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Catalytic Decomposition of Aliphatic Peroxy Acids

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Abstract—The catalytic decomposition of peroxy acids is studied in various solvents in the presence of manganese, cobalt, chromium, nickel, and copper acetates and cerium benzoate. The catalytic activity of the salts in peroxy acid decomposition decreases in the order $Mn^{2+} > Co^{2+} > Ce^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$. The apparent activation energies of the catalytic decomposition of peroxydecanoic acid range between 45.9 and 88.0 kJ/mol. The reaction medium has an effect both on the apparent rate constant and on the activation energy of the reaction. The reaction mechanism includes the fast formation of a catalyst–peroxy acid intermediate complex, which decomposes to release a catalyst molecule and forms the reaction products. The oxidation state of the metal ion of the catalyst can change. The introduction of compounds capable of forming complexes with metal ions of the catalyst substantially slows down the catalytic decomposition.

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Organic peroxy acids are widely used in many processes as epoxidizing, hydroxylating, and disinfecting agents. Use of peroxy acids as oxidizers affords many valuable products in high yields [1]. However, wide use of peroxy acids is hampered by their low stability. They decompose both themselves and in solution, and this process can proceed simultaneously via several mechanisms [2]. Metal ions with a variable oxidation state favor the decomposition of peroxy acids. The main specific features of the catalytic decomposition of the peroxy acids in the presence of cobalt and manganese salts were considered in earlier works [3–5]. It was shown that the mechanism of this reaction resembles in many respects the mechanism of hydroperoxides decomposition in the presence of metal ions of variable valence [6]. At the same time, no data concerning the solvent effect on the catalytic decomposition of peroxy acids are available, although both the rate and mechanism of the process may depend on the composition of the reaction medium.

The regularities of the catalytic decomposition of peroxy acids were mainly considered for cobalt and manganese salts, while the catalytic activity of other metal ions with a variable oxidation state was not studied. The purpose of the present work is to study the stability of peroxy acid solutions in various organic solvents in the presence of copper, nickel, cerium, chromium, cobalt, and manganese salts. We also searched for substances capable of stabilizing peroxy acid solutions.

EXPERIMENTAL

Peroxy acids were synthesized according to an earlier described procedure [7]. Peroxydecanoic acid (PDA) was 98.5% pure in most cases. Decanoic acid was the main impurity in PDA. Peroxyacetic acid (PAA) was synthesized from acetic anhydride and hydrogen peroxide [2]. All solvents were purified by standard procedures [8, 9] and were distilled in an argon atmosphere. Copper, nickel, chromium, cobalt, and manganese acetates, chromium nitrate, and cerium benzoate were used as catalysts (all salts were reagent grade). The catalytic decomposition of PDA was carried out in a glass reactor in the temperature interval from 303 to 323 K under argon. A solution of a peroxy acid in one solvent or another was first maintained at a constant temperature for 20–30 min, and then a prescribed amount of an acetic acid solution of a metal salt was quickly microrsyringed into the solution. This moment was fixed as the onset of the reaction. To determine the PDA decomposition rate, the reaction mixture was sampled and was analyzed iodometrically for the peroxy acid content [10]. The error of determination of the apparent rate constants of the catalytic decomposition did not exceed 3–5%.

RESULTS AND DISCUSSION

Heating of PDA solutions in the temperature range examined for 5–6 h was not accompanied by a change in the peroxy acid concentration, indicating no thermal decomposition of the acid. It was shown [11] that the thermal decomposition of the peroxy acid occurs above 353 K. The introduction of a catalyst into the reaction mixture induces intensive PDA decomposition. The kinetics of this process obeys a first-order kinetic equation (Fig. 1). However, the reaction rate depends on the nature of the catalyst. The apparent rate constants (k_{app}) and activation energies (E_a) of the

catalytic decomposition are given in Table 1. The catalytic activity of the salts estimated from the apparent decomposition rate constants and from the concentration of the catalyst salt (C_{Cat}) decreased in the order $Mn^{2+} > Co^{2+} > Ce^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$.

The apparent activation energies range between 45.9 and 88.0 kJ/mol and are close to the earlier reported values [3–5]. The E_a values for PDA decomposition in the presence of nickel, cobalt, and manganese acetates almost coincide (82.5 ± 5 kJ/mol), whereas they are somewhat lower in the presence of cerium benzoate or copper acetate (65.5 and 45.9 kJ/mol, respectively). The highest E_a value (88.0 kJ/mol) was observed with chromium acetate (Table 1). The difference between the catalytic activities of metal ions (M) in the decomposition of the peroxy compounds is explained in terms of the standard electrode potentials of the $M^{n+}/M^{(n+1)+}$ systems, and the alternating reduction and oxidation of the metal ion are included in the mechanism of the process. In a manganese(II) acetate solution, Mn^{2+} can be oxidized to Mn^{4+} and Mn^{6+}, and this the likely cause of the high catalytic activity of manganese(II).

In all experiments on the catalytic decomposition of PDA in the presence of salts, a weak chemiluminescence was observed, which decreased with a decreasing process rate. This weak chemiluminescence probably indicates that the overall process includes free-radical steps. The results of spectrophotometry and the changes in the chemiluminescence intensity during catalytic PDA decomposition validate the scheme suggested for the process in the presence of the metal salts with a variable oxidation state. In our experiments, the metal salt solutions changed their color on contact with a a peroxy acid solution, indicating that the oxidation state of the metal ion of the catalyst changed during the reaction. The colorless solution of cerium(III) benzoate turned yellow, apparently due to the oxidation of the Ce^{3+} ion to Ce^{4+}. When the reaction mixture contains a peroxy compound, the pale pink solution of cobalt(II) acetate turns dark green. Spectrophotometric data suggest that the different valence forms of the catalytic metal ion are equilibrated already at the earliest stages of catalytic decomposition, and this equilibrium remains unchanged up to the end of the process.

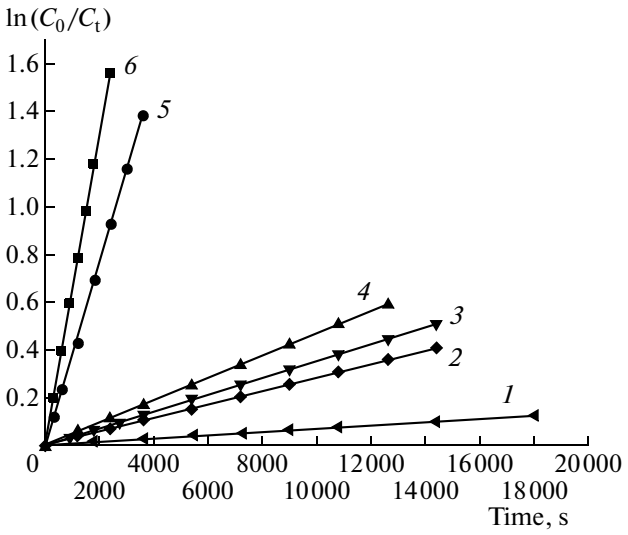

Fig. 1. Kinetics of PDA (0.1 mol/l) decomposition in acetic acid at 308 K in the presence of catalysts: (*1*) copper acetate (6.7×10^{-3} mol/l), (*2*) nickel acetate (3.0×10^{-3} mol/l), (*3*) chromium acetate (8.0×10^{-4} mol/l), (*4*) cerium benzoate (8.0×10^{-4} mol/l), (*5*) manganese acetate (0.8×10^{-4} mol/l), and (*6*) cobalt acetate (4.0×10^{-4} mol/l).

The associative interaction between different valence states of cobalt ions is possible in the systems containing a peroxy compound and cobalt acetate in acetic acid [12]. In addition, spectrophotometric data suggest that the solution contains different salt complexes, whose concentrations depend both on the concentration of the catalyst salt and on temperature. Probably, both catalytic metal ions in different valence

Table 1. Kinetic and activation parameters of PDA decomposition in acetic acid in the presence of various catalysts

Catalyst	$C_{Cat} \times 10^4$, mol/l	$k_{app} \times 10^5$, s^{-1}					E_a, kJ/mol
		303 K	308 K	313 K	318 K	323 K	
$Cu(CH_3COO)_2$	67	0.467	0.670	0.840	–	1.44	45.9
$Ni(CH_3COO)_2$	30	1.89	2.83	5.17	8.17	15.0	80.4
$Ce(C_6H_5COO)_3$	8.0	3.13	4.66	7.29	10.4	15.7	65.5
$Cr(CH_3COO)_3$	8.0	2.15	3.53	6.14	10.4	18.0	88.0
$Co(CH_3COO)_2$	4.0	27.0*	65.4	97.4	151	265	83.1
$Mn(CH_3COO)_2$	0.80	24.1	38.5	66.8	112	192	84.0

Note: The initial PDA concentration is $C_0 = 0.1$ mol/l. The accuracy of E_a determination is ±5.0 kJ/mol.
* $T = 301$ K.

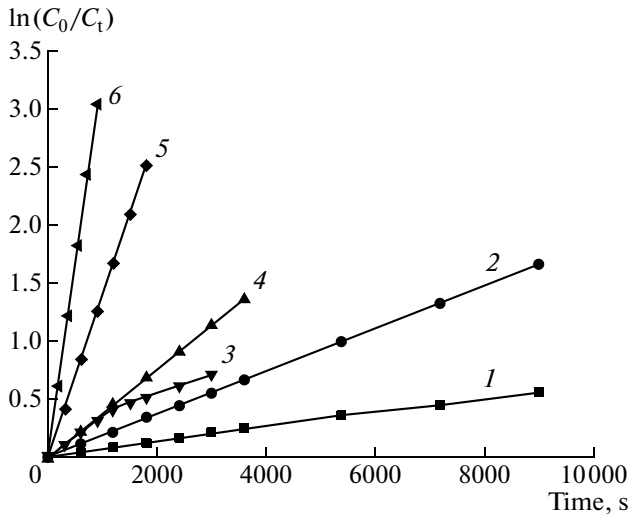

Fig. 2. Kinetics of PDA (0.1 mol/l) catalytic decomposition in the presence of cobalt acetate (C_{Cat} = 2.0 × 10^{-3} mol/l) at 303 K in various solvents: (*1*) acetone, (*2*) dioxane, (*3*) tetrachloromethane, (*4*) propan-2-ol, (*5*) acetic acid, and (*6*) toluene.

states and different complexes have different catalytic activities in PDA decomposition.

The influence of the solvent nature on the rate of catalytic PDA decomposition is illustrated in Fig. 2. The decomposition rate is highest in toluene, being approximately 80 times higher than that in acetone. The apparent rate constants of PDA decomposition in the presence of cobalt acetate ($C_{Cat} = 2 \times 10^{-3}$ mol/l) at the early stages of the process at different temperatures are listed in Table 2. The calculated apparent activation energies of catalytic PDA decomposition in various solvents range between 85.5 and 146.8 kJ/mol. The lowest E_a value (85.5 kJ/mol) was observed in acetic acid, while in toluene at the same catalyst content, E_a = 146.8 kJ/mol. The activation energy varies with the composition of the reaction mixture due to the solvent effect on the reactivity of both PDA and the catalyst. In "inert" solvents, the peroxy acid molecules are cyclic and have an intramolecular hydrogen bond [13]. The solvents capable of forming intermolecular hydrogen bonds with PDA molecules substantially affect the reactivity of the peroxy groups. In addition, the solvent can change the catalytic activity of the catalytic metal salt.

The results obtained show that the mechanism of catalytic PDA decomposition includes the formation of an intermediate complex (IntmC) between the peroxy acid and the catalyst in the initial, fast step

$$\mathrm{PDA} + \mathrm{M}^{n+} \xleftrightarrow{K_{eq}} \mathrm{IntmC}. \qquad \text{(I)}$$

This step can be characterized by the equilibrium constant K_{eq}. Having decomposed, IntmC forms the reaction products and releases the catalytic metal ion:

$$\mathrm{IntmC} \xrightarrow{k_r} \mathrm{M}^{n+} + \text{reaction products}. \qquad \text{(II)}$$

The catalytic metal ion can change its valence state during the decomposition of the intermediate compound IntmC. The overall rate of the process is determined by the decomposition rate of the intermediate compound. The rate of the process can be described by an equation of the Michaelis–Menten type [14]:

$$w = \frac{k_r K_{eq}[\mathrm{PDA}][\mathrm{M}^{n+}]}{1 + K_{eq}[\mathrm{PDA}]}, \qquad (1)$$

where k_r is the true rate constant of decomposition and [PDA] and [M^{n+}] are the concentrations of the peroxy acid and catalyst, respectively.

Equation (1) can easily be transformed into the form convenient for the calculation of K_{eq} and k_r:

$$\frac{1}{w} = \frac{1}{k_r K_{eq}[\mathrm{M}^{n+}][\mathrm{PDA}]} + \frac{1}{k_r[\mathrm{M}^{n+}]}. \qquad (2)$$

The reaction rates were measured at different initial PDA concentrations in the reaction mixture to see whether the proposed mechanism is valid. As was

Table 2. Kinetic and activation parameters of catalytic PDA decomposition in the presence of cobalt acetate in various solvents

Solvent	$k_{app} \times 10^5$, s^{-1}					E_a, kJ/mol
	303 K	308 K	313 K	318 K	323 K	
Acetone	6.82	14.8	31.8	63.3	126	121.0
Dioxane	18.5	42.2	69.0	136	270	107.3
Propan-2-ol	37.8	76.8	175	320	750	121.0
Tetrachloromethane	35.5	67.1	132	287	517	110.8
Ethyl acetate	–	99.4	162	270	573	94.5
Acetic acid	140	274	438	695	1180	85.5
Toluene	338	677	2290	5340	–	146.8

Note: The initial PDA concentration is C_0 = 0.1 mol/l, and the catalyst concentration is $C_{Cat} = 2.0 \times 10^{-3}$ mol/l. The accuracy of E_a determination is ±5.0 kJ/mol.

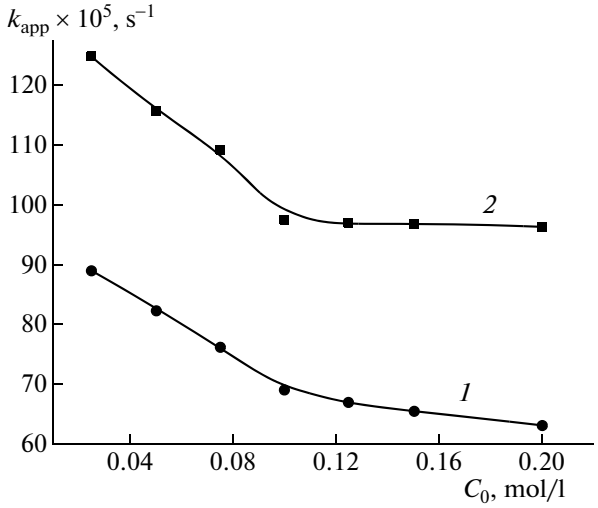

Fig. 3. Dependences of the apparent rate constant of catalytic decomposition on the initial PDA concentration at 323 K in various solvents: (*1*) dioxane ($C_{Cat} = 2.0 \times 10^{-3}$ mol/l) and (*2*) acetic acid ($C_{Cat} = 4.0 \times 10^{-4}$ mol/l).

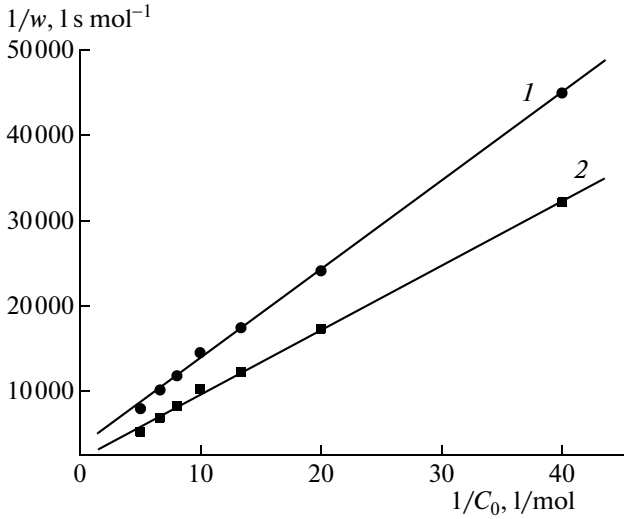

Fig. 4. $1/w$ versus $1/C_0$ for the catalytic decomposition of PDA at 323 K in various solvents: (*1*) dioxane ($C_{Cat} = 2.0 \times 10^{-3}$ mol/l) and (*2*) acetic acid ($C_{Cat} = 4.0 \times 10^{-4}$ mol/l).

expected, an increase in the C_0/C_{Cat} ratio decreases the overall rate of the process (Fig. 3) and the apparent rate constant of catalytic decomposition tends to some limit. The experimental results can be fitted to a linear function in the $1/w$ vs. $1/C_0$ coordinates (Fig. 4). The numerical values of K_{eq} and k_r were derived from the slope ratio of the lines and from the $1/w$ intercept. For dioxane solutions, these parameters are 2.92 l/mol and 0.15 s^{-1}; for acetic acid, 2.56 l/mol and 1.25 s^{-1}, respectively. Clearly, the equilibrium constants of formation of the intermediate compound between PDA and the catalytic metal ion in dioxane and in acetic acid are similar, and the rate constant of PDA decomposition in dioxane is approximately 8 times lower than that for acetic acid.

One of the possible methods for peroxy acid stabilization is to introduce, into the peroxy acid solution, a compound capable of forming a strong, catalytically inactive complex with the catalytic metal ion. We carried out kinetic experiments in which various compounds capable of forming complexes with metal ions were introduced into the reaction mixture, These complexing agents were ionol (2,6-*tert*-butyl-4-methylphenol), an efficient inhibitor of free-radical reactions; α-hydroxynaphthoic acid (HNA); 8-hydroxyquinoline; and α-picolinic acid (APA). The results are listed in Table 3.

As was expected, the efficient inhibitor of free radical processes (ionol) exerted almost no effect on the catalytic decomposition rate. The weak complexing agent HNA exerted an insignificant effect on the rate of the process. At the same time, 8-hydroxyquinoline and APA introduced into the reaction mixture in a 10- to 50-fold excess over the catalyst concentration substantially decreased the rate of PAA and PDA decom-

Table 3. Influence of various compounds on the rates of PAA and PDA catalytic decomposition

Peroxy acid	Concentration of additive, mol/l	Catalyst	$C_{Cat} \times 10^4$, mol/l	$w \times 10^5$, mol l^{-1} s^{-1}				
				without additive	ionol	HNA	8-hydroxy-quinoline	APA
PAA	0.01	$Cr(NO_3)_3$	10.0	41.1	40.7	36.7	23.0	5.03
PAA	0.01	$Co(CH_3COO)_2$	2.0	27.1	27.3	26.8	3.95	0.80
PDA	0.005	$Co(CH_3COO)_2$	1.0	63.3	63.0	54.4	8.48	1.73
PDA	0.005	$Cr(NO_3)_3$	4.0	31.7	32.0	29.4	19.4	2.82

Note: The initial concentrations of PAA and PDA are 1.0 and 0.1 mol/l, respectively. The solvent is acetic acid. The reaction temperature is 323 K.

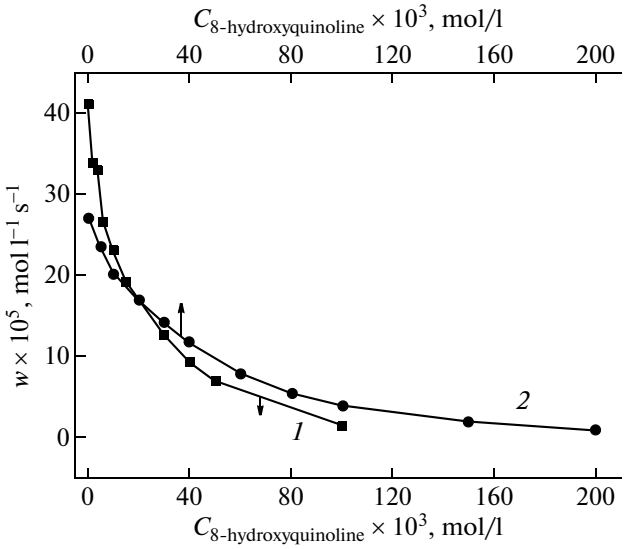

Fig. 5. Influence of the 8-hydroxyquinoline concentration on the rate of PAA catalytic decomposition (C_0 = 1.0 mol/l) at 323 K in the presence of the catalysts (*1*) $Cr(NO_3)_3$ (1.0×10^{-3} mol/l) and (*2*) $Co(CH_3COO)_2$ (2.0×10^{-4} mol/l). The solvent is acetic acid.

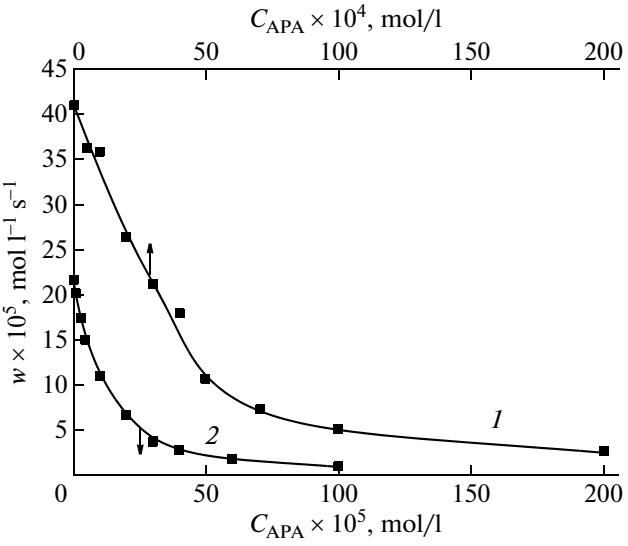

Fig. 6. Influence of the α-picolinic acid concentration on the rate of PAA catalytic decomposition (C_0 = 1.0 mol/l) at 323 K in the presence of the catalysts (*1*) $Cr(NO_3)_3$ (1.0×10^{-3} mol/l) and (*2*) $Co(CH_3COO)_2$ (1.0×10^{-4} mol/l). The solvent is acetic acid.

position in the presence of cobalt acetate and chromium nitrate (Table 3). An increase in the concentration of 8-hydroxyquinoline and APA in the reaction medium decreases the rate of PAA catalytic decomposition to a certain limit (Figs. 5, 6).

According to our data, even in a multifold excess of 8-hydroxyquinoline the limiting rate of PAA decomposition at 323 K in the presence of $Co(CH_3COO)_2$ is 0.98×10^{-5} mol l^{-1} s^{-1}, whereas in the presence of $Cr(NO_3)_3$ it takes a rather large value of 1.49×10^{-5} mol l^{-1} s^{-1} (Fig. 5).

As the APA concentration in the system increases, the rate of catalytic PAA decomposition in the presence of $Cr(NO_3)_3$ decreases by a factor of ~16, while in the presence of $Co(CH_3COO)_2$ it decreases by a factor of ~22 (Fig. 6).

These distinctions can be explained by the different stabilities of the complexes formed by the Co^{3+} and Cr^{3+} ions with 8-hydroxyquinoline and APA. Note that the complexing agents can be oxidized with the peroxy acids. For example, 8-hydroxyquinoline readily forms an N-oxide under the action of the peroxy acid [15]. The oxidation of APA and the well-known complexing agent EDTA was observed in peroxy acid solutions [16, 17]. Probably, the N-oxidation of the complexing agents affects their stabilizing power. Note that the dependences of the rate of catalytic PAA decomposition on the concentration of APA as the stabiliser are satisfactorily linearizable in the coordinates of the $w^{-1} = f(C_{APA})$ equation. This confirms the conclusion that a catalytic metal ion is comparatively inactive in the decomposition reaction when it is bound into a strong complex. In the experiments on the effect of the 8-hydroxyquinoline concentration on the rate of catalytic PAA decomposition, no linear $w^{-1} = f(C_{8\text{-hydroxyquinoline}})$ dependence was observed. This is likely due to the partial N-oxidation of the complexing agent. In this case, 8-hydroxyquinoline is oxidized by the peroxy acid much more rapidly than APA [15].

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