Russian Journal of General Chemistry, Vol. 75, No. 7, 2005, pp. 1125–1130. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 7, 2005, pp. 1187–1193.
Original Russian Text Copyright © 2005 by Dul'neva, Moskvin.

Kinetics of Formation of Peroxyacetic Acid

L. V. Dul'neva* and A. V. Moskvin**

* *Pavlov St. Petersburg State Medical University, St. Petersburg, Russia*
** *St. Petersburg State Chemical and Pharmaceutical Academy, St. Petersburg, Russia*

Received June 3, 2004

Abstract—The kinetics of the reaction of acetic acid with hydrogen peroxide, leading to peroxyacetic acid, were studied at various molar reactant ratios (AcOH–H_2O_2 from 6 : 1 to 1 : 6) at 20, 40, and 60°C and sulfuric acid (catalyst) concentrations of 0 to 9 wt %. The reaction is reversible, and the equilibrium constant decreases as the temperature rises: K = 2.10 (20°C), 1.46 (40°C), 1.07 (60°C); $\Delta_r H^0 = -13.7 \pm 0.1$ kJ mol^{-1}, $\Delta_r S = -40.5 \pm 0.4$ J mol^{-1} K^{-1}. The maximal equilibrium concentration of peroxyacetic acid (2.3 M) is attained at 20°C and a molar AcOH-to-H_2O_2 ratio of 2.5 : 1. The rate constants of both forward and reverse reactions increase with increase in sulfuric acid concentration from 0 to 5 wt %. Further raising the catalyst concentration does not affect the reaction rate. The reaction mechanism is discussed.

Peroxyacetic acid is widely used as component of disinfectants. It is usually prepared *in situ* just before use. An aqueous solution of peroxyacetic acid, which is used as disinfectant, can be obtained by reaction of hydrogen peroxide with acetic acid in water. The process is described by the following scheme.

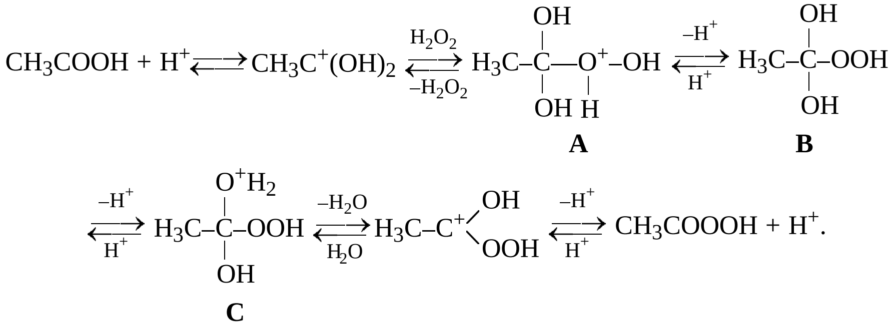
$$AcOH + H_2O_2 \rightleftarrows AcOOH + H_2O.$$

The reaction is reversible, and the concentrations of all four components at the equilibrium state are comparable. Both forward and reverse reactions are fairly slow at room temperature, and a long time is necessary for equilibrium to establish. Therefore, the kinetic parameters and equilibrium constant of this reaction are to be known to predict the equilibration time and equilibrium composition of the solution.

The kinetics of reactions of carboxylic acids with hydrogen peroxide were studied previously. It was shown that the process is of first order with respect to carboxylic acid and hydrogen peroxide [1, 2]. Using an 18O isotope label it was found that the reaction does not involve dissociation of the O–O bond in initial hydrogen peroxide [3]. The hydrolysis of peroxy acids synthesized from $HC^{18}OOH$ or $CH_3 \cdot C^{18}OOH$ and H_2O_2 afforded hydrogen peroxide containing no heavy oxygen (^{18}O). This means that both in the formation and in the hydrolysis of peroxy acids the bond between the acyl group and oxygen atom is cleaved and that the two processes may be described by the following scheme.

$$Ac^{18}OH + H_2O_2 \rightleftarrows AcOOH + H_2{}^{18}O.$$

The reaction is catalyzed by mineral acids; the following mechanism was proposed in [4, 5]:



$$CH_3COOH + H^+ \rightleftarrows CH_3C^+(OH)_2 \underset{-H_2O_2}{\overset{H_2O_2}{\rightleftarrows}} \underset{\mathbf{A}}{H_3C{-}\overset{OH}{\underset{OH}{C}}{-}\underset{H}{O^+}{-}OH} \underset{H^+}{\overset{-H^+}{\rightleftarrows}} \underset{\mathbf{B}}{H_3C{-}\overset{OH}{\underset{OH}{C}}{-}OOH}$$

$$\underset{H^+}{\overset{-H^+}{\rightleftarrows}} \underset{\mathbf{C}}{H_3C{-}\overset{O^+H_2}{\underset{OH}{C}}{-}OOH} \underset{H_2O}{\overset{-H_2O}{\rightleftarrows}} H_3C{-}C^+\!\!\begin{smallmatrix}OH\\OOH\end{smallmatrix} \underset{H^+}{\overset{-H^+}{\rightleftarrows}} CH_3COOOH + H^+.$$

1070-3632/05/7507-1125 ©2005 Pleiades Publishing, Inc.

It is also known that the reaction of acetic acid with hydrogen peroxide in water is accompanied by weak evolution of heat. The heat effect $\Delta_r H^{\neq}$ was estimated by different authors at –4.5 to –7.2 kJ mol^{-1} [6, 7]. Some publications reported on the effect of catalyst concentration on the kinetic parameters of this reaction [8, 9]. The rate of formation of peroxyacetic acid was shown to increase, and the energy of activation, to decrease, as the catalyst (sulfuric acid) concentration rises. As might be expected for a reversible process, the amount of the catalyst does not affect the equilibrium concentration of peroxy acid, other conditions being equal. However, some published data contradict generally accepted views on the effect of some factors on reversible reactions. For example, Havel and Weigner [6] stated that the equilibrium constant for the reaction under study is directly proportional to the sulfuric acid concentration in solution (at a constant temperature) and that the heat effect decreases as the catalyst concentration rises.

According to the data of [5, 6, 10, 11], the maximal equilibrium concentration of peroxyacetic acid depends on the concentration and molar ratio of the initial reactants. However, these data are contradictory, and the corresponding studies were performed under different conditions (reactant ratio, temperature, range of variation of the catalyst concentration); therefore, it is difficult to estimate on a quantitative level the effect of the above factor on the yield of peroxyacetic acid. Some studies were carried out in nonaqueous solvents [12], but the solvent effect was not taken into account; therefore, these data cannot be used.

The goal of the present work was to estimate the effect of the initial AcOH–H_2O_2 molar ratio, sulfuric acid (catalyst) concentration, and temperature on the rate of formation and concentration of peroxyacetic acid in the equilibrium mixture. Experiments were performed in an aqueous solution.

It should be noted that peroxyacetic acid is an unstable compound. Its decomposition is known to follow two paths, catalytic and noncatalytic. Trace amounts of transition metals, dust, and reactor surface are capable of acting as catalysts of decomposition. Among the decomposition products, CO_2, CO, and CH_3OH were detected. Addition of stabilizers, e.g., complexones [13–15], phosphates, or stannates [16] suppresses the catalytic decomposition. To prevent catalytic decomposition of peroxyacetic acid, solutions were stabilized by adding orthophosphoric acid; its concentration in all experiments was 0.057 M (5 wt%). In the absence of catalysts, spontaneous decomposition of peroxyacetic acid occurs according to the following equation:

$$\mathrm{AcOOH} \longrightarrow \mathrm{AcOH} + 0.5\mathrm{O_2}.$$

Therefore, we also tried to estimate how decomposition of peroxyacetic acid affects its equilibrium concentration in solution. First of all, we examined the kinetics of the reaction of hydrogen peroxide with acetic acid at various initial molar reactant ratios (1 : 6 to 1 : 0.167) at 20°C. The progress of the reaction was monitored by measuring the concentration of peroxyacetic acid, and the latter parameter was plotted against reaction time. The kinetic parameters were calculated on the basis of Eq. (1) which takes into consideration the rates of both forward and reverse reactions. In keeping with the data of [1, 2], we assumed that the forward reaction is first-order in acetic acid and hydrogen peroxide and that the reverse reaction is first-order in peroxyacetic acid and water.

$$dx/dt = k_1[c_0(\mathrm{H_2O_2}) - x][c_0(\mathrm{AcOH}) - x] - k_2x[c_0(\mathrm{H_2O}) + x]. \quad (1)$$

Here, x is the current concentration of peroxyacetic acid, M; $c_0(\mathrm{H_2O_2})$, $c_0(\mathrm{AcOH})$, and $c_0(\mathrm{H_2O})$ are the initial concentrations of hydrogen peroxide, acetic acid, and water, respectively, M; and k_1 and k_2 are the second-order rate constants of the forward and reverse reactions, respectively, l mol^{-1} s^{-1}.

In order to calculate the rate constants k_1 and k_2, it was necessary to determine the equilibrium constant K. For this purpose, we measured the equilibrium concentrations of peroxyacetic acid at various molar ratios of the initial reactants at 20°C, the catalyst concentration remaining unchanged, $c(\mathrm{H_2SO_4})$ = 0.057 M. Kinetic experiments showed that the concentration of peroxyacetic acid reached its maximal value in ~36 h after mixing the reactants and that it then remained almost unchanged. Just these values were taken as equilibrium, and the equilibrium constant was calculated by Eq. (2).

$$K = \frac{x_1[c_0(\mathrm{H_2O}) + x_1]}{[c_0(\mathrm{H_2O}) - x_1][c_0(\mathrm{AcOH}) - x_1]}. \quad (2)$$

Here, x_1 is the equilibrium concentration of peroxyacetic acid, M.

Table 1 contains the equilibrium constants determined at 20°C for different initial reactant ratios. Obviously, the equilibrium constant should depend neither on the initial reactant ratio nor on the amount of the catalyst. In the given system, it should depend only on the temperature. Therefore, from the data in Table 1 we calculated the average value of K at 20°C (K = 2.1).

According to published data, the equilibrium

Table 1. Initial reactant concentrations, equilibrium compositions of the reaction mixtures, and equilibrium constants at 20°C, $c(H_2SO_4) = 0.057$ M

Molar ratio H_2O_2 : AcOH, mol mol^{-1}	Initial reactant concentations, c_0, M			Equilibrium concentations ,c_0, M				K
	H_2O_2	AcOH	H_2O	AcOOH	H_2O_2	AcOH	H_2O	
1 : 6	2.42	14.5	8.57	1.75	0.673	12.8	10.3	2.10
1 : 5	2.79	13.9	9.85	1.90	0.889	12.0	11.8	2.09
1 : 4	3.29	13.1	11.6	2.06	1.23	11.1	13.7	2.07
1 : 3	4.00	12.0	14.1	2.24	1.76	9.75	16.3	2.14
1 : 2.5	4.48	11.2	15.8	2.29	2.19	8.91	18.1	2.12
1 : 2	5.10	10.2	18.0	2.26	2.84	7.94	20.2	2.03
1 : 1	7.05	7.05	24.8	1.97	5.08	5.08	26.8	2.04
1 : 0.5	8.71	4.36	30.6	1.42	7.29	2.94	32.0	2.13
1 : 0.4	9.14	3.66	32.1	1.23	7.91	2.43	33.4	2.14
1 : 0.33	9.46	3.15	33.2	1.08	8.38	2.07	34.3	2.14
1 : 0.25	9.88	2.47	34.7	0.84	9.04	1.63	35.6	2.03
1 : 0.2	10.2	2.03	35.7	0.71	9.44	1.32	36.4	2.07
1 : 0.167	10.3	1.72	36.3	0.63	9.71	1.09	37.0	2.19
								Average 2.10 ± 0.05

constant K_2 of the process under study has the following values: 3.27 (35°C) and 2.87 (50°C) [7]; 3.7 (20°C), 4.0 (30°C), 4.3 (35°C) [17]; 1.21 (0°C), 1.2 (5°C), 1.29 (35°C) [18]. These data are contradictory with respect to both values of K_2 and its temperature dependence. Therefore, in the subsequent calculations of k_1 and k_2 at 20°C we used our value of the equilibrium constant at that temperature. In addition, our results allowed us to determine the optimal initial molar ratio of acetic acid and hydrogen peroxide, which ensured the maximal equilibrium concentration of peroxyacetic acid (see figure); this ratio was 1 : 2.5.

It should be noted that Eq. (2) is second-order with respect to peroxyacetic acid concentration x. It has two solutions: x_1 and x_2. Among these, only that satisfying the condition $x_1 < c_0(H_2O_2)$ and $x_1 < c_0(\mathrm{AcOH})$ has physical sense. The second solution, x_2 makes no physical sense. However, both parameters, x_1 and x_2, are necessary to calculate the rate constants k_1 and k_2. The values of x_1 and x_2 are given in Table 2. The parameters x_1 and x_2 fit Eq. (3).

$$x_1 + x_2 = \frac{1}{K-1}\{K[c_0(H_2O_2) + c_0(\mathrm{AcOH}] + c_0(H_2O)\} \quad (3)$$

According to [19], kinetic equation (1) was transformed into Eq. (4).

$$\begin{aligned} dx/dt &= k_1(K-1)(x-x_1)(x-x_2) \\ &= (k_1-k_2)(x_1-x)(x_2-x). \end{aligned} \quad (4)$$

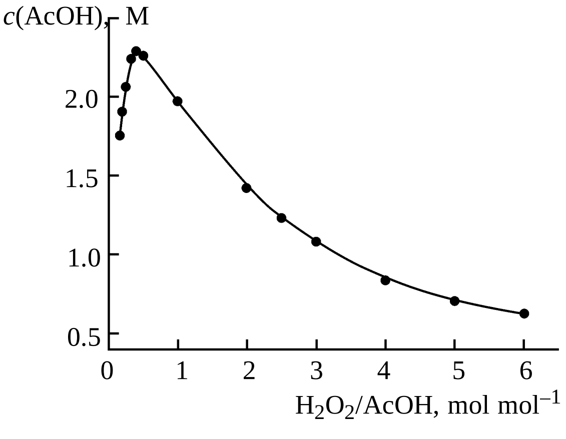
Integration of Eq. (4) gave Eq. (5).

$$\ln[(x_2-x)/(x_1-x)] = \ln(x_2/x_1) + (x_2-x_1)(k_1-k_2)t. \quad (5)$$

From Eq. (5) it follows that the time dependence of $\ln[(x_2-x)/(x_1-x)]$ is linear with the slope $b = (x_2-x_1)(k_1-k_2)$, where k_1 and k_2 are unknown. These parameters can readily be found with account taken of known expression (6). The results of calculations are summarized in Table 2.

$$K = k_1/k_2. \quad (6)$$

Insofar as the reaction under study is catalyzed by acids, we examined the effect of sulfuric acid con-



Dependence of the equilibrium concentration of peroxyacetic acid on the initial reactant ratio.

Table 2. Calculated rate constants of the forward (k_1) and reverse reaction (k_2) of hydrogen peroxide with acetic acid at 20°C, $c(H_2SO_4)$ = 0.057 M

H_2O_2 : AcOH molar ratio, mol mol^{-1}	x_1,[a] M	x_2	$(k_1 - k_2) \times 10^5$, l mol^{-1} s^{-1}	$k_1 \times 10^5$, l mol^{-1} s^{-1}	$k_2 \times 10^5$, l mol^{-1} s^{-1}
1 : 6	1.75	38.5	3.43	6.56	3.13
1 : 4	2.07	39.9	4.02	7.68	3.66
1 : 3	2.23	41.2	4.65	8.89	4.24
1 : 2.5	2.28	42.1	4.95	9.46	4.51
1 : 2	2.30	43.3	3.61	6.90	3.29
1 : 1	2.00	47.5	3.89	7.43	3.54
1 : 0.5	1.41	51.5	2.96	5.65	2.69
1 : 0.4	1.22	52.5	3.51	6.70	3.20
1 : 0.33	1.07	53.3	2.28	4.35	2.08
1 : 0.25	0.86	54.4	4.56	8.72	4.15
			Average	7.23 ± 2.42	3.45 ± 0.55

[a] x_1 is the equilibrium concentration of peroxyacetic acid.

Table 3. Calculated rate constants of the forward (k_1) and reverse reaction (k_2) of hydrogen peroxide with acetic acid at different concentrations of the catalyst

$w(H_2SO_4)$, wt%	$c(H_2SO_4)$, M	x_1	x_2	$(k_1 - k_2) \times 10^5$, l mol^{-1} s^{-1}	$k_1 \times 10^5$, l mol^{-1} s^{-1}	$k_2 \times 10^5$, l mol^{-1} s^{-1}
0	0	1.22	52.8	0.12	0.23	0.11
1	0.011	1.22	52.7	0.23	0.44	0.21
2	0.023	1.22	52.7	044	0.85	0.40
3	0.034	1.22	52.6	0.66	1.26	0.60
4	0.046	1.22	52.6	2.16	4.13	1.97
5	0.057	1.22	52.5	3.57	6.82	3.25
6	0.069	1.22	52.4	3.56	6.79	3.24
7	0.080	1.22	52.4	3.60	6.87	3.27
8	0.091	1.23	53.0	3.54	6.76	3.22
9	0.103	1.24	53.1	3.57	6.82	3.25

centration on the kinetic parameters of the process. For this purpose, we measured the concentration of AcOOH as time elapsed at various sulfuric acid concentrations. The initial mixture was prepared with an H_2O_2–AcOH molar ratio of 2.5 : 1. Orthophosphoric acid was added as stabilizer of peroxyacetic acid; in all experiments, the concentration of orthophosphoric acid was 0.057 M. The rate constants were calculated according to the above-described mathematical model. The results are presented in Table 3.

It is seen that increase in the catalyst concentration from 0 to 5 wt% leads to increase in the rate constants and that further raising the catalyst concentration from 5 to 9 wt% almost does not affects the rate constants; the average values of k_1 and k_2 are 6.81×10^{-5} and 3.25×10^{-5} l mol^{-1} s^{-1}, respectively. This means that there are no reasons to raise the catalyst concentration above 5 wt%. Presumably, the rate-determining stage in the forward reaction is elimination of water molecule from oxonium ion **C** which occurs in dynamic equilibrium with neutral intermediate **B**. When the sulfuric acid concentration exceeds 5 wt%, the equilibrium **B** $\rightleftarrows$ **C** is completely displaced to the right, the concentration of ion **C** reaches is maximal value under the given conditions, and the rate constant of the forward reaction no longer changes. Analogous considerations are also valid for the reverse reaction where the rate-determining stage is elimination of hydrogen peroxide from ion **A**.

The temperature effect on the reaction rate and equilibrium constant was studied by measuring the

Table 4. Compositions of the reaction mixture in the initial moment and in the equiblirium state at different temperatures and equilibrium constants

Temperature, °C	Equilibration time, h	Initial reactant concentrations, c_0, M			Equilibrium concentrations, M				K
		H_2O_2	AcOH	H_2O	AcOOH	H_2O_2	H_2O	AcOH	
20	36	9.88	2.47	34.7	0.840	9.04	35.6	1.63	2.10
40	28	9.88	2.47	34.7	0.678	9.20	35.4	1.80	1.46
60	22	9.88	2.47	34.7	0.544	9.33	35.3	1.93	1.07

kinetic dependences for peroxyacetic acid at 20, 40, and 60°C. The initial molar ratio H_2O_2–AcOH was 1 : 0.25. The concetrations of the catalyst (H_2SO_4) and stabilizer (H_3PO_4) were maintained constant (0.057 M). The initial and equilibrium compositions of the reaction mixture and the equilibrium constant are given in Table 4. It is seen that increase in temperature shortens the time necessary for the equilibrium to establish. The concentration of AcOOH in the equilibrium mixture decreases in parallel, since the equilibrium constant decreases as the temperature rises (Table 4). The obtained data were used to calculate thermodynamic parameters of the reaction according to Eq. (7).

$$\ln K = -\Delta_r H^0/RT + \Delta_r S^0/R, \qquad (7)$$

$\Delta_r H^0$ –13.7 ± 0.1 kJ mol^{-1}, $\Delta_r S^0$ –40.5 ± 0.4 J mol^{-1} K^{-1}; r 0.99996, s 0.00407, n 3.

Using these data, we calculated (as described above) the rate constants of the forward and reverse reactions at different temperatures [$c(H_2SO_4)$ = 0.057 M] and activation parameters of the forward and reverse processes according to the Arrhenius and Eyring equations [Eqs. (8) and (9), respectively].

Temperature, K	293	313	333
$k_1 \times 10^5$, l mol^{-1} s^{-1}	6.81	8.55	13.82
$k_2 \times 10^5$, l mol^{-1} s^{-1}	3.25	5.85	12.92

$$k = Ae^{-E_a/RT}, \qquad (8)$$

$$k = \frac{k_B T}{h} e^{-\Delta H^{\neq}/RT} e^{\Delta S^{\neq}/R}. \qquad (9)$$

	Forward reaction	Reverse reaction
E_a, kJ mol^{-1}	14.22 ± 3.49	27.90 ± 3.39
$\ln A$	–3.804 ± 1.35	1.067 ± 1.31
$\Delta H^{\neq}$, kJ mol^{-1}	11.62 ± 3.45	25.29 ± 3.34
$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	285.24 ± 11.05	244.73 ± 10.72

Both forward and reverse reactions are characterized by fairly low energies (enthalpies) of activation (69.135 [17], 6.20 [7], 42.61 to 56.65 kJ mol^{-1} at various catalyst concentrations [9]) and high negative entropies of activation. In particular, this means that the transition states in both forward and reverse reactions should be much less ordered than the corresponding initial state. On the other hand, this statement contradicts the above hypothesis implying such rate-determining stages of the forward and reverse processes, for which the entropy of activation should be positive. Presumably, the activation parameters determined in the present study are apparent quantities characterizing the entire fairly intricate process rather than a particular reaction stage. Nevertheless, these values may be used to predict the rate of the process as a whole.

By special experiments we showed that decomposition of peroxyacetic acid and hydrogen peroxide in the presence of orthophosphoric acid as stabilizer (0.057 M) occurred (on the average) by 10% in 330 days at 20 + 3°C. Therefore, the change in the concentrations of peroxyacetic acid and hydrogen peroxide as the result of their decomposition during our kinetic experiments was assumed to be negligible.

EXPERIMENTAL

Procedure of kinetic experiments. A reactor (a 2-l glass three-necked flask) equipped with a thermometer and a stirrer (operating at a speed of 100 rpm) was placed in a temperature-controlled unit and charged with a 35 wt% aqueous solution of hydrogen peroxide, and 85% orthophosphoric acid was added to a concentration of 0.057 mol l^{-1}. Specified amounts of glacial acetic acid and sulfuric acid (catalyst) were added under stirring. Samples were withdrawn from the reaction mixture at definite time intervals, and the concentrations of hydrogen peroxide and peroxyacetic acid were measured. The experiment was assumed to be finished than the composition of the mixture almost no longer changed. While studying the effect of the temperature on the rate of formation of peroxyacetic acid, the mixture was maintained at 40 and 60°C for 8 h.

The following reagents were used: 35% hydrogen peroxide of medical grade, glacial acetic acid of chemically pure grade, 85% orthophosphoric acid, and 98% sulfuric acid of chemically pure or analytical grade.

The concentration of hydrogen peroxide was determined by permanganatometric titration [4, 20] using a standard solution of potassium permanganate (0.1 M; technical specification 2642-001-49415344-99 or 6-09-2540-87), sulfuric acid (chemically pure or analytical grade, GOST 4204-77), and distilled water (GOST 6709-72).

The concentration of peroxyacetic acid was determined iodometric titration [4, 21] using sodium carbonate (chemically pure or analytical grade, GOST 83-79) or sodium hydrogen carbonate (chemically pure or analytical grade, GOST 4201-79); potassium iodide (chemically pure grade, GOST 4232-74; 10% aqueous solution prepared according to GOST 4517-87, p. 2.67), a standard solution of sodium thiosulfate pentahydrate (0.1 M, technical specification 6-09-2540-87), soluble starch (GOST 10163-76; a 0.5% aqueous solution prepared according to GOST 4517-87, p. 2.90), and distilled water (GOST 6709-72).

The overall absolute error in the determination of hydrogen peroxide and peroxyacetic acid was 0.15% at a confidence probability of 0.95.

REFERENCES

1. Suzuki, T. and Suzuki, S., *J. Chem. Soc. Jpn., Pure Chem. Sect.*, 1965, vol. 86, no. 12, p. 1318.
2. Suzuki, T. and Suzuki, S., *J. Chem. Soc. Jpn., Pure Chem. Sect.*, 1966, vol. 87, no. 5, p. 476.
3. Bunton, C.A., Lewis, T.A., and Llewelyn, D.L., *J. Am. Chem. Soc.*, 1956, vol. 78, no. 6, p. 1226.
4. Swern, D., *Organic Reactions*, Adams, R., Ed., New York: Wiley, 1953, vol. 7. Translated under the title *Organicheskie reaktsii*, Moscow: Inostrannaya Literatura, 1956, vol. 7, pp. 476–544.
5. Parker, W.E., Wetnauer, L.E., and Swern, D., *J. Am. Chem. Soc.*, 1958, vol. 80, no. 2, p. 323.
6. Havel, S. and Weigner, J.A., *Chem. Prum.*, 1960, vol. 10, p. 293.
7. Suzuki, T., Iwamoto, I., and Suzuki, S., *J. Chem. Soc. Jpn., Pure Chem. Sect.*, 1962, vol. 83, no. 11, p. 1212.
8. Dvorak, J., *Chem. Prum.*, 1959, vol. 9, p. 524.
9. Havel, S., *Sborn. Vedeckych praci. Vysoka Skola Chemickotechnologicka*, Pardubice, 1967, pp. 1, 79.
10. Agnihotri, V.G. and Parikk, D.V., *Res. Ind.*, 1965, vol. 10, no. 6, p. 170.
11. Karetnikova, N.V., Pen, R.Z., and Pen, V.R., *Khim. rastit. syr’ya*, 1999, no. 2, p. 41.
12. Ogata, Y. and Sawaki, Y., *Tetrahedron*, 1965, vol. 21, no. 12, p. 3381.
13. Koubek, E., Haggett, M.L., and Battaglia, C.J., *J. Am. Chem. Soc.*, 1963, vol. 85, no. 5, p. 2263.
14. Dorofeikov, V.V., Shcherbak, I.G., Zemchenkov, A.Yu., and Timokhovskaya, G.Yu., RU Patent no. 2 077 890, 1997; *Byull. Izobret.*, 1997, no. 12.
15. Meloun, D.U.D., RU Patent no. 2 145 879, 2000; *Byull. Izobret.*, 2000, no. 6.
16. Lunenok-Burmakina, V.A., Miroshnichenko, A.G., Kolyadenko, V.G., Mikhno, I.L., Anisimova, I.G., Taran, V.V., Blonskaya, L.F., Emel’yanova, O.B., and Limanov, V.E., USSR Inventor’s Certificate no. 1 683 763, 1991; *Byull. Izobret.*, 1991, no. 38.
17. Shapilov, O.D., *Doctoral (Pharm.) Dissertation*, Moscow, 1978.
18. Doguzova, I.A., *Cand. Sci. (Chem.) Dissertation*, Moscow, 2000.
19. Emanuel’, N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Lectures on Chemical Kinetics), Moscow: Vysshaya Shkola, 1974, pp. 151–156.
20. Schumb, W.C., Satterfield, C.N., and Wentworth, R.L., *Hydrogen Peroxide*, New York: Reinhold, 1955.
21. Sukiasyan, A.N. and Svitova, I.R., *Khim.-Farm. Zh.*, 1983, vol. 17, no. 3, p. 366.