Design of green microorganized systems for decontamination of ecotoxicants*

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Abstract: Due to population upsurge, pesticides (derivatives of organophosphorus acids included) find widespread use in agriculture. The toxicity and long-term environmental hazard of such compounds require detailed studies on decomposition mechanisms of the pesticides and development of efficient, readily available, and inexpensive systems for their decontamination.

A simple and straightforward method for the decomposition of organophosphorus compounds involves their reactions with nucleophiles. Studies on the reactivity of "normal" and α-nucleophiles toward electron-deficient centers allowed us to state a number of basic principles on the nature of the α-effect. One of the most important conclusions is: It is unlikely that the structure variations in the known α-nucleophiles will result in higher reactivity than that of hydroxylamine anion. As a practical matter, the essential disadvantages of decomposition of organophosphorus compounds in water and organic solvents are: (i) instability of active nucleophiles and oxidizing agents, (ii) corrosiveness, and (iii) extremely low solubility of organophosphorus compounds in water. These dictate the strategy of further studies, namely, carrying out the reaction in microorganized media.

The first research line involves the development of the functional imidazole-based detergents functionalized with α-nucleophilic fragments. A number of efficient detergents were first synthesized. An examination of the nucleophilicity of the functional fragments in water and in the micellar phase and quantitative assessment of the factors responsible for the micellar effects showed unambiguously that the main cause of the observed accelerations is the substrate concentrating in the micellar pseudophase.

The second research line consists of studies on the reactivity of versatile oxidative/nucleophilic systems involving H_2O_2/activator and polyhalide ion organocomplexes in water, aqueous alcohols, and micelles of cationic detergents. The novel sources of "active" halogen are highly competitive both with conventional hazardous chlorine derivatives and "green" systems involving H_2O_2/activator.

Keywords: pesticide decontamination; organophosphorus compounds; decomposition mechanisms; α-effect; microorganized media.

INTRODUCTION

The 20th century became an epoch of phenomenal growth of the world economy and continuous improvements in the quality of life in developed countries. However, as a result, there has been an increase in consumption of the Earth's resources and global environmental contamination is happening at an alarming rate. Using the planet's resources responsibly is not just a matter of words, but a matter of mankind's survival

Pesticides, derivatives of phosphorus acids included, find widespread use in agriculture, and their role will grow with further increase of the planet's population [1]. Without pesticides, the survival of millions of people in the poorest countries would be compromised because of illnesses and starvation. However, many of the products that kill pests can lead to fatal poisoning in humans when used in rather small concentrations [1–4].

Paraoxon   Parathion

Phenitrothion   Thymet
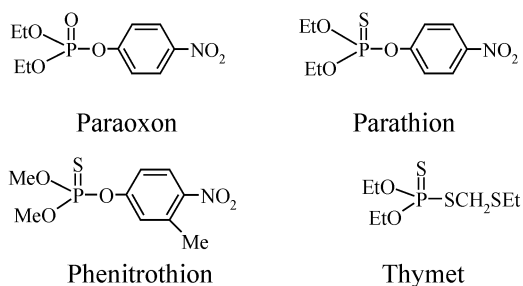
Chemical warfare (CW) agents from among organophosphorus compounds (nerve agents) are similar to pesticides in their chemistry and toxicology. Despite the similarity, the first differ from the latter in having an incomparably higher acute toxicity.

GB   GD   GA   Tammeline ester   VX
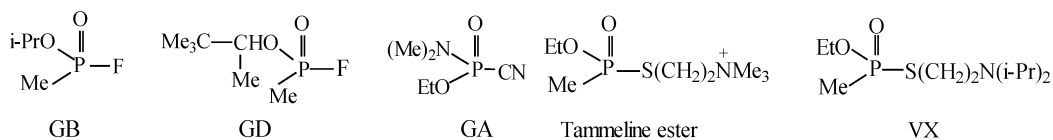
At the same time, inexpensive organophosphorus compounds can be readily synthesized, especially Tabun (GA) and VX. Such compounds do not require an advanced chemical industry, and disarmament treaties have provided information on toxicity and synthesis of these compounds. Huge stocks of CW agents have been accumulated both by the United States and the former Soviet Union. They are in stock for decades, and their further storage represents serious danger.

From the above reasoning, it is clear that the search for and design of reagents for efficient decomposition of organophosphorus ecotoxic substrates is a problem of undoubted importance [5–18].

Green chemistry is an integral component of modern chemical science in the light of "responsible approach" and "sustainable development" principles [19–23]. Green chemistry involves the development of chemical products and processes aimed at the reduction and, finally, complete abandonment of manufacturing of hazardous compounds. However, the principles of green chemistry came to attention only recently, whereas the ecotoxicants have been accumulated by mankind in huge quantities and their manufacture still proceeds.

In solving the problem of decomposition and recycling of ecotoxicants, we proceed from both the green chemistry requirements and providing high reaction rates together with efficient solubilization of hardly soluble organophosphorus.

## α-NUCLEOPHILES IN DECOMPOSITION OF ORGANOPHOSPHORES

Within the last 50 years, the design of reagents and systems efficient in the decomposition of organophosphores is accompanied by the efforts of researchers to study the nature of α-effect, which at the moment still remains one of the intriguing problems of modern physical organic chemistry [24–52]. Indeed, these investigations made it possible to obtain the reactivators of organophosphorous-inhibited cholinesterase and chemically active agents for water-organic and aqueous formulations efficient in the decomposition of ecotoxic pesticides and CW agents [5–18]. Although an intensive search for and design of these compounds proceed, it often has a screening character and the theory of α-effect is far from completed.

Comprehensive studies on the kinetic behavior of a wide class of nucleophiles carried out in our Institute—"normal" (alcohols, phenols, amines) [53–55], α-nucleophiles (inorganic anions [56,57], hydroxylamines [57–59], oximes [60,61], amidoximes [62,63], hydroxamic acids [64,65]) in decomposition of 4-nitrophenyl esters of diethylphosphoric (paraoxon), diethylphosphonic (armin), toluenesulfonic, and *N,N*-dimethylcarbamic acids—has allowed us to make a series of conclusions on the nature of α-effect and substantiate the research lines for the search for novel supernucleophilic reagents.

| Paraoxon | Armine | *p*-Nitrophenyl-toluene sulfonate | *p*-Nitrophenyl-*N,N*-dimethyl carbamate |
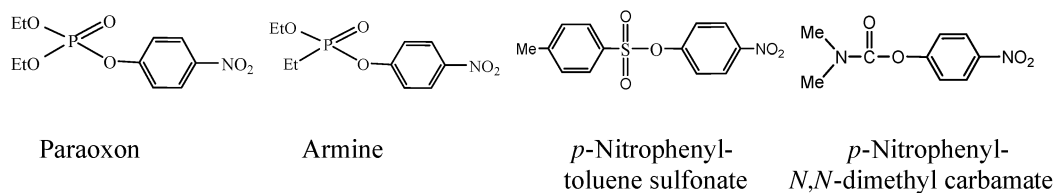
The nature of the α-effect is not uniform. Acid–base catalysis, donor–acceptor interactions, and solvation effects are of greater importance [24–65]. The relationship between reactivity and basicity for the most efficient inorganic α-nucleophiles was first established [56,57]. Hydroxylamine anion was shown to be a typical α-nucleophile and the "leader" in the series of α-nucleophiles (Fig. 1) [57–59]. And, finally, the thesis of the limiting reactivity in α-nucleophiles series was stated. Structure modifications of the known α-nucleophiles will hardly result in the compounds decomposing organophosphores more efficiently than hydroxylamine anion (Fig. 1) [57–59]. Consequently, we have to look for new approaches in the design of supernucleophilic systems.

From a practical point of view, significant disadvantages of organophosphores in water and organic solvents are as follows: (i) low stability of active nucleophiles and oxidizers like peroxides and hypohalogenites, (ii) corrosive inflammable media, and (iii) extremely low solubility of organophosphores in water. The last factor is important because the rate of organophosphore decontamination is governed both by the reactivity and the rate of dissolving of organophosphores. This can lead to confusion—a low decontamination rate for highly reactive α-nucleophile.
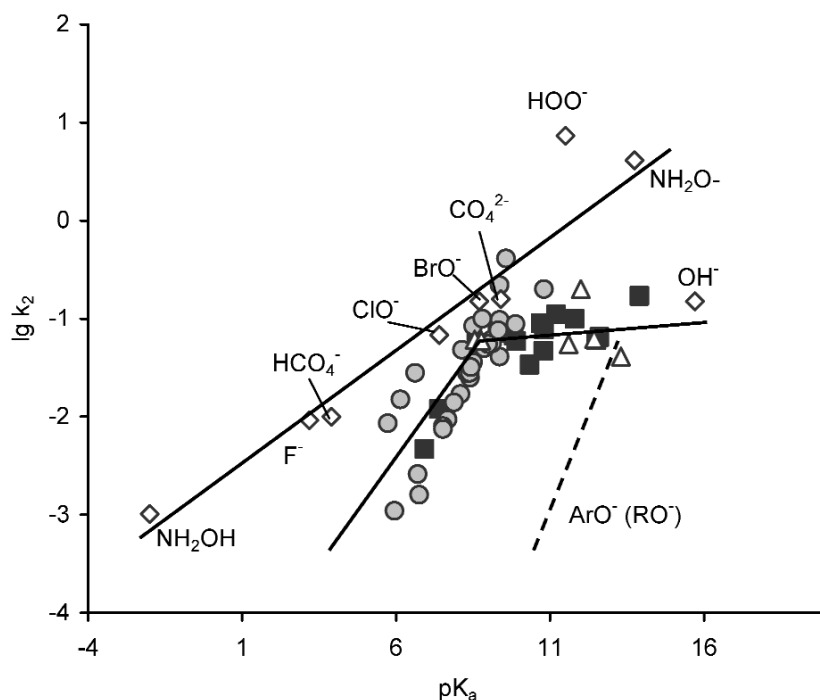
Fig. 1 Brønsted plots for interaction of α-nucleophiles with armine (□ = oximes, $n = 15$; ○ = hydroxamic acids, $n = 30$; △ = amidoximes, $n = 6$; ◇ = inorganic α-nucleophiles); aqueous solution, with ionic strength of 1.0 M (KCl), 25 °C.

SUPERNUCLEOPHILIC SYSTEMS ON THE BASIS OF FUNCTIONAL DETERGENTS

Microorganized medium (micellarized surfactants and microemulsions) is one of the most promising media in the design of supernucleophilic systems for decomposition of ecotoxicants [66–76]. The basic research line is the design of functional surfactants with imidazolium core in their head-groups and α-nucleophiles moiety—oximate, amidoximate, or hydroxamate groups.

The immediate advantage of functional surfactants is that the maximum possible "local" concentration of α-nucleophilic fragment is reached at any micelle concentration and the highest reaction rates are observed for the most hydrophobic esters. In fact, the factors that counteract the dissolving rate of organophosphores in water, in this case, on the contrary, assist an increase in decontamination rate.

We first synthesized a series of surfactants whose structure variations involve exclusively the changes in the nature of the α-nucleophilic fragment in the head-group [77–83].
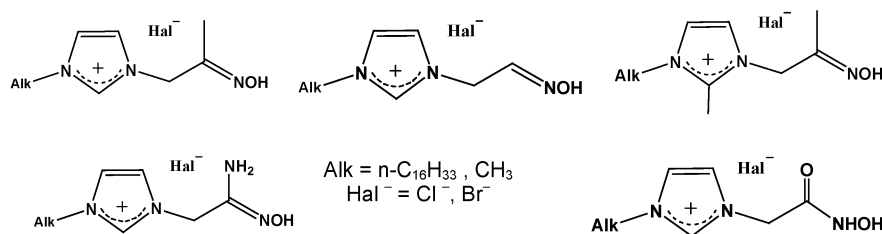
This had made it possible to compare nucleophilicities of functional detergents in water and micellar pseudophase. Transfer of the reaction from water into micelles of functional surfactants is not accompanied by sufficient change in the reactivity of α-nucleophilic centers, and they form the same orders of nucleophilicity as their methyl analogs [81,82]. The conclusion that the order of nucleophilicity remains unchanged is unusual and allows one to predict the changes in reactivity of functional surfactants (i.e., to provide the desirable activity level of functional surfactant).

The micellar effects of functional surfactant can be estimated from the equation

$$\left(\frac{k_{2,\,app}^{m}}{k_{2,\,app}^{w}}\right)_{max} = \frac{k_{2}^{m}}{k_{2}^{w}} \cdot P_{S} \cdot \frac{K_{a,\,app}}{K_{a}} \tag{1}$$

which accounts for changes in nucleophilicity of the reactive center (k_2^m and k_2^w, M^{-1} s^{-1}), its basicity ($K_{a,app}$ and K_a) and substrate concentrating (P_S) in transferring the decomposition reaction from water into micelle [77–83].

An examination of experimental data within the framework of this relationship clearly demonstrates that
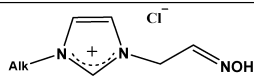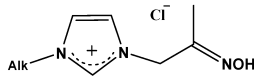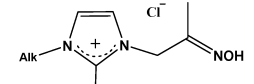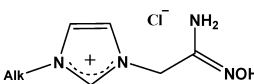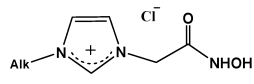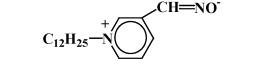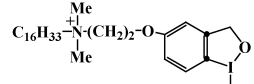
- differences in free energies of activation for reactions in micelles of functional surfactants are negligibly small as compared with those in water;
- the main factor responsible for the micellar effect is the substrate concentration which depends directly on the partition coefficient; the higher the partition coefficient, the more significant an increase in rates. Since the model substrates (simulants) are electroneutral polar compounds, this suggests that the hydrophobic interactions are responsible for concentrating effects;
- methyl analogs will react with the substrates at the same rates as the surfactants if their concentration is comparable with "local" concentration of α-nucleophilic fragment in micelle (i.e., 2–4 M*); it is unlikely that the solutions with so high concentration of methyl analogs can be prepared, therefore, it is clear that the methyl analogs (as nucleophiles) are unable to compete with functional surfactants; and
- optimum conditions in decomposition of organophosphores meet the "green criteria". In comparison with reactions in water, the maximum possible increase in decomposition rate of ecotoxicants is observed at surfactant concentration close to critical micelle concentration (cmc) and acidity of the medium, which is one order of magnitude smaller than acid dissociation constants of functional surfactant in water and micelles (eq. 1). It is this condition in which the observed increase in rate becomes abnormally high and amounts to 10^3–10^4 [79–81].

The half-lives for organophosphores indicate that the new functional surfactants exceed the reactivity of the most efficient surfactants in their reactivity (Table 1). At the same time, it is should not be mistaken that the novel functional surfactants can be used as a basis for nucleophilic decontamination formulations for large surfaces or recycling of a large amount of organophosphores for some reasons, first of all for economic ones. However, the possibility of their use in individual defense kits and mixtures for treating the unique equipment deserves great attention.

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*1 M = 1 mol·dm^{-3}

Table 1 Half-life times ($\tau_{1/2}$) and relative accelerations in decomposition of model organophosphorus substrates (water, 25 °C).

| Compound	Alk	Paraoxon		Armine	
		$\tau_{1/2}$, s	Acceleration	$\tau_{1/2}$, s	Acceleration
(imidazolium, Cl⁻, ...NOH)	CH_3	3650	260	900	~ 10^3
	$C_{16}H_{33}$	14		≤2	
(imidazolium, Cl⁻, ...NOH)	CH_3	8250	190	770	380
	$C_{16}H_{33}$	43		2	
(imidazolium, Cl⁻, ...NOH)	CH_3	6200	140	990	330
	$C_{16}H_{33}$	45		3	
(imidazolium, Cl⁻, NH₂ ...NOH)	CH_3	4100	110	690	230
	$C_{16}H_{33}$	37		3	
(imidazolium, Cl⁻, O NHOH)	CH_3	41000	230	4950	250
	$C_{16}H_{33}$	180		20	
($C_{12}H_{25}$–pyridinium, CH=NO⁻)	--	600 [67]	--	--	--
($C_{16}H_{33}$–N⁺(Me)₂–(CH₂)₂–O– benzofuranone, O⁻)	--	200 [70]	--	--	--

Note: $\tau_{1/2}$ were estimated in terms of full ionization of nucleophilic fragment and substrate binding >99 % adjusted by acidity of medium and concentration of the detergent, respectively.

NEW SOURCES OF "ACTIVE" HALOGEN FOR OXIDATIVE/NUCLEOPHILIC SYSTEMS

Within the modern approaches for the design of active components for fast and irreversible decomposition of ecotoxicants, special attention is given to the development of versatile oxidative/nucleophilic systems. The following observations are noteworthy: (i) nucleophilic systems (concentrated alkaline solutions, oximates, iodosobenzoates, etc.) are efficient toward the esters and acid halides of phosphoric and phosphonic acids; (ii) oxidizing systems (such as oxone (HSO_5^-)), being extremely weak nucleophiles, are efficient in reactions with dialkylsulfides; and, finally, (iii) compounds that contain "active" chlorine, being both excellent oxidizers and reactive nucleophiles, are corrosive and unstable [5–14,84–89].

Hypobromites have a favorable combination of nucleophilic and oxidizing properties, but neither their solutions nor solid salts are able to be stored long-term. An ideal source of "active" bromine would be a safe-to-handle solid substance with low vapor pressure of bromine, high content of active halogen, and readily soluble in water, which enables one to provide a desirable operating concentration of hypobromite and/or hypobromous acid.

As a source of active bromine for decomposition of ecotoxicants, we proposed bis(dialkylamide) hydrogen dibromobromates first synthesized in our Institute [90,91].
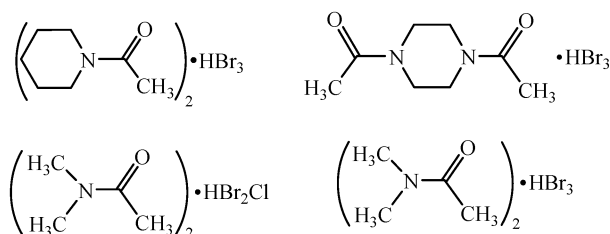
These are solid substances that can be easily synthesized in a sufficiently pure state (graded for analysis) and meet all above requirements. Tribromide ion released in water undergoes fast dissociation to form bromide anion and bromine (eq. 2).

$$Br_3^- \rightleftharpoons Br^- + Br_2 \tag{2}$$

The latter, in its turn, produces hypobromite and/or hypobromous acid depending on the medium acidity. In quantitative estimation of the reactivity, it should be taken into account that hypobromite shows strong oxidizing power and is the efficient α-nucleophile that decomposes acyl substrates and its conjugated acid. UV spectra of the reaction mixtures illustrate variations in absorbance of 4-nitro-phenoxide released at various acidities. The ascending branch of the curve reflects an accumulation of 4-nitrophenoxide in system due to the nucleophilic attack of hypobromite on the electrophilic center in the substrate. The descending ones correspond to oxidation of 4-nitrophenoxide (Fig. 2). In essence, 4-nitrophenoxide ion is an intermediate in this process (Scheme 1) [57].
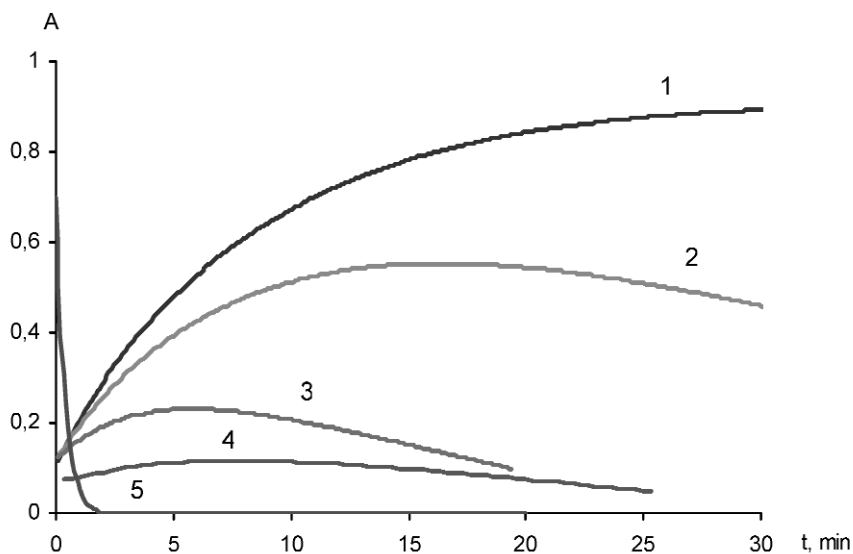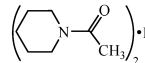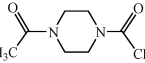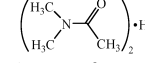
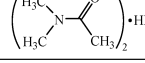

Fig. 2 Time dependences of *p*-nitrophenolate ion absorbance (λ 420 nm) in reaction of BrO⁻/HOBr [formed by bis(*N*-acetylpiperidine)hydrogen dibromobromate] with armine: $[HOBr]_o = 0.01$ M; pH = 11.5 (1), 10.8 (2), 10.40 (3), 10.00 (4), and 9.60 (5); aqueous solution, with ionic strength of 1.0 M (KCl), 25 °C.
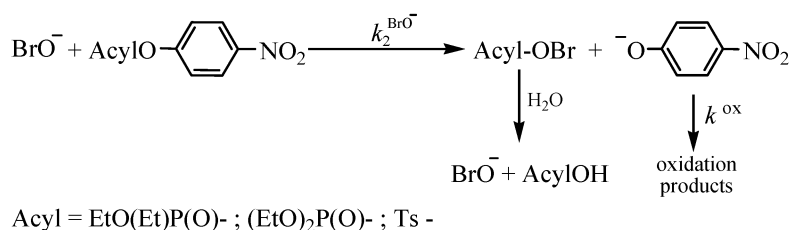
Scheme 1

Reactivity of the hypobromite generated by various sources of "active" bromine is nearly the same (Table 2). BrO⁻ anion is a typical α-nucleophile [92–94]. Being by seven orders of magnitude less basic than hydroxide, it reacts with the substrates under study at the rates close to those in alkaline hydrolysis. The value of α-effect (as measured by the ratio of the second-order rate constants for hypobromite and hypothetical aryloxide of the same acid ionization constant) may have ranges up about 10^3 [92–94].

Table 2 Nucleophilic reactivity of hypobromite ion toward armine (I), paraoxon (II), and p-nitrophenyltoluene sulfonate (III); water, μ 1.0 (KCl); 25 °C.

№	Source of «active» bromine	$k_2^{BrO^-}, M^{-1} \cdot s^{-1}$		
		I	II	III
	Br₂ + H₂O (KOH)	0.156±0.009	0.010±0.002	0.017±0.001
1		0.13±0.01	0.010±0.002	0.015±0.001
2		0.120±0.006	--	--
3		0.116±0.005	0.011±0.001	0.0154±0.0001
4		0.120±0.005	0.011±0.001	0.015±0.001

The systems on the basis of tribromide organocomplexes are multipurpose (i.e., they can be used in decomposition of organophosphores, aryloxides, and toxic sulfides). The optimum pH value for ester decomposition corresponds to the conditions when the observed rates of oxidation and nucleophilic substitution are the same. With consideration of the rate expressions for oxidation and nucleophilic substitution [56,57], the optimum pH value from the relationship

$$pH_{opt} = \frac{\log\left(k^{ox}/k_2^{BrO^-}\right) + pK_a}{2} \tag{3}$$

(where k_2^{ox}, M^{-2} s⁻¹ is the third-order rate constant, $k_2^{BrO^-}$, M^{-1} s⁻¹ is the second-order rate constant, and pK_a is the acid dissociation constant of hypobromous acid) was calculated to be about 10–10.5.

Quaternary ammonium salts like cetyltrimethylammonium dibromobromate are unique reagents capable of generating hypobromite ion and hypobromous acid and of forming the micelles.

As far as we know, there are no detailed kinetic studies on nucleophilic substitution in the presence of cetyltrimethylammonium dibromobromate

$$C_{16}H_{33}\overset{+}{N}(CH_3)_3 \cdot Br_3^-$$

Assuming that both in water and micellar pseudophase the decomposition of organophosphores proceeds by two parallel pathways—alkaline hydrolysis and hypobromite reaction—the overall reaction can be presented by Scheme 2 where k_{2,BrO^-}^m and k_{2,BrO^-}^w, M^{-1} s^{-1}, correspond to the nucleophilic reactivity of the BrO^- anion in micelles and water, respectively; k_{2,OH^-}^m and k_{2,OH^-}^w, M^{-1} s^{-1}, refer to the nucleophilicity of OH^- ion, whose concentration in the experimental conditions is a constant (pH = const) in the micelles and water, respectively; P_S, P_{OH^-}, and P_{BrO^-} are, respectively, the distribution coefficients for the substrate, hydroxide, and hypobromite ions, respectively.
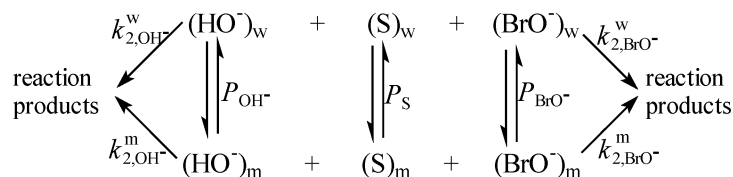
Scheme 2

On the basis of Scheme 2, the quantitative regularities in decomposition of organophosphores can be adequately described by the simple pseudophase model. In surfactant micelles, hypobromite behaves as a typical α-nucleophile, and an increase in observed reaction rates is about 30–40 times [95].

Half-lives of substrates in Table 3 indicate that the systems on the basis of micellarized dibromobromates show promise for feasible decomposition and recycling of ecotoxicants [95,96]. Such surfactants may be an attractive alternative to the green system hydrogen peroxide/activator. It is necessary to emphasize that possible applications of dibromobromates are not restricted to the problem considered. They can find and are finding practical use in thin organic synthesis, as disinfectants (suppression of undesirable microflora in the closed reservoirs, fresh water treatment in extreme conditions, etc.) [97–101], thus emphasizing a uniqueness of these compounds.

Table 3 Half-life times ($\tau_{1/2}$, s) of armine and paraoxon in their reactions with hypobromite ion, generated by dibromobromates of bis-(*N*+acetylpiperidine)hydrogen [complex A, water and in the presence of cetyltrimethylammonium bromide (CTABr) and cetyltrimethylammonium (CTABr$_3$)].

Reaction system	$\tau_{1/2}$, s		
	Complex A		CTABr$_3$
Substrate	[BrO$^-$]$_0$ = 0.01 M	BrO$^-$ + CTABr [BrO$^-$] = [CTABr]$_0$ = 0.01 M	[CTABr$_3$]$_0$ = 0.01M
Armine	600	20	12
Paraoxon	>1 h	270	95

UNIVERSAL "GREEN" SYSTEMS BASED ON HYDROGEN PEROXIDE

The dibromobromate-based compositions can be categorized as green systems with some reservations, whereas the compositions involving hydrogen peroxide/hydroperoxide ion are in full accord with the "green" standards. Such an oxidative/nucleophilic system is versatile [5,10,86]. One of the main re-

quirements for decomposition of ecotoxicants is the rate of chemical reaction. It is obvious that the rate of nucleophilic reaction should increase with increasing pH of aqueous solutions, whereas the oxidizing process should decrease. Therefore, the basic strategy in destruction of pesticides or substances of a similar nature consists of optimization of the operating conditions for systems hydrogen peroxide/hydroperoxide so as to provide the maximum rates for both the nucleophilic reaction and oxidation in mild conditions (i.e., adjacent to the neutral pH). In this case, it is necessary to consider that hydroperoxide is one of the most efficient α-nucleophiles and hydrogen peroxide exhibits rather weak oxidizing properties.

The problem of oxidizing reactivity of hydrogen peroxide can be solved by introduction of activators [102–106], ammonium hydrocarbonate, and boric acid [86,102,107–109]. In combination with hydrogen peroxide, they are sources of peroxocarbonate and peroxoborate, i.e., the species of much higher oxidizing power than that of initial hydrogen peroxide (Scheme 3).
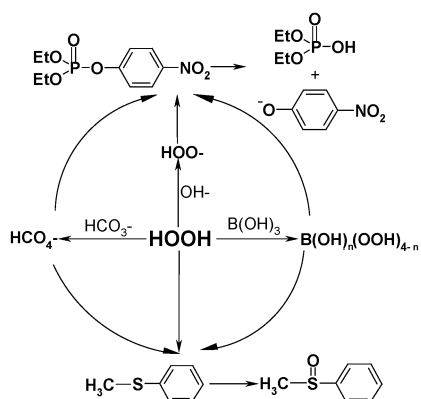
Scheme 3

Table 4 gives the half-lives of thioanisole (mustard gas simulant) in oxidation by hydrogen peroxide with and without the activators. The data demonstrate the powerful catalytic effect of ammonium hydrocarbonate and boric acid—acceleration of the oxidation process amounts to 2–3 orders of magnitude [110].

Table 4 Half-life times ($\tau_{1/2}$) and relative accelerations in oxidation of thioanisol (25 °C, $[H_2O_2]$ = 1 M).

Medium	Oxidation system	$\tau_{1/2}$, s	Acceleration
Water	H_2O_2	495	–
Water	H_2O_2, NH_4HCO_3	3	165
Water	H_2O_2, $B(OH)_3$	5	100
Water/propan-2-ol	H_2O_2	1730	–
Water/propan-2-ol	H_2O_2, NH_4HCO_3	13	130
Water/CTABr	H_2O_2	2000	–
Water/CTABr	H_2O_2, NH_4HCO_3	1.5	1300
Water/CTABr	H_2O_2, $B(OH)_3$	3.5	600

Much more attractive for practical application are aqueous alcohols and micellar systems that provide both high reactivity of hydroperoxide and effective solubilization of hydrophobic substrates [111]. A comparison between oxidizing systems hydrogen peroxide/ammonium hydrocarbonate and hydrogen peroxide/boric acid shows that the latter is more attractive. At insignificant difference in reactivities of peroxoborates and peroxocarbonates, oxidizing system hydrogen peroxide/boric acid is more preferable, since the maximum catalytic effect is observed in pH interval ranges 10.0–10.3. For hydrocarbonate systems, the pH interval is within pH 7.5–9.0. This fact is very important for designing universal decontamination systems—at pH from 8.5 up to 10.5, the concentration of active α-nucleophile HOO^- increases on two orders. Again, the high rates of oxidation reactions and nucleophilic substitution are reached (i.e., the system is versatile).

At those pH which provide optimum conditions in sulfide oxidation [112–115], on the other hand, the system hydrogen peroxide/ammonium hydrocarbonate generates two potentially nucleophilic species—peroxohydrocarbonate and peroxocarbonate (HCO_4^- and CO_4^{2-}) [111,116,117]. As distinct from sulfides, the decomposition of orgnophosphores proceeds via nucleophilic mechanism. This process is complex and includes at least five parallel routes (Scheme 4).
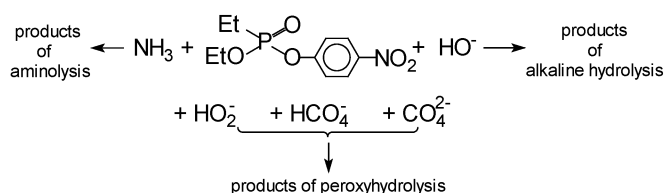
Scheme 4

Taking into account the corresponding equilibria in eq. 4 and rate constants for alkaline hydrolysis, aminolysis, and peroxohydrolysis from independent experiments, we have estimated nucleophilic reactivity of peroxohydrocarbonate and peroxocarbonate ions.

$$NH_4HCO_3/H_2O_2/HO^-$$

$$H_2O_2 \xrightleftharpoons{K_1} H^+ + HO_2^-,$$

$$H_2O_2 + HCO_3^- \xrightleftharpoons{K_2} HCO_4^- + H_2O, \tag{4}$$

$$HCO_4^- \xrightleftharpoons{K_3} H^+ + CO_4^{2-},$$

$$HCO_3^- \xrightleftharpoons{K_4} H^+ + CO_3^{2-}.$$

Points for these anions fall on the Brønsted plots for inorganic α-nucleophiles (Fig. 1) [57]. Therefore, we first showed that peroxohydrocarbonate and peroxocarbonate are typical inorganic α-nucleophiles which provide abnormally fast decomposition of organophosphores [117].

NEW STRATEGIES IN DEVELOPMENT OF THE SYSTEMS FOR EFFICIENT DECOMPOSITION OF ECOTOXICANTS

The list of promising approaches to the design of green systems for decomposition of ecotoxicants would be incomplete without mention of two of them which have been widely accepted by chemists during the last decade and are still unused in solving the problem of ecotoxicant decomposition.

The first line of research is application of nonconventional media such as ionic liquids in decomposition of ecotoxicants. Ionic liquids form the new class of the organic salts that are usually fluid at a temperature below 100 °C [19–23]. In contrast to the traditional volatile organic solvents, the ionic liq-

uids are often classed as "green". Numerous advantages of ionic liquids have become the subject of intensive studies in the last decade [19–23,118–122].
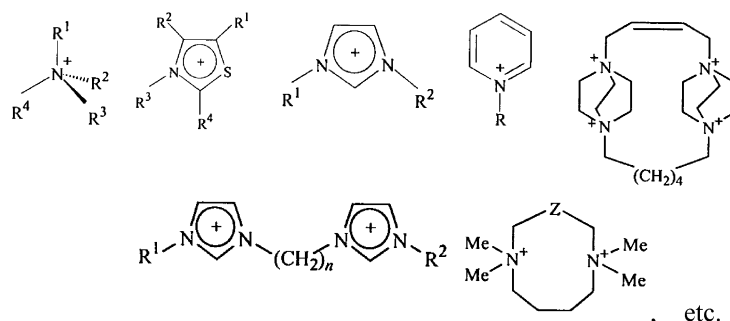
Anions: Cl^-, Br^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, ClO_4^-, etc.

The number of the new ionic liquids being synthesized is far ahead of the studies on their potentialities and the fields of their applications. For example, there are just a few attempts to study nucleophilic substitution at the saturated carbon in such nontraditional media [118–122].

Our studies have shown that nonconventional media such as "salt melts" (e.g., concentrated solutions of tetraalkylammonium salts) can accelerate nucleophilic substitution at tetracoordinated carbon, sulfur, and phosphorus. In going from water or methanol into 4 M solutions of tetraalkylammonium halides, the rate increase amounts to 1–3 orders of magnitude (Fig. 3) [123–125]. The effects of
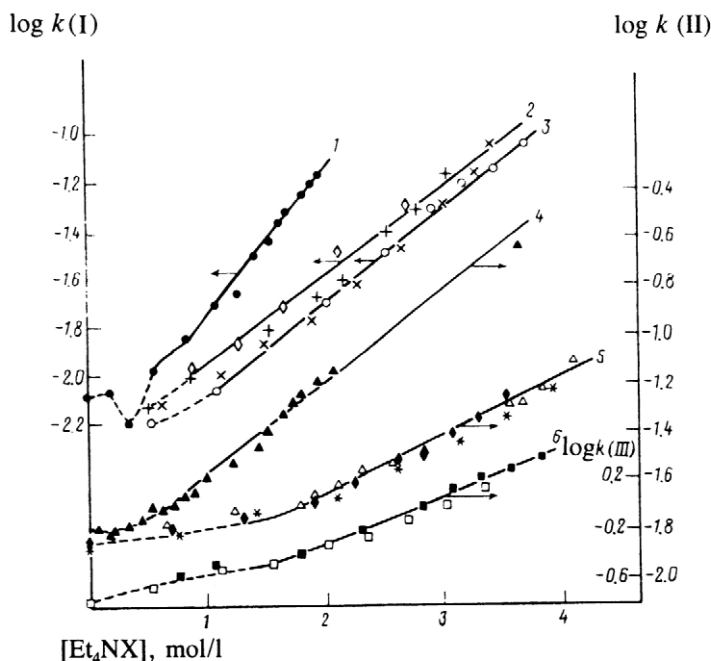
Fig. 3 Dependence of log k on the electrolyte concentration [Et_4NX] for reactions of hydroxide ions with *p*-nitrophenyltoluene sulfonate I (1–3), paraoxon II (4, 5), and armine III (6) in aqueous Et_4NOH solution (1, 4), in Et_4NCl–Et_4NOH–H_2O (2) and Et_4NCl–NaOH–H_2O (3, 5, 6) systems at 25 °C.

quaternary salts on the reaction rates were explained by influence of electrolyte on the structure of solvent, with solvation component of free energy of activation being responsible for the increase in rate. Unfortunately, detailed studies of this system were not carried out due to the limited solubility tetraalkylammonium halides. We suppose that the use of ionic liquids like imidazolium-based, for example, will allow us to develop new systems where the increase in rates of nucleophilic reactions at unsaturated phosphorus will reach several orders of magnitude. The systematic approach that has been used in our recent studies on the development of the new functional surfactants can be used in the design of the nucleophilic systems on the basis of ionic liquids. They are: imidazolium-based ionic liquids (with variable counterion to obtain the sufficiently low fusion point), microheterogeneous systems in combination with the ionic liquids (hydrocarbon chain length in the cation is sufficient for micellarization), and functional ionic liquids (with imidazolium cation modified by introduction of α-nucleophilic moiety).

The second research line consists in design of gemini surfactants and their use in decomposition of organophosphores. This novel class of surfactants features two identical or various amphiphilic fragments which are structurally related to the conventional surfactants connected with a spacer [126,127].

m-n-m 2X gemini   single chain
surfactant   analog
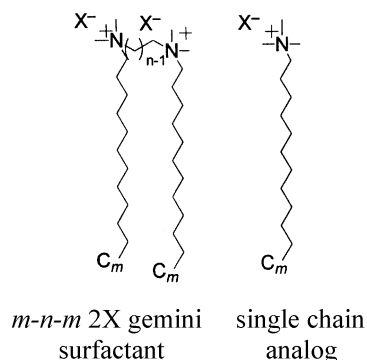
By now, the number of gemini surfactants is really huge and is growing steadily. There are some reasons for generating a boom in research in this field: above all, their extremely low critical micelle concentration (cmc) values, by 2 and more orders of magnitude lower than those for conventional surfactants. There are gemini surfactants with cmc below 10^{-6} M, which is simply difficult to imagine for conventional surfactants. Gemini surfactants exhibit exceptionally high solubilizing ability owing to the fact that their transitions from nominally spherical micelles to cylindrical and giant threadlike micelles are unlike those in the conventional surfactants. The foregoing suggests that the use of such surfactants, both individually and in combination with comicelles of ordinary and functional surfactants will give rise to the micellar systems of extremely low cmc, and, therefore, capable of providing the maximum possible reaction rates at extremely low surfactant concentration.

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