New Sources of "Active" Halogen Bis(dialkylamide)hydrogen Dibromobromates, Efficient Reagents for Destruction of Ecotoxicants

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Abstract—Bis(dialkylamide)hydrogen dibromobromates were synthesized and their reactivity was investigated in decomposition of diethylphosphonic, diethylphosphoric, and 4-toluenesulfonic acids 4-nitrophenyl esters. The nucleophilic reactivity of a typical α-nucleophile, hypobromite ion, is independent of the source of the active bromine. The cetyltrimethylammonium dibromobromate is a unique reagent for destruction of ecotoxicants. In weakly alkaline media the half-life of 4-nitrophenyl diethylphosphonate did not exceed 6 s at $[BrO^-]$ 0.02 mol l^{-1}, and the apparent reaction rate compared to water increased ~40-fold. The main factor governing the micellar effects of surfactants is concentrating the substrate in the micellar pseudophase.

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The development of new efficient reagents for decomposition of ecotoxicants in water requires a search for universal systems operating by oxidative-nucleophilic mechanism that can be applied to utilization of highly toxic phosphorus acids esters, sulfides derivatives etc. (pesticides, chemical warfare agents etc.) [1–3]. A good combination of nucleophilic and oxidative properties is inherent to hypobromites [4], but neither their solutions nor solid salts are suitable for long storage [5]. An ideal source of active bromine would be a safe solid substance with a low pressure of bromine vapor, with a high content of the active halogen, well soluble in water that would furnish the necessary operating concentration of BrO^-/HOBr. As a source of active bromine for ecotoxicants decomposition reagents with labile N–Br and C–Br bonds and also molecular complexes of bromine with N- and O-nucleophiles are widely used [6, 7]. However the compounds of *N*-bromosuccinimide type as a rile are poorly soluble in water [6]. The molecular complexes of bromine with N- and O-nucleophiles (for instance, dioxane-dibromide or the complexes with pyridine N-oxides) are

short-lived [7]. Especially interesting for practice are compounds containing a tribromide anion.*

In water the tribromide anion undergoes a fast and reversible dissociation [reaction (1)] to give a bromide anion and a bromine molecule [8]; the latter in its turn depending on the acidity of the environment generates anion BrO^-, HOBr, or BrO^-/HOBr.

$$Br_3^- \leftrightarrows Br^- + Br_2 \tag{1}$$

We report here on the study of the nucleophilic reactivity of BrO^- ion toward 4-nitrophenyl diethylphosphonate (**I**), diethylphosphate (**II**), and 4-toluenesulfonate (**III**), the α-effect values of BrO^- ions in the cleavage processes of these substrates were estimated, optimum conditions for the reactions were chosen, and the effect of surfactant micelles on the rate of the nucleophilic attack of hypobromite anion on the electron-deficient site of substrate **I** was investigated.

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* Dibromobromates according to the IUPAC nomenclature.

EtO(Et)P(O)OC$_6$H$_4$NO$_2$-p (EtO)$_2$P(O)OC$_6$H$_4$NO$_2$-p
I   **II**

TsOC$_6$H$_4$NO$_2$-p
III
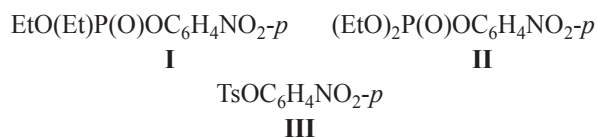
As a source of active bromine bis(dialkylamide)-hydrogen dibromobromates **IV–VII** were used, and also a micelle-formative cetyltrimethylammonium dibromobromate (**VIII**) was employed.

$$C_{16}H_{33}\overset{+}{N}(CH_3)_3 \cdot Br_3^-$$
VIII
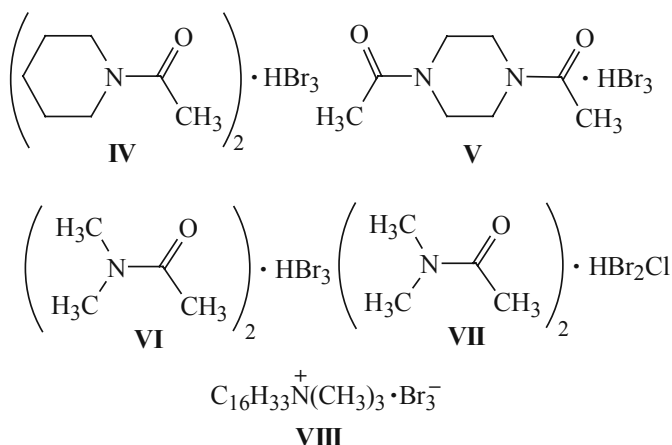
These compounds possess a number of advantages compared to the other known tribromides. They are solid substances easily obtained in an analytically pure state, they dissolve quickly in water solutions of alkali providing relatively stable hypobromites solutions; they are stable under common conditions and can be stored
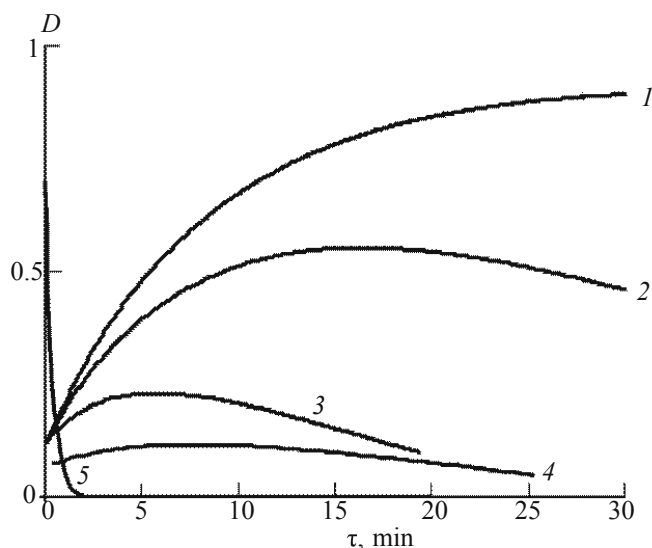
Fig. 1. Variation in time of absorption of p-nitrophenolate ion (λ 420 nm) during the reaction of BrO$^-$/HOBr generated by complex **IV** with ester **I**. [HOBr]$_0$ 0.01 mol l^{-1}, pH 11.5 (*1*), 10.8 (*2*), 10.40 (*3*), 10.00 (*4*) 9.60 (*5*); water, μ 1.0, 25°C.

for a long time* without applying any special precautions; they are not irritant for mucous membranes and dry skin at a short contact.

At the quantitative evaluation of the reactivity of the hypobromite ion it is necessary to take into consideration that BrO$^-$ anion operates as an efficient nucleophile in the cleavage of acyl-containing substrates, and that its conjugate acid HOBr is a strong oxidant. Kinetic curves demonstrating the variation in time of absorption of p-nitrophenolate ion formed in the reaction of complex **IV** with ester **I** at different pH values are presented in Fig. 1. The ascending branch of the curve corresponds to the accumulation in the system of p-nitro-phenolate ion formed at the attack of BrO$^-$ anion on the electron-deficient site of the substrate, and the descending branch of the curve reflects the oxidation of the p-nitrophenolate ion [reaction (2)]; thus in this process p-nitrophenolate ion is an intermediate compound.
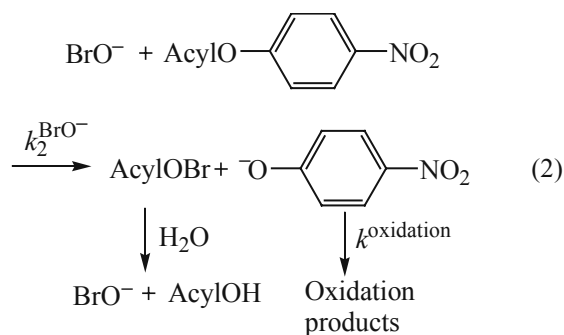
Acyl = EtO(Et)P(O), (EtO)$_2$P(O), Ts.

The nucleophilic reactivity of hypobromite anion generated by various sources of bromine was studied under the conditions when the contribution of the oxidation of the p-nitrophenolate ion was close to zero: during 5–10 half-times of the reaction the p-nitropheno-late ion concentration did not decrease. Therewith the choice of pH depended on the ratio of the rate constants of the nucleophilic attack on the electron-deficient site of the substrate and of the oxidation of the p-nitropheno-late ion. With the reactive ester **I** pH was maintained on the level $\geq$11.15, with compounds **II** and **III** pH was set at >11.35. The apparent rate constant (k_{app}, s^{-1}) under these conditions was described by equation (3).

$$k_{app} = k_{HO^-} a_{HO^-} + k_2^{BrO^-}[HOBr]_0\, \alpha_{BrO^-} \qquad (3)$$

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* After 10 years the decrease in the content of active bromine in compound **VI** did not exceed ~5%.

The term $k_{HO^-} a_{HO^-}$, s⁻¹, in equation (3) corresponds to the contribution of the alkaline hydrolysis; $[HOBr]_0$, mol l⁻¹, is the analytical concentration of hypobromic acid; α_{BrO^-} is the fraction of BrO⁻, and $k_2^{BrO^-}$ l mol⁻¹ s⁻¹ is the second order rate constant characterizing the nucleophilicity of hypobromite anion in water. Inasmuch as the constant of the acid ionization of hypobromic acid pK_a is 8.69 [9], the value $\alpha_{BrO^-} \to 1$ (pH 11.15, α 0.996; pH 11.35, α 0.998), equation (3) may be written in the form (4).

$$k_{app} = k_{HO^-} a_{HO^-} + k_2^{BrO^-}[HOBr]_0 \qquad (4)$$

The second order rate constants were estimated from the linear dependence $k_{app} - [HOBr]_0$ (Fig. 2) and were presented in Table 1. In all events the segment cut on the ordinate corresponded to the contribution of the acid hydrolysis estimated by taking into account k_{OH^-}, l mol⁻¹ s⁻¹, determined in independent experiments [4].

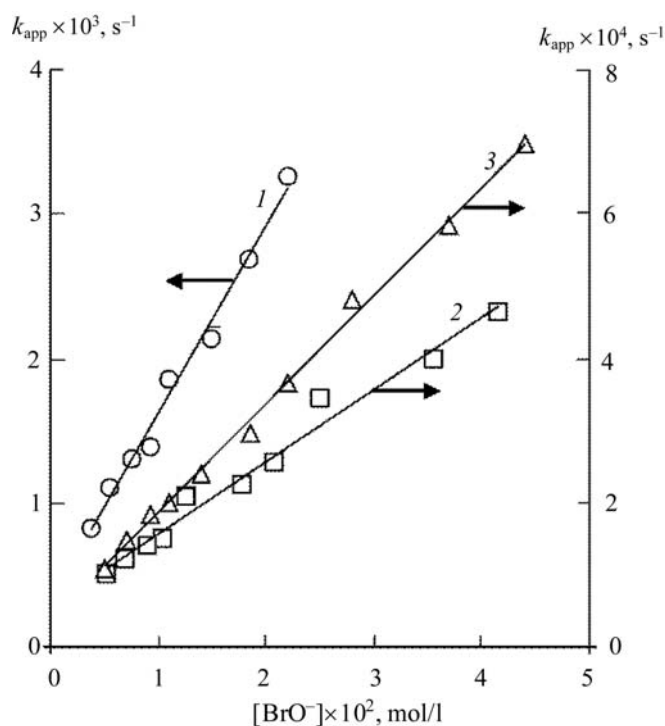The reactivity of hypobromite ion generated by various sources of the active bromine IV–VII virtually coincided. This was not unexpected: the amides contained in the bromine complexes do not react with esters, and the operating concentrations of dibromo-bromates IV–VII are not sufficiently high to affect the environment properties and the nucleophilicity of BrO⁻ anion. The hypobromite ion is a typical α-nucleophile. Although it is by 7 orders of magnitude less basic than the hydroxide ion (pK_a of the conjugate acids is 8.69 [9] and 15.74 [10] respectively), it reacts with substrates I–III at a rate close to that of the alkaline hydrolysis (Table 1). The value of the α-effect is usually evaluated either from the ratio of the second order rate constants $k_2^{\alpha\text{-nucl}}/k_2^{nucl}$, or from the difference $\Delta = \log k_2^{\alpha\text{-nucl}} - k_2^{nucl}$ at the comparable values of constants of acid ionization of the conjugate acids of the α-nucleophile and a "normal" oxygen-containing nucleophile. With the use of Brønsted equations for arylate (alcoholate) ions (5–7) [11] it was possible to calculate the value of the α-effect of the hypobromite ion in reactions with esters I–III.

$$\log k_2^{(ArO^-, RO^-)}(\text{I}) = 0.50 pK_a - 7.95 \qquad (5)$$

$$\log k_2^{(ArO^-, RO^-)}(\text{II}) = 0.57 pK_a - 9.60 \qquad (6)$$

$$\log k_2^{(ArO^-, RO^-)}(\text{III}) = 0.59 pK_a - 9.64 \qquad (7)$$

The reactivity of "normal" oxygen-containing nucleophile, arilate ion with $pK_a^{ArOH} = pK_a^{HOBr} = 8.69$ should

Fig. 2. Dependence of k_{app}, s⁻¹, on [BrO⁻], mol l⁻¹, in reactions of esters I, straight line 1, pH 11.35; II straight line 2, pH 11.35, and III, straight line 3, pH 11.60, with hypobromite ion generated by complex IV; water, μ 1.0, 25°C.

be equal to 2.5×10^{-4} (I), 2.3×10^{-5} (II), and 3.1×10^{-5} (III) l mol⁻¹ s⁻¹. Therefore the magnitude of the α-effect characterized by the ratio of the second order rate constants $k_2^{\alpha\text{-nucl}}/k_2^{nucl}$ is ~600, 500, and 400 and is independent of the source of the active bromine. In the case of ClO⁻ anion the increase in the reaction rate estimated in similar way amounted to $k_2^{\alpha\text{-nucl}}/k_2^{nucl} \geq 10^3$ ($pK_a^{HOCl} = pK_a^{ArOH} = 7.4$) [4].

Table 1. Nucleophilic reactivity of hypobromite ion toward 4-nitrophenyl diethylphosphonate (I), diethylphosphate (II), and toluenesulfonate (III); water, μ 1.0 (KCl), 25°Cᵃ

Source of "active" bromine	k_{app}, l/(mol⁻¹ s⁻¹)		
	I	II	III
Br₂ + H₂O (KOH) [4]	0.156 ± 0.009	0.010 ± 0.002	0.017 ± 0.001
IV	0.13 ± 0.01	0.010 ± 0.001	0.015 ± 0.001
V	0.120 ± 0.006		
VI	0.116 ± 0.005	0.011 ± 0.001	0.0154 ± 0.0001
VII	0.120 ± 0.005	0.011 ± 0.001	0.015 ± 0.001

ᵃ Rate constants of alkaline hydrolysis equal: 0.15 (I), 0.009 (II), 0.008 (III) l/(mol⁻¹ s⁻¹) [4].

We already demonstrated formerly [4] that the hypobromite ion is a typical α-nucleophile. Although the cause of the abnormally high reactivity of α-nucleophiles has been under investigation for over 50 years, it is still under discussion [12]; and the α-effect in all likelihood has no unique nature. The high reactivity of α-nucleophiles is commonly regarded as the result of the stabilization of the transition state of the reaction caused, e.g., by intramolecular general acid-base catalysis [13], by the elevated thermodynamic stability of reaction products [14]; solvation effects of the solvent play a special part [12].

Among the factors governing the α-effect the basicity of the nucleophile [15], hybridization type of the electrophilic site [12, 16] etc. [12] should be mentioned. In the case of hypohalogenite ions it is presumed that the cleavage of esters occurs through a rate-determining state **A**, where the hypohalogenite ion being a Lewis acid functiones as intramolecular general acid-base catalyst [13], namely, the phosphoryl (or sulfonyl) oxygen atom is involved into an interaction with the unoccupied d-orbitals

A
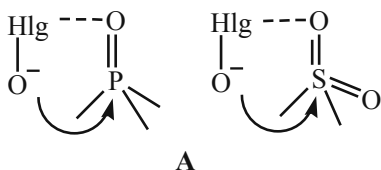
of the halogen atom in the hypohalogenite ion.

However the hypohalogenite ions, in particular, ClO⁻ anion, demonstrate the α-effect toward a saturated carbon atom in reactions with benzyl bromide [17] where this assistance id hardly possible.

In [18] based on the extended version of perturbation theory of molecular orbitals another understanding of the nature of the α-effect is developed proceeding from the destabilization of the initial state. All α-nucleophiles may be divided in two groups. The first group includes ions of ROO⁻, ClO⁻, and RSS⁻ type possessing high repulsion energy of the unshared electron pairs of the α-atom and nucleophilic center in the ground state of the reaction. The second group of nucleophiles includes NH_2NH_2, NH_2OH, hydroxamate and highly basic oximate ions, pyridines N-oxides, and azide ion. The conformations of the latter have a structure where the electron repulsions in the ground state of the reaction are negligible [19]. In the α-nucleophiles of the first group should occur a splitting of hypohalogenite ion p- (or π-) levels and an appearance of higher occupied

p- (or π-) antibonding and lower bonding molecular orbitals [18, 20]. This interaction character is reflected in the physicochemical properties of these compounds [18, 19, 21]. This is beyond question that the higher occupied orbital should interact stronger with the lower unoccupied orbital of the substrate that the nonperturbed p- (or π-) orbital of the nucleophile. Therewith the closer in the energy the reacting orbitals of the nucleophile and substrate, the stronger is the stabilization of the transition state of the reaction and consequently the higher is the rate of the process. These nucleophiles should exhibit the α-effect both in reactions with saturated and unsaturated substrates. Obviously BrO⁻ anion can be classed in this group.

Nonetheless, the explanation of the α-effect based on the destabilization of the initial state has certain drawbacks. Thus if the α-nucleophile is destabilized due to the energetically unfavorable interactions between the unshared electron pairs or by solvation effect of the solvent [12, 22] its nucleophilic reactivity should increase when the degree of destabilization diminishes in the transition state. However simultaneously the basicity of this supernucleophile should also grow for the addition of a proton thereto should even greater decrease its destabilization. Therewith it is expectable that the parallel increase in the reaction rate and basicity of the α-nucleophile should be described by Brønsted relation for the "normal" nitrogen- and oxygen-containing nucleophiles. However actually it is not the case. It is therefore suggested that the protonation of the nucleophile is a process controlled by the charge, whereas the nucleophilic substitution is apparently orbital-controlled [18, 23].

The systems based on the organic complexes of tribromide ion are versatile, i.e., they can be used as oxidants and nucleophiles for neutralization of toxic substrates [4, 24]. The optimum pH value for cleavage of esters **I–III** is that where the apparent rates of

$$k_{app}^{BrO^-} = k_{app}^{oxidation}. \tag{8}$$

nucleophilic substitution and oxidation are equal:

$$k_2^{BrO^-}[HOBr]_0 \; \frac{K_a}{K_a + a_{H^+}} = k^{oxidation}[HOBr]_0 \frac{a_{H^+}^2}{K_a + a_{H^+}}, \tag{9}$$

Accounting for the established laws of these processes [4, 24] expression (8) transforms into (9).

where $[HOBr]_0$, mol l^{-1}, is the analytical concentration of hypobromic acid; K_a is the constant of acid ionization; $K_a/(K_a + a_{H^+})$ and $a_{H^+}/(K_a + a_{H^+})$ are fractions of hypobromite ion and of hypobromic acid at pH = $-\log a_{H^+}$; $k^{\text{oxidation}}$, $l^2/(\text{mol}^2 \text{ s})$ is the rate constant of oxidation. Transforming expression (9) into equation

$$pH = \frac{\log(k^{\text{oxidation}}/k_2^{\text{BrO}^-}) + pK_a}{2} , \qquad (10)$$

it is possible to determine the pH, corresponding to pH_{opt}; considering $k^{\text{oxidation}}$ [4, 24] and $k_2^{\text{BrO}^-}$ for substrates **I–III** it is 10.0–10.7. It should be stressed that ion BrO⁻ being an α-nucleophile makes it possible at concentration 1 mol l^{-1} to achieve half-conversion time ($\tau_{1/2}$) of compounds **I–III** into the reaction products not exceeding 5 s (substrate **I**) and 50 s (substrates **II** and **III**).
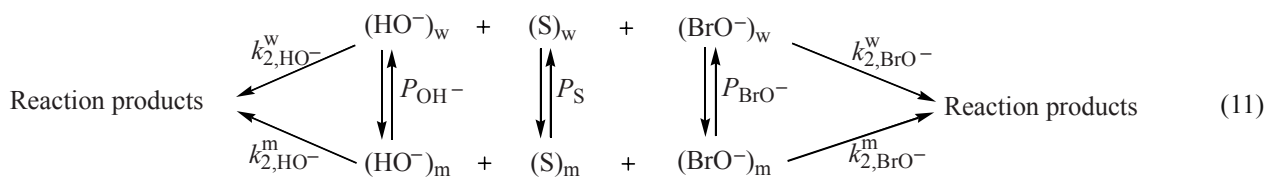
In designing reagents ensuring efficient decomposition of ecotoxicants it is important not only to obtain high apparent reaction rates but to provide the solubilization of substrates poorly soluble in water. The latter factor is often the governing one in substantiation of the routes to modification of the systems for ecotoxicants destruction. We formerly demonstrated that in the micelles of cetyltrimethylammonium bromide (**IX**) the rate of reaction between BrO⁻ anion and esters **I–III** grew 20–30-fold [24]. Unique reagents generating BrO⁻/HOBr and operating as micelle-fomative compounds are quaternary ammonium salts of **VIII** type. Recently compounds **IV–VIII** were widely used in selective bromination of phenols and anilines [25], and also for selective oxidation of sulfides to sulfoxides [26]. However we found no
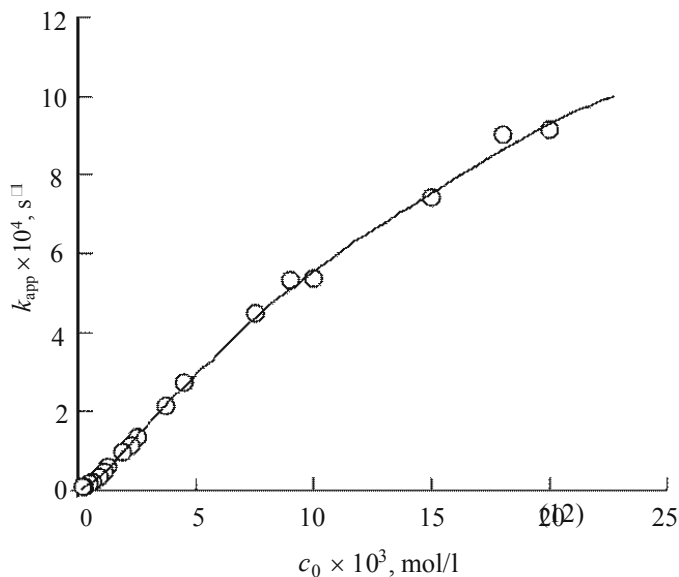
Fig. 3. Dependence of the apparent pseudofirst order rate constants (k_{app}, s⁻¹) on the initial concentration of cetyltrimethylammonium dibromobromate (C_O, mol l^{-1}) in decomposition of ester **I**; pH 11.14–11.20, water, 25°C, ionic force not fixed.

publications on detailed kinetic studies of nucleophilic substitution in the presence of compound **VIII.**

Micellar effects of surfactant **VIII** were studied by an example of the cleavage of ester **I**. The dependence of k_{app} on c_o is of a pattern typical for the reactions of anionic nucleophiles with electroneutral substrate (Fig. 3). The quantitative relationships of the cleavage of ester **I** can be understood in the framework of a simole pseudophase model [27]. Assuming that both in water (w) and in the micellar pseudophase (m) the substrate

$$\text{Reaction products} \xleftarrow[k_{2,\text{HO}^-}^{\text{m}}]{k_{2,\text{HO}^-}^{\text{w}}} \begin{array}{ccccc} (\text{HO}^-)_w & + & (\text{S})_w & + & (\text{BrO}^-)_w \\ \updownarrow P_{\text{OH}^-} & & \updownarrow P_{\text{S}} & & \updownarrow P_{\text{BrO}^-} \\ (\text{HO}^-)_m & + & (\text{S})_m & + & (\text{BrO}^-)_m \end{array} \xrightarrow[k_{2,\text{BrO}^-}^{\text{m}}]{k_{2,\text{BrO}^-}^{\text{w}}} \text{Reaction products} \qquad (11)$$

(S) reacted by two concurrent paths, alkaline hydrolysis and reaction with BrO⁻ anion, the overall scheme of the process may be described by equation (11).

The distribution of the substrate and reagents is described by the corresponding distribution factors: $P_{\text{S}} = [\text{S}]_m/[\text{S}]_w$, $P_{\text{BrO}^-} = [\text{BrO}^-]_m/[\text{BrO}^-]_w$, and $P_{\text{HO}^-} = [\text{HO}^-]_m/[\text{HO}^-]_w$, and the rate of substrate cleavage in the micellar pseudophase, by equation

$$v^{\text{m}} = k_{2,\text{HO}^-}^{\text{m}}[\text{HO}^-]_m[\text{S}]_m cV_m + k_{2,\text{BrO}^-}^{\text{m}}[\text{BrO}^-]_m[\text{S}]_m cV_m, \qquad (12)$$

in water, by equation

$$v^{\text{w}} = k_{2,\text{HO}^-}^{\text{w}}[\text{HO}^-]_w[\text{S}]_w(1 - cV_m)$$
$$+ k_{2,\text{BrO}^-}^{\text{w}}[\text{BrO}^-]_w[\text{S}]_w(1 - cV_m), \qquad (13)$$

where the values k_{2,HO^-}^m, $k_{2,\,BrO^-}^m$ and $k_{2,\,HO^-}^w$, $k_{2,\,BrO^-}^w = k_2^{BrO\ddot{I}}$, 1 mol^{-1} s^{-1}, are second order rate constants corresponding to the reactivities of the hydroxy and hypobromite anions in the micellar pseudophase and in water; $c = c_O - CCM$, mol l^{-1}, is the concentration of the surfactant involved in the micelle formation (CCM, mol l^{-1}, is the critical concentration of micelle formation), V_m, 1 mol^{-1} is the partial molar volume of the surfactant ; cV_m and $(1 - cV_m)$ are volume fractions of the micellar and water phases.

The overall rate of the process (Scheme 11) averaged over the total volume of the system may be expressed through the reaction rates in the micellar and water phases by equation (14).

$$v = v^m + v^w = k_{2,BrO^-}^m[BrO^-]_m[S]_m cV_m$$

$$+ k_{2,HO^-}^m[HO^-]_m[S]_m cV_m + k_{2,HO^-}^w[HO^-]_w[S]_w(1 - cV_m)$$

$$+ k_{2,BrO^-}^w[BrO^-]_w[S]_w(1 - cV_m) \qquad (14)$$

Taking into account the relations between the overall concentrations of reagents and their real concentrations in the respective phases described by the distribution factors and the material balance equations the apparent rate constant can be represented by equation (15).

$$k_{app} = \frac{v}{[S]} = \frac{k_{2,BrO^-}^m P_S P_{BrO^-} cV_m + k_{2,BrO^-}^w(1 - cV_m)}{[1 + (P_S - 1)cV_m][1 + (P_{BrO^-} - 1)cV_m]}[BrO^-]$$

$$+ \frac{k_{2,HO^-}^m P_S P_{HO^-} cV_m + k_{2,HO^-}^w(1 - cV_m)}{[1 + (P_S - 1)cV_m][1 + (P_{HO^-} - 1)cV_m]}[HO^-]_o \qquad (15)$$

In event of dilute solutions of surfactant where the volume fraction of the micellar phase is small ($CV_m \ll 1$) [27] and an efficient uptake of the reagents by the surfactant micelles exists (P_S, P_{BrO^-}, $P_{HO^-} \gg 1$) it is possible to simplify equation (16):

$$k_{app} = \frac{v}{[S]} = \frac{(k_{2,BrO^-}^m/V_m)K_S K_{BrO^-}c + k_{2,BrO^-}^w}{(1 + K_S c)(1 + K_{BrO^-}c)}[BrO^-]_o$$

$$+ \frac{(k_{2,BrO^-}^m/V_m)K_S K_{HO^-}c + k_{2,HO^-}^w}{(1 + K_S c)(1 + K_{HO^-}c)}[HO^-]_o \qquad (16)$$

where the binding constants have the following appearance:

Table 2. Nucleophilic reactivity of hypobromite ion (k_{2,BrO^-}^m) generated by cetyltrimethylammonium dibromobromate, constants of binding of substrate (K_S) and nucleophile (K_{BrO^-}) in the course of decomposition of 4-nitrophenyl diethylphosphonate (**I**), 25°C

$k_{2,BrO^-}^m / V_m$, s^{-1}	k_{2,BrO^-}^m, l mol^{-1} s^{-1}	K_S, l/mol	K_{BrO^-}, l/mol
0.21 ± 0.03^a	0.078^a	220 ± 40^a	50 ± 10^a
0.23 ± 0.02^b	0.085^b	1200 ± 500^b	34 ± 6^b

[a] Calculated by equation (16).
[b] Calculated without accounting for the contribution of alkaline hydrolysis.

$$K_S = (P_S - 1)V_m$$
$$K_{BrO^-} = (P_{BrO^-} - 1)V_m$$
$$K_{HO^-} = (P_{HO^-} - 1)V_m \qquad (17)$$

In processing the experimental data by equation (16) we assumed that $k_{2,HO^-}^m \approx k_{2,HO^-}^w = 0.15$ l/mol [4], $K_{HO^-} \approx 30$ l/mol [28]; [BrO$^-$] = C_o, mol l^{-1} (pH $\approx$ const = 11.14–11.20), and $V_m = 0.37$ l/mol [29]. The optimized values were $k_{2,BrO^-}^m/V_m$, K_S, and K_{BrO^-} that are compiled in Table 2. There are also presented the values of the same kinetic and thermodynamic parameters estimated without accounting for the contribution of the alkaline hydrolysis in water and micelles of compound **VIII**.

The attention is engaged by the fact that the values k_{2,BrO^-}^m and K_{BrO^-} estimated along two approaches are close to each other, whereas the constants of binding the substarate are essentially different. Therewith the K_S value estimated from the kinetic data without accounting for the contribution of alkaline hydrolysis was determined with ~50% error and seemed overestimated. Actually, the constant of binding ester **I** with micelles of functional [30] and cationic [24, 28] surfactants calculated from kinetic data amounted to 150–300 l/mol. This value is consistent with the distribution factor of substrate **II** which is close to ester **I** by the hydrophobicity: from the data on solubility [31] $P_{S(II)} \approx 350$, and $K_{S(II)} = P_{S(II)} V_m \approx 150$ l/mol ($V_m = 0.37$ l/mol). Therefore the account-ing for the reaction of the hydroxide ion in water and in micelles provided more correct description of the micellar effects of the surfactant.

It should be stressed that the analysis of experimental data was based on the simplest pseudophase model not accounting for the exchange of the reactive ions (HO$^-$, BrO$^-$) and inert anion (Br$^-$) between water and the micellar pseudophase. The consideration of these equilibria is obviously very important for the description of the micellar effects of a surfactant since it makes possible to more accurately estimate the concentration of the reactive

ions in water and the micellar pseudophase [32]. However this approach requires the estimation of a number of constants of ion exchange that is frequently a very difficult task.

In the micelles of surfactant the hypobromite ion behaves like a typical α-nucleophile, and the transfer of the reaction from water into micelles of compound **VIII** results in an increase of the apparent reaction rate. Thus at $[BrO^-]_0$ 0.02 mol l^{-1} the value $k_{app}^w = 3.10 \times 10^{-3} - 2.2 \times 10^{-3}$ (calculated based on the values of k_{2,BrO^-}^w, Table 1),

and $k_{app}^m = 9.16 \times 10^{-2}$, then $k_{app}^m/k_{app}^w \; k_{app}^w \approx 30-40$. The reason of it is the effect of substrate concentration in the micellar pseudophase. Actually, the maximum catalytic

$$\left(\frac{k_{2,BrO^-}^{app,m}}{k_{2,BrO^-}^{app,w}} \right)_{max} = \frac{k_{2,BrO^-}^m}{k_{2,BrO^-}^w} \cdot \frac{K_S K_{BrO^-}}{V_m (\sqrt{K_S} + \sqrt{K_{BrO^-}})^2} \quad (18)$$

micellar effect can be evaluated also be equation (18) [27] and it amounts to 30–40.

Table 3. Reaction conditions and apparent rate constants in reactions of BrO$^-$ ion with 4-nitrophenyl diethylphosphonate (**I**), diethylphosphate (**II**), and toluenesulfonate (**III**); water, μ 1.0, 25°C

Source of "active" bromine	I			II					
	pH	[HOBr]$_O$	$k_{app} \times 10^3$, s^{-1}	pH	[HOBr]$_O$	$k_{app} \times 10^4$, s^{-1}	pH	[HOBr]$_O$	
IV	11.35	0.0220	3.26	11.35	0.0415	4.65	11.60	0.044	
	11.35	0.0184	2.69	11.36	0.0356	3.99	11.60	0.037	
	11.36	0.0150	2.14	11.35	0.025	3.45	11.65	0.028	
	11.37	0.0110	1.85	11.37	0.0208	2.55	11.60	0.022	
	11.35	0.0092	1.39	11.36	0.0178	2.25	11.60	0.0185	
	11.35	0.0075	1.30	11.39	0.0125	2.08	11.60	0.014	
	11.36	0.0055	1.10	11.35	0.0104	1.49	11.65	0.011	
	11.35	0.00375	0.819	11.35	0.0089	1.40	11.64	0.0092	
				11.37	0.0063	1.21	11.60	0.007	
				11.35	0.0052	1.01	11.60	0.0051	
V	11.15	0.014	1.85						
	11.15	0.007	1.14						
	11.20	0.0052	0.81						
	11.20	0.0035	0.60						
	11.16	0.0026	0.54						
	11.15	0.0026	0.48						
VI	11.30	0.02	2.60	11.70	0.043	5.04	12.0	0.042	
	11.35	0.018	2.40	11.70	0.035	4.30	12.05	0.036	
	11.35	0.010	1.44	11.70	0.03	3.40	12.05	0.03	
	11.30	0.009	1.30	11.75	0.028	3.23	12.0	0.021	
	11.35	0.005	0.90	11.75	0.0215	3.07	12.05	0.018	
	11.30	0.0025	0.58	11.70	0.014	1.84	12.0	0.015	
				11.75	0.0107	1.20	12.0	0.0105	
				11.70	0.007	1.10			
VII	11.30	0.034	4.20	11.70	0.042	4.45	12.10	0.042	
	11.35	0.026	3.20	11.75	0.03	3.30	12.15	0.038	
	11.35	0.017	2.24	11.75	0.021	2.40	12.10	0.028	
	11.30	0.013	1.65	11,70	0.016	1.90	12.10	0.025	
	11.35	0.0085	1.23	11.70	0.015	1.15	12.15	0.021	
	11.30	0.0065	0.97	11.75	0.0105	0.86	12.15	0.019	
	11.30	0.00425	0.74	11.70	0.008	0.75	12.10	0.014	
	11.35	0.00325	0.63				12.10	0.0125	
							12.15	0.0105	

Inasmuch as $k^m_{2,BrO^-} \leq k^y_{2,BrO^-}$, obviously just the concentrating of ester **I** in the micellar pseudophase governs the observed increase in the reaction rate. Therewith already at the concentration of $[BrO^-]_o$ 0.02 mol l^{-1} the half-conversion time of substrate **I** into the reaction products would reach ~6 s, and it is comparable with $\tau_{1/2}$ value at the decomposition of the ester with water solutions of hypobromite ion at $[BrO^-]_o$ 1 mol l^{-1}.

Kinetic relationships of substrate decomposition and the micellar effects in the micelles of compounds **VIII** and **IX** are practically similar. However the obvious advantage of organic complex **VIII** is its being simultaneously a source of the active bromine and micelle formative compound. Considering that the micelles of compound **IX** accelerate the oxidation of *p*-nitrophenolate ion [24]* the generalized facility based on compound **VIII** is undoubtedly interesting for the practice of decomposition and utilization of ecotoxicants by the oxidative-nucleophilic mechanism of action.

Just similar surfactants may be regarded as an alternative to the "green" systems "hydrogen peroxide–activator". Although the hydroperoxide anion is among the strongest α-nucleophiles, the hydrogen peroxide is relatively weak oxidant that demands the necessary application of activators of acid nature increasing the oxidative ability of H_2O_2 [2, 3]. It commonly requires the reaction to be performed in weakly alkaline media (pH < 10). But in this case the fraction of the hydroperoxide ion as nucleophilic reagent is small, and it is necessary to use high concentrations of the unstable hydrogen peroxide (≥1mol l^{-1}). The organic complexes **IV–VIII** at pH ≈ 10.0 and $[HOBr]_o \ll 1$ mol l^{-1} ensure the desired rate of decomposition of organophosphorus compounds.

It should be noted in conclusion that the possible applications of complexes of type **IV–VIII** are not limited to the problem under discussion. They can find and already have found application as was mentioned above in the fine organic synthesis [26], as disinfectants (to suppress the unwanted microflora in closed reservoirs, purification of sweet water under stringent conditions) [33] etc. showing once more that these compounds are unique.

EXPERIMENTAL

Substrates **I** and **III** were obtained by acylation of 4-nitrophenol with diethyl chlorophosphonate and

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* The effect of compound **VIII** on the oxidation of *p*-nitrophenolate ion was not investigated in this study.

4-toluenesulfonyl chloride respectively in anhydrous dioxane in the presence of triethylamine. After isolation ester **I** was twice ditilled in a vacuum at a pressure of 0.05 mm Hg. Ester **III** was thrice recrystallized from anhydrous ethanol. The physicochemical characteristics (mp, n_D^{20}) and UV spectra were in full agreement with the published data. Substrate **II** was purchased from Aldrich and used without further purification.

Inorganic reagents of "specially pure" and "chemically pure" grades were used without additional purification.

Bis(*N,N*-dimethylacetamide)hydrogen dibromobromate (VI). A solution of 225 ml (1.5 mol) of 40% hydrobromic acid was mixed at cooling with 78 ml (1.5 mol) of bromine. To this mixture was poured at vigorous stirring 225 ml (3 mol) of *N,N*-dimethylacetamide. A heavy red oily substance separated and slowly crystallized at cooling and stirring. The precipitate was filtered off and dried in air. The yield was commonly no worse than 570 g (91%). The reaction product was recrystallized from methanol (~1 ml per 1 g of dibromobromate) avoiding strong heating of the solution, or it was distilled in a vacuum of an oil pump equipped with a liquid nitrogen trap at bp 86–90°C (0.05 mm Hg), mp 81–83°C. The ^1H, ^{13}C, and ^{17}O NMR spectra of compound **VI** were published in [34].

Bis(*N*-acetylpiperidine)hydrogen dibromobromate (IV) was obtained similarly, mp 80–82°C.

(*N,N*'-Diacetylpiperazine)hydrogen dibromobromate (V). To a solution of 1 g (5.9 mmol) of *N,N*'-diacetylpiperazine in 5 ml of water was added a mixture of 0.42 ml (3.9 mmol) of 40% hydrobromic acid and 0.16 ml (3.0 mmol) of bromine, the separated precipitate was filtered off, washed with methanol, and dried, mp 183–184°C.

Bis(*N,N*-dimethylacetamide)hydrogen chlorobromobromate (VII). To a solution of 4.5 ml (56 mmol) of 38% hydrochloric acid was added 2.8 ml (55 μmol) of bromine, the mixture was cooled, and 10 ml (0.11 mol) of dimethylacetamide was added at vigorous stirring. The precipitated yellow-orange crystals were filtered off and recrystallized from methanol, mp 81–83°C.

Cetyltrimethylammonium dibromobromate (VIII). Into a desiccator over a beaker containing ~1 ml (20 mmol) of bromine was placed 2.35 g (6.07 mmol) of cetyltrimethylammonium bromide. Within 24 h an oily red substance formed that was left in air till it solidified. It was crushed and maintained in a vacuum of a water-jet pump. Yield 3.15 g (5.7 mmol).

In all organic complexes **IV–VIII** the content of active bromine corresponded to the stoichiometric composition.

The method of kinetic experiments was described in detail in [4, 30]. The solutions of reagents were prepared just before each series of kinetic measurements. Double distilled water was used. When the initial concentration of the nucleophile was less than 0.02 mol l^{-1}, sodium carbonate was applied as a buffer at the concentration 0.05–0.005 mol l^{-1}. The required pH of buffer solutions was adjusted by KOH and HCl solutions. The acidity of the medium was checked before and after each kinetic run with a pH-Meter-744, Metrohm; when the change in pH after the end of the run exceeded 0.05 pH unit, the run was rejected. The hydrobromic acid concentration was estimated by iodometry. Ionic force was adjusted with 1 M potassium chloride solution (except the experiments with dibromobromate **VIII**). All reactions were studied in water. The reaction progress was monitored by measuring the absorption of the formed *p*-nitrophenolate ion at λ 400–440 nm on spectrophotometers Specord UV VIS and Genesys 10UV. The substrate was charged into the cell from a capillary as a concentrated solution in anhydrous dioxane. In the kinetic runs the initial concentration of substrate (<5 × 10^{-5} mol l^{-1}) was always far less than the initial concentration of the nucleophile. The values k_{app}, s^{-1}, were calculated from the variation in time of the optical density by equation (19).

$$\ln(D_\infty - D_\phi) = \ln(D_\infty - D_o) - k_{app}\phi,$$ (19)

where D_o, D_τ, and D_∞ are optical densities at the initial, running, and final moment of the reaction respectively. In Table 3 conditions are compiled of reactions of BrO$^-$ generated by complexes **IV–VII** with esters **I–III**, and the apparent pseudofirst order rate constants are presented. Linear plots were processed by the least-mean-squares procedures, and their accuracy was shown by the mean square deviations.

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