# Decomposition of 1-Phenylethyl Hydroperoxide in the Presence of Cobalt Acetylacetonates

By Gábor Vasvári and Dezső Gál \*

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, 1025 Budapest, Pusztaszeri ut 59-67, Hungary

Received 10th March, 1976

The decomposition of 1-phenylethyl hydroperoxide has been investigated in the presence of  $Co(acac)_2$  and  $Co(acac)_3$  in argon and oxygen atmospheres.  $Co(acac)_2$  accelerates the decomposition of the hydroperoxide. The decomposition is preceded by the fast formation of a  $Co(acac)_2 + ROOH$  complex which is unaffected by the presence of oxygen in the temperature range studied. The deactivation of the catalyst by the water formed in the decomposition reaction has been confirmed from kinetic evidence. The rate constants for the formation and decomposition of the catalyst + ROOH complex and the overall activation energy were determined.

In the presence of  $Co(acac)_3$  the decomposition starts after an induction period being longer in oxygen than in argon. It is assumed that the actual catalyst of this process is also  $Co(acac)_2$ . The overall activation energy of the decomposition has been determined.

It is generally accepted that the reactions between hydroperoxides and transition metal complexes serve as initiation reactions for catalytic hydrocarbon oxidations.<sup>1-9</sup> We have studied previously the thermal decomposition and autoxidation of cobalt acetylacetonate complexes;<sup>10</sup> the present paper deals with the catalytic decomposition of 1-phenylethyl hydroperoxide (ROOH) in the presence of  $Co^{II}$ , and  $Co^{III}$ -acetylacetonate [Co(acac)<sub>2</sub> and Co(acac)<sub>3</sub>], respectively, studied in chlorobenzene under both argon and oxygen atmospheres.

## EXPERIMENTAL

## MATERIALS

The preparation of  $Co(acac)_2$ ,  $Co(acac)_3$  and the purification of the chlorobenzene used as inert solvent have been described previously.<sup>10</sup> 1-Phenylethyl hydroperoxide (ROOH) was prepared by the thermal oxidation of ethylbenzene at 90°C. The ROOH was precipitated by shaking the reaction mixture with a 50 % solution of sodium hydroxide. The sodium salt was filtered and washed with ether, dissolved in water and neutralized with HCl being careful to avoid an excess of acid. Repeating this procedure three times yielded the hydroperoxide with an impurity of 3 %, consisting of acetophenone (R'COR") and 1-phenylethanol (ROH). Purity was checked by iodometric and g.l.c. analysis.

Argon gas was deoxygenated by metallic copper at 350°C.

## ANALYSIS

The changes in the valency state of the catalysts were followed spectrophotometrically using the method described previously.<sup>10</sup> ROOH, R'COR" and ROH content of the samples were analysed by g.l.c.<sup>11</sup>

## PROCEDURE

The experimental technique is described elsewhere.<sup>11</sup> For the system  $Co(acac)_2$ + ROOH, a modified twin oxidation vessel was used. The flow rate of oxygen was 12 dm<sup>3</sup> h<sup>-1</sup>.

## **RESULTS AND DISCUSSION**

## THE SYSTEM $Co(acac)_2 + ROOH$

Experiments were carried out in the temperature range  $30-70^{\circ}$ C. Initial concentrations were varied in the range  $10^{-4}-10^{-3}$  mol dm<sup>-3</sup> for Co(acac)<sub>2</sub> and  $2 \times 10^{-2}-12 \times 10^{-2}$  mol dm<sup>-3</sup> for ROOH. Typical kinetic curves for the decomposition obtained by changing the initial concentrations of one of the reactants are shown in fig. 1 and 2. The presence of oxygen does not affect the initial rate of the ROOH decomposition.



time/min





time/min

FIG. 2.—Kinetic curves of ROOH decomposition at 50°C in argon (×) and in oxygen ( $\bigcirc$ ). [Co  $(acac)_2]_0: 1 \times 10^{-4}$  (1),  $3 \times 10^{-4}$  (2) and  $1 \times 10^{-3}$  mol dm<sup>-3</sup> (3).

The distribution of the catalyst between its bivalent and trivalent states (fig. 3) during the initial period of the ROOH decomposition was similar whether argon or oxygen was used. The fact that the samples taken after the first minute contain about 50 % of the catalyst in its trivalent form suggests the existence of a fast reaction between  $Co(acac)_2$  and ROOH. Experiments carried out with the stopped-flow method indicated that this fast reaction yielding  $Co^{III}$  species came to an end within 0.3-0.5 s. A similar fast process has been found <sup>12</sup> in the reaction between t-butyl hydroperoxide and  $Co(acac)_2$ ; again oxygen did not affect the reaction.

From the kinetic data the following overall rate expression can be obtained

$$w_0 = k_1 [\text{Co}(\text{acac})_2]_0 [\text{ROOH}]_0^{0.37}.$$
 (1)

With respect to the mechanism based on our measurements and in agreement with the literature data <sup>13, 14</sup> we assume the existence of a fast initial process

$$\operatorname{Co}(\operatorname{acac})_2 + \operatorname{ROOH} \xrightarrow{k_2} \operatorname{Co}(\operatorname{acac})_2 \cdot \operatorname{ROOH}.$$
 (2)

This complex presumably contains a loosened O—O bond and reacts promptly with a second  $Co(acac)_2$  molecule

$$\operatorname{Co}(\operatorname{acac})_{2} \cdot \operatorname{ROOH} + \operatorname{Co}(\operatorname{acac})_{2} \xrightarrow{k_{3}} \operatorname{Co}(\operatorname{acac})_{2} \operatorname{OH} \cdot \operatorname{Co}(\operatorname{acac})_{2} \operatorname{RO}.$$
 (3)



time/min

FIG. 3.—Kinetic curves of the valency change in the system  $Co(acac)_2 + ROOH$  at 50°C in argon  $(\times, +)$  and in oxygen  $(\bigcirc, \bullet)$ . [Co(acac)\_2]<sub>0</sub>:  $1 \times 10^{-3}$  mol dm<sup>-3</sup>, [ROOH]<sub>0</sub>:  $4.7 \times 10^{-2}$  mol dm<sup>-3</sup>.

We suppose that reactions (2) and (3) occur while mixing  $Co(acac)_2$  and ROOH and the binuclear complex formed shows the 1:1 ratio of the valency states as found experimentally. Due to this fast reaction, practically no free  $Co(acac)_2$  remains in the system if  $[ROOH]_0 \ge [Co(acac)_2]_0$  and therefore the initial rates observed are identical both in argon and in oxygen atmosphere. The products detected and measured experimentally might be formed in the following reactions based on literature data

$$\operatorname{RO}_{k_{4}} \xrightarrow{k_{4}} 2\operatorname{Co}(\operatorname{acac})_{2} + \operatorname{H}_{2}\operatorname{O} + \operatorname{R'COR''}$$
(4a)

$$\operatorname{Co}(\operatorname{acac})_2\operatorname{OH} \cdot \operatorname{Co}(\operatorname{acac})_2\operatorname{RO} \cdot - | \stackrel{e}{\longrightarrow} \operatorname{Co}(\operatorname{acac})_2\operatorname{OH} + \operatorname{Co}(\operatorname{acac})_2\operatorname{RO} \cdot$$
(4b)

$$2 \operatorname{Co}(\operatorname{acac})_2 \operatorname{OH} \xrightarrow{\kappa_5} 2 \operatorname{Co}(\operatorname{acac})_2 + \operatorname{H}_2 \operatorname{O} + \frac{1}{2} \operatorname{O}_2$$
(5)

$$2 \operatorname{Co}(\operatorname{acac})_2 \operatorname{RO} \xrightarrow{\kappa_0} 2 \operatorname{Co}(\operatorname{acac})_2 + \operatorname{ROH} + \operatorname{R'COR''}(\operatorname{ROOR})$$
(6)

$$\operatorname{Co}(\operatorname{acac})_2 + n\operatorname{H}_2\operatorname{O} \rightleftharpoons \operatorname{Co}(\operatorname{acac})_2 \bullet n\operatorname{H}_2\operatorname{O}.$$
 (7)

In eqn (4*a*) and (4*b*) *e* denotes the proportion of radicals escaping the cage. Since there is a deficiency of 15-16 % in the material balance we assume the formation of further products (*e.g.* ROOR) undetected in reaction (6).

In order to confirm the existence of reaction (3) we have investigated the catalytic decomposition of ROOH in the presence of 2,6-di-t-butylphenol as inhibitor. We found that the rate of ROOH decomposition in argon was not affected by the inhibitor,

in agreement with the data of Bulgakova *et al.*<sup>15</sup> This means that the radicals formed do not induce the decomposition of the ROOH, or at least that the induced decomposition is negligible. Similar suggestions have been made by Scott<sup>4</sup> and Sapunov.<sup>14</sup> Consequently, propagation processes were not included among the reactions (2)-(7).

Measurements of the accumulation of the products yield a value of  $\sim 1.5$  for the ratio [R'COR'']/[ROH]. Since this ratio should be 1:1 according to reaction (6) we have assumed two directions for reaction (4) *i.e.* the existence of a cage effect. From this point of view step (4a) is a reaction taking place within the cage and leads to the "molecular" decomposition of the ROOH while reaction (4b) represents the "radical" pathway yielding coordinated RO radicals and Co(acac)<sub>2</sub>OH molecules. We succeeded in identifying Co(acac)<sub>2</sub>OH in a CDCl<sub>3</sub> solution of Co(acac)<sub>2</sub> and ROOH by n.m.r. measurements. Both the resonance values and the intensity ratio were identical to those given by Boucher and Herrington.<sup>16</sup>

Reaction (5) cannot be regarded as an elementary process and, though not in contradiction with the experimental results, should be affirmed separately. Co(acac)<sub>2</sub> can also be regenerated by processes (8) and (9)

$$Co(acac)_2OH + ROOH \rightarrow Co(acac)_2 + H_2O + RO_2$$
 (8)

$$Co(acac)_2OH + ROOH \rightarrow Co(acac)_2 + H_2O + R \cdot OOH$$
 (9)

where R-OOH represents the radical  $C_6H_5$ —C-(OOH)—CH<sub>3</sub> formed via abstraction of the tertiary hydrogen.

The existence of reaction (7) is very likely. The kinetic curves of fig. 1 and 2 show the reduction in the rate of the decomposition reaction, and according to fig. 3 Coll accumulates simultaneously in the system, presumably as the inactive Co(acac)<sub>2</sub>. 2H2O.17

By applying the steady-state treatment to the radicals and active catalyst species we obtain the rate equations corresponding to reactions (2)-(7). Assuming  $k_3 \ge k_2$ as suggested by Johnson and Gould<sup>12</sup> and using the stoichiometric expression for the free  $Co(acac)_2$ 

$$[Co(acac)_2]_{free} = [Co(acac)_2]_0 / \{1 + (k_2/k_4)[ROOH] + K_7[H_2O]^n\}$$
(10)

the rate equations are

$$-d[\text{ROOH}]/dt = k_2[\text{Co}(\text{acac})_2]_0[\text{ROOH}]/\{1 + (k_2/k_4)[\text{ROOH}] + K_7[\text{H}_2\text{O}]^n\}$$
(11)

 $d[R'COR'']/dt = (1 - e/2)k_2[Co(acac)_2]_0[ROOH]/\{1 + (k_2/k_4)[ROOH] + (k_2/k_4)[$ 

$$+K_7[\mathrm{H}_2\mathrm{O}]^n\}$$
 (12)

$$d[ROH]/dt = (e/2)k_2[Co(acac)_2]_0[ROOH]/\{1 + (k_2/k_4)[ROOH] + K_7[H_2O]^n\}$$
(13)

$$d[H_2O]/dt = (1 - e/2)k_2[Co(acac)_2]_0[ROOH]/\{1 + (k_2/k_4)[ROOH] + K_7[H_2O]^n\}.$$
 (14)

In order to describe the initial rate of the ROOH decomposition two conditions should be fulfilled: (i) according to the experimental conditions  $[ROOH]_0 \gg$  $[Co(acac)_2]_0$  and thus the consumption of the ROOH during the initial stages of the reaction can be neglected:  $[ROOH] \sim [ROOH]_0$ . (ii) At the beginning of the decomposition there is no water in the system and therefore in the denominator of eqn (10)  $K_7[H_2O]^n = 0$ . Consequently the initial rate of the ROOH decomposition is

$$(-d[ROOH]/dt)_0 = w_0 = k_2[Co(acac)_2]_0[ROOH]_0/\{1 + (k_2/k_4)[ROOH]_0\}.$$
 (15)

In linearized form

$$1/w_0 = 1/k_4 [\text{Co}(\text{acac})_2]_0 + 1/k_2 [\text{Co}(\text{acac})_2]_0 [\text{ROOH}]_0$$
(16)

or

$$1/w_0 = (1/k_4 + 1/k_2[\text{ROOH}]_0) / [\text{Co}(\text{acac})_2]_0.$$
(17)

Relations (16) and (17) are plotted in fig. 4 and the straight line representing eqn (16) is suitable for determining the corresponding rate constants. An expression similar to eqn (15) was suggested by Skibida *et al.*<sup>18</sup> for the decomposition of n-decyl hydroperoxide in the presence of  $Co(acac)_2$ .



 $10^{-5}/[Co(acac)_{2}]_{0}$ 

FIG. 4.—Plot of eqn (16) and (17) at 50°C in argon  $(+, \bullet)$  and in oxygen  $(\bigcirc)$ .

The rate constants at 50°C are

$$k_2 = 22.6 \,\mathrm{dm^3 \, mol^{-1} \, s^{-1}}$$
 and  $k_4 = 0.6 \,\mathrm{s^{-1}}$ .

The value of e can be estimated from the measured product distribution. From eqn (12) and (13) we obtain e = 0.835.

Eqn (11) and (14) enable us to calculate the values of  $K_7$  and n, respectively. Using the kinetic data from fig. 1 we obtain at 50°C

$$K_7 = 1.76 \times 10^5 \,\mathrm{dm^6 \ mol^{-2}}$$
 and  $n = 2$ .

The value n = 2 strongly suggests that the deactivated form of the catalyst is the compound  $Co(acac)_2 \cdot 2H_2O$ . The apparent activation energy of the overall initial rate of the ROOH decomposition both in argon and in oxygen is  $E = 24.3 \pm 2 \text{ kJ mol}^{-1}$ . The error was calculated by the least square method.

## THE SYSTEM $Co(acac)_3 + ROOH$

The following experimental conditions were chosen : temperature range,  $80-120^{\circ}C$ ;  $[Co(acac)_3]_0: 10^{-4}-10^{-3} \text{ mol dm}^{-3}$ ;  $[ROOH]_0: 2 \times 10^{-2}-12 \times 10^{-2} \text{ mol dm}^{-3}$ . The corresponding kinetic curves measured both in argon and oxygen atmosphere are plotted in fig. 5 and 6. A well defined induction period was observed in both cases and as a result of secondary reactions in the presence of oxygen,  $Co(OAc)_2$  appears in the system as an end product of the transformation

$$Co(acac)_3 \rightarrow Co(acac)_2 \rightarrow Co(OAc)_2.$$

The induction period is longer in oxygen and its length varies inversely as the initial concentrations of the reactants and the temperature. Bulgakova<sup>13</sup> has also

observed an induction period during the decomposition of n-decyl hydroperoxide in the presence of  $Co(acac)_3$ . The overall activation energy based on the maximal rates of the ROOH decomposition both in argon and oxygen is ~ 125 kJ mol<sup>-1</sup>.



FIG. 5.—The reaction between Co(acac)<sub>3</sub> and ROOH in argon at  $90^{\circ}$ C. (a) Kinetic curves of the valency change of the catalyst,  $\bullet$  Co(acac)<sub>3</sub>,  $\bigcirc$  Co(acac)<sub>2</sub>; (b) kinetic curves of the ROOH decomposition and product accumulation, • ROOH,  $\bigcirc$  ROH, +R'COR".



FIG. 6.—The reaction between Co(acac)<sub>3</sub> and ROOH in oxygen at 90°C. (a) Kinetic curves of the valency change of the catalyst,  $+Co(acac)_2$ ,  $\bullet Co(acac)_3$ ,  $\bigcirc Co(OAc)_2$ ; (b) kinetic curves of the ROOH decomposition and product accumulation, +R'COR'',  $\bullet ROOH$ ,  $\bigcirc ROH$ ,  $\times$  benzaldehyde.

The existence of an induction period supports the assumption that no direct reaction takes place between Co(acac)<sub>3</sub> and ROOH if Co(acac)<sub>3</sub> represents the coordinatively saturated complex of octahedral configuration with closed ligands. Considering our previous observations <sup>10</sup> on the thermal decomposition and autoxidation of  $Co(acac)_3$  we suggest that the opening-up of one of the ligands represents the first step followed by

$$\operatorname{Co}(\operatorname{acac})_{2}\operatorname{acac} + \operatorname{ROOH} \xrightarrow{k_{18}} \operatorname{Co}(\operatorname{acac})_{2}\operatorname{acac} \cdot \operatorname{ROOH}$$
(18)

$$\operatorname{Co}(\operatorname{acac})_2\operatorname{acac} + \operatorname{O}_2 \xrightarrow{^{n_19}} \operatorname{Co}(\operatorname{acac})_2\operatorname{acac} \cdot \operatorname{O}_2.$$
 (19)

Here  $Co(acac)_2acac$  represents the opened-up chelate. Further reactions are strongly influenced by the readiness of these intermediates either to decompose into active species, eqn (21) and (23), or to regenerate the initial reactants, eqn (20) and (22).

 $\operatorname{Co}(\operatorname{acac})_2 \operatorname{acac} \cdot \operatorname{ROOH} \xrightarrow{k_{20}} \operatorname{Co}(\operatorname{acac})_3 + \operatorname{ROOH}$  (20)

$$\operatorname{Co}(\operatorname{acac})_2\operatorname{acac} \cdot \operatorname{ROOH} \xrightarrow{\kappa_{21}} \operatorname{active species}$$
 (21)

$$\operatorname{Co}(\operatorname{acac})_2\operatorname{acac} \cdot \operatorname{O}_2 \xrightarrow{k_{22}} \operatorname{Co}(\operatorname{acac})_3 + \operatorname{O}_2$$
 (22)

$$\operatorname{Co}(\operatorname{acac})_2 \operatorname{acac} \cdot \operatorname{O}_2 \xrightarrow{\chi_{23}} \operatorname{Co}(\operatorname{acac})_2 + \operatorname{acac}\operatorname{O}_2.$$
 (23)

The length of the induction period is determined in argon by the ratio of the rate constants of the reactions (20) and (21). In the presence of oxygen all four processes might take place and since according to our calculations  $k_{22} \ge k_{23}$ , the length of the induction period increases indicating competition between ROOH and O<sub>2</sub> molecules for the free coordination sites of the Co(acac)<sub>2</sub>acac molecule.

Our hypothesis is strongly supported by the fact that the 125 kJ mol<sup>-1</sup> activation energy found experimentally is in good agreement with literature data, 108-138 kJ mol<sup>-1</sup>, observed in processes starting with the opening-up of one of the ligands of Co(acac)<sub>3</sub>. Banerjea <sup>19</sup> also assumed a ligand opening in the acid-catalysed decomposition of Co(acac)<sub>3</sub> and found an overall activation energy of 138 kJ mol<sup>-1</sup>. The oxidation of  $\alpha$ -naphthol in the presence of Co(acac)<sub>3</sub> studied by Martemianov and Denisov <sup>20</sup> proved to be autocatalytic. It was established that the Co(acac)<sub>2</sub>.  $\alpha$ -naphthol complex plays the role of the accelerating intermediate. The overall activation energy of the process was 126 kJ mol<sup>-1</sup>.

The number of ROOH molecules decomposed by one molecule of  $Co(acac)_3$ , *i.e.* the number of catalytic cycles, increases with increasing [ROOH]<sub>0</sub> and decreases with increasing [Co(acac)<sub>3</sub>]<sub>0</sub>. A retarding effect of oxygen can also be observed causing a significant decrease in the number of cycles.

Data on the number of cycles are given in table 1.

TABLE 1.—NUMBER OF CYCLES IN THE  $Co(acac)_3$  catalysed decomposition of ROOH

[Co(acac) <sub>3</sub> ] <sub>0</sub> /mol dm <sup>-3</sup>	[ROOH] <sub>0</sub> /mol dm <sup>-3</sup>	number of cycles	
		in argon 90°C	in oxygen 100°C
$3 \times 10^{-4}$	$2 \times 10^{-2}$	143	103
$3 \times 10^{-4}$	$4.7 \times 10^{-2}$	244	149
$3 \times 10^{-4}$	$11.8 \times 10^{-2}$	355	197
$1 \times 10^{-4}$	$4.7 \times 10^{-2}$	628	209
$1 \times 10^{-3}$	$4.7 \times 10^{-2}$	88	81

The ratio [R'COR"]/[ROH] calculated from the product distribution was  $\sim 2$ . In the presence of an inhibitor the formation of ketone becomes predominant ([R'COR"]/[ROH]  $\sim 3$ ) while at higher temperatures or at higher catalyst concentrations this ratio decreases to 1.5.

The experimental data cannot be explained by assuming that the mechanism of the ROOH decomposition consists only of reactions (2)-(7) as suggested for the  $Co(acac)_2 + ROOH$  system. Under our experimental conditions the steady state concentration of the active  $Co(acac)_2$  is very low,  $10^{-6}-10^{-7}$  mol dm<sup>-3</sup>, thus the probability of reaction (3) diminishes and simultaneously the monomolecular

decomposition of the  $Co(acac)_2 \cdot ROOH$  complex formed via reactions (21) and (23) becomes significant *, ,* 

$$\operatorname{Co}(\operatorname{acac})_2 \cdot \operatorname{ROOH} \xrightarrow{\kappa_3} \operatorname{Co}(\operatorname{acac})_2 + \operatorname{R'COR}'' + \operatorname{H}_2\operatorname{O}.$$
(3')

Reaction (3') is exothermic <sup>21</sup> even in the absence of catalyst. Assuming that the ratio [R'COR'']/[ROH] = 2 is determined by the ratio of the rates of reactions (3') and (3), it is likely that the use of an inhibitor might enhance this ratio by reacting with the free  $Co(acac)_2$ , *i.e.* decreasing further the rate of reaction (3). An increase of the temperature or of the initial concentration of the Co(acac)<sub>3</sub>, both resulting in the increase of the steady state concentration of  $Co(acac)_2$ , leads to the ratio 1.5 obtained for the system  $Co(acac)_2 + ROOH$ . This means that reaction (3') becomes negligible and consequently it has not been included in the mechanism set up for the latter system.

Since no information is available concerning the changes taking place during the induction period, we assume that the presence of  $Co(acac)_2$  is an essential condition for the catalytic decomposition of the ROOH, and it seems very likely that the fast decomposition is caused by the catalytic cycles realized via valency changes rather than by a free radical chain reaction.

- <sup>1</sup> L. J. Matienko and Z. K. Maizus, Izvest. Akad. Nauk S.S.S.R., Ser. khim., 1972, 7, 1524.
- <sup>2</sup> W. H. Richardson, J. Amer. Chem. Soc., 1965, 87, 247.
- <sup>3</sup> O. Zenjiro, Sh. Tetsuaki, O. Yoshitaka and M. Kei, Kogyo Kagaku Zasshi, 1970, 73, 115.
- <sup>4</sup> E. J. Y. Scott, J. Phys. Chem., 1970, 74, 1174.
  <sup>5</sup> E. T. Denisov and N. M. Emanuel, Uspekhi Khim., 1960, 29, 1409.
- <sup>6</sup> R. Hiatt, T. Mill and F. R. Mayo, J. Org. Chem., 1968, 33, 1416.
- <sup>7</sup> N. M. Emanuel, E. T. Denisov and Z. K. Maizus, Chain Reactions in the Liquid Phase Oxidation of Hydrocarbons (Nauka, Moscow, 1965) (in Russian).
- <sup>8</sup> N. M. Emanuel, Z. K. Maizus and I. P. Skibida, Angew. Chem. Int. Edn, 1969, 8, 97.
- <sup>9</sup> I. P. Skibida, Uspekhi Khim., 1975, 44, 1729.
- <sup>10</sup> G. Vasvári, I. P. Hajdu and D. Gál, J.C.S. Dalton, 1974, 465.
- <sup>11</sup> É. Danóczy, G. Vasvári and D. Gál, J. Phys. Chem., 1972, 76, 2785.
- <sup>12</sup> N. A. Johnson and E. S. Gould, J. Amer. Chem. Soc., 1973, 95, 5198.
   <sup>13</sup> G. M. Bulgakova, I. P. Skibida and Z. K. Maizus, Kinetika i Kataliz, 1971, 12, 76.
- <sup>14</sup> V. I. Sapunov, E. F. Seljutina and N. N. Lebedeva, Kinetika i Kataliz, 1974, 15, 361.
- <sup>15</sup> G. M. Bulgakova, Z. K. Maizus and I. P. Skibida, Kinetika i Kataliz, 1966, 7, 332.
- <sup>16</sup> L. J. Boucher and D. R. Herrington, J. Inorg. Nuclear Chem., 1971, 33, 4349.
- <sup>17</sup> Y. Ohkatsu, T. Osa and A. Misono, Bull. Chem. Soc. Japan, 1967, 40, 2116.
- <sup>18</sup> I. P. Skibida, Z. K. Maizus and G. M. Bulgakova, Proc. 3rd Symp. Coord. Chem., 1970, 1, 375.
- <sup>19</sup> D. Banerjea and S. Dutta Chandhuri, J. Inorg. Nuclear Chem., 1971, 33, 515.
- <sup>20</sup> V. S. Martemianov and E. T. Denisov, Izvest. sibirsk. Otdel. Akad. Nauk S.S.S.R., Ser. khim. Nauk, 1968, 3, 9.
- <sup>21</sup> D. Swern, Organic Peroxides (Wiley, New York, 1970), vol. 1, chap. 2, p. 121.

(PAPER 6/483)