ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2011, Vol. 85, No. 1, pp. 45–50. © Pleiades Publishing, Ltd., 2011.
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CHEMICAL KINETICS AND CATALYSIS

Influence of a Reaction Medium on the Oxidation of Aromatic Nitrogen-Containing Compounds by Peroxyacids

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Received January 13, 2010

Abstract—The influence of different solvents on the oxidation reaction rate of pyridine (Py), quinoline (QN), acridine (AN), α-oxyquinoline (OQN) and α-picolinic acid (APA) by peroxydecanoic acid (PDA) was studied. It was found that the oxidation rate grows in the series Py < QN < AN, and the rate of the oxidation reaction of compounds containing a substituent in the α position from a reactive center is significantly lower than for unsubstituted analogues. The effective energies of activation of the oxidation reaction were found. It was shown that in the first stage, the reaction mechanism includes the rapid formation of an intermediate complex nitrogen-containing compound, peroxyacid, which forms products upon decomposing in the second stage. A kinetic equation that describes the studied process is offered. The constants of equilibrium of the intermediate complex formation (K_{eq}) and its decomposition constant (k_2) in acetone and benzene were calculated. It was shown that the nature of the solvent influences the numerical values of both K_{p} and k_2. It was established that introduction of acetic acid (which is able to form compounds with Py) into the reaction medium slows the rate of the oxidation process drastically. Correlation equations linking the polarity, polarizability, electrophilicity, and basicity of solvents with the constant of the PDA oxidation reaction rate for Py were found. It was concluded that the basicity and polarity of the solvent have a decisive influence on the oxidation reaction rate, while the polarizability and electrophilicity of the reaction medium do not influence the oxidation reaction rate.

Keywords: aromatic nitrogen-containing compounds, peroxyacids, oxidation.

DOI: 10.1134/S0036024411010079

INTRODUCTION

Organic peroxyacids (PAs) are widely used as oxidizers in many reactions. The particulars of the oxidation of olefines, nitrogen- and sulfur-containing compounds by PA were considered in [1–4], where it was proved that these processes are typical electrophilic reactions. The influence of the solvent in oxidation processes with the participation of PA remains poorly studied, but one might expect that the reaction medium would influence both the rate of the reaction and the product yield. In the present work, the results from investigating solvents' influence on the rate of oxidation of acridine (AN), quinoline (QN), α-oxyquinoline (OQN), pyridine (Py), and α-picolinic acid (APA) are given.

EXPERIMENTAL

All solvents and nitrogen-containing heterocyclic compounds were purified by commonly accepted techniques [5, 6] and distilled in an argon atmosphere. Acridine, α-oxyquinoline, and α-picolinic acid were recrystallized from alcoholic solutions. In all tests, peroxydecanoic acid (PDA), the purity of which was no lower than 99.0–99.5%, was used as an oxidizer. Peroxyacid was obtained by the reaction of decanoic acid with hydrogen peroxide in a sulfuric acid medium [7]. After synthesis, the obtained specimen was recrystallized from hexane several times. The main impurity in the PDA samples was decanoic acid. Oxidation was performed in a glass reactor in an argon atmosphere in a temperature range of 303–328 K. The reactor was placed in a thermostat, the temperature in which was maintained with an accuracy of ±0.01 K. The initial solutions of nitrogen-containing compound and PDA were thermostated for 20–30 min, then rapidly poured out, sampled from reaction mixture and analyzed them for peroxyacid content iodimetrically [8]. Constants of the oxidation rate (k) were determined at the initial stages of the process, and the error in determining the values of the rate constant did not exceed 3%. Infrared spectra were measured on a Specord M-80 spectrophotometer.

RESULTS AND DISCUSSION

It was shown by previous tests that in all cases up to deep degrees of conversion, the first order is observed for each of the reagents, and the total kinetic order of the oxidation reaction of nitrogen-containing com-

Table 1. Kinetic and activation parameters of the oxidation of nitrogen-containing compounds by PDA (initial concentrations of PDA and nitrogen-containing compound were 0.05 mol/l)

Compound	$k \times 10^4$, l/(mol s)	$E_{act} \pm 5.0$, kJ/mol	$\Delta H^\#$, kJ/mol	$-\Delta S^\#$, J/(mol K)	$\Delta G^\#$, kJ/mol
Solvent—benzene					
AN	116	40.5	37.8	153	83.7
QN	77.6	44.4	41.7	145	88.4
Py	42.8	49.9	47.2	131	89.6
OQN	37.4	37.9	35.2	171	90.1
Solvent—acetone					
AN	24.6	50.1	47.4	136	91.3
QN	15.7	42.0	39.3	165	92.5
Py	13.8	44.8	42.1	157	92.7
OQN	4.16	39.4	36.7	184	96.1
OQN	8.7	57.4	54.7	121	93.9
APA	1.44	53.1	50.4	150	98.8

Note: The k value ($\Delta k = \pm 0.03k$) was obtained for a temperature of 313 K, while $\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$ was calculated for 323 K. In the case of OQN (second line), the solvent was ethyl acetate.

pounds by PDA is equal to 2. Judging from the obtained results, the reaction products have practically no influence on the process rate. The effective constants of the oxidation rates of the studied nitrogen-containing compounds in acetone and benzene are presented in Table 1.

The degree of oxidation of nitrogen-containing compounds in benzene is considerably higher than in acetone. As is well known [1], the epoxidation process rate of ethylene compounds by PA is strongly reduced in solvents that are able to form intermolecular hydrogen bonds with PA (as compared to “inert” solvents). The peroxyacid molecules of most solvents exist in cyclic form with an intramolecular hydrogen bond [1], and the oxidation rate in such solvents is higher. The reaction rate in both benzene and acetone declines in the series AN > QN > Py. The oxidation reaction rate of compounds containing a substituent close to the reactive centers of OQN and APA is appreciably lower than for their unsubstituted analogues (Table 1).

Products of the interaction between PDA and compounds containing a tertiary nitrogen atom are N-oxide and decanoic acid. The activation energies of the oxidation process of the studied PDA compounds lie in the range of 37.9–57.4 kJ/mol and are close to the numerical values given in the literature [1, 2]. The solvents’ influence on the oxidation rate of pyridine (Py) is considered in detail in Table 2. The oxidation process is slowest in dioxane, while the reaction rate is ~10 times faster in chloroform. The total energies of activation for the process of pyridine oxidation by PDA lie in the range of 64.8–30.6 kJ/mol (Table 2).

The parameters of transition state $\Delta H^\#$, $\Delta S^\#$, and $\Delta G^\#$ were calculated for all oxidation reactions (Table 1, 2). It is noteworthy that the $\Delta S^\#$ values are negative in all cases, demonstrating the greater order of the transition state in comparison with the initial state. The oxidation process of the studied nitrogen-containing compounds in benzene is characterized by lower values of $\Delta G^\#$than in acetone (Table 1). There is a linear interconnection between the values $\Delta S^\#$ and $\Delta H^\#$ of the transition state for the oxidation of pyridine by PDA; i.e., a compensatory effect was observed under the conditions of our tests. The linearity of dependence $\Delta H^\# = f(\Delta S^\#)$ shows the complicated nature of the influence of the solvent on the rate and mechanism of the oxidation process.

Based on the obtained results, we may assume that at the first stage of the reaction, an intermediate compound forms rapidly and yields reaction products upon decomposing at the second stage. The reaction medium will influence both the first and second stage of the oxidation process. These assumptions have been confirmed by infrared spectroscopic tests. In Fig. 1, we present the dependence of the optical density of the absorption band at 3280 cm^{-1} on the PDA concentration in tetrachloromethane solution. It is known from [9] that the absorption band at 3280 cm^{-1} corresponds to the valence vibrations of the OH group associated with the intramolecular hydrogen bond. A change in the PDA concentration in the range of 0.01–0.1 mol/l leads to a proportional increase in the band intensity. The addition of pyridine to the reaction mixture and the fast scanning of the band at 3280 cm^{-1} leads to a change in the band’s intensity (Fig. 1); in this case, it splatters. This confirms our assumption as to the formation at the process’s initial stages of the intermediate compound PyPA. The first stage of the Py oxida-

Table 2. Kinetic and activation parameters of pyridine (Py) oxidation by peroxydecanoic acid (PDA) in the studied solvents (the initial concentration of PDA and nitrogen-containing compound were 0.05 mol/l)

Solvent	$k \times 10^3 \pm 0.03k$, l/(mol s)	E_{act} ±5.0, kJ/mol	$\Delta H^{\#}$, kJ/mol	$-\Delta S^{\#}$, J/(mol K)	$\Delta G^{\#}$, kJ/mol
Dioxane	1.89	68.4	65.7	86	93.5
Propanol-2	2.38	54.9	52.2	126	92.8
Acetone	2.50	44.8	42.1	157	92.7
Ethyl acetate	2.96	47.7	45.0	146	92.3
Toluene	6.76	48.1	45.4	138	90.0
Benzene	7.88	49.9	47.2	131	89.6
Tetrachloromethane	8.12	50.8	48.1	128	90.0
DMFA	10.8	54.0	51.3	116	88.8
Chlorobenzene	11.8	51.2	48.5	124	88.5
Chloroform	19.5	52.3	49.6	116	87.2
Dichloroethane	11.5	32.8	30.1	118	88.6
Nitrobenzene	12.9	30.6	27.9	187	88.3

Note: The value k was obtained for 323 K; $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ were calculated for 323 K.

tion reaction can be characterized by the equilibrium constant K_{eq}:

$$\mathrm{Py} + \mathrm{PA} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \mathrm{PyPA}. \tag{1}$$

The disintegration of the intermediate compound PyPA is the rate-determining stage of the process, which can be described by the "true" rate constant (k_2) of the oxidation reaction:

$$\mathrm{PyPA} \xrightarrow{k_2} \text{reaction products}. \tag{2}$$

The process rate is determined by the equation:

$$W = -\frac{d[\mathrm{PDA}]}{dt} = \frac{k_2[\mathrm{Py}]_0}{K_n + [\mathrm{Py}]_0}[\mathrm{PDA}], \tag{3}$$

where

$$K_n = (k_{-1} + k_2)/k_1, \tag{4}$$

and $[\mathrm{Py}]_0$ is an initial pyridine concentration in solution. Since the pseudomolecular constant is equal to

$$k'_{\mathrm{eff}} = \frac{k_2[\mathrm{Py}]_0}{K_n + [\mathrm{Py}]_0}, \tag{5}$$

we can obtain the numerical values of k_2 and K_n from this dependence in the coordinates $1/k'_{\mathrm{eff}}$ on $1/[\mathrm{Py}]_0$. The inverse value of K_n is symbolized as K_e and is the constant of complex formation for peroxyacid with pyridine. In this case, the k_2 value in expression (4) can be ignored, in comparison with k_{-1}.

Tests at a constant concentration of PDA and various pyridine content were performed to verify proposed equations (2)–(5). In Fig. 2, we present the dependence of the pseudomolecular constants of the oxidation rate on the Py concentration in benzene solution. The pseudomonomolecular constants of the oxidation rate (k'_{eff}) tend to a certain limit with an increase in the Py concentration. The dependence on the Py concentration is straightened satisfactorily in the coordinates $1/k'_{\mathrm{eff}}$ on $1/[\mathrm{Py}]_0$, allowing us to determine the numerical values of k_2 and K_{eq} (Fig. 3). Similar regularities are observed for acetone solutions, but the k_2 and K_{eq} values differ from the corresponding values obtained in benzene (Table 3). The values of the true rate constants of the oxidation reaction in acetone

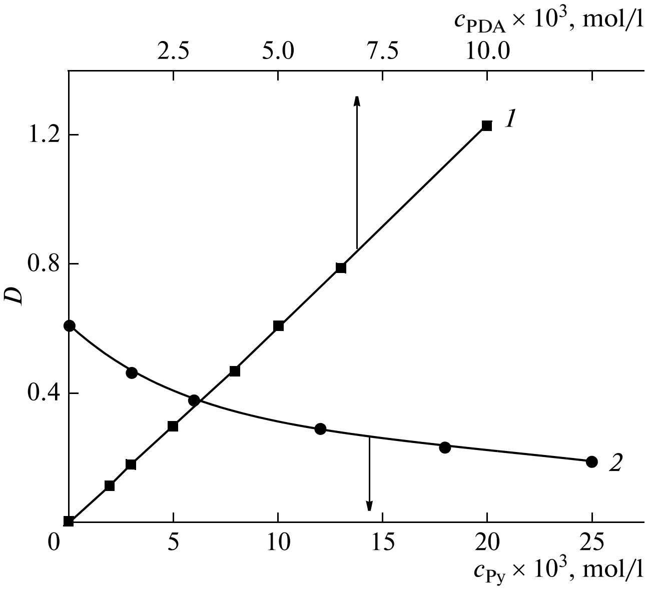

Fig. 1. Dependences of the optical density (D) of absorption band 3280 cm^{-1} on the concentration of PDA (*1*) in tetrachloromethane and pyridine, and (*2*) in tetrachloromethane with 0.05 mol/l of PDA.

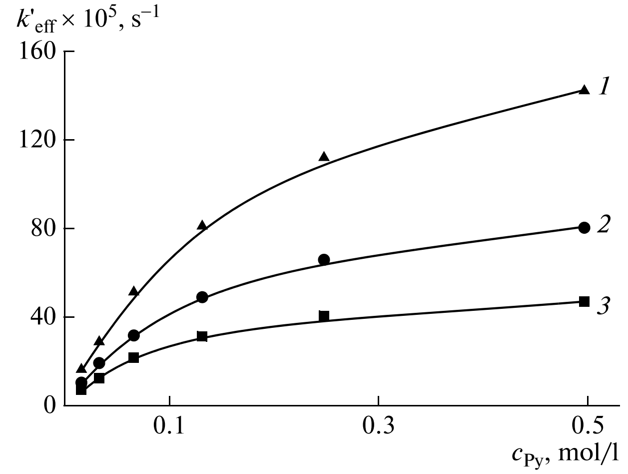

Fig. 2. Dependences of the pseudomonomolecular constant of the oxidation rate on the pyridine (Py) concentration. The solvent was benzene. Temperature, K: (*1*) 303; (*2*) 313; (*3*) 323.

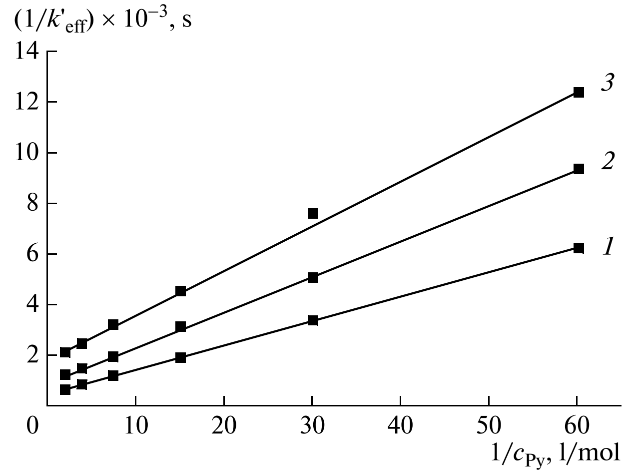

Fig. 3. Dependences $1/k'_{eff}$ on $1/[Py]_0$. The solvent was benzene. Temperature, K: (*1*) 303, (*2*) 313, (*3*) 323.

k_2 are slightly lower than the corresponding values obtained in benzene solution.

The activation energies (E_2) calculated according to the temperature dependences of true oxidation rate constant k_2 are practically the same as the corresponding parameters obtained for value k (Table 1). As in the case of benzene and acetone, the calculated values of K_{eq} increase as the temperature rises (Table 3). As might be expected, the numerical values for the equilibrium constants K_{eq} determined in the benzene solution are slightly higher than the same parameters calculated for the acetone systems (Table 3).

The dependences of K_{eq} on temperature in the coordinates $\ln(K_{eq})$ on $1/T$ are straightened satisfactorily, allowing us to calculate the numerical values for ΔH and ΔS of the first stage of the oxidation reaction: the formation of the intermediate compound PyPA. The obtained values of ΔH and ΔS are negative. The numerical values of ΔH for the tests performed in acetone are higher than the corresponding parameters determined in benzene. The ΔS value of the first stage of Py oxidation by PDA in acetone is −119 J/(mol K). For benzene, this value is considerably higher: −72 J/(mol K). This testifies to the unequal influence of the solvents on the studied reaction.

In most works on the influence of reaction media on oxidation reactions with the participation of PA, the solvents' main influence is associated with a change in the reactivity of the oxidizer. We cannot, however, rule out the solvation of Py by the solvents, or the possibility of subsequent changes in the process rate. We performed tests on the oxidation of Py by PDA using various contents of acetic acid. As is well known, acetic acid forms a stable compound with Py [10]. Py oxidation by PDA will proceed at a moderate rate. The dependences of the overall constant of the oxidation reaction rate k on the content of acetic acid in solutions of tetrachloromethane and chlorobenzene are given in Fig. 4.

As follows from the obtained data, the addition of a small amount of acetic acid to the reaction solutions leads to a significant reduction in the k value. Increasing the acetic acid content from 0.1 to 0.5 mol/l changes k inappreciably. In the case of tetrachloromethane, the k value drops from 8.12×10^{-3} l/(mol s) to 3.02 l/(mol s) when the acetic acid content is increased from 0 to 0.5 mol/l. A similar change in the acetic acid content caused the k value for the reaction mixture in chlorobenzene to fall by 60%.

The obtained results are straightened satisfactorily in coordinates of k on $1/C$, where C is the concentra-

Table 3. Numerical values of the parameters of pyridine oxidation by peroxydecanoic acid in acetone and benzene

Solvent	Parameter	*T*, K			E_2, kJ/mol	$-\Delta H$, kJ/mol	$-\Delta S$, J/(mol K)
		303	313	323			
Acetone	$k_2 \times 10^4$, s^{-1}	3.80	5.63	11.7	45.7		
	K_{eq}, l/mol	2.84	2.17	1.09		38.84	119
Benzene	$k_2 \times 10^4$, s^{-1}	5.36	10.3	19.8	53.2		
	K_{eq}, l/mol	10.4	7.02	5.29		27.6	72

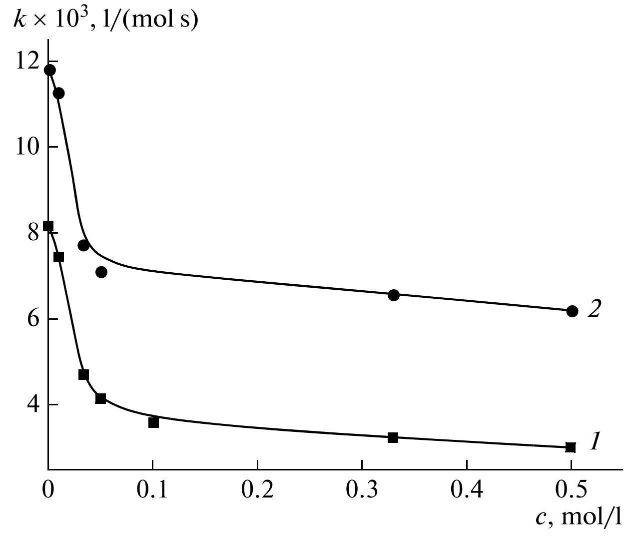

Fig. 4. Dependences of the effective constant of the rate of Py oxidation by PDA (initial concentrations of the components were 0.05 mol/l) on the concentration of acetic acid in solution. Temperature, 323 K. Solvent: (*1*) tetrachloromethane, (*2*) chlorobenzene.

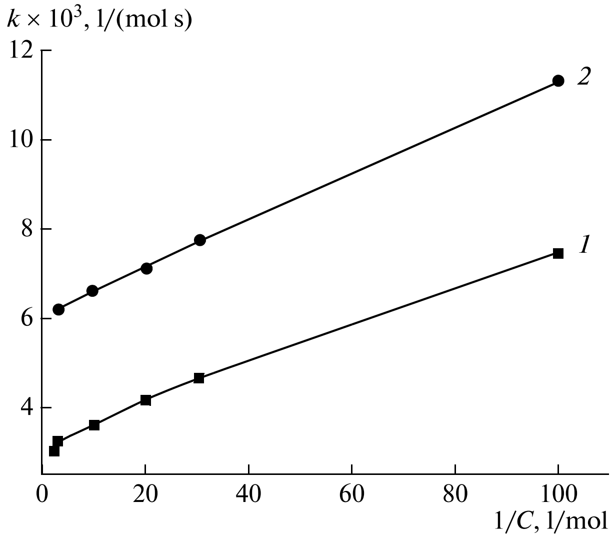

Fig. 5. Dependences of the effective constant of the rate of Py oxidation by PDA (initial concentrations of the components were 0.05 mol/l) on the inverse concentration of acetic acid in solution. Temperature, 323 K. Solvent: (*1*) tetrachloromethane, (*2*) chlorobenzene.

tion of acetic acid in solution (Fig. 5). This confirms that Py bound with acetic acid in a compound is oxidized by PDA at a moderate rate. Judging from the obtained results, the salvation of Py by tetrachloromethane and chlorobenzene is low. Performing similar tests in a solution of dioxane or acetone leads to a reduction in k with a rise in acetic acid concentration by factors of 1.74 and 1.34, respectively, with the obtained dependences being nonlinear in coordinates of k from $1/C$. This points to the solvation of both Py and PDA by dioxane and acetone.

We used the familiar Palm–Koppel equation to find correlation dependences combining the main physicochemical properties of the solvents with the rate constant of the oxidation reaction [11]. The numerical values for polarity (Y), polarizability (P), electrophilicity (E), and basicity (B) were taken from [11]. The equation obtained from our calculations had a low value for the multiple correlation coefficient ($R = 0.812$), indicating a low correlation dependence between the constant of the oxidation rate and the main parameters of the solvents. The constant of the oxidation rate of Py in DMFA solution exhibits the

Table 4. Experimental and calculated (by correlation equation (6)) constants (k) of the rate of pyridine oxidation by peroxydecanoic acid in the studied solvents at 303 K

Solvent	$k \times 10^3$ l/(mol s)	$-\ln k$ experiment	$-\ln k$ calculation	$-\Delta \ln k$
Dioxane	0.386	7.8597	7.7491	0.1105
Propanol-2	0.644	7.3478	6.6089	0.7389
Acetone	0.800	7.1309	6.9854	0.1455
Ethyl acetate	0.924	6.9868	6.3875	0.5993
Toluene	2.04	6.1948	6.0713	0.1235
Benzene	2.48	5.9995	5.9227	0.0768
Tetrachloromethane	2.66	5.9294	5.7364	0.1930
DMFA	2.86	5.8569	7.3774	−1.5205
Chlorobenzene	3.58	5.6324	5.4074	0.2250
Chloroform	5.54	5.1958	5.2111	−0.0153
Dichloroethane	5.46	5.2103	5.0845	0.1258
Nitrobenzene	6.20	5.0832	5.2391	−0.1559

greatest deviation from the obtained dependence (Table 4). Excluding from consideration the results of kinetic tests obtained in DMFA led to the correlation equation

$$\ln k = -7.7240 + 3.8036Y + 3.1195P + 0.071E - 0.0094B, \quad R = 0.975. \tag{6}$$

The R coefficient is increased substantially. The numerical value of the multiple correlation coefficient (0.975) indicates a good correlation. Alternating the parameters excluded from consideration yields a three-parameter equation. Excluding the Y parameter leads to R dropping to a value of 0.823, indicating the influence of polarity on the rate of Py oxidation.

The P polarizability of the solvent has practically no effect on the oxidation process, since excluding this parameter from consideration does not change the numerical value of R (0.967). A similar operation with the E parameter also produces no change in the numerical value of R (0.975).

CONCLUSIONS

Based on the obtained results, we may conclude that the electrophilicity and polarizability of solvents do not influence the rate of Py oxidation by PDA. Solvent basicity greatly influenced the investigated reaction. Excluding this parameter from consideration leads to a considerable reduction in the multiple correlation coefficient R (to 0.532). The reaction medium basicity has a decisive influence on the oxidation reaction rate, while the role of the solvent polarity is less influential. The electrophilicity and polarizability of the reaction medium do not influence the rate of the oxidation reaction.

REFERENCES

1. A. I. Prilezhaeva, *Prilezhaev Reaction. Electrophilic Oxidation* (Nauka, Moscow, 1974) [in Russian].
2. G. A. Tolstikov, *Hydroperoxide Oxidation Reactions* (Nauka, Moscow, 1976) [in Russian].
3. V. L. Antonovskii, *Organic Peroxide Initiators* (Khimiya, Moscow, 1972) [in Russian].
4. V. S. Dutka, Kinet. Katal. **32**, 960–963 (1991).
5. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, *Organic Solvents* (Intersci., New York, 1955; Mir, Moscow, 1958).
6. A. J. Gordon and R. A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques and References* (Wiley, New York, 1972; Mir, Moscow, 1976).
7. W. E. Parker, C. Riccuti, C. L. Ogg, and D. Swern, J. Am. Chem. Soc. **77**, 5459 (1955).
8. V. L. Antonovskii and M. M. Buzlanova, *Analytic Chemistry of Organic Peroxide Compounds* (Khimiya, Moscow, 1978) [in Russian].
9. R. Shriner, R. Fuson, D. Curtin, and T. Morrill, *The Systematic Identification of Organic Compounds* (Wiley, New York, 1980; Mir, Moscow, 1983).
10. A. P. Kreshkov, *Analytical Chemistry of Non-Aqueous Solutions* (Khimiya, Moscow, 1982) [in Russian].
11. V. A. Palm, *Principles of the Quantitative Theory of Organic Reactions* (Khimiya, Leningrad, 1977) [in Russian].