

Reactions of Substituted Phenolate Ions with 4-Nitrophenyl Laurate Catalyzed by Cationic Micelles

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The bimolecular reaction of substituted phenolate ions with 4-nitrophenyl laurate is catalyzed by CTAB (cetyltrimethylammonium bromide). Two types of micellar catalysts are observed: one with ester and phenolate ion in "dilute solution" in the micelle (eq i) and the other when the micelle is "saturated" with phenolate ion (eq ii). The partition coefficients K_{eq} and K'_{eq} refer to equations for increasing CTAB and increasing phenolate ion concentrations and the rate constants obey the saturation rate laws (eqs i and ii, respectively).

$$\text{rate} = k_{ArO}^{cat}[\text{ester}][Ar\bar{O}][CTAB]/([CTAB] + K_{eq}) \quad (\text{i})$$

$$\text{rate} = k'_{ArO}^{cat}[\text{ester}][Ar\bar{O}][CTAB]/([Ar\bar{O}] + K'_{eq}) \quad (\text{ii})$$

The parameters obey the following Brønsted laws (eqs iii-vi).

$$\log k_{ArO}^{cat} = 0.69pK_{ArOH} - 4.9 \quad (\text{iii})$$

$$\log K_{eq} = 0.13pK_{ArOH} - 4.7 \quad (\text{iv})$$

$$\log k'_{ArO}^{cat} = 0.73pK_{ArOH} - 6.2 \quad (\text{v})$$

$$\log K'_{eq} = 0.40pK_{ArOH} - 6.5 \quad (\text{vi})$$

Rate constants were also obtained for the reaction of substituted phenolate ions with 4-nitrophenyl laurate in the absence of CTAB and the bimolecular rate constant obeys the Brønsted law (eq vii).

$$\log k_{ArO} = 0.87pK_{ArOH} - 10.37 \quad (\text{vii})$$

The results are consistent with a less advanced bond formation in the transition state in micellar catalysis compared with that in aqueous solution and with a less polar environment for the oxygen of the attacking phenolate ion at each state of the reaction coordinate.

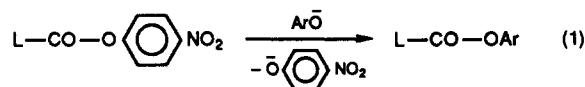
Introduction

It is well known that many bimolecular reactions are catalyzed by micelles. There is extensive evidence that the rate increases caused by the micelles are due largely to increases in local concentrations at the micellar surfaces. Current thought is that these entropy considerations are overriding; nevertheless the microscopic medium of the catalyzed reaction must differ from that of the bulk solvent, otherwise there would be no driving force for adsorption of the substrate. There is evidence that the change in microscopic medium could cause a change in transition-state structure.^{1b} Moreover, the change in microscopic medium at the micelle has been advanced as the cause of a gross change in mechanism in reactions of ester where an E1cB process is an alternative to a BAc2 pathway.^{1c} The present study addresses the problem of the medium effect in bimolecular reactions catalyzed by micelles.

We have recently indicated that partition constants for substituted phenyl laurates and CTAB (cetyl trimethylammonium bromide) micelles are independent of the substituent.^{1d} The effective charge on the leaving aryl oxygen atom in the attack of micelle-bound hydroxide ion on bound aryl laurates is close to that observed in the uncatalyzed reaction in water.^{1d} Bond formation and fission in the hydrolysis reaction are not symmetrical; almost certainly the hydroxide ion enters from an aqueous-like outer "layer" surrounding the micelle whereas

bond fission occurs in the diffuse aqueous-like layer with the phenyl ring partially submerged in the nonpolar core. It is not a simple process to study bond formation in hydroxide ion attack on the aryl esters. An analogous reaction, namely that of substituted phenolate ions with the aryl esters, provides a useful model to investigate this aspect of the transfer reaction where substituent effects will monitor effective charge on the entering nucleophilic oxygen atom. It is likely that the attacking phenolate ion will be more submerged in the micelle than is the hydroxide ion.

In this study we look at the reaction between substituted phenolate anions and 4-nitrophenyl laurate (eq 1) catalyzed by CTAB. The system has the advantage that the



analogous reaction of phenolate ions with aryl acetates in aqueous solvent has been investigated recently in depth and shown to involve a single transition state.² Potential difficulties over changes in the rate-limiting step with a mechanism involving an intermediate should not therefore arise. Moreover, earlier workers have provided precedents for phenolate ion attack on esters catalyzed by cationic micelles.³

(2) Ba-saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 6362; **1989**, *111*, 2647.

(3) (a) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213. (b) Cuccovia, I. M.; Schröter, E. H.; Monteiro, P. M.; Chaimovich, H. *J. Org. Chem.* **1978**, *43*, 2248. (c) Bunton, C. A.; Sepulveda, L. *Isr. J. Chem.* **1979**, *18*, 298. (d) Bunton, C. A.; Cerichelli, G.; Ihara, Y.; Sepulveda, L. *J. Am. Chem. Soc.* **1979**, *101*, 2429.

(1) (a) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975. (b) Rav-Acha, C.; Ringel, I.; Sarel, S.; Katzhendler, J. *Tetrahedron* **1988**, *44*, 5879. (c) Broxton, T. S. *Aust. J. Chem.* **1985**, *38*, 77. (d) Al-Awadi, N.; Williams, A. Submitted 1989.

Table I. Reaction of Substituted Phenolate Ions with 4-Nitrophenyl Laurate^a

substituent	pK _{ArOH} ^b	k _{ArO} × 10 ⁴ , ^c M ⁻¹ s ⁻¹	pH ^c	N ^d	Δ[ArOH], ^e mM	Δk _{obs} × 10 ⁵ /s ⁻¹
4-Me	10.20	410	10.56	3	14-40	30-92
H	9.86	80	10.13	4	11-41	17-33
4-Cl	9.38	56	9.72	4	30-40	1.8-5.7
3-Cl	9.02	36	10.6	4	10-40	60-70
4-Ac	8.05	3.9	10.1	3	32-62	2.3-3.5
4-CN	7.95	2.8	10.6	3	20-60	1.8-3.0
4-CHO	7.66	1.9	9.58	3	37-55	1.6-2.0

^a 25 °C, ionic strength made up to 0.1 M with KCl, wavelength for kinetic study 400 nm, ester concentration in range 0.5–1.0·10⁻⁵ M. ^b Values from Jencks, W. P.; Regenstein, J. in *Handbook of Biochemistry*, 2nd ed.; Sober, H. A., Ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1970, Section j-187. ^c Average pH, buffer component is borate buffer at 0.025 M. ^d Number of data points not including duplicates. ^e Range of total phenol concentrations employed. ^f Range of observed rate constants. ^g Uncertainties on these parameters are not greater than ±10%.

It is necessary to know the value of β_{eq} for the overall equilibrium constant in the pseudo phase if the extent of bond change in the transition state of the transfer reaction is to be measured; this work provides data for such as β_{eq} value.

Experimental Section

Materials. Substituted phenols were obtained commercially and, except where of AR grade, were recrystallised or sublimed. 4-Nitrophenyl laurate was purchased from Aldrich, and CTAB was purified by the method of Duynstee and Grunwald.^{4a} Buffer materials were of AR grade, and water was doubly distilled from glass.

Kinetics. Kinetics of the reaction of phenolate ions with 4-nitrophenyl laurate were measured by adding an aliquot (0.025 mL) of a stock solution of the ester in acetonitrile to buffer (2.5 mL) containing the required reagents in a silica cell in the thermostatted cell compartment of a Unicam SP800 spectrophotometer. The absorbance changes (A_t) at 400 nm were recorded as a function of time and the pseudo-first-order rate constants were obtained from a plot of log A_∞ - A_t against time.

For reactions without CTAB, buffer solutions were prepared from stock solutions containing phenol and buffer component and an identical solution adjusted to the same pH but without phenol. Mixing the stock solutions in the appropriate proportions gives a solution containing varying concentrations of phenol but with every other parameter (ionic strength, total bromide ion concentration, buffer concentration, and pH) constant.

Experiments where CTAB concentration was kept constant were carried out in buffers prepared by the above protocol with CTAB in both stock solutions. When CTAB concentration was varied and phenolate ion kept at 1 mM concentration, the phenolate ion was in both stock solutions and CTAB in one. The composition of the buffer and the ionic components is important because variation of these can cause differential partitioning of the reactant ions into the micellar pseudo phase. It is particularly important that Cl⁻ and Br⁻ concentrations should be constant throughout (see tables) because increasing the concentration of Br⁻ (by adding CTAB) can cause the rate constants to follow a much more complicated rate law than that of eq 3 in Results.

The pH's of the solutions were measured before and after each kinetic run with a micro pH probe inserted into the reaction cell (Russell CMAWL CL5 combination electrode). The pH meter employed was a Radiometer PHM 62 instrument, and the probe was standardized with EIL standard buffers to ±0.01 units. Results of kinetic runs where the pH variation exceeded 0.05 units were discarded. Data were fit with a general program (ENZ-FITTER; Leatherbarrow R., Biosoft, Hills Road, Cambridge, UK, 1987).

(4) (a) Duynstee, E. F. J.; Grunwald, E. *J. Am. Chem. Soc.* 1959, 81, 4540. (b) In both this and previous work^{1d} the cmc of CTAB (≈0.8 mM) is neglected in equations such as eq 3. This is contrary to the protocol of Menger and Portnoy^{4c} who use as the micelle concentration [surfactant] - cmc. This point is interesting as other work seems not to require this procedure. The partition equilibrium constants (K_{eq} or K_e) derived here refer to a molecular concentration rather than to micellar concentration. It is not immediately apparent that the concentration of non-micellized CTAB equals the cmc at total concentrations of added CTAB above the cmc level. The subject presumably needs further careful study. (c) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* 1967, 89, 4698.

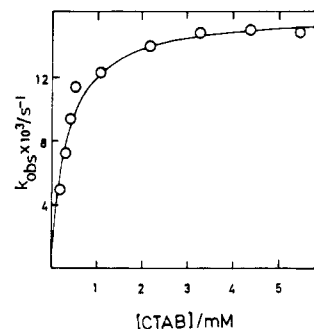


Figure 1. Dependence on CTAB concentration of the rate constant for release of 4-nitrophenol from 4-nitrophenyl laurate in buffers containing 3-chlorophenol (1 mM). Conditions as in Table II; line is calculated from eq 3 with parameters from Table II.

Results

Release of 4-nitrophenol from the 4-nitrophenyl laurate in the aqueous buffers studied here obeys pseudo-first-order kinetics up to at least 90% of the total reaction. All the reactions studied here had rate constants independent of the concentration of the ester within the ranges given in the tables. The critical micelle concentration (CMC) of the ester and its solubility in water are not known, but there is no evidence of aggregation (except by partitioning into the micelles) from the rate constant data. It is noted that there is approximately 1% of acetonitrile in the buffers due to the method of preparation of the ester solution.

The rate constants for reaction in aqueous solution without CTAB are proportional to the phenolate ion concentration; there is negligible background rate under the conditions compared with that due to the added phenol. Second-order rate constants were obtained by division of the slope of the plot of k_{obs} versus total phenol concentration by the fraction of phenolate ion present in the bulk solution (FB). The value of FB was computed from the pH and the pK_a of the phenol employed. There is ample evidence from previous work that reaction of aryl esters in phenol containing buffers is with the phenolate ion (eq 2).² Values of k_{ArO} for reaction of the phenolate ion with the laurate ester in aqueous buffers are recorded in Table I. The rate constants are lower than the corresponding parameters for attack of phenolate ions on 4-nitrophenyl acetate.²

$$k_{\text{obs}} = k_{\text{ArO}}[\text{ArO}^-] \quad (2)$$

Reaction of phenolate ions at low constant concentration (1 mM) with 4-nitrophenyl laurate in buffers containing increasing CTAB concentrations exhibit nonlinear kinetics (Figure 1). Under the current conditions of pH the rate constants were corrected by the small background rate constants in the absence of CTAB compared with those

Table II. Reaction of Substituted Phenolate Ions^a with 4-Nitrophenyl Laurate^c in the Presence of Increasing Concentrations of CTAB^{b,c}

substituent	$k_{\text{ArO}}^{\text{cat}}, \text{M}^{-1} \text{S}^{-1}$	$K_{\text{eq}} \times 10^4, \text{M}$	N^{e}	$\Delta k_{\text{obs}} \times 10^2, \text{s}^{-1}$	pH ^f
H	100 ± 6	4.2 ± 0.8	10	2-9	10.90
4-Cl	29 ± 1	3.6 ± 0.6	10	0.7-3	10.87
3-Cl	16 ± 0.5	3.5 ± 0.4	10	0.9-1.5	10.86
4-Ac	4.6 ± 0.3	3.1 ± 0.8	9	0.1-0.5	9.60
4-CN	4.1 ± 0.2	2.3 ± 0.4	9	0.1-0.4	10.20
4-CHO	2.4 ± 0.2	1.9 ± 0.7	10	0.09-0.25	9.50

^aTotal phenol concentration held at 1 mM throughout. ^bRange of CTAB concentration is 0.1-5.5 mM. ^c25 °C, ionic strength kept at 0.1 M with total [Br⁻] at 5.5 mM, borate buffer at 0.025 M. ^dRange of observed first-order rate constants. ^eEster concentration was between 0.5 and 1.0 · 10⁻⁵ M. ^fAverage pH value quoted. ^gNumber of data points not including duplicates.

Table III. Reaction of Substituted Phenolate Ions with 4-Nitrophenyl Laurate^b in the Presence of CTAB Held at 6 mM Concentration^a

substituent	$k'_{\text{ArO}}^{\text{cat}}, \text{m}^{-1} \text{s}^{-1}$	$K'_{\text{eq}} \times 10^4, \text{M}$	N^{c}	$\Delta k_{\text{obs}} \times 10^4, \text{s}^{-1}$	pH ^e	$\Delta[\text{ArOH}]/\text{mM}$
H	14 ± 1.3	37 ± 10	9	140-740	11.00	0.8-14
4-Cl	3.1 ± 0.2	17 ± 3	11	36-150	10.40	0.6-10
3-Cl	2.9 ± 0.3	8.3 ± 2.2	12	75-150	10.74	0.2-7
4-Ac	0.61 ± 0.03	8.3 ± 1.6	10	6.5-36	9.68	0.3-7
4-CN	0.32 ± 0.01	3.7 ± 0.7	6	6.5-17	9.68	0.4-6
4-CHO	0.32 ± 0.01	3.7 ± 0.3	14	6.5-18	9.68	0.2-7

^a25 °C, ionic strength kept at 0.1 M with total [Br⁻] at 6 mM, borate buffer at 0.025 M. ^bEster concentration was between 0.5 and 1.0 × 10⁻⁵ M. ^cNumber of data points not including duplicates. ^dRange of observed first order rate constants. ^eAverage pH value. ^fRange of total phenol concentration employed.

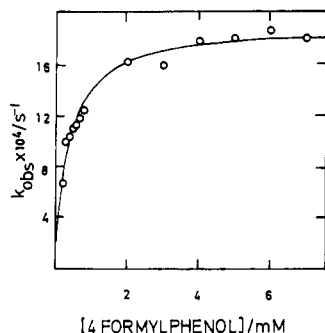


Figure 2. Dependence on 4-formylphenol concentration of the rate constant for release of 4-nitrophenol from 4-nitrophenyl laurate in buffers containing CTAB (6 mM). Conditions are from Table III; line is calculated from eq 7 with parameters from Table III.

in its presence. At constant CTAB concentration (of 6 mM) the rate constants are linear up to 1 mM in phenolate ion concentration (see Figure 2 and the supplementary tables). The pseudo-first-order rate constants (k) fit the rate law of eq 3.^{4b} Bunton and Sepulveda⁵ indicate that

$$k = k_{\text{ArO}}^{\text{cat}}[\text{ArO}^-][\text{CTAB}]/[K_{\text{eq}} + [\text{CTAB}]] \quad (3)$$

the dissociation partition coefficient of the micelle complex with neutral phenol is significantly greater than that of the phenolate ion-micelle complex. The pH's of the experiments here are at a value where the phenols are substantially ionized so that K_{eq} refers to the partitioning of the anion. The derived parameters are recorded in Table II with details of concentration, rate constant ranges, and other conditions. The parameters k_{ArO} , $k_{\text{ArO}}^{\text{cat}}$, and K_{eq} fit Brønsted equations 4-6, respectively.

$$\log k_{\text{ArO}} = (0.85 \pm 0.06)\text{p}K_{\text{ArOH}} - (9.9 \pm 0.6) \quad (4)$$

$$\log k_{\text{ArO}}^{\text{cat}} = (0.69 \pm 0.05)\text{p}K_{\text{ArO}} - (4.87 \pm 0.40) \quad (5)$$

$$\log K_{\text{eq}} = (0.13 \pm 0.03)\text{p}K_{\text{ArOH}} - (4.66 \pm 0.26) \quad (6)$$

Reaction of the 4-nitrophenyl laurate with increasing concentrations of phenolate ion at constant CTAB con-

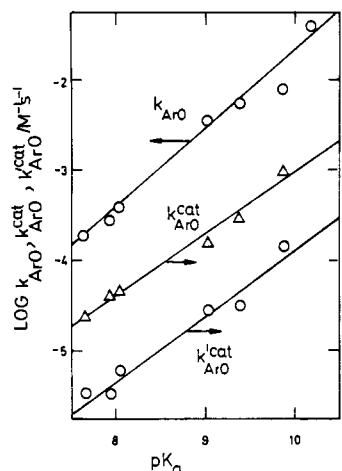


Figure 3. Brønsted dependence of k_{ArO} , $k_{\text{ArO}}^{\text{cat}}$, and $k'_{\text{ArO}}^{\text{cat}}$ on $\text{p}K_{\text{a}}$ of the corresponding phenol. Lines are calculated from eqs 4, 5, and 8, respectively, and the data and conditions are from Tables I-III.

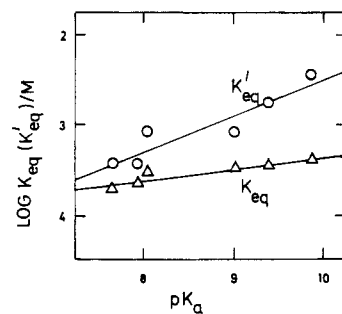
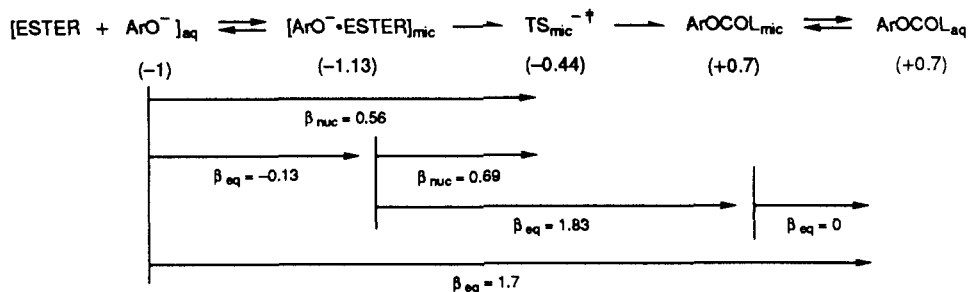


Figure 4. Brønsted dependence of K_{eq} and K'_{eq} on the $\text{p}K_{\text{a}}$ of the corresponding phenol. The lines are calculated from eqs 6 and 9, respectively, and the data and conditions are from Tables II and III.

centration (6 mM) where the ester is completely absorbed by the micelles¹ exhibits a nonlinear dependence of pseudo-first-order rate constant on phenolate ion concentration (Figure 2). The values of observed rate constants have been corrected by subtraction of a *small* background rate constant in the absence of CTAB due to reaction in the

(5) Bunton, C. A.; Sepulveda, L. *J. Phys. Chem.* 1979, 83, 680.

Scheme I.^a Effective Charge Map for the Micelle-Catalyzed Phenolysis of 4-Nitrophenyl Laurate. Ester and Aryl Oxide Ion Are Present as Dilute Solutions in the Micelle



^a Figures in parentheses in this and other schemes are the effective charges⁷ on the aryl oxygen atom at the various states of the reaction; "L" refers to the side chain of the lauric acid moiety "ESTER" is 4-nitrophenyl laurate and "TS" refers to the transition state of the reaction in question.

bulk phase. Reference to Table I for reaction without CTAB indicates that the background rates are indeed small and for practical purposes are neglected. The data fit eq 7, and the derived parameters are recorded in Table III. The parameters of eq 7 may be plotted as a function of $\text{p}K_{\text{ArOH}}$ and yield linear Brønsted eqs 8 and 9. The

$$k_{\text{obs}} = k'_{\text{ArO}^{\text{cat}}}[\text{CTAB}][\text{Ar}\bar{\text{O}}]/[K'_{\text{eq}} + [\text{Ar}\bar{\text{O}}]] \quad (7)$$

$$\log k'_{\text{ArO}^{\text{cat}}} = (0.73 \pm 0.07)\text{p}K_{\text{ArOH}} - (6.2 \pm 0.6) \quad (8)$$

$$\log K'_{\text{eq}} = (0.40 \pm 0.08)\text{p}K_{\text{ArOH}} - (6.5 \pm 0.7) \quad (9)$$

parameter $k'_{\text{ArO}^{\text{cat}}}$ refers to reaction of the ester in micelle "saturated" with phenolate ion; the parameter $k'_{\text{ArO}^{\text{cat}}}$ (eq 3) is the rate constant for reaction of dilute solutions of phenolate ion and ester in the micelle. The Brønsted lines from eqs 4–6, 8, and 9 are illustrated in Figures 3 and 4.

In the experiments quoted in this paper the ionic strength and total bromide ion concentration were kept at standard values to ensure that the micelle surface and bulk solvent had a constant ionic composition.

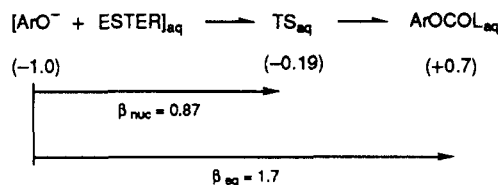
Discussion

This work confirms earlier results where cationic micelles catalyze the bimolecular reaction between anionic nucleophiles and neutral reagents.^{3,6} The rate enhancement for reaction of phenolate ion with 4-nitrophenyl laurate at concentrations of CTAB which abstract all ester and phenolate ion from bulk solution is some 13000:1 ($k_{\text{ArO}^{\text{cat}}}/k_{\text{ArO}}$) over the rate constant in the absence of surfactant. Data for the attack of hydroxide ion on 4-nitrophenyl laurate indicate a 780-fold enhancement for ($k_{\text{OH}^{\text{cat}}}/k_{\text{OH}}$),^{1d} indicating an approximately 20-fold advantage for the catalysis of the phenolate ion reaction.

Bunton and Sepulveda⁵ showed that aryl oxide ions partition into the CTAB pseudo phase with partition (dissociation) coefficients of the order of 10^{-3} M. The ester has a partition coefficient of similar magnitude to that of the phenolate ion so that observed values of K_{eq} which are composite functions of ester and phenolate ion partitioning will not easily be dissected into their component parameters.

The rate constant $k_{\text{ArO}^{\text{cat}}}$ (eq 3) for attack of phenolate ion on ester refers to a ground state where ester and phenolate ion exist as "dilute solutions" in the micellar pseudo phase. There is negligible concentration of the ester and phenolate ion species in the bulk aqueous phase.

Scheme II. Effective Charge Map for Reaction of Phenolate Anions with 4-Nitrophenyl Laurate

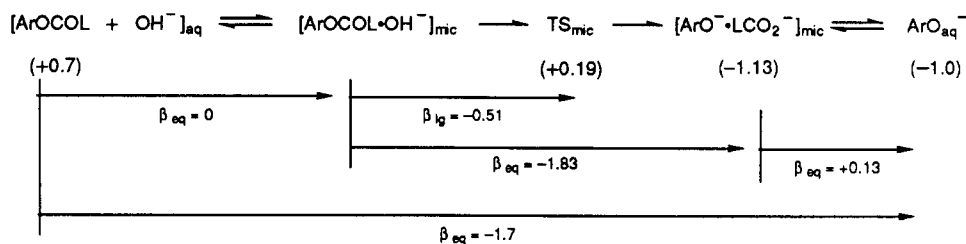


The parameter $k_{\text{ArO}^{\text{cat}}}/K_{\text{eq}}$ refers to a ground state in the bulk aqueous phase and the transition state of the rate-limiting step which resides in the pseudo phase. The Brønsted β_{nuc} coefficient for $k_{\text{ArO}^{\text{cat}}}/K_{\text{eq}}$ (0.56) refers to an overall change in effective charge⁷ of +0.56 on the phenol oxygen from the ground state in the bulk aqueous phase to the transition state in the pseudo phase; this is illustrated in the effective charge map (Scheme I). Previous work has shown that the partitioning of the substituted laurate ester between water and micelle has a β_{eq} value of zero.^{1d} We are thus able to define the β_{eq} value for transfer of the lauryl group in the micellar phase (1.83). The Leffler "α" value is a useful parameter which measures the extent of bond formation or fission in the transition state by comparing the effective charges on a reacting atom in the transition state with those on the atom in reactant and product states. The value of α is given by the ratio $\beta_{\text{nuc}}/\beta_{\text{eq}}$ or $\beta_{\text{fg}}/\beta_{\text{eq}}$ depending on whether bond formation or fission is being studied.⁷ The Leffler α value for the phenolysis of 4-nitrophenyl laurate in the micellar phase possessing "dilute" aryl oxide ions is $0.37 = 0.69/1.83$ and this compares with the result for aqueous solution of $0.51 = 0.87/1.7$ (Scheme II). The rate constants in water for aryl oxide ion and hydroxide ion^{1d} attack on the 4-nitrophenyl laurate are significantly lower than those of the corresponding acetate, presumably due to steric hindrance of the lauryl group bulk caused by "balling up" of the aliphatic side chain in its noncompatible water medium. In the micellar pseudo phase the lauryl side chain will be extended into the hydrophobic core and thus exhibit less steric hindrance to nucleophilic attack at the ester. The bond-forming step in the attack of phenoxide ions on the 4-nitrophenyl laurate ($\alpha = 0.37$) is thus less advanced than it is in the reaction in water, this could reflect a weaker solvation of the aromatic oxyanion in the pseudo phase compared with that in water, and this is consistent with the slightly negative value of β_{eq} for partitioning of the oxyanion into

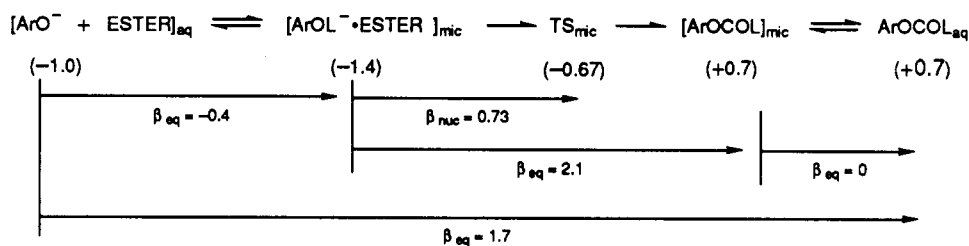
(6) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* 1986, 22, 213.

(7) (a) Williams, A. *Acc. Chem. Rev.* 1984, 17, 425. (b) Thea, S.; Williams, A. *Chem. Soc. Rev.* 1986, 16, 125. (c) The effective charge is measured relative to the charge change in the standard equilibrium namely the ionisation of phenol in water.

Scheme III. Effective Charge Map for the Alkaline Hydrolysis of Aryl Laurates Catalyzed by CTAB



Scheme IV. Effective Charge Map for the Phenolysis of 4-Nitrophenyl Laurate Catalyzed by CTAB Micelles Saturated with Phenoxide Ions



the pseudo phase. The oxyanion thus resides in its ground state in the pseudo phase in a less polar environment than in water.

Knowledge of the β_{eq} for partitioning of phenoxide ion into the pseudo phase (as a dilute "solution") enables us to dissect the micelle-catalyzed alkaline hydrolysis of laurate esters (Scheme III) studied previously.^{1d} The Leffler α value for bond fission in the hydrolysis in aqueous solution ($\alpha = 0.33 = 0.56/1.7$) is greater than that in the micellar phase ($\alpha = 0.27 = 0.51/1.83$). Bond fission is thus less advanced in the pseudo phase for the hydrolysis compared with that for the reaction in bulk water.

The Brønsted dependence for $k'_{\text{ArO}^{\text{cat}}}$ represents the effective charge change on the phenoxide oxygen from the ground to transition state in the pseudo phase of the micelle "saturated" with phenolate ion; the Brønsted β value for $k'_{\text{ArO}^{\text{cat}}}/K'_{\text{eq}}$ represents the change from *bulk aqueous* ground state to the transition state in the "saturated" micellar pseudo phase. The charge changes are shown in the effective charge map in Scheme IV. The Leffler α value ($0.35 = 0.73/2.1$) for the reaction in the pseudo phase indicates a less advanced transition state than in water consistent with a less polar medium for the location of the transition state in the pseudo phase which is "saturated" with phenolate ion.

The values of β_{eq} for the phenolyses in the pseudo phases where phenolate ion is "dilute" and "saturated" are respectively +1.83 and +2.1. These values are greater than that for the phenolysis in water (+1.7), reflecting the less polar environment of the phenoxide in both cases. The micelle "saturated" with phenoxide ion provides an environment which stabilizes the negative charge of the bound phenolate ion less than that of water or the "dilute" micelle. These data are consistent with those of Iyer⁸ who showed that adsorbed aromatic anions are partially buried in the hydrophobic core of the cationic micelle. As the bulk concentration of phenolate ion in the bulk water increases the micelle becomes "saturated" with phenoxide ion; the medium surrounding an adsorbed phenoxide ion under these circumstances is surely different from that for the

case where complete abstraction of the phenolate ion from the bulk solvent is achieved by increasing the CTAB concentration.

The magnitudes of the effective charges on the oxygen of the attacking phenolate ion in its various states in the reaction coordinate in both types of pseudo phase (in parentheses in Schemes I and IV) are considerably more negative than for the corresponding states in bulk water (Scheme II). This is consistent with the oxygen's environment being less polar in the micellar reaction than in water; the increased negative effective charge on the oxygens in the micelles saturated with phenolate ions is presumably due to the effect of the extra adsorbed phenolate species.

The use of the Leffler parameter as an indicator of the extent of bond formation or fission depends on the correct choice of β_{eq} against which to compare the kinetic β value.⁷ Such choice is not usually a problem in the study of reactions in homogeneous solution. The assignment of a β_{eq} for a heterogeneous reaction such as one in micellar solution suffers from the additional complication of a multiplicity of microenvironments ranging from that of the hydrophobic core through the Stern layer to the bulk medium. A further problem concerns the location of the phenolate ion in the pseudo phase; this location might not be the same as that of the transition-state. This problem is eliminated by discussion of the overall term $k_{\text{ArO}^{\text{cat}}}/K_{\text{eq}}$ (or $k'_{\text{ArO}^{\text{cat}}}/K'_{\text{eq}}$) where the nonproductive binding components are cancelled out even though K_{eq} or K'_{eq} might include these. There is a useful analogy with enzyme-substrate reactions where $k_{\text{cat}}/K_{\text{m}}$ does not include the nonproductive binding components present in K_{m} .⁹ The wide variation of Hansch π parameters for substituents employed¹⁰ and the reasonable fit of K_{eq} and K'_{eq} to a single Hammett parameter would indicate that the phenolate ions are binding in a single region of the pseudo phase. Although we are confident of our present assignments we recommend caution in the application of substituent effects in heterogeneous systems.

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Conclusion

In the case where both reactants are absorbed by the hydrophobic core of the micelle the reacting bonds are forced into a region so that the electronic structure of the transition state differs from that in aqueous solution; the nature of the region, as reflected by the effective charges on the attacking oxygen at the various stages of the re-

action path, is not water-like.

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Supplementary Material Available: Tables of rate constants from which parameters in Tables II and III are derived (4 pages). Ordering information is given on any current masthead page.

Photolyses of (3-Naphthoxypropyl)-, (4-Naphthylbutyl)-, and (4-Naphthyl-4-oxobutyl)cobaloxime

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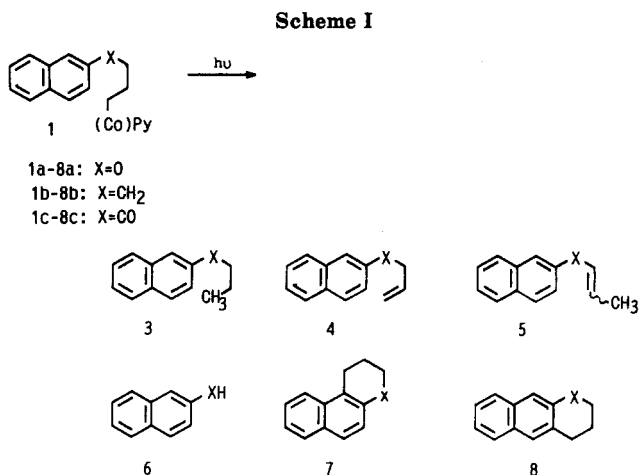
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The cobalt-carbon bond of the titled compounds is photochemically cleaved to generate an organoradical and a cobaloxime(II) radical pair. 3-(1- or 2-naphthoxy)propyl, 4-(1- or 2-naphthyl)butyl, and 4-(1- or 2-naphthyl)-4-oxobutyl radicals thus formed undergo three types of reactions: (a) hydrogen abstraction to give a saturated terminal, (b) hydrogen elimination to give a terminal olefin, and (c) substitution on the naphthalene ring. In benzene and radicals follow process b exclusively (the radicals from (3-(2-naphthoxy)propyl)cobaloxime (1a), (3-(1-naphthoxy)propyl)cobaloxime (2a), and (4-(1-naphthyl)butyl)cobaloxime (2b)) or preferentially (the radicals from (4-(2-naphthyl)butyl)cobaloxime (1b), (4-(2-naphthyl)-4-oxobutyl)cobaloxime (1c), and (4-(1-naphthyl)-4-oxobutyl)cobaloxime (2c)). In chloroform, process a becomes important to the extent as the sum of the other two processes. In water-acetonitrile (4:1), process c becomes important and even takes precedence of others for the radicals from 1b and 1c. This feature is accounted for by the folding of the side chain of hydrophobic radicals. Encapsulation of the radicals in β -cyclodextrin stimulates process c except for the case of the radical from 2c. In the case of cobaloxime 2c, α -cyclodextrin does not affect the partition process of the intermediate radical. This feature is accounted for by the shallow inclusion of the radical due to the hydrogen bonding as depicted in Figure 1d.

We have been concerned with the biomimetic reaction of coenzyme B₁₂ using organobis(dimethylglyoximate)-(pyridine)cobalt(III), organocobaloxime as a model compound,¹ and have exploited the photolytic cleavage of the alkyl-cobalt bond of organocobaloximes to generate an organoradical and cobaloxime(II) radical pair.² In those model studies the organoradicals have phenyl or carbonyl functions at the position β to the radical center. We selected these systems to test the participation of the functional groups in radical rearrangements. Those experiments prompted us to explore the photolysis of alkylcobaloximes having a naphthyl group at the δ -position. The naphthyl group was selected to test the effect of cyclodextrin on the photolyses in an aqueous medium.

Results and Discussion

(3-(2-Naphthoxy)propyl)cobaloxime (1a), (4-(2-naphthyl)butyl)cobaloxime (1b), (4-(2-naphthyl)-4-oxobutyl)cobaloxime (1c), (3-(1-naphthoxy)propyl)cobaloxime (2a), (4-(1-naphthyl)butyl)cobaloxime (2b), and (4-(1-naphthyl)-4-oxobutyl)cobaloxime (2c) were synthesized from the corresponding bromides and cobaloxime(I) anion³



in the same manner as reported in earlier papers.² Elemental analyses and spectroscopic data fully supported the structures of those organocobaloximes. The UV absorption of organocobaloxime has been well characterized, and its absorption at the longest wavelength appears at 440-460 nm. This absorption band is assigned to a ligand to metal charge transfer and is responsible for the radical rupture of the cobalt-carbon bond of organocobaloximes.⁴

Photolyses of the organocobaloximes gave a variety of products, as shown in Schemes I and II. Products 3a,⁵ 4a,⁶ 6a, 7a,⁷ 9a,⁵ 9b,⁸ 9c,⁹ 10a,¹⁰ 12b,¹¹ 13a,¹² 15a, and 16a⁷

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