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STUDY OF THE CATALYTIC DECOMPOSITION OF ALKYL HYDROPEROXIDES BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

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At the present time much attention is being devoted to the study of chemical processes by the method of electron paramagnetic resonance (EPR). Of particular interest is the application of this method in cases where free radicals are generated in the course of a chemical process. The investigations carried out in this direction are few in number ([1]-[6]). Among them, of interest are works on the identification of the free radicals $HO_2\cdot$ ([3]) and $HO\cdot$ ([4]), formed during the decomposition of H_2O_2 in the presence of Ce^{4+} and Ti^{3+}, as well as works ([2], [5]) on the identification of cumyl peroxy radicals formed during the liquid-phase oxidation of cumene by oxygen. In works ([4], [6]), the EPR method was used to detect the formation of radicals during the catalytic decomposition of tert-butyl hydroperoxide.

By the same method we investigated the decomposition of several alkyl hydroperoxides in the presence of cobalt salts, which are catalysts in this reaction. Spectra were recorded on an EPA-2 EPR spectrometer with high-frequency modulation of the magnetic field. The instrument recorded the first derivative of the EPR line. A sample of diphenylpicrylhydrazyl served as the standard. The catalytic decomposition of the hydroperoxide was carried out in a thermostated ampoule placed in the resonator of the instrument. The content of the main substance in the hydroperoxide samples used by us was: tert-butyl hydroperoxide (TBH) and cumyl hydroperoxide (CHP) 99.2–99.6%, diphenylethane hydroperoxide* (DPEH) 96%, and triphenylmethyl hydroperoxide (TPMH) 98%.

Figure 1 shows the spectrum recorded by the EPR spectrometer during the decomposition of TBH in chlorobenzene in the presence of cobalt abietate. The observed EPR spectrum is a single asymmetric line ($\Delta H = 28 \pm 2$ Oe) with a g-factor equal to 2.015 ± 0.002. Comparing the character of the spectrum and the value of the g-factor with literature data ([2], [3], [5]), one may conclude that the recorded signals are due to peroxy radicals $RO_2\cdot$. The width of the signal does not change in the course of the reaction; therefore we characterized the

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

concentration of radicals by the signal intensity (h), measured as the vertical distance between the minimum and maximum of the first derivative of the EPR absorption line.

The intensity of the signals, as well as the character of its change in the course of the catalytic decomposition reaction of the hydroperoxide, depends on the reaction conditions. Peroxy radicals are generated and consumed in the process of hydroperoxide decomposition. It could be expected that, depending on the ratio of the rates of generation (w_1) and loss (w_2) of peroxy radicals in the initial (nonstationary) stage of the process, different types of change in the signal height with reaction time would be observed. Indeed, by varying the reaction conditions, we obtained differ–

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* DPEH was kindly provided to us by the Department of Organic Chemistry of the Lviv Polytechnic Institute.

kinetic curves of this type for the change in the intensity of the signal h over the course of the reaction in its initial stage (Fig. 1). Curves 1 and 2 in this figure correspond to low rates of catalytic decomposition of alkyl hydroperoxides.

It was found earlier (7) that the catalytic decomposition of alkyl hydroperoxides proceeds relatively rapidly in chlorobenzene, more slowly in a mixture of chlorobenzene with acetic acid, and still more slowly in acetic acid. At low temperature and at low catalyst concentrations this reaction proceeds rather slowly even in chlorobenzene.

Fig. 1

Fig. 1. Character of the change in the intensity of EPR signals during the reaction. Initial concentration of TTB –0.2 mol/l.
1 –solvent: equimolar mixture of chlorobenzene and acetic acid. Catalyst: cobalt naphthenate ($5 \cdot 10^{-3}$ mol/l), $t = 25°$;
2 –solvent: chlorobenzene. Catalyst: cobalt abietate ($5 \cdot 10^{-3}$ mol/l), $t = 30°$;
3 –the same, $t = 25°$;
4 –EPR spectrum recorded during the decomposition of TTB in chlorobenzene in the presence of cobalt abietate.

Fig. 2

Fig. 2. Effect of the initial hydroperoxide concentration on the stationary signal intensity, $t = 25°$, $C_k = 5 \cdot 10^{-3}$ mol/l.
1 –solvent: chlorobenzene, TPHP, catalyst: cobalt abietate;
2 –solvent: equimolar mixture of chlorobenzene and acetic acid, TTB, catalyst:

cobalt acetate;
3 –solvent: chlorobenzene, TTB, catalyst: cobalt abietate.

It may be assumed that, in the slow catalytic decomposition of alkyl hydroperoxides, a stationary regime of the reaction is established comparatively rapidly, characterized by an almost unchanged concentration of alkylperoxy radicals. This, in turn, gives rise to an EPR signal intensity that is practically unchanged over a certain interval of observation of the reaction. The kinetic curves 1 and 2 shown in Fig. 1 quite convincingly confirm the above assumption.

If the catalytic decomposition of hydroperoxides in solution proceeds at a high rate, then the kinetic curves for the change in signal intensity with reaction time have the form of curve 3 (Fig. 1). In this case, as in the slow catalytic decomposition of alkyl hydroperoxides, after some interval of time from the beginning of the reaction a stationary regime is also established, under which the intensity h changes very little over the observation time. Thus, for example, as can be seen from Fig. 1 (curve 3), during the first 2.5 min of observation, during which the hyd-

peroxide had decomposed by 30%, the value of h decreased from 260 to 95 mm, whereas during the subsequent 5.5 min only a very slow further decrease in the intensity of the EPR signals occurred. This signal intensity corresponds to an alkyl peroxy radical concentration on the order of $2 \cdot 10^{-5}$ mol/l, as determined by comparison with a standard of diphenylpicrylhydrazyl. After 60 min from the start of the reaction, when the hydroperoxide had decomposed by 92%, the value of h had decreased to 25 mm.

Fig. 3. EPR spectra recorded during the decomposition of GTB (1), GPK (2), GDFE (3), and GTFM (4) in chlorobenzene. Initial hydroperoxide concentration 0.2 mol/l. Catalyst–cobalt abietate ($5 \cdot 10^{-3}$ mol/l), $t = 25°$.

The intensity of the EPR signals is directly related to the rate of catalytic decomposition of alkyl hydroperoxides. As can be seen from Fig. 2, increasing the initial concentration of alkyl hydroperoxides in solution produces only a comparatively small increase in the intensity of the EPR signals. This dependence is manifested more strongly at a low initial hydroperoxide concentration than at a higher one.

Under stationary reaction conditions, the value of h is affected to a certain extent by temperature, as well as by the nature of the alkyl hydroperoxide, the solvent, and the catalyst.

In our experiments on the catalytic decomposition of alkyl hydroperoxides by the EPR method, the temperature was varied from 6 to 45°. It was found that, as the temperature increased, the intensity of the EPR signals in the reaction mixture decreased. This is in complete agreement with the generally accepted ideas concerning the effect of temperature on the lifetime of free radicals in solution.

The results of our experiments show that the rate of catalytic decomposition of alkyl hydroperoxides in the solvents we studied decreases in the following order: GTB > GPK > GDFE > GTFM. Quantitative data from the study of this dependence are summarized in Table 1.

The values of the effective reaction-rate constant given in Table 1 were obtained in experiments in which the decomposition of the corresponding hydroperoxides was carried out in chlorobenzene at 40° in the presence of $1 \cdot 10^{-3}$ mol/l cobalt abietate, in an equimolar mixture of chlorobenzene and acetic acid—at 50° in the presence of $5 \cdot 10^{-3}$ mole/liter cobalt acetate, and in glacial acetic acid—at 70° in the presence of $10 \cdot 10^{-3}$ mole/liter of the same catalyst. In all these experiments the initial concentration of hydroperoxides was 0.1 mole/liter.

Table 1

Effect of the nature of alkyl hydroperoxides on the intensity of the EPR signal, h, and on the effective rate constant of catalytic decomposition of the same hydroperoxides

Hydroperoxide	Chlorobenzene, h, mm	Chlorobenzene, $k \cdot 10^3$, $\text{sec}^{-1} \cdot \text{l} \cdot \text{mol}^{-1}$	Equimolar mixture of chlorobenzene and acetic acid, h, mm	Equimolar mixture of chlorobenzene and acetic acid, $k \cdot 10^5$, sec^{-1}	Acetic acid, h, mm	Acetic acid, $k \cdot 10^4$, sec^{-1}
GTB	55	216	32	45	26	9,0
GPK	26	34	22	31	16	8,3
GDFE	10	–	10	3,9	–	2,6
GTFM	0	0,4	0	2,9	–	2,2

As is seen from the data of Table 1, in terms of the intensity of the recorded EPR signals, h, and consequently in terms of the concentration of alkyl peroxy radicals formed under stationary conditions during the catalytic decomposition of hydroperoxides, the latter may be arranged in the following series: GTB > GPK > GDFE > GTFM. These results were obtained in experiments carried out at 25° in the presence of $5 \cdot 10^{-3}$ mole/liter of the cobalt salt of hydrogenated abietic acid and at an initial concentration of the corresponding hydroperoxides equal to 0.2 mole/liter.

The kinetic curves shown in Fig. 3 demonstrate how strongly the intensities differ for the EPR signals observed under identical conditions of catalytic decomposition in chlorobenzene of the four hydroperoxides studied: GTB, GPK, GDFE, and GTFM. The nature of the solvent has a large influence on the intensity of the signals characterizing the concentration of peroxy radicals formed during the catalytic decomposition of alkyl hydroperoxides. Table 2 summarizes the results of our experiments carried out at 25° in the presence of $5 \cdot 10^{-3}$ mole/liter cobalt acetate. Here h_0 is the intensity of the EPR signals at the initial moment of observation, and h, as usual, is the intensity of the EPR signals under stationary conditions.

Table 2

Effect of the nature of the solvent on the intensity of EPR signals during the catalytic decomposition of GTB and GPK

Hydroperoxide	Signal intensity, mm	Benzene	Chlorobenzene	Toluene	n-Nonane
GTB	h_0	273	260	168	102
GTB	h	–	85	78	48
GPK	h_0	80	72	61	45
GPK	h	39	28	–	21

From the data of Table 2 it is seen that the intensity of the recorded EPR signals in the reaction mixture, characterizing the concentration of alkyl peroxy radicals, is greater in those cases where benzene, toluene, or chlorobenzene served as the solvent. It may be assumed that this effect is to a certain extent due to the formation of π-complexes of alkyl peroxy radicals.

The introduction of inhibitors into the reaction mixture, for example alkylphenols, causes a strong decrease in the intensity of the EPR signals. Conversely, additives of compounds, for example carbonyl peracids, which initiate the decomposition of alkyl hydroperoxides, substantially increase the intensity of the EPR signals. A preliminary check showed that under these conditions the peracid radicals formed during the catalytic decomposition do not give EPR signals.

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

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