

Nucleophilic Reactivity of Hydroxide and Hydroperoxide Ions in Aqueous–Alcoholic Media and of HCO_3^- Ion in Water

V. A. Savelova, A. F. Popov, L. N. Vakhitova, T. N. Solomoichenko, Yu. S. Sadovskii, T. M. Prokop'eva, A. V. Skrypka, and B. V. Panchenko

Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine,
ul. R. Lyuksemburg 70, Donetsk, 83114 Ukraine
e-mail: prokop'eva@infou.donetsk.ua

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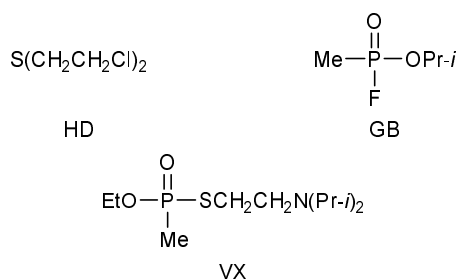
Abstract—Nucleophilic reactivity of hydroxide and hydroperoxide ions toward ethyl 4-nitrophenyl ethylphosphonate, diethyl 4-nitrophenyl phosphate, 4-nitrophenyl 4-toluenesulfonate, and 4-nitrophenyl dimethylcarbamate in the system H_2O_2 –KOH was studied in aqueous–alcoholic solutions at 25°C. The rate of reactions of both anions with ethyl 4-nitrophenyl ethylphosphonate, diethyl 4-nitrophenyl phosphate, and 4-nitrophenyl dimethylcarbamate and of hydroxide ion with 4-nitrophenyl 4-toluenesulfonate increases with rise in the fraction of the alcohol in mixtures of water with isopropyl and *tert*-butyl alcohols, while the reaction rate of hydroperoxide ion with 4-nitrophenyl 4-toluenesulfonate decreases. The rate of reactions of both anions with all the above substrates in mixtures of water with ethylene glycol decreases as the fraction of the latter rises. The apparent rate of the reaction of ethyl 4-nitrophenyl ethylphosphonate with anionic nucleophiles in the system H_2O_2 – HO^- – HCO_3^- in water at pH 8.5 almost does not depend on the concentration of ammonium hydrogen carbonate up to a value of 1 M, and it increases when the NH_4HCO_3 concentration exceeds 1 M. Mixtures of water with the lower monohydric alcohols were recommended for use as components of H_2O_2 – HO^- – HCO_3^- systems for oxidative decomposition of ecotoxicants.

The problem of utilization (degassing) of active components of chemical weapons has now become especially important, for it is closely related to increasing ecological safety requirements. Accumulation of huge amounts of chemical weapons and terroristic threat enhance the hazard. The chemical origin of chemical weapons, such as mustard gas (HD), sarin (GB), and VX, suggests that they should be decomposed by oxidative nucleophilic systems. Oxidants are known to be effective with respect to compounds like HD [1–3], GB decomposes by the action of nucleophiles [4, 5], while oxidative nucleophilic systems containing an HOX – OX^- couple ($\text{X} = \text{OH}$, Hlg , etc.) [6, 7] are preferred for compounds like VX or mixtures

of these substances. Presumably, this approach is promising as applied to the general ecological problem involving detoxication (neutralization) of substances hazardous for humans and environment. Among these, a large group includes pesticides, the most hazardous of which are esters derived from phosphoric and phosphonic acids.

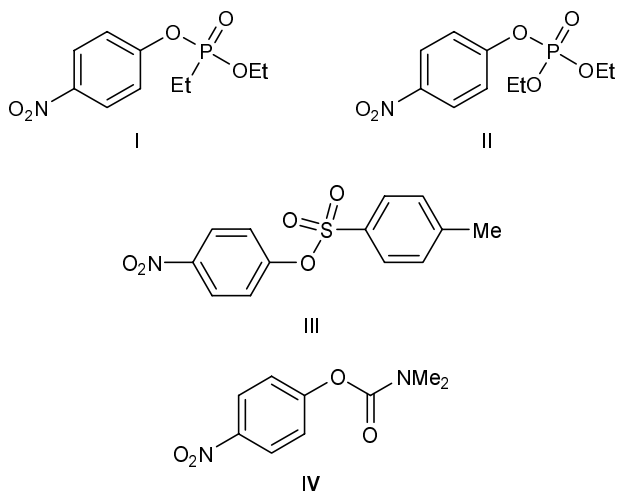
At least six requirements are imposed on degassing systems [6], the main of which is the reaction rate. Obviously, the rate of nucleophilic reaction should increase while the rate of oxidative process should decrease with rise in pH of aqueous systems based on HOX – OX^- couple. Therefore, the main strategy in utilization of chemical weapons and related substances implies optimization of HOX – OX^- systems to attain the maximal rates of both nucleophilic and oxidation reaction under mild conditions, i.e., at a nearly neutral pH value [3, 6, 7].

From the practical viewpoint, especially attractive are systems based on hydrogen peroxide. Hydroperoxide ion HO_2^- is one of the strongest α -nucleophiles [5], but hydrogen peroxide is a relatively weak oxidant



[8]. In order to enhance oxidative properties of H_2O_2 , various acid activators are used to obtain peroxy acid [1, 3, 9]. As applied to the chemical weapon utilization problem, activation of H_2O_2 with hydrogen carbonate ion attracts interest [1]. The rate of oxidation of sulfides (analogs of mustard gas) with hydrogen peroxo-carbonate ion HCO_4^- in water is higher by more than two orders of magnitude. However, the application of this method is limited due to very poor solubility of poison-gases (which are usually viscous oily substances) in water. For that reason, the reaction rate even in a highly active system may be limited by the substrate solubility. As shown in [1], in the case of sulfides the problem may be solved by using the $\text{H}_2\text{O}_2\text{-HCO}_3^-$ system in aqueous-alcoholic medium.

The goal of the present work was to examine the reactivity of anionic species in the systems $\text{H}_2\text{O}_2\text{-HO}^-$ and $\text{H}_2\text{O}_2\text{-HO}^-\text{-HCO}_3^-$ ($\text{Nu}^- = \text{HO}^-, \text{HO}_2^-, \text{HCO}_4^-$) with respect to electrophilic substrates **I-IV** (S) in aqueous-alcoholic mixtures. Ethyl 4-nitrophenyl ethylphosphonate (**I**) (Armin) and diethyl 4-nitrophenyl phosphate (**II**) (Paraoxon) can be regarded as models of organophosphorus anticholinesterase ecotoxicants and analogs of neuroparalytic poisons of the G series [4, 6, 10]. These compounds, as well as low-reactive esters, 4-nitrophenyl 4-toluenesulfonate (**III**) and 4-nitrophenyl dimethylcarbamate (**IV**), were repeatedly used as model substrates in reactions with participation of α -nucleophiles [5, 11, 12].



As aqueous-alcoholic media we selected those analogous to the media examined in [1] for the oxidation of organic sulfides (mustard gas analogs) with the system $\text{H}_2\text{O}_2\text{-HCO}_3^-$. The alcohol components were isopropyl and *tert*-butyl alcohols and ethylene glycol.

The kinetic studies were performed at 25°C with excess nucleophile ($[\text{S}] \ll [\text{Nu}^-]$).

Reactions with hydroxide ion. Alkaline hydrolysis of compounds **I-IV** in aqueous solutions of KCl ($\mu = 1 \text{ M}$) was studied previously [5, 11]; the corresponding rate constants k_{HO} calculated with the use of hydroxide ion activities were also given. While studying the kinetics of alkaline hydrolysis of esters **I-IV** in aqueous-alcoholic mixtures, constant ionic strength of solution was not maintained, and the rate constants were calculated from the concentration dependence

$$k_{\text{ap}} = k_{\text{HO}}[\text{MOH}], \quad (1)$$

where k_{ap} (s^{-1}) is the apparent pseudofirst-order rate constant, and $[\text{MOH}]$ (M) is the alkali concentration. In most cases, the straight lines described by Eq. (1) pass through the origin (Fig. 1), indicating insignificant contribution of neutral hydrolysis (alcoholysis) to the apparent reaction rate. Probably, k_{HO} values include some contribution of the process with participation of alkoxide ion, especially when the alcohol concentration in the mixture is high. However, we did not examine this aspect specially.

In going to an alkali concentration of 0.1 to 2 M, the dependence of k_{ap} upon $[\text{MOH}]$ becomes curvilinear (Fig. 1, curves 2, 3) and is described by Eq. (2).

$$k_{\text{ap}} = k_{\text{HO}}[\text{MOH}] + k'_{\text{HO}}[\text{MOH}]^2. \quad (2)$$

Linearization of Eq. (2) gives Eq. (3) which is illustrated by curves 2' and 3' in Fig. 1.

$$k_{\text{ap}}/[\text{MOH}] = k_{\text{HO}} + k'_{\text{HO}}[\text{MOH}]. \quad (3)$$

When the alcohol concentration exceeds 30 vol %, the rate constants k_{HO} and k_{HOO} for the reactions of esters **II** and **IV** with HO^- and HO_2^- in the presence of potassium hydroxide are higher than in the presence of NaOH. In 90% isopropyl alcohol, the difference reaches ~30% for the hydrolysis of ester **II** and ~40% for ester **IV**; the corresponding difference for the reaction with hydroperoxide ion is ~20 and 30%, respectively. Therefore, the k_{HO} values given in Table 1, as well as k_{HOO} in Table 2, refer to reactions performed with the same alkali, namely potassium hydroxide. Taking into account limited solubility of KOH in mixtures with high concentration of alcohol, the reactions were carried out in the presence of 18-crown-6 (CW) at a $[\text{KOH}]:[\text{CW}]$ ratio of 1:1. By special experiments (under the conditions ensuring complete solubility of

Table 1. Rate constants (k_{OH}) for the reactions of hydroxide ion with ethyl 4-nitrophenyl ethylphosphonate (**I**), diethyl 4-nitrophenyl phosphate (**II**), 4-nitrophenyl 4-toluenesulfonate (**III**), and 4-nitrophenyl dimethylcarbamate (**IV**) in water and aqueous–alcoholic mixtures at 25°C

Alcohol concentration, vol %	Isopropyl alcohol		<i>tert</i> -Butyl alcohol		Ethylene glycol	
	[KOH] × 10 ² , M	$k_{\text{HO}} \times 10^2$, ^a l mol ⁻¹ s ⁻¹	[KOH] × 10 ² , M	$k_{\text{HO}} \times 10^2$, ^a l mol ⁻¹ s ⁻¹	[KOH] × 10 ² , M	$k_{\text{HO}} \times 10^2$, ^a l mol ⁻¹ s ⁻¹
Ethyl 4-nitrophenyl ethylphosphonate (I)						
0		12 ± 1 ^b				
30	0.5–4	7 ± 1	0.2–1.2	15.2 ± 0.4	2–18	8.8 ± 0.5
50	–	–	–	–	2–10	7.9 ± 0.2
70	1–4	25 ± 2	0.1–0.6	33 ± 1	2–18	6.4 ± 0.3
90	0.2–2.8	83 ± 7	0.05–0.4	104 ± 6	2–18	10.1 ± 0.6
Diethyl 4-nitrophenyl phosphate (II)						
0	0.5–3.7	1.17 ± 0.02 ^b				
30	0.6–5	5.6 ± 0.4	4.6–36	0.78 ± 0.02 ^c	0.4–3	0.90 ± 0.03
70	0.15–2.3	11.7 ± 0.3	1.3–9	2.8 ± 0.1 ^c	0.4–3	0.82 ± 0.03
90	0.16–1.5	17.5 ± 3.2	0.4–1.5	8.2 ± 0.8 ^c	0.4–3	0.67 ± 0.06
4-Nitrophenyl 4-toluenesulfonate (III)						
0	6–150	0.46 ± 0.01 ^b				
30	10–50	0.42 ± 0.03 ^c	34–116 ^d	0.25 ± 0.01 ^c	10–44	1.1 ± 0.1
70	15–50 ^d	0.44 ± 0.02 ^c	10–50 ^d	0.33 ± 0.02 ^c	17–66	0.85 ± 0.01
90	10–47 ^d	1.20 ± 0.05 ^c	4–20 ^d	2.2 ± 0.01 ^c	13–32	0.55 ± 0.02
4-Nitrophenyl dimethylcarbamate (IV)						
0	10–100	0.040 ± 0.001 ^b				
10	–	–	–	–	2–20	0.037 ± 0.002
30	4–30	0.083 ± 0.002	4.6–10	0.030 ± 0.005 ^c	2–20	0.033 ± 0.003 ^c
70	1–10	0.45 ± 0.02	0.6–1.2	0.17 ± 0.02 ^c	5–100	0.031 ± 0.001
90	0.25–1.5	0.91 ± 0.07 ^c	0.4–3.1	0.38 ± 0.01 ^c	3–30	0.024 ± 0.002

^a The rate constants k_{HO} in water ($\mu = 1.0$ M, KCl) were calculated using the activity of HO⁻ (except for ester **IV**), and in all aqueous–alcoholic mixtures, using KOH concentration.

^b According to the data of [5], the rate constants k_{HO} in water ($\mu = 1.0$ M, KCl) are as follows: 0.15 (**I**), 0.0096 (**II**), 0.008 (H₂O + 5% EtOH, **III**), 0.00056 (**IV**).

^c In the presence of 18-crown-6, [KOH]:[CW] = 1:1.

^d For the given concentration range, the rate constants k_{HO} were calculated by Eq. (3).

^e Concentration of ethylene glycol 40 vol %.

potassium hydroxide) we showed that addition of crown ether almost does not affect the reactivity of the alkali.

Reactions with hydroperoxide ion. The kinetics of the reactions of esters **I–IV** with hydroperoxide ion were studied under the same conditions as with hydroxide ion (water, $\mu = 1$ M, KCl). The calculated second-order rate constants k_{HO_2} (Table 2), as well as k_{HO} values (Table 1), coincided with those found previously in [5, 11] within experimental error.

The reactions of substrates **I–IV** with hydroperoxide ion generated in the system H₂O₂–KOH in aqueous–alcoholic medium were performed without maintaining a constant ionic strength. The concentration of hydrogen peroxide was usually greater than or equal to that of potassium hydroxide (in a few cases, [H₂O₂] < [KOH]). Figure 2 shows that the plots of k_{ap} (s⁻¹) versus reagent concentration ([KOH] or [H₂O₂], [KOH] ≤ [H₂O₂]) are straight lines. This means that in aqueous–alcoholic mixtures neutralization of hydrogen

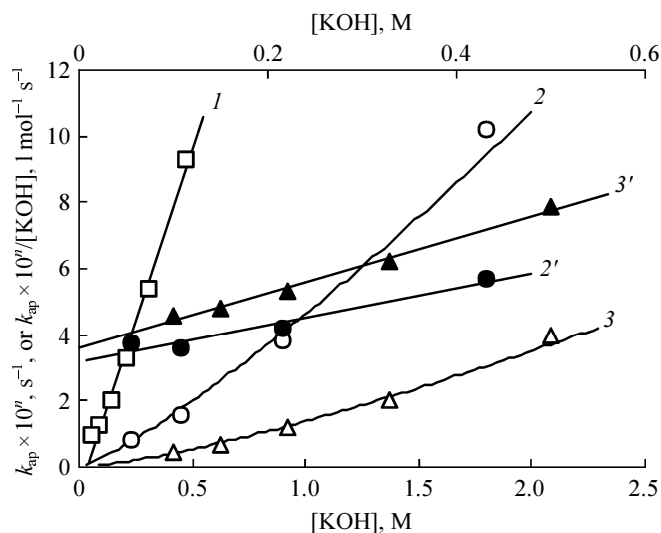


Fig. 1. Plots of the apparent rate constants (1–3) $k_{\text{ap}} \times 10^n$ and (2', 3') $k_{\text{ap}} \times 10^n / [\text{KOH}]$ versus potassium hydroxide concentration $[\text{KOH}]$ for the hydrolysis of (1, 3, 3') 4-nitrophenyl 4-toluenesulfonate and (2, 2') 4-nitrophenyl dimethylcarbamate in aqueous–alcoholic mixtures at 25°C: (1) isopropyl alcohol, 90 vol % (with addition of 18-crown-6); (2, 2') ethylene glycol, 40 vol %; (3, 3') *tert*-butyl alcohol, 70 vol % (with addition of 18-crown-6); (1, 3, 3') $n = 3$; (2, 2') $n = 4$.

peroxide is almost complete even at an equimolar ratio of H_2O_2 and KOH . Therefore, the rate constants k_{HOO} were calculated by Eq. (4):

$$k_{\text{ap}} = k_{\text{HOO}}[\text{KHO}_2], \quad (4)$$

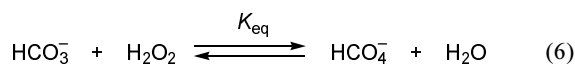
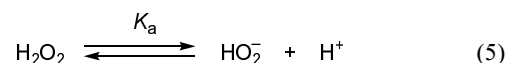
where $[\text{KHO}_2]$ is equal to the concentration of alkali (or hydrogen peroxide) if $[\text{KOH}] \leq [\text{H}_2\text{O}_2]$.

When $[\text{KOH}]_0 > [\text{H}_2\text{O}_2]_0$, the contribution of alkaline hydrolysis is as a rule negligible (<5%). In a few cases when the contribution of alkaline hydrolysis was greater, we used in Eq. (4) $k'_{\text{ap}} = k_{\text{ap}} - k_{\text{HO}}[\text{MOH}]$, where $[\text{MOH}] = [\text{KOH}]_0 - [\text{H}_2\text{O}_2]_0$, instead of k_{ap} . The k_{HOO} values calculated in such a way are given in Table 2 together with the $k_{\text{HOO}}/k_{\text{HO}}$ ratios which are frequently used to characterize α -effect [13].

Reactions in the system $\text{H}_2\text{O}_2\text{--HO}^-\text{HCO}_3^-$.

Table 3 contains the results of studying the kinetics of nucleophilic cleavage of ester **I** in the system $\text{H}_2\text{O}_2\text{--KOH--NH}_4\text{HCO}_3$ in water ($\mu = 1 \text{ M}$, KCl , phosphate buffer). The data for 4 reaction series are given (total of 47 kinetic curves). In the first series, the concentration of hydrogen peroxide was varied, while pH and $[\text{NH}_4\text{HCO}_3]$ were maintained constant. In the second series, pH was varied, $[\text{H}_2\text{O}_2]$ and $[\text{NH}_4\text{HCO}_3]$ being

constant. In the third and fourth series, the concentration of ammonium hydrogen carbonate was varied over a wide range at constant pH value and hydrogen peroxide concentration. In addition, the ranges of variation of the equilibrium concentration ratio of HCO_4^- and HO_2^- are presented in Table 3. The equilibrium concentrations $[\text{HCO}_4^-]_{\text{eq}}$ and $[\text{HO}_2^-]_{\text{eq}}$ were calculated using $\text{p}K_{\text{a}} = 11.5$ [5] for equilibrium (5) and $K_{\text{eq}} = 27$ for equilibrium (6) [14]. Dissociation of HCO_3^- ($\text{p}K_{\text{a}} = 10.33$ [15]) and HCO_4^- ions ($\text{p}K_{\text{a}} \approx 9.4$ [1]) was not taken into account due to low experimental pH values (Table 3). The concentration ratio $[\text{HCO}_4^-]_{\text{eq}}/[\text{HO}_2^-]_{\text{eq}}$ was varied from ~ 1 to ~ 50 .



Treatment of the data for the first two series gave rate constants k_{HOO} which coincided (within the experimental error) with those found without addition of NH_4HCO_3 ($7.3 \text{ l mol}^{-1} \text{ s}^{-1}$) [5]. However, the absence of NH_4HCO_3 effect on the reaction rate under the given conditions may be rationalized in terms of a small excess of HCO_4^- over HO_2^- ($[\text{HCO}_4^-]_{\text{eq}}/[\text{HO}_2^-]_{\text{eq}} = 2\text{--}20$). In the third series, the ratio $[\text{HCO}_4^-]_{\text{eq}}/[\text{HO}_2^-]_{\text{eq}}$ was raised to 50. Nevertheless, the reaction rate remained constant over the whole range of variation of the NH_4HCO_3 concentration and coincided with the apparent reaction rate in the absence of NH_4HCO_3 ($k_{\text{ap}} = 0.0021 \text{ s}^{-1}$). The maximal change in the apparent rate constant was attained in the fourth series of experiments where the ratio $[\text{HCO}_4^-]_{\text{eq}}/[\text{HO}_2^-]_{\text{eq}}$ reached ~ 700 .

Analysis of the results and discussion. Let us consider the data in Table 3 for series no. 4 in more detail. We previously [5] deduced the Brønsted equation ($\log k = -2.9 + 0.25 \text{p}K_{\text{a}}$) describing the reactivity of three inorganic anionic α -nucleophiles (ClO^- , BrO^- , and NH_2O^-) with respect to ethyl 4-nitrophenyl ethylphosphonate (**I**) in water at 25°C ($\mu = 1 \text{ M}$, KCl). It was noted that $\log k$ values for the reaction with HO_2^- ions deviate from the above straight line toward larger values ($\Delta \log k = 0.93$), which was explained by general acid catalysis in the transition state formed by phosphorus acid esters. An analogous relation was observed in the reaction of hydroperoxide ion with diethyl 4-nitrophenyl phosphate (**II**) [5].

Calculation of the rate constant for nucleophilic reaction of HCO_4^- with ester **I** by the given Brønsted equation with the use of $\text{p}K_{\text{a}}(\text{H}_2\text{CO}_4) \approx 4$ ("by

Table 2. Rate constants (k_{HOO})^a for the reactions of hydroperoxide ion with ethyl 4-nitrophenyl ethylphosphonate (**I**), diethyl 4-nitrophenyl phosphate (**II**), 4-nitrophenyl 4-toluenesulfonate (**III**), and 4-nitrophenyl dimethylcarbamate (**IV**) in water and aqueous-alcoholic mixtures at 25°C and rate constant ratios $k_{\text{HOO}}/k_{\text{HO}}$

Alcohol concentration, vol %	Isopropyl alcohol			<i>tert</i> -Butyl alcohol			Ethylene glycol					
	$[\text{H}_2\text{O}_2] \times 10^2, \text{ M}$	$[\text{KOH}] \times 10^2, \text{ M}$	$k_{\text{HOO}}/k_{\text{HO}}$	$[\text{H}_2\text{O}_2] \times 10^2, \text{ M}$	$[\text{KOH}] \times 10^2, \text{ M}$	$k_{\text{HOO}}/k_{\text{HO}}$	$[\text{H}_2\text{O}_2] \times 10^2, \text{ M}$	$[\text{KOH}] \times 10^2, \text{ M}$	$k_{\text{HOO}}/k_{\text{HO}}$			
Ethyl 4-nitrophenyl ethylphosphonate (I)												
0	0.33	0.1–0.9	6.7 ± 0.6^b	56	1.7	0.05–0.19	5.7 ± 0.1	38	1.45	0.04–0.19	2.15 ± 0.03	24
30	1.5	0.07–0.55	7.1 ± 0.2	42	–	–	–	–	1.6	0.1–0.6	1.32 ± 0.02	–
50	–	–	–	–	–	–	–	–	–	–	–	–
70	1.5	0.04–0.27	11 ± 1	44	1.5	0.05–0.4	11.3 ± 0.4	34	1.45	0.04–0.19	1.15 ± 0.04	18
90	1.4	0.02–0.08	48 ± 3	58	1.5	0.026–0.2	22.0 ± 0.6	21	1.45	0.04–0.19	0.67 ± 0.04	7
Diethyl 4-nitrophenyl phosphate (II)												
0	3.16	0.1–1.2	0.53 ± 0.04^b	45	3	0.14–1.1	0.43 ± 0.01	55	1.55	0.18–2.9	0.32 ± 0.01	36
30	3.1	0.1–1	0.41 ± 0.01	7	3	0.2–3.7	0.47 ± 0.01	17	1.55	0.18–2.9	0.16 ± 0.03	19
70	1.55	0.2–0.75	0.85 ± 0.01	7	3	0.18–1.5	1.54 ± 0.03	19	1.55	0.18–2.9	0.084 ± 0.002	13
90	1.55	0.1–0.75	1.5 ± 0.1	9	3	–	–	–	–	–	–	–
4-Nitrophenyl 4-toluenesulfonate (III)												
0	4.7	0.2–1.6	1.2 ± 0.1^b	261	8.3	0.2–1.6	0.77 ± 0.01	–	–	–	–	–
15	8.3	0.2–1.6	0.73 ± 0.04	–	14	0.4–3.3	0.26 ± 0.01	104	14	0.4–2.4	0.58 ± 0.02	53
30	8.5	0.3–1.8	0.32 ± 0.01	79	14	0.6–3.3	0.22 ± 0.01	67	14	0.4–2.2	0.22 ± 0.01	26
70	14	0.5–2.2	0.31 ± 0.02	70	14	0.7–2.4	0.065 ± 0.003	3	28	0.7–5.5	0.11 ± 0.01	20
90	14	0.7–1.6	0.22 ± 0.01	18	14	–	–	–	–	–	–	–
4-Nitrophenyl dimethylcarbamate (IV)												
0	–	6–18	0.022 ± 0.001^b	55	3	0.14–1.1	0.013 ± 0.001	43	3.1	0.45–3.6	0.012 ± 0.001	36
30	3.1	0.75–3	0.019 ± 0.002	23	3.1	0.23–1.9	0.015 ± 0.001	9	3	0.2–0.9	0.016 ± 0.001	52
70	1.55	0.2–1.5	0.014 ± 0.001	3	1.5	0.2–1.5	0.030 ± 0.003	8	3.1	0.2–1.8	0.0038 ± 0.0003	16
90	1.55	0.1–0.75	0.043 ± 0.002	5	–	–	–	–	–	–	–	–

^a The rate constants k_{HOO} in water ($\mu = 1 \text{ M}$, KCl) were calculated as described in [5] using $\text{p}K_{\text{a}} = 11.5$ for H_2O_2 ; the rate constants k_{HOO} in aqueous-alcoholic mixtures were calculated by Eq. (4).

^b According to the data of [5], the rate constants k_{HOO} in water ($\mu = 1.0 \text{ M}$, KCl) are as follows: 7.3 (**I**), 0.55 (**II**), 0.99 ($\text{H}_2\text{O} + 5\% \text{ EtOH}$) (**III**), 0.016 (**IV**).

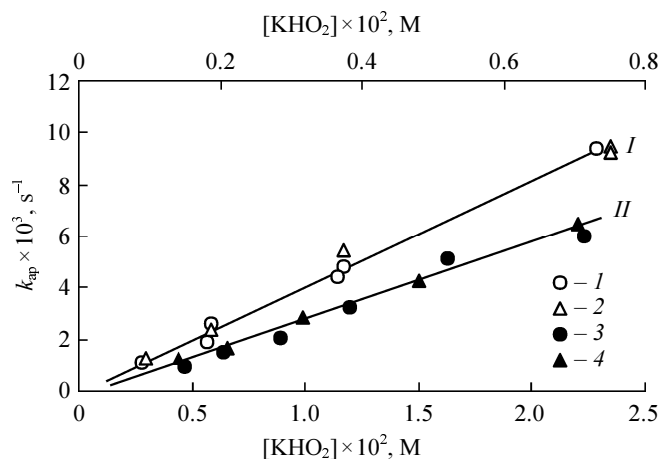


Fig. 2. Plots of the apparent rate constants k_{ap} versus KHO_2 concentration ($[KHO_2] = [KOH]$ at $[H_2O_2] > [KOH]$ and $[KHO_2] = [H_2O_2]$ at $[H_2O_2] < [KOH]$) for the perhydrolysis of (I) diethyl 4-nitrophenyl phosphate in 90% aqueous isopropyl alcohol and (II) 4-nitrophenyl 4-toluenesulfonate in 70% aqueous isopropyl alcohol at 25°C; concentrations, M: (1) $[H_2O_2] = 1.53 \times 10^{-2}$, $[KOH] = (0.1-0.75) \times 10^{-2}$, (2) $[KOH] = 0.75 \times 10^{-2}$, $[H_2O_2] = (0.1-0.75) \times 10^{-2}$, (3) $[H_2O_2] = 14.2 \times 10^{-2}$, $[KOH] = (0.5-2.2) \times 10^{-2}$, (4) $[KOH] = 14.2 \times 10^{-2}$, $[H_2O_2] = (0.5-2.2) \times 10^{-2}$. If $[KOH] > [H_2O_2]$, the k_{ap} values were corrected for the contribution of alkaline hydrolysis, k_{HO} ($[KOH] - [H_2O_2]$).

analogy” estimate [1]) gives $k_{HCO_4} \approx 0.013 \text{ l mol}^{-1} \text{ s}^{-1}$. Curve 1 in Fig. 3 corresponds to the reaction rate expected when HCO_4^- ion does not participate in nucleophilic attack on ester I ($k'_{ap} = 7.3[H_2O_2]_{eq}$). Curve 2 in

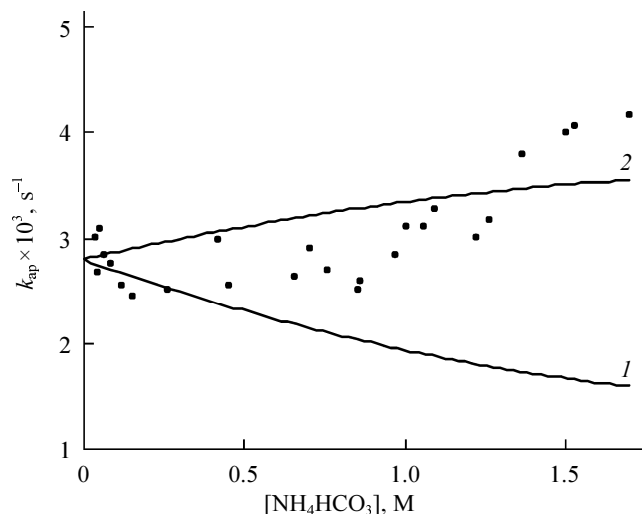


Fig. 3. Plots of k_{ap} (s^{-1}) versus NH_4HCO_3 concentration (M) for the reaction of ethyl 4-nitrophenyl ethylphosphonate (I) with the system H_2O_2 – KOH – NH_4HCO_3 in water at 25°C (phosphate buffer, pH = 8.5; $[H_2O_2] = 0.35 \text{ M}$), calculated by the formulas (1) $k'_{ap} = 7.3[H_2O_2]_{eq}$ and (2) $k''_{ap} = 7.3[H_2O_2]_{eq} + 0.013[HCO_4^-]_{eq}$; dark circles correspond to experimental values.

Fig. 3 describes the case when HCO_4^- ion, as well as HO_2^- , reacts with the substrate with a second-order rate constant of $0.013 \text{ l mol}^{-1} \text{ s}^{-1}$ ($k''_{ap} = 7.3[H_2O_2]_{eq} + 0.013[HCO_4^-]_{eq}$). Dark circles in Fig. 3 correspond to experimental values of k_{ap} (total of 25 experiments). There is no appreciable effect (within the error in determination of k_{ap}) of NH_4HCO_3 on the apparent reaction rate up to a concentration of 1 M. In the NH_4HCO_3 concentration range from 1 to 1.7 M, the experimental values of k_{ap} (10 points) are closer to curve 2 rather than 1. Estimation of k_{HCO_4} from k_{ap} corresponding to the above concentration range $\{k_{HCO_4} = (k_{ap} - k'_{ap})/[HCO_4^-]_{eq}\}$ gives values varying from 0.01 to $0.017 \text{ l mol}^{-1} \text{ s}^{-1}$, i.e., approaching a value of $0.013 \text{ l mol}^{-1} \text{ s}^{-1}$, which was obtained from the Brønsted equation for three inorganic anionic α -nucleophiles [5].

Although the authors [5] treated the obtained estimate of k_{HCO_4} with care, we can state with some certainty that HCO_4^- ion is an α -nucleophile whose pK_a value is the lowest among inorganic anions known so far. The deviation of $\Delta \log k_{HCO_4}$ from the Brønsted dependences for reactions of aroxide ions [16] and amines [17] is about 4. Even though we assume pK_a value for the conjugate acid (H_2CO_4) to be the same as for carbonic acid ($pK_a = 6.37$ [15]) rather than 4 [1], deviations from the Brønsted dependences would remain considerable: 2.7 from the plot for aroxide ions and 3.2 from the plot for amines. In view of the above stated we believe it to be reasonable to perform a special study on the reactivity of HCO_4^- ion.

The ratios k_{HO_2}/k_{HO} given in Table 2 show that hydroperoxide ion acts as an α -nucleophile in all aqueous–alcoholic media. On the other hand, the α -effect appreciably weakens as the fraction of alcohol increases. It is known [18] that, among other factors, the strength of the α -effect is determined by solvation interactions. In the general case, just that solvation constituent of the Gibbs activation energy which changes in going from water to alcohol is responsible for variation of the α -effect. Most probably, the gain in the activation energy upon desolvation of hard HO^- ion (with a localized negative charge) is greater than upon desolvation of softer HO_2^- ion in which the negative charge is delocalized to a stronger extent.

Analysis of the k_{HO} and k_{HO_2} values (Tables 1, 2) revealed, at first glance, qualitatively similar dependences of the reaction rates with hydroxide and hydroperoxide ions on the composition of aqueous–alcoholic mixtures. For example, the rate of reactions of HO^-

Table 3. Nucleophilic cleavage of ethyl 4-nitrophenyl ethyl-phosphonate (**I**) with the system H₂O₂–KOH–NH₄HCO₃ in water at 25°C ($\mu = 1$ M, KCl, phosphate buffer)

Series no.	pH	[H ₂ O ₂], M	[NH ₄ HCO ₃], M	Number of runs	[HCO ₄ ⁻] _{eq} /[HO ₂ ⁻] _{eq} , ^a M	$k_{ap} \times 10^3, s^{-1}$	$k_{HCO}, l mol^{-1} s^{-1}$
1	8.5	0.11–0.28	0.01	4	4.3–4	1–2.3 (6.9±1.0) ^b	–
2	8–9	0.079	0.016	6	2–21	0.18–1.8 (6.7±0.5) ^b	–
3	9.02	0.076	0.01–0.4	12	1–53	2.0–2.2 ^c	–
4	8.5	0.35	0.035–1.7	25	14–700	2.5–42	0.01–0.017 ^d

^a Ratio of equilibrium concentrations; see equilibria (5), $pK_a = 11.5$ [5], and (6), $K_{eq} = 27$ [15].

^b In parentheses are given the rate constants k_{HOO} ($l mol^{-1} s^{-1}$) calculated with the use of equilibrium concentrations of hydroperoxide ion (cf. $k_{HOO} = 7.3 \pm 0.8 l mol^{-1} s^{-1}$ obtained for the system containing no NH₄HCO₃ [5]).

^c In the absence of NH₄HCO₃, $k_{ap} = 2.1 \times 10^{-3} s^{-1}$.

^d Range of variation of k_{HCO} , calculated for NH₄HCO₃ concentrations ranging from 1 to 1.7 M.

and HO₂⁻ with all the examined substrates (except for esters **III**; see below) in mixtures of water with isopropyl and *tert*-butyl alcohols decreases as the alcohol concentration rises, whereas the reaction rate in mixtures of water with ethylene glycol decreases in all cases. Presumably, this analogy is illustrated by almost linear correlation (7) which covers the whole array of data given in Tables 1 and 2.

$$\log k_{HOO} = (1.30 \pm 0.15) + (0.93 \pm 0.07) \log k_{HO}; \quad (7)$$

$$r = 0.9, N = 40.$$

A more detailed analysis revealed differences indicating a complex mechanism of solvation in aqueous–alcoholic media. First, as noted above, the reaction rate changes in the opposite direction, depending on the alcohol nature. Increase in the fraction of monobasic alcohols (*i*-PrOH, *t*-BuOH) favors the process, while ethylene glycol inhibits the reaction. Reactions with ester **III** occupy an intermediate place: the rate of its alkaline hydrolysis in going from water to 90% isopropyl or *tert*-butyl alcohol increases, passing through a weakly defined minimum, and the rate of perhydrolysis continuously drops down. Second, the absolute variation of the rate constant ($\Delta k = k_{H_2O} - k_{H_2O/ROH}$) strongly depends upon both reactant and alcohol nature, which is reflected in differences in the α -effect.

Without going into details of the mechanism of the reactions under study and assuming concerted bimolecular substitution mechanism as the most probable [5], the observed relations may be interpreted on a qualitative level as a joint effect of various solvation interactions, each contributing something to variation of the solvation constituent of the Gibbs activation energy in going from water to alcohol. These inter-

actions include: (1) desolvation of nucleophilic anionic species (increase of the reaction rate); (2) solvation of the departing group (decrease of the reaction rate); and (3) decrease of the polarity of the medium and variation of its structure (both positive and negative effect on the reaction rate is possible).

Taking into account the above stated, increase in the reaction rate in going from water to 90% aqueous alcohols is likely to result mainly from the contribution of desolvation of HO⁻ and HO₂⁻ ions (reactions with esters **I**, **II**, and **IV** and reaction of HO⁻ with ester **III** in aqueous isopropyl and *tert*-butyl alcohols), while decrease in the reaction rate is caused mainly by solvation of the departing 4-nitrophenoxide ion (reactions of all substrates in water–ethylene glycol mixtures and of ester **III** with HO₂⁻ in H₂O–*i*-PrOH and H₂O–*t*-BuOH).

As shown in [1], hydrogen carbonate catalysis of the oxidation of mustard gas analogs with the system H₂O₂–HCO₃⁻ in water mixtures with both mono- and dihydric (propylene glycol) alcohols decelerates the reaction. Nevertheless, aqueous–alcoholic mixtures considerably improved the solubility of the substrate and oxidant and were recommended for degassing of mustard gas.

Hydroxide and hydroperoxide ions react with sarin (neuroparalytic gas) in water with the rate constants $k_{HO} = 0.35$ and $k_{HOO} = 36 l mol^{-1} s^{-1}$ [19]; these values approach those found for ester **I**. The reactions of the same nucleophiles with VX are characterized by the rate constants $k_{HO} = 0.004$ and $k_{HOO} = 0.17 l mol^{-1} s^{-1}$ [20], which are similar to those found for ester **II**. Therefore, from the viewpoint of decomposition of chemical weapons, the most interest is the effect of alcohols on the reactions of HO⁻ and HO₂⁻ with phosphorus acid esters **I** and **II**. In going from water to

90% isopropyl and *tert*-butyl alcohols, the rate of alkaline hydrolysis increases by a factor of 7 to 15, and of perhydrolysis, by a factor of 3 to 7. These data, in combination with the absence of negative effect of NH_4HCO_3 on the apparent rate of nucleophilic substitution under mild conditions (pH \sim 8.5), lead us to contend (with account taken of the recommendation given in [1, 14]) that mixtures of water with monobasic alcohols are quite suitable for the development of $\text{H}_2\text{O}_2\text{-HO}^-\text{-HCO}_3^-$ nucleophilic oxidative systems for decomposition of ecotoxicants.

As concerns mixtures of water with dihydric alcohols, our prognosis is less optimistic. According to our data, ethylene glycol appreciably reduces the nucleophilic reactivity of hydroxide and hydroperoxide ions; therefore, it is unlikely to be preferred for the preparation of the corresponding degassing systems. On the other hand, mixtures of water with dihydric alcohols (such as propylene glycol) were recommended for oxidative degassing of mustard gas, for propylene glycol reduces the oxidation rate to a lesser extent than do monohydric alcohols [1]. Glycols also attract interest from the viewpoint of preparing on their basis of low-temperature microdispersion compositions. As we already noted, high rate of decomposition of a toxic substrate is only one among at least six requirements to degassing systems [6]. Undoubtedly, recommendations concerning the rate of decomposition are taken into account while developing really operating compositions, but these recommendations are not always fulfilled rigorously.

The above stated may be illustrated by the data of Menger and Rourk [6] and Wagner and Yang [7] who developed by a semiempirical method low-temperature microdispersions on the basis of the $\text{H}_2\text{O}_2\text{-HO}^-$ and $\text{H}_2\text{O}_2\text{-HO}^-\text{-HCO}_3^-$ systems. These systems decomposed a mixture of HD, GB, and VX at a high rate. It should be emphasized that monohydric alcohols are usually indispensable components of various microdispersions like water–oil and oil–water.

EXPERIMENTAL

Ethyl 4-nitrophenyl ethylphosphonate (**I**), 4-nitrophenyl 4-toluenesulfonate (**III**), and 4-nitrophenyl dimethylcarbamate (**IV**) were synthesized and purified by the procedures described in [5]. Their physical parameters (melting points and refractive indices) and UV spectra were consistent with published data. Commercial diethyl 4-nitrophenyl phosphate (**II**) (from Aldrich) was used without additional purification.

Hydrogen peroxide (a \sim 30% solution in water, analytical grade) was preliminarily distilled under reduced pressure (5 mm). Commercial potassium hydroxide and sodium hydroxide (Lacheme), ammonium hydrogen carbonate of chemically pure grade, potassium chloride, and sodium hydrogen phosphate (buffer component) were used without additional purification. 18-Crown-6 was recrystallized from benzene to a constant melting point (34°C) [21]. Isopropyl and *tert*-butyl alcohols were dried over calcium oxide and then distilled over a fresh portion of CaO and without it [15]. Ethylene glycol was purified as described in [22]. Solutions were prepared using doubly distilled water.

Procedure for kinetic measurements. Solutions of reactants were prepared just before each series of kinetic experiments. Solutions of alkalis and hydrogen peroxide were prepared, and their concentration (activity) was determined, by exactly the same procedure as that reported in [5]. The acidity of solutions was monitored using an OP 211/1 Radelhis pH-meter (Hungary) with an accuracy of ± 0.05 pH unit; the concentration of hydrogen peroxide was determined by permanganatometric titration [23]. Buffer solutions were adjusted to a required pH value by adding a concentrated solution of KOH or HCl. The concentrations of ammonium hydrogen carbonate and other additives were calculated from the sample weight. Solutions of nucleophilic reagents in aqueous–alcoholic mixtures were prepared by mixing required amounts of the alcohol and aqueous solution of the reagent with a known concentration. The reagent concentration was calculated from the overall volume of the alcohol and aqueous solution (change of the volume on mixing was neglected). The reagent concentration was varied by dilution of the initial solution either with pure solvent or with a solution containing an appropriate component (or components) whose concentration was maintained constant in a given series of experiments. Aqueous solutions were mixed with the corresponding alcohols just before kinetic measurements to exclude distortion of the kinetic parameters as a result of possible decomposition of hydrogen peroxide under alkaline conditions (which is accelerated by alcohols [24]). The kinetic data were characterized by a good reproducibility, and the kinetic laws were strictly fulfilled.

The progress of the reactions was monitored by spectrophotometry (Specord UV-Vis, SF-26), following variation in the absorption of 4-nitrophenoxide ion ($\lambda = 400\text{--}410$ nm). Concentrated solutions of substrates in anhydrous ethanol or dioxane were introduced into

a spectrophotometric cell through a capillary. The initial substrate concentration in kinetic experiments ($\sim 5 \times 10^{-5}$ M) was always much lower than the initial nucleophile concentration. The apparent pseudofirst-order rate constants (k_{ap} , s^{-1}) calculated as described in [5] did not change up to 5–10 half-conversion periods of the substrate. The k_{HO} and k_{HOO} values were determined by least-squares treatment of linear dependences (1), (3), and (4) and were characterized by mean-square deviations. As a rule, the correlation coefficients were no less than 0.99.

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