STUDY OF THE FORMATION OF FREE RADICALS DURING IRRADIATION OF PALMITIC ACID AND ITS DERIVATIVES BY THE E.P.R. METHOD

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Abstract

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A. A. Revina, Sh. A. Aripdzhanov, and N. A. Bakh*

STUDY OF THE FORMATION OF FREE RADICALS DURING IRRADIATION OF PALMITIC ACID AND ITS DERIVATIVES BY THE E.P.R. METHOD

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Studies, by means of the e.p.r. method, of radicals formed during the radiolysis of organic compounds provide additional information on the nature of primary radiation-chemical processes. Of great interest is the question of the influence of the character of the bonds in a molecule on the formation of radicals and on their radiation yield. Palmitic acid and its derivatives were chosen for the investigation. The data available in the literature on the character of e.p.r. spectra in irradiated carboxylic acids are not systematic in nature ([1], [2]). Recently, papers have appeared devoted to the study of e.p.r. spectra of irradiated dicarboxylic acids ([3]-[5]). Comparison of e.p.r. spectra and gas-evolution data made it possible to conclude that, under radiation, it is primarily the carboxyl groups of the molecules that undergo destruction ([5]).

In order to determine the influence of the character of the bonds in the carboxyl group on the primary processes in the radiolysis of carboxylic acids, we investigated the kinetics of radical accumulation in palmitic acid ($C_{15}H_{31}COOH$), in potassium palmitate ($C_{15}H_{31}COOK$), and in the triglyceride of palmitic acid $(C_{15}H_{31}COO)_3C_3H_5$. Irradiation was carried out at $-196°$ with γ-rays from Co^{60}. The source of γ-radiation, constructed in the form of a beaker, made it possible to carry out uniform irradiation of samples in a Dewar vessel at different temperatures. The dose rate, determined by the ferrous sulfate dosimetry method with subsequent recalculation in accordance with the electron density of the substance, was equal to $\sim 5 \cdot 10^{16}$ eV/g • sec. Measurements of e.p.r. spectra were made on an electron paramagnetic radiospectrometer of the RE1301 type at $-196°$. The spectra were recorded as the first derivative. The radical content was determined by comparing the areas under the integral curves of resonance absorption of the sample under study and of a standard. As the latter, vacuum samples of solid α, α'-diphenyl-β-picrylhydrazyl, recrystallized from chloroform, were used. The substances studied were placed in ampoules made of special glass, which gives practically no e.p.r. signal after irradiation at $g \sim 2$ ([6]). Before irradiation the samples were thoroughly degassed at $\sim 10^{-6}$ mm Hg for 6-

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Fig. 2. Initial portions of the radical-accumulation curves upon irradiation of palmitic acid (1, 2), tripalmitin (3, 4), and potassium palmitate (5, 6): 1, 3, 5 —in the presence of air; 2, 4, 6—in vacuum

Figure 2: Fig. 2. Initial portions of the radical-accumulation curves upon irradiation of palmitic acid (1, 2), tripalmitin (3, 4), and potassium palmitate (5, 6): 1, 3, 5—in the presence of air; 2, 4, 6—in vacuum

10 hours at room temperature. Separate measurements showed that increasing the temperature of the vacuum treatment to 50°C does not lead to noticeable changes. To determine the influence of oxygen on the radiation yield of radicals, a series of experiments was carried out with samples irradiated in the presence of air.

The e.p.r. spectra recorded at −196° after irradiation of palmitic acid, potassium palmitate, and tripalmitin are shown in Fig. 1. The energy absorbed by these samples was $7.2 \cdot 10^{20}$ eV/g. Examination of the resonance-absorption signals of samples that had received different doses leads to the conclusion that a characteristic feature is a change in the relative intensity of individual lines in the spectra during irradiation. This indicates the presence of different radicals and different regularities in the kinetics of their accumulation. Thus, the EPR signals are a superposition of the spectra of several radicals. The extent of the spectra is ~ 200 oersted. In the spectrum of palmitic acid a doublet with a splitting of 28–30 oersted is clearly manifested, characteristic of all irradiated carboxylic acids ($^{1-5}$). Figure 2 shows the dependence of the concentration of the radicals formed on dose. As can be seen from

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* Yu. B. Yakovlev and N. I. Mitina took part in carrying out the experiments.

Fig. 3. Dependence of radical concentration on dose in palmitic acid (1, 2), tripalmitin (5), and calcium palmitate (3, 4): 1, 3, 5—in the presence of air; 2, 4—in vacuum

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the figure, the highest concentration of radicals is reached in palmitic acid. We give the radiation-chemical yields of radicals (in radicals/100 eV), calculated from the linear initial portions of the accumulation curves:

	In vacuum	In the presence of air
Palmitic acid	20	20
Tripalmitin	12	7
Potassium palmitate	9	7

The yield of radicals in palmitic acid is substantially higher than that reported for succinic acid in work (^{5}). It should be noted that in our experiments the measurement of EPR spectra at −196° was carried out under conditions excluding saturation of the paramagnetic-resonance signal. In addition, irradiation at −196° and at a low dose rate, $\sim 3 \cdot 10^{16}$ eV/g • sec, promoted a more complete detection of the primary radicals. The results obtained, indicating different radiation stability and a different character of the spectra of primary radicals in the case of the fatty acid, on the one hand, and its salt and ester, on the other, can be compared with the literature data on gas evolution in palmitic acid, calcium palmitate, and palmitinocetyl ester subjected to the action of α-rays (^{7}). In that work it was shown that the greatest total gas yield is observed in the case of the free acid and that the yield of CO_2 falls sharply on going to the salt and to the ester. This permits the conclusion that the formation of the primary radicals detected by us is closely connected with the processes leading to the formation of the final products of radiolysis. Comparison of the radical yields in vacuum and air samples shows that the presence of oxygen does not cause a change in the radical yield in the acid and leads to a decrease in the salt and ester. It is essential to note that at −196° it was not possible to detect, from the EPR spectra, the formation of peroxide-type radicals. Figure 3 presents the curves

accumulation of radicals up to comparatively high irradiation doses, $\sim 3 \cdot 10^{21}$ eV/g. The concentration of radicals in palmitic acid reaches, at this dose, $\sim 3 \cdot 10^{20}$ rad/g and still shows no tendency toward the establishment of a stationary value.

Fig. 3. Dependence of the radical concentration on dose in palmitic acid (1, 2), tripalmitin (5), and calcium palmitate (3, 4): 1, 3, 5—in the presence of air; 2,

4—in vacuum.

The results obtained in our work lead to the conclusion that the influence of the nature of the bonds in the molecule on radiolysis processes can be detected by studying the formation of free radicals by the EPR method.

Institute of Electrochemistry
Academy of Sciences of the USSR

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