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Figure 1. Decomposition of dicyclohexyl percarbonate. $C_0 = 0.1$ mol/l. 1 –in CCl_4, $t = 50°$; 2 –in C_6H_6, $t = 50°$; 3 –in C_6H_6, $t = 60°$. a –without DPPH; b –with DPPH.

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Figure 2. Decomposition of dicyclohexyl percarbonate in iso-C_3H_7OH. $C_0 = 0.06$ mol/l, $T = 25°$; 1 –without DPPH; 2 –with DPPH; 3 –DPPH added 15 min after the beginning of decomposition.

Figure 2: Figure 2. Decomposition of dicyclohexyl percarbonate in iso-C_3H_7OH. $C_0 = 0.06$ mol/l, $T = 25°$; 1 –without DPPH; 2 –with DPPH; 3 –DPPH added 15 min after the beginning of decomposition.

Abstract

Full Text

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STUDY OF THE MECHANISM OF THERMAL DECOMPOSITION OF PERCARBONATES IN SOLUTION

In our work (1) on the decomposition of dibenzyl and dicyclohexyl percarbonates in various solvents, it was found that RO radicals formed as a result of peroxide

$$\text{cyclo-}C_6H_{11}OCOOCOC_6H_{11} \longrightarrow 2C_6H_{11}OCO^{\bullet} \longrightarrow 2C_6H_{11}O^{\bullet} + 2CO_2 \quad (1)$$

Fig. 1. Decomposition of dicyclohexyl percarbonate. $C_0 = 0.1$ mol/l. 1 –in CCl_4, $t = 50°$; 2 –in C_6H_6, $t = 50°$; 3 –in C_6H_6, $t = 60°$. a –without DPPH; b –with DPPH.

Fig. 2. Decomposition of dicyclohexyl percarbonate in iso-C_3H_7OH. $C_0 = 0.06$ mol/l, $T = 25°$; 1 –without DPPH; 2 –with DPPH; 3 –DPPH added 15 min after the beginning of decomposition.

in some solvents, such as benzene, CCl_4, and acetic acid, disproportionate

$$\text{2-cyclo-C}_6\text{H}_{11}\text{O}^{\bullet} \longrightarrow \text{cyclo-C}_6\text{H}_{11}\text{OH} + \text{cyclo-C}_6\text{H}_{10}\text{O}, \qquad (2)$$

and the solvent does not participate in the reactions of the radicals. It is very probable that process (2) occurs in the solvent cage. In alcohols we observed the participation of the solvent, which, by donating hydrogen to RO radicals, is converted into an aldehyde or ketone.

In the present work the mechanism of interaction of RO radicals with the solvent was investigated with the aid of the radical scavenger α,α-diphenyl-β-picrylhydrazyl (DPPH), as well as by the use of the labeled-atom method. In Figs. 1 and 2, in coordinates $\ln \frac{C_0}{C}$—t, where C_0 is the initial concentration of percarbonate in solution, and C is its concentration at time t, there are presented

the rate of decomposition of dicyclohexyl peroxydicarbonate in carbon tetrachloride and benzene (0.1 mole/l) and in isopropyl alcohol (0.06 mole/l) was determined. As is seen from Figs. 1 and 2, additions of DPPH have absolutely no effect on the rate of decomposition in carbon tetrachloride and benzene, which indicates the absence of initiated decomposition of the percarbonate in these solvents, whereas during decomposition in isopropyl alcohol additions of DPPH completely inhibit the process.

For a more detailed study of the mechanism of decomposition of percarbonates in alcohols, which proceeds according to the general equation

$$\text{ROC(= O)OOC(= O)OR} + \text{R}'\text{OH} \rightarrow 2\text{ROH} + 2\text{CO}_2 + \text{R}'\text{O} \quad \text{(ketone or aldehyde)},$$

a system was investigated in which $R = R'$. The use of $R = R^1 =$ iso-C_3H_7 proved most convenient. We introduced the C^{14} label both into the isopropyl radical of the peroxide and into that of the alcohol. The acetone isolated from the reaction mixture during decomposition of labeled C^{14} diisopropyl percarbonate in inactive isopropyl alcohol proved to be completely inactive.

When the same reaction was carried out with inactive peroxide in C^{14}-labeled alcohol, the activity of the acetone corresponded to that of the alcohol (Table 1).

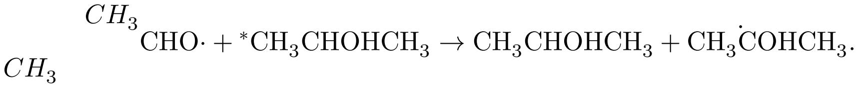
Table 1

Decomposition of diisopropyl percarbonate in isopropyl alcohol
$C_0 = 0.2$–0.4 mole/l; $t = 50$–$60°$

Activity, imp/min*	Activity, imp/min*	Activity of acetone 2,4-dinitrophenylhydrazone, imp/min*	Activity of acetone 2,4-dinitrophenylhydrazone, % of initial	Activity of isopropyl alcohol isolated after the reaction, imp/min*	Activity of isopropyl alcohol isolated after the reaction, corrected for dilution	Activity of isopropyl alcohol isolated after the reaction, % of initial
diisopropyl percarbonate**	isopropyl alcohol**	in imp/min*	in % of initial	in imp/min*	corrected for dilution	in % of initial
Inactive	48,300	43,920	91.2	–	–	–
72,000	Inactive	1170	1.6	1890	74,000	102.5

* Radiometric analysis was carried out on an internal-filling counter. Error of measurement ±3%.
** The peroxide and the alcohol were taken labeled at the secondary C.

On the basis of the data obtained one may conclude that the iso-$C_3H_7O\cdot$ radical formed from the peroxide according to equation (1) is converted entirely into alcohol by abstraction of hydrogen from the solvent



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\mathrm{CHO}\cdot + {}^{*}\mathrm{CH_3CHOHCH_3} \rightarrow \mathrm{CH_3CHOHCH_3} + \mathrm{CH_3\dot{C}OHCH_3}. \tag{3}$$

On the basis of the work of Harash(2) it is known that free radicals abstract hydrogen from the C–H group of isopropyl alcohol, and a new alcohol radical is formed, which in our case is isomeric with the radical obtained from the peroxide.

It should be assumed that this radical also initiates the decomposition of the peroxide:

$$\text{iso-}C_3H_7OC(=O)OOC(=O)OC_3H_7 + \mathrm{CH_3\dot{C}OHCH_3} \rightarrow \mathrm{CH_3COCH_3} + 2CO_2 + \text{iso-}C_3H_7OH + \mathrm{(CH_3)_2CHO}\cdot. \tag{4}$$

Thus it is explained that acetone is formed only from the alcohol solvent. (In view of the low concentration of peroxide in the solution, one may neglect the amount of alcohol that is formed from the peroxide and can then participate in reactions with radicals. By the end of the decomposition its amount will be only 5 g/l.)

It may be assumed that, in addition to equation (4), acetone could be formed by the disproportionation reaction of the alcohol radical:

$$2CH_3\dot{C}OHCH_3 \rightarrow CH_3CHOHCH_3 + CH_3COCH_3. \tag{5}$$

This reaction is usually accepted for explaining the formation of acetone in the radical dehydrogenation reaction of isopropyl alcohol (2). To decide whether such a reaction actually takes place, we used, as the solvent in the decomposition of diisopropyl percarbonate, isopropyl alcohol deuterated in the hydroxyl group, which according to equation (5) should have given acetone and $CH_3CDODCH_3$.

The alcohol, washed free of hydroxyl deuterium, showed no deuterium content by isotope analysis and by the IR spectrum. Our observations are in agreement with a recently published work (3), in which optically active secondary butyl alcohol was used in the photolysis of benzophenone. From the retention of the optical activity of the solvent alcohol, the absence of the disproportionation reaction (5) was demonstrated.

Table 2

Initiation of the reaction between CCl_4 and *iso*-C_3H_7OH at 60°
(in moles of liberated HCl per 1 mole of peroxide taken)

	Peroxide concentration, mol/l	Peroxide concentration, mol/l	Peroxide concentration, mol/l	Peroxide concentration, mol/l
	0.04	0.02	0.01	0.005
Benzoyl peroxide	–	5.27	5.65	13.65
Dibenzyl percarbonate	–	19.7	39.4	66.0
Dicyclohexyl percarbonate	12.0	41.0	64.5	112

Thus, the reaction of diisopropyl percarbonate in isopropyl alcohol can be represented successively by reactions (1), (3), and (4).

On the basis of the data obtained, it could be expected that percarbonate would prove to be an active initiator of the previously described reaction of CCl_4 with alcohols (4). The data for this reaction are summarized in Table 2.

When benzoyl peroxide and other acyl peroxides were used to initiate this process, it remained unclear how this reaction begins: through the $CCl_3\cdot$ radical formed in the interaction of peroxide radicals with CCl_4, or through CH_3COHCH_3-radicals formed in the interaction with *iso*-C_3H_7OH.

Using percarbonate as an example, it has been shown that the primary process is the reaction of the radicals formed according to equation (1) with the alcohol.

Since $RO\cdot$ radicals, unlike $R\cdot$ radicals, do not react with CCl_4, the yield of active $CH_3\dot{C}OHCH_3$ radicals per mole of peroxide will be considerably higher in the case of initiation by percarbonates.

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