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L. A. TIKHOMIROV, N. Ya. BUBEN

RADIOLYSIS OF SOLID SOLUTIONS OF STABLE RADICALS IN ISOPROPYL ALCOHOL

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As is known, in the radiolysis of liquids stable radicals (for example, diphenylpicrylhydrazyl) are used as acceptors of radicals formed in the solvent. Measurement of the acceptor concentration during irradiation in this case makes it possible to determine the number of short-lived radicals that have reacted with the acceptor. The application of the electron paramagnetic resonance method has made it possible to establish ($^{1-3}$) that, when ionizing radiation acts on solid organic solutions, a significant transfer of energy occurs from the solvent to the dissolved substance. This is manifested, in particular, in a change in the radiation yield, the limiting concentration, and sometimes the nature of the radicals formed. However, as a rule, the investigator has no information on how effectively the radiation acts on the dissolved substance. The use of stable radicals, it seems to us, can provide additional information on this question. On the basis of the foregoing, it appeared of interest to study the kinetics of destruction of stable radicals during irradiation of frozen solutions of them in an organic solvent, which makes it possible simultaneously to follow the radicals formed in it. As the object of investigation in the present work we chose solutions of 2,2,6,6-tetramethylpiperidine nitroxide (^{4}) in isopropyl alcohol. The EPR spectrum of the stable radical in such solutions at a temperature of 100° K, according to our measurements, is a triplet with a splitting between the outer components of 65 oersted, whereas the spectrum of radicals formed in isopropyl alcohol consists of 7 lines of hyperfine structure with a total splitting of 120 oersted (^{5}). Such a difference in the width of the spectra makes it possible to record the outer lines of the alcohol radical practically without superposition of the signal from the stable radical up to a content of the latter in the solution of $1.6 \cdot 10^{20}$ g^{-1}. By determining the total number of radicals in the solution and calculating the number of alcohol radicals from measurement of the outer components of the spectrum, it is possible to follow the concentrations of both radicals during irradiation.

Samples of the mixture weighing 20–40 mg, from which the air had previously been evacuated, were sealed in thin-walled ampoules made of "Luch" glass and irradiated with electrons of energy 1.6 MeV directly in the resonator of the EPR spectrometer. The procedure for determining the concentration and dose is described in (^{6}). The total dose was 100-200 Mrad. The dose rate was varied from 1.4 to 10 Mrad/min. The experiments were carried out at a constant temperature of 100° K, for which purpose the samples were blown with a jet of cold gaseous nitrogen. The temperature of the jet was measured with a copper-constantan thermocouple.

The dependence of the concentration of stable radicals and of radicals formed in the alcohol on the irradiation dose at a temperature of 100° K was studied at various initial concentrations of stable radicals N_0 from $2.6 \cdot 10^{19}$ to $2.5 \cdot 10^{20}$ g^{-1}. Figure 1a gives the results of one

from the measurements: the change in the total concentration of radicals is represented by the upper curve, the accumulation of alcohol radicals by curve N_2; the dose dependence of the concentration of stable radicals (N_1) was obtained by subtracting the second curve from the first. At the end of the experiment the mixture was heated to a temperature of 190°K, at which recombination of the alcohol radicals occurred, and the final concentration of stable radicals was measured. As is seen from Figs. 1b and c, which give linear anamorphoses of the curves $N_1(D)$ and $N_2(D)$, the destruction of stable radicals in an alcohol solution under the action of radiation is satisfactorily described by the law:

$$N_1 = N_0 e^{-k_1 D}, \tag{1}$$

where D is the dose, k_1 is a constant, and the accumulation of alcohol radicals occurs according to the law

$$N_2 = N_{2\text{pr}} \left[1 - e^{-k_2 D}\right], \tag{2}$$

where $N_{2\text{pr}}$ is the limiting concentration of alcohol radicals and k_2 is a constant. These dependences were fulfilled for all the initial concentrations N_0 studied. Special experiments showed that the constants k_1 and k_2 do not depend on the dose rate when the latter was varied from 1.4 to 10 Mrad/min, nor on the rate of freezing of the solution. The values of the initial radiation yields of destruction of stable radicals $G(-R_{\text{stab}})$ and formation of alcohol radicals $G(R_{\text{sp}})$ were determined from expressions (1) and (2), respectively, as

$$G(-R_{\text{stab}}) = (dN_1/dD)_{D \to 0} = k_1 N_0$$

and

$$G(R_{\text{sp}}) = (dN_2/dD)_{D \to 0} = k_2 N_{2\text{pr}}.$$

Fig. 1. a —Dependence of radical concentration on irradiation dose; b —linear anamorphosis of the curve for destruction of stable radicals; c —the same for accumulation of alcohol radicals

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The error in determining the constants k_1 and k_2 did not exceed 20%. Table 1 gives the values of N_0, k_1, $N_{2\mathrm{pr}}$, k_2, and the radiation yields $G(-R_{\mathrm{stab}})$ and $G(R_{\mathrm{sp}})$, calculated per 100 eV of energy absorbed by 1 g of solution. In parentheses are also given the radiation yields obtained from the mean values of the constants k_1. The last columns of the table give the electron fractions E of stable radicals in the solution and the ratios $G(-R_{\mathrm{stab}})/E = G'(-R_{\mathrm{stab}})$, i.e., the radiation yields of destruction of stable radicals recalculated per 100 eV of energy absorbed only by the radicals.

Along with measurements of radical concentration, the yields of molecular hydrogen upon irradiation of pure isopropyl alcohol and of an alcoholic solution of stable radicals containing $3\cdot 10^{20}$ radicals/g at a temperature of 100°K were compared by the mass-spectrometric method. It turned out that the hydrogen yield in the radiolysis of the solution differs little (decreases by approximately 25%) from the yield in the alcohol. In a number of experiments the number of stable radicals that had reacted with atomic hydrogen was also measured. For this purpose, after irradiation the mixture was heated and lead peroxide was added to the liquid solution; this quantitatively converts 2,2,6,6-tetramethylpiperidine hydroxylamine into the free-radical state. In this way it was shown that no more than 25% of all stable radicals destroyed during radiolysis enter into reaction with atomic hydrogen formed during irradiation.

As is seen from Table 1, in solid solutions stable radicals are destroyed with a very large radiation yield $G'(-R_{\mathrm{stab}})$, amounting to

amounting, when calculated per energy absorbed by the radicals themselves, on average to 240 radicals per 100 eV. Measurement of the destruction kinetics of the same stable radicals when they were irradiated in the form of a polycrystalline powder without solvent showed that the radical concentration changes with dose in accordance with law (1), but with the constant $k_1 = 4\cdot 10^{-4}$ Mrad^{-1} and a radiation yield $G'(-R_{\mathrm{stab}}) = 2/100$ eV. Thus, in a frozen solution of isopropyl alcohol the stable radicals are destroyed under the action of radiation approximately 100 times more efficiently than in the absence of solvent.

Table 1

$N_0 \cdot 10^{-19}$, g^{-1}	0	2.6	3.5	5.2	9.7	12	16	25
$k_1 \cdot 10^2$, Mrad^{-1}	–	4.2	3.3	5.2	5.1	2.6	3.4	3.5*
$G(-R_{\text{stab}})$, eV$\cdot 10^{-2}$		1.7	1.8	4.3	7.9	5.0	8.7	14
		(1.7)	(2.2)	(3.3)	(6.2)	(7.7)	(10)	
$N_{2\text{pr}} \cdot 10^{-19}$, g^{-1}	3.6	3.5	4.0	3.4	3.9	3.9	3.5	
$k_2 \cdot 10^2$, Mrad^{-1}	4.4	3.7	3.9	5.2	4.6	4.9	5.2	
$G(R_{\text{sp}})$, eV$\cdot 10^{-2}$	2.4	2.1	2.5	2.8	2.9	3.0	2.9	
$E \cdot 10^3$		6.8	9.2	13	25	30	42	66
$G'(-R_{\text{stab}})$, eV$\cdot 10^{-2}$		250	196	330	316	167	207	212

* The value of the constant k_1 at this concentration was calculated from the slope of the curve of the total radical concentration at low doses, since it was not possible to record the initial portion of the alcohol-radical accumulation curve.

This effect cannot be explained by recombination of radicals with hydrogen atoms split off from alcohol molecules, since the radiation yield $G(\text{H}) = G(R_{\text{sp}}) \simeq 3/100$ eV, whereas $G(-R_{\text{stab}})$ reaches values of 10-14 per 100 eV. In addition, direct measurements of the yields of molecular hydrogen and of the fraction of radicals regenerated by lead peroxide are in contradiction with such an assumption.

It seems to us that an essential role in the mechanism of destruction of stable radicals by radiation is played by their destruction—the rupture of chemical bonds with the formation of mobile secondary radicals. The large values of $G(-R_{\text{stab}})$ indicate that a large amount of energy absorbed by the solvent is transferred to the radicals. It should be noted that the observed radiation yields for radical destruction are difficult to explain either by energy transfer through electronic excitation levels of the solvent or by charge transfer: these mechanisms apparently cannot provide the decomposition of 10-14 radicals when 100 eV of energy is absorbed by the solvent. This remark applies to an even greater extent to work (7), in which the radiolysis of frozen solutions of ferric chloride in organic solvents was studied, and for the solution in benzene a value $G(-\text{FeCl}_3) = 23/100$ eV was obtained, the authors considering that the energy is transferred via the $^1B_{2u}$ level of benzene.

One of the most important results obtained in the present work is the practical equality of the constants k_1 and k_2. From equations (1) and (2) it is seen that they represent the rate constants for destruction of stable and alcohol radicals during irradiation, calculated per unit dose rate. Their equality means that the probability of destruction by radiation of stable radicals is the same as for alcohol radicals during their accumulation. It should be noted that in solid isopropyl alcohol the radicals $(CH_3)_2COH$ are apparently also destroyed mainly by radiation. This is indicated by the large radiation yield of acetone in the radiolysis of frozen isopropanol (8).

On the basis of the experimental data, one can estimate the ratio of the probabilities of formation of a new radical and destruction of an already existing one. The rate constant for radical formation by radiation, k_0, calculated

per unit dose rate, i.e., the radiation yield of alcohol radicals referred to one alcohol molecule, is evidently expressed as $k_0 = G(R_{\text{sp}})/n = k_2 N_{\text{pr}}/n$, where n is the number of alcohol molecules in one gram of solution. For isopropyl alcohol at 100°K, $k_0/k_2 \cong 4 \cdot 10^{-3}$. Consequently, the probability that a radical is destroyed by radiation is approximately 250 times greater than the probability of the birth of a new one. This may be associated with the weakening of chemical bonds in the radical (^{9}), as a result of which the energy transferred through the solvent effectively destroys radicals.

We believe that the high probability of radical destruction by radiation is in many cases the principal cause determining the regularities of radiation accumulation of radicals in organic substances at low temperatures and, in particular, their low limiting concentrations. This is indicated by the validity of formula (2) and by the close values of the constants k_2 for a number of the compounds investigated (^{10}).

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Institute of Chemical Physics
Academy of Sciences of the USSR

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