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Thermal Decomposition of Aliphatic Peroxy Acids

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Abstract—The thermal decomposition reactions of aliphatic peroxy acids containing from 8 to 16 carbon atoms in a molecule were studied. It was found that the carbon radical length had no effect on the thermal stability of peroxide groups. The apparent rate constants of thermolysis of peroxydecanoic acid in various solvents and the activation energies of the test reaction were found. The thermal degradation of peroxy acids involved secondary reactions of induced chain degradation in addition to the primary homolysis of the peroxide group. The rate constants of induced chain degradation were found.

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INTRODUCTION

Organic peroxy acids are commonly used as oxidizing agents in many processes [1, 2]. Aliphatic peroxy acids can be successfully applied to modify polymers [3]; they are also intermediates in the synthesis of peroxide initiators for radical processes. Both in a pure form and in solutions, peroxy acids can simultaneously undergo decomposition by several mechanisms. Transition metal ions cause the intense degradation of peroxy acids [4, 5]. In water-containing solutions, the hydrolysis reaction can occur, in the course of which hydrogen peroxide and a corresponding carboxylic acid are formed [6]. The thermal degradation reactions of peroxy acids are not clearly understood, and available data are incomplete and contradictory [7, 8]. Here, we report the results of a study on the thermal decomposition of higher aliphatic peroxy acids in various organic solvents. These results can be useful in studying oxidation processes occurring at various temperatures and accompanied by the thermal degradation of an oxidizing agent.

EXPERIMENTAL

Aliphatic peroxy acids were prepared by the interaction of a corresponding carboxylic acid with hydrogen peroxide in a sulfuric acid solution [9]. The synthesized products were repeatedly recrystallized from hexane. Peroxy acid samples of 99% purity or greater; the main impurities were the corresponding carboxylic acids. The following peroxy acids were prepared and characterized in this study: peroxyoctanoic ($\mathbf{C_8}$), peroxynonanoic ($\mathbf{C_9}$), peroxydecanoic ($\mathbf{C_{10}}$), peroxylauric ($\mathbf{C_{12}}$), peroxytridecanoic ($\mathbf{C_{13}}$), peroxytetradecanoic ($\mathbf{C_{14}}$), peroxypentadecanoic ($\mathbf{C_{15}}$), and peroxypalmitic ($\mathbf{C_{16}}$) acids. All of the solvents were purified in accordance with published procedures [10, 11] and distilled in an atmosphere of argon. The thermal degradation constants of the test peroxy acids were determined over the temperature range of 358–393 K.

An ampoule procedure was used to find the rate constants of thermolysis of peroxy acids. A peroxy acid solution with a specified concentration was placed in a glass ampoule and purged with argon, and the ampoule was sealed. Thereafter, the ampoule was transferred to a thermostat, in which the temperature was maintained to within ±0.05 K. After a certain lapse of time, the ampoule was removed from the thermostat, sharply cooled, and opened; the contents were analyzed by iodometry to determine peroxy acid concentration [12].

Thermogravimetric analysis was performed on a Derivatograph Q-1500 D instrument at a sample heating rate of 5 K/min. The thermal degradation of peroxy acids was performed in ceramic crucibles. Before heating, the samples of peroxy acids were mixed with highly dispersed Al_2O_3.

RESULTS AND DISCUSSION

The test peroxy acids began to decompose at a noticeable rate in the used solvents at temperatures higher than 358 K. Their thermal degradation was adequately described by a first-order reaction rate equation. In this case, the results obtained in the course of a process performed in toluene suggest that the hydrocarbon radical length had almost no effect on the apparent rate constant k_{app} (Table 1). The numerical values of apparent activation energies (E_a) were calculated from the temperature dependences of k_{app}; these values were similar for all of the test peroxy acids, and they varied from 95 to 116 kJ/mol (Table 1). Note that the values of E_a for peroxy acids containing even numbers of carbon atoms in a molecule were somewhat lower than those for peroxy acids with odd numbers of C atoms (Table 1). The numerical values of E_a

Table 1. Apparent rate constants and activation energies of the thermolysis of aliphatic peroxy acids in toluene

Peroxy acid	$k_{app} \times 10^5$, s^{-1}						E_a, kJ/mol
	Temperature, K						
	358	363	368	373	378	383	
C_8	–	6.32	9.83	14.5	23.1	34.4	99
C_9	3.18	4.89	7.65	13.1	23.8	33.6	112
C_{10}	3.92	6.79	10.6	15.8	24.9	33.7	96
C_{12}	–	–	8.78	15.2	25.3	34.0	109
C_{13}	2.77	4.73	7.69	13.0	23.1	35.4	116
C_{14}	–	6.40	10.0	14.7	23.4	32.3	95
C_{15}	–	5.66	8.96	14.2	20.6	32.5	104
C_{16}	–	–	10.2	14.2	23.9	34.1	96

Note: Initial peroxy acid concentration: 0.05 mol/l. The error in the determination of E_a was ±5 kJ/mol, and the values of k_{app} were measured to within 3%.

suggest that, evidently, the thermolysis of peroxy acids in toluene occurred by a radical mechanism. It was found [13, 14] that the thermal degradation of peroxybenzoic and peroxyacetic acids in hydrocarbon solvents occurred by a homolytic mechanism and E_a = 125 kJ/mol. Levush et al. [15] studied the decomposition of low-molecular-weight peroxy acids in a gas phase and found that the overall reaction involved both homogeneous and heterogeneous degradation. The activation energy of a homogeneous process varied from 118.6 to 138.6 kJ/mol.

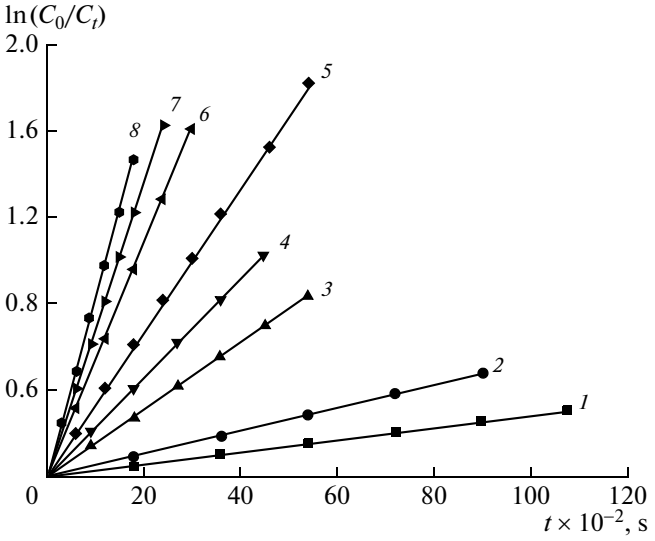

Fig. 1. Kinetic curves of the thermal degradation of C_{10} at 383 K. Solvents: (*1*) chlorobenzene, (*2*) benzene, (*3*) dichloroethane, (*4*) acetic acid, (*5*) toluene, (*6*) acetone, (*7*) dioxane, and (*8*) decane. Initial C_{10} concentration: 0.05 mol/l.

We studied the effect of a reaction medium on the rate of thermal degradation of peroxy acids with the use of 13 solvents of different nature. The thermal degradation of C_{10} in the test solvents was adequately described by first-order reaction rate equation (Fig. 1). In the $\ln(C_0/C_t) - t$ coordinates (t is reaction time), the kinetic curves remained linear to high degrees of conversion. The apparent rate constants (k_{app}) were determined at the initial stages of C_{10} decomposition in the test solvents at various temperatures (Table 2). At 373 K, the thermal degradation of peroxy acids occurred at the lowest rate in benzene, whereas the rate of the process in dimethylformamide (DMF) was higher by a factor of about 140. The apparent activation energies of the process and the activation parameters of the test reaction were determined from the temperature dependences of the overall rate constants of the thermal degradation of peroxy acids (Table 3). The numerical values of E_a varied from 55 to 119 kJ/mol. The comparatively low values of E_a in acetone, DMF, and chloroform can suggest a contribution from the bimolecular reaction of a peroxy acid with a solvent to the overall decomposition process. The possibility of this reaction occurring in DMF was found by polarography and calorimetry [16]. Because the overall rate constants of degradation of peroxy acids in toluene were almost independent of the length of a hydrocarbon radical, it is believed that this behavior will be also observed in other solvents.

Table 3 summarizes the parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\#}$ corresponding to a transition state. The numerical values of $\Delta H^{\neq}$ varied from 51.8 to 115.8 kJ/mol, whereas the values of $\Delta S^{\neq}$ can be not only positive but also negative. The values of $\Delta G^{\#}$ varied to a lesser extent and fell within the range of 65.5–76.6 kJ/mol. There is a linear correlation between the parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 3); that is, a compensation effect was observed under conditions of our experiments.

Table 2. Apparent rate constants and activation energies of the thermolysis of C_{10} in various solvents

Solvent	$k_{app} \times 10^5$, s^{-1}							E_a, kJ/mol
	Temperature, K							
	363	368	373	378	383	387	393	
Chlorobenzene	–	–	1.20	1.84	2.86	4.17	6.23	101
Benzene	–	–	1.01	2.31	5.33	8.52	12.3	104
Tetrachloromethane	–	–	4.30	6.23	8.15	12.5	16.9	85
Dichloroethane	–	–	8.16	11.8	15.5	25.5	35.3	86
Chloroform	–	–	12.5	16.6	20.5	29.1	37.8	67
Acetic acid	5.97	7.73	11.6	15.8	22.8	–	39.6	70
Toluene	6.79	10.6	15.8	24.9	33.7	–	68.4	96
Ethyl acetate	6.43	11.0	20.0	33.4	52.9	–	–	119
Acetone	20.3	28.9	37.5	45.5	53.4	–	–	55
Dioxane	9.16	14.6	25.5	41.3	67.7	–	–	118
Decane	11.9	20.7	35.9	51.9	81.4	–	–	104
DMF	68.5	104	138	176	-	–	–	57
Nitrobenzene	4.22	8.52	12.5	24.6	37.0	–	–	100

Note: Initial peroxy acid concentration: 0.05 mol/l. The error in the determination of E_a was ±5 kJ/mol, and the values of k_{app} were measured to within 3%.

Table 3. Activation parameters of the reaction of C_{10} thermolysis in various solvents at 383 K

Solvent	$k_{app} \times 10^5$, s^{-1}	E_a, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta G^{\neq}$, kJ/mol
Chlorobenzene	2.86	101	97.8	54.4	76.6
Benzene	5.33	104	100.8	67.6	74.6
Tetrachloromethane	8.15	85	81.8	21.8	73.2
Dichloroethane	15.5	86	82.8	30.8	71.2
Chloroform	20.5	67	63.8	−17.5	73.5
Acetic acid	22.8	70	66.8	−8.0	70.1
Toluene	33.7	96	92.8	61.6	68.7
Ethyl acetate	52.9	119	115.8	127.6	70.5
Acetone	53.4	55	51.8	−40.4	70.5
Dioxane	67.7	118	114.8	127.2	69.7
Decane	81.4	104	100.8	90.3	69.7
DMF	138*	57	53.8	−23.0	65.5
Nitrobenzene	37.0	100	96.8	74.1	68.4

* Temperature: 373 K.

The occurrence of this effect suggests a complex character of the influence of a solvent on the thermal decomposition reaction of a peroxy acid. The isokinetic temperature found from the slope of the $\Delta H^{\neq} = f(\Delta S^{\neq})$ function is 417 ± 15 K, which is somewhat higher than the temperature of our experiments.

The experimental results suggest that the primary reaction of C_{10} homolytic degradation was complicated by induced chain decomposition processes. This conclusion was supported by the results of a study on the effect of the initial peroxy acid concentration in a toluene solution at 373, 383, and 393 K on the numerical value of k_{app} (Fig. 2). The increase in the concentration of C_{10} in toluene from 0.01 to 0.2 mol/l resulted in an increase in k_{app}. For example, at 373 K, the constant k_{app} increased by a factor of 2.3. The same increase in the concentration of C_{10} in decane resulted in an increase in k_{app} from 16.3×10^{-5} to 61.9×10^{-5} s^{-1}. In the reaction performed in dioxane, the overall rate constant of thermolysis at the same change in the concentration of C_{10} increased to a lesser extent, namely, from 20.5×10^{-5} to 37.7×10^{-5} s^{-1}.

The overall reaction of the thermal decomposition of peroxy acids in solutions can be described by the well-known equation

$$-\frac{dC}{dt} = k_0 C + k_i C^n, \quad (1)$$

where k_0 is the rate constant of the primary homolytic degradation, k_i is the rate constant of induced chain decomposition, C is the peroxy acid concentration,

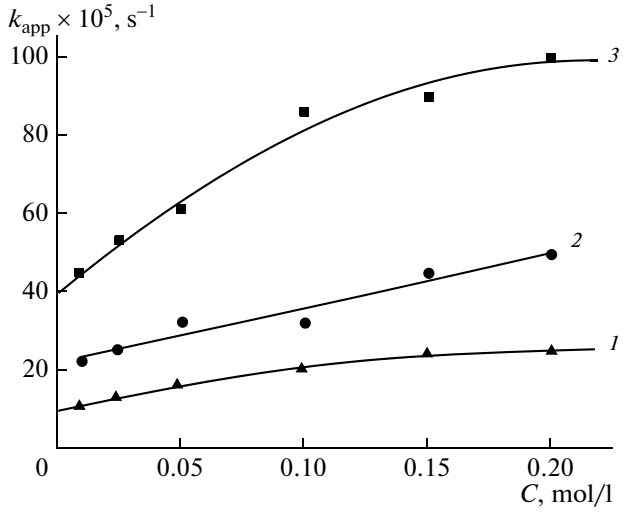

Fig. 2. Dependence of the apparent rate constants of C_{10} thermolysis in toluene on the initial peroxy acid concentration at temperatures of (*1*) 373, (*2*) 383, and (*3*) 393 K.

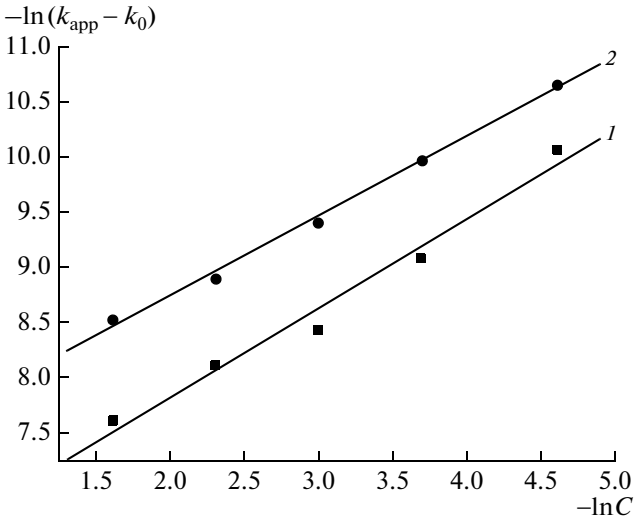

Fig. 3. Dependences of $\ln(k_{app} - k_0)$ on $\ln C$ obtained in a study of C_{10} degradation in (*1*) decane and (*2*) acetic acid at 373 K.

and n is the order of induced chain decomposition reaction. Equation (1) can be easily transformed to the following form, which is suitable for calculating the numerical values of k_i and n:

$$\ln(k_{app} - k_0) = \ln k_i + (n-1)\ln C. \quad (2)$$

The dependence of $\ln(k_{app} - k_0)$ on $\ln C$ is linear (Fig. 3). Its slope is $(n - 1)$, and the intercept on the axis of ordinates is $\ln k_i$. The numerical values of k_0 were found by extrapolating k_{app} to the zero concentration of peroxy acids (Fig. 2). Table 4 summarizes the reaction parameters of induced C_{10} degradation in toluene, decane, acetic acid, and dioxane. The numerical values of n in the test solvents were close and fell within a range from 1.70 to 1.84. The rate constants of primary homolytic degradation of C_{10} at 373 K increased in the order acetic acid < toluene < decane < dioxane from 3.40×10^{-5} to 18.3×10^{-5} s^{-1} (Table 4). The rate constants of induced chain degradation k_i in acetic acid, toluene, and dioxane were almost the same; this fact suggests the similarity of decomposition mechanisms in these solvents. The numerical value of k_i in decane was higher than that in toluene, acetic acid, or dioxane by a factor of about 4. The activation energy of the process was calculated from the temperature dependence of k_i constants; it was found somewhat lower than the apparent values of E_a (Table 1) and equal to 90.1 kJ/mol.

Table 4. Kinetic parameters of the induced degradation of C_{10} in various solvents

Solvent	Temperature, K	$k_0 \times 10^5$, s^{-1}	$k_i \times 10^4$, l mol^{-1} s^{-1}	n
Toluene	373	8.80	5.99	1.79
Toluene	383	19.2	12.3	1.77
Toluene	393	40.4	26.1	1.84
Acetic acid	373	3.40	6.11	1.70
Decane	373	12.0	20.3	1.80
Dioxane	373	18.3	5.53	1.70

The thermolysis of peroxy acids in the absence of a solvent came into play at 323–333 K. As the reaction in solution, this process can be described by a first-order reaction rate equation. The following apparent rate constants of C_{10} thermal degradation in the absence of a solvent were obtained:

Temperature, K	338	343	348	353	358	363
$k_{app} \times 10^5$, s^{-1}	3.24	4.82	7.71	11.9	18.5	27.8

The total activation energy of the C_{10} thermolysis process in the absence of a solvent was calculated from the temperature dependence of k_{app}; it was 87 kJ/mol.

Aliphatic peroxy acids have a crystal structure. Thus, the C_9 acid forms crystals that belong to the $P2_1/c$ structural class, $Z = 4(1)$. In this case, intermolecular hydrogen bonds are formed between peroxy acid molecules; the bond length is 2.74 Å [17]. In a melt, the crystal state was partially retained; in the thermal decomposition of peroxy acids, this facilitated a high contribution of induced degradation reactions to the overall process.

The results of thermal analysis suggest that the thermal degradation of the test peroxy acids in a molten state came into play at 320–328 K. The melting temperature of C_{10} is 317 K [6]. Figure 4 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves obtained in the thermal analysis of a sample of C_{10} mixed with Al_2O_3. We failed to perform this analysis without the use of Al_2O_3 because the degradation of the peroxy acid in the absence of a fill-

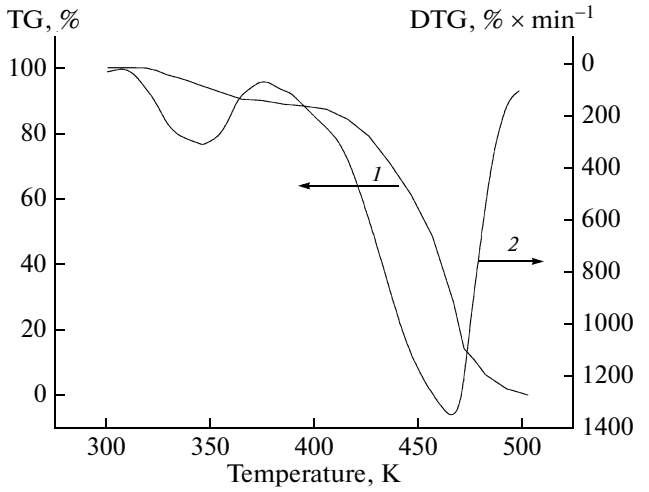

Fig. 4. (*1*) TG and (*2*) DTG curves of a sample of C_{10} in a mixture with Al_2O_3. Heating rate: 5 K/min.

ing agent occurs uncontrollably and the results are irreproducible. As judged from the experimental data, the degradation of the peroxy acid occurred in two steps. At the first step over the temperature range of 323–373 K, the degradation of the peroxide groups of peroxy acid molecules occurred; in the course of this degradation, volatile low-molecular-weight products were formed. At this step, the change in the sample weight was 9–10%. The results of the thermal analysis are consistent with kinetic data obtained in the study of C_{10} degradation in a molten state (see above), according to which the degradation occurred over the temperature range of 338–363 K. At the second step, which corresponds to a maximum in the DTG curve over the range of 413–483 K, the degradation of high-molecular-weight products, which were formed at the first step and adsorbed on the surface of Al_2O_3, occurred. We calculated the activation energy and the order of reaction n for the first step of C_{10} thermal degradation using the Freeman–Carol method [18]. The numerical value of E_a is 53 ± 7.0 kJ/mol, which is somewhat lower than the corresponding value obtained under isothermal conditions using an ampoule procedure. The order of reaction n is 0.45 ± 0.07. It is likely that the surface of the Al_2O_3 filling agent had a considerable effect on the values of E_a and n in thermal analysis experiments.

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