JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 74–80

Effects of inert organic and inorganic anions on the rates of intramolecular general base-catalyzed reactions of ionized phenyl salicylate (PS^-) with piperidine in the presence of cationic micelles

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Received 27 April 2000; revised 30 June 2000; accepted 29 August 2000

ABSTRACT: Pseudo-first-order rate constants (k_{obs}) for piperidinolysis of PS^- follow the relationship $k_{obs} - k_0 = k_n^{obs}[Pip]_T$ ($[Pip]_T$ = total concentration of Pip) at a constant $[CTABr]_T$ (total concentration of cetyltrimethylammonium bromide), [MX] (inert salt concentration) and 35 °C. The values of k_n^{obs} at different $[CTABr]_T$ (ranging from 0.005 to 0.02 M) and [MX] follow the relationship $k_n^{obs} = (k^n_W + k^n_W \Psi [MX] + k^{ns}_M K_N K_S^0[CTABr]_T)/(1 + \Psi [MX] + K_S^0 [CTABr]_T)$, where $k^n_W = k_n^{obs}$ at $[CTABr]_T = [MX] = 0$, Ψ is an empirical parameter and K_S^0 is the CTABr micellar binding constant of PS^- in the absence of MX. The magnitude of Ψ is attributed to the ability of X^- to expel PS^- from micellar pseudophase to the aqueous pseudophase. The values of Ψ vary in the order Ψ(sodium cinnamate) $>$ Ψ(sodium 4-methoxybenzoate) $>$ Ψ(sodium 2-chlorobenzoate) $>$ Ψ(disodium isophthalate) $>$ Ψ(disodium phthalate) $>$ Ψ(sodium sulfate) $>$ Ψ(disodium fumarate). The values of $k^{ns}_M K_N$ ($k^{ns}_M = k^n_M/V_M$, where k^n_M is the second-order rate constant for the reaction of Pip with PS^- in the micellar pseudophase and V_M is the micellar molar volume in M^{-1} and K_N represents CTABr micellar binding constant of Pip) are not significantly affected by the presence of MX into the reaction mixtures. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: phenyl salicylate; piperidine; aminolysis; hydrolysis; intramolecular general base catalysis, sodium salts of organic and inorganic acids; micelles; cationic surfactants

INTRODUCTION

The occurrence of ion exchange appears to be a ubiquitous feature observed in ionic micellar-mediated reactions involving ionic reactant(s) where ionic reactant(s) and counterions carry similar charge. The pseudophase ion exchange (PIE) model was developed to explain the reaction kinetics of ionic micellar-mediated reaction involving only one ion-exchange process.[1] The PIE model has been also used in a few reactions involving two ion-exchange processes but with additional restrictive reaction conditions.[2,3] The weaknesses of PIE model started to appear in the literature.[4] The rates of alkaline hydrolysis of esters[5] and *N*-hydroxyphthalimide,[6] in the presence of inert salt (MX) and cationic micelles, have been discussed in terms of PIE model coupled with an empirical linear equation which measures the effect of MX on cationic micellar binding constant (K_S) of anionic organic substrate. The rates of methanolysis[7] *n*-butylaminolysis[8] and piperidinolysis[8] of PS^-, in the presence of MX and CTABr micelles, showed that the variation of K_S with [MX] did not follow an empirical linear equation. In continuation of our work on the effects of inert inorganic and organic salts on rates of hydrolysis, alkanolysis and aminolysis of PS^- in the presence of cationic micelles, we now report the effects of a few organic anions and sulfate ions on the rate of reaction of PS^- with piperidine.

EXPERIMENTAL

Materials. All the reagents used were supplied by Fluka, BDH and Aldrich and were of the highest commercially available purity. Stock solutions of phenyl salicylate were prepared in acetonitrile. Stock solutions of organic acids (mono- or dicarboxylic) were prepared in aqueous NaOH solution containing an excess of 0.05 M NaOH. An excess of 0.05 M NaOH was maintained to avoid the possibility of the presence of non-ionized organic acids in the stock solutions. The stock solutions of piperidine were freshly prepared in distilled water.

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Contract/grant sponsor: National Scientific Research and Development Council of Malaysia; *Contract/grant number:* 09-02-03-0003.

Kinetic measurements. The rate of piperidinolysis of PS^- was studied by monitoring the disappearance of PS^- as a function of time at 350 nm. The required amount of the sodium salt of an organic acid was introduced into the reaction mixture by using a stock solution (y M) of an organic acid (containing a monocarboxylic group) prepared in ($y + 0.05$) M NaOH aqueous solution. The stock solutions (0.25 or 0.5 M) of NaOH were used to introduce 0.02 M NaOH into the reaction mixture in each kinetic run. Thus, the total concentration of NaOH added to the reaction mixture in each kinetic run was >0.02 and ≤ 0.04 M. The details of the kinetic procedure, data analysis and product characterization study were as described elsewhere.[9]

RESULTS AND DISCUSSION

In order to find the effects of total concentration of piperidine ($[Pip]_T$) on the rate of reaction of PS^- with Pip, three kinetic runs were carried out at different $[Pip]_T$ ranging from 0.04 to 0.10 M within the [NaOH] range >0.02 to ≤ 0.04 M at a constant concentration of inert salt (MX = sodium salt of an organic acid or sodium sulfate) and cetyltrimethylammonium bromide (CTABr). Pseudo-first-order rate constants (k_{obs}) obeyed the equation

$$k_{obs} - k_0 = k_n^{obs}[Pip]_T \qquad (1)$$

where k_0 is pseudo-first-order rate constant for hydrolysis of PS^- and k_n^{obs} is the nucleophilic second-order rate constant for the reaction of Pip with PS^-. The values of k_0 at different $[CTABr]_T$, in the absence of MX, were obtained from the literature.[10] Although the values of k_0 are expected to increase with increase in the concentration of MX (owing to the increase in $[HO^-]$) at a constant $[CTABr]_T$, the effectiveness of such an increase would have caused the appearance of definite intercepts in the plots of $k_{obs} - k_0$ versus $[Pip]_T$ and the magnitudes of such intercepts should have increased with increase in [MX]. However, some representative plots of $k_{obs} - k_0$ versus $[Pip]_T$ for the most effective salt (sodium cinnamate) among all the salts in the present study, as shown in Fig. 1, did not reveal any definite intercept. It may be noted that the maximum contribution of k_0 (obtained at the lowest $[Pip]_T$ = 0.04 M, 0.005 M CTABr and 0.2 M sodium cinnamate) is <9 % even if k_0 is considered to be six times larger than k_0 at 0.005 M CTABr with (sodium cinnamate] = 0.

The values of k_n^{obs}, under different reaction conditions, were calculated from Eqn. (1) and the results, obtained in the presence of sodium cinnamate, sodium 2-chlorobenzoate, sodium 4-methoxybenzoate, disodium phthalate, disodium isophthalate, disodium fumarate and sodium sulfate, are summarized in Tables 1 and 2. The reliability of the fitting of the observed data to Eqn. (1) is

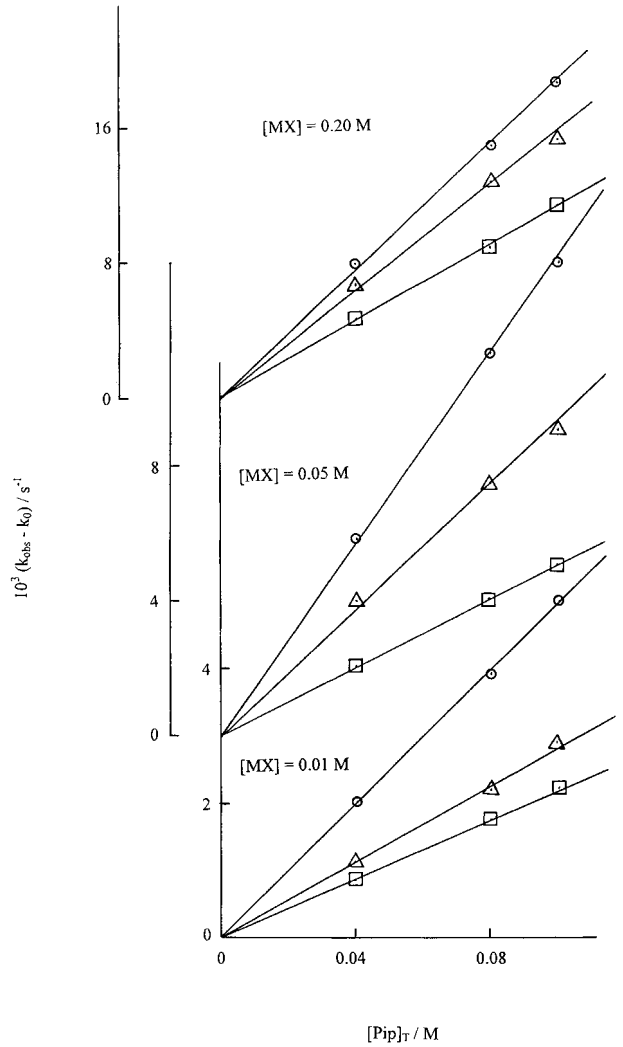


Figure 1. Plots showing the dependence of $k_{obs} - k_0$ on $[Pip]_T$ for the reaction of Pip with PS^- at a constant concentration of sodium cinnamate ([MX]) and (○) 0.005, (△) 0.01 and (□) 0.02 M CTABr. The solid lines are drawn through the calculated data points using Eqn. ((1))

evident from some representative plots in Fig. 1 and from the standard deviations associated with the values of k_n^{obs} (Tables 1 and 2). It is known that the presence of additives (such as inert salts of organic and inorganic acids) in the aqueous micellar solution changes the shape, size and characteristic intrinsic properties of micelles.[11] However, the satisfactory fit of the observed data to Eqn. (1) indicates that any change in the shape, size and characteristic intrinsic properties of micelles due to the change in $[CTABr]_T$, $[Pip]_T$ and [MX] (MX = sodium salt of an organic or inorganic acid) at 2×10^{-4} M PS^- is kinetically insignificant.

The effects of sodium 2-chlorobenzoate on k_n^{obs} were also studied at different $[CTABr]_T$ where 0.5 M stock solutions of 2-chlorobenzoic acid were prepared in 1.0 M NaOH aqueous solution. These results are summarized in Table 1. In these kinetic runs, an increase in [MX] from

Table 1. Effects of [MX] and [CTABr] on second-order rate constants (k_n^{obs}) for the reaction of piperidine with PS^- at 35 ° C[a]

[MX] (M)	[CTABr] (M)	$10^3 k_n^{obs}$ $(M)^{-1} s^{-1}$	$10^3 k_n^{cal}$ $(M)^{-1} s^{-1}$	$10^3 k_n^{obs}$ $(M)^{-1} s^{-1}$	$10^3 k_n^{cal}$ $(M)^{-1} s^{-1}$	$10^3 k_n^{obs}$ $(M)^{-1} s^{-1}$	$10^3 k_n^{cal}$ $(M)^{-1} s^{-1}$	$10^3 k_n^{obs}$ $(M)^{-1} s^{-1}$	$10^3 k_n^{cal}$ $(M)^{-1} s^{-1}$
		MX[b]		MX[c]		MX[d]		MX[e]	
0.005	0.005	35.4 ± 0.3[f]	37.6						
0.005	0.010	23.7 ± 0.4	26.5						
0.005	0.015	23.2 ± 0.1	22.6						
0.005	0.020	21.2 ± 0.3	20.6						
0.010	0.005	49.8 ± 0.8	50.9	30.3 ± 0.6[f]	32.7	32.1 ± 0.8[f]	33.8	34.4 ± 0.7[f]	35.0
0.010	0.010	28.2 ± 0.7	33.8	23.6 ± 0.2	24.6	25.3 ± 1.7	25.2	26.1 ± 0.4	25.8
0.010	0.015	25.0 ± 0.5	27.6	23.6 ± 0.2	21.8	22.6 ± 0.3	22.3	22.4 ± 0.8	22.6
0.010	0.020	22.0 ± 0.4	24.4	21.4 ± 0.5	20.4	22.8 ± 0.5	20.8	21.9 ± 0.3	21.0
0.020	0.005	85.5 ± 2.8	74.1	37.7 ± 2.0	40.4	42.1 ± 1.3	42.4	45.1 ± 1.2	44.8
0.020	0.010	45.7 ± 1.0	47.4	29.0 ± 0.2	28.8	29.4 ± 1.4	29.9	32.3 ± 0.5	31.1
0.020	0.015	32.9 ± 0.4	37.2	23.8 ± 0.3	24.6	25.5 ± 0.8	25.4	25.3 ± 0.8	26.2
0.020	0.020	24.7 ± 0.7	31.9	23.2 ± 0.1	22.5	23.8 ± 0.4	23.2	23.7 ± 1.7	23.7
0.050	0.005	143 ± 2	125	68.3 ± 1.2	61.3	65.2 ± 1.0	65.3	77.0 ± 3.1	70.6
0.050	0.010	94.6 ± 4.0	81.5	41.0 ± 0.6	40.5	44.8 ± 0.3	42.9	45.6 ± 3.5	45.9
0.050	0.015	63.8 ± 1.7	62.6	33.9 ± 1.1	32.8	35.4 ± 2.2	34.5	35.3 ± 1.2	36.6
0.050	0.020	50.8 ± 0.9	52.1	28.1 ± 1.1	28.8	29.5 ± 2.2	30.1	28.8 ± 1.4	31.7
0.050	0.020					28.5 ± 0.7	30.1		
0.100	0.005	188 ± 4	175	95.0 ± 1.6	90.0	101 ± 1	96.2	109 ± 3	104
0.100	0.010	127 ± 2	123	62.3 ± 1.8	58.1	61.1 ± 2.0	62.2	69.2 ± 2.2	67.6
0.100	0.015	106 ± 1	96.3	46.1 ± 1.0	45.4	50.0 ± 0.9	48.4	52.9 ± 2.0	52.4
0.100	0.020	82.7 ± 2.6	80.2	36.9 ± 1.7	38.6	42.2 ± 1.1	41.0	41.6 ± 3.8	44.1
0.100	0.020	82.8 ± 2.4	80.2						
0.200	0.005	192 ± 7	225	134 ± 4	132			146 ± 5	151
0.200	0.005			130 ± 5	132				
0.200	0.010	161 ± 8	174	81.0 ± 1.6	87.4	93.7 ± 2.8	93.8	102 ± 2	102
0.200	0.015	138 ± 5	143	64.8 ± 0.4	67.6	67.2 ± 0.6	72.7	75.4 ± 0.6	79.3
0.200	0.020	115 ± 3	122	53.0 ± 4.9	56.4	59.4 ± 4.2	60.6	67.4 ± 3.4	66.0

[a] [phenyl salicylate]$_0$ = 2 x 10^{-4} M, [NaOH] = 0.02 m, 35 °C, λ = 350 nm and aqueous solvent for each kinetic run contained 2% (v/v) CH_3CN.
[b] MX = sodium cinnamate.
[c] MX = sodium 2-chlorobenzoate (0.5 M stock solution of 2-chlorobenzoic acid was prepared in 0.55 M NaOH).
[d] MX = sodium 2-chlorobenzoate (0.5 M stock solution of 2-chlorobenzoic acid was prepared in 1.0 M NaOH).
[e] MX = sodium 4-methoxybenzoate.
[f] Error limits are standard deviations.

0.01 to 0.20 M increased the added [NaOH] from 0.03 to 0.22 M. However, even under such conditions, the contribution of k_0 turned out to be negligible compared with k_n^{obs} $[Pip]_T$ in Eqn. (1), as can be seen from the following discussion.

The rate of hydrolysis of phenyl salicylate is independent of $[HO^-]$ within the range ~0.005–0.060 M and, under such conditions, the rate of hydrolysis involves PS^- and H_2O as the reactants.[12] The rate of reaction between PS^- and HO^- becomes significant only at $[HO^-] >\sim 0.06$ M. The value of the second-order rate constant (k_{OH}) for the reaction between PS^- and HO^- is $1.24 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 30 °C in the absence of CTABr micelles.[9a] These results show that the value of k_0 (= pseudo-first-order rate constant for hydrolysis of PS^-) should be nearly 50% higher at 0.2 M MX than at 0.01 M MX and $[CTABr]_T$ = 0. However, the least-squares calculated respective values of k_0 and k_n^{obs} at 0.2 M MX are $(-0.6 \pm 6.2) \times 10^{-4}\ s^{-1}$ and $(96.8 + 8.0) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 0.01 M CTABr, $(1.4 \pm 0.5) \times 10^{-4}\ s^{-1}$ and $(66.8 \pm 0.6) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 0.015 M CTABr and $(0.9 \pm 8.2) \times 10^{-4}\ s^{-1}$ and $(59.6 \pm 10.5) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 0.02 M CTABr. The respective values of k_0 and k_n^{obs} at 0.01 M MX are $(2.1 \pm 0.4) \times 10^{-4}\ s^{-1}$ and $(30.8 \pm 0.6) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 0.005 M CTABr, $(-0.7 \pm 0.6) \times 10^{-4}\ s^{-1}$ and $(28.4 \pm 0.8) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 0.01 M CTABr, $(1.3 \pm 0.4) \times 10^{-4}\ s^{-1}$ and $(22.4 \pm 0.5) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 0.015 M CTABr and $(1.2 \pm 1.0) \times 10^{-4}\ s^{-1}$ and $(22.7 \pm 1.3) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 0.02 M CTABr. These calculated values of k_0 and their standard deviations merely indicate the insignificant contribution of k_0 compared with k_n^{obs} $[Pip]_T$ in Eqn. (1) and consequently the increase in $[HO^-]$ from 0.021 to 0.22 M could not have any effect on k_0 values. The values of k_n^{obs}, obtained by using 0.5 M stock solutions of 2-chlorobenzoic acid prepared in 1.0 M NaOH, are essentially similar to the corresponding k_n^{obs} obtained by using 0.5 M stock solutions of 2-chlorobenzoic acid prepared in 0.55 M NaOH (Table 1). These results show the absence of a kinetically detectable amount of protonated piperidine ($PipH^+$) within the [NaOH] range 0.021–0.040 M.

The values of k_n^{obs} increased from 35.4×10^{-3} to $192 \times 10^{-3}\ M^{-1}\ s^{-1}$ with increase in [sodium cinnamate] from 0.005 to 0.2 M at 0.005 M CTABr (Table 1). Such an

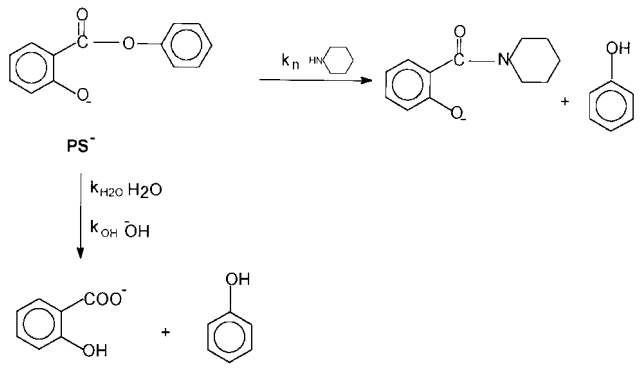
Table 2. Effects of [MX] and [CTABr] on second-order rate constants (k_n^{obs}) for the reaction of piperidine with PS^- at 35 °C[a]

[MX] (M)	[CTABr] (M)	$10^3 k_n^{obs}$ (M^{-1} s^{-1})	$10^3 k_n^{cal}$ (M^{-1} s^{-1})	$10^3 k_n^{obs}$ (M^{-1} s^{-1})	$10^3 k_n^{cal}$ (M^{-1} s^{-1})	$10^3 k_n^{obs}$ (M^{-1} s^{-1})	$10^3 k_n^{cal}$ (M^{-1} s^{-1})	$10^3 k_n^{obs}$ (M^{-1} s^{-1})	$10^3 k_n^{cal}$ (M^{-1} s^{-1})
		MX[b]		MX[c]		MX[d]		MX[e]	
0.005	0.005	28.7 ± 0.7[f]	29.2	33.7 ± 0.3[f]	32.4			29.5 ± 1.0[f]	31.3[g]
0.005	0.010	23.2 ± 0.7	24.7	22.5 ± 2.6	27.7			25.9 ± 0.5	26.4
0.005	0.015	22.5 ± 0.4	23.2	19.0 ± 0.7	26.1			24.6 ± 0.2	24.8
0.005	0.020	17.8 ± 0.6	22.4	23.9 ± 0.4	25.3			22.0 ± 0.3	24.0
0.010	0.005	28.3 ± 1.0	29.8	35.5 ± 0.2	33.5	27.5 ± 0.3[f]	28.2	31.1 ± 0.3[f]	32.7[h]
0.010	0.005	32.6 ± 1.4	29.8						
0.010	0.010	24.1 ± 2.8	25.1	29.0 ± 0.4	28.3	23.7 ± 0.6	24.0	27.6 ± 0.3	27.2
0.010	0.015	22.8 ± 1.9	23.4	23.5 ± 2.6	26.5	23.6 ± 0.7	22.5	24.8 ± 0.2	25.3
0.010	0.020	22.2 ± 2.1	22.6	21.0 ± 2.0	25.6	20.5 ± 0.5	21.8	24.2 ± 0.3	24.4
0.010	0.020	22.2 ± 0.9	22.6						
0.020	0.005	29.8 ± 1.1	31.0	44.3 ± 3.9	35.7	29.3 ± 0.4	28.3	38.8 ± 0.3	41.1[i]
0.020	0.010	23.3 ± 0.5	25.7	32.2 ± 1.3	29.4	23.5 ± 0.2	24.0	34.6 ± 1.1	31.6
0.020	0.015	22.0 ± 2.1	23.9	24.6 ± 0.4	27.3	22.9 ± 0.1	22.6	31.7 ± 0.6	28.3
0.020	0.020	20.7 ± 2.4	22.9	24.5 ± 0.4	26.2	21.1 ± 0.4	21.8	26.4 ± 3.3	26.6
0.050	0.005	44.3 ± 0.9	34.6	55.0 ± 3.9	42.2	28.5 ± 0.3	28.8	44.2 ± 2.1	46.4[j]
0.050	0.010	30.0 ± 3.2	27.6	35.4 ± 0.6	32.9	26.0 ± 0.3	24.2	39.1 ± 2.1	34.5
0.050	0.015	26.0 ± 2.3	25.1	32.8 ± 0.7	29.6	22.7 ± 1.0	22.7		
0.050	0.020	26.1 ± 0.2	23.9	28.8 ± 0.6	28.0	21.4 ± 1.4	21.9		
0.100	0.005	48.0 ± 3.2	40.5	65.0 ± 3.0	52.3	30.5 ± 0.7	29.5		
0.100	0.005	47.0 ± 3.2	40.5						
0.100	0.010	33.6 ± 2.1	30.7	41.4 ± 2.1	38.4	26.6 ± 0.7	24.6		
0.100	0.015	28.9 ± 2.3	27.2	34.1 ± 1.7	33.4	24.4 ± 0.9	23.0		
0.100	0.020	27.2 ± 2.2	25.5	28.4 ± 1.9	30.8	22.0 ± 0.5	22.1		
0.200	0.005	45.0 ± 2.7	51.4	63.4 ± 3.0	70.6	30.1 ± 1.2	30.9		
0.200	0.010	31.5 ± 1.9	36.6	44.3 ± 0.8	48.8	26.6 ± 0.9	25.3		
0.200	0.015	26.5 ± 1.2	31.3	35.4 ± 3.1	40.7	22.6 ± 0.5	23.4		
0.200	0.020	26.0 ± 2.3	28.6	30.9 ± 1.6	36.4	18.7 ± 0.4	22.5		

[a] [phenyl salicylate]$_0$ = 2 x 10^{-4} M, [NaOH] = 0.02 M, 35 °C, λ = 350 nm and aqueous solvent for each kinetic run contained 2% (v/v) CH_3CN.
[b] MX = disodium phthalate.
[c] MX = disodium isophthalate.
[d] MX = disodium fumarate.
[e] MX = sodium sulfate.
[f] Error limits are standard deviations.
[g] [MX] = 0.05 M.
[h] [MX] = 0.10 M.
[i] [MX] = 0.40 M.
[j] [MX] = 0.60 M.

increase in k_n^{obs} cannot be attributed to ionic strength and medium effects because an increase in [Na_2SO_4] from 0.05 to 0.6 M revealed only a modest increase in k_n^{obs} from 29.4 × 10^{-3} to 44.2 × 10^{-3} M^{-1} s^{-1} at 0.005 M CTABr (Table 2). The nucleophilic reactivity of carboxylate anion towards the carbonyl carbon of PS^- may be considered to be extremely weak because the pK_a or pK_{a2} values of mono- or dicarboxylic acids used in the present study are in the range 2.9–5.4. The value of the second-order rate constant for the reaction between PS^- and HO^- (pK_a = 15.4) is 1.24 × 10^{-3} M^{-1} s^{-1} at 30 °C in the absence of CTABr micelles.[9a] Pseudo-first-order rate constants (k_{obs}) for the cleavage of PS^- in the presence of >0.01 M NaOH at 35 °C showed a mild decrease (from 7.6 × 10^{-4} to 6.4 × 10^{-4} s^{-1}) with increase in [sodium benzoate] from 0.0 to 0.8 M. It may also be noted that the kinetically significant carboxylate reactivity with PS^- in the presence of CTABr micelles must have produced significant intercepts in the plots of $k_{obs} - k_0$ versus [Pip]$_T$ (where k_0 represents rate constant for hydrolysis of PS^- in the absence of sodium cinnamate). However, such intercepts are not visible in the plots is Fig. 1. Thus, the increase in k_{obs} with increase in [carboxylate anion] in the presence of CTABr micelles at [NaOH] >0.02 M cannot be attributed to the nucleophilic reaction between carboxylate anion and PS^-.

The value of k_n^{obs} is nearly 13 times larger in aqueous pseudophase than in the micellar pseudophase.[10] Hence the most obvious cause of the observed effects of [MX] on k_n^{obs} may be attributed to the occurrence of ion exchange between X^-_W and PS^-_M (where the subscripts W and M represent aqueous pseudophase and micellar pseudophase, respectively). The possible ion-exchange processes in the present reacting system are HO^-–Br^-, HO^-–X^-, HO^-–PS^-, Br^-–X^-, Br^-–PS^-, and X^-–PS^-. The kinetic effectiveness of HO^-–PS^-, HO^-–Br^-, Br^-–X^-, X^-–HO^- and Br^-–PS^- ion-exchange processes may be ignored based on evidence



Scheme 1

described elsewhere.[13] The X^-–HO^- ion-exchange would be kinetically significant only when it decreased $[HO^-_M]$ to the extent that the concentration of non-ionized phenyl salicylate ([PSH]) no longer remained insignificant. However, the spectral evidence revealed the absence of PSH under the experimental conditions of the entire kinetic runs of present study. Hence the occurrence of probably the most effective ion exchange, X^-–PS^-, caused an increase in k_n^{obs} with increase in [MX] at a constant $[CTABr]_T$.

Experimental procedures, described elsewhere,[14] were used to affirm that PSH was not present in the reaction mixtures at concentrations at a detectable level under the experimental conditions of the present study. Nucleophilic reactions of primary and secondary amines with PS^- involve the intramolecular general base catalysis and the detailed mechanisms of these reactions have been discussed elsewhere.[9] We presume the occurrence of similar mechanism(s) in the micellar pseudophase also. The reaction scheme for the cleavage of PS^- in the presence of piperidine may be as shown in Scheme 1.

The significant decrease in k_n^{obs} with increase in $[CTABr]_T$ at a constant [MX] (Tables 1 and 2) may be explained using the pseudophase model of micelles.[15] As described elsewhere in detail,[18,13] the observed rate law for the cleavage of PS^- in the presence of piperidine (Pip), inert salt (MX) and micelles (D_n) (rate = k_{obs} $[PS^-]_T$ where $[PS^-]_T = [PS^-_W] + [PS^-_M]$), a reaction scheme in terms of the pseudophase model[15] of micelles and Eqn. (1) can lead to Eqn. (2)

$$k_n^{obs} = \frac{k_W^n + k_M^{ns} K_N K_S [D_n]}{1 + K_s [D_n]} \qquad (2)$$

where $k^{ns}_M = k^n_M/V_M$ (with V_M representing the micellar molar volume in M^{-1}),[16] K_N and K_S are the CTABr micellar binding constants of piperidine and PS^-, respectively and $1 \gg K_N$ $[D_n]$ under the experimental conditions imposed.

As concluded earlier, kinetically the most effective ion exchange which may indirectly affect the values of k_n^{obs} is X^-–PS^-. Such an ion exchange is expected to decrease K_S with increase in $[X^-]$. The values of K_S, obtained in methanolysis,[7] *n*-butylaminolysis[8] and piperidinolysis[8] of PS^- at different [MX] (MX = KBr and NaBr), followed the equation

$$K_S = K_S^0/(1 + \psi[MX]) \qquad (3)$$

where the magnitude of the empirical parameter Ψ is a measure of the ability of X^- to expel PS^- from the micellar pseudophase to the aqueous pseudophase. If it is assumed that Eqn. (3) is applicable in the present reaction system then Eqns (2) and (3) yield

$$k_n^{obs} = \frac{k_W^n + K_W^n \psi[MX] + k_M^{ns} K_N K_S^0 [D_n]}{1 + \psi[MX] + K_S^0 [D_n]} \qquad (4)$$

The values of the critical micellar concentration (cmc) are considered to be negligible compared with $[CTABr]_T$ under the present experimental conditions[13] and hence $[D_n] \approx [CTABr]_T$. The unknown parameters, Ψ and k^{ns}_M K_N, were calculated from Eqn. ((4)) with known values of k^n_W and $K_S{}^0$ using the non-linear least-squares technique. The values of k^n_W (= 0.324 M^{-1} s^{-1}, obtained in the absence of micelle at [MX] = 0 [10]) and $K_S{}^0$ (= 7000 M^{-1}, obtained spectrophotometrically in the absence of Pip and MX[17]) were obtained from the literature. The least-squares calculated values of Ψ and k^{ns}_M K_N for various salts of organic and inorganic acids are summarized in Table 3. The study of the effects of $[CTABr]_T$ on k_n^{obs} for the reaction of Pip with PS^- at [MX] = 0 yielded $K_S{}^0$ = 8400 M^{-1}.[10] This value of $K_S{}^0$ was also used to calculate Ψ and k^{ns}_M K_N from Eqn. ((4)). These calculated values of Ψ and k^{ns}_M K_N for various MX are also summarized in Table 3. The fitting of the observed data to Eqn. (4) seems to be satisfactory, as is evident from the values of k_n^{cal} listed in Tables 1 and 2 and from the standard deviations associated with the values of Ψ and k^{ns}_M K_N (Table 3).

The values of k^{ns}_M K_N obtained in the presence of different MX are not very different from those obtained in the absence of MX.[10] A detailed discussion on the k^{ns}_M K_N value at [MX] = 0 is given elsewhere.[10]

The degree of micellar affinity of a solubilizate depends largerly upon the electrostatic interaction (if both micelle and solubilizate are ionic), hydrophobic interaction and packing constraints (i.e. steric hindrance). Usually electrostatic interaction is much stronger than hydrophobic interaction. For instance, the values of the binding constants (K_S) of phenyl benzoate (PB) with CTABr and sodium dodecylsulfate (SDS) micelles are 300 [18] and 500 M^{-1},[18] respectively, while the respective values of K_S of PS^- (the structural difference between PB and PS^- is only the presence of $o-O^-$ group in PS^-) with CTABr and SDS micelles (determined kinetically) are 7000[17] and 5.9 M^{-1}.[19] The relative water solubility of monocarboxylic acids may be attributed to their relative

Table 3. Values of Ψ and $k^{ns}_{M}K_N$ calculated from Eqn. ((4)) for various MX

MX	$K_s^0 = 7000\ M^{-1}$		$K_s^0 = 8400\ M^{-1}$		SL[a]
	$\Psi(M^{-1})$	$10^3\ k^{ns}_{M}\ K_N\ (M^{-1}\ s^{-1}$	$\Psi(M^{-1})$	$10^3\ k^{ns}_{M}\ K_N\ (M^{-1}\ s^{-1}$	
Sodium cinnamate	367 ± 23[b]	14.4 ± 3.6[b]	441 ± 28[b]	15.0 ± 3.6[b]	
Sodium 2-chlorobenzoate	101 ± 2.9	16.1 ± 1.0	121 ± 3.6	16.6 ± 1.1	0.22
Sodium 2-chlorobenzoate	113 ± 3	16.2 ± 0.7	136 ± 3	16.8 ± 0.8	0.22
Sodium 4-methoxybenzoate	131 ± 3	16.0 ± 0.9	157 ± 4	16.5 ± 1.0	0.04
Disodium phthalate	15.1 ± 2.2	20.1 ± 1.0	18.7 ± 2.8	20.8 ± 1.0	0.70
Disodium isophthalate	27.9 ± 3.8	22.9 ± 1.5	34.0 ± 4.8	23.5 ± 1.6	0.01
Disodium fumarate	1.7 ± 0.8	19.6 ± 0.4	2.7 ± 1.0	20.2 ± 0.4	0.70
Sodium sulfate	3.6 ± 0.5	21.4 ± 0.8	4.5 ± 0.5	22.0 ± 0.8	
Sodium benzoate [c]	124	14.8	153	15.4	0.34

[a] SL represents solubility in g per 100 g H_2O and obtained from Ref. 30.
[b] Error limits are standard deviations.
[c] Obtained from Ref. 13.

hydrophobicity.[20 21] The value of Ψ for X^- must increase with increase in hydrophobicity of X^-. Thus, the values of Ψ for 2-chlorobenzoate ion (Ψ = 101–113 M^{-1}) and benzoate ion (Ψ = 124 M^{-1})[13] are consistent with the water solubilities of the corresponding benzoic acids (Table 3). However, although the water solubility of 4-methoxybenzoic acid is more than eight times smaller than that of benzoic acid, the value of Ψ (= 131 M^{-1}) for 4-methoxybenzoate ion is not very different from that for benzoate ion. This shows that the electrostatic and hydrophobic ineractions are not the only factors which affect the CTABr micellar affinity of X^-. The dodecyltrimethylammonium bromide (DTABr) micellar binding constant of diethyl ether (K_S = 1.4 M^{-1}) is significantly smaller than the CTABr micellar binding constants for ethane (K_S = 8.7 M^{-1}) and propane (K_S = 33 M^{-1}).[22] Similarly, the CTABr micellar binding constants for benzene, methylbenzene and methoxybenzene are 38–46, 83–146 and 37–54 M^{-1}, respectively.[22] These results predict that the Ψ values for benzoate and 4-methoxybenzoate ions should be nearly same.

The value of Ψ for the phthalate dianion is nearly half of that for isophthalate dianion, and this may be attributed to their relative hydrophobicity as reflected from the water solubility data for phthalic and isophthalic acids (Table 3). The values of ion-exchange constants, obtained directly by physical techniques, for *m*-nitrobenzoate ion[23] and *m*-phthalate ($\equiv$ isophthalate) dianion[24] are significantly larger than those for corresponding ortho-isomers. Although the value of Ψ for isophthalate dianion is slightly more than four times smaller than that for benzoate ion, the water solubility of benzoic acid is 34 times larger than that of isophthalic acid. These results cannot be explained in terms of electrostatic and hydrophobic interactions only. The most obvious reason for the low Ψ values for phthalate and isophthalate dianions compared with those for benzoate, 2-chlorobenzoate and 4-methoxybenzoate ions may be ascribed to the different distances of penetration into the micellar pseudophase by benzoate monoanions and phthalate dianions. It appears that the micellar surface is not homogeneous in terms of polarity, water concentration[1b,25] and distribution of solubilizates of different hydrophobicity.[19,26] Thus, phthalate ions (with two anionic groups) remain in the micellar region of high water concentration, while benzoate and PS^- ions (with only one anionic group) can reach to the micellar region of relatively low water concentration. A similar conclusion has been proposed for related systems.[23,27,28]

The value of Ψ for fumarate dianion is more than 200 times smaller than that for cinnamate ion (Table 3). The replacement of one of the two carboxylate groups of fumarate dianion by a C_6H_5 group produces cinnamate ion. The value of Ψ for cinnamate ion is nearly three times larger than that for benzoate ion. Furthermore, the value of Ψ for fumarate dianion is nearly half of that for sulfate ion (Table 3). However, the sulfate ion cannot be more hydrophobic than the fumarate dianion. The energetically favorable electrostatic interaction between CTABr micellar head-groups and phthalate or isophthalate dianions should apparently be stronger than that between CTABr micellar head-groups and benzoate ion. However, the lower values of Ψ for phthalate and isophthalate dianions compared with that for benzoate ion indicate that the higher favorable electrostatic interaction of the CTABr micellar surface with phthalate or isophthalate dianion than that with benzoate ion is offset by hydrophobic and some other possible interactions. Although a micelle is a dynamic molecular aggregate,[29] the micellar surface or Stern layer which contains the headgroups is a well-defined structural entity. Bulky and geometrically constrained dianions such as fumarate, phthalate and isophthalate dianions are expected to experience geometric constraint (i.e. packing constraint or steric hindrance) in the cationic micellar pseudophase. Probably for this reason, the phthalate dianion (the two carboxylate groups are in *cis*-like positions) can penetrate in to the CTABr micellar surface deeper than the fumarate dianion (where the two carboxylate groups are in *trans* positions), despite the

fact that the water solubilities of both phthalic acid and fumaric acid are same (Table 3).

The empirical definition of $\Psi_{X/PS}$ [=Ψ in Eqn. ((3))], where the magnitude of $\Psi_{X/PS}$ is the measure of the ability of X^- to expel PS^- from the cationic (CTABr) micellar pseudophase to the aqueous pseudophase, shows that $\Psi_{X/PS}$ must be proportional to the ion-exchange constant K_X^{PS}. The reported value of $\Psi_{Br/PS}$ is nearly 20 M^{-1}.[7] Thus, the ratios $\Psi_{PTL/PS}/\Psi_{Br/PS}$ ($\approx$1.0) and $\Psi_{IPTL/PS}/\Psi_{Br/PS}$ ($\approx$1.6) may be compared with the respective ion-exchange constants K_{PTL}^{Br} (= 2.0) and K_{IPTL}^{Br} (= 3.4) determined by using an ion specific electrode,[24] where PTL and IPTL represents phthalate and isophthalate dianion, respectively. Similarly, the ion-exchange constants K_X^{Br} for X = *o*-, *m*- and *p*-nitrobenzoate ions, obtained by ^{1}H NMR spectroscopy are 3.8, 11 and 3.3, respectively,[23] which may be compared with $\Psi_{2\text{-chlorobenzoate/PS}}/\Psi_{Br/PS}$ ($\approx$6–7) and $\Psi_{4\text{-methoxybenzoate/PS}}/\Psi_{Br/PS}$ ($\approx$8). The solubilities of *o*-, *m*- and *p*-nitrobenzoic acids are 0.75, 0.34 and 0.03 g per 100 g H_2O, respectively.

Acknowledgements

The authors thank the National Scientific Research and Development Council of Malaysia under the IRPA program for financial support (Grant No. 09-02-03-0003).

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