Nucleophilic Oxidizing Systems Based on Hydrogen Peroxide for Decomposition of Ecotoxicants

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Abstract—The kinetics of oxidation of methylsulfanylbenzene and nucleophilic decomposition of diethyl 4-nitrophenyl phosphate with hydrogen peroxide in the presence of ammonium hydrogen carbonate or boric acid in aqueous, aqueous–alcoholic, micellar, and microemulsion media were studied. Quantitative parameters of the examined processes were determined, and the possibility of using hydrogen peroxide for the design of oxidative nucleophilic decontaminating systems was demonstrated.

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Taking into account huge worldwide stocks of chemical weapons [1–6], the problem implying utilization of highly toxic chemical agents has recently become especially important. The most common chemical weapons may be divided into three main groups: (1) phosphorus acid esters (neurotoxins and structurally similar pesticides, e.g., GB, GD, and Metaphos); (2) organosulfur compounds (blister agents, e.g., Yperite or HD); and (3) compounds with combined (neuroparalytic) action (VX).



Procedures for chemical degradation of organophosphorus compounds are based on hydrolysis in aqueous alkali, oxidative chlorination with a mixture of chlorinated lime and calcium hypochlorite, and alcoholysis with 2-aminoethanol or potassium butoxide, followed by thermal bituminization and stocking of salt concentrates [7–10]. Organosulfur compounds are decomposed by selective oxidation [11–14]. The optimal system for decontamination of toxic chemical agents should ensure their solubilization and simultaneously high rate of decomposition. Therefore, organized nanosize systems such as micellar solutions and microemulsions are promising from the viewpoint of development of ecologically safe decontaminating compositions [11, 12, 15–21]; these systems provide increased reagent concentration at the phase boundary between micelles (oil drop) and water and create favorable conditions for nucleophilic attack on electrophilic centers of toxic substrates [21, 22].

While searching for chemically active components capable of rapidly and irreversibly decomposing toxic chemicals, specific attention is now given to the design of universal oxidative nucleophilic systems for degradation of chemical agents of different natures. For example, nucleophilic reagents are efficient toward phosphorus acid esters and halides (GB) [23, 24], dialkyl sulfides like HD are decomposed by the action of oxidants [16, 25, 26], whereas oxidative nucleophilic systems containing an HOX– OX^- couple (X = OH, Hlg, etc.) are preferred for decontamination of chemical agents like VX or mixtures of compounds belonging to the above three types (GB, HD, VX) [20, 27]. In this respect, hydrogen peroxide due to its dual nature (it is an effective oxidant toward HD analogs [15, 25] and reactive α -nucleophile toward phosphorus acid esters [1, 24, 28]) may be regarded as universal agent in the design of mild and ecologically safe decontaminating systems. The problem related to simultaneous occurrence of oxidative and nucleophilic processes, especially in the presence of activators, implies additional studies aimed at determining the optimal pH value, i.e., that ensuring maximal rates of both oxidation and nucleophilic substitution.

The goal of the present work was to find optimal and universal oxidative nucleophilic decontaminating systems by studying the reactivity of hydrogen peroxide and its derivatives toward electrophilic substrates in microorganized catalytic media with a high solubilizing ability with respect to hydrophobic compounds.

As model substrates we used diethyl 4-nitrophenyl phosphonate (I) (Paraoxon), which is a structural analog of organophosphorus neuroparalytic agents and pesticides [1, 20, 21, 23], and methylsulfanylbenzene (II, thioanisole) as analog of HD in both reactivity and hydrophobic properties [17, 29–34].



As the main decontaminating agent we examined hydrogen peroxide which is a mild and ecologically safe oxidant toward HD analogs, and its anionic form HOO⁻ shows supernucleophilic properties with respect to organophosphorus compounds. In order to enhance the oxidizing power of H_2O_2 , it was activated using ammonium hydrogen carbonate NH_4HCO_3 or boric acid B(OH)₃; the latter are known to convert hydrogen peroxide into peroxo acids which are efficient oxidants [15, 19, 25, 29, 35]. Nucleophilic activity of peroxo anions was studied very poorly [1, 36], though it attracts strong practical interest from the viewpoint of creation of oxidative nucleophilic decontaminating systems.

With a view to overcome mutual insolubility of substrate and decontaminating agent, decomposition of compounds **I** and **II** was performed in nanosize multicomponent systems such as microemulsions, micellar solutions, and aqueous–alcoholic mixtures in the presence or in the absence of surfactant. As the latter we used cetyl(trimethyl)ammonium bromide and Triton X-100 [4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol], taking into account that anionic surfactants were shown previously [37–39] to inhibit processes in the above systems.

Transformations of ester I in the presence of H_2O_2 - HO^- in all the examined media take two main path-

ways, perhydrolysis by the action of HOO⁻ ion generated according to the reaction $H_2O_2 + HO^- \leftrightarrow H_2O +$ HOO⁻ and alkaline hydrolysis by the action of hydroxide ion HO⁻ (Scheme 1). The contribution of the latter process is minimal; it does not exceed 1–5% of the overall rate of substrate consumption [40]. By special experiments we found that no neutral hydrolysis or alcoholysis of I or oxidation of 4-nitrophenoxide ion with hydrogen peroxide occurred in our kinetic experiments or the rates of these reactions were very low. The pK_a value of hydrogen peroxide in water is 11.6, which implies an appreciable concentration of HOO⁻ ions at high pH values.



According to the GLC data, the only product of oxidation of sulfide **II** with hydrogen peroxide under the conditions of kinetic measurements ([**II**] = 2.0×10^{-3} M, [H₂O₂] = 1.1 M, [NH₄HCO₃] ≤ 0.5 M) was methyl phenyl sulfoxide [31] (Scheme 2). No subsequent oxidation of methyl phenyl sulfoxide to the corresponding more toxic sulfone [27] was observed, at least during 24 h after oxidation of **II** started.

Scheme 2.

$$H_2O_2$$
 + PhSMe \longrightarrow PhS(O)Me + H_2O
II

The activating effect of hydrogen carbonate ion in the oxidation of sulfides with hydrogen peroxide is related to generation in the system H_2O_2 -NH₄HCO₃ of hydrogen peroxycarbonate ion HCO₄⁻ which is a stronger oxidant than hydrogen peroxide [15, 25, 30, 41] (Scheme 3).



Equilibrium (1) at pH 8–9 establishes relatively rapidly (in \sim 5–30 min) [25]. Within this pH range

acid–base dissociation of HCO_3^- (p $K_a = 10.3$ [25]) and HCO_4^- ions may be neglected [31].

Peroxoborates are mainly formed in the system H_2O_2 -B(OH)₃ [29, 33] (Scheme 4). The ratio of peroxoborates depends on the initial concentrations of B(OH)₃ and H₂O₂ and pH [33]. At relatively low concentrations of B(OH)₃ and H_2O_2 (<1 M), pH 6–14, the main products are mono- and diperoxoborate ions $B(OH)_3(OOH)^-$ and $B(OH)_2(OOH)_2^-$; whereas at high reactant concentrations polyperoxoborates like $B_2(O_2)_2(O_2H)_n(OH)_{4-n}$ (*n* = 0, 2, 4) predominate [35]. Therefore, distinct separation of oxidation pathways with determination of the reactivity of peroxoborates generated in the system is often difficult; nevertheless, the reaction of sulfides with H_2O_2 is accelerated in the presence of $B(OH)_3$, as compared with oxidation of the same substrate with hydrogen peroxide in the absence of an activator [29, 35].

Scheme 4.

$$B(OH)_{3} + H_{2}O \longrightarrow B(OH)_{4}^{-} + H^{+}$$

$$B(OH)_{4}^{-} + H_{2}O_{2} \longrightarrow B(OH)_{3}(OOH)^{-} + H_{2}O \quad (3)$$

$$B(OH)_{3}(OOH)^{-} + H_{2}O_{2} \longrightarrow B(OH)_{2}(OOH)_{2}^{-} + H_{2}O \quad (4)$$

There are no published data on nucleophilic reactivity of peroxoborates, but peroxo anions HCO_4^- and CO_4^{2-} are known [36] to act as typical nucleophiles. The second-order rate constants for the reactions of HCO_4^- and CO_4^{2-} with ester I are equal to 0.01 and 0.105 1 mol⁻¹ s⁻¹, respectively. It might be expected that activation of hydrogen peroxide with borates and hydrogen carbonates would give rise to additional paths of decomposition of organophosphorus compounds according to nucleophilic mechanism with participation of peroxo anions generated in the systems B(OH)₃–H₂O₂ and NH₄HCO₃–H₂O₂.

Figure 1 shows the pH dependences of the apparent rate constants for decomposition of substrates I and II with hydrogen peroxide in the presence and in the absence of activators. The general trend is sharp reduction of the rate of oxidation of sulfide II with hydrogen peroxide (Fig. 1a, 1b; curve 2) and hydrogen peroxy carbonate HCO₄ (Fig. 1c, 1d; curve 2) with rise in pH (pH >9.5). The observed pH dependences may be rationalized as follows (on a qualitative level): the oxidation process involves both neutral hydrogen peroxide and its anion HO₂; the concentration of the latter increases as pH rises, whereas its oxidizing power is weaker than that of neutral species [30, 35]. Increase of pH also leads to reduction of the concentration of the active oxidant species as a result of dissociation of HCO_4^- ions to CO_4^{2-} ; like HO_2^- , CO_4^{2-} is a weaker oxidant than its protonated form [32, 36].

The presence of B(OH)₃ in the system containing hydrogen peroxide gives rise to extremal dependence of the apparent rate constants for the oxidation of sulfide **II** versus pH of aqueous solution, the maximum being located at pH ~10 (Fig. 1e, 2). This pattern is consistent with the corresponding variation of the concentration of the active species, B(OH)₃(OOH)⁻ and B(OH)₂(OOH)₂⁻ (Fig. 2), calculated according to equilibria (3) and (4) [35].

The pH dependences of the apparent rate constants for decomposition of substrate I with peroxide ion in the presence and in the absence of activators in aqueous and aqueous-alcoholic media are traditional. A more or less significant nucleophilic substitution pathway appears at pH \geq 10, and the reaction rate further increases in parallel with pH (Fig. 1, 1). It is interesting that the rate of nucleophilic process increases almost twofold upon activation of hydrogen peroxide with $B(OH)_3$ (Fig. 1e; cf. curves 1 and 3) and by a factor of 1.3 in the presence of NH_4HCO_3 (Fig. 1c, I) as compared to the reaction rate in the absence of an activator (Fig. 1c, 3). The only reasonable explanation is participation of peroxo anions HCO₄, B(OH)₃(OOH)⁻, B(OH)₂(OOH)⁻₂, etc. in nucleophilic substitution. In other words, peroxycarbonate and peroxoborate ions are characterized by dual oxidative-nucleophilic nature, which may be regarded as an additional preference (apart from economical and ecological) for using hydrogen carbonate and borate catalysis in the design of universal decontaminating compositions.

The given data unambiguously indicate that the main problem in the development of oxidative nucleophilic systems on the basis of hydrogen peroxide is proper choice of the activating agent and acidity of the medium to ensure maximal rate of decomposition of ester I and of oxidation of sulfide II.

Figure 3 shows the dependence of the apparent rate constant for decomposition of ester I in the system H_2O_2 -HO⁻ in the presence of cetyl(trimethyl)ammonium bromide (CTAB) upon concentration of the latter in the pH range from 8.5 to 12.5 (micellar solution). These data clearly demonstrate that the absolute value of the observed micellar effect increases more than twofold as pH decreases from 12.5 to 8.5. Change of pK_a value of hydrogen peroxide in going to micellar



Fig. 1. Dependences of the apparent rate constants upon pH for (*1*, 3) nucleophilic replacement in diethyl 4-nitrophenyl phosphate (**I**) and (*2*) oxidation of methylsulfanylbenzene (**II**) with hydrogen peroxide in the absence and in the presence of activators at 25°C: (a) water, phosphate buffer, (*1*) $[H_2O_2]_0 = 1.12$, (*2*) 1.12 M; (b) water–propan-2-ol (74.8:25.2, wt %), (*1*) $[H_2O_2]_0 = 1$, (*2*) $[H_2O_2]_0 = 1.13$ M; (c) water, (*1*) $[H_2O_2]_0 = 1$ M, $[NH_4HCO_3] = 0.1$ M; (2) $[H_2O_2]_0 = 1.13$ M, $[NH_4HCO_3] = 0.066$ M; (3) $[H_2O_2]_0 = 1$ M; (d) water–propan-2-ol (74.8:25.2, wt %), (*1*) $[H_2O_2]_0 = 1$ M, $[NH_4HCO_3] = 0.066$ M; (2) $[H_2O_2]_0 = 1.13$ M, $[NH_4HCO_3] = 0.066$ M; (3) $[H_2O_2]_0 = 1$ M; (3) $[H_2O_2]_0 = 1$ M, $[B(OH)_3] = 0.1$ M, (2) $[H_2O_2]_0 = 1$ M, $[B(OH)_3] = 0.1$ M; (3) $[H_2O_2]_0 = 1$ M.

solution [42] (which is especially appreciable in weakly alkaline medium) in combination with micellar catalytic effect (up to 15-fold) makes the rate of decomposition according to nucleophilic mechanism at pH 8.5 comparable to the rate of analogous process at pH ~10.2 at a constant concentration of hydrogen peroxide.

The results of studying decomposition of compounds I and II in micellar systems H₂O₂-CTAB (Fig. 4a), H₂O₂-NH₄HCO₃-CTAB (Fig. 4b), and H_2O_2 -B(OH)₃ (Fig. 4c) allowed us to draw some preliminary conclusions. In particular, micellar catalysis is effective in nucleophilic and redox reactions involving anionic species [HOO⁻, HCO⁻₄, B(OH)₃(OOH)⁻, $B(OH)_2(OOH)_2$ in the presence of cationic surfactant (CTAB) in weakly alkaline medium (pH 8.5-9.5), whereas the rate of oxidation of sulfide II with hydrogen peroxide sharply decreases in the presence of CTAB (Fig. 4a); activation of hydrogen peroxide with $B(OH)_3$ in the reaction with ester I increases the micellar effect by a factor of ~ 1.5 (Fig. 4c; cf. curves 1 and 3), whereas the catalytic effect of CTAB in the presence of NH₄HCO₃ is weaker (Fig. 4b; cf. curves 1 and 3).

Table 1 contains the second-order apparent rate constants for the oxidation of sulfide $\mathbf{II}(k_{ap,ox}^2)$ and nucleophilic replacement in ester $\mathbf{I}(k_{ap,nu}^2)$ with hydrogen peroxide in different media in the absence and in the presence of NH₄HCO₃ and B(OH)₃ as activators at pH 9. The rate constants were calculated from the overall concentration of H₂O₂ (oxidation) and HOO⁻ (nucleophilic replacement) with no account taken of their distribution over pseudophases (surfactant micelles or oil drops) and contributions of pathways involving peroxo anions generated according to reactions (1), (3), and (4). This approach seems to be more informative for comparison of the rates of substrate decomposition in dynamic media that are prone to phase and aggregation transitions and are characterized by different solubilizing effects on hydrophobic sub-strate. In addition, the ratios i_{ox} (i_{nu}) of $k_{\text{ap,ox}}^2$ ($k_{\text{ap,nu}}^2$) for all the examined systems and the apparent rate constants in water in the absence of activator are given (Table 1, no. 1). The $i_{ox/nu}$ values were assumed to characterize the efficiency of oxidative (nucleophilic) system in going from aqueous to nanosized and/or activated media, and the product i_{ox} i_{nu} was assumed to quantitatively characterize the efficiency of universal system for simultaneous oxidation of sulfide II and decomposition of ester I.



Fig. 2. Dependences of the concentration of (1) monoperoxoborate $B(OH)_3(OOH)^-$ and (2) diperoxoborate $B(OH)_2(OOH)_2^-$ on pH of aqueous solution, 25°C; water, $[H_2O_2]_0 = 1 \text{ M}$, $[B(OH)_3] = 0.1 \text{ M}$.



Fig. 3. Dependences of the rate of decomposition of diethyl 4-nitrophenyl phosphate upon concentration of cetyl(trimethyl)ammonium bromide in the system H_2O_2 -HO⁻ at pH (1) 8.5, (2) 9.5, (3) 10.5, (4) 11.5, and (5) 12.0; [HOO⁻] = 0.002 M, 25°C.

The data in Table 1 indicate the absence of strict relation between properties of the reaction medium and reactivity of the main decontaminating species in the absence (H₂O₂, HOO⁻) and in the presence of activator [H₂O₂, HOO⁻, HCO⁻₄, B(OH)₃(OOH)⁻, B(OH)₂(OOH)²₂] in both oxidation of sulfide **II** and nucleophilic decomposition of ester **I**. Nevertheless, some general trends in variation of the efficiency of hydrogen peroxide systems in going from aqueous to aqueous–alcoholic and organized media may be noted, and the reactivities of the examined decontaminating systems may be compared. Activation of hydrogen peroxide with am-

Table 1. Apparent second-order rate constants k_{ap}^2 ($1 \text{ mol}^{-1} \text{ s}^{-1}$) for the oxidation of sulfide II and nucleophilic substitution in ester I with H_2O_2 in different media

	Reaction medium ^a		Oxidation		Nucleophilic replacement		
No.		Activator	$k_{\rm ap, ox}^2 \times 10^4,$ 1 mol ⁻¹ s ⁻¹	$i_{\rm ox}{}^{\rm b}$	$k_{\rm ap, nu}^2 \times 10^2,$ 1 mol ⁻¹ s ⁻¹	<i>i</i> _{nu} ^c	i _{ox} i _{nu}
1	$H_{2}O(1)$	—	14.3	1.00	53.0	1.00	1.00
2	$H_{2}O(1)$	NH ₄ HCO ₃	85.8	6.00	95.6	1.80	10.8
3	$H_{2}O(1)$	B(OH) ₃	170	11.9	132	2.50	30.0
4	H_2O –propan-2-ol (2)	-	4.00	0.30	41.0	0.80	0.24
5	H_2O –propan-2-ol (2)	NH ₄ HCO ₃	20.5	1.40	35.1	0.70	1.00
6	H_2O -butan-2-ol (3)	-	2.00	0.14	43.4	0.80	0.10
7	H_2O -butan-2-ol (3)	NH ₄ HCO ₃	10.6	0.74	38.8	0.73	0.54
8	H ₂ O–ethylene glycol (4)	_	8.32	0.60	32.0	0.60	0.36
9	H ₂ O–ethylene glycol (4)	NH ₄ HCO ₃	40.6	2.80	30.1	0.60	1.70
11	H ₂ O–propan-2-ol–CTAB (5)	NH ₄ HCO ₃	50.1	3.50	68.5	1.30	4.60
12	H ₂ O–ethylene glycol– CTAB (6)	_	20.2	1.40	86.4	1.63	2.30
13	H ₂ O–ethylene glycol– CTAB (6)	NH ₄ HCO ₃	94.4	6.60	100	1.90	12.5
14	H ₂ O–ethylene glycol– CTAB (6)	B(OH) ₃	67.0	4.70	250	4.70	22.0
15	H ₂ O–ethylene glycol– X-100 (7)	_	12.8	0.90	35.2	0.70	0.63
16	$H_2O-CTAB(8)$	_	6.77	0.47	602	11.4	5.40
17	$H_2O-CTAB(8)$	NH ₄ HCO ₃	75.5	5.30	142	2.70	14.3
18	$H_2O-CTAB(8)$	B(OH) ₃	165	11.5	721	13.6	156
19	H ₂ O–X-100 (9)	-	12.3	0.86	116	2.20	1.90
20	Microemulsion (10)	_	4.72	0.33	74.0	1.40	0.46
21	Microemulsion (10)	NH ₄ HCO ₃	6.23	0.44	34.1	0.64	0.30
22	Microemulsion (10)	B(OH) ₃	4.68	0.33	21.2	0.40	0.13

^a In parentheses is given the number of the reaction medium according to Table 3. ^b i_{ox} is the ratio of the oxidation rate constant $k_{ap,ox}^2$ to the corresponding constant in water. ^c i_{nu} is the ratio of the rate constant $k_{ap,nu}^2$ for nucleophilic substitution to the corresponding constant in water.

monium hydrogen carbonate and boric acid increases the rate of oxidation of sulfide II by at least an order of magnitude, and the rate of decomposition of ester I, by a factor of 1.5-2 (Table 1, entry nos. 2, 3, 13, 14, 18). The use of $B(OH)_3$ as activator is more advantageous as compared to NH₄HCO₃; unlike peroxycarbonate ion active at pH 7-9, the maximal oxidizing power of peroxoborates is retained at pH 10, the accelerations of both processes being comparable.

Comparison of the i_{ox} i_{nu} values for entry nos. 2 and 17, 3 and 18, 5 and 11, and 9 and 13 (Table 1) showed that the presence of cationic surfactant (CTAB) in activated media enhances its decontaminating efficiency. In addition, micellar and aqueous-alcoholic surfactant mixtures, especially in the presence of salt activators, considerably improve the solubility of substrates (Table 2), which is one of the main advantages of these media from the viewpoint of development of oxidative nucleophilic compositions for decontamination of toxic chemical agents. The most effective universal decontaminating system on the basis of hydrogen peroxide is a micellar solution of CTAB in the presence of $B(OH)_3$ (Table 1, no. 18); it ensures the highest reactivity of anions in oxidative nucleophilic processes with high constants $K_{\rm S}$ (Table 2, no. 3) for binding of both substrates I and II by CTAB micelles.



Fig. 4. Dependences of the apparent rate constants upon concentration of cetyl(trimethyl)ammonium bromide for (1, 3) nucleophilic replacement in diethyl 4-nitrophenyl phosphate (I) and (2) oxidation of methylsulfanylbenzene (II) with hydrogen peroxide in the absence and in the presence of activators at 25°C: (a) water–CTAB, $[H_2O_2]_0 = 1$ M, (1) pH 8.5, (2) pH 8.2; (b) water–CTAB, (1) $[H_2O_2]_0 = 1$ M, $[NH_4HCO_3] = 0.5$ M, pH 8.5; (2) $[H_2O_2]_0 = 1.14$ M, $[NH_4HCO_3] = 0.083$ M, pH 8.5; (3) $[H_2O_2]_0 = 1$ M; (c) water–CTAB, (1) $[H_2O_2]_0 = 1$ M, $[B(OH)_3] = 0.1$ M, pH 9.5; (2) $[H_2O_2]_0 = 1$ M, $[B(OH)_3] = 0.1$ M, pH 9.5; (3) $[H_2O_2]_0 = 1$ M, pH 9.5.

Despite obvious appeal of microemulsions as strongly solubilizing media (Table 2, no. 6), carrying out oxidative nucleophilic processes in these media is not free from some disadvantages. First, microemulsions are as a rule multi-component systems necessarily containing an oil (i.e., toxic organic solvent), which considerably reduces their ecological safety. Second, the data in Table 1(nos. 20–22) show that both oxidative and nucleophilic processes in microemulsions are characterized by lower rates relative to analogous reactions in aqueous, aqueous–alcoholic, and micellar systems, the K_s values being comparable for both substrates (Table 2, cf. nos. 1 and 6).

Thus our results showed that weakly alkaline (pH 8–9) aqueous and aqueous–alcoholic mixtures containing hydrogen peroxide, cationic surfactant, and activator ensure high degree of substrate solubilization

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and enhance the reactivity of oxidants and nucleophiles (as compared to aqueous solutions); in addition, such systems are simple to prepare and are ecologi-

Table 2. Binding constants $(K_S, 1 \text{ mol}^{-1})$ of substrates I and II in different media

No	Prostion modium	K _S , l/mol			
INO.	Reaction medium	Ι	Π		
1	H ₂ O–CTAB	350 [42]	400 [38]		
2	H ₂ O-CTAB-NH ₄ HCO ₃	700 [38]	900 [38]		
3	H ₂ O-CTAB-B(OH) ₃	500	300		
4	H ₂ O-ethylene glycol-CTAB	50	150		
5	H ₂ O–ethylene glycol–CTAB– NH ₄ HCO ₃	90	250		
6	Microemulsion	250	300		

No.	Reaction medium	Water	CTAB	Propan-2-ol	X-100	Butan-1-ol	Ethylene glycol	Hexane
1	Water	100						
2	Water-alcohol	74.8		25.2				
3		74.7				25.3 ^a		
4		67.7					32.3	
5	Water-alcohol-surfactant	70.0	5.0	25.0				
6		68.8	1.8				29.4	
7		70.0			0.1		29.9	
8	Micellar solution	99.7–99.5	0.3-0.5					
9		99.9			0.1			
10	Microemulsion	88.0	5.0			5.0		2.0

Table 3. Compositions of the reaction media (wt %)

^a Butan-2-ol.

cally safe. Therefore, they may be regarded as promising for decontamination of toxic chemicals according to oxidative nucleophilic mechanism.

EXPERIMENTAL

Commercial diethyl 4-nitrophenyl phosphate (Aldrich), ammonium hydrogen carbonate of chemically pure grade, sodium hydrogen phosphate Na₂HPO₄·2H₂O of chemically pure grade, boric acid of chemically pure grade, cetyl(trimethyl)ammonium bromide and Triton X-100 (Aldrich), and potassium hydroxide (Lachema) were used without preliminary purification. Propan-2-ol, butan-1-ol, butan-2-ol, and ethylene glycol were purified by standard methods [43]. Solutions were prepared using doubly distilled water. Methylsulfanylbenzene was synthesized according to the procedure described in [44]. Hydrogen peroxide of analytical grade (33% aqueous solution) was preliminarily distilled under reduced pressure (5 mm), and its concentration was monitored by titration with potassium permanganate.

The compositions of the examined reaction media are given in Table 3. Solutions of reactants were prepared just before kinetic measurements. Aqueous– alcoholic solutions (Table 3, nos. 2–4) were prepared by mixing required volumes of alcohol and aqueous solutions of reactants with accurately determined concentrations and pH values. The reactant concentrations were calculated on the overall volume of aqueous– alcoholic mixture. Mixtures alcohol–water–surfactant (Table 3, nos. 5–7) with different reactant ratios (by weight) were prepared by mixing all components. In doing so, the aqueous phase was a solution of potassium hydroxide and hydrogen peroxide with accurately determined concentrations. The concentrations of oxidants and nucleophiles in the mixture were calculated on the overall volume of the alcohol–water– surfactant mixture.

The concentration of surfactants in micellar solutions (Table 3, nos. 8–9) was varied by dilution of a stock solution containing components whose concentration remained constant in a given series of experiments.

Butan-1-ol-water-surfactant-hexane microemulsion (Table 3, no. 10) was prepared by mixing the components in the following order: aqueous solution of reactants with required concentrations, surfactant, alcohol, hexane. Mixing and subsequent shaking over a period of no longer than 1 min gave a transparent microemulsion. Peroxide-hydrogen carbonate solutions were kept for at least 30 min for equilibration [Eq. (1)].

The acidity of solutions was monitored using a Metrohm-827 pH-meter (Switzerland) with an accuracy of ± 0.05 pH unit. Solutions were adjusted to a required pH value by adding a concentrated solution of potassium hydroxide. Special experiments showed that no side decomposition of hydrogen peroxide occurred at high pH values over a period of 5 h (this time was sufficient to perform kinetic measurements for one series of experiments). No oxidation of 4-nitrophenol liberated in the course of nucleophilic substitution process was observed.

The progress of oxidation and nucleophilic substitution was monitored by spectrophotometry according to the procedure described previously [31, 38]. Nucleophilic substitution was monitored by measuring the absorbance at λ_{max} 405 nm (4-nitrophenoxide ion) at $[\text{HOO}^-] >> [\mathbf{I}]$. Oxidation reactions were examined under the condition $[\mathbf{II}]_0 \ll [\text{NH}_4\text{HCO}_3]_0 \ll [\text{H}_2\text{O}_2]_0$; the concentration of \mathbf{II} did not exceed 2×10^{-3} M.

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