Hungarian Chemical Society

7th "Tihany" Symposium
on
Radiation Chemistry

9—14 September, 1990

Balatonszéplak

Hungary

Abstracts

Hungarian Chemical Society

7th "Tihany" Symposium
on
Radiation Chemistry

9—14 September, 1990

Balatonszéplak

Hungary

CONTENTS

EFFECT OF MINERAL FIRTELIZERS ON ACCUMULATION OF GROSS STRONTIUM-90 AND CAESIUM-137 ON THE YIELD OF DIFFERENT AGRICULTURAL PLANTS

M.A.Abdullaev

Azerbaijan Scientific Research Institute of Agriculture,
Sovkhoz-2, 370098, Baku, USSR

Effect of NPK on the gross strontium-90 and caesium-137 accumulation in the yield of winter barley and chick-pea on the chestnut (grey-brown) soils of Apsheron were studied in the field experiments of 1987-1988. Concentrations of radionuclides in the soil and plant samples were determined radiochemically. Radioactivity of the isolated strontium-90 and caesium-137 was measured on the low background equipment of UMF-1500M type with SBT-13 counter.

The results showed that application of optimal doses of mineral firtelizers significantly decreases strontium-90 and caesium-137 accumulation in the grain and straw of winter barley and chick-pea. They also promote the radionuclides accumulation coefficients (AC) decrease in the yield of the cultures under study. AC of strontium-90 is decreased in the grain (from 0,121 to 0,099) and in the straw (from 0,454 to 0,357) of winter barley and AC of caesium-137 was decreased in the grain (from 0,076 to 0,05) and in the straw (from 0,169 to -0,137) of winter barley. AC of strontium-90 is decreased in the grain (from 0,17 to 0,109) and in the straw (from 0,647 to 0,487) of chick-pea and AC of caesium-137 is decreased in the grain (from 0,065 to 0,046) and in the straw (from 0,242 to 0,182) of chick pea.

It was found that application of optimal doses of mineral firtelizers have a positive effect on the yield quantity of winter barley and chick-pea. Optimal doses of mineral fertilizers providing the maximal increase of yield promote low (per cent) accumulation of radionuclides both in grain and in straw.

FORMATION OF BIOLOGICALLY RELEVANT COMPOUNDS OF INTEREST IN CHEMICAL EVOLUTION FROM THE RADIOLYSIS OF SUCCINONITRILE.

G. Albarrán., C. Juárez. and A. Negrón-Mendoza.
Instituto de Ciencias Nucleares, U.N.A.M., Circuito Exterior, C.U.
04510-México, D.F., MEXICO.

Ionizing radiation has been proposed as an energy source on the Primitive Earth. However, very little attention has been paid to it. The purpose of this paper is to summarize the results of how ionizing radiation may have effective in producing compounds with biological significance from the radiolysis of succinonitrile (SN). The CN group may have made it appearance in the early stages of the chemical evolution, for this reason, the radiolytical behavior of nitriles have relevance in the study of prebiotic chemistry. In order to accumulate radiolytic products we used very high radiation dose, more than those normally used in radiation chemistry studies.

The deaerated samples were prepared by the syringe technique. The solutions were 0.1 moles dm^{-3} with an initial pH of 6.0. Irradiations were carried out using two gamma souces of 3.6 kCi and 50 kCi. The irradiation dose were from 0.22 to 750 kGy. Only freshly solutions were used for irradiation. Inmediately after irradiation measurements were made on the solutions. If no otherwise stated the materials, instruments and techniques used in this work were the same as those described previously(1). The determination of ammonia was with a ion selective electrode.

Search for gaseous products.- Carbon monoxide, carbon dioxide, hydrogen and ammonia were identified among radiolytic products. The concentration of those was a funtion of dose.

Policarboxylic acids.- Many carboxylic acids were detected in this radiolysis and their amount increase with the radiation dose. Among them are malonic, succinic, tricarballylic, 1,2,4- butanetricarballylic and 1,2,3,4-butanetetracarboxylic acids.

Peptidic like material.- Some oligomeric products were formed as radiolytic products. The biuret reaction was positive in all samples. The IR data show bands which can be correlated to the presence of an amide bond. All this suggest that peptide bond is present and the oligomeric material consist of heteropolyamides.

From the observed products it seems that in the case of the dinitriles such as SN, the CN group is very reactive and it is the target attack of primary products of water decomposition. The $H^{\cdot}$, e^{-}_{aq} and $^{\cdot}OH$ adducts react further to yield the observed products.

Low doses initiate a large variety of chemical changes in the SN with a G_{-SN}=5.5. The formation of carboxylic acids is explain by abstraction reactions. This radicals dimerized and hydrolized yielding carboxylics acids. The convertion of SN into acids is dose dependent. Some of the acids are biological significance, specially in the Krebs cycle. An oligomeric products with (+) biuret test (peptide bond) was formed. The amount of oligomers depend of the dose up to 19.3 kGy. After this dose the yield reach a plateau.

In the Primitive Earth was very likely that ionizing radiation was abundant and available to induce reactions on molecules and transform them into complex compounds. This process may also occur in the interstellar dust and comets.

1.-Negrón-Mendoza, A., Albarrán, G., Treviño, C. and Torres J.L.
J. Radioanal. Nucl. Chem. 124 (1988) 281.

EB CURABLE COATING SYSTEM ON THE BASE OF CHLORINATED POYOLEFIN AND ACRYLATE MONOMERS

J.B.Adjaoud, E. Takács

Research Institut for the Plastics Industry, Budapest

Currently, the main film-forming constituents of the electron beam curable coatings are unsaturated oligomers dissolved in acrylic monomers.
The drawbacks of some of these systems are the sensitivity to oxygen and the high dose requirement.
In the present research work chlorinated polyolefin and acrylate monomer systems were studied as EB curable coating systems.
The polymerisation of such systems requires less than 50 KGy dose on the low-voltage Electrocurtain accelerator CB 175/15/10 lab unit.

Hardness and hot water resistance of the crosslinked coatings in function of the curing dose and the oxygen content in the atmosphere was studied in detail.

The system containing chlorinated polyolefin and acrylate monomers allows to produce high quality coating with suitable hardness and hot water resistance even at low curing dose /$<$ 40 KGy/ delivered at relatively high oxygen content up to 10 000 ppm.

STERILIZATION OF NEOMYCIN SULPHATE BY GAMMA RADIATION

ALIAOUI. S, CHAREF .A, HADJADJ.A,
Laboratoire de Technologie de l'Irradiation, CDTN,.Alger,

The thermolabile nature and incompatibility of neomycin sulphate with ethylene oxide necessitated to investigate the effects of the use of ^{60}Co-irradiation to sterilize antibiotic.
The results of the relevants dose range which for sterilization purposes are between 20 and 50 kGy.
Physico-chemical parameters such as colour,solubility, PH, melting point of control and irradiated sample were determined by standard methods. Irradiated samples showed slight change in colour which may be attributed to presence of free radicals.
Thin layer Chromatography showed that chromatographic patterns of control and irradiated samples were alike and no spot other than due to neomycin was obtained. No changes are indicated by UV and IR Spectra.
A test for sterility of irradiated sample at 25 KGy and microbiological assay for potencies of the samples were carried out by standard pharmacopoeial procedures. There was no change indicated by chemical assay and microbiological assay reveald no loss in potency. Pharmacological test were carried out by determining LD_{50} values by injecting graded doses of aqueous solutions of the samples intravenous to albino mice.
To determine the radiolytic degradation scheme and the stability of the antibiotic following irradiation, high performance liquid Chromatographic methods were developped. Neomycin sulphate, upon irradiation, undergoes hydrolytic cleavage at a glycosidic bound to from neanune.
Neomycin sulphate irradiated at 25 KGy can be released for marketing as sterile without final sterility testing.

FORMS OF URANIUM-238 AND THORIUM-232 FOUND IN SOME SOIL TYPES OF AZERBAIJAN

J.A.Aliev, M.A.Abdullaev

Azerbaijan Scientific Research Institute of Agriculture,
Sovkhoz-2, 370098, Baku, USSR

Migration and mobility of natural radionuclides, uranium-238 and thorium-232 in particular, are to a marked degree specified by their forms in the soil-plant cover. To determine the different forms of uranium-238 and thorium-232, 5 gramms of air-dry soil sifted through the sieve with diameter of 1mm, were successfully treated with 1n solution of ammonium acetate, 6n HCl and concentrated HF. When treated with the acetate solution the soil was mixed during 30 min. with the 2-fold amount of the solution and the suspension was left overnight thus providing the most full exchange. After filtration the residue was washed by acetate solution till the soil/solution ratio was 1/8. When treated with 6n HCl this ratio was 1/2. In the solutions obtained uranium-238 was isolated from thorium-232 by passing them through the column packed with anionite of EDE-10n type. Uranium-238 and thorium-232 were determined spectrophotometrically with arsenaso-III. Grey-brown, mountain-forest, mountain-brown and yellow-podzolic types of soils were investigated.

The results obtained showed that uranium-238 and thorium-232 in all the horizons of the soil types studied are present in three forms (exchangeable, acid soluble and fixed). Their main mass (more than 50% from the gross content) in all the horizons is in the form (fixed or acid soluble) which is hardly accessible for the plants. It is obvious that because of this reason uranium-238 and thorium-232 are recieved by the different agricultural plants in very small quantities.

MATRIX EFFECTS IN PHOTO- AND γ-RADIOLYSIS OF ORGANIC SULPHIDES

Hanna B. Ambroż, Grażyna K. Przybytniak and Teresa Wrońska

Institute of Nuclear Chemistry and Technology
Dorodna 16, 03-195 Warszawa, Poland

The character of intermediates affords information on the mechanism of reactions of organic sulphur compounds which are very important in medicine (as radioprotectors), ecology and industry. Two distinct paramagnetic species were found in photochemical studies of organic sulphides (Reference). Matrix effects are very significant in photo- and radiation-chemical studies of organic sulphides in determining the nature of intermediates. One of the most important factor appears matrix acidity. At high acidic matrices sulphur-centered radical cations and in low acidic systems carbon-centered radicals are detected as the intermediates. The low pH matrices in solid-state esr studies at 77 K stabilize monomer radical cation $R_2S^{+\cdot}$ or dimer radical cation $[R_2S \mathbin{\dot{-}} SR_2]^+$ of three electron bond, depending on parent sulphide concentration. The high pH matrices stabilize solely carbon-centered species.

Reference: H.B.Ambroż and T.J.Kemp, J.Chem.Res., 1985, 290 and references given therein.

LYOLUMINESCENCE OF SOME SACCHARIDES IN METHANOL

Juan Azorín N. and Alicia Gutiérrez C.
Instituto Nacional de Investigaciones Nucleares
Salazar, Méx., MEXICO

The field of lyoluminescence (LL) in non-aqueous media is almost unexplored. However, LL of saccharides in water has been extensively studied because of its high LL yield and close tissue equivalence(1).

In this paper we present results of changing of solvent from water to methanol. LL response of mannose, sucrose and commercial sugar was compared for these two solvents.

Samples were irradiated with different doses of gamma radiation in a ^{60}Co Vickrad unit (8325 GBq) under electronic equilibrium conditions. Solvents used were deionised bidistilled water and analytical grade methanol. Luminol and lucigenin were used as sensitizers dissolved in water and in methanol.

Readings were made in the LL reader (modified TL analyser) described elsewhere(2) by injecting 5 ml of solvent in the dissolution cell in which 10 mg of the sample were previously placed. The chosen cut-off times of integration were 30 seconds when water was used as solvent and 3 minutes for methanol.

The LL yield appears to be more efficient by a factor of about 20 when solvent is changed from water to methanol. The dose response curves of the saccharides studied in methanol are very similar to those in water. However, for accurate LLD of these saccharides in methanol the solvent temperature must be controlled more than in the case of water.

References

1.- Puite, K.J. and Ettinger, K.V. Lyoluminescence Dosimetry Part II. State-of-the-Art. Int. J. Appl. Radiat. Isot. 33, 1139-1157 (1982).

2.- Azorín, J., Gutiérrez, A. and Guadarrama, L. Lyoluminescence of Tris (Hydroxymethyl) Aminomethane in Gamma Dosimetry. Radiat. Prot. Dosim. 17, 423-426 (1986).

REACTIVE INTERMEDIATES FROM THE REACTION OF HYDROGEN PEROXIDE, AND RADIATION-PRODUCED FREE RADICALS WITH COPPER(I) COMPLEXES

AYAD N. BAGA
Radiochemistry Department
Tajura Nuclear Research Centre
P.O. Box 30878 Tripoli
Great Jamahiriya

Abstract

Evidence is accumulating to show that reaction of Copper(I) Complexes with hydrogen peroxide and radiation-produced free radicals in aqueous solution give not, as previously commonly assumed, the OH. Free radical, but a species that can be regarded as a copper-hydrogen-peroxide complex [formally Copper(III)], that can itself react as intermediate in oxidation processes.

In the case of the reaction of the 2, 9-dimethyl 1,10-phenanthroline complex of Copper(I) with hydrogen peroxide, a stable copper-peroxide appears to be formed [1]. The reactions leading to this species, and some of its properties, are discussed.

It is concluded that information about the reactivities of copper-peroxide intermediates is essential to an understanding of the role of the Copper(I)/hydrogen peroxide reaction in biological oxidative mechanisms.

[1] K.D. Karin, J. Zubieta (eds), "Biological and Inorganic Copper Chemistry", Adenine Press, New York, pp. 61 (1985).

RADIATION EFFECTS ON ALUMINUM AND HYDROGEN RELATED POINT DEFECTS IN ALPHA QUARTZ

Harish Bahadur
National Physical Laboratory
Hillside Road, New Delhi
110012, India.

In recent years studies on radiation effects in alpha quartz have received considerable attention due to a variet of scientific and technological applications for which it is an unique material. At present, most of the industrial demand on quartz crystals is met by the different grades of commercially available cultured quartz except for those where a radiation resistant quartz is required for various aerospace applications. In almost all cases of high purity cultured quartz, natural quartz is the starting material from which they are grown hydrothermally. Therefore,it is of interest to investigate the radiation effects on different impurities present in natural quartz.

We have carried out a study of electrodiffusion and irradiation on high quality clear natural quartz from Arkansas, USA and Brazil. In particular, OH^- related defects have been monitored using infrared absorption measurements in the 3100-3700 cm^{-1} range. Out of a variety of hydroxyl defect centers we have focused our attention on the major bands viz. $Al\text{-}OH^-$, $N_1\text{-}M^+$ and $N_1\text{-}H^+$; where M^+ is either Na^+ or Li^+. The $Al\text{-}OH^-$ centers show absorption bands at 3306 and 3367 cm^{-1}; the $N_1\text{-}Li^+$ absorbs at 3476 cm^{-1}; $N_1\text{-}Na^+$ absorbs at 3451 cm^{-1} and $N_1\text{-}H^+$ exhibits absorption at 3468 cm^{-1}. It is believed that all the $N_1\text{-}Li^+$, $N_1\text{-}Na^+$ and $N_1\text{-}H^+$ centers arise due to a common defect and represent specific configuration of LiOH, NaOH and H_2O molecules perturbed by theSiO_4 tetrahedra in quartz lattice. Irradiation effects were monitored on the major bands in the high quality natural quartz. Irradiation was carried out by a van de Graaff accelerator using electron beams accelerated to 1.75 MeV. Radiation dose of 2 Mrads was given to samples at all stages of investigation. The $N_1\text{-}M^+$ centers show a relatively fast decay at room temperature irradiation than at 77K irradiation while the reverse is the case for $N_1\text{-}H^+$ centers. The room temperature irradiation of $Al\text{-}OH^-$ centers increases their strength. The irradiation replaces some of the alkali ions from the aluminum centers with hydrogen in the limit to saturate all aluminum with hydrogen. In thethe case of the crystals electrolyzed in the hydrogen atmosphere the $N_1\text{-}H^+$ and the long bond $Al\text{-}OH^-$ centers behave identically. They decay to about 90% of their original strength. Isochronal annealing shows that the recovery of all these centers is essentially complete by 760K.

THE EFFECT OF γ RADIATION ON VOLATILE IODINE COMPOUNDS IN DILUTE AQUEOUS SOLUTIONS

J. Balog
Central Research Institute for Physics
P.O.B. 49, Budapest H-1525, Hungary

The volatility and oxidation-reduction reactions of iodine compounds in dilute aqueous solutions are studied by ^{131}I tracer method with a view to nuclear safety problems. The effect of pH, concentration and γ irradiation on the I^-/IO^- equilibrium and the OI^-/HOI dissociation is investigated in detail. The role of volatile HOI in radioactive I-release is discussed.

A RETARDED DNA-CHAIN GROWTH AND FORK-DISPLACEMENT RATE AND A HIGH NUMBER OF SPONTANEOUS SISTER-CHROMATID EXCHANGES IN XERODERMA PIGMENTOSUM (FORM II)

L.S.Barenfeld, S.G.Nergadze*, N.M.Pleskach, V.M.Mikhelson
Institute of Cytology of the Academy of Sciences of the USSR, Tikhoretsky Prospect 4, Leningrad 194064, (USSR).
* Scientific Resaerch Institute of Informatics and Complex Automation of Public Health of the Ministry of Public Health, Georgien SSR, Tbilisi, (USSR).

The cytogenetic observation that the frequency of spontaneous sister-chromatid exchanges (SCE) in a special form of xeroderma pigmentosum (XPII) is about 3 times higher compared to that seen in normal cells, prompted an investigation of DNA replication in that rare disorder. XPII is unique in having g-ray sensitivity in addition to UV-sensitivity . Using DNA fiber autoradiography, an estimation of fork-displacement rate as well as the incidence of fusion between neighbouring clusters of replicons was made. The fork-displacement rate in XPII dermal fibroblasts in tissue culture was found to be significantly slower than that in normal control cells, however, similar to that obtained earlier in Bloom's syndrome cells. Here we also present evidence on a new defect in DNA replication lying in a significantly decreased number of simultaneously operating clusters of replicons which resuts in a significantly decreased rate of DNA-chain growth. (The two components of ongoing DNA replication were found to be normal in classical XP and Cockayne's syndrome cells). According to Painter's replicative model of SCE the exchanges arise due to double-strand DNA breaks occurring at the border between two adjacent clusters of replicons, one of which is completely while another partially replicated. A retarded fork-displacement rate together with decreased rate of DND-chain growth will cause this situation to persist longer than normal. Thus our data provide further support for replication model for SCE.

THE RADIATION DESTRUCTION OF DYES IN POLYMERS: THE NEW METHOD OF INCREASING OF DYED POLYMERS STABILITY BASED ON VIBRATIONAL CROSS-RELAXATION

A. S. Belichenko, K. M. Dyumaev, A. P. Maslyukov, G. A. Matyushin and V. S. Nechitailo

All Union Medical Polymers Institute, USSR, Moscow, Nauchny pr., 10

In this work we discuss the mechanism of radiation destruction of dyes in polymers connected with solid-phase chemical reaction between dye molecules and oxyradicals forming by oxidation of primary radicals generated under irradiation. If this is the case, the rate of dye bleaching under irradiation can be influenced by the additives decreasing the rate of primary radicals generation.

The new physical method of increasing of dyed polymers stability against high power electromagnetic irradiation of UV- and γ-range was proposed. The essence of the method is: chemically inert additives are introduced into polymeric matrix, vibrational spectra of additives overlap with spectra of macromolecules. The condition for resonance energy transfer for vibrational exitation from macromolecules onto additive molecules (vibrational cross-relaxation) is fullfilled, life time of excited vibrational states is shortened sharply, rate constant of chemical bond cleavage in macromolecules is decreased and therefore the formation of primary radicals in polymers and subsequent proceeding radical dye destruction processes in polymers are suppressed.

The aim of this work is to check experimentally whether this mechanism of dye destruction in polymers under irradiation is correct. The studies were carried out on the widely used polymer (polymethylmethacrylate) impregnated with dyes (vanadyl phtalocyanin and nickel dithiobenzyl complex). The polymer samples were irradiated at 300 K in air with a ^{60}Co source at a dose rate of 1.2 Gy/s. The UV-irradiation was accomplished with high power continuous and impulsive lamps in different spectral ranges. The application of offered vibrational cross-relaxation method allowed us to increase in 10-100 times the dyes stability in polymers against UV-and γ-irradiation.

REMOVAL OF ORGANIC AND INORGANIC ADMIXTURES FROM ATMOSPHERIC AIR BY MEANS OF DC- AND PULSED STREAM CORONA ENERGIZATION

E.V.Belousova, V.A.Goncharov, A.V.Polyakova, A.Z.Ponizovskii,
A.P.Shvedchikov, S.G.Gostev, V.A.Potapov. A.A.Fatkin, A.A.Abramov

Institute of Chemical Physics USSR Academy of Sciences
Horizon, 117334 Moscow V-334, Kosygin st., 4 , USSR

A series of experiments of the pulse corona induced plasma chemical removal of NO_x, SO_2, NH_3 and organic admixtures (phenol, benzene, p-benzoquinone, etc.) from wet air has been carried out. An electrostatic technology based on the effect produced in the moist air by the DC- and pulse corona discharge occuring when a nanosecond pulse voltage of very fast rising front is applied to an electrode structure very similar to that used in electrostatic wet precipitatiors has been used.

The test cell consists of concentric stainless-steel cylinder electrod (diameter 60 mm, length 250 mm) with stainless-steel filament.

The experiments in static and flow conditions at 25-50°C has been studied. The influence of temperature, concentration, pulse frequency, dose, flow rate etc. on the kinetics of admixtures decay and several intermediates production has been obtained.

The possible mechanism of admixtures removal with participation of atoms (H, O, N), radicals (OH, HO_2, PhO, $HOSO_2$, NO_3, etc.), excited states and ions has been considered. The analysis of influence of corona energy on the efficiency of admixtures removal has been made.

KINETICS AND MECHANISM OF GAS PHASE REACTIONS OF ORGANIC AND NONORGANIC POLLUTANTS IN WET AIR UNDER IRRADIATION BY FAST ELECTRONS

E.V.Belousova, A.V.Polyakova, A.P.Purmal, A.P.Shvedchikov, S.O.Travin

Institute of Chemical Physics USSR Academy of Sciences
117334 Moscow, V-334, Kosygin st., 4, USSR

A general kinetic mechanism for fast electrons (dose rate 8 kGy/s, dose 0-200 kGy, temperature 50-200°C) induced transformations of NO_x, SO_2, phenol, p-benzoquinone in wet air is formulated.

We used a reaction set with more than 40 measured rate constants for H, N, O, S atoms, OH, HO_2, $HOSO_2$, $HOSO_3$, SO, NO_3, C_6H_5O radicals and intermediate species (O_3, SO_3, N_2O, semiquinone, hydroquinone, etc.) to fit the available data.

Dose dependence of NO_x, SO_2, C_6H_5OH, $C_6H_4O_2$ (the initial concentrations are $\leq 5\cdot10^2$, 10^4, 10^3, 10^3 ppm accordingly) decay and production of intermediates (atoms, radicals, molecules) and final products have been calculated. The main oxidizing particles are OH, O, HO_2 species, the dominant removal mechanism of SO_2 includes the reaction $SO_2 + OH \dashrightarrow HOSO_2$ with production of H_2SO_4 as a final product in the presence of H_2O. When NO_x is present $G(-SO_2)$ considerably decreases. In the presence of NO_2 and O_3 the rate of C_6H_5OH decay increases through the reaction $C_6H_5OH + NO_3 \dashrightarrow$ products ($K_{298} = 1.32\cdot10^{10}$ l/mole·s). High values of phenol and benzoquinone conversion in the range 10-30 kGy have been observed.

7th TIHANY SYMPOSIUM ON RADIATION CHEMISTRY
(Balatonzeplak 9-14 Sept 1990)

PHOTOIONIZATION OF WATER OR AQUEOUS SOLUTES : ON THE ELECTRONIC STRUCTURE OF LIQUID WATER

A. Bernas*, T. Goulet† and J.P. Jay-Gerin†

*Laboratoire de Photophysique Moléculaire, U. Paris Sud, 91405 Orsay
†Groupe C.R.M. en Sciences des Radiations et Département de Médecine Nucléaire et de Radiobiologie, Faculté de Médecine,
U. de Sherbrooke, Sherbrooke (Québec), Canada J1H 5N4.

The photoionization yield curves -i;e. the excess electron yield $\varphi_{e^-_{aq}}$ as a function of the photon energy E_{ph} - for either pure water⁽¹⁾ or aqueous solutes⁽²⁾⁽³⁾ are shown to present an exponential behavior in the ionization threshold region.

Such an exponential law, also characteristic of an Urbach tail, suggests that : i) the final electronic states in the photoionization of liquid water might belong to such a tail extending below the bottom V_0 of the conduction band ; ii) the variation of the $\varphi_{e^-_{aq}}$ with E_{ph} reflects the energy dependent density of states in the latter⁽⁴⁾ .

Combining some photoionization and photoemission literature data allows to estimate the liquid water band gap E_G at 8.9 ± 0.2 eV and the extension T of the Urbach tail at 2.4 ± 0.7 eV⁽⁴⁾ .

With respect to the ionization potential E_i of H_2O vapor, the transition to localized states below V_0 for photoionized liquid water obviously contributes to a further lowering of E_i. So does the water electronic instantaneous polarization around the positive charge. The magnitude of the three additive terms V_0, T and P_+ might then account for the exceedingly large difference (~ 6 eV) between the $E_{i\ vap}$ and $E_{i\ liquid}$ values reported for water.

(1) D.N. NIKOGOSYAN, A.A. ORAEVSKY and V.I. RUPASOV, Chem. Phys. 77, 131, 1983.

(2) E. AMOUYAL, A. BERNAS and D. GRAND, Photochem. Photobiol. 29, 1177, 1979.

(3) A. BERNAS, D. GRAND and E. AMOUYAL, J. Phys. Chem. 84, 1259, 1980.

(4) T. GOULET, A. BERNAS, C. FERRADINI and J.P. JAY-GERIN, Chem. Phys. Lett. in press.

INDUCTION AND SUBSEQUENT REPAIR OF DNA DAMAGE IN QUIESCENT AND PROLIFERATING HEPATOCYTES OF RATS IRRADIATED WITH NEUTRONS AND X-RAYS

L. Bezdrobnaya
The Research Institute of Oncology, Kiev, Ukrainian SSR

We used a model of intact and regenerating (following partial resection) rat liver to compare effectiveness of 6 MeV neutrons and X-rays on cells with various proliferative activity, demonstrated by the induction and repair of DNA damage, namely single-strand breaks.

We found that during inhibition of repair events, neutrons (3-24 Gy) induce more DNA lesions in quiescent cells than in proliferating ones, while X-rays (2,5-10 Gy) gave a reverse pattern. An increased output of primary neutron-induced DNA damage in quiescent cells seems to be due to densety packed chromatin in the latter, since neutrons, in passing throug the cell, produce a significantly higher, than X-rays, linear density of ionization per unit of treck of charged particles formed by them, while the contribution of neutron indirect action due to radicals is significantly lower. As the photon exposure produces up to 70% primary DNA damage due to interaction with OH radicals, a greater frequency of inducing DNA damage by X-rays in proliferating cells is determined by increased availability of DNA to radicals due to chromatin depacking. In rats irradiated at 10 Gy, neutron-induced DNA damage is repaired in quiescent hepatocytes within 12 h, while in proliferating cells within 6 h, the duration of repair after X-rays being 5 h and less than 1 h, respectively. In the postrepair period residual DNA damage is observed. G_0hepatocytes show a linear-quadratic dependence on the dose of irradiation (up to 30 Gy) within 20 h of exposure. The relative biologic effectiveness of neutrons for residual damage to quiescent cells is 1.55 and 1.3 at 10 and 30 Gy, respectively. The extent of reparability of DNA depends on the stage of the cell cycle during irradiation of animals. Following neutron exposure, the highest DNA damage is observed in G_0, while with X-rays in G_1. A mixed cell population G_1+S and a significant increase in differences between quiescence and proliferation (2.3-fold versus 1.4) due to significantly augmented residual DNA damage in G_0 cells. More close DNA-histone contacts in the chromatin of quiescent cells seem to contribute more than less condensed chromatin in proliferating cells, to the interaction of the ends of DNA broken strands and proteins developing within a treck of one charged particle, which significantly increases the probability of developing more complex irreparable damage of DNA. Thus, our findings suggest that, in the absence of proliferation, neutron-induced damage are poorly repaired.

THE ROLE OF DNA POLIMERASES IN THE REPAIR OF DNA RADIATION INDUCED DAMAGE IN PROLIFERATING AND QUIESCENT MAMMALIAN CELLS

Bildin V.N., Seregina T.B., Plotivenkova O.A., Zhestyanikov V.D.
Institute of Cytology, Acad.Sci.USSR, Leningrad

The involvement of DNA polimerases in the repair of DNA radiation induced damages has been investigated. The rates of the elimination of the single- (ssb) and double-strand breaks (dsb) in the presence of the inhibitor of DNA polimerases α and δ, aphidicolin (Aph), and the inhibitor of DNA polymerase β, 2',3'dideoxythymidine-5'-threephosphate (ddTTP), have been compared. The work has been carried out on mouse Swiss 3T6 cells and human epidermal carcinoma A431 cells using the methods of alkaline sedimentation (after X-ray irradiation at the 10 Gy dose) and neutral elution on the filters at pH 7.2 (after γ-irradiation at the 100 Gy dose).

It is shown that the Aph (30 μM) does not influence on both ssb and dsb DNA repair in proliferating 3T6 cells but inhibits them for 60-70 % in quiescent cells. The addition of hydroxyurea (10 mM) to Aph leads to a decrease in efficiency of the ssb DNA repair for 20% in proliferating cells but does not result in the additional inhibition of the process in quiescent cells. ddTTP inhibits ssb and dsb DNA repair for 15-20% both in proliferating and quiescent 3T6 cells. Aph inhibits the ssb DNA repair in quiescent human A431 cells completely. Data presented allow us to conclude that DNA polymerases α and δ are of great importance for the processes of the repair of DNA radiation induced damages in mammalian cells.

STUDY OF THE ELEMENTARY REACTIONS OF THE ACTION OF PHENOLIC STABILIZERS BY TIME-RESOLVED OPTICAL UV-VIS SPECTROSCOPY

O. Brede and L. Wojnařovits [x]

Central Institute of Isotope and Radiation Research of the
Academy of Sciences of the G.D.R., Leipzig, G.D.R.-7050

With pulse radiolysis and detection by optical emission and absorption spectroscopy elementary reactions of antioxidant action of sterically hindered phenols were studied. Despite of radiation-chemical pecularities the pulse radiolysis experiments give information on the reaction of alkyl and alkylperoxi radicals with the phenol which generates phenoxyl radicals.
Besides of the radical reaction path the phenols are also very active as light absorbers (direct phenoxyl formation), as singlet quenchers and in a reaction with ketone triplets (electron transfer to with subsequent protonation of ketones).

For the case of 2,6-di-tert.-butyl-4-methylphenol it is experimental evidence that its phenoxyl radical rearranges to a radical of a probable benzyl type structure which should play a key role in the phenol oxidation mechanism.

On the basis of the time-domain experiments a critical analysis of the reaction mechanism of the stabilization of liquid hydrocarbons as well as polyolefine polymers is given.

---

[x] Institute of Isotopes of the Hungarian Academy of Sciences,
H-1525 Budapest, P.O.Box 77, Hungary

RADIATION TRANSFORMATIONS OF POLYVINYL ALCOHOL IN AQUEOUS SOLUTION

K.Burczak, R.Łubis, J.Rosiak, J.Kroh
Institute of Applied Radiation Chemistry, Wróblewskiego 15,
93-590 Lodz, Poland

Polyvinyl alcohol (PVA) hydrogels are the basic materials in a variety of biomedical applications [1]. Macroscopic effects of the influence of ionizing radiation on the PVA aqueous solutions were a subject of a number of papers [2-4].

The aim of our work was to study some radiation induced transformations of PVA in aqueous solution leading to its crosslinking or degradation. They have been investigated using pulse radiolysis in connection with the measurements of light scattered intensity (LSI) as well as optical absorption.

In the solution saturated with Ar at [PVA] = 3.4×10^{-2} b.M the LSI increased after the pulse (crosslinking) and decreased in the presence of oxygen at $[O_2] = 1.4\times10^{-3}$ M (main chain scission).The rate constant of bimolecular reaction of crosslinking of PVA macroradicals on the basis of LSI experiments is equal to $k_2 = 1.7\times10^{8}\ M^{-1}\ s^{-1}$. ° OH radical is the main transient species attacking the polymer in aqueous solution and responsible for the formation of the PVA macroradicals [5].

Some results have been obtained on the basis of ordinary sol-gel analysis of crosslinked PVA samples using new ROCH equation [6] to calculate $G_{(x)}$ - radiation yield of crosslinking. The experimentally obtained values of $s + \sqrt{s}$ have been interpreted on the basis of modified Charlesby-Pinner equation [7].

References

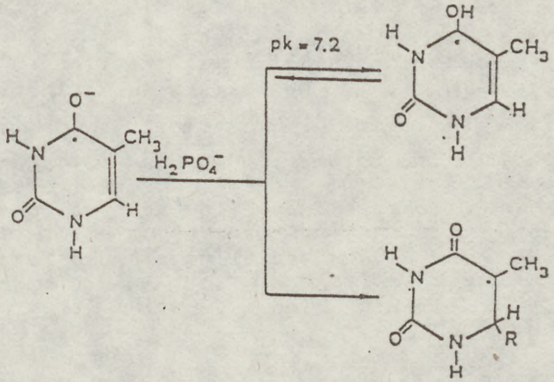
1. Peppas A.N.: Hydrogels in Medicine and Pharmacy, CRC Press, Inc., Boca Raton, Florida, Vol.I 1986, Vol.II and III 1987.
2. Bray J.C., Merrill E.W.: J.Appl.Pol.Sci., 17, 3779, 1973.
3. Ikada Y., Mita T., Horii F., Sakurada I., Hatada M.: Radiat. Phys.Chem., 9, 633, 1977.
4. Chen Wenxiu, Bao Huaying, Radiat.Phys.Chem., 26, 43, 1985.
5. Łubis R., Olejniczak J., Rosiak J., Kroh J.: Radiat.Phys. Chem., 36, 249, 1990.
6. Rosiak J., Olejniczak J., Charlesby A.: Radiat.Phys.Chem., 32, 691, 1988.
7. Olejniczak J., Rosiak J., Charlesby A.: Radiat.Phys.Chem., in press.

REDOX INVERSION PROCESS OF PYRIMIDINE AND PURINE ANIONS IN IRRADIATED AQUEOUS SOLUTION

F. BUSI[1], P. O'NEILL[2], O. TUBERTINI[3]

[1] ISTITUTO SCIENZE CHIMICHE, UNIVERSITA' DI BOLOGNA
[2] MRC RADIOBIOLGY UNIT, Chilton, Didcot, Oxon, U.K.
[3] CENTRO RADIOCHIMICA AMBIENTALE, UNIVERSITA' DI BOLOGNA

Purine and pyrimidine irradiated in aqueous solution undergo fast reactions with the radicals H, OH, and $e^-_{solv.}$ produced in the radiolysis of water.It has been reported that the reducing radical anions formed by the reaction of pyrimidines with solvated electron undergo fast protonation at O(4) in competition with a slower protonation process at C(6) yielding radicals with strong oxidizing property. The pyrimidine protonations processes are rapresented by the reaction scheme:



the slow protonation at C(6) is catalysed by phosphate.
The electron adduct or its protonated O(4) derivative reacts with molecular oxygen or other oxidant by electron transfer restituting the original pyrimidine resulting, therefore, in a radiation protection process.If the protonation at C(6) occurs prior the reaction with the oxidant, due to low solute concentration or to the presence of phosphate, the process lead to chemical irreversible damage resulting in a possible sensitization effect. Purine electron adducts react with water and may be converted into oxidizing radicals.
The knowledge of electrochemical properties of the intermediates formed by the decay of the electron adducts have, therefore, implication in the potential mechanism of radiation induced damage in living cells.

We report the voltammetric studies, using the photocurrent and the galvanostatic-pulse radiolysis techniques,on the properties of purine and pyrimidine electron adducts and their decay products.The pyrimidines have been investigated in the presence of phosphate at different concentrations and the results are in agreement with those reported from optical absorption measurements. The phosphate catalysed protonation occurs at C(6) with rates in the order thymine> uracil> 6-methyluracil.Adenine electron adduct and its protonated derivatives are oxidized at a dropping mercury electrode in the potential range up to -1.6 V vs SCE indicating that redox inversion processes are not involved in the decay mechanism.In irradiated solutions of dAMP and dGMP the observed photocurrent signals indicate the partial conversion of the primary electron adducts to oxidizing radicals.

THE MECHANISM AND KINETICS OF DECOMPOSING SOLUTIONS OF SURFACE-ACTIVE SUBSTANCES UNDER THE ACTION OF ACCELERATED ELECTRONS

Buslaeva S.P., Vanjushkin B.M., Gogolev A.V.,
Kabakchi S.A., Medvedovsky L.I., Panin Yu.A.,
Putilov A.V., Upadishev L.B.

USSR

Moscow

All-Union Research Institute of Technical Physics and Automation

Stationary and pulse radiolysis of necal water solutions, i.e. anionic surface-active substance (SAS) mixture, isomer sodium isobutylnaphthalenesulfonates, containing admixtures, typical of the technology of emulsion synthetic rubber production has been investigated.

With the use of NMR-(I)H and ultra-violet (UV) spectrophotometry methods it was shown, that isobutylnaphthalenesulfonate (N) under radiolysis equally effectively reacts as with oxidizing, so with recovering water radiolysis products.

Reaction rate constants N with hydrated electron, OH radicals and H atoms as well as rate constants of forming electron, OH and H adducts with oxygen have been found. With doses less than 0.5 Mrad, molecule N damage yield is $G=1.95\pm0.20$ molecules/100 eV.

When conducting, liquid-phase radiochemical processes in inhomogeneous radiation fields, kinetic dependencies are of a special value.

A mathematic model has been developed, ensuring selection of an optimal hydrodynamic mode depending on kinetic parameters of surface-active substance decomposition in water solutions.

A technological scheme of liquid waste purification combining electron-beam machining with biological additional decontamination has been developed.

The facility with two process lines, has been designed and put into operation.

The complete sanitary-and-chemical analysis confirming the compatibility of the new method with usual biological purification of synthetic rubber production wastes has been conducted.

IMMOBILIZATION OF CATALASE ON POLY(ACRYLONITRILE)-G.CO-HYDROXYETHYL METHACRYLATE

M.C.Cavaco[1], A.P.Piedade[2], M.E.Andrade[1] and M.H.Gil[2]

[1] - Departamento de Física - ICEN/LNETI - E.N. 10, 2685 Sacavém - Portugal

[2] - Departamento de Química - Universidade de Coimbra - Portugal

Different poly(acrylonitrile)-g.co-hidroxyethyl methacrylate graft copolymers were prepared by using gamma irradiation at 400 $Gy.h^{-1}$ for different intervals of time. The influence of the monomer concentration and time of irradiation on the yield of grafting were analysed.

Some of the samples were used for the immobilization of catalase. The enzyme was coupled covalently to the hydroxyl groups of the support after being activated either with epichlorohydrin or with p-toluene sulphonyl chloride.

The hydrophilicity of the polimeric supports was calculated by determining the water and buffer sorption and the contact angle.

From the results obtained we can conclude that the hydrophilicity as well as the critical wetting tension is dependent on the presence of the poly(hydroxyethyl methacrylate).

The yield of the enzyme coupling increases when hexamethylenediamine was used as a "spacer". The results obtained showed that these polymeric supports are promising for the immobilization of catalase.

SELECTED ASPECTS OF THE CHEMISTRY AND RADIATION CHEMISTRY OF LIGNIN

Claudio A. Chuaqui

Radiation Applications Research Branch,
Whiteshell Laboratory,
AECL Research
Pinawa, Manitoba,
CANADA ROE 1L0

After cellulose, lignin is the most abundant constituent of wood, accounting for about 25% of the bulk material. Chemically, lignin is an irregular, highly branched, three-dimensional polymer of an amorphous and complex nature. Its basic blocks are phenylpropanoid units linked together in a variety ways, yielding at least ten different types of bonds between the units. The result is a highly complex and unreactive polymer.

The structure of lignin is not completely understood. However, many important structural features of lignin are known, particularly those related to reactivity modes during its degradation, derivatization and delignification in pulping processes. The efficient utilization of lignocellulosics in biomass processing is limited mainly by the inability to use lignin. It is recognised that lignin offers a great potential for the production of lignin and lignin-derived products, once controlled derivatization and degradative processes are discovered and implemented.

In the present work, lignin was subjected to electron and gamma radiation as part of a study to determine the effects of radiation on its structure. Some of the factors that influence the outcome of the treatment are the dose, the nature of the atmosphere surrounding the sample, and the physical state and nature of the irradiated lignin itself. We have obtained data to describe some of the free radical intermediates formed during irradiation and how the variation of certain factors affects the magnitude and direction of the effects induced by irradiation. The data were obtained using electron spin resonance spectroscopy, size exclusion chromatography and other high performance liquid chromatography techniques, gas chromatography-mass spectroscopy analysis, and chemical degradative methods. The substrates used were several types of isolated lignins and wood, and some compounds that are useful as lignin models. Depending on the experimental conditions, the results show that radiation treatment may lead to either polymerization or degradation processes. The factors that determine the outcome are discussed in terms of substrate structures and the chemical processes that take place.

THE USE OF N-VINYLIMIDAZOLE IN POLYMER RADIATION CHEMISTRY

ADOLPHE CHAPIRO
C.N.R.S. 94320 THIAIS, FRANCE

N-vinylimidazole (NVI) was used in studies of radiation induced polymerization, and grafting. Poly(NVI) was also cross-linked to a hydrogel by irradiation of aqueous solutions of the polymer. The monomer was polymerized in bulk and in various solvents at tempeartures ranging from 20 to 60°C. In all systems the reaction was slow. Irradiation of concentrated monomer solutions resulted in the formation of a crosslinked-linked gel which indicates that the double-bonds in the imidazole ring react in the process. However, no retardation was observed. In aqueous or methanol solutions containing 9.0 mol./liter of monomer or less the polymerization proceeds homogeneously and the polymer remains soluble. Auto-catalytic conversion curves are observed even in dilute solutions, indicating the operation of a "matrix effect". NVI was grafted into Teflon-FEP films giving rise to permselective membranes. PNVI forms complexes with many organic and inorganic substances. The stability of these complexes is pH dependant. At low pH, the imidazole rings become partly ionized. These versatile properties make NVI grafted membranes interesting canditates for specific separation processes. Aqueous solutions of PNVI undergo cross-linking under irradiation with the formation of gels. These exhibit good biocompatibility. The reaction occurs with a much higher efficiency than that of a similar water-soluble polymer : poly(N-vinylpyrrolidone) (PNVP). There is evidence that here again the double bonds in the imidazole rings contribute to the gelation process. Although PNVI gels exhibit properties similar to those of PNVP gels, their ability to complex some molecules, such as proteins, is much greater and this opens interesting prospects for potential uses of such gels.

CHEMICAL QUALITY OF IRRADIATED ARGENTINIAN ONION DURING LONG-TERM STORAGE

C.A. CROCI, S.A. BANEK and O.A. CURZIO
Laboratorio de Radioisótopos, Universidad Nacional del Sur
8000 Bahía Blanca, Argentina

The influence region of the UNS is a great producer of the "Valenciana sintética 14" onion variety, which is the most important in the country for the internal market as well as for exportation.

The effectiveness of 50 Gy of cobalt-60 gamma rays for inhibiting sprouting in this variety had been proven(1), but the effect of treatment on chemical parameters of this variety is unknown.

The aim of this study was to evaluate the effects of treatment, storage time and crop year on the main chemical parameters of bulbs. Bulbs from two campaigns, 1984 and 1985, were irradiated and stored in ordinary conditions. The contents of dry matter, total carbohydrates, vitamin C and acidity were measured at 1-month intervals for 10 months. The flavour strength in terms of total piruvate were determined in the 1985 trial.

The two trials results show that in stored irradiated and control bulbs carbohydrates and vit.C behaviours were identical ($p > 0.05$). For both parameters irradiated bulbs showed to have higher contents ($p < 0.01$) than control ones; highest contents ($p < 0.05$) were found in 1984 trial's samples. Dry matter and acidity in irradiated and control bulbs showed to have identical behaviour ($p > 0.05$). Neither irradiation treatment nor crop year affected the contents of these parameters ($p > 0.05$). Piruvate contents in irradiated and control bulbs of the 1985 trial showed to have identical behaviour ($p > 0.05$). Irradiation treatment had no significant effect ($p > 0.05$) on piruvate of the bulbs.

The results indicate that irradiation treatment, long-term storage and crop year do not adversely affect the principal chemical parameters of "Valenciana sintética 14" onion variety. The practical implications of these results are discussed.

(1) Curzio,O.A. and Croci,C.A.(1988). Radiat.Phys.Chem. 31, 203-206.

CHANGES IN PEROXIDASES ASSOCIATED WITH RADIATION-INDUCED SPROUT INHIBITION IN GARLIC (Allium sativum L.)

C.A. CROCI*, J.A. ARGUELLO+ and G.A. ORIOLI++

*Laboratorio de Radioisótopos and ++Departamento de Agronomía
Universidad Nacional del Sur, 8000 Bahía Blanca, Argentina
+Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina.

In a preliminary study of the effect of cobalt-60 gamma rays on garlic cloves, low doses during post-dormancy were found to provide interesting material for studying the biochemical and physiological aspects of radiation-induced sprout inhibition⁽¹⁾.

The aim of this study was to analyze the effect of an acute dose (10.0 Gy) on post-dormant garlic cloves up to 100 days after treatment in relation to: a) inner sprout growth and b)changes in peroxidase and soluble proteins. Irradiation was found to bring about modifications in the inner sprout but not in the storage leaf. Sprout growth radio-inhibition became evident after 25 days of treatment and was synchronous with a marked increase in peroxidase activity. Thin layer isoelectrofocusing revealed that radiation induced an increase in the number of anodic peroxidase isoenzymes at 100 days, suggesting modifications in the vascularization process. Neither the soluble protein content nor the protein pattern was affected by irradiation. These results are discussed in terms of a possible mediating effect of peroxidase on radiation-induced sprout inhibition in garlic.

(1) C.A. Croci, J.A. Argüello and G.A. Orioli (1987). Environmental and Experimental Botany 27, 1-5.

A COMPARATIVE STUDY OF COATINGS CURED BY EB AND UV

I.Czajlik, E.Takacs, M.Zohdy*, T.Czvikovszky

Research Institute for the Plastics Industry
H-1950 Budapest, Hungary.

* National Center of Radiation Research and Technology
Nasr.C. Cairo, Egypt.

In the field of radiation technology curing by UV light or electron beam are often considered to be competiting processes. A number of papers (1-4) deal with the similarities and differences of these technologies and give conflicting results.

The aim of this study is to investigate the influence of curing parameters on the UV and EB cured film properties in order to determine which technology is superior in a particular application.

The films of different oligomer/monomer mixtures were cured by UV and EB on glass plates. The equipment used for UV curing was a Super Six UV lamp system of Fusion System Corporation. The electron beam curing was carried out under argon gas (200-300 ppm oxygen) using an Electrocurtain CB 150/15/180L accelerator.

The pendulum hardness, the gel content and the double bound content of the cured films were measured as a function of dose, dose rate and (in case of UV curing) as a function of photoinitiator concentration, too.

References.
1.K.J.O'Hara FC 85-421 Radcure 85 SME Conference Basel 1985.
2,V.P.Thalacker, T.F.Boettcher Radiat.Phys.Chem. 25 323-32 (1985)
3,E.G.Larson, D.S.Spencer, T.E.Boettcher, M.A.Melbauer, R.P.Skarjine Pol.Mat. Science and Engineering 547-551 (1986).
4,S.A.Allen, P.J.Robinson, N.J.White, G.GF.Skelhorne Eur. Pol. J. 20 No.1. 13-18 (1984).

MEASUREMENT OF OER AND RBE FOR p(18MeV)+Be FAST NEUTRONS

Dám, A., Rétlaki, M., Gazsó, L., [+]Fenyvesi, A., [+]Molnár, T., [+]Mahunka, I.

OSSKI, Budapest 1221. Pentz K. u. 5.
[+]ATOMKI, Debrecen 4026. Bem tér 18/c.

With the increasing use of high energy neutrons for cancer therapy has been raised the need of basic radiobiologycal studies. One of the advantages of neutrons for therapy is that the neutron has a lower oxygen enhancement ratio (OER), than conventional low LET (Linear Energy Transfer) radiations, because it is supposed that most tumor contain more viable hypoxic cells than do normal tissues. Tolerance dose, wich have been established for conventional low LET radiations can not be directly translated into corresponding neutron doses, because the relative biological effectiveness (RBE) of neutrons varies with the dose, the object or end point studied. The biological effects depend on the energy (MeV) and output (μA) of radiation and the gamma-proportion, wich are determined by the facility and the high LET particle used, releasing from the nuclear reaction.

Present study was carried out to establish the basic biological parameters of MGC-20E Cyclotron in ATOMKI (Debrecen), wich was planned for subsequent medical applications as well.

The most important parameters RBE and OER were determined in bacterial model system and survival was investigated as end point. The absorbed dose from p(18 MeV)+Be fast neutron source was determined by calculation based on ECNEU (European Clinical Neutron Dosimetry Group) recommendations. A thimble type ionization chamber (Extradin T2) constructed of A-150 tissue equivalent plastic and a miniature energy compensated GM counter (FWF GM-1) were used for evaulation for the separate neutron and gamma absorbed dose components of mixed n-gamma fields.

RBE of neutron beam for Escherichia coli B/r (ATCC. No. 23227) was determined in nitrogen and under oxic condition, using ^{60}Co γ-ray as a reference radiation. It follows:

$RBE_{anoxic} = 3,92$ $RBE_{oxic} = 2,46$

OER was also calculated from both quality of radiations:

$OER_{neutron} = 1,31$ $OER_{gamma} = 2,10$

High LET radiation afford distinct advantages for clinic as a tool for improved radiotherapy. With that object the effect of different radiomodifying agent was also studied, such as elektronaffinic sensitizers (Misonidazole) and radioprotective drugs (WR 1065). Their effectiveness was found to be lower in modulation of neutron-induced cell lethality than that observed for ^{60}Co γ-rays.

THE X-RAY DAMAGE OF PROTEINS IN AQUEOUS SOLUTION

II. CORRELATION OF FUNCTIONAL AND STRUCTURAL PARAMETERS OF MALATE SYNTHASE

H.Durchschlag[1] and P.Zipper[2]

[1] Institute of Biophysics and Physical Biochemistry, University of Regensburg, Federal Republic of Germany
[2] Institute of Physical Chemistry, University of Graz, Austria

The damage of the sulfhydryl enzyme malate synthase upon X-irradiation was investigated by both functional and structural studies (e.g., activity measurements and small-angle X-ray scattering). In both cases irradiation was performed in the absence or presence of additives of different nature. Enzyme activity was registered after stop of irradiation and in the post-irradiation phase; additionally a repair of irradiated enzyme was performed by addition of dithiothreitol. Results have been presented in a series of papers (cf. [1-5] and references therein). In order to quantify the protective and repair-promotive efficiencies of various additives, appropriate normalized efficiency parameters were derived from activity measurements [3,4]. In the present study we additionally introduce similarly defined efficiency parameters, which are derived from the X-ray scattering data and quantify the protective effects of additives against radiation-induced structural changes (aggregation, fragmentation). This approach enables the convenient comparison of additives with respect to their efficiencies to modulate functional and structural effects of radiation damage. We investigated the correlations between various functional parameters, structural parameters, and their interrelationships. Based on the correlations of the efficiency parameters various features of the action of the additives can be unveiled. Our results indicate a distinct correlation of primary and post-irradiation inactivation. Additionally, correlations of primary inactivation and different sorts of structural alterations could be deduced. There is a striking similarity of the radioprotective efficiency of various groups of additives against both structural and functional damages. This follows impressively from cumulative indices for the protective power of additives, which can be derived from various combinations of efficiency parameters.

[1] Durchschlag, H., Zipper, P.: Proc. 6th Tihany Symp. on Radiat. Chem., Balatonszéplak 1986, pp. 835-842, Akadêmiai Kiadó, Budapest 1987.
[2] Zipper, P., Durchschlag, H., Gatterer, H.G., Kriechbaum, M., Wilfing, R.: Proc. 6th Tihany Symp. on Radiat. Chem., Balatonszéplak 1986, pp. 797-801, Akadémiai Kiadó, Budapest 1987.
[3] Durchschlag, H., Zipper, P.: FEBS Lett. 237, 208-212 (1988).
[4] Durchschlag, H., Zipper, P.: Z. Naturforsch., in press.
[5] Zipper, P., Durchschlag, H.: cf. separate abstract.

NUCLEAR ACCIDENT DOSIMETRY IN VIEW OF RECENT ADVANCES IN MATHEMATICAL MODELING OF ACUTE RADIATION EFFECTS

I. Dvornik and S. Miljanić
Ruđer Bošković Institute
YU 41000 Zagreb, P.O. Box 1016, Yugoslavia

Exposure to ionizing radiation in case of nuclear accidents or catastrophic events is always characterized by nonuniform distribution of dose within the body of exposed persons. The nature of the event and the geometry of exposure cannot be known in advance. The problem of diagnosis of radiation injury and the prognosis of the severity of acute radiation sickness (ARS) can be solved by adequate personal dosimetry if the dose-effect relation is known. We shortly describe the recently published mathematical models (Gozembuk and Keirim-Markus, 1988) of different types of ARS. For the first time they make possible the comparatively accurate quantitative prognosis for exposures to gamma rays and neutrons with any type of dose distribution to critical organs (hematopoietic tissue, small intestine, skin). For some typical gamma and gamma plus neutron radiation fields we have calculated the dose distributions and related accute effects showing possible relations between the dose measured at the body surface and the ARS. Therefrom we deduce criteria for the optimization of nuclear accident dosimetry (NAD), both for the basic system of personal NAD, and for complete dosimetric characterization of accidents.

Reference:

1. Gozembuk, V.L., Keirim-Markus, I.B.: "Dozimetritcheskie kriterii tjazhesti ostrogo oblutchenija tcheloveka" ("Dosimetric Criteria of the Severity of Acute Exposure of Man"), Energoatomizdat, Moscow, 1988 (in russ.).

POSSIBLE MECHANISM OF RADIATION THERMAL CONVERSIONS IN INORGANIC SYSTEMS.

Egorov G.B., Arshakuni R.G., Pirogov F.V., Chibisov N.P.,
Kapralova R.M., Oganesyan P.L., Panin Yu.A., Snegirev V.E.

Proceding from theory of defect formation in a solid an interpretation of the phenomena of intensification of high-temperature chemical conversions in a number of inorganic systems during their irradiation with high intensive electron fluxes produced by high-power accelerators is given. The intensification phenomena are observed during experiments. The intensification process becomes apparent when equal levels of chemical conversions are reached at temperatures which are tens and even hundreeds degrees lower at usial heating with similar rates (the exposure time being the same).

A possible mechanism concept of radiation thermal (RT) conversions is assumed. The mechanism satisfactorily interprets the above-mentioned nonleanerity of relation ship between the process rate and the exposure rate. The nonlinearity is experimentally oserved as well. It is stated that at high dose rate, along with generaltive - recombination aggregation of defects resulting in phase transition intensification, additional intensification of phisico-chemical conversions is possible because of defect clustering cherged differently. Large needle-shaped crystal of calcium oxyorthosilicate observed against substantial number of small ones produced during the radiation-thermal synthesis of portland-cement clinker are indicative of it. Quantitative assessment of relations obtained in application to certain inorganic systems provides a good basis for designing radiation-chemestry systems and equipment having commercial-scale electron accelerators.

INVESTIGATION OF FORMATION AND GAMMA RADIATION EFFECT OF CERIUM /III/ AMPICILLIN COMPLEX

Mohamed M. El-Desseuky[x] - Abd-El-Klah A. El-Tavil[xx]

[x] Military Technical College, Kobry El Kobbah, Cairo, Egypt
[xx] Military Central Lab. for Medical Analysis, Kobry El Kobbah, Cairo, Egypt

Abstract

The complex of cerium /III/ and ampicillin has been investigated spectrophotometrically. The effects of pH and molar ratio of ampicillin to cerium /III/ on the formation of complex were studied. The stability constants of the formed complex K at different pH values as well as the dissociation constand K_2 of ampicillin were determined.

Gamma radiolysis of cerium /III/ - ampicillin complex at doses from 20 - 100 Gy using ^{137}Cs source at ph 5 , 7 , and 9 was studied. The IR + UV spectra as well as the variations in pH before and after their radiolysis were executed.

Results showed that the formed cerium /III/ ampicillin complex was more stable against decomposition by gamma radiation than ampicillin only. This result is important for future radiation technology of ampicillin.

Moreover, the results proved the posibility of a new utilization of ampicillin for internal radioactive decontamination of human beings from some radioactive lanthanide elements like cerium. These dangerous radioactive elements are usually formed in nuclear accidents.

GAMMA RADIATION STUDIES ON CIS,BUTADIENE RUBBER REINFORCED WITH SHORT ORGANIC FIBRES

By

A.A. EL MILIGY, E.M. ABDEL-BARY*, M.M. ABDEL-AZIZ
AND M.M. SHAKER

National Centre For Radiation Research And Technology
AEA, Nasr City, Cairo, EGYPT
*Chemistry Department, Faculty of Science
Mansoura University, Mansoura, EGYPT

Short organic fibres, namely, polyetheleneterphthate, (PET), and poly-p-phenyleneterephthalamide, (PPTA) were utilized in this study as a main reinforcing component when preparing cis,butadiene rubber composites. The obtained composites were also loaded with (HAF) carbon black. Composites containing 30 phr HAF carbon black and PET ranging between 5 to 25 phr were subjected to gamma radiation doses between 5 and 25 Mrad. Same range of irradiation dose was used for composites containing 50 phr of HAF carbon black and either 10 or 20 phr of (PPTA) Also, the effect of coupling agents namely, reasorcinonl and hexamethlenetetramine was followed up. Mechanical, physico-chemical and thermal characteristics of prepared composites were carried out as a function of concentration of reinfrocing short fibers as well as radiation exposure dose. The obtained results were evaluated and showed an enhancement in properties of prepared composites.

LOW-TEMPERATURE RADIATION-INDUCED PROCESSES IN POLYETHYLENE IRRADIATED AT 10 - 20 K

V.I.Feldman, S.M.Borzov, F.F.Sukhov, N.A.Slovokhotova
Karpov Institute of Physical Chemistry
ul. Obukha,10 - 103064, Moscow, USSR.

The problem of localization of primary radiation events and transport of charge,excitation and active species in heterogenious systems is concerned with the very nature of the radiolysis of polymers.Low-temperature radiation-induced processes occuring under the conditions of extremely reduced molecular motion seem to be of considerable interest for radiation chemistry as well as for investigation of low-temperature dinamics of polymers. In present paper we report the results of extensive studies of stabilization and reactions of active species in polyethylene of different structure and morphology irradiated at 10-20 K by means of ESR and IR spectroscopy.

The polymer samples investigated were low density polyethylene (LDPE), high density polyethylene (HDPE), polyethylene with extended chain crystals(ECC PE) and perdeuteropolyethylene(DPE). Irradiation of the samples with fast electrons and spectroscopic measurements were carried out in original homemade cryostats.

The principal feature of low-temperature radiation-induced processes is inhomogenious spatial distribution of primary radiolysis products. Alkyl radicals in polyethylene irradiated at 10-20 K are trapped mainly as correlated radical pairs, which recombine efficiently even below 100 K. It was shown that the change in the spatial distribution of alkyl radicals upon post-irradiation UV-photolysis of the sample had a pronounced effect on their subsequent thermal decay.

Analysis of experimental results makes us conclude that a very specific low-temperature reaction - selective intra-chain recombination of radical pairs (proceeding, probably,via tunnel mechanism) took place in crystalline region of HDPE and ECC PE. Activation of radical decay reaction at ca.65 K is probably due to low-temperature phase transition in polymer crystal.Generally speaking,anomalous morphology effect is observed for radical decay below 100 K:in contrast with classic viewpoint,decay in crystalline region is more effective then that in amorphous region. Regularity of crystalline region facilitates one-dimensional tunnel H-atom migration along the polymer chain.In contrast with this "ordered" situation, the possibility of three-dimensional migration cannot be neglected in irregular amorphous region of the polymer,and recombination probability decreases markedly. Another marked feature of low-temperature radical reactions in irradiated polyethylene is anomalous isotopic effect:radical decay in DPE is more effective than that in LDPE.We can tentatively explain this effect by the difference in the primary radical spatial distribution in LDPE and DPE due to the specific mechanism of radical pair formation.

The effects of crystal size, structural and radiation-induced defects on the processes of charge, excitation and radical site transport are discussed.

CORRELATION BETWEEN CHEMICAL NATURE AND SWELLING PROPERTIES OF SOME COPOLYMERIC GELS

Maria Fiti, M. Dragusin
Institute of Atomic Physics, Bucharest - Romania

Our previous investigations concerning the influence of chemical composition of swelling aqueous medium on the bulk properties of hydrophylic gels of acrylamide-acrylic acid copolymers pointed out new and unexpected correlations.

In this work attention is foccused on the physical and swelling properties of some new amphyphylic gels, consisting in copolymers of tho monomers, one hydrophylic and another hydrophobic. This class of gels is of great interest because it enlarges considerably the chemical composition structures and respectively the properties of these new materials.

The results concerning the preparations by radioinduced polymerisation and crosslinking acrylic and methacrylic acid with dibutylmaleate copolymers are obtained.

A preliminary study of the swelling properties of these copolymers pointed out new and interesting results, which will allow a systematic investigation with the aim to clarify how the properties of network structure of the gel are influenced by the chemical composition of the copolymer containing basic unit of different polarity.

PILOT SCALE PLANT FOR IRRADIATION PRODUCTION OF POLYACRYLAMIDE

Maria Fiti; C. Ponta; Rodica Moraru; M. Dragusin; C. Floru
INSTITUTE FOR ATOMIC PHYSICS - BUCHAREST ROMANIA

The hydrosoluble polymers and copolymers of acrylamide have a wide variety of applications, being prepared in industry by all classical methods.

The radiation technology, of great promise, consist of the following important steps:

Monomer solution preparation	Irradiation polymerisation	Chopping gel-plates

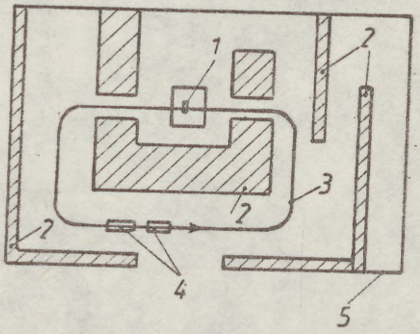
It is a continous, reliable process leading to high quality products. The main features of this process are:

1. A very small radiation dose is used: 0.2-0.5 kGy, with high conversion: ≥98 %, at high monomer concentration, ≥40 %.
2. Composition of monomer solution, i.e. special additives, and irradiation conditions keep under control all process.
3. The polymerisation reaction heat and disolved oxygen are turned into promoting agents of the process.
4. The versatility of the technology permits directing the characteristics of final products. A typical polymer has:

$$M_w \geq 5.10^6 \quad ; \quad k_H \leq 0.4 \quad ; \quad \text{anionicity: 0-30 \%}$$

5. The final product (wet gel grains) is twice cheaper than dry product.

Specifical components of the pilot plant are presented in the figure:



1. ^{60}Co - 10kCi
2. Biological protection
3. Conveyor
4. Irradiation trays
5. Interlocked entrance

The maximum pilot capacity is 200-300 t/year, depending on the impurities level in raw materials.

RADIATION CHEMISTRY OF CYCLO-OCTANE: EFFECT OF IONIZATION DENSITY

G.Földiák, M.Roder, L.Wojnárovits

Institute of Isotopes of the Hungarian Academy of Sciences
H-1525 Budapest, P.O. Box 77, Hungary

The chemistry of cyclo-octane is influenced by the strain in the molecule which results in an excess energy of formation of about 42 kJ mol^{-1}. This strain is mainly due to repulsive interactions of the hydrogen atoms in the molecule.

As a result of dehydrogenation in cyclo-octane, *cis*-cyclo-octene, bicyclo-octyl and a cross-bridged compound, pentalane (bicyclo[3.3.0]octane) are formed with G-values of 3.2, 1.9 and 0.6 in γ-radiolysis by ^{60}Co (LET ≈ 0.2 eV/nm) and 2.2, 1.1 and 0.16 in α-radiolysis by ^{210}Po (LET ≈ 200 eV/nm).

Studying the effect of iodine in liquid hydrocarbon solutions in γ-radiolysis the G-values both of the cyclo-octene and bicyclo-octyl decrease close to the limiting values at as low a concentration of iodine as 1 mM. In the α-radiolysis, however, the effect of iodine is smaller and approaches the limiting values in the case of cyclooctene at 2-3 mM and of bicyclo-octyl at about 20 mM.

Some results got at the α-radiolysis of cyclo-octane are significantly different from that of cyclohexane, e.g. the limiting values of cyclo-octene are ca 50% higher. The reason lies in the different ratio of some reaction steps in the high LET tracks of cyclo-octane and cyclohexane interpreted by the higher viscosity and hence by the smaller diffusivity in C_8 than in C_6 hydrocarbons.

THE INFLUENCE OF DOSE AND DOSE RATE ON METABOLIC PROCESSES IN MAIZE ROOTS STUDIED BY PHOSPHORUS NMR SPECTROSCOPY

U.Franck
Central Institute for Isotope and Radiation Research,
Academy of Sciences
G.D.R. Permoserstr. 15, Leipzig, DDR-7050

Phosphorus NMR is a powerful tool which sheds some light into the metabolic processes involving soluble phosphorus compounds. This method allows to quantify the damage evoked by ionizing radiation already 48 h after irradiation. The measurements were provided after reactivation of the samples hermetically closed over 10 h. The compartimentation of free inorganic phosphate between cytoplasma and vacuole seems to be useful for the evaluation of the degree of pertubation of the metabolic processes in plants.
An inverse dose rate effect was observed.

RADIATION-INDUCED GRAFTING OF STYRENE ONTO CHLORINATED PVC FOR PLASTIC FOAMS

K. Friese, F. Tannert

Academy of Sciences of the G.D.R., Central Institute of Isotope and Radiation Research, Permoserstraße 15, DDR-7050 Leipzig

The grafting of styrene onto chlorinated PVC is carried out in an aqueous dispersion. Polymer and monomer are stirred in water at elevated temperature till the styrene is absorbed by the polymer quantitatively. After that the grafting is initiated by γ-irradiation. Granules of this graft polymer are impregnated with pentane in an autoclave at temperatures between 100 and 120 °C. After heating with superheated steam we obtained a plastic foam like polystyrene with a density lower than 0,05 g/cm^3.

The foam shows good mechanical stability and is not inflammable.

CONTROL OF ELECTRICAL DYNAMIC CHARACTERISTICS OF INSULATED GATE BIPOLAR TRANSISTORS BY ELECTRON IRRADIATION.

[1]F. Frisina, [1]N. Tavolo, [1]C.G. Aniceto, and [2]P.G. Fuochi

[1]SGS-Thomson Microelectronics, Stradale Primosole 50, Catania, Italy
[2]Istituto F.R.A.E.-C.N.R., via de' Castagnoli 1, Bologna, Italy

Since 1982 interest has developed in Italy in the application of high-energy electron irradiation for control of carrier lifetime in power silicon devices. Research has been conducted extending its scale from an experimental basis to a semi-industrial level on fast recovery diodes, fast switching silicon controlled rectifiers, gate turn-off thyristors and power MOSFETs [1-3]. The good results so far obtained have induced the SGS-Thomson Microelectronics Company to apply this technology to a new family of bipolar devices, the so-called insulated gate bipolar transistors (IGBT). The electron irradiation process, using a 12 MeV linear accelerator, has been optimized in order to have a homogeneous distribution of the radiation all over the surface of large area silicon wafers (12 cm diameter). IGBT devices ($BV_{CES} > 500$ V) have been irradiated in order to enhance their switching speed, by controlling the fall time (t_f) and to increase their latch-up current. The irradiation dose was in the range $8x10^4 - 2.8x10^5$ Gy ($1.9x10^{14} - 6.5x10^{14}$ e^-cm^{-2}). Latch-up current density higher than 8 A/mm^2 and reduction of the collector current fall time from over 9 µs to less than 400 ns have been achieved with a dose of $2.8x10^5$ Gy. No appreciable negative effects on the leakage current has been observed whilst an increase in the V_{CEsat} together with a decrease in the thresold voltage has been measured. This reduction in the thresold voltage, caused by the damage produced in the gate oxide of the device by electron irradiation, has been removed by an appropriate annealing at temperature > 315°C without significant variations of carrier lifetime, parameter strictly connected to the fall time [4]. Long-term stability of the irradiated devices has been checked by annealing them for 1000 h at the maximum operation junction temperature (150°C). No variations of the electrical characteristics has been observed. A set of curves related to the variations of the key electrical parameters vs. irradiation dose has been obtained. From these data a trade-off curve has been derived that allows to obtain the best performances of the device (Fig. 1).

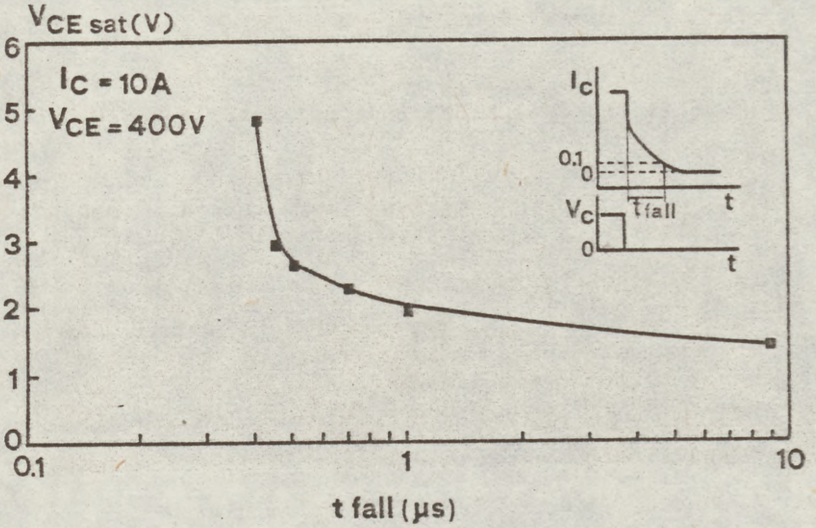


Fig. 1. - Trade-off curve between forward voltage drop and collector current fall time for n-channel IGBT after irradiation and annealing treatments.

REFERENCES:

1. - P.G. Fuochi, P.G. Di Marco, G.M. Bisio, E. Di Zitti, B. Passerini, S. Tenconi, and M. Zambelli, Alta Frequenza, 55, 47 (1986).
2. - P.G. Fuochi, B. Passerini, F. Fasce, and M. Zambelli, ESSDERC 89, Berlin, 1989, p. 539.
3. - F. Frisina, N. Tavolo, E. Gombia, R. Mosca, P. Chirco, and P.G. Fuochi, Radiat. Phys. Chem., 35, 500 (1990).
4. - D.S. Kuo, J.Y. Choi, D. Giandomenico, C. Hu, S.P. Sapp, K.A. Sassaman, and R. Bregar, IEEE Electron Device Lett., EDL-6, 211-214 (1985).

STABILIZATION OF ENHANCED RADIOSENSITIVITY OF BACILLUS MEGATERIUM SPORES BY PRETREATMENT OF THIOL REACTIVE AGENTS

L. G. Gazsó, L. +Wojnárovits, A. Dám, M. Rétlaki

OSSKI, Budapest 1221. Pentz K. u. 5.
+Institute of Isotopes, 1525. Budapest Konkoly-Thege u. 29-33.

Glutathione (GSH) can be depleted either by thiol reactive agents such as di-ethyl-maleate (DEM) and diamide (DAM) or chemically blocking GSH biosynthesis using BSO.
10 mmol/l DEM and 1 mmol/l DAM were applied during cultivation and preparation of Bacillus megaterium spores. Radiation responses of treated spores were investigated at various oxygen concentrations (0.7% O_2, 1.4% O_2, 1.89% O_2 in N_2 and pure nitrogen). DEM and DAM pretreatment did not influence the radiosensitivity of spores under anoxic conditions but an enhanced radiation response could be obtained when oxygen was present. (indirect effect)
Increasing oxygen concentration resulted a decreased radiation sensitization. Enhanced radiation response was seen when DEM and DAM were present during irradiation under both hypoxic and anoxic conditions (direct effect).
These data indicate that DEM and DAM have two different modes of action and only one of them is due to the reduction of GSH level.
In pulse radiolysis experiments (carried out with optical detection) di-ethyl-maleate was found to scavenge hydrated electrons with a rate parameter of $(2.2 \pm 0.5) . 10^{10}$ mol^{-1} dm^3 s^{-1}. In the reaction DEM electron adduct is formed that below pH 5 quickly protonates.
Electron transfer from thymine radical anion was also demonstrated ($k \approx 6.10^8$ mol^{-1} dm^3 s^{-1}).
These reactions indicate that DEM in biological systems can also accept electrons (free electrons or electrons attached to biopolymers) delivered by ionizing radiations and therefore can act as an electron affinic radiation sensitizer.

THE EFFECT OF GAMMA IRRADIATION ON THE THERMAL EXPANSION BEHAVIOUR OF ORIENTED POLYPROPYLENE

L. Godjevargov[*], Lj. Novaković and D. Kostoski

[*]Higher Institute of Chemical Technology,
8010 Bourgas, Bulgaria

"Boris Kidrič" Institute of NUclear Sciences, Vinča
P.O. Box 522, 11001 Belgrade, Yugoslavia

Quenched and air-cooled samples of oriented polypropylene have been irradiated to 250 kGy absorbed dose at a dose rate of 10 kGy/hour in the presence of air at room temperature, using a Co-60 gamma ray source. The orientation has been performed by drawing at 383 K. The thermal expansion behaviour of irradiated and unirradiated samples has been measured by Thermo-mechanical Analyser over the temperature range 223 to 293 K. For high draw samples the thermal expansion coefficient in the axial direction is negative and increases in magnitude with increasing temperature.

For low draw samples in axial direction and for all drawn samples in the transverse direction the thermal expansion coefficient is positive and increases in magnitude with increasing temperature. The effect of absorbed dose on the thermal expansion behaviour has been related to the effects of degradation and crosslinking of gamma irradiated oriented polypropylene.

RADIATION-CHEMICAL PLANT GAMMATOK-100

V.A.Goldin V.A.Rudoy P.Yu.Lushchik

Karpov Institute of Physical Chemistry
Moscow, USSR

The first two radiation-chemical plants type Gammatok-100 were put into operation in the USSR.

Plants type Gammatok-100 were designed on the base of the rational designs which have been tested at the prototype - the pilot plant PXYHD - 20 000 /1/ operated in the Karpov Institute of Physical Chemistry since 1966 as well as calculations and experimental investigations of coaxial-cylindrical units /2/.

Possible field of application of such plants is environmental protection measures conserning the portable water treatment and sewage disinfection /3/.

These plants can be used for the development of the following process chain:"ampule investigations ↔ pilot-plant experiments ↔ pilot-commercial production". This ensures wide experimental means for investigation of dependences of speeds of radiation-chemical conversions of liquid and solid-phase objects at different rates of absorbed doses, temperatures and pressures. Units of different designs (in particular, mixing and coaxial cylindrical ones) and volumes (40 and 400 litres) allow to study influence of streem of liquids (laminar, transient or turbulent flow) and feed of liquid for radioactive irradiation (uninterrupted and periodical) to radiation-technology characteristies of plant (uniformity of irradiation, output, efficiency et al.).

References

1. Goldin V.A., Mendelson E.L., Breger A.Kh. et al. - Proceedings of the Third Tihany Symposium on Radjation Chemistry 1972.
2. Mendelson E.L., Goldin V.A., Breger A.Kh. - Proceedings of the 5th Tihany Symp. on Radiation Chemistry, 1982.
3. Рябченко В.А., Арбузова Н.А., Гольдин В.А., Мендельсон Э.Л.- Санитария и гигиена, I976, № 5, с.I03.

RADIATION MODIFICATION OF THE FILLED MIXTURES BASED ON ETHYLENE POLYMERS AND COPOLYMERS

T.N. Gordiichuk, V.P. Gordienko

L.V. Pisarzevsky Institute of Physical Chemistry of the
Ukrainian SSR Akademy of Science, Prospekt Nauki, 31,
252028 Kiev, USSR

The effect of ionizing radiation on the mixtures of polyethylene and ethylene-vinylacetate copolymer (EVAC), with the additional fillers was investigated in our work. The mixtire of low pressure polyethylene and ethylene-vinylacetate copolymers containing 5,5; 11,2; 19,8; 30,5 weight % of vinylacetate was used as a researsh sample. EVAC was added into polyethylene until EVAC constitued 30 % of the total weight. Aerosyl A-175 and needle-looking form mullite ($Al_2O_3:2SiO_2$) was used as a filler. The resulting sample underwent radiation in the electron accelerator, as well as on the gamma-source Co^{60} in absorbtion integral doze of 0,02 - 1,0 MGy.

In the process of investigation the effect of uncompatible polyolefins compatibility increasing as a result of crosslinking between various macromolekules was revealed under ionizing radiation. This provided a bettering physical-mechanical properties of these compositions.

It was found that the presence of mullite in the polyethylene mixtures made possible the increasing of the free radical consentration in the polymer over unfilled mixtures and filled-with-aerosyl mixtures. Owing to the change of the free radical concentration during irradiation of polymer composition with an inorganic fillers occurs the posibility to regulate the level of radiation-chemical crosslinking of such materials.

The optimized concentration levels of the most effective influense of the fillers and polymer additions in the radiation modification structure and properties of the composition based on polyethylene, was determined. It is found that the introduction the filler into the polymer composition and their following irradiation yeilds a bettering of the physical-mecanical properties of the composite materials in a wide temperature range.

THE RADIATION DESTRUCTION OF BLOOD COMPARTIBLE BLOCKCOPOLYMERS

B.A.Gorelik, I.M.Rajgorodsky, O.G.Fortunatov, E.Sh.Goldberg, A.V.Tresvova, O.V.Dubinskaya, E.V.Zolotova, G.I.Listvoib.

All Union Medical Polymers Institute, USSR, Moscow

In this work we submit the last results on the investigation of radiation destruction of siloxane containing polymers and polyurethanes possessing the high blood compatibility.

During studing of radiation oxidation it was shown that the process of destruction is localized in soft polyether block and does not depend on the MW of soft block when the MW is more than 600. The introduction into the system of hard isocyanate block can results in significant increase of polymer stability. The degree of stabilization very depends upon the nature of hard block. In the case of phenylcontaining isocyanate hard block the evident increase of radiation stability is observed if compared with polyether oligomer. The introducing of cycloolefinic hard block into polyurethane does not give rise to enhance of radiation stability. In presented work the main reason of mentioned phenomenon is discussed in terms of inter and intra molecular mechanism of stabilization. During the investigation of polysiloxane containing polymers by means of GPC method the changes of MW and MWD of irradiated polymers were studied. We carried out our experiments with usage of copolymers with various ratious of soft and hard blocks concentrations. It was shown that the process of radiation destruction is localized in hard polycarbonate block and on phase boundary between soft and hard blocks.

On this work the attempt was done of studing the influence of supermolecular structure of blockcopolymers on their radiation resistance.

ON THE VERY EARLY ($< 10^{-10}$s) DECAY KINETICS OF HYDRATED ELECTRONS PRODUCED BY PHOTOLYSIS*

by

Thomas Goulet and Jean-Paul Jay-Gerin

Groupe du Conseil de Recherches Médicales du Canada en Sciences des Radiations et Département de médecine nucléaire et de radiobiologie, Faculté de médecine, Université de Sherbrooke, Sherbrooke, Québec, Canada J1H 5N4.

ABSTRACT

We investigate the possible reactions that hydrated electrons (e^-_{aq}) can undergo in pure deaerated water immediately after they have been created by photoionization. Under the usual conditions where the concentration of e^-_{aq} is small, the two main competing reactions are:

$$e^-_{aq} + OH^{\cdot} \longrightarrow OH^- \tag{1}$$

and

$$e^-_{aq} + H_3O^+ \longrightarrow H_2O + H^{\cdot} . \tag{2}$$

Using Monte Carlo simulation techniques, we study the effect of the initial spatial distribution of species on the decay kinetics of e^-_{aq}. We also examine the effect of the Coulombic attraction on reaction (2) and treat the case where this last reaction is not considered to be diffusion-controlled.

From comparisons between the calculations and the results of femtosecond photoionization experiments, we obtain some information on the initial spatial distribution of hydrated electrons. This, in turn, brings a better understanding of the behaviour of the electrons prior to their hydration.

---

* Work supported by the Medical Research Council of Canada and by the ministère de l'Enseignement supérieur et de la Science du Québec.

Picosecond pulse radiolysis. The use of the laser photoionization effect to study the mechanism of fast radiation chemical processes.

V.M.Grigoryants. Institute of Chemical Kinetics and
Combustion, Novosibirsk-90, 630090, USSR

The time profiles of fluorescence of BBOT liquid solutions in decalin during irradiation by fast electron pulses of picosecond duration were studied in our experiments. It is possible to achieve the good agreement betweem the observed and the theoretically calculated profiles of fluorescence in subnanosecond range in the assumption of the energy transfer from highly excited solvent molecules to additive molecules.

To verify this assumption we have made an attempt to include the additional channel of the decomposition of highly excited states due to their photoionization by infrared light of powerful laser.

The instant laser heating of the sample was taken into account by the comparision of the obtained time profiles of fluorescence in the case when the laser pulse preceeds to the electron one with the situation of their overlap.

The experimentally observed decrease of the fluorescence intensity and also the shortening of its time parameters (Fig. 1) may serve as an evidence in favor of the model employed. The measured cross-section of photoionization is $10^{-19} - 10^{-18}$ cm^2 by the order of magnitude.

The decrease of fluorescence intensity during the laser irradiation has not been found in isooctane. Moreover, some increase of the signal was observed (Fig.2).

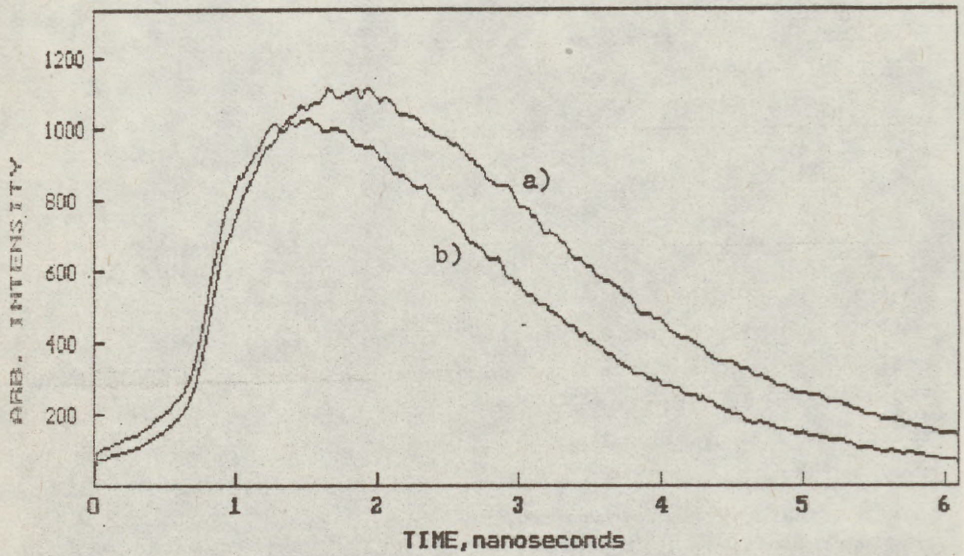


Figure 1. The time profiles of Fluorescence $5\cdot10^{-4}$ M BBOT in trans-decalin at room temperature: a)lazer off, b) lazer on (100-150 mDJ in light pulse).

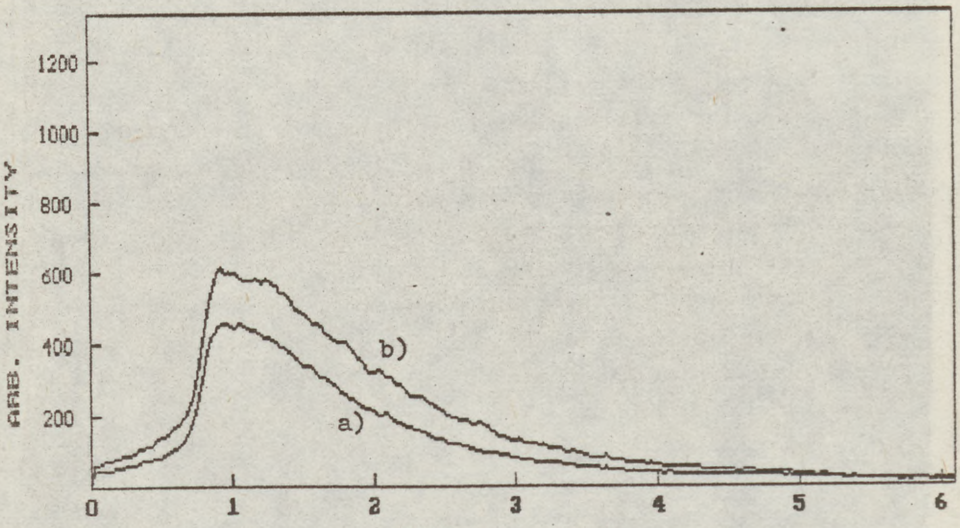


Figure 2. The time profiles of fluorescence 5.10^{-4} M BBOT in isooctane at room temperature: a) lazer off, b) lazer on (100-150 mDJ in light pulse).

RADIATION CHEMICAL STABILITY OF CROWN ETHERS COMPLEXES WITH METAL SALTS IN THE SOLID STATE

Grigor´yev E.I., Ivakina L.V., Mikhalitsina O.V.,
Myasoedova T.G., Storogenko P.A., Trakhtenberg L.I.
NIFHI im. L.Karpova, MHTI im. D. Mendeleeva, GNIIHTEOS, Moscow
Adress: ul. Obukha 10, 103064, Moscow K-64, USSR

Molecular adducts of magnesium, calcium, iron chlorides with oxoligandes have been synthesized and the effect of γ-radiation on them has been studied too.

ESR spectra of stabilized paramagnetic centers in the complexes $MgCl_2 18C6$, $MgCl_2 \cdot 15C5$, $CaCl_2 \cdot 18C6$, $CaCl_2 \cdot 15C5$, $FeCl_3$ 18C6, $FeCl_2 \cdot 15C5$ have been measured. ESR spectra of radicals of crown ether complexes with Mg^{2+} and Ca^{2+} ions have essential differences. It has been shown that the temperature relation of spectrum linewidth and lineshape is intricate and individual for every complex substance. So the spectrum of $CaCl_2 \cdot 18C6$ adduct radical at T=77 K involves 7 broadened lines hyperfine structure, which transform under effect of temperature to triplet first and then to quartet of lines of about equal intensities. Paramagnetic species of 4 types are observed in complexes of $MgCl_2$. Apparently it shows that metal ion has different effect on crown ether radiolysis mechanism and polyether ligande nature has some influence too. These conclusions are confirmed with the values of radiation chemical yield of radicals (G_R) which are 5.7; 3.3; 8.1; 3.1 radical/100ev for 18C6, $MgCl_2 \cdot 18C6$, $CaCl_2 \cdot 18C6$, $CaCl_2 \cdot 15C5$ respectively. In forming complex with metal a macrocyclic polyether undergoes conformation restructuring which apparently has an effect on radiation chemical conversion mechanism.

Spectra of unirradiated complexes $FeCl_3$ with 18C6 and 15C5 are singlet of $g=2.0281$, $\Delta H^{pp}=782$ Gs and $g=2.0090$, $\Delta H^{pp}=118$ Gs respectively. This difference in magnetic parameters is probably dependent on variation in the symmetry of ligande sphere crystalline field. Sufficient variation in linewidth and the presence of atomic hydrogen ($\Delta H=499.8$ Gs) are observed for irradiated samples of $FeCl_3$ crownates.

Thus radiation chemical processes in crown ether molecular complexes are influenced by polyether ligande sphere and complex cation nature to a great measure.

RA

Gr

Ka

DC
(3-
3,
by
rac
of
bor
re-
app
H-a
in
tes

the
sub
int
of
enc
sub

of
sor
ben
grea
unde

ring
The
enla

RADIATION-CHEMICAL TRANSFORMATION IN SOLID CROWN ETHERS.

Grigoryev E.I., Myasoedova T.G., Nesterov S.V., Trakhtenberg L.I.

Karpov Institute of Physical Chemistry, Moscow, USSR.

γ-radiolysis products of crown ethers (CE) 15C5, 18C6, DCH18C6, DB18C6, B12C4, DB24C8 and alkylsubstituted DB18C6 (3-metyl(DB18C6), 3,12-dymetyl(DB18C6), 3-butyl(DB18C6), 3,12-dybutyl(DB18C6), 3,12-dyhexyl(DB18C6)) have been studied by the methods of gas chromatography and ESR. The complex character of ESR spectra indicates that several primary processes of radiolysis take place simultaneously. The breaking of C-O bond of polyether ring, accompanied by the intramolecular re-arrangement and by the formation of aldehyde groups, is apparently the main process of the CE radiolysis. Besides, H-atom may drop from $-CH_2-$ groups of the polyether ring, and in case of alkylsubstituted DB18C6 - from the alkyl substitutes.

Radiation stability of the studied crown ethers depends on the size of the polyether ring and on the character of the substitutes. The introduction of cyclohexyl and benzene groups into the ring of 18C6 causes significant reduction in the yield of radicals GR and molecular hydrogen, which proves the efficiency of intramolecular energy transfer from macrocycle to the substitute.

The increase of polyether ring size leads to the increase of the yield of GR. It connects both with reduction of the absorbed energy transfer efficiency from the macrocycle to the benzen substitutes (in case of DB24C8 and DB18C6) and with the greater probability of several C_2H_4O fragments elimination under CE decay.

The introduction of the alkyl substitutes into polyether ring of DB18C6 results in reduction of radiation stability. The increase of the number of alkyl groups and the chain length enlarge the yield Gr.

INTERMEDIATE RADIOLYSIS PRODUCTS OF DMSO AND DMSO/H_2O SOLUTIONS OF SOME SOLUTES

J. Grodkowski, D. Pogocki and M. Tomasik
Institute of Nuclear Chemistry and Technology
Dorodna 16, 03-195 Warszawa, Poland

Dimethylsulfoxide (DMSO) is an aprotic, polar solvent completely miscible with water. Solvent and biological properties of DMSO and its binary mixture with water have initiated radiolysis studies concerning reducing and oxidizing species. In the present work we discuss the scavenging of oxidizing products by appropriate solutes in DMSO and DMSO/H_2O mixtures.

The pulse radiolysis experiments have been carried out using 2.5 μs and 5.5 μs, 10 MeV electron pulses from linear electron accelerator LAE 13/9. The following systems have been investigated: DMSO/KBr, DMSO/KBr/CCl_4, DMSO/CCl_4,DMSO/CBr_4, DMSO/H_2O/KCNS, solutions saturated with Ar, O_2 or N_2O. $Br_2^{-\cdot}$ and $(CNS)_2^{-\cdot}$ radicals were used to calculate G values of oxidizing species. The highest yield approaching 6.9 was observed in the DMSO/KBr/CCl_4/O_2 system. In the appropriate conditions there were also postulated the existence of DMSO·Cl and DMSO·Br intermediate adducts characterized by absorption in the range 380-450 nm. In the DMSO/H_2O/KCNS solutions, depending on the DMSO content, there were observed: 1-concurrence between DMSO and KCNS on OH radicals and 2-for concentration of DMSO 0.2M an increase of $(CNS)_2^{-\cdot}$ formation. The results cannot be interpreted in terms of direct effect, possible explanation could be scavenging of OH radical precursor. This work has been supported by The Program CPBP 01.19. 02.07.

EFFECT OF HYDROGEN BONDING IN BENZOIC ACID ON FREE RADICAL REACTIONS IN FBX SYSTEM OVER PROLONGED PERIODS

B.L. GUPTA

Division of Radiological Protection, Bhabha Atomic Research Centre, Trombay.
Bombay - 400 085, India.

ABSTRACT

The paper describes the studies on slow thermal and radiolytic oxidation of ferrous ions in the FBX system (1). Benzoic acid increases the radiolytic oxidation of ferrous ions through a chain reaction. The xylenol orange is more effective than ferric ions in reducing this chain length. Benzoic acid increases the rate of thermal oxidation of ferrous ions by xylenol orange also. Benzoic acid itself without xylenol orange produces thermal oxidation of ferrous ions through a chain reaction. The rate of this oxidation considerably depends on the benzoic acid concentration in the solution. The ferric ions are more effective than xylenol orange in reducing the chain length of thermal oxidation. The long chains are produced at low rates of thermal oxidation only, when the ferric ion concentrations in the solution are low. The thermally excited benzoic acid molecules form free radicals which initiate the chain which is later propagated by the chemically excited benzoic acid molecules. The association of benzoic acid molecules through hydrogen bonding plays an important role in energy transfer processes which lead to free radical formation in the triplet state of benzoic acid. The excitation and emission spectra of benzoic acid change due to the association of molecules. In radiolysis of the FBX system at low dose-rates, the G(Fe^{3+}) values are very high (2) since the chemically excited benzoic acid molecules in free radical reactions initiate and carry the chain. Because of the low concentration of ferric ions, the excited molecules are not quenched. In biological systems also such as in DNA where molecules are connected through hydrogen bonding, chain reactions may be produced due to excited molecules formed in slow thermal and radiolytic reactions. In other words, the radiation effects on biological systems at very low dose-rates may be higher than at acute dose-rates.

REFERENCES

1. B.L. Gupta, Dosimetry in Agriculture, Industry, Biology and Medicine, I.A.E.A. (1973) 421.
2. B.L. Gupta and U. Madhvanath, Int. J. Appl. Radiat. Isot. 12 (1985) 985.

FREE RADICAL SCAVENGER PROPERTIES OF SILYBIN - A NATURAL BIOFLAVONOID DRUG

I. György,[1] A. Blázovics,[2] S. Antus,[3] J. Fehér,[2] and G. Földiák[1]

[1]Institute of Isotopes of the Hungarian Academy of Sciences,
H-1525 Budapest, P. O. Box 77, Hungary

[2]Second Department of Medicine of the Semmelweis Medical
University, Budapest

[3]Department of Organic Chemistry, Technical University,
Budapest

The reactivity of silybin - a natural flavonolignane - the active substance of the liver-protecting drug, Legalon^R (Madaus, Cologne) was investigated in various in vitro free radical generating systems.

Silybin reacts with $^\bullet OH$ radicals with a diffusion controlled reaction rate, $k(^\bullet OH + silybin) = 1.8 \times 10^{10}\ M^{-1}\ s^{-1}$, as established by pulse radiolysis using a competition kinetic method. Various sites of attack on the silybin molecule by $^\bullet OH$ radicals were identified by comparing the transient spectra with those obtained using adequate model compounds. The effect of deprotonation of the polyphenolic type molecule on its reactivity in scavenging electrophilic free radicals was examined (e.g. $^\bullet N_3$, $^\bullet CCl_3O_2$). It is concluded, that oxidising radicals of moderate reactivity exhibit remarkable selectivity in their attack on the phenolic rings and the rate constants strongly depend on the electron-withdrawing/donating properties of the co-substituents.

Free radical chain processes in both enzymic and non-enzymic systems, attended by formation of O_2^-, are inhibited by silybin (xanthine/xanthine oxidase, autooxidation of epinephrine). The effects were compared with the reactions with O_2^- produced by pulse radiolysis.

A possible relation between biological and chemical reactivity of silybin is shortly discussed.

RADIATION INITIATED GRAFTING OF METHYL METHACRYLATE AND METHYLACRYLATE ONTO WOOL

LE HAI, Radiation Chemistry Lab., Nuclear Res. Institute
Dalat, Vietnam and
M.H. RAO, Chemistry Division, Bhabha Atomic Research Centre,
Trombay, Bombay-400 085, India

Abstract

Radiation initiated grafting of Methyl Methacrylate and Methyl Acrylate onto wool fibre /dyed and undved/ has been carried out under variety of conditions. The importance of swelling in obtaining appreciable amounts of grafting has been stressed. The rate of grafting at low dose rate is found to be lesz than that at high dose rate. The percent graft of dyed wool is observed to be less than for undyed wool and these results are explained on the basis of protection offered by moieties of the dye. The graft yield of Methyl Methacrylate is also found to be higher than in the case of Methyl Acrylate and graft rate was increased in the case of mixtured solution of monomer of Methyl Methacrylate and Methyl Acrylate. The efficiency of monomer utilization has been found to be around 52 % at low monomer concentrations, when $CuSO_4$ was used as the scavenger. Reasonable hydrophobicity is achieved in Ca. 81.76 % Methyl Methacrylate grafted undyed wool, 140 % for grafted dyed wool and 160 % mixture of MMA and MA grafted undyed wool.

Experimental

The grafting experiments were carried out in Borsil tubes 16 mm in diameter and 150 mm in length. A weighed wool sample around 0.17 gram, was placed in the tube and 10 ml of methanolic solution of the monomer saturated with $CuSO_4$ was added. All samples are placed in a water bath at 60°C for thrs and then flushing with Argon gas before irradiation. The samples were irradiated in gamma source AEE /Bhabha Atomic Research Centre/ with dose rate of 0.42 and 0.18 Mrad hr, at room temperature. The sample tubes were then immediately opened and the homopolymer in solution was isolated by precipition in methanol and filtering drying. The wool samples were followed by extraction with chloroform for 8hrs and Acetone for 8hrs and then dried to constant weight in vacuo at 60 C. The amounts of grafting and efficiency were calculated in following formular

$$\% \text{ grafting} = \frac{W_1 - W_o}{W_o} \times 100$$

$$\text{and } \% \text{ Efficiency} = \frac{W_1 - W_o}{W_2} \times 100$$

Where W_o, W_1 and W_2 are the weight of the orgiginal of woolen sample, the grafted wool sample after extraction and drying and monomer taken for grafting, respectively.

The moisture absorption of grafted wool sample, a measure of hydrophobicity, was determined on the basis of the gravimetry.

The Main results

Table 1 Percentage of moisture absorption /% M/ by MMA and mixture of MMA and MA grafted wool sample.

Grafted undyed wool with mixture of MMA and MA		Grafted undyed wool with MMA		Grafted dyed wool with MMA	
% Graft	% M	% Graft	% M	% Graft	% M
0.00	16.00	0.00	16.00	0.00	15.00
10.20	14.24	11.85	12.95	17.62	13.91
30.18	13.04	23.64	9.68	59.98	9.10
79.69	9.12	35.15	7.91	142.08	6.63
111.02	9.34	81.76	6.50	208.40	3.00
142.02	7.99	128.50	3.54	218.79	2.00
161.96	7.23	204.68	3.48		
321.96	5.74	208.90	3.00		
325.79	5.76	241.68	2.35		
357.47	5,02	268.64	2.18		
443.18	4.61	304.16	1.96		

References

1. A.A. Armostrong, JR and H.A. Rutherford, Textile Res. J. 33,246 /1963/ Industrial Uses of Large Radiation Sources. Vol.I.IAEA Vienna. 1963,p.257-287.
2. K.N. Rao and M.H. Rao, H.T. Lokhande, N.R. Mody and A.G. Jog, J.Appl. Polym.Sci.Vol. 23,2133 /1979/

3. D.D. Kale and H.T. Lokhande, K.N. Rao and M.H. Rao, J.Apll. Polym.Sci. Vol 19,pp 461 /1975/

4. A. Hebeish, A. Bendak and A. Kantouch, J.Appl.Polym. Sci. 15,2733 /1974/

5. B.N. Misra and K. Mentai, J.Polym.Sci. Chem.Edt.18,1911 /1973/

6. Kozo Arai, Michiharu Negishi, Tashu Tomu Suda and Shinti Arai, J.Appl.Polym.Sci.17, 483 /1973/

7. Bendaka and Hebeish, J.Appl.Polym.Sci.Chem.Edt.11, 3283 /1973/

8. Kozo Arai, Masamichi Shimisu and Machiko Shimada, J.Polym. Sci.Chem.Edt. 11, 3271 /1973/

9. V.Stanett, K. Araki, J.A. Gervasi and SW. Meleskey, J.Polym.Sci. A-3, 3763 /1965/

10. A. Chapiro and V. Stannett. J.Radiat. Isotopes, 8, 164 /1960/

11. M. Kumar and M.H. Rao. Die Angewandte Makromolekulare Chemie 152 /1987/ 133-147 /Nr. 2482/

12. A. Chapiro, Radiat.Chem.Polym.Systems 196 /1961/ Newyork, London.

THERMODYNAMIC RELAXATION AND RADICAL DECAY IN SOLID POLYMERS

P.Hedvig
Research Institute for Plastics
Budapest 1950, Hungary

Thermodynamic(volume) relaxation is known [1] to occur in such solids which are not in thermodynamic equilibrium. Chemical reactions in such states are highly influenced by the process of approaching equilibrium accompanied by large scale molecular rearrangement. This process results in a shift of the relaxation (correlation) time spectrum to longer times. A temperature - jump upward makes the relaxation time spectrum move to the opposite direction resulting in increase of mobility [2].

The aim of the present paper is to study thermodynamic relaxation under such experimental conditions as the decay of free radicals is measured. In order to characterize molecular mobility under non equilibrium conditions results of mechanical stress relaxation experiments are analyzed on the basis of the autocorrelation function $f(\lambda) = \exp\{-(\lambda/\tau)^n\}$, where τ and n are temperature dependent parameters, λ is the effective time of thermodynamic relaxation which depends on the storage time and on an experimental temperature dependent parameter. By an iterative fitting procedure these parameters are determined and the relaxation time distribution calculated.

Using the results of these studies the "stepwise" [3] character of the radical decay in glassy amorphous as well as crystalline polymers can be explained by considering molecular mobilities merely without the need of assuming two different chemical kinetical processes. The initial fast decay is due to the process which makes the relaxation time distribution shift to shorter times accompanied by decreasing density, increasing mobility. This is a thermally activated process with an activation energy in the order of 80 kJ/M/K. After a certain time, depending on the thermal history of the sample, the shift of the relaxation time distribution is reversed, the mobility decreases resulting in slowing down the chemical reaction.

REFERENCES

1 A.J.Kovacs, J.Polymer Sci 30,131, (1958)
2 L.C.E.Struik, Polymer, 29,1347 (1988(
3 V.V.Voevodsky, Proc 1 Tihany Symposium on Radiation Chemistry (ed.J.Dobo) 111, Hungarian Ac. Sci. 1964

MEASUREMENT OF THE RADIATION FIELD OF AN INDUSTRIAL ELECTRON ACCELERATOR

H.-J. Heinrich1), W. Hädrich1), K. Posselt1), F. Lübbe2), U. Jurjanz2), P. Küllig2)

1) Central Institute for Solid State Physics and Materials Research, Academy of Sciences of the GDR, Helmholtzstr. 20, 8027 Dresden, GDR

2) Kabelwerk Nord, 2767 Schwerin-Sacktannen, GDR

The application of a high power accelerator demands measurements for characterization of its field of high energy electrons. Among other things it is important to know the course of the intensity distribution in the scanned electron beam, especially the ranges of homogeneity, the field at the boundaries, the effect of the beam scanning in two directions etc. The measurements were performed at an 1.5 MeV-, 50 kW-electron accelerator, type UW 70, with a double scanning system. For the measurement of the field in the irradiation chamber using a remote controlled conveyor system current density collectors of different types as well as foil dosimeters from polyethylene and blue cellophane were applied. With the aim to improve the total productivity of crosslinking of the PE insulation of cables a special simultaneous irradiation technique is employed. According to this technique several cable lines being independent to each other are arranged in three different irradiation planes. The field distributions measured without and with covered cable lines are discussed and compared with calculated results.

INTERPRETATION OF ELECTRONIC ENERGY TRANSPORT EXPERIMENTS ON A SENSITIZED ORGANIC PHOTOCONDUCTOR

W. Helmstreit

Academy of Sciences of the G.D.R., Central Institute of Isotope and Radiation Research, Permoserstraße 15, DDR-7050 Leipzig

Electronic energy transport was studied in thin layers (thickness 5-10 µm) of a sensitized organic photoconductor. Transient trapping experiments are described in this disordered media by exciton processes.

As indicated by the fluorescence depolarization the migration of excitation energy is fast with respect to the fluorescence lifetime. From these experiments the number of migrational steps is estimated for the different energy transport (Sensitizer S, photoconductor PC):

S --> S, PC --> PC, S --> PC.

KINETICS OF ELECTRON-BEAM EXCITED SPECIES IN RARE GAS / ALKYL - AND SILICON TETRA - FLUORIDE MIXTURES

R. Hermann

Central Institute of Isotope and Radiation Research of the Academy of Sciences of the G.D.R., Permoserstr. 15, 7050 Leipzig, G.D.R.

The evolutions of rare gas monomer and dimer excited state absorptions and emissions were studied in absence and presence of additives where electron irradiation served as source for pulsed excitation of the matrix gases. Quenching dynamics were investigated by decreasing the decay of the excited rare gas transients in dependence of the scavenger concentration. Rates for the energy transfer processes were derived by numeric simulation of the observed rare gas species kinetic behaviour where the rate equation systems were solved by a Runge-Kutta approach. By analyzing the quenching rates in respect to the energy differences of the excited state levels between the rare gas and the admixed fluoride species it was concluded that the energy transfer process is governed by a collision mechanism. Theories of the transfer of electronic excitation energies give only a qualitative description of the experimental data.

As a result of energy transfer the admixed alkyl fluorides decompose mainly in CF_2 and CF_3 radicals and by pulse radiolysis the corresponding emission time profiles were detected. The observed UV-emissions were dominant due to CF_2 transitions and the visible emissions around 600 nm due to CF_3 transitions. In the case of SiF_4 addition decomposition in SiF_2 and SiF_3 radicals was expected and the kinetics as well as the emission spectra of this transitions were investigated. The formation of the radical states will be discussed in respect to the precursers which transfer their excitation energy to the additives and the threshold energies for dissoziation of CF_3H and CF_3D as well as CF_4 and SiF_4. Collision-free fluorescence lifetimes of the excited radical states could be achieved by pressure variation of the pure alkyl fluorides and the pure silicon tetrafluoride. The obtained optical spectra confirmed previous results.

MECHANISM OF REDOX REACTIONS INDUCED BY LIGHT AND ELECTRON PULSE IN SOLUTIONS OF MIXED LIGAND IRON(II) COMPLEX CYANIDES

A. Horváth, J. Szőke
Department of General and Inorganic Chemistry
Veszprém University, H-8201 Veszprém, P.O.Box 158 (Hungary)
L. Wojnárovits
Institute of Isotopes of the Hungarian Academy of Sciences
H-1525 Budapest, P.O.Box 77 (Hungary)

Redox reactions initiated by UV excitation and pulse radiolysis in aqueous solutions of $[Fe(L)(CN)_4]^{2-}$ and $[Fe(L)_2(CN)_2]$ complexes (where L = 2,2'-bipyridine and its derivatives) have been investigated. Hydrated electrons formed in light induced reactions of iron(II) complexes or produced by electron pulse are shown to disappear in a diffusion controlled reaction with $[Fe(L)(CN)_4]^{2-}$ and $[Fe(L)_2(CN)_2]$ complexes to form iron(I) compounds [1]. These reactive intermediates have been characterized by their reactions and visible absorption spectra obtained by time resolved spectroscopy.

Addition of other electron savengers (NO_3^-, MV^{2+}) leads to formation of oxidizing ($\cdot NO_2$) or reducing ($\cdot MV^+$) intermediates. It has been pointed out that $\cdot MV^+$ (methylviologen radical) is also produced by an electron transfer reaction from iron(I) compounds, and disappears in reactions with ground state iron(II) and iron(III) complexes.

Using the established kinetic model the quantum yield of reduced methylviologen $\cdot MV^+$, the energy rich species which can transform the light to chemical energy, can be optimized.

References

[1] A. Horváth and Zs. Uzonyi: Inorg. Chim. Acta, 170 (1990) 1

Synthesis and application of EB-reactive epoxy-acrylate oligomers

A.Ille, T.Czvikovszky, E.Takács, I.Czajlik, E.Banai

Research Institute for Plastics

Budapest, 1950. Hungary

Hygh reactivity oligomers of medium molecular mass are the main components of EB- and UV crosslinked coating systems.

Aliphatic and aromatic epoxy-acrylate oligomers have been synthesised by using different amine catalysts. The progress of oligomer formation as monitored by HPCL will be presented on some example of a multicomponent catalyst systems.

The EB-reactivity of the synthesised epoxy-acrylates was measured under the beam of an ELECTROCURTAIN 170/15/10 LAB VNIT.

The conversion measured by the pendulum hardness of the disappearance of double bounds /detected by IR/ as well.

The aliphatic epoxy-acrylates are more reactive systems, resulting in highly flexible coatings, as compared to the aromatic ones.

RADIATION TECHNOLOGY FOR A CLEANER ENVIRONMENT

Stuart L. Iverson

Radiation Applications Research
Whiteshell Laboratory
AECL Research
Pinawa, Manitoba
CANADA R0E 1L0

There is a growing realization that human civilization cannot continually increase the discharge of pollutants and the intensity of land, water and air use. Significant negative impacts are already being observed on human health and environmental systems in some parts of the world. If living conditions are to improve, particularly in the highly populated but less developed countries, methods of minimizing these impacts must be found. The term "sustainable development" expresses the concept that economic growth can be achieved with controlled environmental impact through the use of improved technology. Our work in Radiation Applications Research suggests that radiation processing is a very clean and energy-efficient technology, and can make an important contribution to sustainable development.

This contribution can be made through various avenues, including improved process efficiency and the reduction of chemical emissions and residues. Ionizing radiation can be used to improve the efficiency of a process by substituting for heat, or by directly producing the desired chemical, microbiological or physiological effect. Radiation curing of advanced composites, such as carbon fibre/epoxy, saves a significant amount of energy compared to heat treatment in an autoclave, while many of the food irradiation applications use the direct effects of radiation to minimize waste and spoilage, thereby improving the overall efficiency of the food production process. Efficiency can also be improved by converting wastes (sewage sludge, straw, stover) into useful materials using radiation as part of a process.

In radiation processing of plastics, chemical emissions are minimized by processing at a lower temperature, and by re-formulating resins with decreased concentrations of volatiles, promoters and catalysts. In biological applications, emissions and residues are avoided by using the direct action of radiation on microbes and insects as a substitute for chemical fumigants or sterilizing agents.

There are also a number of other potential applications that require further research and development. Examples of these are water/liquid waste treatment where work is required to significantly improve process efficiency, recycling (particularly plastics) where innovative processing methods are required, and adhesives where inexpensive radcure systems with little inhibition due to oxygen would significantly expand possible applications.

THE INFLUENCE OF THE TEMPERATURE ON THE CHANGES OCCURING IN THE BLENDS OF POLYETHYLENE WITH ANTIOXIDANTS PHENOLIC TYPE

E. Jaworska, I. Kałuska, G. Strzelczak-Burlińska
and J. Michalik

Institute of Nuclear Chemistry and Technology, Dorodna 16,
03-195 Warsaw, POLAND

The influence of the temperature on the changes in esr spectra of radicals originated from antioxidants phenolic type and their blends with polyethylene has been studied. It was found that in the range of temperatures 77-273 K in pure antioxidants exposed to the ionizing radiation the phenoxyl radicals are formed.
In the case of the polyethylene blend with Irganox 1081 it was observed that at 77 K the phenoxyl radicals are formed which do not change their spectra up to 230 K.
Above that temperature the spectra of alkyl and allyl radicals from polymer appear. The decrease of phenoxyl radicals concentration is interpreted as an effect of grafting phenoxyl radicals to polymer chain.
In the case of the polyethylene blend with Irganox 1010 in the temperature up to 230 K the spectra of alkyl radicals formed from polymer appear. Their concentration decrease with the increase of the temperature.
However, above 250 K the phenoxyl radicals predominate in the spectrum. The changes in the spectra as observed in present study suggest the decay of polymer radicals by their recombination whereas the reactions of phenoxyl radicals with polymer chain are hindered because of the size and steric effect in the molecule of Irganox 1010.

REFERENCE

E. Jaworska, I. Kałuska, G. Strzelczak-Burlińska and J.Michalik "Irradiation of Polyethylene in the Presence of Antioxidants", Radiat. Phys. Chem., in press.

THE REACTION OF α-HYDROXYETHYL RADICAL IN THE RADIOLYSIS OF ETHANOL-INHIBITOR SYSTEM

Wu Jilan and Wei Genshuan
Department of Technical Physics, Peking University
Beijing 100871, P.R.of China

ABSTRACT

THE G-values of the major radiolysis products [H_2, CH_3CHO, $(CH_3CHOH)_2$] of gamma-irradiated liquid ethanol have been determined by using AA(Acryl-acid), St(Styrene) and MPP(4-Methyl-4-Phenyl-2-Pentanone) as inhibitors.

The kinetics of α-hydroxyethyl radical reacting with inhibitors has been investigated.

$$\text{inhib.} + CH_3\dot{C}HOH \xrightarrow{k_6} P$$

$$2\ CH_3\dot{C}HOH \longrightarrow (CH_3CHOH)_2$$

The kinetic equation of α-hydroxyethyl radical reacting with these inhibitors can be described as follows:

$$G' = G_0 - \frac{k_6}{2(k_7)^{1/2}} \left(\frac{G}{\dot{D}K'}\right)^{1/2} [\text{inhib.}]$$

Herein G' is the G value of 2,3-butanediol in the presence of inhibitor, K' is the conversion factor.

Acetaldehyde may come from the fast process in spur but not from the disproportionation of α-hydroxyethyl radical as reported before.

The mechanism of inhibition effect of ethanol by benzene under gamma-irradiation has been discussed.

RADIATION-INDUCED CROSSLINKING OF AROMATIC POLYMERS WITH CARDO GROUP

Xu Jun and Zhang Wanxi
Changchun Institute of Applied Chemistry, Chinese
Academy of Sciences, Changchun 130022, China

Aromatic polymers with cardo group, such as polyetherketone with cardo group(PEK-C) and polyethersulfone with cardo group (PES-C), are a novel engineering plastic with good resistance to high temperature. In this paper, we firstly reported radiation-induced crosslinking of these two polymers.

1. Radiation Crosslinking

It may be expect from the structure of PEK-C and PES-C that they are difficult to crosslink at ambient temperature under irradiation. It was found from the relationship between gel content and radiation dose of PEK-C and PES-C that the crosslinking degree of PEK-C and PES-C are far larger at high temperature than at amibent temperature. The glass transition temperature(Tg) of PEK-C irradiated at high temperature is higher than at room temperature, whose valuc is about 20℃ higher than that (227℃) of unirradiated PEK-C.

2. Estimation of Gelation Dose by Shake-up Peak of XPS

It was found by us that the intensity of shake-up peak of X-ray photoelectron spectroscopy (XPS) for PEK-C and PES-C varies as irradiation dose. The experimental results have shown that relative intensity of shake-up peak of XPS (Ps) (relative area ratio for the shake-up peak with respect to the C_{1s} main peak) decreases with increasing of irradiation dose (R) for PEK-C, and Ps for PES-C increases with increasing of irradiation dose. Ps of crosslinked PEK-C and 1/Ps of crosslinked PES-C were plotted against R and a straight line was obtained (shown in

Figs. 1 and 2), and then make a straight line parallel to the R-axis using Ps value of uncrosslinked samples for PEK-C or 1/Ps for PES-C as the intercept at the Ps or 1/Ps ordinate. The dose corresponding to the intercrossing point of the two straight lines may be considered as the gelation dose (Rg). Rg values obtained by this method are 1.2×10^6(Gy) for PEK-C and 7×10^5(Gy) for PES-C.

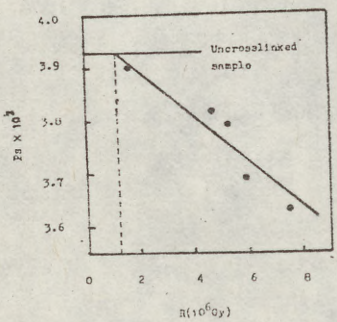


Fig. 1. The relationship between Ps and R of PEK-C.

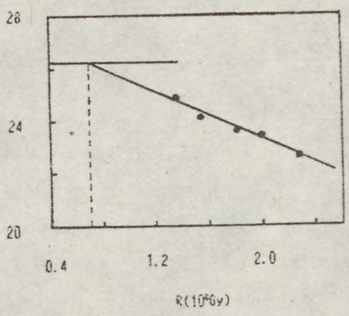


Fig. 2. The relationship between 1/Ps and R of PES-C.

RADIATION INDUCED IRON RELEASE FROM TRANSFERRIN AND ITS EFFECT ON LIPID PEROXIDATION IN LIPOSOMES

R.K. Kale and Sandhya L. Sitasawad

Radiation Biology Laboratory, School of Life Sciences, Jawaharlal Nehru University, New Delhi-110 067, India.

It is now well established that free iron is involved in several degenerative diseases. Free iron ions initiate as well as catalyze a variety of free radical reactions that lead to damage or death of cell (1). *In vivo* most of the iron is bound to proteins and not available to promote deleterious free radical reactions. However, iron-proteins may not withstand all of the insults inflected by nature and man.

The iron used in Life sustaining processes might be potentially harmful if released from proteins (2). Free radicals are considered to be responsible for release of iron. This phenomenon is of paramount importance from the radiation biology point of view. Radiation is mainly detrimental to life due to free radicals generated through indirect effect. However, there is lack of information regarding the radiation mediated iron release from proteins.

Iron salts are absorbed through gut and transported by transferrin. Iron from transferrin enters the various cells for use in synthesizing various proteins (3). Transferrin, therefore, can be one of the major source of iron. A question of paramount importance is whether iron would be available for participation in deleterious effect of radiation.

The release of iron from transferritin was determined by using the iron chelator bathophenanthroline (BPS) as a chromophore. Liposomes were prepared from L-α-phosphatidyl choline.

Radiation induced release of iron from transferrin and its effect on lipid peroxidation was studies after r-irradiation. The released iron was found to stimulate lipid peroxidation. Under anaerobic condition, the iron release was more than aerobic condition. Moreover, iron release was inversely related to dose rate. Catalase, SOD, GSH and peroxidase inhibited iron release but not liposomal lipid peroxidation. The chelates like EDTA, EGTA and ferrozine showed no appreciable change in lipid peroxidation.

The results indicate that transferrin could be one of the sources of iron in event of *in vivo* irradiation. In addition the findings also suggest the involvement of lipid molecules in iron release as well as transferrin dependent lipid peroxidation.

1. Halliwell, B. & Gutteridge J.M.C. (1985) Mol. Asp. Med., 8, 89.
2. Dunford, (1987) Free Radical Biol. Med., 3, 405.
3. Halliwell, B. & Gutteridge, J.M.C. (1989) Free Radical Biol. Med. (Oxford Press).

THE RADIATION CHEMISTRY OF SOME TRANSITION METALS ACETYLACETONATES IN AQUEOUS - ALCOHOLIC SOLUTIONS

E.Kalecińska

Institute of Chemistry, University of Wrocław, Joliot-Curie 14,
50-383 Wrocław, Poland

The radiation-chemical processes of acetylacetonates solutions: $Fe(acac)_3$, $Co(acac)_3$, $Mn(acac)_3$, $Cr(acac)_3$, $Ce(acac)_3$, $Cu(acac)_2$, $Ir(acac)_3$, $Rh(acac)_3$ and $Ru(acac)_3$ in gamma-irradiated liquid methanol and methanol-water mixtures have been studied. It has been shown by pulse radiolysis method that the electron scavenging rate constants are very high: $1.2\ 10^{10}\ M^{-1}s^{-1}$ for $Ru(acac)_3$ and $Rh(acac)_3$ to $9.1\ 10^{9}\ M^{-1}s^{-1}$ for $Ir(acac)_3$. These high rate constants are in contrast with considerably low complex decomposition yields: about 0.1 molecules per 100 eV for $Fe(acac)_3$ and $Ir(acac)_3$ increasing through Co, Cr, Rh and Ru acetylacetonates to the yields equal to 5.6 and 7.0 molecules per 100 eV for $Mn(acac)_3$ and $Cu(acac)_2$, respectively. Exceptional high decomposition yield equal to 16 molecules per 100 eV has been observed for $Ce(acac)_3$ but only in aerated solutions.

The mechanisms of radiation-chemical decomposition of examined acetylacetonates have been discussed. The main role in the decomposition mechanisms play the scavenging of the primary radiolysis products by the acetylacetone ligand and the further transfer of electrons to or from the central metal atom.

$$\mathrm{Me(acac)}_n \xrightarrow{R,\ e^-_{solv}} \mathrm{Me(acac)}_{n-1} + \mathrm{acac} \qquad (1)$$

Such produced metal complex: $Me(acac)_{n-1}$ depending on the stability can by decomposed to the free acetylacetone and solvated metal and/or can be oxidized to the initial complex.
Hence, the different decomposition yields and the strong influence of oxygen have been observed in the examined systems.

RADIATION-CHEMICAL PROCESSES IN SOME AQUEOUS GLASSES

J.Kaleciński

Polish Academy of Sciences, W.Trzebiatowski Institute of Low Temperature and Structure Research, Wrocław, Poland

Rapid cooling of concentrated aqueous solutions of some inorganic compounds like H_3PO_4, H_2SO_4, $Ca(NO_3)_2$, LiCl, $MgCl_2$ and $CaCl_2$ gives good glasses very convenient for optical studies of intermediates occuring as the result of gamma irradiation of these systems. The addition of scavengers of ion-radicals or electrons to the examined systems makes the unique possibility for examination of the processes carried on during the increase of temperature.

In the present paper the yields of intermediates and the processes occuring during the increase of temperature have been examined in the following systems:

a. Concentrated aqueous Li, Mg and Ca chlorides with the presence of Br^-, I^-, SCN^- ions as well as with acetylacetone. The last has been examined in the mixed system: aqueous chlorides - alcohols. As the result of the processes the transients of XCl^- type have been created, where X is the radical from the corresponding scavenger.

b. Concentrated H_3PO_4 and H_2SO_4 with addition of NO_3^- ions. It has been shown that in these systems the reaction:

$$Y + NO_3^- \longrightarrow NO_3 + Y^- \qquad (1)$$

takes place, where Y is the ion-radical from the corresponding acid.

c. Concentrated aqueous chlorides - nitrates. In this system reaction (1) does not occur but only the significant increase of the primary yield of Cl_2^- ion-radicals has been observed.

STRUCTURE AND MOBILITY OF PEROSY RADICALS IN SOLID POLYMERS: POLYETHYLENE AND POLYPROPYLENE

Kashiwabara H., Nagoya Institute of Technology, Showa-ku,
Nagoya 466, Japan

A general rule for analyzing the data of ESR method applied to the study of peroxy radicals in solid polymers will be presented. And the examples of the cases of polyethylene and polypropylene will be discussed.

Also a characteristic consideration on the true activation energy associated with a motional narrowing of the magnetic resonance spectra will be presented. This is based on the fact that a broad distribution of relaxation time must be taken into consideration in the case of solid polymers. The analysis is also applied to the motion associated with a drastic change of ESR spectrum of peroxy radicals in polyethylene observed for ureapolyethylene canal complex.

DETERMINATION OF DIFFUSION COEFFICIENT OF OXYGEN INTO POLYMERS THROUGH POST-IRRADIATION OXYDATION

Y. Katırcıoğlu, Y. Kaptan*, O. Güven

Department of Chemistry and Physics*
Hacettepe University
Beytepe, Ankara, 06532
TURKEY

The Electron Spin Resonance Spectroscopy has been used to follow the kinetics of decay of radicals produced by irradiation with gamma rays in polymers upon exposure to air. The oxygen uptake of gamma irradiated spherical poly(methyl methacrylate), poly(vinyl acetate) and cylindirical poly(methacrylonitril) samples has been determined from the changes in the intensity of some bands in their ESR signal. By using Fick's second law of diffusion, the diffusion coefficient of oxygen into polymers were determined.

The diffusion coefficient of oxygen determined by this technique showed an inverse dependence on dose. The values obtained after correction for dose effects; $D=3.7 \times 10^{-8}$ cm^2/s for PMMA, $D=4.5 \times 10^{-8}$ cm^2/s for PVAc and $D=1.1 \times 10^{-8}$ cm^2/s for PMAN are in very good agreement with the values reported in the literature.

CAROTENOIDS IN IRRADIATED DRY FOODS AND MODEL SYSTEMS

B. Katušin-Ražem, S. Đurić-Bezmalinović, D. Ražem
Ruder Bošković Institute
41000 Zagreb, Yugoslavia

Carotenoids are important as vitamin A precursors, antioxidants and colorants in foods. Food irradiation can jeopardize these functions, so it is important to understand radiation-induced depletion of carotenoids in irradiated foods and factors influencing it.

This paper describes radiation-induced changes of carotenoids in dry carrots, dog-rose hips, egg powder, and a model of egg powder, as measured by spectrophotometry. Carotenoids are relatively stable in irradiated dry foodstuffs in the absence of lipids (carrots and dog-rose hips and mechanical mixture of egg powder components without lipids). If the mixture of model egg powder prepared with the addition of lipids or a natural egg powder were irradiated, the depletion of carotenoids with dose was much stronger and dependent on the availability of oxygen. While in absence of oxygen hydroperoxide formation approached saturation, the decay of carotenoids proceeded with dose in evacuated samples along a single linear curve. In presence of oxygen the formation of hydroperoxides and decay of carotenoids in egg powder are coupled to each other, the corresponding curves looking like mirror images: both are characterized by an induction phase followed by a linear part. Linear decay of carotenoids with dose starts above about 2 kGy. Linear parts extrapolated back to zero dose give the effective concentration of carotenoids as if 35 % higher than the actual one. In model systems, on the other hand, no shoulder was observed on the decay curve of carotenoids, and the decay was a stronger function of dose.

Postirradiation decay of carotenoids in whole egg and egg yolk powder critically depends on the presence of oxygen at the time of irradiation. While the rate of decay in evacuaated samples (to which air was admitted upon irradiation) only weakly depends on the irradiation dose, the rate of carotenoids decay in samples irradiated in equilibrium with air shows an exponential increase with dose.

Carotenoids in dry carrots decreased linearly with time showing no dependence on radiation dose.

IDENTIFICATION OF IRRADIATED DRY FOODS CONTAINING LIPIDS

B. Katušin-Ražem, B. Mihaljević, D. Ražem
Ruder Bošković Institute
41000 Zagreb, Yugoslavia

Radiation-induced chemical changes in foods are generally very small at the usual processing doses. A possible use of lipid hydroperoxides (LOOH) as indicators of irradiation is described for egg and milk powder, soya flour and hazelnuts as representatives of various classes of lipid containing foods. A sensitive and reproducible spectrophotometric method based on ferric thiocyanate, as modified in our laboratory, was applied. Lowest detection limit of 0.05 mmol LOOH per kg lipid could be measured. The formation of LOOH with dose and the influence of age, irradiation conditions and storage time on LOOH were investigated in various batches by the same producer, as well as in samples supplied by various producers. Background levels of LOOH in all unirradiated materials were established.

Hydroperoxides produced in all irradiated materials decay with time, except in milk powder, where a strong postirradiation increase was observed first, followed by a decrease. Nevertheless, after a twelve months' storage it was still possible unambigously to identify samples irradiated with 1 kGy. In whole egg and egg yolk powder, after an initially fast decay, the level of LOOH continued to decrease by the first-order decay. Nevertheless, after a six months' storage it was still possible unambigously to identify samples irradiated with 2 kGy. Alternative methods of generation of LOOH in egg powder were investigated, as well as possible methods of destroying it after irradiation. Keeping egg powder at an elevated temperature for an extended period of time or boiling in water proved unsuccessful in either generating or destroying LOOH.

The level of LOOH in soya flour reached the background level in less than 3 months after irradiation. The level of LOOH in hazelnuts induced by the dose of 1 kGy was low,but an unambigous identification was still possible after six months' storage at 8°C in dark.

Radiation-induced peroxidation of lipids is potentially suitable for the identification purposes because many foods contain lipids, irradiations are generally performed in presence of air, and sensitive methods for the measurement of lipid oxidation are available.

RADIATION-HETEROGENEOUS PROCESS APPLICATION FOR INCREASING OF EFFICIENCY OF SEWAGE WATER TREATMENT

Knakninov V.V., Rjazantzev A.A., Najdanov O.D.

Institute of Natural Sciences, Buryat Branch of the Siberian Department of the Academy of Sciences of the USSR, Ulan-Ude, U.S.S.R.

Radiation treatment of sewage water has great opportunities to work out a wide range of pfoblems such as the oxidation of the organic and inorganic substances including biologically non-decomposive and strongly toxic. A high degree of treatment by the given method is achieved at high exposure dose, owing to which this method is rather expensive.

One of the ways of increasing of the sewage water treatment efficience may be a combination of the radiation-chemical method with the oxidative catalysis.

There are some experimental data in this work on the radiation-catalytic seware water treatment of the sulphate cellulose production as well as the data on the oxidation of the model solution of sodium sulphide. Researches have been carried out on the ULY-6 type electrous accelerator with the energy range from 0,5 to 2 MeV. The stable products of radiolysis have been studied by methods of chromatography and spectroscopy. The dependence of the oxidation depth of sulfur compounds on the exposure dose, type of catalyzer and adsorbent has been determined. Solution aeration during radiation process promotes more complete oxidation of the sulfur-containing components of sewage water, decreasing chemical oxygen consumption and pH, and for the sodium sulphide solutions in the end it brings to sulphate formation.

The mechanism of the adsorbtion-catalytic process worhing under quich electrons influence has been discussed.

The conclusion about the efficiency of the complex method of the radiation treatment of sewage water has been drawn on the basis of the given researches.

THE INVESTIGATION OF POLYMERIZATION-DEPOLYMERISATION EQUILIBRIUM AT γ-IRRADIATION OF POLYMETHYLMETHACRYLATE

S.Kilichev, U,N.Musaev, A.Karimov, Tashent State University, Chemical Department, 700095, Tashent, Vyzgorodok, USSR.

In this work the processes of polymerization-depolymerization equilibrium under γ-irradiation were investigated. Intensive decreasing of seen under the small dosage of irradiation (up to 10-20 Mrad). The reaction of depolymerisation follows simultaneously with the radiational depolymerization reaction of the permanent monomer in polymethylmethacrylate under increasing the dosage of irradiation from 20 and above.

The constants of the reaction additional polymerization were calculated and it was found the equation which permitted to calculate the rapid change of the concentration of methylmethacrylate in the process of γ-irradiation of polymethylmethylacrylate in a wide doze interval.

EFFECT OF 3-AMINOBENZAMIDE ON X-IRRADIATED CHO CELLS REPLICATING IN MEDIUM CONTAINING 5-BROMODEOXYURIDINE

Kirillova T.V., Seregina T.B., Spivak I.M.

Institute of Cytology, Acad.Sci.USSR, Leningrad

In order to obtain more information about the involvement of poly(ADP-ribosyl)ation (ADP-R) during DNA repair, studies have been performed using the ADP-R inhibitor 3-aminobenzamide (3AB). In present paper a possible role of ADP-R in repair processes on cellular and molecular levels in X-irradiated CHO K1 cells, cultivated with 5-bromodeoxyuridine (BDU-cells) has been studied.

It has been shown that:
1. 3AB, 6 mM, in CHO K1 cells, irradiated with X-rays in a dose of 5 Gr, leads to a) a decrease in cell survival; b) a decreased efficiency of the recovery of the DNA single-strand breaks, evaluated by sedimentation in alkaline sucrose density; c) an increase in S- and G_2-delays while progressing through the cell cycle, evaluated by flow cytometry. 2. While noneffective in the normal CHO K1 cells, 3AB is effective in unirradiated BDU-cells (BDU, 10 mkM): a) cell survival is reduced; b) G_2-delay appears. 3. 3AB has been much more effective in X-irradiated BDU-cells while progressing through a cell cycle; G_2-delay is significantly increased, this increase depending on 3AB treatment: 5 times increase for the treatment during the first and two first cell cycles and 2 times during the second cycle only.

Data obtained point to the involvement of ADP-ribosylation in a repair activity of the cell. ADP-ribosylation may be involved in keeping a normal chromatine structure, necessary for effective DNA replication.

FORMATION OF 3-ELECTRON BONDED INTERMOLECULAR AND INTRAMOLECULAR S-CENTERED SPECIES IN THE PULSE RADIOLYSIS OF DIETHYL DITHIO CARBAMATE AND DISULFIRAM

K. Kishore and P.N. Moorthy
Applied Chemistry Division, Bhabha Atomic Reasearch Centre
Trombay, Bombay-400085, India

ABSTRACT

Diethyl dithiocarbamate(RS^-) is an antioxidant and a radioprotective agent and disulfiram(RSSR), is its oxidation product. Pulse radiolysis studies of these compounds have shown that the one electron oxidation of RS^- leads to the formation of a dimer anion radical of the type $[RS\therefore SR]^-$ having absorption in the visible region with λ_m at 570 nm. The one electron oxidation can be brought about by $^\bullet OH$, $Br_2^{-\bullet}$, $N_3^\bullet$, $I_2^{-\bullet}$ etc. and the resulting radical is rather unreactive which may explain its radioprotective effect. The same species is also produced by the reaction of e_{aq}^- with disulfiram. Such a 3-electron bonded species is similar to the one observed in the case of $^\bullet OH$ radical reaction with thiols(RSH)(1) and is attributed to the inter-molecular interaction between the initial $RS^\bullet$ radical and the parent compound RS^-.

One electron oxidation of disulfiram with $Br_2^{\bullet -}$ gave a transient absorption with λ_m at 490 nm which could be attributed to the formation of intra-molecular 3-electron bonded species of the type $[RS\overset{\therefore}{-}SR]^+$ reported earlier in the case of one electron oxidation of alkyl disulfides. However in this case the bond is $2\sigma/2\pi/1\pi^*$(2) whereas in the case of $[RS\therefore SR]^-$ species it is $2\sigma/1\sigma^*$(3) bond. $^\bullet OH$ radical reaction with disulfiram did not lead to such a transient. The transient produced in this case had very weak absorption in the uv region. Even $\dot{N}_3$ radicals did not oxidize disulfiram. The oxidation potential of this compound is inferred to be between 1.3-1.7V vs NHE.

REFERENCES

1. M.Z. Hoffman and E. Hayon, J. Phys. Chem. 77, 990 (1973).
2. K.-D. Asmus, in "Radioprotectors and Anticarcinogens"(O.F. Nygaard and M.G. Simic, eds.), p.23. Academic Press, New York, 1984.
3. K.-D. Asmus, Acc. Chem. Res. 12, 436 (1979).

CALIBRATION OF FRICKE DOSIMETRY BY WATER CALORIMETRY

Norman V. Klassen, Ken R. Shortt and Carl K. Ross
Division of Physics, National Research Council of Canada
Ottawa, Ontario, Canada, K1A 0R6

The Fricke dosimeter has a long tradition in radiation chemistry. Its mechanism is well understood, allowing it to be used as a diagnostic tool in radiation chemistry as well as a dosimeter. The increasing emphasis on absorbed dose to water by standards labs, especially for high energy photons, necessitates a fresh look at the Fricke dosimeter as a standard. It makes it important to know the value of $G\epsilon(Fe^{3+})$ for a wide range of photon and electron energies and to place realistic uncertainties on those values.

The large uncertainty associated with the determination of the dose to water obtained using graphite calorimetry (estimated to be 2% for high energy photons) encouraged efforts to make measurements directly in water. We have developed a standard for absorbed dose to water for 20 MV photons based on water calorimetry. The accuracy of water calorimetry is strongly related to the understanding of the radiation chemistry which takes place in the water, or the dilute aqueous solutions, present in the calorimeter. By using a variety of aqueous solutions in our calorimeter, and by comparing the results to computer simulations, we believe that we can measure the absorbed dose to water to within an uncertainty of ±0.6%. We chose the Fricke dosimeter as a transfer standard and calibrated it using our water calorimeter. We measured $G\epsilon(Fe^{3+}) = 3.505(\pm 0.021) \times 10^{-3}\ l\ cm^{-1}\ J^{-1}$ for Fricke containing NaCl and irradiated and read at 25°C.

The most reliable values of $G\epsilon(Fe^{3+})$ have been determined by graphite calorimetry or by fully stopping a beam of electrons of known energy and current in Fricke solution. In 1979, Svensson and Brahme (Svensson H. and Brahme A., Acta Radiol. Oncol., **1979**, *18*, 326) evaluated measurements of $G\epsilon(Fe^{3+})$ made using electron beams and recommended a value of $3.515(\pm 0.024) \times 10^{-3}\ l\ cm^{-1}\ J^{-1}$. More recent, as well as the older determinations of $G\epsilon(Fe^{3+})$ will be reviewed in the light of our new calibration.

Application of electron beam - chemical curing process for the production of composite electroinsulating materials

Authers : Kopchjonov V.I.,Ogonkov V.G.,Shic V.B.
Grozdov A.G.,Tevlin A.B.,Kovalenko V.Ja.

Currently world's production of various insulating materials(laminates, incl. copper-clad laminates , varnished fabrics, prepregs, glass-mica materials,composites based on polymer films etc.) for electrical engineering, machinebuilding and electronics amounts to thousands tonns.

Application of e-beam - chemical curing for this purposes helps to avoid some disadvantages of the traditional methods.

The most important problem in this context is development of special thermosetting binders without organic solvents, capable of complete or partial curing under the influence of accelerated electrons.

It is proposed for the production of laminates and clad laminates to use a binder capable of being cured by two following mechanisms: radical polymerisation at the irradiation stage and polyconnection at the pressing stage. Composition of radiation cured part includes diluents - monomers as well as various reaction capable unsaturated olygomers (polyesters, acrilated epoxy resins,acril-urethans)

It is possible to make necessary corrections of some properties of the final product by introduction into the composition of different olygomers. Thermosetting component of the binders includes epoxy olygomer with preliminary added hardener. In order to avoid stickage of prepregs it is possible to use hard epoxy resins or products of their modifications.

A special line is used for the production of materials. This process line consisits of transport system,unit for impregnating (varnishing) of glass-fabric (polymer film) with a binder, unit for doubling(buildup) of layers and curing with accelerated electron beam with energy of 200-550 keV.

Application of electron beam - chemical curing process provides production of insulating materials with technical properties being in accordance with standard specifications.

The process as well provides for the decrease of production cost based on energy saving, smaller working area , decrease of maintenance expenses and expenses for the measures necessary for enviroment protection.

Relationship between the radiation chemical processes and the applicability of the ethanol-monochlorobenzene solution

A.Kovács, L.Wojnárovits, G.Földiák

The radiation chemical processes, taking place in the ethanol-monochlorobenzene solution have been studied by means of electron pulse, as well as gamma radiolysis. The optical absorption spectra of the solution and its components were taken after the 2.6 μs electron pulse both in aerated and dearated solutions. The formation of HCl, which is used to determine the absorbed dose, was studied by using thymolsulphonphthalein indicator by means of 80 ns pulses. The yields of benzene, hydrochloric acid and some dimer products were determined by gamma radiolysis.

The effect of light and temperature on the yield of HCl was also investigated and relationship between the radiation chemical processes and practical applicability of the ECB solution was established.

Radiation chemistry of halogenphenol novolacs

R. Kunze +), M. Wäsche +), A. Lippitz +), I. v. Lampe ++)

+) Zentralinstitut für physikalische Chemie, AdW der DDR, 1199
Berlin, Rudower Chaussee 5

++) Zentralinstitut für organische Chemie, AdW der DDR, 1199
Berlin, Rudower Chaussee 5

Halogenphenol novolacs are an interesting group of polymers for microlithography. This paper presents results of the radiation chemistry of 4-halogenphenol novolacs after irradiation with Al K_α - X-ray and low energy argon ions (E = 1 keV). Furthermore, it is reported on the reactions of these polymers in an oxygen plasma environment.

The effects of there processes are observed by monotoring the variation in the XPS-spectra.
As for the irradiation, the XPS results revealed a crosslinking mechanism in the halogenphenol novolacs via halogen elimination. The halogen elimination increased in the order fluorine, chlorine, bromine and iodine in correspondence with the decrease of the dissoziation energies of the C-halogen bonds.

The etching rates were measured in a diode-etching reactor, which allows both reactive ion etching and plasma etching. It was found that the novolacs containing iodine showed a high resistance to the oxygen plasma in comparison with the other polymers. The XPS-studies indicated that the oxygen plasma converts the iodo substituents to iodine oxides, and this iodine oxide layer is responsible for the high plasma resistance, i.e. the small etching rate.

COMBINED EFFECT OF IRRADIATION AND DIELECTRIC HEATING ON CHEMICAL PROPERTIES OF SOYBEANS(POSTER)

N.D.Lam; J.Beczner and I.F.Kiss
Central Food Research Institute
1o22 Budapest,Herman Ottó u.15

The gamma-irradiation with o, 6, 1o, 2o kGy dose and dielectric heating at 27,12 MHz with 9o and 1o5 ^{0}C were applied.Irradiation alone did not affect on trypsin inhibitor activity (TIA) in soybeans.

A low inactivation (5,21%) was observed az 2o kGy. In contrast,TIA rapidly decreased by increasing the dielectric heat - treatment temperature : 16,78% inactivation at 9o^{0}C and 32,26% at 1o5^{0}C. The inactivation in combined treatment proceeds more rapidly. Corresponding values at 9o and 1o5^{0} C are 37,66 and 64,44% respectively when the samples were preirradiated at 1o kGy. These results and additional data of the second experiment, illustrate the complementary effect of heating and irradiation in inactivating soybean trypsin inhibitors.

The Response Surface Analysis (RSA) was used to study the effect of two variables, dose of irradiation (o,5,1o, 15 and 2o kGy), dielectric heating temperature(95, 1oo, 1o5, 11o and 115^{0}C) on TIA, lipoxygenase (LOX) activity and nitrogen solubility (NSI). Response surfaces were represented mathematically by regression equations which showed that the irradiation did not contribute to inactivation of LOX and NSI by dielectric heating. The highest inactivation of TIA was observed at 1o kGy plus 11o^{0}C which could be reached with dielectric treatment only at 12o ^{0}C.

THE RADIOLYSIS OF CYCLOHEXANE WITH ^{4}He IONS

Jay A. LaVerne and Robert H. Schuler
Radiation Laboratory, University of Notre Dame, Notre Dame, IN, 46556, USA
Gabor Foldiak
Institute of Isotopes, Hungarian Academy of Sciences, Budapest, Hungary

The role of cyclohexyl radicals in the radiolysis of cyclohexane has been studied. Neat solutions and solutions with added iodine have been irradiated with ^{60}Co gamma rays and with helium ions of 5 MeV (LET = 90 eV/nm) to 20 MeV (LET = 30 eV/nm). The yields of cyclohexene, bicyclohexane and cyclohexyl iodide have been determined at very low doses using gas chromatographic-mass spectrometric techniques. Gamma radiolysis studies show that the yields of cyclohexene and bicyclohexane decrease from 3.12 and 1.76 molecules/100 eV to 1.74 and 0.27 molecules/100 eV, respectively, with the addition of 0.1 mM iodine. With 10 MeV helium ions, the addition of 0.1 mM iodine there is a much smaller decrease in the yields of cyclohexene and bicyclohexane, from 2.25 and 1.10 molecules/100 eV to 1.93 and 0.79 molecules/100 eV, respectively. The lifetime of the cyclohexyl radical is about 1 μs at this concentration of iodine and the results suggest that the radical combination processes are largely complete in helium ion tracks. The yield of cyclohexyl iodide does not increase with further addition of iodine in gamma radiolysis which could be due to the interference of iodine with precursors to the cyclohexyl radical. Cyclohexyl iodine yields increase with increasing iodine concentration using 10 MeV helium ions which is expected since the iodine can scavenge more radicals from the track before they recombine. Iodine apparently does not significantly interfere with ionic processes in the tracks of heavy ions. The yields of cyclohexene and bicyclohexane decrease with increasing iodine concentration and at 40 mM they appear to reach the limiting values of 0.48 and 0.20 molecules/100 eV, respectively, for gamma rays and 0.61 and 0.30 molecules/100 eV, respectively, with 10 MeV helium ions. The similarity in yields for the two types of radiation suggests that the production of cyclohexene and bicyclohexane can occur to a minor extent via processes not involving radical precursors. At 40mM of iodine the lifetime of the cyclohexyl radical is about 2 ns and most cyclohexyl radicals should be scavenged. There is probably a minor, fast ionic process for the production of some of the observed cyclohexene and bicyclohexane.

GENERAL PROPERTIES OF DOMESTIC RADIOCHROMIC DYE FILM ELECTRON DOSIMETERS*

Chen Lishu, Wang Lianyan, Wen Youqin
Institute of Atomic Energy, Beijing, People's Republic of China

ABSTRACTS

Owing to the limited range, scatter and absorbed characteristics of electron beams passing through material, moreover the definite volume of most common dosimeters and varying radiation field of electron accelerators, this dosimetry becomes a much more complex problem. All things considered the research project has established a system for routine measurement of electron doses and has brought about a complete experimental approach for high-dose dosimetry. The system consists of five parts : the radiochromic dye thin films, a thickness gauge, irradiation equipment, radiation fields and a standard instrument for calibration.

Some general characteristics of the domestic PR-CN(PVB) electron dosimeters have been determined and the results obtained are as follows :

(1) The optical absorption spectra have an absorption maxima at the wavelength about 550 nm. The half-width of the peaks is about 74 nm.

(2) The background optical density per unit thickness follows a lognomal distributions. The median(50%) reading is 0.52 O.D./mm.

(3) The median spread of the responses to identical doses is 2.8%.

(4) A good linear relationship exists between the change in optical densities per unit thickness and electron absorbed doses in the range of 0.5 to 120 kGy.

(5) A linear increase in the optical densities with temperature during irradiation can be characterised by a positive temperature coefficient of about +0.5% per centigrade degree in the renge of 5-50°C.

(6) The effect of storage conditions indoor on the background and responses of the dosimeters irradiated would not appear if the dosimeters were stored in a desiccator and wrapped in a sealed plastic package.

(7) After 12 hours or post-irradiation heating treatment for 10 min under the temperature of 60-65°C, all colour centres have already arrived at a stable value.

(8) The distributions of the background have decided the lowest detectable limit value of decades Gy estimated for electron doses.

(9) The effect of various light exposure has been carried out especially.

Reference:W.L.Mclaughlin et.al., Rad.Phys.Chem.,V.14,p.535 1979.

---

* Supported by the IAEA under the research Contract No. 4236/RB.

RADIOPROTECTIVE EFECTS OF DIMETHYL SULFOXIDE IN TWO BIOLOGICAL SYSTEMS

Nélida L. del Mastro, Dulcila M.L. Bernardes &
Anna Lúcia C. H. Villavicencio

COMISSÃO NACIONAL DE ENERGIA NUCLEAR - SP
INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES
Caixa Postal 11049 - Pinheiros
05499 - São Paulo - BRAZIL

Some chemicals are known to offer protection to "in vivo" or "in vitro" systems exposed to gamma radiation. Dimethyl sulphoxide (DMSO) is a well-known chemical protector against radiation damage for bacteria as well as mammalian cells grown in vitro (Chapman et al., 1973, Radiat. Res. 56:291-306). The present study was conducted: a) to confirm data from others (Ashwood-Smith, 1961, Int. J.Radiat. Biol. 3:41-48) describing a radioprotective capacity of DMSO in mice; b) to establish whether this protective behavior could be evidenced in an in vitro chemical system utilizing bovine crystalin proteins as target. Heterozigous female albino mice were used for the 30-day-survival studies after 9 Gy ^{60}Co gamma irradiation (dose rate: 4.5 Gy/min) injected 1 h prior with 2000 mg/kg DMSO intraperitoneally. Total body weight curves during the same period were also analysed. For the molecular level studies 1 M DMSO was added to a series of aqueous protein solutions (previously extracted from bovine lens) and 10 min later irradiated with 5,000; 10,000; 15,000; 20,000 and 25,000 Gy ^{60}Co (average dose rate 14 Gy/min). After irradiation, spectrophotometric reading at 600 nm and free thiol group determinations were performed in order to evaluate the radiation-induced modifications. DMSO was able to protect against the increase of turbidity of the solutions produced by irradiation, as well as the radiation-induced augmentation of free sulphydrylic groups. The results shown that this chemical provided a significant amount of protection preventing lethality in mice following gamma radiation exposures in the range expected to inhibit the functional capacity of the hematopoietic system and gastrointestinal tract. Nevertheless, mechanisms of the protective action have not been established. Our results could substantiate the generalized version of the oxygen-fixation hypothesis (Alexander, 1962, Trans. N. Y. Acad. Sci 24:966-978). Moreover, the sulfonyl peroxyl radical and its suggested high reactivity (Sevilla et al, 1990, Int. J. Radiat. Biol. 57: 65-81) may be of significance to interpret our data on the interaction of DMSO with biological thiols.

THE EFFECT OF IRRADIATION ON THE DYNAMIC MECHANICAL PROPERTIES OF BLENDS OF LDPS AND PS

M. Mateev, Plovdiv University, 4000 Plovdiv
M. Nikolova, Scientific and Ind. Enterprise of Electron
Processing of Materials 34, 3-20 Str. 1324 Sofia

Blends of low density polyethylene /LDPE/ and polystyrene /PS/ have been investigated. Two types of experiments have been carried out. One series comprises mixing of PS with irradiated LDPE. The doses in this case are below the gel point for the LDPE. Plates have been prepared from the mixture by compression moulding, and their dynamic mechanical properties have been studied. In a second series, PS and LDPE have been mixed and the plates, prepared from the mixture in the same manner, have been irradiated to various doses. In both cases irradiation has taken place in air, in a ^{60}Co source with a dose rate of 0,33 Mrad/h. The tensile strength, the elongation at break and the tensile modulus have been tested on a Zwick dynamometer.

It has been established, that thedynamic mechanical parameters are very sensitive to the concentration of LDPE in the first series, and less sensitive to the irradiation dose. There is an increase in the compatibility of the blends with the increase of the dose, and the concentration of LDPE is responsible for the resulting properties of the blends. In the second series of experiments, the influence of the irradiation dose on the properties of the blends in very strong. It increases with the increase of the LDPE concentration. The results are explained by the radiation crosslinking of LDPE and the intensified interphase interaction with the PS domains.

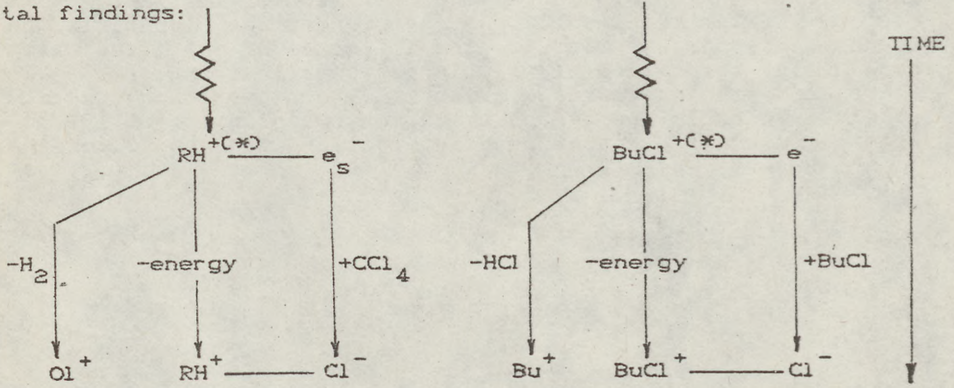
FRAGMENTATION OF RADICAL CATIONS IN LIQUIDS

R. Mehnert
Central Institute of Isotope and Radiation Research of Academy of
Sciences of the G.D.R., Permoserstraße 15, Leipzig, DDR-7050

After electron-pulse irradiation of liquids such as alkanes or butylchloride parent as well as fragment radical cations are observed by optical absorption spectroscopy. The fragment radical cations are of olefinic nature formed (mainly) by H_2 or HCl elimination.

From the coexistence of parent and fragment cations in the time scale of pico- and nanoseconds it is concluded that fragmentation of vibrationally excited parent radical cations takes plase. If vibrational energy relaxation is competing with fragmentation, parent radical cations can be stabilized.

Experiments are discussed, which were performed in liquid alkanes containing carbon tetrachloride as electron scavenger and in neat liquid n-(s)-butylchloride. The following (simplified) schemes of ion-pair transformation can be used to explain the experimental findings:



Ol^+ = olefinic radical cation, RH^+ = alkane radical cation,
Bu^+ = butene radical cation

The question is further discussed, whether or not a similar simple fragmentation mechanism can be used to explain the coexistence of parent and fragment cations in carbon tetrachloride.

ISOTOPE EFFECTS IN RADIATION-INDUCED DECARBOXYLATION OF SOLID PHENYLALANINE ENANTIOMERS

O. Merwitz, G.H. Schleser
Institut für Chemie, Forschungszentrum Jülich GmbH
Postfach 1913, D-5170 Jülich, Federal Republic of Germany

The radiation-induced decarboxylation of solid phenylalanine-1-^{14}C enantiomers was measured for the first time in 1976 (1). Different $^{14}CO_2$ cleavage yields for D- and L-phenylalanine were reported. Investigations with D- and L-leucine-1-^{14}C showed similar results (2).

To elucidate the reason of this behaviour more profoundly, irradiation experiments were planned by using D- and L-phenylalanine-1-^{13}C. A first step in starting the stable isotope work was the mass-spectrometrical analysis of the $^{13}C/^{12}C$ ratios of non-labeled phenylalanine enantiomers.

These experiments exhibit small yet distinct differences in their isotopic composition. The L-form, the dominant form in nature, has a higher ^{13}C content than the D-form.

The $^{13}C/^{12}C$ ratio of CO_2, cleaved by ^{60}Co-γ-radiation, depends exponentially on the dose and is different from the $^{13}C/^{12}C$ ratio of the non-irradiated phenylalanine enantiomers. The latter indicates the existence of a kinetic isotope effect during decarboxylation.

The results are discussed with respect to the role of isotope effects in asymmetric selection mechanisms.

1. O. Merwitz, Rad. and Environm. Biophys. 13, 63-69 (1976).
2. B. Norden, J.O. Liljenzin, R.K. Tokay, J. Mol. Evol. 21, 364-370 (1985).

RADIATION - INDUCED PEROXIDATION OF LIPIDS IN DRY FOOD COMMODITIES

B. Mihaljević, B. Katušin-Ražem, D. Ražem
Ruđer Bošković Institute
41000 Zagreb, Yugoslavia

Food irradiation has been recognized as an important method for preventing food spoilage and foodborne diseases. In fat containing foods, however, it can bring about undesirable peroxidation of lipids.

This paper describes radiation-induced formation of lipid hydroperoxides in whole egg and egg yolk powder, dry milk, soya flour, hazelnuts and poppy seeds. Various batches by the same producer and samples supplied by various producers were analyzed. Our modification of analytical technique based on spectrophotometry of the coloured complex between thiocyanate ion and ferric ion (produced by oxidation of ferrous ions by hydroperoxides) was applied.

The build up of hydroperoxides with dose depends on the nature of foods, their physical status and age. In egg powders, soya flour and aged dry milk the increase is slow at lower doses, and rises linearly with dose after an induction period (dose) if oxygen is available. The extrapolations of the linear parts of these curves intercept the dose axis at about 2 kGy for egg powder, about 1 kGy for soya flour, and 0.2 kGy for aged dry milk. This is interpreted as the dose required to overcome natural radioprotective capacity. In hazelnuts, fresh dry milk and evacuated egg powder, on the other hand, peroxidation initially increases with dose to approach saturation at higher doses (above 5 kGy). No increase of peroxidation in irradiated poppy seeds was observed.

In practice, decontamination of egg and milk powder would not require doses higher than 3 kGy, while disinfestation requirements for hazelnuts, soya flour and poppy seeds would not exceed 1 kGy. The amount of hydroperoxides formed at these dose levels is neither nutritionally nor toxicologically significant, but nevertheless, it was shown that it can be further reduced by reducing the availability of oxygen, either directly (by evacuation, sealing, etc.), or by increasing the dose rate.

INDUCTION OF SISTER-CHROMATID EXCHANGES IN THE CELLS OF PATIENTS WITH TWO DIFFERENT FORMS OF PREMATURE AGING

Mikhelson V.M., Pleskach N.M., Prokofjeva V.V., Bildin V.N., Barenfeld L.S.

Institute of Cytology, Acad.Sci.USSR, Leningrad

Study of hereditory human syndroms wyth premature aging provides a framework for understanding of the mechanisme of natural aging. In this work the study has been focused on the specificity of radiation-induced damage in the cells derived from patients with two forms of premature aging, progeria and Cockaine's syndrome (CS).

In both types of premature aging cells unlike normal cells there is a high (by a factor of 3) incidence of spontaneous sister chromatid exchanges (SCE). Exposure to ionizing radiation increases significantly the frequency of SCE in both CS and normal lymphocytes while that in progeria lymphocytes does not increas but even somewhat decreases frequency of SCE at a dose range of about 1 Gy. The frequency of SCE increases with dose not reaching however the level available in the cells derived from normal donors all the more that in CS cells. Exposure to 4 J/m^2 of UV light sharply enhances the level of SCE in both CS and normal cells, however does not influence the frequency in progeria cells.

Such a difference in the reaction of chromosomes derived from patients with the two forms of premature aging is accompained by a different radiosensitivity in terms of replicative DNA synthesis. There is radiosensitive DNA synthesis in CS cells as well as in normal cells while that in progeria cells appeared to be radioresistant.

The cause of this difference remains to be established. Now we may only suggest that unlike progeria, CS is not a real disease of premature aging, but only is an imitation of it.

EFFECT OF RADIATION ON FUNCTIONAL ACTIVITY OF NUCLEAR MEMBRANE FROM PREGNANT ANIMALS AND THEIR FETUS.

Mirakhmedov A.K.,Mirkhamidova P.,Shamsutdinova G.T.
Institute of Biochemistry, Uzbek Academy of Sciences
Prospect M.Gorky,56, 700143, Tashkent, USSR.

It has been shown, that in vivo irradiation in the doses of I and 2 Gr caused the changes in nuclei of pregnant animals and their fetus. Rats were irradiated on the 3rd, 13th and 17th day of pregnancy. Investigations were carried out on the 21st day of pregnancy, To study RNA transport, the animals were injected intraperitoneally ^{3}H-orotic acid (50 Cu/100g body weight), and in a 40 minutes they were sacrificed. It has been shown that irradiation caused changes in RNA transport in isolated liver cell nuclei of maternal organism and fetus at all stages of development. The most profound inhibition of RNA transport in isolated liver nuclei of maternal organism and embryo was observed on the 13th and 17th day of pregnancy after total irradiation in the dose of 2 Gr. The irradiation caused the changes in cytochrome-c-oxidase,ATPase,RNAase activity in liver nuclei of embryo and maternal organism. The irradiation in the dose of 2 Gr also caused the profound inhibition of enzymes activities.The most profound inhibition of RNAase, cytochrome-c-oxidase activity was observed on the 13th and 17th day of pregnancy upon the dose of 2 Gr. This dose (2 Gr) decreased cytochrome-c-oxidase activity by 44% on the 3rd day of pregnancy, by 52% on the 13th day, and by 64% on the 17th day. It has been established that cytochrome-c-oxidase, NAD$^+$-cytochrome c-reductase, ATPase and RNAase activity in embryo liver nuclei is more sensitive to the irradiation on the 13th and 17th day of embryonal development.Thus, irradiation caused functional changes in enzymes activities and RNA transport in nuclei of maternal organism and their embryos.

EFFECT OF IONIZING RADIATION ON THE CONTENT OF LIVER MITOCHONDRIA PHODPHOLIPIDS FROM FETUS AND MATERNAL ORGANISM AT DIFFERENT STAGES OF EMBRYONAL DEVELOPMENT.

Mirakhmedov A.K.,Shirinova I.A.,Almatov K.T.,Djuraeva M.M. Institute of Biochemistry, Uzbek Academy of Sciences,Prospect M.Gorky,56,700143,Tashkent,USSR.

It has been established that a single action of ionizing radiation on pregnant rats in the dose of I Gr on the 3rd day of pregnancy caused changes in the content of liver mitochondria phospholipids from fetus and maternal organism.Changes in composition of liver mitochondria membrane phospholipids were of unequivocal character with the exception for phosphatidic acid.The content of phosphatidylcholine decreased by 19 and 13%,of phosphatidylethanolamine by 22 and 36%, of cardiolipin by 23 and 48%, while the minor fractions of phospholipids - phosphatidylserines increased by 34 and 214%, of phosphatidyl inositols by 31 and 63%, and of sphingomyelins by 136 and 86%. Double increase of irradiation dose considerably enhanced the deviation of some phospholipids contents from the standard. Thus, irradiation in the dose of 2 Gr caused I,I7 fold decrease in the level of phosphatidylethanolamine of liver mitochondria from maternal organism, while the level of phosphatidyl inositols, phosphatidic acid and sphingomyelins increased I,I6, I,23 and I,34 times subsequently. At the same time,the level of cardiolipins in fetus liver mitochondria decreased I,II times, while the level of phosphatidylserines and phosphatidylinositols increased I,43 and I,3I times as compared to that after irradiation in the dose of I Gr.

With the development of embryos (on the 13th and 17th day of conception) the deviation in phospholipid content in liver mitochondria from fetus and maternal organism considerably decreased upon the action of ionizing radiation.

Thus, it has been shown that the effect of ioninzing radiation on rats on the 3rd, 13th and 17th day of pregnancy caused the changes in phospholipid content in liver mitochondria from fetus and maternal organism.

RADIATION DAMAGE STUDIES BY ESR SPECTROSCOPY: ELECTRON-LOSS AND - GAIN CENTRES IN HIO_3

Shuddhodan P. Mishra, Nucl. and Rad. Chem.Lab., Dept. of Chem.
Banaras Hindu Univ. Varanasi 221005, India

Salts of non-metal oxyanions have been extensively studied by radiation/hot-atom chemists, and in particular, e.s.r. spectroscopy has been widely used to probe the nature of paramagnetic centres trapped in such solids in poly-cristalline and single crystal states. Informations deduced have greatly helped in the understanding of radiation damage mechanism.

Alkali-metal perchlorates, perbromates and periodates have been studied, and all the expected primary electronloss $/\dot{X}O_4/$ and - gain $/\dot{X}O_4^{2-}/$ species have been reported /1-3/. Similarly, solid state radiolysis of chlorates and bromates have provided good information on the unstable intermediates including $XO_3^{\cdot}$ and $\dot{X}O_3^{2-}$ centres /4/. However, there has been a dearth of such information in iodates. A species described as a iodine atom was trapped in X/γ-irradiated HIO_3/5/, and a comparable species, thought to be $\dot{I}O_3^{2-}$, was formed in γ-irradiated $LiIo_3$ crystals /6/. Both these identifications are ope to question. The former is chemically improbable, whilst the latter is confusing because the data, as reported, give a negative value for the anisotropic coupling, which is quite exceptional, and if correct, probably reflects some form of motional averaging.

In an attempt to resolve the identity of electronloss and - gain species formed as a result of solid state radiolysis /X/ γ-rays/ ond HIO_3, single crystal + poly-crystalline materials were irradiated at R.T. and 77K + resulting paramagnetic species studied by esr spectroscopy. 77K irradiations did not give appreciable concentration of species but warming upto room temperature of such materials or irradiations at room temperature gave clear features for e-loss /HIO$_3^{\dot{+}}$ or IO$_3$ and their breakdown projects/ and e-gain /H$\dot{I}$O$_3^-$ or H/H$^{\dot{+}}$/$\dot{I}$O$_3^-$/ centres. The g-values, the hyperfine coupling constants + possible structures presented and radiation damage mechanism proposed.

References:

1. J.R. Byberg and S.J.K. Jensen, J.Chem.Phys., 52, 5902 /1970/
2. J.R. Bybergy, J.Chem.Phys., 55, 4867 /1971/
3. M.C.R. Symons and S.P. Mishra, J.Chem.Soc./Dalton/, 2183 /1981/
4. S.P. Mishra and M.C.R. Symons, J.Chem.Soc./Faraday 1/, 72, 747 /1976/ and references cited
5. C.E. Bailey, J.Chem.Phys., 59, 1599 /1973/
6. V.O.Martirosyan, M.L.Meilman, I.N.Marov and V.V.Shukov, Phys.Status Solidi, B68, 791 /1975/

RADIATION OF ADSORBED NUCLEOTIDES ON CLAYS

F.G. Mosqueira., G. Albarrán. and A. Negrón-Mendoza.
Instituto de Ciencias Nucleares, U.N.A.M., Circuito Exterior, C.U.
04510-México, D.F., MEXICO.

In this article it is proposed that ionizing radiation from the decay of radioactive elements such as potassium-40, uranium-235, uranium-238, and thorium-232 (all of them with half-lifes of 10^9 years or more) might have induced within clays chemical changes relevant to prebiotic chemistry.

At present, the overall radiation effects due to radionuclides in the terrestrial crust seem to be almost null. However, they could have been fairly important for prebiotic synthesis. Indeed it has been calculated that radiation energy per unit time was three to four times greater in the primitive earth ($4.5X10^9$ years ago) than it is at the present time (1). For example, it can be calculated that the amount of energy liberated from the decay of potassium-40 in the form of beta and gamma radiation during a period of $3.5X10^9$ years was about $2.05X10^{20}$ calories per year. It is quite important to note also that potassium-40 is evenly distributed in the crust, specially in perisilicic rocks, clays and oceans.

The presence of dissolved radionuclides in watery reservoirs such as oceans and lakes may induce chemical reactions with dissolved gases to form simple organic compounds. After their synthesis such compounds may diffuse away from radioactive deposits and avoid further radiolytic effects.

It has been calculated that at present potassium-40 in sea water varies within the range of 3 to $5X10^{-10}$ Ci/l, although it may be observed larger variations. This quantity was much greater $4.5X10^9$ years ago. For this reasons potassium-40 in sea water or any other enviroment appears to be the element that determines in a large extent the radioactivity level.

Besides, it has been shown that clays are quite effective to fix potassium selectively. As a results of this it is found a high level of radioactivity in different sorts of clay. It has been calculated that they present a dose intensity of about 15 mrem per year and it was four times greater $4.0X10^9$ years ago (2). Further, the crystalline structure of clays sometimes forms interlayer channels where water may be adsorbed, together with organic molecules and dissolved ions such as K^+, Na^+, Ca^{++}, etc. In particular it has been observed that purine and pyrimidine bases are easily adsorbed in carbon and montmorillonite clays.

From the point of view of chemical evolution such considerations are quite important due to the fact that an adsorption mechanism may act to concentrate such organic molecules on clays. In turn, these molecules would be then exposed to ionizing radiation to form radiolytic products, even at low doses. This may happen because adsorption occurs at the interlayer channel and radiolytic products of water, as for example $H^\bullet$, $^\bullet OH$, and e^-_{aq} may diffuse and attack to heterocyclic rings, preferentially at carbons 5 and 6. It is discussed thus that the products of these reactions rapidly decompose to form other molecules that do not seem to contribute to the synthesis of prebiotic oligonucleotides.

(1) Bullard, E. (1954), in The Earth as a Planet. Ed. by G.P. Kuper., University Chicago Press, Chicago. Pags. 57-137.

(2) Eisenbud, M. (1963), in Enviromental Radioactivity., Mc Graw Hill Book, Pags. 159-204.

DISTRIBUTION OF PRIMARY IONIZATION AND EXCITATION IN WATER RADIOLYSIS.

A. Mozumder, Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA.

This paper aims at the calculation of entity-specific ionization and excitation probabilities for water radiolysis at low LET with due attention to ionization efficiency and threshold(s). Mean numbers of ionizations and excitations, together with their statistical fluctuations, are provided for a given energy loss ε which may be further averaged over the distribution of ε. Explicit computations are presented for the gas phase while the procedure for the liquid phase is broadly indicated.

The probability $\omega(\varepsilon)\Delta\varepsilon$ that an energy loss between ε and $\varepsilon+\Delta\varepsilon$ will occur on the complete absorption of a primary radiation has been calculated for electron radiolysis of water from fundamental principle.[1,2] If the energy spent in an ionization process is denoted by I', the maximum number of ionizations corresponding to energy loss ε is given by n_m ε/I'. Calling the probability for $(n_m-\nu)$ ionizations and η excitations at energy loss ε by $P(N_m-\nu,\eta;\varepsilon)$ the overall ionization and excitation probability is given by:

$$W(k,\eta) = \sum_{\varepsilon} P(k,\eta;\varepsilon)\,\omega(\varepsilon)\Delta\varepsilon.$$

We have evaluated P as a product of a probability of a given number of ionizations and a conditioned probability of having another given number of excitations. Each of these factor probabilities can be given as a Bernoulli distribution in terms of the maximum number of events and the normalized probability of occurrence of an event (ionization and excitation). In the gas phase, the energy dependent occurrence probabilities may be obtained from cross-sections of ionization, excitation and other processes involving neither ionization nor excitation.[3] The liquid phase calculations depend on experimental ionization efficiency (up to ~ 9.3 eV), W-value of ionization and a plausible form of variation of event occurrence with energy.

It is found that a median spur (20-25 eV) in liquid water has the maximum probability of having one ionization and one excitation while a typical energy loss in the gas phase (30 eV) results in 1 or 2 ionizations and 0-2 excitations. Fates of ionizations and excitations leading to the primary species are speculated.

1. A. Mozumder and J.L. Magee, Radiat. Res. 28, 203 (1966).
2. S.M. Pimblott, J.A. LaVerne, A. Mozumder and N.J.B. Green, J. Phys. Chem. 94, 488 (1990).
3. M. Hayashi, "Atomic and Molecular Data for Radiotherapy," IAEA-TECDOC, Vienna, 1989, pp193-9.

RADIATION-THERMAL TRANSFORMATIONS OF PENTADECANE AND PENTADECANE-SUBBITUMINOUS COAL MIXTURE

I.I.Mustafaev, K.M.Yakubov, N.K.Gulieva, O.M.Makhmudov

Sector of Radiation Researches, Azerbaijan SSR Academy
of Sciences. 3I"A", Narimanov Avenue, Baku 370I43, USSR

The experimental results are given concerning the investigations of H_2, CH_4, C_2H_4, C_2H_6, C_3H_8 and liquid olefins formation regularities at radiation-thermal transformation of pentadecane (PD) and its mixtures with subbituminous coal in the interval of γ -irradiation dose rate and accellerated electrons $\Delta\dot{D}$ =28-9740 kGy/hr, absorbed dose ΔD =2.8-2088 kGy, temperature ΔT= 370÷ 550°C.

PD conversion into gases varies from 2 to I7 per cent under the influence of γ -irradiation ($\dot{D}$ =28 kGy/hr) and D =42 kGy and ΔT=370÷ 435°C in dependence with temperature. The value of iodic number at these conditions for liquid products Δn = 30÷ 95. At more high temperatures the yield of liquid olefins decreases due to intensive gas formation.

Under the influence of accellerated electrons ($\dot{D}$ =2088-8352 kGy/hr) and temperature (ΔT=370-435°C) the summary radiation-chemical yield of gaseous products varies in the interval G= 23.I÷ 50.6 that corresponds G(-PD)= 2.9÷ 6.9.

In the flow conditions at $\Delta\dot{D}$ =2435-9470 kGy/hr and ΔT=450÷550°C the chain regime of PD decomposition is observed: G(-PD) 500÷ 600.

Rate ratio of radiation-thermal (RT) and thermal (T) processes of PD transformation is the function $\dot{D}$ and T: at T=425°C the variation of $\dot{D}$ from 28 up to 5352 kGy/hr leads to the increase of W_{Rt}/W_T from I,9 to I5.3 and at the same time the increase of temperature from 450°C to 550°C at $\dot{D}$ =9740 kGy/hr leads to the decrease of W_{RT}/W_T from I20 to 87.

At $T > 370$°C the yield of gases from the binary mixture (W_3) is less than the sum of gases yield from PD (W_1) and subbituminous coal (W_2): $W_3 < W_1 + W_2$. Relative decrease of gases yield (S) in the investigated parameters interval lies within the limits 6.I÷ 35.4 per cent for H_2; I5.3÷ 64.4 per cent for methane; I2.5÷ 56.2 per cent for ethylene; I7.0÷ 48.I per cent for ethane; I5.6÷53.3 per cent for propane. The values of total gasformation lies within the limits 25.2÷ 70.3 per cent.

Double bonds are formed in the liquid part, the iodic numbers of liquid products of combined pyrolysis reach n ~ 50. Breach of double bonds additivity is negligible.

REACTIONS OF REDUCING AND OXIDIZING SPECIES OF WATER RADIOLYSIS WITH HYDROXYPYRIDINES

D.B.Naik and P.N.Moorthy
Applied Chemistry Division
Bhabha Atomic Research Centre
Trombay, Bombay 400085

ABSRACT

Hydroxypyridines(pyridinols) exibit varying degrees of keto-enol tautomerism depending on the position of OH group. In the case of 2- and 4- pyridinols, the pyridone/pyridol ratio in aqueous solution is 340:1 and 2200:1 respectively(1), whereas 3-pyridinol exists only as the enol. 3-pyridinol is the model compound for pyridoxine(vitamin B_6) and is found to have antihypoxic and antiamneastic activities in mice(2). These compounds also exist in different conjugate acid-base forms in the 0-14 pH region(3) and the reactivities of the different forms may differ. The rate constants for reactions of the different forms of all the three pyridinols with e^-_{aq} were determined by monitoring the first order decay of e^-_{aq} absorbance at 720 nm in N_2 saturated 0.1 moldm^{-3} t-butanol matrices at different pHs. The rate constants of the neutral forms(pH 6.8) of pyridinols were found to be of the order of 10^{10} dm^{3}mol^{-1}s^{-1} whereas the deprotonated forms were found to be much less reactive($k \sim 10^9$ dm^{3}mol^{-1}s^{-1}). The transient species formed by e^-_{aq} reaction absorb in the 220-550 nm region and decay by good second order kinetics. Rate constants for reactions of the pyridinols with $^{\bullet}OH/O^{\bullet -}$ were determined by following the pseudo-first order build-up of the product transient absorbance at the respective λ_{max} in N_2O/O_2 saturated solutions, or by competition kinetics. Rate constants for OH radical reaction with the neutral forms of the pyridinols were higher by almost an order of magnitude compared with the protonated forms. With O^- also the rate constants were of the order of 10^9 dm^{3}mol^{-1}s^{-1}. In the case of one-elecron oxidant radicals such as $\dot{N}_3$, $\dot{Br}_2^-$, $\dot{Cl}_2^-$, etc only the deprotonated forms of 3- and 2- pyridinols were found to be reactive whereas 4-pyridinol is difficult to be oxidized by any of these oxidants.. Similarly e^-_{aq} reaction with 4-pyridinol is quite slow. These results show that 4-pyridinol which predominantly exists in the keto form is very difficult to be oxidized and reduced whereas in the case of the other two isomers these processes readily occur. One electron reduction potentials of all the three pyridinols are more negative than -1.0 V at neutral pH.

REFERENCES

1. A.Albert and J.N.Phillips, J.Chem.Soc., 1294 1956.
2. T.A.Varonina, T.L.Garibova, I.V.Khromoso, U.M.Tilekiva, Farmakol. Toksikol., Moscow, 50 1987.
3. S.F.Mason, J.Chem.Soc., 1253 1959.

RADIATION-CHEMICAL SYNTHESIS OF CARBOXYL-CONTAINING COPOLYMERS OF N-VINYLPYRROLIDONE.

Panarin E.F., Ushakova V.N., Kiriukhin D.P., Munikhes V.M.

The Institute of Macromolecular Compounds of the Academy of Sciences of the USSR, Bolshoy pr., Leningrad, 199004, USSR

The copolymers of N-vinylpyrrolidone (VP) with unsaturated carboxylic acids: acrylic, methacrylic, crotonic etc. are widely used as modifiers of biologically active compounds.

The polymers used as carriers of biologically active compounds should meet several requirements: they should be highly water-soluble, nontoxic, immunoinert and should be completely released from the organism. In this connection, it is very important that low molecular weight impurities and high molecular weight fractions should be absent in polymers. The radiation method of initiation makes it possible to obtain polymers without residues of initiators and catalysts over a wide molecular range and is very promising for the synthesis of these polymers.

The purpose of the present paper is to investigate the main features of the radiation-induced copolymerization of VP with unsaturated carboxylic acids: acrylic, methacrylic, crotonic and undecylenic acids and of the properties of copolymers depending on the process conditions. It was shown that the method of radiation-induced initiation makes it possible to obtain VP copolymers with the carboxyl group content from 5 to 50 mole% in high yields from 60 to 100 mass% over a wide molecular weight range from 10 thousands to 3.5 millions and molecular weight distribution from 1.4 to 2.5 depending on the polymerization conditions.

PULSE RADIOLYSIS STUDY OF CARNOSINE WITH SUPERIXIDE RADICALS INTERACTION IN WATER SOLUTIONS

Andrey R. Pavlov[a], Alexandra A. Revina[b], Alexander I. Yaropolov[a]
a) A.N.Bach Institute of Biochemistry, USSR Academy of Science, Leninsky prospect 33, Moscow, 117071, USSR
b) A.N.Frumkin Institute of Biochemistry, USSR Academy of Science, Leninsky prospect 31, Moscow, 117071, USSR.

The histidine-containing dipeptide carnosine (β-alanyl-L-histidine) and its N_1- and N_2- methylated derivatives anzerine and ofidine are the main dipeptide components extracted from skeletal muscles of vertebrates. It was found that carnosine possesses pronounced antioxidant properties (Dupin A.M. et al, 1984). This dipeptide inhibited ascorbate-dependent peroxidation of lipids in biological membranes reacted with its products of peroxidation. Also, it was shown that equimolar complexes of carnosine with ions of Zn and Cu decrease peroxide concentration in a manner similar to superoxide dismutase. (Gulyaeva, 1987). However, the mechanism of carnosine antioxidant effect remained unclear, primarily because of the indirect system of generation and detection of superoxide radicals.

The antiradical activity and the radiation stability of carnosine in water solutions was studied by pulse radiolysis technique with spectrophotometric registration of absorbance. For our experiments we used a linear accelerator U 12 (E=4.5 m.e.v., τ=2.2 s, D= 30-40 Gy per pulse). The transient spectra were recorded in the range 245-670 nm during $2*10^{-5}$-20 s after the pulse using a flow system for continuous change and saturation of the samples by different gases. Also, the spectra of the stable products of radiolysis were studied.

The results obtained give evidence that carnosine in water solutions at the presence of oxygen behaves like a multifunctional antioxidant. Even at low concentrations dipeptide forms a charge-transfer complex (Car...$O_2^{-\cdot}$, λ_{max}=265 nm) with superoxide radical which changes the reactivity of $O_2^{\cdot}$. The absorbance band of the complex was shifted towards the lower energy as compared to superoxide radical (λ_{max}=255 nm). The interaction of carnosine with OH-radicals proceeding at very high rate and resulting in the formation of a stable product suggested an another type of dipeptide activity.

The kinetic mechanism of the interaction of carnosine with products of radiolysis of water in aerobic conditions is discussed.

REFERENCES

Dupin A.M., Boldyrev A.A., Arkhipenko Yu.D., Kagan D.E.(1984) Bulleten experimentalnoi biologii i Medicini (USSR),**47**, p.186-188.

Gulyaeva N.V.(1987) Biokhimia (USSR), **52**, p. 1216-1220.

IDENTIFICATION OF IRRADIATED FOODS BY THERMOLUMINESCENCE

Sinikka Pinnioja and Timo Autio
Department of Radiochemistry, University of Helsinki
Unionink. 35, SF-00170 Helsinki, Finland

The thermoluminescence of irradiated foodstuffs seems to originate more from mineral contamination rather than from food material itself. Thermoluminescence of minerals common in agricultural topsoil and wind-transported dust, quartz, feldspars and limestones is very sensitive to ionizing radiation and the signal is stable (Autio and Pinnioja, 1990). The aim of the present work was to find foodstuffs, mostly spices and herbs, which contain identifiable minerals for TL analysis.

A large number of spices and herbs totalling 85 lots of 27 different species and berries was studied. The material was irradiated using a cobalt-60 source to a 10 kGy dose and stored thereafter in darkness at room temperature. The TL method is based on determining TL of contaminant minerals separated from foodstuffs. Separation of minerals (1 mg is enough) was done in three ways: picking directly from the material. If not successful, centrifugation in sodium polytungstate solution (density ~1.6 g/cm³) was done. For herbs, berries and potatoes washing with water was the most suitable method. Thermoluminescent spectra were measured using a Danish Riso TL-DA-10 instrument. For identification of radiation treatment the low temperature part (90-250°C) of TL glow curve was used. Re-irradiation was used to eliminate spurious TL results arising from organic residues and nonluminescent minerals in original samples.

Results from mineral separation are given in Table 1. Minerals could be found from most samples. Mineral amounts varied widely between different species and lots. Out of 30 species studied two gave unsuccessful mineral foundings, freeze-dried onions and three lots out of six dried paprikas. Radiation treatment was detectable from spices and herbs half a year after irradiation treatment when the TL intensity of the irradiated samples still differed by a factor 100 or more from the highest blanks.

Table 1. Mineral sampling from foodstuffs for TL analysis

Specimen	Number of		Minerals for TL analysis found by			
	species	lots	picking	water	h.d.liq.	not found
Spices	17	66	34		26	6
Herbs	5	14		14		
Spice mix	5	5	5			
Berries	2	6	4	2		
Potatoes		3	3			

Reference: Timo Autio and Sinikka Pinnioja (1990). Identification of irradiated foods by the thermoluminescence of mineral contamination. Zeitschrift für Lebensmittel-Untersuchung und -Forschung 190: In press.

MODELING OF RADIONUCLIDE MIGRATION FROM A LOW-LEVEL RADIOACTIVE WASTE IN CEMENT - WASTE COMPOSITION

I.Plećaš, A.Perić
Boris Kidrič Institute of Nuclear Sciences-Vinča
11001 Belgrade, P.O.Box 522, Yugoslavia

ABSTRACT

Determination of diffusion coefficients, D_e(cm²/s), retardation factors, K_F, and coefficients of distribution, k_d(ml/gr), using simplified mathematical model for analysing the migration of Co-60 and Cs-137 contained in radioactive waste composition has been developed.

Apparatus for concrete leakage test has been constructed in Institute of Nuclear Sciences "Boris Kidrič"-Vinča. This original method provides a virtual image about the ability of concrete to prevent "washing out" of solidified waste materials by underground flows. The apparatus made possible simulation of real process with concrete disks. Leakage test results enable time calculation with a great degree of approximation after which radionuclide washing out from real system can be expected. There is no suggested IAEA standard procedure, worked out by E.Hespe!

Analysing results presented in this paper, $D_e=10^{-15}-10^{-14}$(cm²/s), $K_F \sim 45$ and $k_d=2-6$(ml/gr) it is noticed that calculated values are similar to the literature data, what proves that one dimensional model used in this experimental work can be used for calculating of parameters of migration process. That also proves that the system of engineering concrete trenches permit secure preservation of radionuclides for more than 300 years. These results will be used for future Yugoslave radioactive waste storing center.

REFERENCES

1. I.Plećaš, "Comparative Study of French and Yugoslav Radioactive Waste Forms", Proc.Waste Management, Tucson, Arizona, Feb.27 - March 3, 1983, Vol.2, p.186 (1983).
2. I.Plećaš, "Some Important Characteristics of Concrete Containers in Radioactive Waste Package", Proc. XI Regional.Conf. of IRPA, Vienna, 1983, Vol.2, p.206 (1983).
3. I.Plećaš, "Optimization of Concrete Containers Composition in Radioactive Waste Technology", RWMADW, 6(2), 161 (1985).
4. I.Hashimoto, "Peclet Numbers and Retardation Factors for Ion Exchange Columns", IEC Fundamentals, 3, 213 (1964).
5. A.H.Lu, "Modeling of Radionuclide Migration from a Low-Level Radioactive Waste Burial Site", Health Physics, 34, 39 (1978).
6. E.D.Hespe, "Leach Testing of Immobilized Radioactive Waste Solids", Atomic Energy Rev., 9, 195 (1971).

RECENT ADVANCES IN LOW TEMPERATURE STUDIES ON REACTIVITY OF RADIATION PRODUCED SPECIES IN CONDENSED MEDIA: FROM TIME-DEPENDENT REACTIVITY TO DISPERSIVE KINETICS

Andrzej Plonka
Institute of Applied Radiation Chemistry
Technical University of Lodz
Wroblewskiego 15, 93-590 Lodz, Poland

The advantages of low-temperature trapping as alternative to pulse methods are well recognized for determination of the structure of radiation produced intermediates. Now it is turning out that studies on reactivity of species trapped in vitrified systems may be more than complementary to those by pulse techniques at the ambient temperature (Plonka 1990). Due to the high viscosity, glasses are less favourable to internal rearrangements than liquids and therefore the reactions, by their very nature, disturb the initial distribution of reactant reactivity. For the first-order reactions, taken as an example, if reaction rates exceed markedly those of internal rearrangement, the reactant reactivity changes with reaction time t as

$$f(\tau,t) = f(\tau,0)\ \exp(-t/\tau)$$

where $f(\tau,0)$ denotes the initial distribution expressed in terms of lifetimes. The system is depleted of more reactive species and this results in time-dependent reactivity (Plonka 1986) recently interpreted phenomenologically in terms of distributions of activation energy for reactions (Plonka 1989). If the same distribution of reactivity $f(\tau,0)$ was that present in the liquid it would be presumably preserved during the reaction course due to efficient internal rearrangements and evolve in time according to

$$f(\tau,t) = f(\tau,0)\ \exp(-\langle 1/\tau\rangle t)$$

with the rate coefficient $\langle 1/\tau\rangle$ equal to the mean value of the reciprocals of species lifetimes. The resulting reactant decay would be monoexponential. Thus we are allowed to conclude that the distribution in reactant reactivity becomes evident when it is not preserved during the reaction course. Studies are undertaken to show if the constant value of activation energy, often reported in the studies by pulse techniques, can be regarded as some mean value of the distribution of activation energy seen upon vitrification of the system. Of course, this distribution would be of first importance for reaction modelling also at the ambient temperature. At present it is encouraging that the dynamic models rationalizing the use of the time-dependent rate constant in solids on longer time scales are seen to be operative for reactions in liquids on picosecond time scale (Plonka 1990).

References:

A. Plonka (1986) Time-Dependent Reactivity of Species in Condensed Media, Lecture Notes in Chemistry No. 40, Springer-Verlag, Berlin Heidelberg New York London Paris Tokyo.

A. Plonka (1989) Dispersive kinetics in condensed phases, Annual Reports on the Progress of Chemistry <u>85</u>, 47.

A. Plonka (1990) ESR studies on reactivity of radiation produced species in condensed media, Magnetic Resonance Reviews - in press.

EXAMINATION OF RADIATION CROSSLINKED POLYMERS APPLICABLE FOR HEAT SHRINKABLE PRODUCTS

K. Posselt, W. Koch

Central Institute for Solid State Physics and Materials Research, Academy of Sciences of the GDR, Helmholtzstr. 20,
8027 Dresden, GDR

The most important properties of materials applicable for heat shrinkable products are high extensibility in the heat and sufficient shrinking force. However, to a certain extent these are opposite requirements. To value the quality of a suitable material it is recommendable to apply special test methods: Measurement of the mechanical stress during a cooling and heating cycle on samples pre-extended at a temperature above the melting point, derived from a procedure suggested by Forgács and Dobó /1/; tensile test with notched test specimens and determination of the shrinking force, both in the entropy-elastic state of the material (e.g. at 150 °C), according to a practice published by Murata, Yamamoto, and Yamakama /2/; determination of the insoluble fraction in dependence on dose as a measure of the yield of crosslinking.
The results show that the fracture toughness of several commercial LDPE-types proves to be too low for achieving heat shrinkable products of good quality. Properties essentially better in this way are found with crosslinked linear LDPE or with compounds made from LLDPE and LDPE, resp.

References:

/1/ P. Forgács, J. Dobó; Radiat. Phys. Chem. 11 (1978) 3, 123 - 127

/2/ N. Murata, F. Yamamoto, S. Yamakawa; Rev. Electr. Comm. Lab. 30 (1982) 4, 629 - 638

THE CHANGES OF DC-CURRENT CONDUCTIVITY ACTIVATION ENERGY DURING RADIATION INITIATED CURING OF UNSATURATED POLYESTER RESINS

I. PUCIĆ MILIČIĆ and F. RANOGAJEC

"RUĐER BOŠKOVIĆ" INSTITUTE, 41000 ZAGREB
pob 1016 YUGOSLAVIA

Two different activation energies of DC-conductivity of unsaturated polyester resins with and without styrene were determined between room temperature and 350 K, in the range above the glass transition temperature. The change in the slope of DC-conductivity vs. inverse temperature was assigned to upper liquid-liquid transition, T_{lp}.

Radiation curing was performed in steps and after each irradiation DC-conductivity temperature dependence in the same temperature range (R.T. to 350 K) was measured. Dose increase is accompanied by decrease of absolute current values and by increase of the activation energies except in the case of pure unsaturated polyester resin without styrene. The increase of the activation energies vs. dose reached plateau at the dose at which the vitrification occured.

The radiation crosslinking did not affect the liquid-liquid transition T_{lp} which is consistent with the assumption that intramolecular local ordering based on H-bonding disintegrated at that temperature.

REACTIONS OF IMIDAZOLINE-TYPE NITROXIDES WITH $OH^{\bullet}$ RADICALS

Putyrskaya G.V., Matus I., Rockenbauer A., Győr M. és
Kovács L.

Central Research Institute for Chemistry of the Hungarian
Academy of Sciences, H-1525 Budapest, P.O. Box 17.

The reactions of some imidazoline-type nitroxides with $OH^{\bullet}$ radicals generated by γ-irradiation have been studied in order to clear the mechanism of their interactions.

It was found that the primary reaction between nitroxide and $OH^{\bullet}$ radicals takes place not with the nitroxide group but with the phenyl group of the stable radical yielding a cyclohexadienyl-type biradical. This latter disappears either in disproportionation or in the interaction with another molecule of the nitroxide radical. The G-value of these reactions are about the half of the G-values for the forming of $OH^{\bullet}$.

A simple method has been elaborated for distinction of this newly formed stable radical from the initial one by ESR and for the calculation of their concentrations.

Five nitroxides with different functional groups have been investigated. The best acceptor was the nitroxide, containing tolyl-group among the screening groups of the nitroxide fragments. The G-value of the disappearing of this nitroxide was equal to the G-value of $OH^{\bullet}$ radicals.

Experiments were carried out in the presence of aliphatic and aromatic alcohols and a mechanism of these reactions is suggested.

STUDY OF THERMALIZATION LENGTHS OF SLOW ELECTRONS AND LIFETIMES OF RADICAL-ANIONS IN POLAR LIQUIDS BY PHOTOINJECTION METHODS

A.M.Raitsimring, A.I.Kalugin, V.V.Konovalov
Institute of Chemical Kinetics and Combustion, Novosibirsk.

The method of electron photoinjection from metal to electrolyte solutions (PIMES) has been used to study the dependences of thermalization lengths of slow electrons on their energy in water and methanol. The range of maximal energies within which the measurements were undertaken was 0.2-5 eV. The range of mean energies 0.1-3 eV. The energy of of injected electrons was changed by varying both potential and light wave length which illuminated of photocathode within 427-193 nm Four different variants of PIMES method have been employed in measurements. These were acceptor, kinetic, recombination, and the method based on the measurement of photocurrents in diluted electrolyte solutions. In the energy range under discussion the thermalization lengths of electrons varied from 5 to 120 A in water, and from 5 to 40 A in methanol. The dependence of thermalization length on energy is interpreted in terms of the theory of non-local losses with taking into account the elastic scattering of electrons during thermalization

This method has also been used to study the lifetimes of aromatic radical-anions of halobenzoic acids. The times ranged from 10^{-3} to 10^{-9}s. Having studies a few tens of objects we conclude that the lifetime of radical-anions depends on the nature of halogen and its position in the ring relative to a carboxylate group. It increases in the series F>Cl>Br and metha>para>ortho (Cl, Br) and metha<para<ortho (F). The PIMES metod has been compared to the conventional method of pulsed radiolysis.

Thus, we report various means to realize the PIMES technique and its potentialities in solving fundamental and applied problems of radiation chemistry.

RADIATION INDUCED REACTIONS IN AQUEOUS SOLUTIONS OF CITRIC ACID

S. Ramos., A. Negrón-Mendoza. and G. Albarrán.

Instituto de Ciencias Nucleares, UNAM
Circuito Exterior, C.U., A.P. 70-543
04510 México, D.F., México.

The radiation-induced decomposition of citric acid in aqueous solutions has been study at their natural pH (2.4). This is a part of a systematic studies for the radiolysis of carboxylic acids related to the Krebs cycle in connection with chemical evolution studies, due to the important role that citric acid plays in biological systems. As first step, our principal interest was focused to detect in this radiolysis other carboxylic acids from the Krebs cycle.

The experimental procedures involving several steps. Citric acid was recrystallized twice from water. Distilled water was purified according to the standards procedures used in Radiation Chemistry. Irradiations. The preparation and handling of the solutions was using the syringe technique. Freshly prepared aqueous solutions (0.1 moles.dm^{-3}) were prepared each time. They were irradiated in two 60-cobalt sources with a dose rate of 10 kGy/h and at 32 kGy/h. The absorbed doses varied in the range from 12 to 730 kGy. It is worth notice that we used very high radiation dose, non conventional in Radiation Chemistry, the reason is our interest in chemical evolution process.

For the analysis of the radiolytic products we used mainly mass spectroscopy chromatographic techniques.

Gas chromatography shows the presence of dicarboxylic and tricarboxylic acids. The principal nonvolatile products was tricarballylic acid. Other carboxylic acids founded were succinic, malonic, isocitric, 1,2,4-butanetricarboxylic, and 1,2,3,4-butanetetracarboxylic.

The total carboxylic acids formed from this system varied with absorbed doses. The amount of them gradually increased with the absorbed doses up to 290 kGy. After this doses, the total amount of carboxylic acids began to decomposed.

The radiation chemical yield for decomposition of citric acid was obtained from a plot of yields vs doses and was 1.62. This value is quite different from other hydroxyacids studied such as malic acid with a G°5.2.

The ready formation of citric acids from several sources, its resistant toward the radiation, and the formation of other carboxylic acids is important from the point of view of chemical evolution.

INTERACTION OF MANGANESE TETRATOLYLPORPHYRIN WITH MOLECULAR OXYGEN AND SUPEROXIDE ANION-RADICAL.

A.A.Revina, ˣV.V.Volod'ko.

Frumkin Institute of Electrochemistry of Academy of Sciences of the USSR, Moscow.
ˣAll-Union Scientific Research Institute of Oil Refining, USSR, Moscow.

Nowadays a considerable attention is paid to mechanism of metalloporphyrins reactions with superoxide radical $O_2^{-\bullet}$ due to its probable participation in cytochrome P-450 enzyme processes as well as numerous catalytic oxidation reactions.

In this work the transient stages of reactions between manganese(III) tetratolylporphyrin (Mn(III)TTP) and anion-radicals $O_2^{-\bullet}$ and $CH_3CN^{-\bullet}$ as well as interaction of reduced porphyrin Mn(II)TTP with molecular oxygen in acetonitrilic solutions are investigated by pulse radiolysis and spectrophotometric electrochemical technique.

Mn(II)TTP was detected during Mn(III)TTP electrochemical reduction in the absence of O_2 :

$$\mathrm{Mn(III)TTP} \xrightarrow[\mathcal{E}=-0,4V]{+e^-} \mathrm{Mn(II)TTP} \qquad (1)$$

The radiolytic reduction of Mn(III)TTP by acetonitrilic anion-radical $CH_3CN^{-\bullet}$ included two stages and resulted in the formation of Mn(II)TTP too:

$$\mathrm{Mn(III)TTP} + CH_3CN^{-\bullet} \longrightarrow \mathrm{Mn(III)TTP}\ldots CH_3CN^{-\bullet} \qquad (2)$$

$$\mathrm{Mn(III)TTP}\ldots CH_3CN^{-\bullet} \longrightarrow \mathrm{Mn(II)TTP} + CH_3CN \qquad (3)$$

Electrochemical and radiation induced reduction of Mn(III)TTP in the presence of oxygen led to the formation of two oxygen containing adducts: $\mathrm{Mn(II)TTP}\ldots O_2$ and $\mathrm{Mn(IV)TTP}\ldots O_2^{2-}$. Mn(III)TTP interaction with $O_2^{-\bullet}$ resulted in $\mathrm{Mn(III)TTP}\ldots O_2^{-\bullet}$ complexe formation:

$$\mathrm{Mn(III)TTP} + O_2^{-\bullet} \longrightarrow \mathrm{Mn(III)TTP}\ldots O_2^{-\bullet} \qquad (4)$$

Equilibrium between the detected oxygen containing complexes was observed:

$$\begin{tikzcd} & \mathrm{Mn(III)TTP}\ldots O_2^{-\bullet} \arrow[dl, shift left] \arrow[dr, shift left] & \\ \mathrm{Mn(II)TTP}\ldots O_2 \arrow[ur, shift left] \arrow[rr, shift left] & & \mathrm{Mn(IV)TTP}\ldots O_2^{2-} \arrow[ll, shift left] \arrow[ul, shift left] \end{tikzcd} \qquad (5).$$

RADIATION AND SUPRATHERMAL CHEMISTRY BY SOLAR WIND

Kurt Roessler

Institut für Chemie 1 (Nuklearchemie), Forschungszentrum
Jülich,
Postfach 1913, D-5170 Jülich, Germany

Solar wind consists of 95 % protons, 4 % He^{2+} and 1 % heavier ions with an average velocity of 400 km s^{-1} and a flux of 2 to $3 \cdot 10^8$ ions $cm^{-2}s^{-1}$ at 1 A.U. The resulting energies are about 1 keV p, 3 keV He^{2+}, 10 keV C^{6+}, etc. From a computer simulation of their collisions with solid matter it follows that the energy is distributed almost equally by nuclear stopping S_n which creates atomic displacements and by electronic stopping S_e which creates excited states and ions. Many of the displaced atoms possess kinetic energies $\geq$ 2 eV and, thus, can undergo suprathermal (hot) reactions with neighboring matrix molecules. A comparison of G-values for suprathermal reactions by hot secondaries and classical radiolytical reactions in H_2O-ice, frozen CH_4, SiO_2, etc. shows that the first are much more important for chemistry than the latter ones. The interaction of solar UV-photons increases the amount of radiolytic (photolytic) reactions but also creates hot atoms via photodissociation processes.

Typical reaction sites in the inner solar system are discussed with respect to the competition of the two principal reaction pathways. Gaseous systems include the inner coma of comets and the outer atmospheres of plants. Solid systems are the icy layers on interstellar grains, comets, rings of planets, asteroids and surfaces of icy satellites. It is shown by simulation experiments and theoretical calculations that suprathermal reactions constitute an important factor in extraterrestrial chemistry [1].

[1] K. Roessler, in Solid State Astrophysics, E. Bussoletti, G. Strazzulla, eds., North Holland, Amsterdam 1990.

HOT CARBON AND RADIATION CHEMISTRY IN SOLID METHANE

K. Roessler, G. Eich, E. Zádor

Institut für Chemie 1 (Nuklearchemie), Forschungszentrum Jülich,
Postfach 1913, D-5170 Jülich, Germany

Frozen methane at 77 K was irradiated with 20 MeV $^3He^{2+}$ ions from a cyclotron. Primary, suprathermal (hot) carbon atoms were created via the nuclear reaction $^{12}C(^3He,^4He)^{11}C$. Secondary hot carbon atoms (^{12}C) were formed by collisions (nuclear stopping S_n) of the $^3He^{2+}$ ions and the ^{11}C-recoils with the CH_4 matrix molecules. The two kinds of species underwent specific hot reactions, e.g. insertion into CH bonds or H abstraction, which together with radical combination led to a variety of products ranging from simple aliphatic or olefinic compounds (in particular unsaturated such as C_2H_2) to long chain aliphatic but also cyclic and aromatic molecules (e.g. cyclopropane, cyclohexane, benzene). Analysis was performed by GC/FID, GC/MS, and HPLC/UV. The concommitant radiolysis effects were studied over five orders of magnitude of $^3He^{2+}$ radiation dose from $D^* = 10^{-3}$ to almost 10^2 eV per target molecule [1].

The most interesting result was the observation of polycyclic aromatic hydrocarbons (PAH) up to coronene and related amorphous hydrogenated carbonaceous compounds (a-C:H) with yields up to 6 % of the total products. The finding of these molecules with $n_c > 20$ also at lowest doses led to the postulation of a new type of solid state reaction in collision cascades: the multicenter reaction of hot target atoms which are stopped in a very close zone. Their metastable reaction products can easily combine to larger, cyclic and partially aromatic structures. This mechanism is confirmed by computer simulation of collision cascades in solid CH_4 which show the clustering of hot carbon atoms [2].

[1] A. Patnaik, K. Roessler, E. Zádor, Radiochim. Acta 50 (1990) 75/85.

[2] K. Roessler, G. Eich, A. Patnaik, E. Zádor, Lunar Planet. Sci. Conf. 21 (1990) 1035/1036.

CRYSTALLIZATION KINETICS OF RADIATION CROSSLINKED POLYETHYLENES

A. Šafranj and V. Marković*
"Boris Kidrič" Institute of Nuclear Sciences,
P.O.Box 522, 11001 Beograd, Yugoslavia

One of the most important irradiation effect on polyethylene is the formation of cross-links between the chains(1). These cross-links can transform a linear structure into three-dimensional network, thus changing the viscoelastic and mechanical properties of the material. Also, crosslinks reduce the overall crystallinity and affect the crystallization kinetics.

Our earlyer work(2) showed, that crosslinking strongly influence the crystallization behaviour, rates and temperatures. At the low degrees of crosslinking two different crystallization procedure take place in the same polymer. The two processes are separated on the time/temperature scale and can be easily identified by DSC. It has been postulated(3,4) that this separation is caused by the fact that irradiated polyethylenes are blends of crosslinked and un-crosslinked fractions forming separate phases with different thermodynamic stabilities. The separation thus corresponds to the degree of crosslinking.

The object of our work was to investigate this phenomenon in more detail and to answer the question why some types of polyethylenes failed to show this kind of separation.

In our studies we used high-density (HDPE), low density (LDPE) and linear low-density (LLDPE) polyethylenes, irradiated at different doses up to 300 kGy. The non-isotermal DSC kinetic analysis of crystallization was used in this work.

REFERENCES:

1. Dole, M., Howard, W.H., J.Phys.Chem., <u>61</u>, 137 (1957)
2. Marković, V., Šafranj, A., J.Radiat.Res.Radiat.Processing, 4(3), 1 (1986)
3. Forgacs, P., Dobo, J., Proceeding of the 6th Tihany Symposium, Hedvig, P., Nyikos, L., Schiller, R., eds., Akadémiai Kiadó, Budapest 1987, p. 523
4. Hikmet, R., Keller, A., Radiat.Phys.Chem., <u>29</u>(4), 275 (1987)

---

* present address: IAEA, P.B. 100, A-1400 Vienna, Austria

PHYSICAL AND LIPIDS ALTERATIONS OF IRRADIATED MEAT

F.A. Salem [xx] - T.M. Dessouki [x] - M.I. Shehata [xx] -
M.M. Abd El-Baki [xx] - M.M.E. El-Ebzary [x]

Summary

The physical and lipids changes were studied during storage of irradiated camel meat. Irradiated with 200 and 100 krad aided in acoleration of meat aging and increased of tenderness at room temperature without bacterial decomposition when compared with aging of unirradiated meat at 4°C. The use of CTC and propolis reduced the lipids changes and deterioration of meat color during aging of irradiated meat. Heating of meat before irradiation, altbugh inoreazed the storage life, was found to reduce the tenderness, water holding capacity and color intensity, while enhanced the lipids oxidation.

---

[x] Fish and Meat Research Lab., Food Techn. Branch,
Agricultural Research Center, Egypt
[xx] Food Science Dept., Faculty of Agriculture,
Zagazig University, Egypt

ELECTRON BEAMS

- Industrial Applications -

Crosslinking

by

Wolfram R. Scheerer

Scheerer + Partner
Johannesstr. 11
D - 6780 Pirmasens
Germany

Abstract

The article consists of a brief summary which covers direct ionizing radiation and particularly the crosslinking application. Furthermore it reflects the view from an equipment supplier, since electron beam treatment gained acceptance as a reliable and economical production technique, machinery and associated equipment grew into a new generation.

Transparent processing parameters make the electron beam treatment a sure, safe, efficient way to make products stronger, tougher, heat resistant, or even impart certain properties to the products which only can be achieved by using electron beams.

While the opportunity for new applications of electron accelerators in the field of crosslinking still exists, it is appropriate at this time to take stock of those applications where electron accelerators have been used profitably.

SELF-TRAPPING OF ELECTRONS WITHOUT DELAY

Robert Schiller
Central Research Institute for Physics
P.O.B. 49, Budapest H-1525, Hungary

Electron trapping brought about by polarization interaction of the electron and the medium is usually regarded as a slow process which takes a period of time in the order of ϑ, the constant-charge (i.e. longitudinal) dielectric relaxation time. This problem is being reconsidered by treating the electron as a non-classical entity embedded in the relaxing continuum of the medium. Self-trapping can be shown to be much faster than dielectric relaxation, in some cases even proceeding "instantaneously" i.e. on the time scale of infrared frequencies.

ANALYTICAL CHARACTERIZATION OF THE EBC-PROCESS

J. Schmidt, U. Decker
Central Institute of Isotope and Radiation Research of the Academy of Sciences of the G.D.R., Permoserstr. 15, 7050 Leipzig, G.D.R.

The aim of our investigations is the characterization of the curing course of solvent-free radiation curable acrylates and binders, e.g. unsaturated prepolymers, with different methods in order to contribute to the description of the mechanism and the kinetics of polymerization and crosslinking processes in multifunctional acrylates.
Energetic electrons absorbed in the coating create excited species and ions as precursors of free radicals initiating the polymerization and crosslinking. The start of these processes can be observed by pulse radiolysis with optical detection and further by the decrease of double bond content by IR spectroscopy and the increase of the gel content of the investigated systems. For comparisons the photoinitiated polymerization and crosslinking of the same samples have been investigated using the differential scanning calorimetry with UV and laser excitation.
The influence of dose, additives and oxygen on the curing process was investigated.
The results of the different methods were discussed and compared.

DETECTION OF SOME IRRADIATED SPICES USING DAMAGED STARCH AS INDICATION METHOD

M.M. Sharif, J. Farkas and Á. Koncz
Institute of Preservation and Livestock Products Technology,
University of Horticulture and Food Industry,
P.O.Box 53, 1118 Budapest, Hungary

ABSTRACT

A rotational viscosimeter type Rheotest was used to determine the apparent viscosity of heat-gelatinised suspensions of irradiated and non-irradiated spices e.g. white and black peppers, nutmeg and ginger, obtained from different origin. The radiation doses were 4, 8, 16 and 32 kGy, plus the zero kGy.

Promising results were obtained for black pepper, white pepper, ginger and nutmeg, while no signficant differences showed by allspice, garlic powder and onion powder between irradiated and non-irradiated samples.

A special storage experiment for black pepper was carried out to study the effect of storage conditions (a_w=0.25, 0.50 and 0.75, respectively) upon the rheological properties during a period of 100 days. The apparent viscosity for ground black pepper stored at a_w=0.75 showed some decrease during long-term storage.

Generally, the difference between the irradiated samples and the control could be enlarged by measuring the apparent viscosities of heat-gelatinised suspensions at higher temperature, e.g. at 50 °C.

REACTIONS OF ELECTRONS WITH SULFOXIDE MOLECULES IN GASEOUS AND CONDENSATION PHASES

Shishlov N.M., Sadykov R.A., Vasil'ev Yu.V., and Burmistrov E.A.

Institute of Chemistry, Bashkirian Research Centre, Ural Department
of the USSR Academy of Science, Ufa, SU-450054, U.S.S.R.

Intermediate paramagnetic species (PMS) of three types $\dot{C}H_3$, $\dot{C}H_2SOCH_3$, $[CH_3SOCH_3]^{\dot{-}}$ ($\dot{C}D_3$ and $[CD_3SOCD_3]^{\dot{-}}$) were registered by the ESR- and UV-spectral methods in mixtures DMSO-h_6 + H_2O (DMSO-d_6 + H_2O) exposed to X-ray radiation at 77 K. A single line in the ESR pattern and an optical absorption band at λ(max) ~350 nm were assigned to an anion-radical (AR) of DMSO. Photochemical and thermal transformations of the species were studied in detail. In particular, the photolysis of AR (λ(max)= 365 nm) led to an increased number of radicals $\dot{C}H_3$ and $\dot{C}H_2SOCH_3$ ($\dot{C}D_3$).

Experimented photoionization of ferrocyanide ions with an eximer laser (λ= 223) nm) proved the electronic origin of the three types of PMS.

The mass-spectrometry method was used to register negative ions in the gaseous phase, which showed the lowest energy resonance to occur at 1.8 eV of the electron energy with the formation of ions CH_3SO^- (CD_3SO^-). An isotope effect was observed within the cross-section of the dissociative electron attachment at 1.8 eV for DMSO-h_6 (σ_1) and DMSO-d_6(σ_2) ($3\sigma_2 \sim \sigma_1 = 3.0\cdot10^{-19} cm^2$). This allows to assess an essential role played by the reaction of electron autodetachment in the case of the above resonance.

The process of electron attachment by DMSO molecules in the gaseous phase was compared to that in the condensation phase. The results of the comparison, the electron energies estimated from the photochemical data as well as uneffectiveness of the electron acceptors for the yields of PMS upon radiolysis of sulfoxides and water-sulfoxide mixtures forced us to assume that the formation of PMS is closely connected with the trapping of non-thermalyzed electrons. A bell-like pattern of the PMS yields plotted against the composition of a (DMSO + H_2O) mixture can be rationalyzed in terms of the effect produced by the medium upon a probability of an autodetachment of the attached electron.

THE RESPONSE OF LiF THERMOLUMINESCENT DOSIMETERS TO HIGH ENERGY ELECTRONS

H.Silva*, A.Ramalho**, M.Moreira***, J. Gomes da Silva** and H.Matos**

*Instituto de Ciências e Engenharia Nucleares
Estrada Nacional No. 10, 2685 Sacavém, Portugal
**Serviço de Radioterapia do Instituto Português de Oncologia
Rua Prof. Lima Basto, Palhavã, Lisboa, Portugal
***Instituto Superior de Engenharia de Lisboa
Rua Conselheiro Emídio Navarro, Lisboa, Portugal

ABSTRACT

The high energy electron beams have a large application in fields such as radiotherapy and radiation processing of polymers. The LiF thermoluminescent dosimeters have a large utilization in obtaining the absorbed gamma doses in biological and polymeric materials, because its characteristics, concerning the radiation absorption, are similar to those materials. In this work, the response of LiF dosimeter as a function of the electron energy, ranging from 1 to 50 MeV, and dosimeter characteristics is obtained using two different calculation models, based respectively on the BURLIN (1) and ALMOND (2) theories, and the concept of electronic equilibrium. The results are compared with the experimental ones obtained in this work and from other authors. The experimental results are in good agreement with the theoretical ones obtained from the ALMOND theory. One can conclude that the electronic energy dependence is larger for lower energies and smaller dosimeters. Above the 10 MeV the variations of dosimeter response do not exceed 1%, for all dimensions considered, and, for dosimeters with particle mean pathlengths higher than 0.5 $g.cm^{-2}$, those variations do not exceed 0.5% for the energies considered.

(1) T.E. BURLIN, Br. J. Radiol. 39 (1966) 727.

(2) P.R. ALMOND and K. McGRAY, Phys. Med. Biol. 15 (1970) 335.

RADIATION INDUCED LIPID PEROXIDATION IN LIPOSOMES: NON-LINEAR RELATIONSHIP WITH DOSE

Sandhya L. Sitasawad and R.K. Kale

Radiation Biology Laboratory, School of Life Sciences, Jawaharlal Nehru University, New Delhi-110 067, India.

Membranes are vital elements and are extremely essential for the cell integrity. It has been suggested that the damage to membrane organization is an initial step in triggering cell death (1). Apart from DNA, the membranes are considered to be one of the critical targets of radiation action.

Lipid peroxidation is an important effect of radiation on cellular membranes. It is highly destructive process. The cell organs or whole animal lose biochemical function and/or structural architecture (2). Biological membranes are very complex and limit the understanding of the chemical aspect of radiation induced lipid peroxidation. Liposomes provide an excellent model for cellular membranes (3).

Liposomes were prepared from L-α-phosphatidylcholine. Lipid peroxidation was determined by TBA method and expressed in terms of MDA formed.

Lipsomes irradiated with various doses of γ-rays (0-776 Gy). Lipid peroxidation was found to increase with increase in radiation dose in the lower dose region (upto 400 Gy) and decrease with increase in a higher dose region (beyond 400 Gy). Our observations have clearly shown that lipid peroxidation is not a linear function of radiation dose. These observations are very important from biological point of view. Vitamin E, Fe^{2+} ions and oxygen could not alter non-linear pattern. It seems in lower dose region (upto 400 Gy) initiation and propagation is operative without much inhibition. The decrease in lipid peroxidation in higher dose region (beyond 400 Gy) might be due to high rate of termination or recombination reactions of free radicals or both. The termination reactions might bring about deleterious changes in the structure and function of biological membranes. On the other hand in recombination processes relatively stable and uncreactive molecular products are formed. The latter may significantly reduce the biological damage while former may not. Therefore, relative contribution of these processes would determine the extent of biological damage.

Lipid peroxidation process appears to be more complex than thought to be and needs further investigation which would unfold some hidden facts about its initiation, propagation and termination steps.

1. Kerr et al. (1972) Br. J. Cancer, 226, 239.
2. Leyko, W. & Bartosz, G. (1986) Int. J. Radiat. Biol., 49, 743.
3. Kale, R.K. & Sitasawad, Sandhya L. (1990) Radiat. Phys. Chem. In Press.

MAS-NMR STUDIES ON CROSS LINKS INDUCED BY γ-IRRADIATION TO POLYETHYLENE.

J.Sohma*, Qun Chen**, Xue-wen Wu**, G.scholtyssek***,
G.H.Zachmann***
*School of Science, Kanagawa University, 2496
Tsuchiya, Hiratsuka, 259-12, JAPAN
**Department of Physics, East China Normal University,
Shanghai, PR of China
***Institute of Polymer Chemistry, Hamburg University,
Hamburg, FRG

Detection of cross links induced by γ-irradiation to polymers is mainly based on changes in physical properties of irradiated polymers. Chemistry of cross links, such as chemical species responsible for cross links and concentrations of the species, is little known. Also no information on preferential sites of cross links, either in crystalline or amorphous parts, is obtained. One of the aims of this presentaion is to report the chemical species for cross links formed by γ-irradiation in polyethylene(PE). Both high density PE and low density PE were heavily irradiated up to 900 Mrad. Bruker CXP-300 spectrometer was used for CP-MAS NMR measurements. High resolution(HR) NMR spectra were observed from the irradiated PEs in a solid state. Chemical species formed by the irradiation were identified through the observed chemical shifts in the NMR spectra. Majority of the chemical species responsible for the cross links was found to be tertiary carbon even in such a heavy irradiation. It was also found that short branches were generated selectively in amorphous parts of the irradiated PEs. Taking advantage of the Torchia pulse sequence[1] in NMR measurements, we observed separately the HR spectra from either the crystalline or amorphous parts in the irradiated PEs. The results derived from the observed HR spectra indicated us that the cross links were preferentially formed in the amorphous parts, that is the relative concentration of the cross links in the amorphous region is 3.6 times larger than that in the crystalline region.

The other aim is to present a new finding that MAS-NMR is a more sensitive method to detect cross links than the conventional pulse NMR. The roataion frequency in the MAS-NMR is a variable parameter in the MAS-NMR and this frequency acts as a kind of time window, which gives us information on molecular motion of polymers. The cross links hinder the mobility of polymer molecules and hindrance is detected either by measurements of spin-spin relaxation time or by the variable rotation frequency in the MAS-NMR. It was found that the sensitivity of the MAS-NMR in the detection of cross links is higher than the conventional measurement of the spin-spin relaxation time. The effect of γ- irradiation of 40 Mrad to the molecular motion was detected by the MAS-NMR, while 100 Mrad at least was needed for the detection of the cross links by the conventional pulse technique.

---

1) D.A.Torchia:J.Mag.Res.30,613,(1978)

SOME PRECULIARITIES OF THE IRRADIATED MICROTUBULES POLYMERIZATION. APPLICATION OF THE TARGET THEORY.

Sorochinsky B.V., Prohnevsky A.I., Hrodzinsky D.M.

Institute of Cell Biology Ukrainian Acad. Sci., Lebedeva stI
Kiev 252I43, USSR

The microtubules system is the central element in the cell organization. That's why the cytosceleton demages may be the central stages in the forming of cell reaction after irradiation. It's interesting to note in this connection about cytosceleton's proteins possibility of polymerization in vitro under the influence of some external medium's conditions. The microtubules assembly process is the cooperative process which is characterized with some kinetic parameters.

We have investigated the influence of gamma-irradiation on the bovine brain microtubules assembly using the methods of electron microscopy and turbidimetry. It was shown that high doses of irradiation (IO Gy - IOOO Gy) can considerably modificate the assembly processes. The violations in the polymerization kinetic and in the morphology of the structures may be determined with irradiation-induced microtubules proteins demages. The target volume was calculated, it's compareble with the size of the molecular aggregats forming on the some stages of microtubule assembly. It's assume that stages of nucleation and lateral growth are the critical stages in the microtubules polymerization.

SET-UP FOR HIGH-LET RADIATION RESEARCH IN JINR, DUBNA

Z.Stuglik[1], I.Zvara, S.N.Timokhin, A.B.Yakushev, K.A.Gavrilov
Joint Institute for Nuclear Research, 141980 Dubna, USSR

The high-LET radiation experiments are of interest not only for radiation chemistry but also for radiobiology and nuclear medicine. Stricly defined experimental conditions can be obtained when irradiation is performed by accelerated ion beams. Recently we have had the possibility of carrying out experiments in JINR, Dubna. At present we work in stationary regime and investigate liquid systems. The set-up for the radiation experiments is placed on a beam of the 4-meter cyclotron U-400 which supplies accelerated ions from ^{11}B to ^{129}Xe with energies of 13 to 3 MeV/amu, respectively. The intensity of the ion beam is $10^{14}\div10^{12}$ ions/sec and may be easily attenuated to the desired values. The range of the ions in water, l, is ≤ 0.7 mm, LET is $10\div100$ eV/Å and higher. The ion beam may be focused to an area of $10\div20$ mm in diameter and spread over an area of 100 mm in diameter. The exit windows are done from thin metal (Al, Ti) foils. The vertical direction of the beam is very convenient for the bombardment of liquid-phase. Dosimetry is performed by an ionization chamber. The ion energy is measured by a semiconductor detector.

---

[1] on leave from Institute of Nuclear Chemistry and Technology, Warsaw, Poland

DIELECTRIC STUDY OF RADIATION CROSSLINKING OF OLIGOMER - MONOMER MIXTURES

E.Takacs and P.Hedvig

Research Institute for Plastics
Budapest 1950, Hungary

The temperature domain dielectric technique [1] was used for monitoring the crosslinking reaction in mixtures of an unsaturated poliester oligomer with hexane diol diacrylate monomer. The dielectric transition was measured at different stages of crosslinking at different frequencies from 100 Hz to 100 kHz and the resulting permittivity versus temperature curves were interpreted on the basis of the autocorrelation function $F(t) = \exp\{-(t/\tau)^n\}$ [2] . This function was transformed first to the frequency scale and then to the temperature scale considering the temperature dependence of τ and that of the relaxed permittivity.The transformed real permittivity $\varepsilon = u + \Delta\varepsilon\ f'(\nu\ T,\Delta H,n)$ was fitted to the measured curve in two stages:first the temperature dependence of the amplitude $\Delta\varepsilon$ was determined from the high temperature part then the transition temperature T, activation enthalpy of the transition ΔH, and exponent n were varied until chi square became minimum. The unrelaxed part u and the frequency ν was directly measured.

This procedure has made it possible to reveal multiplicity of the transition of the crosslinked product. Below the irradiation temperature typically two transitions are observed: the lower-temperature one , interpreted as being due to the uncrosslinked part which becomes less and less plasticized as crosslinks are formed by the monomer,and the higher temperature part related to the glass-transition of the crosslinked network. At high radiation doses the transition is shifted through the reaction temperature indicating that the reaction is not stopped when the matrix becomes glassy.The results are in agreement with those obtained earlier [3] for unsaturated polyester-styrene mixtures.

Besides the shift and multiple character of the dielectric transition information from the decrease of its intensity is also derived and the results are compared with those obtained by mechanical and differential thermal methods.

REFERENCES
1 P.Hedvig, Dielectric Spectroscopy of Polymers
A.Hilger, Bristol 1977
2 P.Hedvig, J.Polymer Sci.Pt.IV, 15, 375,(1980)
3 Z.Jelcic,P.Hedvig,F.Ranogajec,I.Dvornik
Angew.Makromol.Chemie 130,21, (1985)

ABSTRACT

THE EFFECTS OF SMALL CONCENTRATIONS OF METHANOL ON THE RADIATION POLYMERIZATION OF STYRENE

by

Fuh-Wei Tang, Mohamad Al-Sheikhly and Joseph Silverman

Laboratory for Radiation and Polymer Science
University of Maryland, College Park, Maryland 20742, U.S.A.

The mechanisms whereby ionizing radiation produce the species which initiate neutral free radical and ionic polymerization are investigated. Of particular interest is the remarkable enhancement effect on radiation induced polymerization of styrene by small concentrations of methanol. The approach is to compare the effects of methanol and other alcohols on the steady state polymerization of styrene induced by two different initiation methods: (1) gamma ray; (2) ultraviolet light (UV). In addition to these steady state reaction studies, microsecond pulse radiolysis with 6 MeV electrons is used to study the transient aspects of styrene polymerization and especially, the effect of methanol on the initiation step.

The results for photopolymerization initiated with wavelengths above 280 nm, and therefore dominated by free radical polymerization, show that methanol has no sensitizing effect. This eliminates methanol from the initiation stage of the free radical polymerization. By means of studies with different alcohols and an analysis of the dimer and trimer yield, a proton donor mechanism is successfully established for the enhancement effect of methanol on the radiation induced polymerization of styrene. Methanol serves as a rapid proton donor to the anion radical converting the latter to a neutral propagating free radical. The resulting methoxide anion then neutralizes the cation radical converting it to an additional neutral propagating free radical.

Trace amounts of methanol (less than 0.05 M) in system with 2-3 mM water is found to have a desensitizing effect because of a quenching influence of methanol on propagating free ionic species; this effect is not observed in the water saturated (35 mM water) system or even at higher concentrations of methanol in the system with 3 mM water.

In pulse radiolysis, a quantitative agreement between steady state polymerization and pulse radiolysis is for the first time obtained in the analysis of the radiation yield of propagating radicals. This agreement gives rise to quantitative values for the extinction coefficient of the propagating free radical (1782 M^{-1} cm^{-1}) and the bimolecular rate constant for the termination reaction (5×10^{8} m^{-1} s^{-1}).

PECULIARITIES OF CAGE RADICAL ABSTRACTION REACTIONS R + R'H → RH + R' IN ORGANIC SOLIDS

V.A.Tolkatchev
Institute of Chemical Kinetics and Combustion, Novosibirsk,
630090, USSR

The regularities of the cage reaction of hydrogen atom abstraction from matrix molecules by free radicals were studied using the method of isotopic substitution of molecules in monocrystal lattices. Free radicals were obtained either under γ-irradiation or photochemically from matrix or additives. A quantitative method to describe abstraction kinetics was found which allows the determination of the individual probabilities of the transfer of H atoms occupying the different sites in the radical environment. As a result, it is possible to analyse the transfer probability dependence on the distance between the reagents.

The initial section of the curve are described in terms of the kinetic law which is specific of a liquid phase:

$$d[R]/dt = -\sum K_i[C_i][R] \qquad (I)$$

where $[C_i]$ is the reagent mole fraction. The analysis of the initial transformation sections gives the kinetic characteristics of the process. When a certain point of the solid has its own rate constant, law (I) is transformed to that of rate constant-distribution which is experimentally verified. The rate constant of the chemical reaction was observed to change with time in the glasses of low-molecular compounds. In these cases the kinetics may be described by the law:

$$d[R]/dt = -K(t)[R][C]$$

and is not reduced to the rate constant-distribution. Two possible reasons for such a behavior were discussed: (i) the structure relaxation of the nearest radical environment to an equilibrium state; and (ii) the peculiarities of the defect motion in the solid which affect the process.

The experimental data testifying to a collective character of an elementary transfer act were discussed. These involve: the levelling of the isotopic effect in atomic hydrogen transfer, the levelling of the dependence of the tunneling transfer probability on the transfer distance, matrix isotopic effect. Whereas the latter may be assigned to the role of intermolecular vibrations, the former require the introduction of new concepts on the process of an elementary act. To our opinion it is necessary to take into account the multiplicity of the potential minima of the potential energy surface over which the system (radical-reagent-surrounding molecules) moves during the reaction.

The experimental data are presented which confirm the existence of such potential minima in the transitions of a neighbouring molecule pair by about 0.2 Å. The data were obtained by analysing the transitions of radical pairs in γ-irradiated potassium hydromalonate.

QUANTITATIVE EVALUATION OF SOME ADVANTAGES OF RADIATION RADICAL POLYMERIZATION OVER THERMAL POLYMERIZATION

O.Ch.Touronok

L.V.Pisarzevsky Institute of Physical Chemistry of the
Ukrainian SSR Academy of Sciences, Prospekt Nauki, 31,
252028 Kiev, USSR

On the basis of the Talroze's general theory /1/, the approach to define optimal conditions for realizing radiation induced polymerization had been developed. It implies grafical findings within of the doze rates and within the temperature regions where radiation polymerization has advantages in comparison to thermal polymerization, and while in the meantime, can satisfy some additional conditions. These regions are determined by crossing of the halfplanes satisfying the following criteria:

i-criterion - the rate of the radiation polymerization should be hihger than the rate of thermal polymerization;

p-criterion - the average polymerization degree of radiation formed polymer should be more than the one for thermal initiation;

ν-criterion - the chain radiation process is still existing;

$\nu_{ч}$-criterion - the average polymerization degree of radiation formed polymer should be more than the needed practical value;

w-criterion - the radiatin polymerization rate should be higher than the needed practical value.

Under certains conditions the plots i- and p-criteria coincide. This means that the radiation polymerization, due to this conditions, cannot supply simultaneosly both the rate and the polymerization degree higer, than of those of thermal polymerization. Then by crossing the halfplanes determined by above criteria two regions of essential radiation polymerization (ESR-region) will be formed: the essential polymerization rate region and the essential polymerizatiorn degree region. Their values depend on the monomer nature and the given polymerization rate as well as the polymerization degree of the last two criteria. The present approach is illustrated by the concrete examples.

/1/ Tal'rose V.L.: Khim. Visok. Energii, 8 /6/, 519-527 /1974/.

SOLID PHASE REACTIONS OF METHYL RADICALS IN INERT GAS METHANE CONTAINING MATRIX

Trakhtenberg L.I.,Grigoryev E.I.,Zhykov D.C.
USSR, Moscow, L.Ya.Karpov Physical Chemistry Research Institute

The process of diffusion and recombination of CH_3 radicals and H atoms at 77 and 90 K in solid xenon with methane additive are studied. The diffusion coefficient of methyl radicals appeared to be proportional to methane concentration C_o, contained in the sample.

To describe the transfer process of methyl radicals the following assumptious were made for this very case:

1) vacansy diffusion mechanism of radicals in solid xenon;
2) methan molecules interaction ability with one another and with vacansics;
3) concurrention of this processe between each other.

Now the following dependence diffusion coefficient methyl radical can be given by:

$$D_{Rad} \sim \left\{1 + C_o \exp\left(-\frac{\Delta G_1}{RT}\right) - 2 C_o^2 \exp\left(-\frac{\Delta G_1 + \Delta G_2}{RT}\right)\right\}^{-1}$$

where ΔG_1-change in Gibbs free energy during methan-methan, and ΔG_2 during methan-vacancy complex formation, and subsiguently egual: -0,40 and -0,86 Kkal/mol; that is physically reasonable.

At 90 K diffusion coefficient did't depends on methan concentration, and eguals $1,34 \cdot 10^{-15}$ $cm^2 . s^{-1}$.

The value of methyl radicals diffusion coefficient derived from experimental date of their kinetic recombination at various methane concetration in matrix.

In a sample containing 2,0 mol.% of methane the value of methyl radical diffusion coefficient is $6,5 \cdot 10^{-18} cm^2 . s^{-1}$ while the value of H-atom diffusion coefficient is $8,0 \cdot 10^{-15} cm^2 . s^{-1}$. This value proves that H-atoms concentration is determined by their recombination with each other. H-atoms and methyl radical interaction is described by H-diffusion model.

The rate constant of recombination of methyl radicals and atoms is less than the rate constant of recombination of H atoms with each other and is egual to $2,0 . 10^{-11} cm^3 . s^{-1}$. The achieved result is elevated, as the adsorbtion H-atoms characteristics on xenon are not taken into account, for the value of Henry constant for hydrageh in xenon is not known.

ACCELERATED ELECTRON ENERGY SELECTION, WHEN IRRADIATING THICK-WALLED POLYMERIC PIPES

Upadishev L.B., Aktabaeva L.S., Vanjushkin V.M.,
Mazurov V.M., Semenov V.P.

USSR, Moscow

All-Union Research Institute of Technical Physics
and Automation

At the present time in the world tens of electron accelerator facilities operate for radiation treatment of polymeric pipes in order to impart to them new useful operating properties.

The nomenclature of irradiated pipes has been considerably widened, and in new developments a trend has been outlined to the increase of pipe diameter and their wall thickness. But demands made to inhomogeneity of the absorbed dose are rather strict. Inhomogeneity, as a rule, should not exceed ±20%.

To ensure the preset inhomogeneity, the use of accelerators with a high energy of accelerated electrons results in the increase of the facility cost because with increasing the energy the accelerator cost and radiation shielding increase, input and output systems of irradiated material become more complicated.

Problems of ensuring the preset inhomogeneity due to irradiation of multi-side pipes, wall thickness of which achieves 20% of outer pipe radius, have been considered. Calculation and experimental results, which have shown, that multi-side irradiation made it possible to reduce accelerated electron energy in 2.7-5.6 times in comparison with two- and one-side irradiation and to increase the radiation-utilization factor, have been given.

MAIN FEATURES OF THE KINETICS OF RADIATION-INDUCED HOMOPOLYMERIZATION OF N-VINYLPYRROLIDONE AQUEOUS AND ORGANIC MEDIA

Ushakova V.N., Panarin E.F., Leliukh A.I., Kiriukhin D.P.
and Munikhes V.M.

The Institute of Macromolecular Compounds of the Academy of Sciences of the USSR, Bolshoy pr. 31, Leningrad, 199004, USSR

Polyvinylpyrrolidone (PVP) is used in medicine and biology as a plasma expander and a modifier of biologically active compounds. The method of radiation-induced polymerization is one of the promising methods for obtaining PVP. In this connection, the aim of the present paper was to investigate in detail the kinetics of the radiation-induced homopolymerization of N-vinylpyrrolidone (VP) in bulk, in water and in alcohols with different lengths of the alkyl radical from ethanol to decanol. This investigation was carried out with the aid of the calorimetric method which makes it possible to measure the process rate in the field of γ-irradiation and the structure and properties of polymers depending on the process conditions were also studied. It was shown that the homopolymerization of VP in bulk in the range of dose rates 0,7Gr/s-3,36Gr/s in aqueous and organic solutions proceeds at high rates. In this case when the process is carried out in bulk and in concentrated solutions (70mass%), the gel effect is observed. The investigation of the dependence of polymerization on the dose rate of γ-irradiation made it possible to obtain the dependence of the process rate (w) on the dose rate(I) for various VP conversions. It was found out that w is proportional to $I^{0,5}$ up to very high conversion (90mass%). This fact indicates that even in the stage of the gel effect, chain termination proceeds by the free-radical mechanism. The investigation of the molecular weight characteristics of the molecular weight characteristics of PVP showed that an increase in molecular weight and a certain broadening of molecular weight distribution are observed with increasing conversion. This phenomena are most pronounced in the range of the gel effect.

STUDY OF MATRIX MICROSTRUCTURE OF IRRADIATED POLYSTYRENE AND POLY(METHYL METHACRYLATE) BY DOUBLE MODULATION ESR

S. Valić, F. Ranogajec and Z. Veksli
Ruđer Bošković Institute, POB 1016, 41001 Zagreb, Croatia, Yugoslavia

The double modulation ESR - spin probe method has been applied to study changes in the matrix microstructure induced by γ-irradiation in polystyrene (PS) and poly(methyl methacrylate) (PMMA). The line width broadening of DMESR spectra below the glass transition temperature is very sensitive to small differences in the local free volume and the side grupe motions. Slower line width broadening with increasing radiation dose reflects the restricted spin probe motions due to the crosslinking of PS. At higher doses (~ 400 kGy) PS matrix appears to be highly heterogeneous in terms of free volume sizes.

The spin probes embeded in irradiated PMMA matrix sense lower local density as the chain scission increases. It was shown that the DMESR spectra enable to detect free volume changes affected by a small decrease of molecular mass.

Alanine as reference and routine dosimeter for electron beam irradiations.

K.Van Laere$^{(1)}$, F.Callens $^{(2)}$, E.Boesman$^{(2)}$ and J.Buysse$^{(1)}$.

(1) Nuclear Physics Laboratory
Proeftuinstraat 86

Ghent State University
9000 Gent - Belgium

(2) Laboratory for Crystallography
and Solid State Physics
Krijgslaan 281, S1

The Electron Spin Resonance readout technique, which is now commonly accepted as reference technique for high-dose irradiations, as well as the electrochemical quantification, by means of an ion-selective electrode, of radiolytically produced ammonia upon irradiation of alanine, have both been investigated on their applicability for reference and routine high-dose evaluations.

The Electron Spin Resonance methodology (dose range 0.1 - 300 kGy) is depicted by means of the most important detector characteristics, the inclusion of a DPPH/NaCl reference sample and a number of irradiation and read-out related correction factors. The overall accuracy estimated for this method is 3.5 %, although slightly increasing at the lowest (<1 kGy) and highest (>100 kGy) dose levels. The complete automation procedure for the collection and analysis of the readout data is included in more detail.

The NH_3-ISE read-out technique (dose range currently 0.5 - 1500 kGy), which been described in more detail elsewhere (Van Laere et al., 1990), is compared to the ESR system from the angle of the radiation chemical reaction scheme.
A thermostatted phantom for electron beam irradiations at constant temperatures from -30 °C up to +90 °C (max. 1 kW power input), allows the accurate measurement of irradiation temperature coefficients for both read-outs. These were found to be different for both radiation chemical paths (ESR : 0.235 (+/- 0.017) $\%^{o}C^{-1}$; NH_3-ISE : 0.34 - 0.46 $\%^{o}C^{-1}$, latter depending on dose level). Post-irradiation effects for both radiolytic yields were shown to be negligible during the first six months. Consistency in dose measurements between ISE/ESR is demonstrated over the complete common dose range.

For the high-dose electron beam calibration irradiations (electron energy > 5 MeV), reference conditions and a reference procedure were developed. These include the complete detailed simulation of the irradiation set-up by means of a Monte Carlo algorithm ELGA50 describing coupled electron-photon transport and the automated scanning of the radiation field before each calibration irradiation. Correction factors for the field size and dosimeter wall interactions were also calculated by means of the algorithm.

Reference

K.Van Laere and J.Buysse (1990) : Operation and methodology of an alanine-Ion Selective Electrode dosimetric system.
Part I : Electrode Characteristics and Data Analysis.
Part II : Dose Response.
Both accepted for publication in Int.J.Appl.Radiat.Isot.

THE INFLUENCE OF GLASS STRUCTURE NONUNIFORMITY ON FREE RADICAL FORMATION AND OXIDATION IN γ-IRRADIATED SQUALANE GLASS

S.V.Vasenkov, V.A.Bagryansky, V.V.Korolev, V.A.Tolkatchev
Institute of Chemical Kinetics and Combustion, Novosibirsk,
630090, USSR

There is experimental evidence for the fact that glass structure is nonuniform and may often be represented as two regions of a different density, i.e. well-packed and porous. If these models exist in reality, the structure peculiarities may have a substantial effect on both the regularities of radical formation during radiolysis and postradiation chemical transformations. The present report gives the data confirming such an effect using squalane of a glassy $C_{30}H_{62}$ hydrocarbon as an example.

The reaction of tertbutyl radicals, $R+O_2 \rightarrow RO_2$, obtained from tertbutylchloride additives by the reaction of dissociative electron addition in squalane radiolysis was studied. Oxygen was dissolved in matrix before freezing. The oxidation kinetics is described by the Smoluchovskii equation:

$$d[R]/dt = -4\pi \rho D(1 + \rho/\sqrt{\pi D t})[R][O_2]$$

where ρ is the reaction radius; D is the diffusion coefficient; t is the time. The reaction radius in quenched glass samples has a very large value (12 Å). Measuring the phenanthrene luminescence quenching with oxygen in the same matrix allows the independent determination of the oxygen diffusion coefficient which coincides with that found from the oxidation kinetics.

The conclusion was made on a preeminant radical formation in porous glass regions whose oxygen diffusion coefficient substantially exceeds that in the main matrix. Hence, the mean size of porous regions will represent the reaction radius in the formal oxidation laws. The existence of porous regions was also confirmed by studying the relation between the peroxide and alkyl radicals formed at 77 K during radiolysis as a function of a dissolved oxygen amount. If the mobility of oxygen in porous regions is very high, the resulting radicals will be oxidized when an oxygen molecule enters their environment. Then the fraction of oxidized radicals is:

$$\frac{[RO_2]_0}{[R]_0 + [RO_2]_0} = 1 - \exp(-v[O_2])$$

where v is the value of the high mobility volume. The experiments correspond to this relation. The radius calculated from the v value is also ≈12 A.

Glass annealing near the glass transition point destroys the porous regions. When tertbutylchloride additives are absent in squalane, no porous regions are formed by freezing.

ON THE RADIATION MODIFICATION OF POLYVINYLIDENE FLUORIDE

A. Vokál and M. Palanová

Nuclear Research Institute
250 68 Řež, Czechoslovakia

The article is devoted to the study of radiation modification of polyvinylidene fluoride and thermoplastic copolymer of vinylidene fluoride with hexafluorpropylene focused mainly on their use in wire and cable industry.

Samples in the form of pressed or extruded foils were irradiated in air using the linear electron accelerator. They were examined by measuring the gel fraction, degree of swelling, heat elongation under constant load, mechanical properties and absorbances both immediatelly after the irradiation and subsequent aging.

It was found that thermoplastic copolymer of vinylidene fluoride with hexafluorpropylene is more easily crosslinkable by ionizing radiation when compared to homopolymer. The thermomechanical resistance of all irradiated samples, if they are not annealed after irradiation at temperatures near or above their melting point, decreases during the storage at room temperature. The significant sensitizing effect of triallylcyanurate and m-phenylenedimaleimide was confirmed. The use of m-phenylenedimaleimide, however, may substantially deteriorate the extrudability of polymer. The ultimate elongation of all samples under study drastically decreased after irradiation. The loss of elasticity of copolymer samples depends on their preirradiation morphology. The wire insulated with irradiated copolymer of vinylidene fluoride with hexafluorpropylene ensures a problem-free operation for hundreds of hours at temperatures about 250 °C. The irradiated samples have a significant tendency to darken, if they are exposed to elevated temperatures. This tendency is diminished by the presence of some pigments.

ELECTRON SCAVENGING IN IRRADIATED NONPOLAR LIQUIDS. A COMPUTER SIMULATION STUDY.

Mariusz Wojcik and Witold M. Bartczak

Institute of Applied Radiation Chemistry, Technical University,
Wroblewskiego 15, 93-590 Lodz, Poland

The competing processes of electron scavenging and electron-cation recombination in radiation-induced spurs of several ion pairs in liquid hydrocarbons are analyzed by the Monte Carlo simulation method. The calculations are carried out for the ion-pair clusters which contain initially from one to five ion pairs, for a range of scavenger concentrations and for different initial electron-cation distances.

During the simulation the ions move both due to diffusion and the electric field and the scavengers perform only the diffusive motion. In order to save the computer time the periodic boundary conditions for scavengers as well as the variable time step are applied. The simulation is carried out until all the electrons disappear and the number of scavenging and recombination reactions is recorded. The scavenging probability is averaged over an ensemble of $2*10^4$ independent spurs.

The results of the simulation show the decrease of the scavenging probability for multi-pair clusters as compared with the predictions of the analytical single-pair theory. The decrease is caused by the scavenger depletion and it ranges from about 30% for the spurs with two ion pairs to about 50% for the case of five ion pairs. The role of the multi-pair effects in interpreting the experimental results is discussed.

OPTICAL ABSORPTION SPECTRA OF SOLVATED ELECTRON IN MOLTEN ALKALI HALIDES AND THEIR MIXTURES. A COUPLED MOLECULAR DYNAMICS AND MULTIPLE SCATTERING METHOD.

Mariusz Wojcik, Witold M. Bartczak and Jerzy Kroh

Institute of Applied Radiation Chemistry, Technical University,
Wroblewskiego 15, 93-590 Lodz, Poland

The electronic states and the optical absorption spectrum of excess electron in molten alkali halides and their mixtures are studied by the Molecular Dynamics method coupled with the quantum - chemical SCF-Xalpha-SW method.

First step of the calculations consists in the computer simulation of the system of alkali and halide ions plus a model anion which represents the solvated electron. The trap geometries obtained by the simulation are then used as an input for the SCF-Xalpha-SW program and the energy of electron states and electron transitions for these traps are calculated.

It was found that the structures containing 3 cations closer to the trap center than the first anion make the most probable trapping sites in molten KBr/LiBr systems. The ensemble averaged energy of the basic optical transitions of the trapped electrons calculated for these mixtures correctly reproduce the experimental dependence of the optical absorption maximum on the composition.

ANTIOXIDANT ACTION OF 4-METHYL-2,6-DI-T-BUTYLPHENOL IN CYCLOHEXANE

L. Wojnárovits, O. Brede[x], G. Földiák
Institute of Isotopes of the Hungarian Academy of
Sciences, H-1525 Budapest, P.O.Box 77, Hungary

[x]Central Institute of Isotope and Radiation Research of the
Academy of Sciences of the G.D.R., DDR-7050 Leipzig

Natural or artificially produced sterically hindered phenols serve as antioxidants, e.g. in membranes, foodstuffs, lipids or polyolefins. The chemistry of the antioxidant action has been studied many times but our knowledge of the subject is rather controversial. This is partly due to the complexity of chemistry, and partly to the fact that only few papers deal with the elementary steps of processes based on time resolved kinetic spectroscopic measurements.

We have carried out comprehensive work on oxidation induced by radiation in cyclohexane in the presence of 4-methyl-2,6-di-t-butylphenol. Pulse radiolysis, laser kinetic spectroscopy, final product measurements by GC and UV-VIS spectroscopy were used in the experimental work. In radiolysis formation of phenoxyl radical intermediate was demonstrated which decays with a first order rate parameter of $k \cong 4.10^4$ s^{-1} yielding a transient product terminating in a slow second order reaction with $2k \cong 6 \cdot 10^6$ mol^{-1} dm^3 s^{-1}. These decay characteristics were independent of the phenol concentration, dose/pulse value and the presence of oxygen did not modify the processes. In radiolysis in the absence of O_2 a dimer of cyclohexane and phenol, in the presence of O_2 a compound with quinomethid structure forms as main product of phenol decomposition. The results are interpreted in terms of a rearrangement of the phenoxyl radical to benzyl type radical.

STRUCTURE-REACTIVITY-RELATIONSHIPS IN RADIATION-INDUCED CROSSLINKING OF POLYETHYLENES

K. Wunsch*, H.-J. Dalcolmo**

* Central Institute of Isotope and Radiation Research, Permoserstr. 15, Leipzig, 7050, G.D.R.
** VEB Leunawerke "Walter Ulbricht", Merseburg, 4220, G.D.R.

Various different polyethylenes characterized by their analytical data were crosslinked radiation-chemically to find the specific radiation doses for a fixed crosslinking state.

The main interest was focused on the following aspects:
- proof of those parameters that influence the crosslinking reaction anyway and
- calculation of the necessary radiation dose on the basis of these parameters.

It can be shown that most of the molecular (data of molecular weights, degree of short chain branching, content of double bonds) and supermolecular parameters (density, degree of crystallinity, lamellae thickness) depend on each other in a very complex manner, i.e., the variation of one parameter causes changes of the others.

Hence, the influence of a single parameter on the crosslinking efficiency can be observed, but it is impossible to find a quantitative correlation for it.

On the basis of a multiple linear regression a mathematical formulation was found to calculate approximative the goal radiation dose. From the experimental results it was concluded that to the mentioned parameters influence the crosslinking efficiency different importance has to be assign within the principal polyolefinic structures (LDPE, LLDPE, HDPE). In accordance with this the computations show minor differences between calculated and experimental determined radiation doses for these single groups.

CATION DEPENDENT ISOTHERMAL LUMINESCENCE (ITL) OF γ-IRRADIATED IONIC ICES AT 77 K

M.Wypych and J.Kroh
Institute of Applied Radiation Chemistry, Wróblewskiego 15,
93-590 Łódź, Poland

The γ-radioluminescence and pulse radiolysis study of e_t^- in glassy alkaline and halogen ices indicate important role of Me^+ (Me^{2+}) cations in the radiative recombination (1,2).

To confirm the influence of cation nature on the electron localization and decay in aqueous matrices we have decided to examine the ITL of the wide range of polycrystalline ices containing the same amount of electrolyte -
4 mol dm^{-3} (Li^+, Na^+, K^+, Rb^+) OH^- or
(Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+})Cl^-.

The decay kinetics of ITL was analysed in terms of first order reaction with a time-dependent rate constant of the form
$k(t) = Bt^{\alpha - 1}$, $0 < \alpha \leq 1$(3).

The comparative, quantitative measurements indicate that ITL of both alkaline and chloride matrices is strongly dependent on the nature of cation Me^+(Me^{2+}) as observed for glassy ices.

These dependences are confirmed by analysis of kinetic parameters of ITL decay both in the presence and in the absence of e_t^- and hole scavengers.

The results are consistent with the model of Bartczak et al.(4).

References

1. M.Wypych, J.Kroh and S.Kuberski, Bull.Pol.Acad.Sci.Chem. 34, 403, 1986.
2. M.Wypych and J.Kroh, Radiat.Phys.Chem. 17, 47, 1981; 33, 139, 1989; 36, 127, 1990.
3. A.Płonka, Ann.Rep.Progr.Chem. 85, Sec.C, 47, 1988.
4. W.M.Bartczak, M.Hilczer and J.Kroh, Radiat.Phys.Chem. 17, 431, 1981.

REACTION MECHANISM FOR RADIATION-INDUCED DEGRADATION OF POLY(METHYL METHACRYLATE) AS STUDIED BY ESR AND ESE

Hiroshi Yoshida and Tsuneki Ichikawa

Faculty of Engineering, Hokkaido University,
Kita-ku, Sapporo, 060, Japan

The study is aimed at elucidating the reaction mechanism for the radiation-induced degradation of poly(methyl methacrylate), a typical radiation-degradable polymer, based on the nature and behavior of free radicals in γ-irradiated PMMA observed by the ESR and ESE (electron spin echo) methods.[1]

PMMA was irradiated at 77 K in vacuum and heated stepwisely to room temperature. Formation and decay of the radicals during the heat-treatment were examined by the ESR method with the microwave power lowered to 10 μW to avoid the power-saturation effect. The ESE method was complementally used to discriminate the coexisting radicals based on the difference in the rate of paramagnetic relaxations. Attention was paied to remove residual monomer in the sample, because the monomer readily adds to the radicals derived from PMMA and converts them to the propagating-type radical (identical to the propagating radical in radical polymerization.

Major radicals observed immediately after the irradiation at 77 K are the side-chain radical $-COO\dot{C}H_2$ (triplet spectrum with hyperfine coupling constant of 2 mT, G=2.0), the main-chain radical $-\dot{C}H-$ (doublet spectrum with hfc of 2 mT, G=1.0), and the anion radical (broad singlet spectrum, G=1.2). The formyl and methyl radicals are generated though with low yield.

The behavior of radicals are summarized as: (1)The anion radical is photobleached with visible light and partially (10 %) transforms into the methyl radical. (2)The methyl radical decays at 77-180 K. (3)At 230-265 K, the side-chain radical transforms, without loss of total radical concentration into the propagating-type radical, so that the the *G* value of the propagating-type radical present at room temperature is 2.0 (4)The main-chain radical partly disappears above 265 K but most of the radical (G=0.8) survives at room tempera-ture. The decay of this radical does not accompany the forma-tion of any new radical. (4) If the sample is warmed without photobleaching, the anion radical decays at 77-180 K. There is no difference in the spectral features above 180 K between the photobleached and unbleached samples.

It is indicated that the precursor of the propagating-type radical is the side-chain radical. Therefore, the scission of the main chain proceeds very probably as shown below:

$$-CH_2-CCH_3(COO\dot{C}H_2)-CH_2- \longrightarrow -CH_2-\dot{C}CH_3-CH_2- + CO + CH_2O$$

$$-CH_2-\dot{C}CH_3-CH_2- \longrightarrow -CH_2-CCH_3{=}CH_2 + \dot{C}(CH_3)COOCH_3-CH_2-$$

The transient radical $-\dot{C}CH_3-$ has not yet been observed successfully. However, the effect of the uv-illumination on the side-chain radical strongly supports the the $-\dot{C}CH_3-$ radical as being the immediate precursor.

[1]T.Ichikawa, H.Yoshida, *J.Polym.Sci.Part A*, 28, 1185 (1990)

APPLIED ASPECTS OF SOLID STATE PULSE RADIOLYSIS

Z.P.Zagórski
Department of Radiation Chemistry and Technology
Institute of Nuclear Chemistry and Technology
03-195 Warszawa, Poland

Pulse radiolysis is executed mainly on liquids, giving important information concerning the identities and reactions of short living species. However, the majority of objects of radiation processing are solid or at least rigid and conclusions drawn from the results of pulse radiolysis of liquids have little application. Chemical basics referring to the radiation processing of objects in the solid and rigid state, derive from esr spectrometry, radiothermoluminescence, lyoluminescence, product analysis etc. These methods seldom give a clue as to the mechanism of reactions. They only identify products, stable at the temperature of irradiation and storage. In an attempt to look into the mechanisms of reactions in the solid state we have intensified our efforts towards the application of pulse radiolysis to solid samples [1]. Experimental work is much more difficult here. The transparency of the samples is usually poor. In few cases only, e.g. of aqueous clathrates, the transparency is not worse than in the case of frozen glasses and conventional experimental arrangement, i.e. with the external analytical light may be applied. In other cases samples are opaque and the conventional approach is not possible. We have applied, in such cases, our Čerenkov Light Selfabsorption Method (ČLSM), which enables us to measure the transient absorption spectrum of an intermediate. Experiments have shown that in the majority of cases there is no need to change the sample after every pulse Usually, one sample is sufficient to obtain several spectra. The ČLSM has an advantage over the reflection spectroscopy method, which may cause undesirable photochemical effects generated by the high intensity of the source of analytical light. Our experience is exemplified by pulse radiolysis of crystalline biogenic amino acids. Many of them show transients which are identified as free radicals before deamination and/or decarboxylation. All measurements [2] were performed at room temperature and transients disappeared in miliseconds. Alanine is among the amino acids showing the transient clearly. The light absorbing species are precursors of a deaminated free radical, observed by esr spec- spectrometry. Thus the better insight is presented into the well known, solid state dosimetric system. The importance of pulse radiolysis in solid state for looking into new dosimetric systems of potential applied value is stressed. Pulse radiolysis of solid samples also gives important results if the intermediates decay with the emission of light. In general, solid state pulse radiolysis offers insight into phenomena which escape the observation in liquid systems, where rapid diffusion plays an important role. Other examples refer to solid crystalline aqueous clathrates, which may be investigated at practically same temperature in the liquid state.

[1]. Z.P. Zagórski, Solid state pulse radiolysis, in

New Trends and Developments in Radiation Chemistry,
IAEA-TECDOC-527, 1989, p.79.

[2]. Z.P. Zagórski and Z. Tomasiński,
part of the results submitted for publication as a "letter"

GEMINATE ELECTRON-ION PAIRS RECOMBINATION IN RADIOLYSIS OF TRI-N-BUTYLPHOSPHATE AND HEXANE-TRI-N-BUTYLPHOSPHATE MIXTURE

Zaitsev V.D., Khaikin G.I., Tsarevsky A.V.

A.N.Frumkin Institute of Electrochemistry of Academy
of Sciences of the USSR, Moscow

On the base of the concentration dependence of the electron scavenging efficiency by diphenyl employing modificated empyrical Warman-Asmus-Schuler equation the yields and the effective frequencies of the recombination of correlated electron-ion pairs and the free-ions yields of excess electrons were stated in tri-n-butylphosphate(TBP) and its mixture with hexane. At temperature 213 K these values we found to be 3.21 particles/100eV, $3.52*10^7 s^{-1}$, 0.84 particles/100eV for TBP and 3.71, $4.5*10^8$, 0.28 for TBP(30v.%)-hexane mixture accordingly.

The adequacy of the values obtained to kinetic parameters of real electron-ion pairs decay has been demonstrated by compairing of calculated temporal dependences of survived geminate pairs fraction obtained by inverse Laplace trasformation of the equation for rectangular radiation pulse of limited duration with experimental kinetic curves of solvated electrons(e_s^-) produced in the solvents by 20 ns-pulse of accelerated electrons.

Spectral characteristics and kinetic parameters of some reactions of e_s^- in TBP and TBP-hexane mixture were studed. The possible origins of observed dilution effects just as practical importance of obtained results from the point of view their applications for simulating radiation processes in extraction systems used in radiochemical technology are discussed.

THE X-RAY DAMAGE OF PROTEINS IN AQUEOUS SOLUTION

I. CORRELATION OF STRUCTURAL PARAMETERS OBTAINED FROM SMALL-ANGLE X-RAY SCATTERING STUDIES

P.Zipper[1] and H.Durchschlag[2]

[1] Institute of Physical Chemistry, University of Graz, Austria
[2] Institute of Biophysics and Physical Biochemistry, University of Regensburg, Federal Republic of Germany

Small-angle X-ray scattering was introduced by us into the field of radiation biology as a novel technique for studying radiation-induced structural changes of biopolymers [1,2]. The method turned out to be a very potent tool for establishing several structural parameters obtained under various conditions and characterizing different phenomena of radiation damage. Both time-resolved experiments (monitoring the damage in situ) and studies on pre-irradiated samples were performed in the absence or presence of additives. Parameters obtained include: mean degree of aggregation, radius of gyration, shape factor, extent of fragmentation, rate constants describing the effects of aggregation. As shown by a series of studies on proteins (cf. [3] and references therein) additives provided quite different protective effects against aggregation and fragmentation, depending on the nature and concentration of additives. The present study attempts to correlate and compare the structural parameters obtained in previous studies. In particular, the following comparisons and correlations of parameters were carried out: in situ vs. in situ, pre-irradiated vs. pre-irradiated, in situ vs. pre-irradiated. The findings show a good consistency of quantities derived from the two lines of experiments (in situ, pre-irradiated) and some parallelism of aggregation and fragmentation. The results indicate different modes of aggregation with different proteins and additives. A correlation of structural and functional parameters will be presented in a separate contribution [4].

[1] Zipper, P., Durchschlag, H.: Radiat. Environ. Biophys. 18, 99-121 (1980).
[2] Zipper, P., Gatterer, H.G., Schurz, J., Durchschlag, H.: Monatsh. Chem. 111, 981-1004 (1980).
[3] Zipper, P., Durchschlag, H., Gatterer, H.G., Kriechbaum, M., Wilfing, R.: Proc. 6th Tihany Symp. on Radiat. Chem., Balatonszéplak 1986, pp. 797-801, Akadêmiai Kiadô, Budapest 1987.
[4] Durchschlag, H., Zipper, P.: cf. separate abstract.

SPIN TRAPPING IN RADIATION AND PHOTOCHEMISTRY

Zubarev V.E.
Department of Chemistry Moscow State University
117234 Moscow USSR

Spin trapping method, firstly introduced in 1969 by Janzen & Blackburn(1969) has been successefully used during recent 10-15 years for the structure and reactivity studies of radicals and to investigate the mechanism of various processes involving short-lived radicals in chemistry, biology and medicine(Zubarev 1984).

Starting in radiation chemistry from the very informative work of Wargon & Williams(1972) on the study of structure of short-lived radicals formed under the radiolysis of methanol(CH_3O and CH_2OH) at present Spin trapping method is a quantitative kinetic method especially in radiation and photochemistry.

After a discussion of previous results on spin trapping studies in radiation and photochemistry new own results as well as results in chemistry of spin traps will be presented , including new possibilities for the study of radical processes with the aim of spin trapping technique. The most important from this is the formation, structure and reactions of anion- and cation-radicals of spin traps.

Taking into account the chemistry of spin traps, one can obtain essentially new information about the mechanism of radiation and photochemical reactions involving reactions of holes, electrons and free radicals.

References.

Janzen E.G. & Blackburn J.(1969) J. Am. Chem. Soc., 90,7141-43.
Wargon J.A. & Williams F.(1972) J. Am. Chem. Soc., 94, 7917-19.
Zubarev V.E. (1984) Spin trapping method. Use in chemistry, biology and medicine. Moscow State University Publishing House. Moscow, 187pp. (Russ.).

EFFECT OF IRRADIATION TEMPERATURE ON RELATIONSHIP BETWEEN SOL FRACTION AND DOSE OF FLUOROPOLYMERS

Zhang Wanxi and Xu Jun
Changchun Institute of Applied Chemisrty, Chinese
Academy of Sciences, Changchun 130022, China

The experimental results have shown that behaviors of radiation crosslinking for some fluoropolymers do not fit Charlesby-Pinner's expression[1] relating sol fraction (S) to radiation dose (R). We have proposed a general expression,

$$R\,(S + \sqrt{S}\,) = 1/q_0U_1 + \alpha_0 R^{\beta}/q_0 \qquad (1)$$

where β is a crosslinking parameter characterized the relationship between the structure of polymer chain and the behavior of radiation crosslinking. β may be expressed as a function of Tg and difference ($\triangle T$) between irradiation temperature (Ti) and glass transition temperature of polymer (Tg), i. e $\beta = f(Tg, \triangle T)$ where $\triangle T = Tg - Ti$. Taking account of that β is linear with Tg[2], β may be expressed by

$$\beta = 2.2\times10^{-3}Tg + 3\times10^{-4}\,(Tg-Ti) + 0.206 \qquad (2)$$

in which the physics of $3\times10^{-4}\,(Tg-Ti)$ is the contribution of irradiation temperature to the probability of crosslinking. When $Ti > Tg$, $3\times10^{-4}\,(Tg-Ti)$ is a negative number. It is therefore implied that the increasing of irradiation temperature may bring about decreasing of β value, which increases the crosslinking probability of polymer.

On the basis of Tg and Ti for fluoropolymers, the values of β calculated from Eq. (2) are in good agreement with the experimental values obtained by substituting the experimental value of R and S into Eq.(1) (as shown Table I) .

Table I β value of fluoropolymers

polymer	Tg (k)	Ti (k)	$\beta_{exp.}$ [3] (r)	$\beta_{cal.}$ From Eq.(2)
F-30	337	423	1 (1)	0.92
F-46	356	513	0.91 (0.980)	0.94
F-406	283	373	0.77 (1)	0.80
F-40	320	513	0.85 (0.994)	0.85
FPI	546	593	1 (0.980)	1.39
PVF2	236	298	0.70 (0.995)	0.71

r- Correlation coefficient fitting Eq.(1)

REFERENCES

[1] Charlesby, A. and Pinner, S.H., Proc. Roy. Soc., A249, 367(1959).

[2] Zhang, W.X., He, T.B, Sun, J.Z. and Qin, B.G., Kexue Tongbao, 3, 189(1986)

[3] Zhang, W.X. et al., J. Radiat. Res. and Radiat. Proc., 4(3), 35(1986).

MTESZ - egyesületi használatra !

Kiadja: Magyar Kémikusok Egyesülete
Készült: 160 példányban
90/995 MTESZ Házinyomda, Budapest.
Felelős vezető: Boncza Gábor

ISSN 0231-0317

ISBN 963 8191 29 2