Micellar effect of ionic surfactants in the reaction of *o*-dimethylaminomethylphenol with *p*-nitrophenyl diphenyl phosphate

I. S. Ryzhkina, R. A. Shagidullina, L. A. Kudryavtseva, I. E. Ismaev, and B. E. Ivanov*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 8420083 Kazan', Russian Federation. Fax: +7 (843) 275 2253

The effect of cetylpyridinium bromide (CPB) and sodium dodecyl sulphate (SDS) on the direction and the rate of the reaction of *o*-dimethylaminomethylphenol (MP) with *p*-nitrophenyl diphenyl phosphate (**1**) has been studied by ^{31}P NMR and spectrophotometry. It was shown that the reaction of MP with **1** proceeds in two steps both with and without the surfactant. The product of transesterification is formed in the first step. The second step is hydrolysis catalyzed by the aminomethyl group yielding equal amounts of diphenyl phosphate and *o*-dimethylaminomethyl phenyl phosphate. The reaction of MP with **1** is catalyzed by CPB and inhibited by SDS. The ratio between the rates of the first and the second stages changes in the presence of surfactant. The parameters of the reaction of MP with **1** inhibited by micellar SDS were calculated.

Key words: micellar effect, transesterification, hydrolysis, rate constant, *p*-nitrophenyl phosphate, ^{31}P NMR, spectrophotometry.

In a continuation of our earlier studies of the reactivity of bifunctional nucleophiles in reactions with *p*-nitrophenyl phosphates and the effect of various factors on this reaction[1–3] we investigated the kinetics of the reaction of *p*-nitrophenyl diphenyl phosphate (**1**) with *o*-dimethylaminomethylphenol (MP) in aqueous micellar solutions of cationic (cetylpyridinium bromide (CPB)) and anionic (sodium dodecyl sulfate (SDS)) surfactants. In aqueous alcohol, the interaction of **1** and MP proceeds in two stages. The first stage is the formation of *p*-nitrophenolate as a result of transesterification and the formation of phosphorylated MP; the second stage is the hydrolysis of the latter promoted probably by intramolecular catalysis by the aminomethyl group. It was of interest to investigate the effect of surfactants on the rate and direction of these processes. We used ^{31}P NMR spectroscopy in our studies as it is known[4,5] that *p*-nitrophenol or phenol may split off in aqueous micellar solutions and microemulsions of **1** thus hampering spectrophotometric kinetic measurements in these systems.

Experimental

MP and compound **1** were synthesized by the known procedures (see Refs. 6 and 7, respectively). CPB (reagent grade) and SDS were purified by the published procedure.[8] ^{31}P NMR spectra were recorded on a Bruker MSL 400 spectrometer with working frequency 161.97 MHz at 308 K. Chemical shifts were taken relative to 85 % H_3PO_4. Kinetics of transesterification in the presence of SDS was studied using a Specord UV-VIS spectrophotometer by monitoring the optical density of the reaction mixture at 400 nm under pseudomonomolecular conditions. Apparent rate constants, activation parameters, substrate binding constants (K_{bn}), rate constants in the micellar phase (k_m), and critical micellar concentrations (C_{cmc}) (CMC) were calculated on an Elektronika D3-28 microcomputer using standard and original programs.

Results and Discussion

The reaction of **1** with MP proceeds in alkaline solution. Therefore, we studied alkaline hydrolysis of **1** with and without added CPB and SDS by ^{31}P NMR spectroscopy and determined the yield of *p*-nitrophenolate (NP) by spectrophotometry.

In the absence of surfactants, the ^{31}P NMR spectra of an alkaline (pH 11.6) water-alcohol solution of **1** ($\delta^{31}P$ −19.3) exhibited signals at $\delta^{31}P$ −11.2 and −12.4 assigned to diphenyl phosphate[1] and, possibly, *p*-nitrophenyl phosphate, respectively. The spectrophotometric yield of NP was ~85 %. The kinetics of alkaline hydrolysis of **1** (pH 11.6) in the presence of SDS (C_{SDS} = 0.07 *M*) was monitored by following the intensity of the signals in the ^{31}P NMR spectra and is shown in Fig. 1. A decrease in the intensity of the signal of substrate **1** is accompanied by an increase in the intensity of the diphenyl phosphate and *p*-nitrophenyl phosphate signals. According to the signal intensities, in the final reaction mixture the amount of diphenyl phosphate is 4.5 times greater than that of *p*-nitrophenyl phosphate. The yield of NP (spectrophotometry) in the presence of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 242—245, February, 1994.

1066-5285/94/4302-0219 $12.50

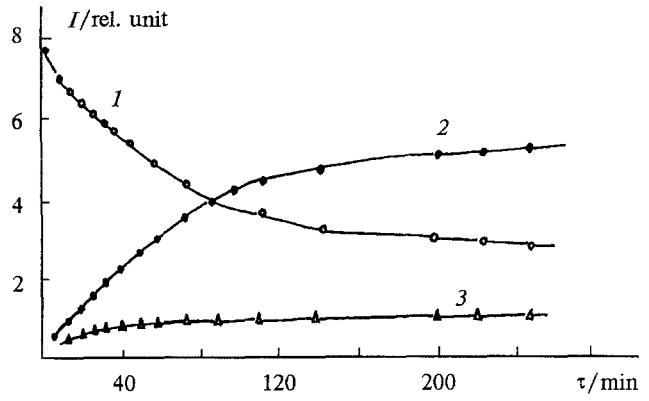


Fig. 1. Variation in intensities of the signals in the ^{31}P NMR spectra during alkaline hydrolysis of **1** ($C_1 = 5 \cdot 10^{-3}$ *M*) in the presence of SDS ($C_{SDS} = 7 \cdot 10^{-2}$ *M* at pH 11.6 and 35 °C). Chemical shifts δ^{31} P: −19.3 (*1*); −11.2 (*2*); −12.4 (*3*).

CPB and SDS is about 87—90 %. The first-order rate constant of the decomposition of substrate **1** ($k = 2.5 \cdot 10^{-4}$ s^{-1}) is practically the same as that of diphenyl phosphate formation ($k = 2.3 \cdot 10^{-4}$ s^{-1}), *i.e.* NP formation. This attests to the applicability of spectrophotometry to the investigated systems for determination of the decomposition rate of **1**.

Analysis of the ^{31}P NMR spectra obtained in the course of the reaction of **1** with MP under pseudomonomolecular conditions in 40 % aqueous ethanol in the absence of surfactants (see Fig. 2) showed that in the first step the intensity of the signal for intermediate **2** increases ($\delta^{31}P$ −18.7) as the intensity of the signal for substrate **1** decreases. In the second reaction step, hydrolysis of intermediate **2** results in the appearance of two signals ($\delta^{31}P$ −11.2 and −11.1) due to the formation of diphenyl phosphate (**3**) and possibly *o*-dimethylaminomethyl phenyl phosphate (**4**). The signals in the

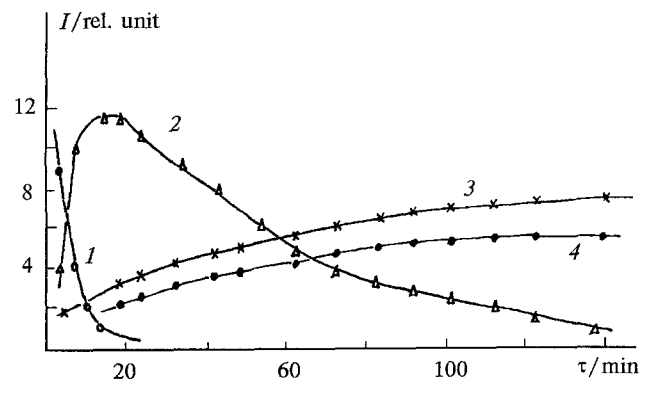
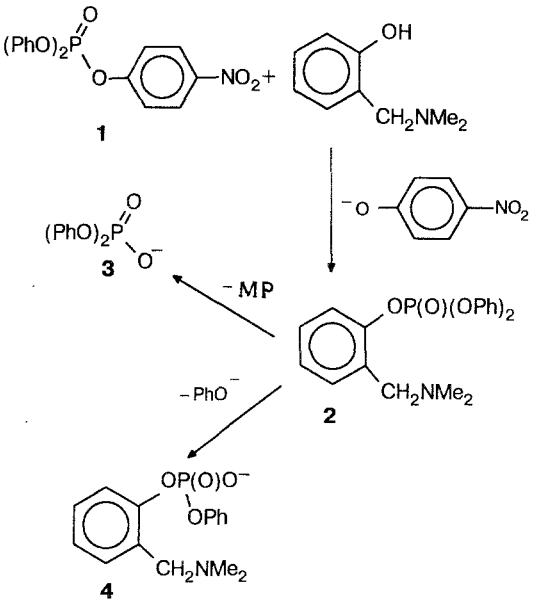


Fig. 2. Variation in intensities of the signals in the ^{31}P NMR spectra during the reaction of MP ($C_{MP} = 0.51$ *M*) with substrate **1** ($C_1 = 1.5 \cdot 10^{-2}$ *M*) in aqueous ethanol at pH 10.0 and 35 °C. Chemical shifts δ^{31}P: −19.3 (*1*); −18.7 (*2*); −11.2 (*3*); −11.1 (*4*).

Scheme 1



^{31}P NMR spectra were assigned by comparing them with the chemical shifts of the products of model hydrolysis, alcoholysis, and transesterification reactions.[1]

Spectrophotometric determination of the yield of NP in the reaction of **1** with MP showed that both in the presence and in the absence of surfactants the concentration of NP formed is equal to the initial substrate concentration. ^{31}P NMR analysis showed that under the reaction conditions (pH 9—10.5, 25—60 °C, $C_{SDS} = 0 \div 0.8$ *M*, $C_{CPB} = 0 \div 2 \cdot 10^{-3}$ *M*) hydrolysis of **1** proceeds very slow and can be neglected. Consequently, the formation of acids **3** and **4** is the result of two-directional decomposition of **2** which may be caused by intramolecular catalysis by the aminomethyl group (Scheme 1).

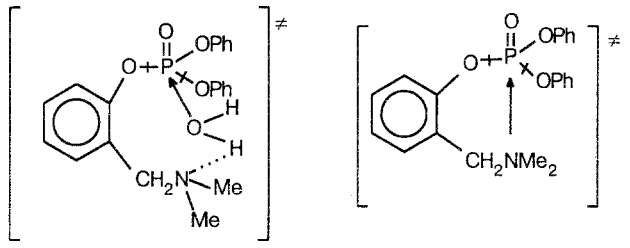
Below are listed the apparent and bimolecular (overall) transesterification rate constants of the reaction of **1** with MP in 40 % aqueous alcohol (k^1), hydrolysis of intermediate **2** (k^2), and formation of acids **3** (k^3) and **4** (k^4) calculated from ^{31}P NMR-monitored kinetics (see Fig. 2) ($C_{MP} = 0.51$ *M*, $C_1 = 1.5 \cdot 10^{-2}$ *M*, pH 10.0, 35 °C):

$k^1 \cdot 10^3/s^{-1}$ ($M^{-1} \cdot s^{-1}$)	3.0(5.9);
$k^2 \cdot 10^4/s^{-1}$ ($M^{-1} \cdot s^{-1}$)	4.2(8.2);
$k^3 \cdot 10^4/s^{-1}$ ($M^{-1} \cdot s^{-1}$)	1.5(2.9);
$k^4 \cdot 10^4/s^{-1}$ ($M^{-1} \cdot s^{-1}$)	2.6(5.1).

It can be clearly seen that in the absence of surfactants, the transesterification rate constant of **1** is nearly 10 times greater than the hydrolysis rate constant of intermediate **2**. The sum of the rate constants of the formation of acids **3** and **4** is equal to k^2, thus confirming the above-proposed reaction mechanism.

The intramolecular catalysis of nucleophilic substitution in various derivatives of carboxylic and phosphorus

acids is well known.[9] The intramolecular catalysis in the hydrolysis of intermediate **2** possibly proceeds through the participation of the aminomethyl group $-CH_2NMe_2$ by general basic or nucleophilic mechanisms *via* the following transition states:



The formation of nearly equal amounts of acids **3** and **4** with similar chemical shifts can be explained by the similarity of the acidic properties of phenol (pK_a 10.0) and *o*-dimethylaminomethylphenol (pK_a 10.8) as the leaving groups.

In order to obtain evidence for intramolecular catalysis by the *ortho*-aminomethyl group in the hydrolysis of **2** we studied the kinetics of the reaction of **1** with phenol under the same conditions. In this case, the apparent rate constants of the decomposition of **1** and the formation of triphenyl phosphate ($k = 3 \cdot 10^{-4}$ s^{-1}) were 10 times smaller than in the reaction of **1** with MP due to the bifunctional nature of the latter.[10] Triphenyl phosphate formed ($\delta^{31}P$ −18.7) undergoes virtually no hydrolysis. Although the ^{31}P NMR spectra include a signal with chemical shift −11.2 ppm, which corresponds to that for diphenyl phosphate, its intensity is very low and practically does not change with the time.

The rate constants of the reaction studied in the presence of CPB and SDS micelles are listed in Table 1. As expected from electrostatic micellar theory,[11] CPB favors both nucleophilic substitutions: the bimolecular transesterification rate constant is twice as high and the rate constant of hydrolysis of intermediate **2** increases by an order of magnitude compared to the reactions in a water-ethanol medium. Thus, CPB increases the rate of the second reaction step significantly, which becomes only two times smaller than that of the first one.

Table 1. Apparent and bimolecular rate constants of the reaction of MP with **1** in the presence of surfactants ($C_1 = 4 \cdot 10^{-3}$ *M*, 35 °C)

$k^1 \cdot 10^2$ /s^{-1}($M^{-1} \cdot s^{-1}$)	$k^2 \cdot 10^3$ /s^{-1}($M^{-1} \cdot s^{-1}$)	$k^3 \cdot 10^3$ /s^{-1}($M^{-1} \cdot s^{-1}$)	$k^4 \cdot 10^4$ /s^{-1}($M^{-1} \cdot s^{-1}$)
$C_{CPB} = 2 \cdot 10^{-3}$, $C_{MP} = 5.7 \cdot 10^{-2}$, pH 10.0			
0.07(1.2)	0.35(6.2)	0.16(2.8)	2.0(36)
$C_{SDS} = 0.1$, $C_{MP} = 5.0 \cdot 10^{-2}$, pH 10.5			
0.23(4.6)	3.0(60)	1.5 (30)	12.0(240)
$C_{SDS} = 0.6$, $C_{MP} = 5.4 \cdot 10^{-2}$, pH 10.5			
0.072(1.3)	1.6(30)	0.58(11)	8.0(150)
$C_{SDS} = 0.83$, $C_{MP} = 6.0 \cdot 10^{-2}$, pH 10.5, 45 °C			
0.18(3.0)	0.68(11)	0.36(6.0)	3.8(63)

Table 2. Apparent rate constants of the transesterification of MP and **1** in the presence of SDS at various temperatures ($C_{MP} = 5.0 \cdot 10^{-3}$ *M*, $C_1 = 1 \cdot 10^{-4}$ *M*, pH 9.25)

C_{SDS}/M	$k \cdot 10^{-4}/s^{-1}$	C_{SDS}/M	$k \cdot 10^{-3}/s^{-1}$
45 °C		60 °C	
—	4.5	—	1.92
0.025	3.9	0.025	1.71
0.075	3.4	0.075	1.09
0.10	3.2	0.15	0.89
0.15	2.75	0.25	0.67
0.30	2.15	0.35	0.63
0.60	1.5	0.60	0.48
1.00	1.1	0.88	0.46
—	—	1.00	0.31

The influence of SDS on the reaction of **1** with MP was studied in more detail at various SDS concentrations (0.1 *M*, 0.6 *M*, 0.83 *M*). As SDS concentration increases from 0.1 *M* to 0.6 *M* the transesterification rate decreases fourfold and the rate of decomposition of the intermediate decreases twofold. Thus, in the presence of surfactants the rates of formation and decomposition of the intermediate of the reaction of **1** with MP became comparable, and product 2 is not accumulated, unlike the reaction in aqueous alcohol (*cf.* Figs. 3 and 4).

The dependences of the apparent first-order transesterification rate constants of **1** and MP on SDS con-

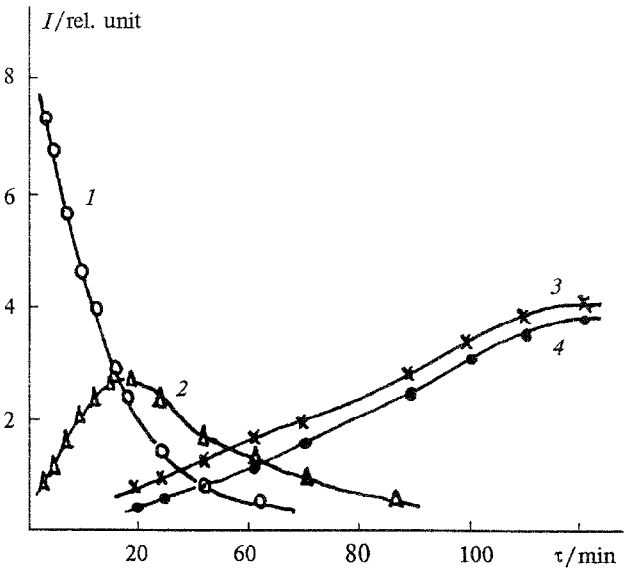


Fig. 3. Variation in intensities of the signals in the ^{31}P NMR spectra during the reaction of MP ($C_{MP} = 5.68 \cdot 10^{-2}$ *M*) with substrate **1** ($C_1 = 4.0 \cdot 10^{-3}$ *M*) in the presence of CPB ($C_{CPB} = 2.0 \cdot 10^{-3}$ *M*) at pH 10.0 and 35 °C. Chemical shifts $\delta^{31}P$: −19.3 (*1*); −18.7 (*2*); −11.2 (*3*); −11.1 (*4*).

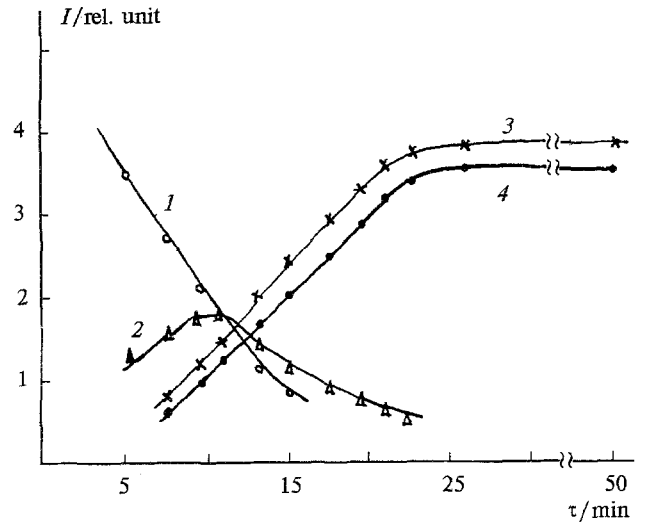


Fig. 4. Variation in intensities of the signals in the ^{31}P NMR spectra during the reaction of MP ($C_{MP} = 6.0 \cdot 10^{-2}$ *M*) with substrate **1** ($C_1 = 4.0 \cdot 10^{-3}$ *M*) in the presence of SDS ($C_{SDS} = 0.83$ *M*) at pH 10.5, 45 °C. Chemical shifts $\delta^{31}P$: −19.3 (*1*); −18.7 (*2*); −11.2 (*3*); −11.1 (*4*).

Table 3. Parameters of SDS micelle-inhibited transesterification of MP and **1** at various temperatures

T/°C	$C_{cmc} \cdot 10^2/M$	$k_m \cdot 10^3/c^{-1}$	K_{bn}/M	k_w/k_m
45	0.21	0.052	5	9
60	0.84	0.32	14	6
25*	0.30	0.17	3000	81

* Data on alkaline hydrolysis of **1** in the presence of SDS ([NaOH] = 0.08 *M*).

centration at various temperatures were obtained by spectrophotometry (Table 2). Increasing the SDS concentrations results in a decrease in the rate constants, which then become constant. The obtained curves can be explained in terms of a pseudophase model of micellar catalysis, considering the distribution of the substrate between the micellar and aqueous phases and that the parameters of the micelle-inhibited reaction, *viz.*, (K_{bn}), CMC, and k_m, can be calculated according to the Fendler equation[11] (Table 3).

The activation parameters of the transesterification reaction in the micellar and aqueous phases (E_a= 84.6 kJ · mol^{-1}, log*A* = 10.5 and E_a = 106.7 kJ · mol^{-1}, log*A* = 13.2, respectively) were calculated from the temperature dependence of the apparent rate constant of the reaction of **1** with MP in water (k_w), and k_m. According to the published data,[11] the values of E_a for the alkaline hydrolysis of **1** in water and in micellar SDS solutions are 42.2 and 91.2 kJ · mol^{-1}, respectively. In the transesterification reaction, weak binding of the substrate with SDS micelles is observed, although, as can be seen from Table 4, the binding constant for this substrate in alkaline hydrolysis in micellar SDS solutions is about ~3000. This weak binding of substrate **1** with the SDS micelle is possibly the reason for its insignificant inhibitory effect in this reaction (k_w/k_m = 6÷9) as compared with alkaline hydrolysis (k_w/k_m = 81).

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Received December 16, 1992