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Abstract

Full Text

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FORMATION OF ION-RADICALS UNDER THE ACTION OF γ-RADIATION ON THE TETRAHYDROFURAN–STYRENE SYSTEM AT −196°

(Presented by Academician S. S. Medvedev on 29 X 1962)

Under the influence of ionizing radiation, many organic substances at −196° acquire coloration and paramagnetic properties (ˆ1). It is assumed that in frozen alcohols and ethers the colored centers are trapped electrons (ˆ2). The addition to such substances of compounds possessing strong electron-acceptor properties leads to the formation of the corresponding anion-radicals (ˆ3). It has also been shown that upon γ-irradiation at −196° of dilute solutions of aromatic amines in polymethyl methacrylate or in hydrocarbons, formation of amine cation-radicals occurs (4,5).

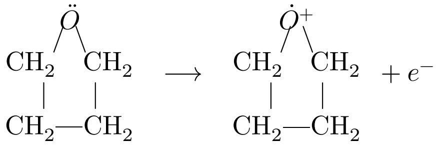
In the present work new data have been obtained on the formation of ion-radicals upon irradiation, frozen at −196°, of tetrahydrofuran (THF) and solutions of styrene in THF. The spectra of electron paramagnetic resonance (e.p.r.) were investigated on a superheterodyne radiospectroscope with high-frequency modulation of the magnetic field at 500 kc and a cylindrical resonator for the H_{011} mode (ˆ6). The investigated samples of tetrahydrofuran, styrene, and their mixtures were purified by the method described in (ˆ7) and freed of air in a high vacuum. Irradiation was carried out on a γ-source of Co^{60} at −196° with doses from 0.14 to 6 Mrad.

Fig. 1. E.p.r. spectra of γ-irradiated THF: *a*—−196°, *b*—−160°.

The e.p.r. spectra of irradiated polycrystalline THF at −196 and −160° are presented in Fig. 1. As is seen from Fig. 1, the spectrum of irradiated THF consists of 5 components of hyperfine structure (h.f.s.), which may be attributed to the interaction of an unpaired electron with four protons. The ratio of the intensities of the h.f.s. components at −196° differs from the binomial distribution. With increasing temperature the ratio of the intensities of the h.f.s. components approaches the binomial distribution corresponding to the case of interaction with four equivalent protons. The spectrum obtained, apparently, may be assigned to the THF cation-radical.

Fig. 2. EPR spectra of a solution of styrene in THF (2.18 mol/l), irradiated with a dose of 0.14 Mrad at −196°, at different power levels of the signal generator: a –power 5 mW; b, c, d, e –obtained at powers respectively lower by 6, 10, 16, 20, and 26 dB

Figure 2: Fig. 2. EPR spectra of a solution of styrene in THF (2.18 mol/l), irradiated with a dose of 0.14 Mrad at −196°, at different power levels of the signal generator: a –power 5 mW; b, c, d, e –obtained at powers respectively lower by 6, 10, 16, 20, and 26 dB



In Fig. 2 are presented the e.p.r. spectra of a solution of styrene in THF (2.18 mole/l), irradiated with a dose of 0.14 Mrad at −196°. This system is a transparent glass, which after irradiation acquires

red coloration. It is of interest that, upon irradiation of pure styrene with the same doses, no EPR signals were detected. The observed line shape of the EPR signal depends substantially on the power level of the signal generator. At a power of 5 mW and with a cylindrical resonator tuned to the H_{011} wave, a saturated signal is observed, the shape of which approaches that of the THF signal. As the power level of the signal generator is lowered, there is at first some increase in the signal intensity

Fig. 2. EPR spectra of a solution of styrene in THF (2.18 mol/l), irradiated with a dose of 0.14 Mrad at −196°, at different power levels of the signal generator: a –power 5 mW; b, c, d, e –obtained at powers respectively lower by 6, 10, 16, 20, and 26 dB

with a slight deterioration in the resolution of the structure, and then a decrease in the signal and disappearance of the hyperfine structure. At low power levels ($p = 5$ μW) the signal is an unresolved singlet.

In order to interpret the indicated spectra, a detailed study was made of THF and of solutions of styrene in THF at various irradiation doses. It was found that, in the absence of saturation, the signal shape of γ-irradiated pure THF does not depend on the irradiation dose (within the range from 0.14 Mrad to 6 Mrad), while the intensity is proportional to the dose. The power of the signal generator at which distortion of the signal shape sets in owing to the saturation effect depends on the irradiation dose. At low irradiation doses, distortion of the signal shape begins at considerably lower power levels. Thus, the power level of the signal generator at which saturation occurs at a dose of 0.14 Mrad is approximately 20 times lower than at a dose of 0.84 Mrad. The signal shape of irradiated THF (dose 0.84 Mrad) at signal-generator powers below 1 mW and a magnetic-field modulation amplitude $H_m = 7$ Oe does not depend on the power level, and the amplitude is proportional to the square root of the power. However, at a power of 1 mW, reducing the modulation amplitude by a factor of 10–100 leads to distortion of the absorption-signal shape, which, as experiments show, is due to an increase in the magnitude of the dispersion signal relative to the absorption signal. At a power of 1 mW and a modulation amplitude $H_m = 7$ Oe, a well-resolved structure of the dispersion signal is observed. As the modulation amplitude is decreased, the structure of the dispersion signal becomes smeared, and its magnitude does not depend on the modulation amplitude down to $H_m = 0.07$ Oe.

In the absence of saturation, the magnitude of the absorption signal for the styrene—THF system in the composition range from 1:3 to 1:1 is proportional to the THF concentration. With increasing dose, the shape of the absorption signal of the styrene—THF system depends to a lesser degree on the power level of the signal-

generator. At a dose of 0.84 Mrad, the signal shape, at the power levels used and $H_m = 7$ oersteds, coincides with the signal shape in Fig. 2 corresponding to low power levels.

Illumination of a sample of the irradiated solution of styrene in THF in a glass ampoule at −196° with the total light of a mercury lamp causes its bleaching; at the same time, the singlet characteristic of the EPR spectrum of the γ-irradiated solution disappears, and a signal appears corresponding to irradiated pure THF (Fig. 3). The dependence observed at a dose of 0.14 Mrad of the shape of the EPR spectra of a solution of styrene in THF on the power level of the signal generator (Fig. 2), as well as the disappearance of one of the signals upon illumination with ultraviolet light, are direct evidence for the formation of two radicals during γ-irradiation of this system.

The change in signal shape for a solution of styrene in THF at a dose of 0.14 Mrad, as a function of the power level, can be explained by different spin-lattice relaxation times T_1 and cross-relaxation times T_{21} of these two radicals. The relaxation times of the THF radical at a dose of 0.14 Mrad are shorter than the relaxation times corresponding to the other radical; therefore, at high power levels of the signal generator the THF radical is saturated less strongly, and its magnitude proves to be relatively larger and determines the observed signal shape. An increase in the dose of γ-irradiation leads to an increase in the concentration of radicals and to a decrease in the average distance between them, which causes a decrease in the cross-relaxation time (^{8}). The change in cross-relaxation time with irradiation dose is confirmed by experiments with γ-irradiated pure THF. The increase observed here, with increasing irradiation dose, in the power level of the signal generator at which no saturation effect is yet observed is associated with a decrease in the cross-relaxation time.

Fig. 3. EPR spectra of a solution of styrene in THF (2.18 mole/liter). Irradia-

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

tion dose 1.14 Mrad at −196°: *a*—before illumination with ultraviolet light; *b*—after illumination.

Fig. 4. EPR spectrum of the styrene anion-radical at −196°.

The width of the components of the h.f.s. of THF at −196° is due to the anisotropy of the hyperfine structure, as follows from the dependence of the spectrum shape on the power level and on the amplitude of modulation of the magnetic field, and also from the fact that the widths of the components narrow with increasing temperature. Therefore, at low irradiation doses a case of inhomogeneous saturation is observed. As the concentration of radicals increases, the cross-relaxation time T_{21} becomes shorter than the spin-lattice relaxation time, and the saturation becomes homogeneous, even in the case of inhomogeneous line broadening (^{9}). The small changes in the signal shape for a solution of styrene in THF as a function of the power level (at a dose of 0.84 Mrad) can be explained by a decrease in the cross-relaxation time in the radicals studied, as a result of which, at the given power levels, the difference in relaxation times is not manifested. The disappearance of one of the signals upon illumination of the styrene—THF system with ultraviolet light gives grounds to suppose that γ-irradiation of this system leads to the formation of anion-radicals with the low ionization potential characteristic of them. Apparently, under these conditions the styrene anion-radicals are formed as a result of capture of thermal electrons by styrene molecules. In Fig. 4

the EPR signal of these anion radicals, obtained by subtracting the residual signal after irradiation of the sample with ultraviolet light from the initial signal. By comparing the yields of cation and anion radicals, one can estimate the probability of electron capture by the electron-acceptor additive under these conditions. A comparison of the EPR spectra presented in Fig. 3 shows that the concentration of THF cation radicals is approximately half the total concentration of radicals in the styrene—THF system. It follows from this that the probability of electron capture by styrene at a concentration of the latter of 2.18 mole/liter is close to unity. Under ultraviolet irradiation, the electron apparently passes from the styrene molecule into the THF lattice and finds itself in the same state as upon irradiation of pure THF. It is interesting that styrene anion radicals are stable in the styrene—THF system, whereas they are not formed in appreciable concentrations upon irradiation of pure styrene, although it would seem that in both systems the probability of formation of anion radicals should be the same.

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REFERENCES

1. R. S. Alger, T. H. Anderson, L. A. Webb, J. Chem. Phys., **30**, 695 (1959).
2. H. Linschitz, M. G. Berry, D. Schweitzer, J. Am. Chem. Soc., **76**, 5833 (1954).
3. P. S. Rao, J. R. Nash et al., J. Am. Chem. Soc., **84**, 500 (1962).
4. Kh. S. Bagdasar' yan, V. A. Krongauz, N. S. Kardash, DAN, **144**, 101 (1962).
5. Kh. S. Bagdasar' yan, Z. A. Sinitsyna, DAN, **147**, No. 6 (1962).
6. V. I. Muromtsev, A. K. Piskunov, N. V. Verein, Radiotekhnika i elektronika, No. 7, 1070 (1962).
7. A. P. Sheinker, A. D. Abkin, Vysokomolek. soed., **3**, 716 (1961).
8. N. Bloembergen, S. Shapiro, P. S. Pershan, Phys. Rev., **114**, 445 (1959).
9. S. A. Al' tshuler, B. M. Kozyrev, *Electron Paramagnetic Resonance*, Moscow, 1961.

Note: Figure translations are in progress. See original paper for figures.