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STABILIZATION OF FREE RADICALS IN IONIC CRYSTALLINE MATRICES

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For the study of free radicals, the method of stabilizing them in various matrices is widely used (1). In this case the stability of the radicals—the temperature at which their recombination is observed at an appreciable rate—is determined to a considerable degree by the properties of the matrix. Radicals formed during radiolysis and photolysis of frozen organic substances rapidly recombine on heating to the glass-transition temperature in amorphous substances and to near the melting temperature in crystalline substances (2). In individual cases recombination also occurs at a lower temperature—in the region of the thawing of certain molecular motions in the matrix. Therefore it may be expected that the use of stronger matrices will make it possible to prevent recombination of organic radicals up to higher temperatures. An attempt to use an ionic crystal lattice for these purposes was made in work (3): a mechanical mixture of KCl with small additions of certain solid organic substances was subjected to photolysis. The small effect observed in this case is associated, in the opinion of the authors themselves, with stabilization of radicals on the surface of microcrystals.

It is of interest to ascertain the possibility of stabilizing organic radicals in an ionic lattice as a matrix under conditions where the initial organic molecules and the matrix material are present in comparable amounts and form a chemically homogeneous system. For this purpose one can use, for example, crystallosolvates—molecular compounds of inorganic salts with organic solvents—which are crystals of known composition (4). Upon irradiation of such compounds with gamma rays or fast electrons, one may expect a substantial increase in the stability of the radicals formed. Although this method of introducing organic compounds into an ionic crystal lattice is not universal, it is applicable in many cases, since the number of compounds of this type is fairly large. In the present work we investigated radicals formed upon irradiation of compounds of normal alcohols (methyl, ethyl, *n*-propyl) with magnesium chloride and calcium chloride of the type $MgCl_2 \cdot 6ROH$ and $CaCl_2 \cdot 4ROH$ (5). The indicated compounds were obtained by the procedure described in work (6). Irradiation of the samples was carried out at −170° with fast electrons of energy 1.6 MeV to a dose of about 40 Mrad. The radicals formed were recorded by the method of electron paramagnetic resonance (e.p.r.). The concentration of paramagnetic centers in the irradiated samples was $\sim 10^{20}$ paramagnetic centers per 1 g. The

Fig. 1. EPR spectra of irradiated alcohols in the $MgCl_2$ matrix: a —methyl at −150°, b —the same at −40°, c —ethyl at −80°, d —n-propyl at −150°, e —the same at −90°

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e.p.r. spectra observed upon irradiation of alcohols in $CaCl_2$ and $MgCl_2$ matrices coincide with the spectra of the corresponding alcohols irradiated at the temperature of liquid nitrogen (^{7}). This permits the conclusion that in both cases mainly identical radicals are formed. For three of the investi-

The EPR spectra of the irradiated compounds are shown in Fig. 1 (*a, b, c*). It is of interest that the spectra lack the lines usually observed upon irradiation of ionic crystals and associated with the formation of capture centers. This can be explained by loosening of the crystal lattice when compounds with alcohol are formed, as a result of which the depth of the energy traps for electron capture decreases.

For obtaining information on the comparative stability of alcohol radicals in frozen alcohol and in an ionic crystalline matrix, the change in radical concentration with increasing temperature was investigated. For this purpose the irradiated sample was blown, together with a standard, by a stream of dry nitrogen of a specified temperature. When the sample reached the temperature of the stream, the EPR spectrum of the radicals was recorded; then the temperature of the stream was raised, and so on. The time for which the sample remained at constant temperature was about 15 min; during this time no appreciable decrease in radical concentration occurred. Such measurements do not make it possible to obtain quantitative information on the kinetics of radical recombination, but they immediately show in what temperature interval rapid disappearance of the radicals begins. Figure 2 gives curves for the change in concentration of free radicals with increasing temperature for frozen methyl alcohol and the compound $MgCl_2 \cdot 6CH_3OH$.

Fig. 1. EPR spectra of irradiated alcohols in the matrix $MgCl_2$:
a —methyl at −150°, *b* —the same at −40°, *c* —ethyl at −80°, *d* —*n*-propyl at −150°, *e* —the same at −90°.

As is seen from comparison of these curves, in the ionic crystal lattice alcohol radicals can readily be observed at temperatures considerably exceeding the melting point of methyl alcohol. Up to a temperature of −30°, recombination of radicals in the matrix proceeds slowly: during 15 min their concentration does not change noticeably. At higher temperatures a rapid decrease in radical concentration with time is observed, but apparently this is connected chiefly with decomposition of the compound $MgCl_2 \cdot 6CH_3OH$ itself when the sample is blown by a stream of nitrogen. Radicals formed upon irradiation of ethyl

Fig. 2. Change in concentration of the radical CH_2OH (arb. units) with temperature: 1 —in frozen methyl alcohol, 2 —in $MgCl_2 \cdot 6CH_3OH$

Figure 2: Fig. 2. Change in concentration of the radical CH_2OH (arb. units) with temperature: 1 —in frozen methyl alcohol, 2 —in $MgCl_2 \cdot 6CH_3OH$

Fig. 3. Temperature dependence of the ratio of the amplitudes of the central and outer components of the hyperfine structure for the first derivative of the spectrum of the $\dot{C}H_2OH$ radical

Figure 3: Fig. 3. Temperature dependence of the ratio of the amplitudes of the central and outer components of the hyperfine structure for the first derivative of the spectrum of the $\dot{C}H_2OH$ radical

and *n*-propyl alcohols were also observed in $CaCl_2$ and $MgCl_2$ matrices up to a temperature of $-30°$.

Fig. 2. Change in concentration of the radical $\dot{C}H_2OH$ (arb. units) with temperature:
1 —in frozen methyl alcohol, 2 —in $MgCl_2 \cdot 6CH_3OH$.

The possibility of observing, over a wider temperature range, the free radicals formed in the radiolysis of normal alcohols made it possible to obtain new information on the nature and properties of these radicals.

1. The EPR spectrum of the radical $\dot{C}H_2OH$, observed in irradiated $MgCl_2 \cdot 6CH_3OH$ at $-150°$, is shown in Fig. 1a. The ratio of the amplitudes of the components of the hyperfine structure of the first derivative of the spectrum at this tem-

at a temperature is approximately equal to $1 : 1.7 : 1$. As the temperature is raised, a relative increase in the amplitude of the central component is observed. This is illustrated by Fig. 1 , which gives the spectrum of the same radical at $-40°$. The temperature dependence of the ratio of the amplitude of the central component (H_1) to the amplitude of the outer components (H_2) in the first derivative of the spectrum is shown in Fig. 3. These changes in the EPR spectrum are reversible; i.e., when the temperature is lowered, H_1/H_2 decreases according to the same law. Analysis of the spectrum of the $\dot{C}H_2OH$ radical leads to the conclusion that the change of H_1/H_2 with temperature is associated with a decrease in the width of the central component of the hyperfine structure of the spectrum as the temperature is raised; the width of the outer components in this case remains practically unchanged.

Fig. 3. Temperature dependence of the ratio of the amplitudes of the central and outer components of the hyperfine structure for the first derivative of the spectrum of the $\dot{C}H_2OH$ radical.

As shown in works (8, 9), effects of this kind are general for radicals of the type $R\dot{C}H_2$ and are associated with the unfreezing of rotation of the CH_2 group about the R—C bond as the temperature is raised. With sufficiently rapid rotation, for the central component of the triplet the broadening caused by anisotropy of the hyperfine interaction is completely removed, whereas for the side components this broadening remains.

Thus, stabilization of $\dot{C}H_2OH$ radicals in an ionic crystalline matrix makes it possible to observe the unfreezing of internal rotation of the $\dot{C}H_2$ group in these radicals.

2. In a number of works (10, 11) it was noted that, in the radiolysis of normal alcohols, removal of a hydrogen atom in the α-position occurs predominantly, with formation of radicals $RCH_2\dot{C}HOH$. The EPR spectrum observed upon irradiation of frozen ethyl alcohol is a quintuplet with a binomial distribution of intensities, which is well explained by the formation of the radical CH_3—$\dot{C}HOH$, in which the hydrogen atoms in the α- and β-positions are equivalent. Certain difficulties arose in interpreting the EPR spectra of *n*-propyl alcohol and other higher normal alcohols irradiated at low temperature. The point is that in the spectra of all these alcohols 5 principal lines are observed with an intensity distribution of $1:2:2:2:1$. In order to assign such a spectrum to the radical $RCH_2\dot{C}HOH$, it must be assumed that the unpaired electron interacts with 3 hydrogen atoms, but that the interaction constant with one of the β-hydrogens is twice as large as the interaction constants with the other two hydrogen atoms*. However, there was no direct evidence that such an interpretation of the spectra is correct. In the present work, in the EPR spectra of *n*-propyl and *n*-amyl alcohols irradiated in the matrix, when the temperature was raised to approximately −100°, a reversible transition of the quintuplet into a quartet with an intensity ratio close to $1:3:3:1$ was found. This is illustrated by the spectra of *n*-propyl alcohol at −150° and −90°, shown in Fig. 1 , . In the spectrum of irradiated ethyl alcohol, no transitions were observed upon raising the temperature.

The observed change in the parity of the spectrum with temperature in irradiated higher normal alcohols** indicates the unfreezing of rotation CH_2 groups in the radical $RCH_2\dot{C}HOH$, as a result of which both β-hydrogens become equivalent and a spectrum is observed that is characteristic of the interaction of the unpaired electron with three equivalent hydrogen atoms. These observations confirm the correctness of the proposed interpretation of the EPR spectra of radicals formed in the radiolysis of higher normal alcohols.

In the future, the proposed stabilization method will be extended to other classes of organic radicals; it is also planned to clarify the question of the magnitude of

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* Such an interpretation of the EPR spectra of irradiated higher normal alcohols was proposed by V. K. Ermolaev and Yu. N. Molin.

** A change in the parity of the EPR spectrum at a temperature of −160° was previously observed for isopropyl alcohol (12).

the limiting concentration of free radicals in ionic crystalline matrices.

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