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Effective Charge Development in Ester Hydrolysis Catalyzed by Cationic Micelles

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Reaction of hydroxide ion with substituted phenyl laurates is catalyzed by micelles containing CTAB (cetyltrimethylammonium bromide). The observed rate constants for ester consumption obey a Michaelis–Menten-like rate law, $k_{\mathrm{obsd}} = (k_{\mathrm{OH}}K_{\mathrm{eq}} + k_{\mathrm{OH}}^{\mathrm{cat}}[\mathrm{CTAB}])[\mathrm{OH}]/(K_{\mathrm{eq}} + [\mathrm{CTAB}])$, where $k_{\mathrm{OH}}^{\mathrm{cat}}$ is the second-order rate constant for reaction of hydroxide ion with micelle-bound ester, K_{eq} is a partition coefficient for dissociation of ester from the micelle-bound ester, and k_{OH} is the second-order rate constant for reaction of free ester with hydroxide ion. The value of the parameter K_{eq} is independent of the nature of the substituent on the ester. The ratio $k_{\mathrm{OH}}^{\mathrm{cat}}/K_{\mathrm{eq}}$ represents the free energy change from ester in aqueous solution to the transition state of the ester reaction in the micellar pseudophase. The dependence of log $k_{\mathrm{OH}}^{\mathrm{cat}}/K_{\mathrm{eq}}$ on the pK_a of the leaving phenol obeys a linear Brønsted equation with $\beta_{\mathrm{lg}} = -0.51$, and log k_{OH} obeys a linear Brønsted equation with $\beta_{\mathrm{lg}} = -0.56$. Since both Brønsted parameters refer to catalyzed and uncatalyzed reactions starting from the same standard state (aqueous solution), the effective charge in the transition states of both reactions is almost the same. The microscopic medium is thus similar for both cases, consistent with the COOAr moiety's residing in an aqueous-like region of the pseudophase in the catalytic process.

Introduction

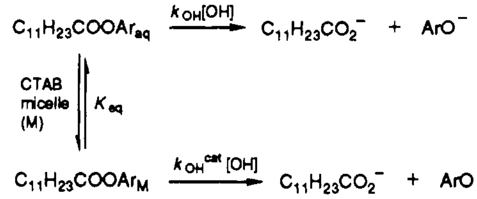
The dominant factor in the efficiency of micellar catalysis of bimolecular reactions has been recognized as the increased concentration of reactants in the pseudophase caused by partitioning from bulk solvent.[1] There is no doubt that the pseudophase region possesses considerable variation of polarity. Investigation of the pseudophase based on static parameters which give rise to data relating to global polarity[2–6a] are of importance but do not relate to polarity at a reaction center. Moreover, the "reporter" molecules employed in such studies are usually completely absorbed into the core of the micelle. Intrinsic polarity "reporter" molecules where the "reporter" groups lie in the pseudophase region (such as 1-methyl-4-dodecylpyridinium iodide)[6b] will refer to ground-state polarity.

The advantage of measuring polarity by observations of polar substituent effects on rates is that polarity differences may be measured between ground and transition states. This approach is essentially "blind" to effects not directly concerned with catalysis such as "nonproductive" binding of substrate in the micelle.

The present contribution concerns the reaction of hydroxide ion with substituted phenyl laurates catalyzed by CTAB (cetyltrimethylammonium bromide). The stoichiometry of the reaction is shown in Scheme I, where the ester is partitioned into the micelle, which already has a local concentration of hydroxide ions in its Stern layer.

The effect on the various kinetic parameters of varying the substituent on the leaving phenolate ion enables us to compare the effective charge[7,8] (see Appendix) on the leaving oxygen in the transition state of the micellar process with that for the process in water. This comparison should give us information about the polarities of the microscopic medium of the micellar transition state compared with that for the water reaction related to that of the ester in the standard state in water.

Scheme I. Stoichiometry of Reaction of Aryl Laurates with Hydroxide Ion Catalyzed by CTAB



Several workers have reported investigations of substituent effects on micellar catalyses to study polarity factors. These include acetal and ortho ester hydrolysis with "oil in water" and "water in oil" systems[9] as well as nucleophilic reactions of esters.[10] These studies provide Hammett or Brønsted data referring to reaction of the substrate in the pseudophase and hence yield polarity differences *within* that phase. In order to compare effective charges for different transition states, it is necessary to determine Brønsted parameters relating to the transfer of substrate between the *bulk* phase and the pseudophase. This work determines the Brønsted slopes for kinetic and equilibrium parameters (k_{OH}, $k_{\mathrm{OH}}^{\mathrm{cat}}$, and K_{eq}) for reaction of hydroxide ion with aryl laurates catalyzed by CTAB. With this data we can compare the polarity of the microscopic medium of the ester transition state in the pseudophase with that in the aqueous phase.

Experimental Section

Materials. Substituted phenyl laurates were prepared by reacting lauroyl chloride with phenols in the presence of triethylamine in dichloromethane solvent cooled in ice. The esters were obtained by evaporating the dichloromethane after extraction with dilute HCl and drying ($MgSO_4$). The 4-nitrophenyl ester was purchased from Aldrich. The esters were characterized by analysis (supplementary table), and their structures are consistent with the ^{1}H NMR spectra measured with a JEOL 100-MHz instrument. CTAB was purchased from Aldrich and was purified by the method of Duynstee and Grunwald.[11]

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Table I. Hydrolysis of Substituted Phenyl Laurates over a Range of pH Values in the Presence of 6 mM CTAB at 25 °C[a]

substituent	mp,[b] °C	pK^{ArOH}	$k'_{OH}{}^{cat,c}$ M^{-1} s^{-1}	ΔpH^d	N^e	$\Delta k_{obsd} \times 10^{4,f}$ s^{-1}	λ^g
2-NO_2-4-Cl	48-9	6.05	31	10-11.0	4	32-320	423
4-NO_2		7.16	14	10-11.0	4	23-140	400
2-NO_2	34-5	7.21	11	10-11.0	4	20-100	412
4-CN	60-1	7.95	9.5	10-11.0	5	13-96	280
3-NO_2	43-4	8.37	4.5	10.3-11.0	3	6-36	266
3-Cl	29-30	9.02	2.0	10-11.0	4	2-20	250
4-Cl	38-9	9.38	1.6	11.3-12.3	4	16-330	244
parent	liquid	9.95	0.57	11.5-12.5	3	8-190	245
4-Me	liquid	10.2	0.39	11.5-12.5	4	8-130	243

[a] Ester concentration was in the range (0.5–1) × 10^{-5} M. [b] Melting point of the laurate ester. [c] Obtained by division of the rate constants by hydroxide ion concentration. Uncatalyzed hydrolysis rates were negligible compared to the catalytic rates under these conditions. [d] Range of pH over which measurements were made. [e] Number of data points not including duplicates. [f] Range of observed rate constants. [g] Wavelength for kinetic studies.

Buffer materials were of analytical reagent grade, and water used throughout the investigation was doubly distilled from glass.

Methods. The reaction under investigation was studied initially by repetitively scanning the UV–vis spectrum to determine the best wavelength for kinetic measurements. Ester hydrolyses were followed by adding an aliquot (0.05 mL) of the ester in acetonitrile (ca. 0.001 M) to the buffer solution (2.5 mL) in a silica cell in the thermostated cell compartment of a Unicam SP 800 spectrophotometer. The buffer solution was prepared with various CTAB concentrations by mixing a stock solution of buffer containing CTAB with an identical stock buffer solution without CTAB. The technique enables one to keep pH, buffer, and ionic strength constant while varying one component; it was also used in experiments where bromide ion concentration was kept invariant. The effect on pH of ion partitioning between micellar and bulk phases was nullified by adjusting the pH's to the required values.

The absorbance change during reaction was measured as a function of time, and pseudo-first-order rate constants were determined from the slope of linear plots of $A_\infty - A_t$ against time on two-cycle semilogarithmic graph paper. The pH of the buffer solution in the spectrophotometric cell was measured after the completion of the reaction with a Radiometer PHM26 pH meter calibrated with EIL standard buffers to ±0.01 pH units. The difference in pH between reaction solution and original buffer was less than 0.1 pH units for the reported data.

Data were fit with a BBC microcomputer using Basic language programs.

Results

Liberation of substituted phenol from the aryl laurates in buffer solutions with and without added CTAB obeyed excellent pseudo-first-order kinetics up to about 90% of the total reaction. The rate constants for hydrolysis of the esters are linear in hydroxide ion concentration in borate buffers (0.01 M) containing 6 mM CTAB with ionic strength made up to 0.1 M with KCl (Figure 1). Rate constants for the esters varied with increasing CTAB concentration as shown in Figure 2 at constant pH and with no added bromide ion except that of the surfactant. The variation is similar to that observed by Cordes[12] for the hydrolysis of 4-nitrophenyl hexanoate in CTAB-containing buffer. The results illustrated in Figure 2 are characteristic of the ion-exchange effect[13] whereby increasing the bulk bromide ion concentration displaces hydroxide ion from the Stern layer of the micelle. The pseudo-first-order rate constants for hydrolysis of the substituted esters at 6 mM CTAB at a constant bromide ion concentration of 6 mM and chloride ion at 0.094 M were corrected for background hydrolysis, and division by the hydroxide ion concentration (computed from pH and pK_w) gave the rate constants $k'_{OH}{}^{cat}$, which are recorded in Table I.

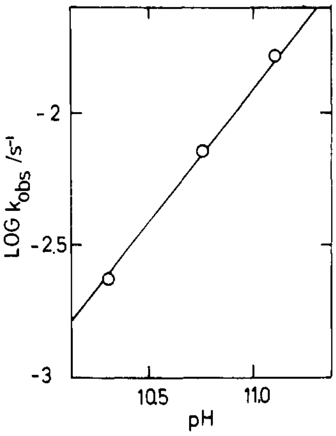

Figure 1. Dependence on pH of the hydrolysis of 4-nitrophenyl laurate in buffer containing 6 mM CTAB, borate buffer (0.01 M); temperature maintained at 25 °C and ionic strength kept at 0.1 M with KCl.

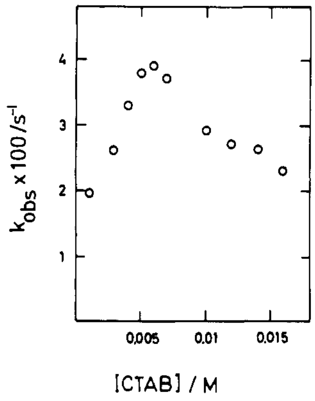

Figure 2. Dependence on CTAB concentration of the hydrolysis of 4-nitrophenyl laurate at pH 11.45, 25 °C. Borate buffer at 0.025 M and ionic strength 0.1 M maintained with KCl. The total bromide ion concentration is not maintained at a constant level.

The effect of CTAB concentration on the hydrolysis rate of the esters at bulk bromide ion concentration held constant at 0.09 M differs from that shown in Figure 2 (see Figure 3); the data obey a saturation-type rate law, 1,[14a] for concentrations of CTAB up to 0.09 M.

$$k_{obsd} = \frac{(k_{OH}{}^{cat}[CTAB] + k_{OH}K_{eq})[OH]}{K_{eq} + [CTAB]} \tag{1}$$

The rate constant $k_{OH}{}^{cat}$ refers to the apparent bimolecular rate constant of micelle-bound ester with bulk hydroxide ion. The parameter K_{eq} (an apparent dissociation constant or a partition coefficient) is the same as $1/K_s$

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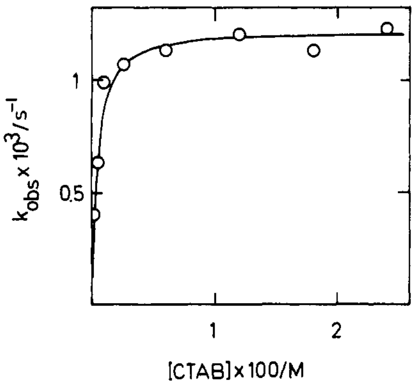


Figure 3. Dependence on CTAB concentration of the hydrolysis of 3-chlorophenyl laurate at pH 11.66 and 25 °C with borate buffer at 0.01 M and bromide ion maintained at 0.09 M. Line is calculated from data in Table III.

Table II. Hydrolysis of Substituted Phenyl Laurates over a Range of pH Values in the Absence of Surfactant at 25 °C[a]

substituent	$k_{OH} \times 10^{3,b}$ M^{-1} s^{-1}	ΔpH[c]	N^d	$\Delta k_{obsd} \times 10^{5,e}$ s^{-1}
2-NO_2-4-Cl	46	11.6–12.6	4	12–190
4-NO_2	18	11.6–12.8	4	8–160
2-NO_2	14	12.0–13.2	4	14–250
4-CN	13	12.1–13.3	3	16–180
3-NO_2	6.3	12.0–13.4	3	6–250
3-Cl	1.8	11.8–13.4	4	1–50
4-Cl	1.0	12.5–13.4	4	3–25
parent	0.39	12.5–13.4	3	0.4–16
4-Me	0.22	12.0–13.6	4	0.2–9

[a] Ester concentration was in the range (0.5–1) × 10^{-5} M. Wavelengths as in Table I. [b] Obtained by division of pseudo-first-order rate constants by the hydroxide ion concentration. [c] Range of pH over which measurements were made. [d] Number of data points not including duplicates. [e] Range of observed rate constants.

Table III. Rate Parameters for CTAB-Catalyzed Alkaline Hydrolysis of Substituted Phenyl Laurates at Constant Bulk Bromide Ion Concentration[a]

substituent	k_{OH}^{cat}, M^{-1} s^{-1}	$K_{eq} \times 10^4$, M	$\Delta k_{obsd} \times 10^{4,b}$ s^{-1}	Δ-[CTAB],[c] mM	N^d
2-NO_2-4-Cl	5.8 ± 0.3	3.9 ± 0.7	68–230	1–5	11
4-NO_2	4.8 ± 0.1	4.1 ± 0.7	80–190	1–45	9
2-NO_2	4.5 ± 0.1	4.1 ± 0.7	80–180	0.5–45	12
4-CN	3.3 ± 0.1	4.0 ± 0.4	40–130	0.2–24	7
3-NO_2	0.55 ± 0.03	4.3 ± 0.2	6–22	0.2–24	7
3-Cl	0.30 ± 0.01	3.8 ± 0.6	4–12	0.2–24	8
4-Cl	0.28 ± 0.01	3.9 ± 0.7	4–11	1–20	6
parent	0.101 ± 0.008	4.0 ± 0.2	0.6–3.6	0.1–20	7
4-Me	0.088 ± 0.005	4.2 ± 0.1	1.2–3.4	1–30	7

[a] Total bromide ion concentration kept constant at 0.09 M by addition of KBr; borate buffer at 0.01 M and pH at 11.66; 25 °C. [b] Range of rate constants. [c] Range of CTAB concentrations employed. [d] Data points not including duplicates.

defined by Bunton and Savelli[1] and is used by us because its unit is molarity and it is analogous to K_m, the Michaelis–Menten parameter for enzyme substrate kinetics. The parameter k_{OH} is the rate constant for reaction of hydroxide ion with ester in the absence of CTAB. Background hydrolysis, although it is included in eq 1, is negligible under the conditions of our experiments in CTAB-containing buffers. Data for k_{OH} are recorded in Table II. The data were fit to eq 1 and the results are recorded in Table III. Goodness of fit to eq 1 is illustrated in Figure 3 for reaction of the 4-chlorophenyl laurate; standard deviations on the parameters are recorded in Table III.

The effect of the borate buffer concentration on the kinetics was found to be negligible within the experimental error of the determined rate constants for 4-nitrophenyl laurate hydrolysis at 18 mM CTAB, 0.09 M bulk bromide ion concentration, and pH 11.21. The borate concentration was varied between 0.01 and 0.03 M.

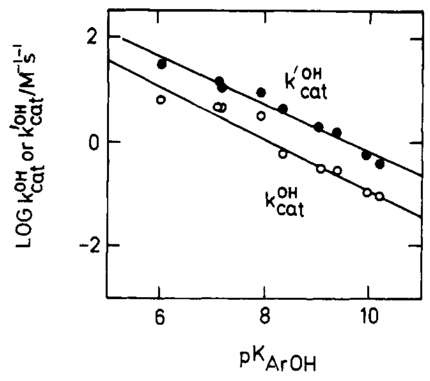


Figure 4. Brønsted dependences on the pK_a of the leaving phenol for $k'_{OH}{}^{cat}$ and $k_{OH}{}^{cat}$ for micelle-catalyzed hydrolyses of substituted phenyl laurates. Data and conditions are from tables I and III, and lines are calculated from eq 2 and 3.

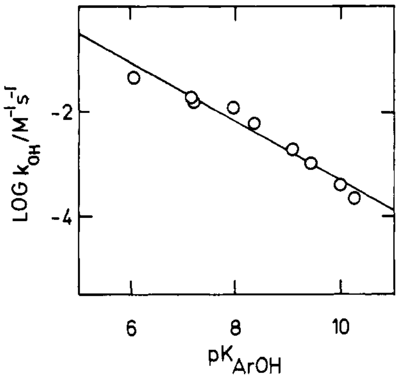
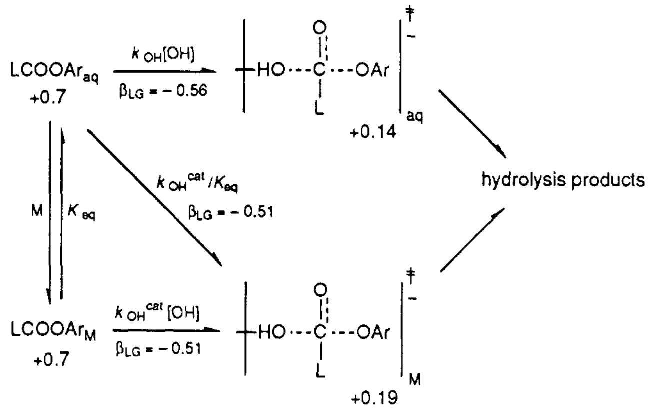


Figure 5. Brønsted dependence of k_{OH} on the pK_a of the leaving phenol in the hydrolysis of substituted phenyl laurates. Data and conditions are from Table II, and line is calculated from eq 4.

Scheme II. Effective Charge Map for Alkaline Hydrolysis of Aryl Laurates in the Presence and Absence of CTAB[a]



[a] [M = micelle].

Brønsted plots of the kinetic paramters $k'_{OH}{}^{cat}$ and $k_{OH}{}^{cat}$ (Tables I and II) are recorded in Figure 4. Figure 5 illustrates the Brønsted dependence of k_{OH}. Equations 2, 3, and 4 govern the rate constants $k'_{OH}{}^{cat}$, $k_{OH}{}^{cat}$, and k_{OH}, respectively, and refer to constant bulk bromide ion concentration.

$$\log k'_{OH}{}^{cat} = (-0.46 \pm 0.03)\,\mathrm{p}K^{ArOH} + (4.41 \pm 0.27) \quad (2)$$

$$\log k_{OH}{}^{cat} = (-0.51 \pm 0.06)\,\mathrm{p}K^{ArOH} + (4.17 \pm 0.49) \quad (3)$$

$$\log k_{OH} = (-0.56 \pm 0.05)\,\mathrm{p}K^{ArOH} + (2.30 \pm 0.4) \quad (4)$$

Discussion

The general result of this work, namely, that a cationic surfactant catalyzes the alkaline hydrolysis of an ester, is in good agreement with the results of other workers.[10,12,15-18] The catalytic effect is reduced by added bromide ion, consistent with partial ion exchange of the hydroxide ion in the Stern layer of the micelle.

The dissociation partition coefficient for the ester, K_{eq}, exhibits no change with substituent (Table III). Consideration of Hansch π parameters[19] indicates that the substituent should have a significant effect if the ester were dissolved completely in the hydrophobic core of the micelle. The π parameters, derived from the partition coefficient for transport of substituted phenoxyacetic acids between 1-octanol and water, vary between -0.3 and $+0.76$ for the substituent range studied (the π values for the 2-nitro-4-chloro species are not known).[19] The data are consistent with a model where the aliphatic backbone of the laurate ester is absorbed in the core of the micelle with the phenyl and ester moieties in the interfacial region so that the substituent is surrounded by bulk water or a water-like medium.

The ratio $k_{OH}{}^{cat}/K_{eq}$ or $k'_{OH}{}^{cat}/K_{eq}$ relates to the free energy change from *aqueous solution* to the transition state of the reaction in the pseudophase. There is a useful analogy with enzyme–substrate reactions between the kinetically determined enzyme parameters k_{cat}/K_m and the present $k_{OH}{}^{cat}/K_{eq}$. The ratio cancels out nonproductive binding terms even though K_{eq} and K_m might include these.[20,21] In the micellar catalysis case, a nonproductive binding mode could involve complete incorporation of the ester in the hydrophobic core, which would thus protect it from hydrolysis.

The slope of the Brønsted dependence of k_{OH} measures the effective charge difference between the ground state in aqueous medium to the transition state in the same solvent; it agrees with that from other work on other aryl esters.[22] The slope of the Brønsted dependence for $k_{OH}{}^{cat}/K_{eq}$ measures the effective charge difference from aqueous solution to the transition state in the pseudophase. The effective charge map of the reactions is shown in Scheme II.

The main result of this work is that the effective charge on the transition state in the micelle is almost the same as that in bulk water. The simplest explanation of this result is that the microscopic medium for the ester moiety in the micelle (at the transition state) has similar polarity to that in bulk water. Thus a model for the transition state would involve "solution" of the laurate side chain in the core of the micelle leaving the ester function (COOAr) in that part of the interfacial region that is bulk solvent like. The current view of the interfacial region of the micelle (oil in water) is that is has a significant amount of water molecules and ions in mobile equilibrium with the bulk solution.[1,3,13] Our results are consistent with no electronic enhancement of ester hydrolysis. Presumably the absorption of the lauryl side chain in the micelle core automatically places the polar ester group into the interfacial region.

Iyer and his co-workers[23] have indicated that simple hydroxy benzoate anions bind with CTAB micelles, placing part of the phenyl ring within the hydrophobic region. It is unlikely that the binding of the aliphatic backbone of the laurate esters in the micelle will allow a similar configuration of the phenyl ring in the interfacial region; nevertheless, Iyer's results would probably predict that the phenyl group does not extend into bulk water. This is consistent with our results; it is possible that part of the phenyl group of the ester could be influenced by the hydrophobic core while the substituent and ester functions remain in the interfacial region. The interfacial region possesses significant polarity due presumably to charged groups and water molecules.

If both the phenyl ring and the lauryl side chain of the ester were in the hydrophobic micellar core with the ester moiety in the interfacial region, the configuration of the ester would be the more energetic "cis" form.[24] We do not believe that the data available at present can indicate if this is a factor in micellar catalysis of ester hydrolysis.

Acknowledgment. We thank the University of Kuwait for sabbatical leave and funds (N.A.-A.).

Appendix

Unit effective charge is defined by a standard ionization equilibrium (against which β is measured in the Brønsted plot) under standard conditions.[7,8] In the present study, the standard reaction is the ionization of phenols (eq A1). Effective charge change on an atom in a reaction (such as in eq A2) is the hypothetical charge change required to produce the observed substituent effect compared with that in the standard equilibrium. The charge change in

$$\underset{0}{\mathrm{ArOH}} \xrightleftharpoons{K_a} \underset{-1}{\mathrm{ArO^-}} + \mathrm{H^+} \tag{A1}$$

$$\underset{+0.7}{\mathrm{ArOCOR}} + \mathrm{Nu} \xrightleftharpoons{K_{eq}} \underset{-1}{\mathrm{ArO^-}} + \mathrm{RCONu} \tag{A2}$$

eq A1 is defined as -1, and of course the Brønsted β for this reaction is exactly -1 unit. The Brønsted β for K_{eq} of eq A2 is -1.7 so that the effective charge change will be -1.7 units for this reaction. Since the product phenoxide is the same for both equations, it is as if $+0.7$ unit of effective charge resides on the aryl oxygen in the ester. It should be appreciated that effective charge is a hypothetical quantity; the change in absolute charge on the oxygens in eq A1 is certainly not unity.

Registry No. CTAB, 57-09-0; phenol, 108-95-2; 2-nitrophenol, 88-75-5; 3-nitrophenyl, 554-84-7; 4-chloro-2-nitrophenol, 89-64-5; 4-cyanophenol, 767-00-0; 3-chlorophenol, 108-43-0; 4-chlorophenol, 106-48-9; 4-methylphenol, 106-44-5; lauroyl chloride, 112-16-3; phenyl laurate, 4228-00-6; 4-chloro-2-nitrophenyl laurate, 125357-83-7; 4-nitrophenyl laurate, 1956-11-2; 2-nitrophenyl laurate, 2639-52-3; 4-cyanophenyl laurate, 90149-61-4; 3-nitrophenyl laurate, 125357-84-8; 3-chlorophenyl laurate, 125357-85-9; 4-chlorophenyl laurate, 83491-06-9; 4-methylphenyl laurate, 10024-57-4.

Supplementary Material Available: Table of analytical and physical data for substituted phenyl laurates (1 page). Ordering information is given on any current masthead page.

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(20) The parameter $k_{OH}{}^{cat}/K_{eq}$ is an apparent third-order rate constant; it can only be a true microscopic rate constant when the rate-limiting step is the encounter between hydroxide ion, ester, and micelle.

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