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MECHANISM OF MICELLAR EFFECTS ON ACYLATION OF ARYL OXIMES BY *p*-NITROPHENYL CARBOXYLATES

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Abstract—The *m*-bromobenzaldoxime acylation by *p*-nitrophenyl carboxylates is strongly accelerated (by 3 to 4 orders) in the presence of micelles of cationic detergent of cetyltrimethylammonium bromide. The micellar catalysis is explained by a general approach to the kinetics of bimolecular reactions in the presence of micelles. The kinetic conception proposed takes into consideration a heightening of the reagent concentration in the micellar phase, the simultaneous course of the reaction in the aqueous and micellar phases and the shift of the apparent ionisation constant of the functional group of one of the reagents under the action of the surface micelle charge. This concept is used to derive the equation for the apparent second-order rate constant. k_{app}. The equation is applied to calculate rate constants. k_m, of oxime acylation by carboxylates $R—C(O)OC_6H_4NO_2$ in the micelle surface layer from experimental data, k_{app}. The partition constants of carboxylates between the aqueous and micellar phases are thereby evaluated from the data of their solubility dependence on the detergent concentration. The apparent values of oxime dissociation constant at different detergent concentrations are measured by spectrophotometric titration. The change in rate constants of acylation on going from the aqueous phase into the micellar phase is dependent on the nature (aliphatic or aromatic) and the size of the side group R of the carboxylate. This result is interpreted as due to a different orientation of the reagent molecules in the micelle.

INTRODUCTION

THE catalytic properties of ionic detergent micelles on acid or alkaline hydrolysis[1–5] and on nucleophilic substitution or addition[6–11] have been revealed. Although these reactions are all bimolecular no general approach to this phenomenon has been reported. This paper describes the kinetics of the bimolecular reaction which depends on pH and proceeds in the presence of detergent micelles.

Most kinetic studies of micelle catalysed reactions point out that incorporation of the substrate into the micellar phase brings it into proximity with the reagent which may be attracted to the micelle electrostatically[1, 4–6, 10, 11] or chemically incorporated in it.[7–9] Besides heightening of reagent concentration in the micellar phase the chemical interaction can be considerably increased by suitably orienting the reagent molecules in or on the surface of the micelles. Since micelles have structure,[12] the nature of the substrate may determine its positioning within a micelle. It should, therefore, be possible to create a micelle possessing catalytic sites relatively specific toward a substrate of designated structure. The relation between the structure of reagents and their reactivity in the surface layer of the micelle is known for compounds with charged molecules only.[8] We now describe the kinetics of the bimolecular acylation (I) of *m*-bromobenzaldoxime by *p*-nitrophenyl carboxylates which proceeds in the presence of micelles of the cationic detergent of cetyltrimethylammonium bromide (CTAB). The carboxylates are listed in the Table. In this detergent, the absorbed molecules of aliphatic and aromatic compounds are located in different

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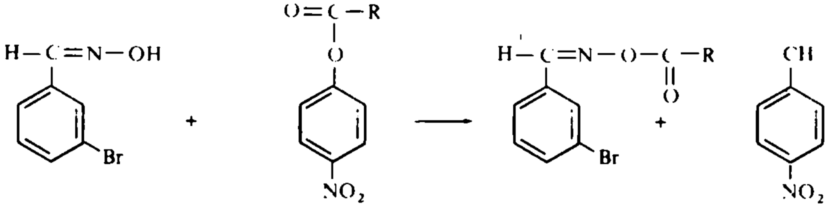

I

portions of the micelle.[13] Accordingly we decided to elucidate the reactivity of *p*-nitrophenyl carboxylates having a peculiar side hydrocarbon group R in the micellar phase, thus extending our previous investigation[14] which revealed the catalytic action of CTAB micelles on salicylaldoxime acylation by NPA and NPTMA.

THEORY

Concentration and pH effects on the rate of bimolecular reaction in the presence of micelles. Considering the kinetics of the chemical interaction of reagents A and B one of which has the ionogenic group.

$$A \rightleftharpoons A^- + H^+. \tag{1}$$

suppose that the reactive form of A is represented by its anion. Then

$$A^- + B \rightarrow \text{products}. \tag{2}$$

The apparent second-order rate constant, k_{app}, of this reaction has been estimated by the equation:

$$v = k_{app}[A]_t[B]_t \tag{3}$$

with $[A]_t$ and $[B]_t$ being the overall concentrations of the reagents. On the other hand, the observed rate, v, of the bimolecular reaction occurring in the solution, which consists of two "phases", i.e. the bulk phase and the micellar phase, equals the sum of two processes, the reaction in the micellar phase and the reaction in the bulk phase (see Appendix to Reference 7):

$$v = k_m[D]\bar{V}[A^-]_m[B]_m + k_b(1 - [D]\bar{V})[A^-]_b[B]_b \tag{4}$$

at $[D]_t \geqslant$ cmc, or

$$v = k_b[A^-]_b[B]_b \tag{5}$$

at $[D]_t \leqslant$ cmc.

Here indices m and b refer to the micellar and bulk phases, respectively; k_m and k_b stand for second-order rate constants; $[D] = [D]_t -$ cmc where $[D]_t$ is the overall detergent concentration; $\bar{V}$ is the molar detergent volume; $[A^-]_m$, $[B]_m$, $[A^-]_b$ and $[B]_b$ denote the concentrations of the corresponding components of reaction (2).

The actual concentration of A^- and B in the bulk and micellar phases can be determined by suggesting a definite distribution of reagents between the two phases.[11]

Let us introduce the partition coefficients P for all reaction components:

$$P_A = [A]_m/[A]_b$$
$$P_{A^-} = [A^-]_m/[A^-]_b \qquad (6)$$

and

$$P_B = [B]_m/[B]_b$$

The material balance equations must also be taken into account. Thus:

$$[A]_t = (1 - [D]\bar{V})([A]_b + [A^-]_b) + [D]\bar{V}([A]_m + [A^-]_m) \qquad (7)$$
$$[B]_t = (1 - [D]\bar{V})[B]_b + [D]\bar{V}[B]_m \qquad (8)$$

From (4)–(8) the apparent second-order rate constant, k_{app} in equation (3) can be expressed as follows:

$$k_{app} = \frac{k_m P_{A^-} P_B [D]\bar{V} + k_b(1 - [D]\bar{V})}{\{1 + (P_{A^-} - 1)[D]\bar{V}\}\{1 + (P_B - 1)[D]\bar{V}\}\{1 + [H^+]_b/K_{a(app)}\}} \qquad (9)$$

at $[D]_t \geqslant$ cmc, or

$$k_{app} = \frac{k_b}{1 + [H^+]_b/K_a} \qquad (10)$$

at $[D]_t \leqslant$ cmc, where

$$K_{a(app)} = K_a \frac{1 + (P_{A^-} - 1)[D]\bar{V}}{1 + (P_A - 1)[D]\bar{V}} \qquad (11)$$

and

$$K_a = [A^-]_b[H^+]_b/[A]_b \qquad (12)$$

Eqs (9) and (11) can be conveniently transformed using K values equal to

$$K = (P - 1)\bar{V} \qquad (13)$$

which can be measured experimentally.[11] Provided that

$$P_A, P_{A^-}, P_B \gg 1 \qquad (14)$$
$$[D]\bar{V} \ll 1 \qquad (15)$$

(9) and (11) lead to approximate Eqs (16) and (17),

$$k_{app} = \frac{\bar{k}_m K_{A^-} K_B [D] + k_b}{(1 + K_{A^-}[D])(1 + K_B[D])(1 + [H^+]_b/K_{a(app)})} \qquad (16)$$

$$K_{a(app)} = K_a \frac{1 + K_{A^-}[D]}{1 + K_A[D]} \qquad (17)$$

In Eq. (16)

$$\bar{k}_m = k_m/\bar{V}. \qquad (18)$$

Eqs (9), (11) are based on the assumption that reagents do not affect the micelle properties and, in particular, do not shift cmc. Hence these equations hold only at sufficiently low concentrations of reacting substances which must be considerably lower than that of the detergent. These conditions do not only minimise the effect of reacting substances on the micelle formation but also provide for the correctness of relations in (6) which seem to be true for dilute solutions only.

Let us consider some consequences arising from (16) assuming $k_b \ll \bar{k}_m K_{A^-} K_B[D]$. The correctness of this assumption under experimental conditions will be substantiated in the Experimental.

Equation (16) leads to the usually observed type of detergent concentration–rate profile[15] characterised by the presence of a maximum. Physically this phenomenon consists in the following: the growing volume of the micellar phase (at detergent concentration above cmc) results, on the one hand, in increased amount of reacting substance passing into it from water, and, on the other hand, the concentration of this substance in the micellar phase is lowered. The former process leads to accelerated reaction and is predominant at low detergent concentration until the amount of the substance passed into the micelles is small. The latter process involving the reagent dilution in the micellar phase retards the reaction and is predominant at high detergent concentrations when the reagents are, essentially in the micellar phase only.

The optimal detergent concentration and the value of maximal acceleration depend, in a general case, on the pH. Taking into consideration (10) and (17) Eq (16) gives:

$$[D]_{opt} = \left(\frac{1 + [H^+]_b/K_a}{K_B(K_{A^-} + K_A[H^+]_b/K_a)}\right)^{\frac{1}{2}} \tag{19}$$

$$\left(\frac{k_{app}}{k_{app,[D]_t=0}}\right)_{max} = \frac{\bar{k}_m}{k_b} \frac{K_{A^-}K_B(1 + [H^+]_b/K_a)}{(\sqrt{\{K_{A^-} + K_A[H^+]_b/K_a\}} + \sqrt{\{K_B(1 + [H^+]_b/K_a)\}})^2} \tag{20}$$

The dependence of (19) and (20) on $[H^+]$ disappears in extreme cases:

(a) at $[H^+]_b \ll K_a$, when

$$[D]_{opt} = (1/K_{A^-}K_B)^{\frac{1}{2}} \tag{19a}$$

and

$$\left(\frac{k_{app}}{k_{app,[D]_t=0}}\right)_{max} = \frac{\bar{k}_m}{k_b} \frac{K_{A^-} K_B}{(\sqrt{K_{A^-}} + \sqrt{K_B})^2} \tag{20a}$$

(b) at $[H^+]_b \gg K_a$, when

$$[D]_{opt} = (1/K_A K_B)^{\frac{1}{2}} \tag{19b}$$

and

$$\left(\frac{k_{app}}{k_{app,[D]_t=0}}\right)_{max} = \frac{\bar{k}_m}{k_b} \frac{K_{A^-}K_B}{(\sqrt{K_A} + \sqrt{K_B})^2} \tag{20b}$$

It can be shown that the reaction rate (k_{app} value in essence) increases more rapidly at low [D] than it falls at high [D]. Here we confine ourselves to the case at $[H^+]_b \ll K_a$ (with $[H^+]_b \gg K_a$ the result is similar). At $[D] \to 0$ the value of $\partial k_{app}/\partial[D]$ is $\bar{k}_m K_{A^-} K_B$ whereas that of $\partial k_{app}/\partial[D]$ at $[D] \gg [D]_{opt} = (1/K_{A^-}K_B)^{\frac{1}{2}}$

is $\bar{k}_m/[D]^2$. Hence it can be concluded that

$$\left|\frac{\partial k_{app}}{\partial[D]}\right|_{[D]\to 0} \gg \left|\frac{\partial k_{app}}{\partial[D]}\right|_{[D]\gg[D]_{opt}} \tag{21}$$

RESULTS AND DISCUSSION

Incorporation of p*-nitrophenyl carboxylates into the micellar phase*

The partition of *p*-nitrophenyl carboxylates between the micellar and bulk phases is considered in terms of their changing solubility in aqueous detergent solutions. The substrate solubility in the presence of detergent micelles. $S_{b,m}$. is associated with that in their absence. S_b. as follows:

$$S_{b,m}/S_b = 1 + K_B[D], \tag{22}$$

where K_B follows from (13). The experimental results are presented on Fig 1 in terms of coordinates of (22) and the K_B values calculated on these data are given in the Table. K_B for NPA is known.[5]

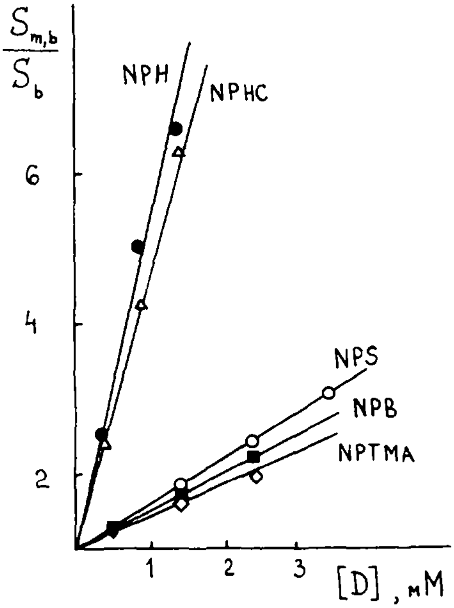

FIG 1. Effect of detergent (CTAB) on the solubility of *p*-nitrophenyl carboxylates in water at 25°. *p*H 4·8. 1 v.% of acetonitrile

Incorporation of the oxime into the micellar phase

Determination of p$K_{a(app)}$. The values of K_{A^-} and K_A, characterising the partition of the anion and, accordingly, that of the non-ionic form of *m*-bromobenzaldoxime between the micellar and bulk phases could not be evaluated by the same method as applied to carboxylates owing to the very high solubility of the oxime. They were therefore estimated from the dependence of $K_{a(app)}$ on [D]. The apparent value of the oxime ionisation constant, $K_{a(app)}$ observed at various detergent concentrations were determined by spectrophotometric titration[16] at 310 nm. It will be seen from

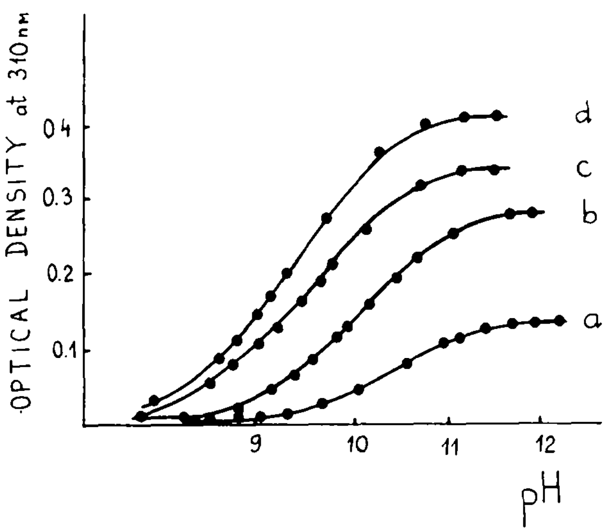

FIG 2. Ionisation of *m*-bromobenzaldoxime (5×10^{-5} M) at 25°, 1 v.% of acetonitrile with detergent (CTAB) concentration (mM): a – 0, b – 0·65, c – 1·5, d – 5

Fig 2 that at selected wavelength the non-ionic form of oxime does not practically absorb light. Hence $pK_{a(app)}$ can be taken as the abscissa of half the height of the sigmoidal curve.

The analysis of the dependence of the obtained $pK_{a(app)}$ values on the detergent concentration is complicated because of the inconsistency of the ionic strength in experiments at different CTAB concentrations. The effect of this factor on the dissociation constant of the substance sorbed on the surface of the CTAB micelle has been described.[17] Increased concentration of counter ions in the solution results in lowered surface potential of the micelle and, hence, in lowered sorption energy of the anionic form of the oxime, causing the lowering of K_{A^-} with K_A remaining practically unaffected. It is thus seen from (17) that the increased concentration of counter ions in the solution leads to lower $K_{a(app)}$. To estimate this effect we used equations given in[17]. At the maximal ionic strength created by the buffer (0·03 M) a decrease of the ionisation constant does not exceed 2%. As the Br^- anions are sorbed on the micelles of cationic detergents much stronger than many other anions (F^-, Cl^-, $SO_4^=$), they can be more effective.[5] Nevertheless, the maximal decrease of $K_{a(app)}$ calculated, assuming the ionic strength to depend on the CTAB concentration only, does not exceed 50%. The actual error does not therefore appear to be higher than 20–30%.

Fig 3 shows the dependence of $K_{a(app)}$ on the detergent concentration. The observed shift of apparent pK_a, $pK_{a(app)} < pK_a$, is characteristic of solutions with CTAB micelles[17] and due to the additional electrostatic interaction of oxime anion and the positively charged micelle. Using Eq (17) and data from Fig 3, the approximate values of K_{A^-} are 3×10^4 and $K_A = 2 \times 10^3$ 1/mole.

Dependence of the reaction rate on pH. Oximes are acylated by *p*-nitrophenyl esters in the anion form.[18] As seen from Fig 4, the observed dependence of log k_{app} (at $[D]_t = 0$) on *p*H is described by Eq (10). The Table lists the values of second-order rate constants, k_b, measured for carboxylates used in the absence of detergent.

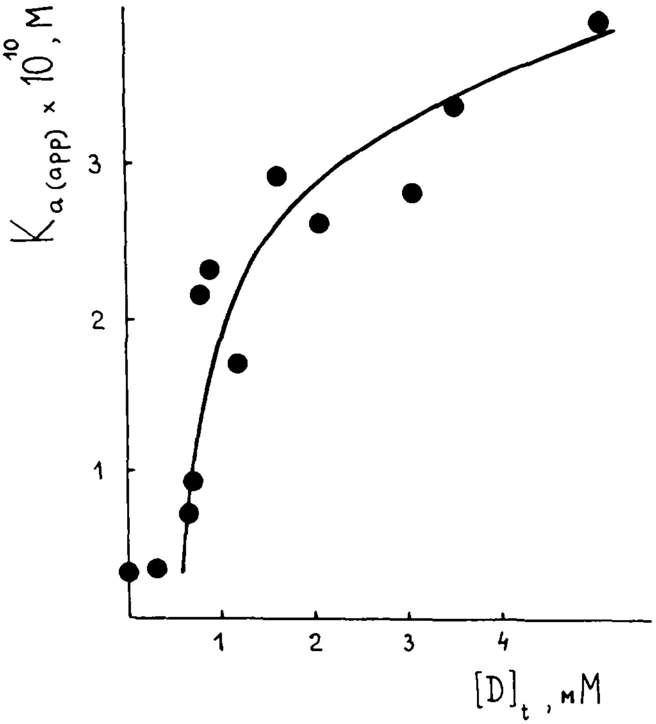

FIG 3. The influence of detergent (CTAB) on the apparent ionisation constant of *m*-bromobenzaldoxime. The experimental conditions are given in the subscript to Fig 2

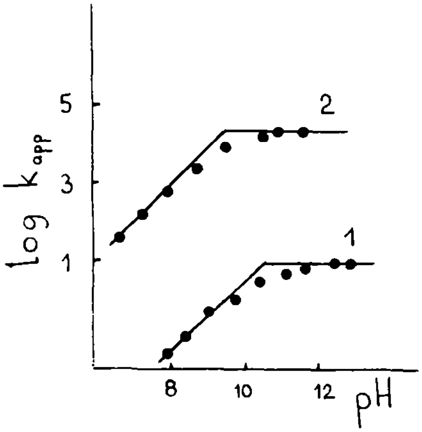

FIG 4. The *p*H-dependence of the apparent second-order rate constant for *m*-bromobenzaldoxime acylation by NPTMA in the absence (curve 1) and in the presence (curve 2) of CTAB ($[D]_t$ = 1·5 mM) at 25°, 1 v% of acetonitrile. The oxime concentration was varied from 5×10^{-5} to 4×10^{-3} M with carboxylate concentration being $1{\cdot}25 \times 10^{-4}$ M.

Fig 4 also contains the dependence of k_{app} on pH in the presence of detergent (curve 2). The values of $pK_{a(app)}$ which follow from curves 1, 2 in Fig 4 are in agreement with those evaluated by spectrophotometric titration of *m*-bromobenzaldoxime and given in Fig 3.

Detergent concentration–rate profiles. In Figs 5 and 6, the apparent values of second-order rate constants for reaction (I) involving NPA and NPTMA in dilute aqueous CTAB solution are plotted against the detergent concentration. The detergent concentration–rate profile is multiphasic.[15] Above cmc the rate constants rise rapidly with increasing CTAB concentration. After reaching an optimal detergent concentration, k_{app} falls comparatively slowly in accord with the concept presented in the theoretical part.

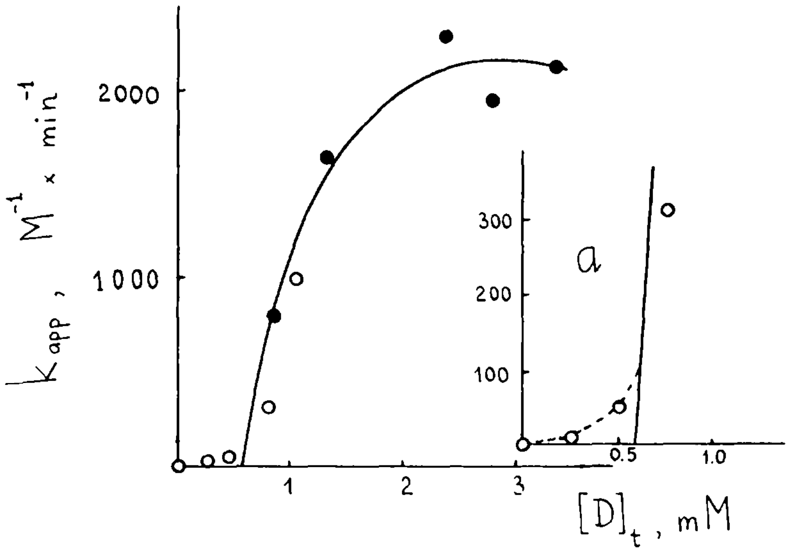

FIG. 5. The apparent second-order rate constants for *m*-bromobenzaldoxime acylation by NPA in the presence of CTAB at 25°, pH 7·3. 1 v% of acetonitrile. The oxime concentration was varied from 2×10^{-5} to 4×10^{-4} M with carboxylate concentration being $1{\cdot}6 \times 10^{-4}$ M. The k_{app} values (——●- - -) were calculated using equaton (16) and the data obtained at pH 6·3

A marked increase in k_{app} is observed at $[D]_t <$ cmc, as shown in Figs 5a and 6a, and also recorded by other authors.[6] This fact is usually interpreted as due to reagents inducing the micelle formation or else, it is believed that the detergent molecules start aggregating before cmc. It is further possible that the detergent molecules display a certain catalytic effect, although a much weaker one than that of the micelles.[4] A similar curvature of detergent concentration–rate profiles is also observed on *m*-bromobenzaldoxime interaction with other carboxylates under study.

TABLE 1

Carboxylates $R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OC_6H_4NO_2$	R	K_B 1/mole	$k_b \times 10^{-3}$ 1/mole/min	$\bar{k}_m \times 10^{-2}$ min^{-1}	$(k_{app}/k_{app} \cdot [D]_t = 0)_{max} \times 10^{-2}$ experimental values	$(k_{app}/k_{app} \cdot [D]_t = 0)_{max} \times 10^{-2}$ calculated[a] values	k_m/k_b[b]
NPA	CH_3	27	3·4	130	10	9·3	1·3
NPTMA	$(CH_3)_3C$	440	0·08	0·91	35	89	0·40
NPB	$CH_3(CH_2)_2$	530	2·7	9·4	8	99	0·12
NPH	$CH_3(CH_2)_5$	4500	5·8	5·5	9·5	310	0·033
NPHC	$C_6H_5(CH_2)_2$	3800	2·2	21	75	290	0·33
NPS	orto-HOC_6H_4	630	2·4	150	170	110	2·2

[a] The values calculated according (24) from measured K_{A-}, K_A, K_B with $\bar{V}$ taken as 0·35 1/mole[14] and $k_m/k_b = 1$.

[b] The values calculated from experimental constants $\bar{k}_m$ and k_b assuming $\bar{V} = 0{\cdot}35$ 1/mole[14]

Application of kinetic Eq (16) *to experimental data*

In order to obtain experimental proof of the validity of the kinetic Eq (16) constants K_B (see the Table), K_{A-} and $K_{a(app)}$ (see the section "Incorporation of the oxime into the micellar phase") have been determined independently. The knowledge of these values makes it possible to calculate in (16) the factor:

$$\alpha = \frac{K_{A-}K_B[D]}{(1 + K_B[D])(1 + K_{A-}[D])(1 + [H^+]_b/K_{a(app)})} \tag{23}$$

When using (16) we supposed that $k_b \ll \bar{k}_m K_{A-} K_B[D]$, for already at cmc the value of k_{app} is an order higher than k_b (e.g. see Figs 5a, 6a).

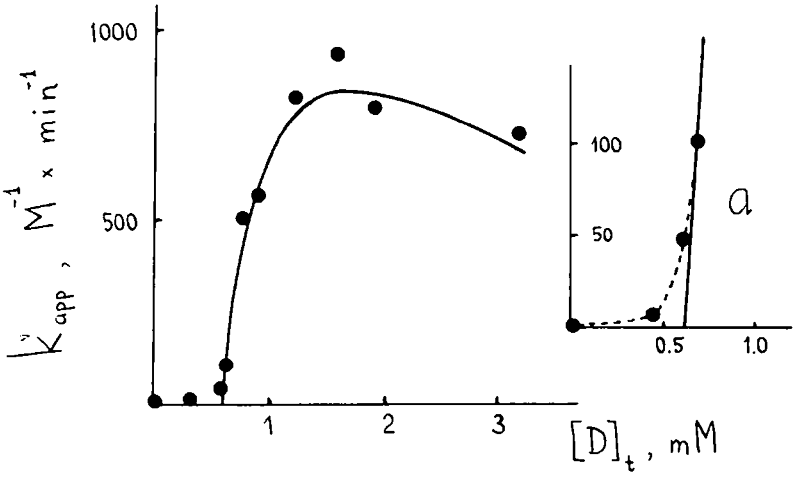

FIG 6. The apparent second-order rate constants for *m*-bromobenzaldoxime acylation by NPTMA in the presence of CTAB at 25°. pH 8·0 1 v% of acetonitrile. The oxime concentration was varied from 4×10^{-5} to 4×10^{-3} M with carboxylate concentration being $1{\cdot}25 \times 10^{-4}$ M. The k_{app} value at $[D]_t = 0$ is taken from Fig 4

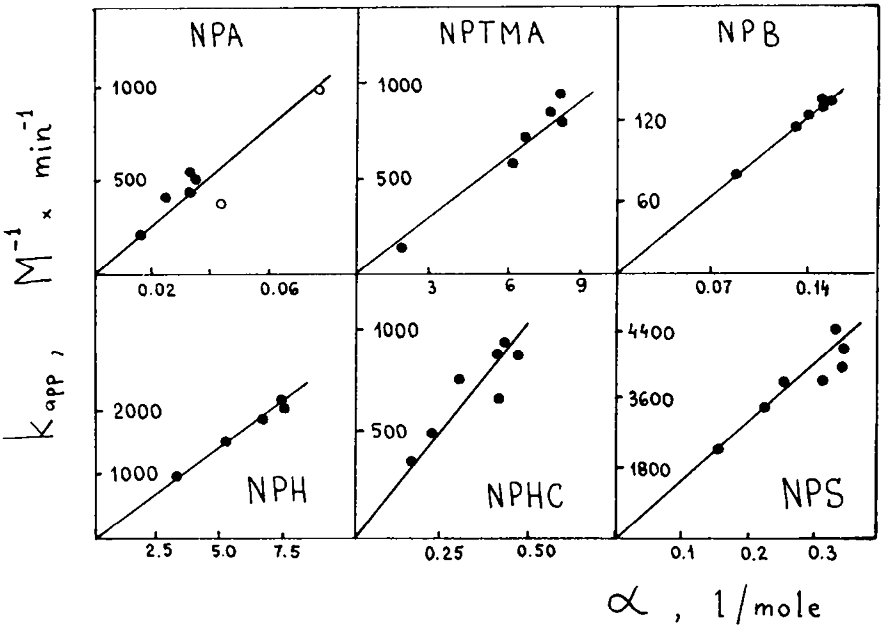

Fig 7. The apparent second-order rate constant for *m*-bromobenzaldoxime acylation by *p*-nitrophenyl carboxylates plotted as a function of the factor α at 25°, 1 v% of acetonitrile. The values of α were calculated using equations (23), (17) from measured K_A –, K_A, K_B. CTAB concentration was varied from 0 to 3 mM. NPA and NPTMA, the experimental conditions are given in the subscripts to Fig 5 and Fig 6, respectively. NPB, *p*H 6·2 with the concentrations of oxime and carboxylate being 2×10^{-4} M and $1{\cdot}4 \times 10^{-4}$ M, respectively. NPH, *p*H 7·3 with the concentrations of the oxime and carboxylate 5×10^{-4} M and 8×10^{-5} M, respectively. NPHC, *p*H 6·2 with the concentrations of oxime and carboxylate 4×10^{-4} M and 1×10^{-5} M, respectively. NPS, *p*H 6·5 with the concentrations of oxime and carboxylate 2×10^{-5} M and 3×10^{-5} M, respectively.

Fig 7 gives the k_{app}/α dependence for all carboxylates studied. The observed linear dependence (corresponding at α both to different [D] and *p*H) demonstrates the validity of Eq (16). The values of $\bar{k}_m$, equal to the slope of the straight lines in Fig 7 are presented in the Table.

The curves on Figs 5 and 6 plotting the detergent concentration–rate profiles have been calculated theoretically (using values of $\bar{k}_m$ taken from Fig 7). In spite of deviations near cmc (see above) the theoretical Eq (16) which takes into account only the micelle effect on the reaction (micellar catalysis) gives a satisfactory description of the experimental results. Eq (16) is an approximation as it does not take into account the possible effect of increased counter ions concentration with rising CTAB concentration. It appears that deviations caused by this effect do not exceed the limits of the experimental errors.

Mechanism of micellar effects on reaction rate

(i) *The pH dependent concentration effect.* The motive force for a heightening of the concentration in the micellar phase of reagents conctaining a non-polar fragment in the molecule is provided by the hydrophobic interaction.[12] When the reagent molecule contains in addition a charge, the effectiveness of sorption is strongly enhanced by the electrostatic interaction of this charge with that in the micelle.[17] It is therefore obvious that the concentration in the micellar phase should be different for ionic and non-ionic forms of the dissociating reagent. This causes the shift of the apparent pK_a value of the oxime observed in the presence of the detergent micelles and gives rise to the pH dependence of the concentration effect.

As in the reaction studied $K_{A^-} > K_A$ (see the section "Incorporation of the oxime in the micellar phase"), then the maximal acceleration, $(k_{app}/k_{app,[D]_t=0})_{max}$ observed in the presence of detergent micelles, reaches its peak at $[H^+]_b \gg K_a$, as follows from (20), with (20b) valid under these conditions. The latter equation is expedient to transform to

$$\left(\frac{k_{app}}{k_{app,[D]_t=0}}\right)_{max} = \frac{k_m}{k_b} \times \underset{(a)}{\frac{K_A K_B}{\bar{V}(\sqrt{K_A} + \sqrt{K_B})^2}} \times \underset{(b)}{\frac{K_{A^-}}{K_A}} \tag{24}$$

The factor of k_m/k_b in Eq (24) defines the maximal contribution of the pH dependent concentration effect to the micellar catalysis. The a fraction in the right part of (24) represents the heightening of the reagent concentration (i.e. the non-ionic form of the oxime and carboxylate) in the micellar phase. The b fraction denotes, as seen from Eq (17), the maximal shift of the oxime $K_{a(app)}$, that is $K_{a(app)}/K_a$ at a sufficiently high detergent concentration. It follows from the data presented in the section "Incorporation of the oxime into the micellar phase" that K_{A^-}/K_A is 15.

The values of $(k_{app}/k_{app,[D]t=0})_{max}$ calculated from measured K_{A^-}, K_A, K_B assuming $\bar{V} = 0{\cdot}35$ l/mole and $k_m/k_b = 1$ are given in the Table. This shows that the pH dependent concentration effect accelerates the reaction rate by three or four orders. The same Table lists the values of experimentally found accelerations of the reaction rate at $[H^+]_b \gg K_{a(app)}$ which also amount three to four orders. The concentration effect is thus seen to play the main part in the micellar catalysis, whereas the fact that the reaction as such proceeds in the micellar phase does not contribute to its marked acceleration, on the contrary, it does even often decellerate (see below).

(ii) *The influence of the reaction medium. The orientation effect.* The change in the reaction rate by replacing water for micellar medium depends on the relation of the second-order rate constants k_m/k_b. To calculate the true value of rate constant in the micellar phase, k_m, from experimental $\bar{k}_m$ (Table) one must know the molar detergent volume. The approximate values of k_m/k_b given in the Table are calculated assuming[14] $\bar{V} = 0{\cdot}35$ l/mole. One would expect k_m/k_b to be constant, for the mechanism of reaction (I) could be considered as being similar for all the p-nitrophenyl carboxylates studied. The Table shows that the reaction in the micelle medium leads either to a small rise in the reaction rate (NPS) or does not affect it (NPA), whereas in most cases the reaction is decellerated. The difference in reactivity, k_m/k_b for NPH and NPS is two orders as high. We believe that the observed dependence of reactivity change, k_m/k_b, on the structure of the side group R points to the difference in orientation of the ground states of reagents in the micellar phase. The NMR studies[13] suggest that CTAB absorbs aromatic molecules such as those of benzene and nitrobenzene into the aqueous portion of the interior of the micelles (not far from the surface) whereas aliphatic molecules are absorbed in the inner hydrocarbon portion of the micellar phase. Therefore, the relation k_m/k_b decreases as the side group R of the substrate is accumulating more "aliphatic" C atoms (Fig 8). This suggests the following mechanism of the orientation effect of reaction (I) proceeding in the micellar phase.

The *m*-bromobenzaldoxime anions seem to be all in the surface micelle layer with the reactive anion group turned towards water. The carboxylate molecule in ground state of acylation is situated so that the aliphatic part of its side group R is immersed into the hydrocarbon portion of the micelle. Therefore as the aliphatic part of the side group R is enlarged the ester group of the substrate becomes increasingly oriented to the inner hydrocarbon portion of the micelle thus becoming gradually less available for the oxime anion. Consequently, in the transient state of acylation the aliphatic part of the side group R should be transfered together with the ester bond into the interior of the micelle. The free energy increment of such a transfer forms a part of the overall free energy of activation. As a first approximation we shall assume the increment of the free energy of this transfer to be equal for the methyl and methylene groups and independent of their place in the side group R. In that case there must be a linear dependence of log (k_m/k_b) on the number of methyl and methylene groups in the acyl part. It is seen from Fig 8 that these values are in fact

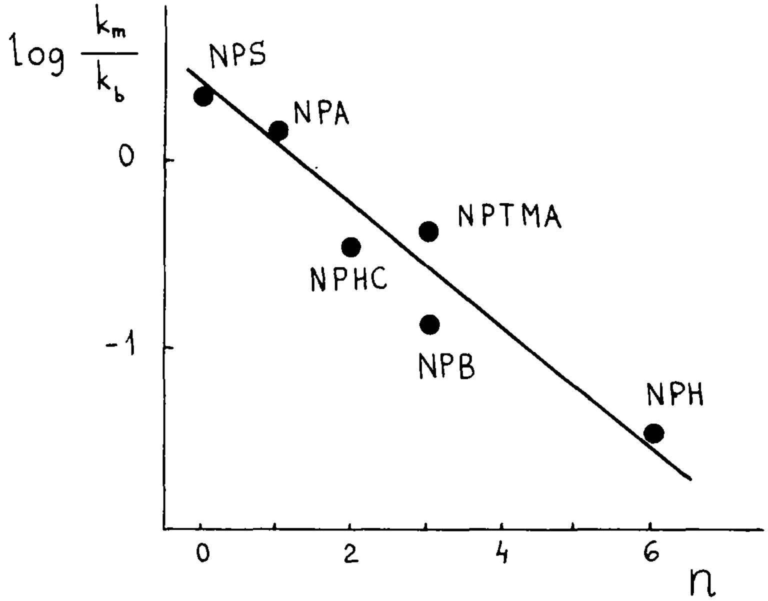

Fig 8. Variation in the logarithm of ratio of second-order rate constants for *m*-bromobenzaldoxime acylation by *p*-nitrophenyl carboxylates in micellar (k_m) and bulk (k_b) phases as a function of the number (n) of methyl and methylene groups in the acyl part of the carboxylate molecule (see the Table)

in a fair linear correlation. The slope of the straight line (−0·32) points to the free energy increment of a transfer of the CH_3— (or CH_2) group from the non polar micelle nucleus into its surface layer as being 430 cal/mole. This value is characteristic of the hydrophobic interaction.[19]

CONCLUSION

In order to explain the catalytic properties of the detergent micelles in similar reactions, recourse is often had to the concept of the surface micelle charge stabilising the ionic transient state.[15] Such an assumption seems to be superfluous. It is seen from the present work that the observed micellar effects can all be described satisfactorily in terms of concept of a heightening of reagents concentration in the micellar phase, their orientation in the micelle and the $pK_{a(app)}$ shift of the reagent under the action of the surface charge. The fact that a number of workers[2,6,20] have discovered decreased activation energy in the presence of micelles with the pre-exponent remaining constant or even being lowered, cannot be interpreted unequivocally, for the experimental activation energy reported by the authors pertains to the complex rate constant of the k_{app} type that involves the binding constants of reagents by the micelle whose temperature behaviour is unknown.

EXPERIMENTAL

Materials. m-Bromobenzaldoxime was prepared as recorded,[21] m.p. 73° (lit. 71·5°). *p*-Nitrophenyl salicylate (NPS) used was commercial reagent of Soyuzkhimreactiv. The following *p*-nitrophenyl carboxylates were obtained by Dorovska in accordance with the literature procedures: acetate (NPA),[22] m.p. 77° (lit. 77–78°); trimethyl acetate (NPTMA),[23] m.p. 95° (lit. 94–95°); butyrate (NPB),[24] b.p. 162–164° at 7–8 mm of Hg (lit. 162–164° at 7 mm of Hg); heptanoate (NPH),[25] b.p. 205–206° at 12 mm of Hg; hydrocinnamate (NPHC),[26] m.p. 99° (lit. 99–100°). *p*-Nitrophenol was supplied by Carlo Erba Co (for analysis grade).

Cetyltrimethylammonium bromide (CTAB) was a commercially available sample (Chemapol) recrystallised as recorded.[10] The critical micelle concentration (cmc 6×10^{-4} M at 25° and pH 8·3, borate buffer, 1 v% of acetonitrile) was estimated by the dye method.[6]

Components of buffer solns used were analytical grade reagents of Soyuzkhimreactiv. Composition of buffer solns: phosphate buffer 0·006 M $Na_2HPO_4.H_2O$ + 0·006 M KH_2PO_4 for pH 4·8–8·0; borate buffer 0·02 M H_3BO_3 + 0·005 M $Na_2B_4O_7$ + 0·01 M KOH for *p*H 7·5–11·5. Values of pH were measured with the Radiometer TTT 1c instrument at 25°.

Solubility measurements. The solubility of *p*-nitrophenyl carboxylate in the aqueous detergent soln was evaluated after equilibration by hydrolysing (as a result of addition of alkali soln to have the final pH value exceeding 12) to *p*-nitrophenolate ion which was determined spectrophotometrically (400 nm).

Kinetics. The general procedure for measuring the rate of reaction (I) involved the addition of a soln of *p*-nitrophenyl carboxylate in acetonitrile (0·03 ml) to the buffer solution containing CTAB and *m*-bromobenzaldoxime at the desired concentration (3·00 ml). The initial rate, *v*, of *p*-nitrophenolate ion liberation was followed spectrophotometrically (400 nm). The apparent second-order rate constant, k_{app}, was estimated by Eqn (3) with $[A]_t$ and $[B]_t$ being the overall concentrations of the oxime and carboxylate, respectively.

Spectrophotometry. The measurements were carried out in a Hitachi Perkin–Elmer 124 recording spectrophotometer, equipped with a cuvette holder through which water was circulated at 25 ± 0·1°. To determine the solubility of carboxylates and to obtain kinetic data the apparent molar absorptivity of *p*-nitrophenol at 400 nm depending on the detergent concentration and the *p*H value of respective buffer solution was measured.

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