ACID-CATALYZED DECOMPOSITION OF HYDROPEROXIDES IN THE PRESENCE

OF KETONES

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Ketones and aldehydes accelerate decomposition of hydroperoxides in acetonitrile solution in the presence of strong acids. An explanation of the effect, due to the formation of semiperketals (semiperacetals) which undergo rapid acid-catalytic decomposition, is proposed. The macrostage character of the reaction of acid-catalyzed decomposition of cyclohexyl hydroperoxide was demonstrated for the first time. The initially slow decomposition takes place homolytically and yields the product cyclohexanone, which accelerates decomposition.

Homolytic transformation takes place parallelly to ionic transformation during acid-catalyzed decomposition of hydroperoxides, and its proportion is usually small in overall decomposition [1]. The intense study of acid-catalytic decomposition of hydroperoxides began in the 1950s, but the question of the effect of the products of decomposition on the decomposition reaction has been poorly illuminated up to now. It can be concluded from the data below that the correlation of acid-catalyzed homolysis and heterolysis is more complex than previously indicated. In particular, the intense overall decomposition can be the consequence of accumulation of products of a catalyzed homolytic reaction.

EXPERIMENTAL

Cyclohexylhydroperoxide (CHHP) was synthesized by oxidation of cyclohexane [2]. Solutions prepared by vacuum distillation with a 75 and 90% concentration of CHHP were used in the study, and cyclohexanol was almost the only contaminant component. The rate of overall decomposition of the hydroperoxides was determined iodometrically. Processing of the kinetic curves for calculating the values of the pseudomonomolecular rate constants from the slope of the logarithmic anamorphoses was described previously in [1]. The products of decomposition of the hydroperoxides were analyzed chromatographically at 323 K (20% Carbowax-6000 or 30% dioctyl phthalate on Chromaton N-AW). The products of decomposition of CHHP, cyclohexanol (COL) and cyclohexanone (CON) were analyzed after decomposing the residual CHHP in the samples by addition of a twofold (with respect to the hydroperoxide) amount of triphenylphosphine, forming an alcohol according to the reaction

$$(C_6H_5)_3P + ROOH \rightarrow (C_6H_5)_3PO + ROH$$
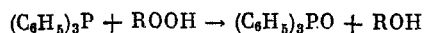
Combining the data from GLC analysis of COL and CON with the data from iodometry, the amount of COL formed during the kinetic experiment was determined. Acetonitrile was purified by the method in [1], and perchloric acid [3], COL, and tert-butyl hydroperoxide (TBHP) were purified by vacuum rectification.

RESULTS AND DISCUSSION

The concentration dependences of the pseudomonomolecular rate constants of consumption of CHHP are shown in Fig. 1. Curve 2 is completely analogous to the previously obtained data on the decomposition of TBHP catalyzed by $HClO_4$ [1] and $SbCl_5$ [4], i.e., for $[HClO_4] \geq [ROOH]$, the value of the pseudomonomolecular consumption rate constant k attains the limiting value, $k = k_\infty$. This finding is treated most simply by analogy with schemes 1 and 2 in [5], whose essence consists of the simple transformation of protonated molecules of the hydroperoxide $ROOH_2^+$ into the products of reactions basically along ionic pathways. However, the

TABLE 1.   Kinetics of Catalyzed Decomposition of CHHP and Accumulation of Products ($[HClO_4]$ = $4.06 \cdot 10^{-2}$, $[CHHP]_0$ = $4.33 \cdot 10^{-2}$ mole/liter, 302 K, acetonitrile)

Time, min	$[CHHP] \cdot 10^2$	$[CON] \cdot 10^2$		$[COL] \cdot 10^2$	$\Sigma c_i^{\dagger}$
		IR*	GLC		
0,5	4,22	—	0,14	—	—
1,5	4,04	0,22	0,18	—	4,44
2,5	3,84	0,30	0,26	0,62	4,76
3,5	3,70	0,32	0,36	0,63	4,65
4,5	3,52	0,40	0,45	0,68	4,60
9,0	2,62	0,65	0,66	1,06	4,33
15,0	2,02	0,90	0,89	1,23	4,15
25,5	1,69	1,20	1,04	0,99	3,88
40,0	1,22	1,40	1,34	1,32	3,94
60,0	0.94	1,74	1,35	1,47	4,15

*The analysis of ketone was duplicated by IR spectroscopic analysis.

$\dagger \Sigma c_i$ = [CON] + [COL] + [CHHP].

dependence of k on [ROOH] (Fig. 1, curve 1) is more complex than in [1, 3-5]: $k = k_0 + k_1 \cdot$ [ROOH], i.e., decomposition can be formally represented as parallelly occurring first- and second-order reactions (the equality $k = k_\infty$ holds for curve 1, since all of the experiments in this series were conducted with [ROOH] < $[HClO_4]$.   From the slope of curve 1 (Fig. 1), k_1 = $4.3 \cdot 10^{-3}$ liter/mole·sec, and the value of interception at the ordinate is k_0 = $3 \cdot 10^{-3}$ sec^{-1}.   The value of the activation energy of overall decomposition, E_{inf} = 64 kJ/mole, was determined with the values k of decomposition of $2.1 \cdot 10^{-2}$ mole/liter CHHP in the presence of $3.3 \cdot 10^{-2}$ mole/liter $HClO_4$ in an atmosphere of air ($18.7 \cdot 10^{-3}$, $14.6 \cdot 10^{-3}$, $10.2 \cdot 10^{-3}$, $7 \cdot 10^{-3}$ sec^{-1} for 333, 328, 323, and 318 K, respectively).   This value is much less than the analogous characteristic of uncatalyzed overall decomposition of CHHP (E = 144 kJ/mole), i.e., the acid greatly facilitates decomposition of CHHP [2].

The results of the analysis of the products of catalyzed decomposition of CHHP are reported in Table 1.   Note that ketone and alcohol are formed in acid-catalytic decomposition of CHHP in the ratio of approximately 1:1.   The marked imbalance of products (Σc_i > $[CHHP]_0$), probably due to the insufficient precision of the determination of [COL] for low degrees of decomposition, corresponds to the manifest excess of [COL] > [CON] in the first minutes of decomposition.

It follows from the data reported that the mechanism of decomposition of CHHP in the presence of $HClO_4$ is complex.   In particular, it is difficult to explain the contribution of the second-order reaction in CHHP, as the first-order in the hydroperoxide corresponded to acid-catalyzed overall decomposition in all preceding studies.   In addition, the nature of the formation of the marked amount of COL and the ratio of [COL] ≥ [CON] is not understood
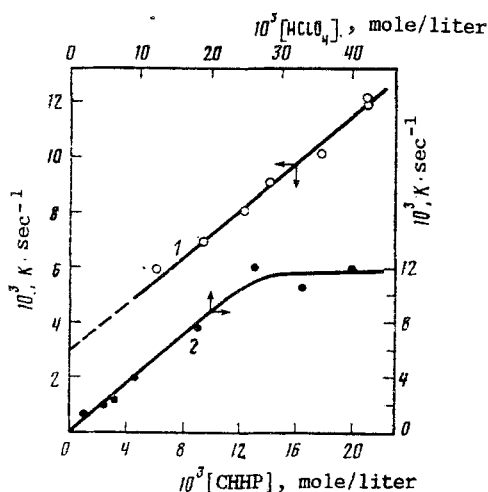

Fig. 1.   Dependences of the pseudo-monomolecular rate constants of decomposition of CHHP on the concentrations of CHHP (1) and $HClO_4$ (2) in acetonitrile; air, 323 K: 1) $[HClO_4]$ = $3.3 \cdot 10^{-2}$ mole/liter; 2) $[CHHP]_0$ = $2.1 \cdot 10^{-2}$ mole/liter.
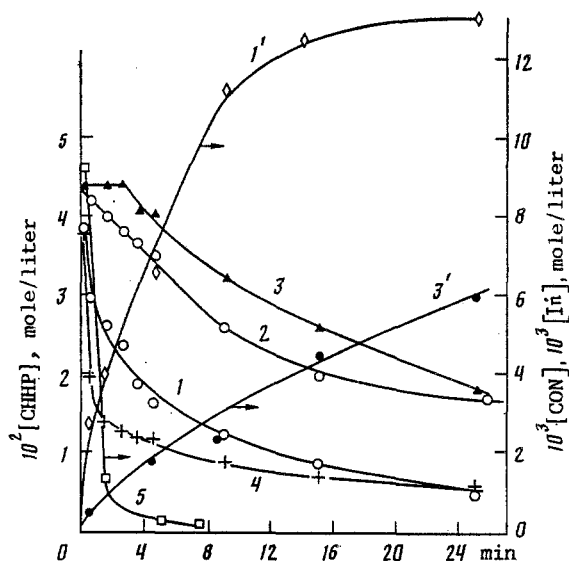
Fig. 2. Kinetic curves: 1-4) decomposition of CHHP at 302 K and $[HClO_4] = 4.1 \cdot 10^{-2}$ mole/liter; 1) in argon; 2) in oxygen; 3) in argon in the presence of $8.9 \cdot 10^{-3}$ mole/liter of nitroxyl radical (inhibitor); 4) in oxygen in the presence of $1.5 \cdot 10^{-2}$ mole/liter CON; 5) quenching of nitroxyl radical. 1', 3') Accumulation of CON in experiments 1 and 3.

from the point of view of the probable transformation of the CHHP molecule according to a scheme with predominant formation of CON
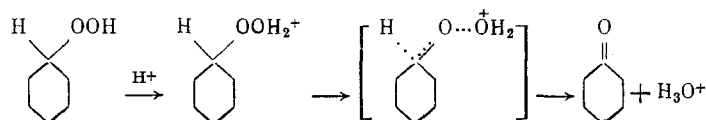
The comparative experiments on decomposition of CHHP in bubbling of argon, air, and oxygen was an additional complexity. It was shown that $k_{Ar} = 9.3 \cdot 10^{-3}$, $k_{air} = 7.4 \cdot 10^{-3}$, and $k_{O_2} = 4.8 \cdot 10^{-3}$ sec^{-1} for $[CHHP]_0 = 0.016$ and $[HClO_4] = 2.8 \cdot 10^{-2}$ mole/liter, 318 K. From the point of view of a purely ionic (molecular) mechanism of decomposition, the dependence of the rate on the presence of this dependence could most probably indicate the marked role of radical stages in the decomposition of CHHP. Finally, the key, in our opinion, results were obtained in studying decomposition at a low temperature (Fig. 2). The effect of the nature of the bubbling gas is preserved here (curves 1 and 2), and decomposition is faster in argon. The inhibitor added at the beginning of the experiments: 2,2,6,6-tetramethyl-4-benzoylhydro-piperidine-1-oxyl, causes pronounced slowing of decomposition (curve 3). The end of the induction period is due to the rapid transformation of the inhibitor in the strongly acid medium (curve 5). The rates of accumulation of CON in the experiments with and without the nitroxyl radical (curves 3' and 1') differ very significantly: The inhibitor decreases the rate of accumulation of ketone. Finally, addition of ketone at the beginning of the reaction (curve 4') causes fast consumption of the hdyroperoxide, which is not slowed by the inhibitor.

This set of data is in agreement with the following mechanism of decomposition of CHHP. 1. Decomposition of the individual hydroperoxide in our conditions takes place very slowly even in the presence of an acid. 2. Addition of an acid causes homolysis of the hydroperoxide, resulting in the formation of ketone and alcohol according to the following reactions
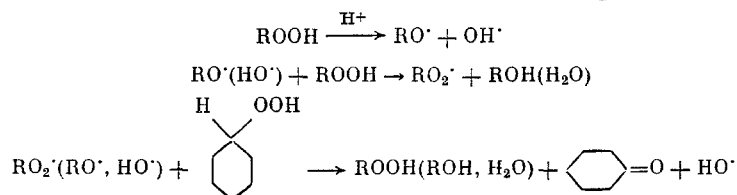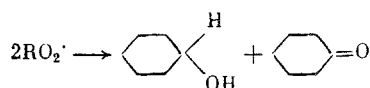
$$ROOH \xrightarrow{H^+} RO^\cdot + OH^\cdot$$

$$RO^\cdot(HO^\cdot) + ROOH \rightarrow RO_2^\cdot + ROH(H_2O)$$

Time, min	Catalyst					
	HCl	HCl+CON	HCl+CON +H₂O	HClO₄+CON	HClO₄	HClO₄+PA
	$10^2[CHHP]$, mole/liter					
0	2,48	2,3	2,6	2,4	--	2,25
1	2,42	2,0	2,26	2,1	2,43	--
2	2,45	1,74	2,1	1,9	--	--
4	2,54	1,36	1,9	1,6	--	2,3
6	2,40	1,1	1,7	1,4	2,5	1,24
8	2,40	0,9	1,55	1,4	--	0,9
10	2,38	0,7	1,52	1,2	2,46	0,85
12	2,50	0,68	1,6	1,2	--	0,9
14	--	--	1,58	--	2,48	--

$$2RO_2 \cdot \longrightarrow \overset{H}{\underset{OH}{\bigcirc\!\!\!<}} + \bigcirc\!\!=\!\!O$$

3. CON, which accumulates during radical-induced decomposition of CHHP, causes fast decomposition of the hydroperoxide, playing the role of a cocatalyst of the acid catalyst (addition of a secondary alcohol in a concentration commensurate with the concentration of ROOH does not cause acceleration).

4. Addition of an inhibitor slows the reaction of acid-catalytic decomposition, blocking the "trigger mechanism of decomposition," the reaction of chain radical formation of ketone from CHHP.

The data which confirm these statements are contained in Table 2, from which it is clear that pronounced decomposition of the hydroperoxide does not take place in the presence of a strong mineral acid alone. Addition of ketone to the acid solution causes decomposition whose rate decreases on subsequent addition of water. The comparison shows that decomposition in the systems HCl + CON + H₂O and HClO₄ + CON takes place with a similar rate. This is also understandable: perchloric acid was added to the solution in the form of a 75% aqueous solution and water was actually present in the solution in the concentration of $6.8 \cdot 10^{-2}$ mole/liter in the experiment with perchloric acid, i.e., in a concentration comparable to $[H_2O]$ in the experiment with HCl. Addition of propionaldehyde (PA) to the solution containing a mineral acid also results in rapid consumption of the hydroperoxide. The effect of water is understood: its addition decreases the acidity of the medium

$$SH^+ + nH_2O \rightleftharpoons nH_2O \cdot H^+ + S$$
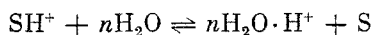
i.e., the strength of the acid catalyst in the solvent S decreases. For this reason, acid-catalytic decomposition does not take place in a solvent with a high basicity: methanol, even in relatively rigorous conditions (333 K, 0.03 mole/liter $HClO_4$).

The results of the detailed kinetic study of catalyzed decomposition of TBHP in the presence of $HClO_4$ and CON are reported below. This compound was more convenient for investigation than the preceding CHHP + $HClO_4$ + CON system in which CON is formed in decomposition, i.e., the concentration of the catalyst changes, making quantitative processing of the data and interpretation of the calculated overall constants difficult. Examples of the kinetic curves of decomposition of TBHP are shown in Fig. 3. The presence of ketone alone or an acid alone (curves 1, 2) does not result in decomposition of TBHP. Their combined presence causes rapid decomposition. Methyl ethyl ketone (MEK) in the presence of $HClO_4$ also causes consumption of the hydroperoxide, and the effect of this ketone is weaker than the effect of CON (compare curves 5 and 4). Carbonyl-containing compounds (ketones, aldehydes) thus cause rapid decomposition of hydroperoxides in acetonitrile in the presence of perchloric and hydrochloric acids. The effect of H_2SO_4 in these conditions is virtually not observed, however, and addition of AcOH also does not cause decomposition of ROOH in the presence of ketones.

The question of the stoichiometry of the reaction of ketone and hydroperoxide arises. The data reported in Table 3 show that even a fivefold change in the concentration of $HClO_4$

Fig. 3   Fig. 4

Fig. 3. Kinetic curves of decomposition of TBHP at 302 K in
acetonitrile, argon: 1) $[CON]_0 = 1.47 \cdot 10^{-2}$ mole/liter, with-
out $HClO_4$; 2) $[HClO_4] = 4 \cdot 10^{-2}$ mole/liter, without CON; 3)
$[CON]_0 = 1 \cdot 10^{-3}$, $[HClO_4] = 4 \cdot 10^{-2}$ mole/liter; 4) $[CON]_0 =$
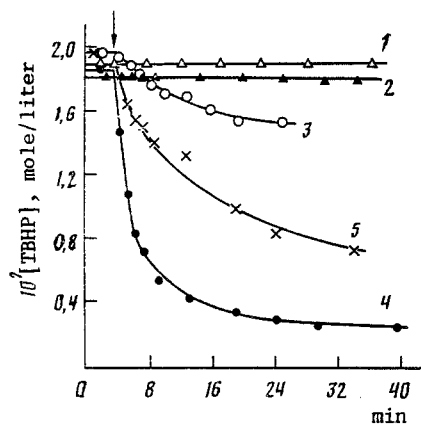$1.5 \cdot 10^{-2}$, $[HClO_4] = 4.1 \cdot 10^{-2}$ mole/liter; 5) $[MEK]_0 = 1.54 \cdot$
10^{-2}, $[HClO_4] = 4 \cdot 10^{-2}$ mole/liter.
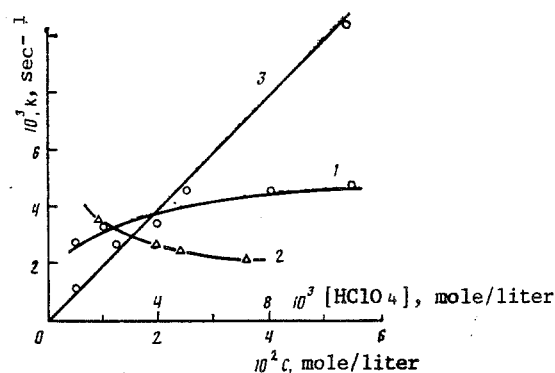
Fig. 4. Dependence of k of decomposition of TBHP in aceto-
nitrile at 302 K, argon: 1) on $[HClO_4]$, $[TBHP]_0 = 2 \cdot 10^{-2}$,
$[CON]_0 = 5 \cdot 10^{-3}$ mole/liter, external scale; 2) on $[TBHP]_0$,
$[CON]_0 = 2.5 \cdot 10^{-3}$, $[HClO_4] = 4 \cdot 10^{-2}$ mole/liter, external scale;
3) on $[CON]_0$, $[TBHP]_0 = 2 \cdot 10^{-2}$, $[HClO_4] = 4 \cdot 10^{-2}$ mole/liter,
internal scale.

weakly affects the kinetics of consumption of CON. The rates and degrees of decomposition
of TBHP also differ little from these experiments (the data are not reported in Table 3).
The average value of the ratio of the decrease in the hydroperoxide and ketone in the ex-
periments with a variable concentration of $HClO_4$ is $\Delta[TBHP]/\Delta[CON] \approx 2.3$. The role of the
products of conversion of CON in decomposition of TBHP is unclear, but if they have no cata-
lytic effect, then approximately two molecules of hydroperoxide are decomposed with the par-
ticipation of one molecule of ketone. The ratio $[ROOH]/[CON]_0$ correlates with the value of
$[ROOH]_0/[CON]_0$; see Table 4.

Table 4 shows that for small ratios of the initial concentrations of the reactants, the
reaction takes place with the stoichiometry $ROOH:CON \approx 2:1$, and for large ratios, the reac-
tion resembles the catalytic reaction. The dependences of the pseudomonomolecular rate con-
stant of decomposition of TBHP on the concentrations of the acid, ketone, and hydroperoxide
are shown in Fig. 4. The first order in ketone, the slight increase in k with an increase
in the concentration of the acid, and the decrease in k with an increase in [ROOH] are ob-
served experimentally.

The study of the composition of the products of decomposition of TBHP in the presence
of CON and $HClO_4$ showed that four basic compounds are formed: acetone, di-tert-butyl perox-
ide, isobutylene, and methanol. In approximately 90% conversion of TBHP (for $[TBHP]_0 =$
$2.1 \cdot 10^{-2}$, $[HClO_4] = 5 \cdot 10^{-2}$, $[CON]_0 = 5 \cdot 10^{-2}$ mole/liter, 302 K), the molar ratio of the prod-
ucts listed is 2:1:1:0.6, and the balance of products is 65% based on the equation $0.25 \times$
$\sum_i n_i C_i$ [4], i.e., 35% of the decomposed TBHP produces unidentified products. In the exper-
iment with the deep decomposition by 35% ($[TBHP]_0 = 2.5 \cdot 10^{-2}$, $[HClO_4] = 5 \cdot 10^{-2}$, $[CON]_0 =$
$2 \cdot 10^{-2}$ mole/liter, 302 K), the balance equals 90%, and the ratio of the products indicated
above is 2.5:1:2.5:0.5.

These ratios are in general close to the previously obtained ratios [1, 4] in studies
of the decomposition of TBHP in the presence of $HClO_4$ and $SbCl_5$ at a slightly higher (by
20°C) temperature in the absence of ketone.

The mechanism of decomposition of the hydroperoxides in light of the findings reported
above can be attributed to the formation of a new peroxide from ketone (or aldehyde) and

TABLE 3. Kinetics of Consumption of CON in Catalyzed Decomposition of TBHP in Acetonitrile (302 K, argon)

Time, min	$10^2 [HClO_4]$, mole/liter			$10^2 [TBHP]$, mole/liter	
	1,0	2,0	5,5	1,0	2,0
	$10^3 [CON]$, mole/liter			$10^3 [CON]$, mole/liter	
0,5	3,2	4,1	4,1	1,65	0,77
1,5	2,88	3,9	2,8	1,58	0,67
2,5	2,42	3,2	2,42	1,15	0,45
4	2,4	2,5	1,36	1,1	0,3
7	1,9	1,8	1,2	0,8	0,12
12	1,4	1,54	0,8	0,5	0,04
17	1,0	1,1	0,7	0,45	0,02
23	0,9	0,84	0,6	0,45	0,02

$[TBHP]_0 = 2 \cdot 10^{-2}$ mole/liter
$[CON]_0 = 5 \cdot 10^{-3}$ mole/liter

$[CON]_0 = 2,5 \cdot 10^{-3}$ mole/liter
$[HClO_4]_0 = 4 \cdot 10^{-2}$ mole/liter

TABLE 4. Dependence of $\Delta[ROOH]/[CON]_0$ on the Initial Ratio of Concentrations of Hydroperoxide and Ketone

$\dfrac{[ROOH]_0}{[CON]_0}$	20	8	4	2
$\dfrac{\Delta[ROOH]}{[CON]_0}$	5	3	2	1,7

hydroperoxide, and it decomposes in acid medium more rapidly than the starting hydroperoxide. The existence of these forms is well known: They are semiperacetals or semiperketals [5], and the kinetics of their formation are studied in detail in [6]. The formation of perketals

with the structure of $\diagdown$C—OOR from CON and TBHP is possible [7], and this question requires
$\diagup$ $\diagdown$OOR

special investigation. The hypothesis of the more rapid decomposition of these adducts in acid medium in comparison to the starting ROOH explains the effect of the combined action of the carbonyl compounds and acids. In a first approximation, the mechanism of decomposition of TBHP can be represented by the scheme

$$ROOH + H^+ \overset{K_1}{\rightleftharpoons} ROOH_2^+$$
$$R'O + H^+ \overset{K_2}{\rightleftharpoons} R'OH^+$$
$$R'OH^+ + ROOH \overset{K_3}{\rightleftharpoons} X \qquad (1)$$
$$X \overset{K'}{\longrightarrow} P$$

In the scheme, K_1, K_2 are the equilibrium protonation constants of the hydroperoxide and ketone R'O, and K_3 is the equilibrium constant of formation of the intermediate product, semi-

perketal X of the hypothetical structure $\langle\!\!\!\bigcirc\!\!\!\rangle\!\!\!<^{OH}_{OOR}$. In accordance with scheme (1), the expression of the rate of consumption is

$$W = -d[ROOH]/dt = k'[X] = k'K_3 [R'OH^+][ROOH]$$
$$[ROOH] = [ROOH_2^+]/K_1 [H^+] \qquad W = k'K_3 [R'OH^+] \frac{[ROOH_2^+]}{K_1[H^+]}$$

In consideration of the material balance $[H^+]_0 = [ROOH_2^+] + [R'OH^+] + [H^+]$ (it is assumed that all of the perchloric acid added to the acetonitrile solution dissociates, and the protons exist in three forms: in the form of protonated hydroperoxide and ketone, and in the form of free H^+), we have

$$W = k'K_3[\text{R'OH}^+] \frac{[\text{ROOH}_2^+]}{K_1\{[\text{H}^+]_0 - [\text{ROOH}_2^+] - [\text{R'OH}^+]\}}$$

The concentrations of the protonated forms of ketone and hydroperoxide $K_2[\text{R'O}][\text{H}^+]_0$ are correspondingly

$$[\text{R'OH}^+] = \frac{K_2[\text{R'O}][\text{H}^+]_0}{1 + K_2[\text{R'O}] + K_1[\text{ROOH}]}$$

$$[\text{ROOH}_2^+] = \frac{K_1[\text{ROOH}][\text{H}^+]_0}{1 + K_2[\text{R'O}] + K_1[\text{ROOH}]}$$

and the rate of decomposition is

$$W = \frac{k'K_2K_3[\text{R'O}][\text{ROOH}][\text{H}^+]_0}{1 + K_2[\text{R'O}] + K_1[\text{ROOH}]}$$

Based on the determination, the pseudomonomolecular first-order rate constant of decomposition is W/[ROOH] = k, i.e.,

$$k = \frac{a[\text{R'O}][\text{H}^+]_0}{1 + K_2[\text{R'O}] + K_1[\text{ROOH}]} \tag{2}$$

where $a = k'K_2K_3$, $[\text{H}^+] = [\text{HClO}_4]$.

Let us compare the analytical dependences of k with the experimental dependences (Fig. 4). The specific rate of decomposition k is proportional to [R'O] (Fig. 4, curve 3), and consequently, the contribution of term $K_2[\text{R'O}]$ to the value of the denominator is small, $K_2[\text{R'O}] < 1 + K_1[\text{ROOH}]$. The basicity of the ketone is apparently lower than the basicity of the hydroperoxide, and in our experiments [R'O] < [ROOH]. Then (2) is transformed into the following

$$k = \frac{a[\text{R'O}][\text{H}^+]_0}{1 + K_1[\text{ROOH}]} \tag{3}$$

According to (3), the value of k is directly proportional to [R'O] but decreases with an increase in [ROOH], which is in agreement with the experimental findings (Fig. 4, curves 2 and 3).

According to the last equation, k should increase proportionally to the increase in the concentration of acid, but the increase is small in the experiment (Fig. 4, curve 1). Scheme (1) apparently only approximately reflects the processes which take place in the complex system studied.

The question of the contribution of the homolytic pathway to the overall decomposition in ROOH + H^+ + ketone systems requires special investigation. The experiments with the inhibitor (Fig. 2, curve 3) make it necessary to assume the presence of a macrostage character of decomposition in these systems, i.e., the complex interaction of homolysis and heterolysis catalyzed by acids. The fact that the CON + CHHP + acid system distinctly react to the concentration of oxygen in the system (Fig. 2, curves 1 and 2) can also be treated as evidence of the important role of homolytic processes. The high concentration of alcohol in the products of decomposition of CHHP in the presence of the ketone and acid is difficult to explain by assuming a purely heterolytic occurrence of the process.

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