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Effects of [NaBr] on the Rates of Intramolecular General Base-Catalyzed Reactions of Ionized Phenyl Salicylate (PS^-) with *n*-Butylamine and Piperidine in the Presence of Cationic Micelles

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Effects of cetyltrimethylammonium bromide (CTABr) micelles on second-order rate constants (k_n^{obs}) for nucleophilic reactions of amines (piperidine and *n*-butylamine) with ionized phenyl salicylate (PS^-) reveal a nonlinear decrease with the increase in [D_n] (where $[D_n] = [CTABr]_T - cmc$) at a constant [NaBr] and 35 °C. The observed data, at a constant [NaBr], fit reasonably well to a pseudophase model of micelles, and such a data fit gives kinetic parameters such as CTABr micellar binding canstant (K_S) of PS^-. The effect of [NaBr] upon K_S is explained with the empirical relationship $K_S = K_S^0/(1 + \psi[NaBr])$, where ψ is an empirical parameter.

Introduction

It is becoming increasingly clear that the two-state micellar model is an approximation.[1] The concept of a multistate micellar model seems to be more accurate and realistic. The occurrence of ion exchange in ionic reactions in the presence of ionic micelles has been ascertained beyond any doubt. However, the theoretical model known as the pseudophase ion-exchange (PIE) model[2] does not appear to be perfect, although it explains a large body of data in an apparently satisfactory sense. The PIE model has been used in reactions with only one ion-exchange process involved. To the best of our knowledge, there is only one series of reports[3,4] in which the PIE model has been used for ionic reactions involving two ion-exchange processes, and the use of the PIE model required relatively more restrictive conditions. The effects of inert salt (MX) on the rates of alkaline hydrolysis of a few moderately hydrophobic anionic esters[5] and imide[6] in the presence of cationic micelles have been discussed in terms of the PIE model coupled with an empirical equation (eq 1), where K_S and K_S^0 represent micellar binding constants

$$K_S = K_S^0 - L[MX] \tag{1}$$

of an anionic solute (ester or imide) in the presence and absence of an inert salt, MX, respectively, and L is an empirical parameter. The rate of methanolysis of PS^- at different [KBr] in the presence of CTABr micelles showed that the values of K_S followed an empirical equation (eq 2), where Ψ is an

$$K_S = K_S^0/(1 + \Psi[KBr]) \tag{2}$$

empirical parameter.[7] Equation 2 has been found to be applicable in a few other related studies.[8] The presence of 0.05−0.50 M KBr did not show a detectable effect on pseudo-first-order rate constants for hydrolysis of PS^- in the presence of 0.05 M CTABr.[9] In the continuation of our work on testing the validity of eq 2, we now report the effects of [NaBr] on rates of reactions of PS^- with *n*-butylamine and piperidine. The results and their probable explanations are described in this article.

Experimental Section

Materials. All of the reagents used were supplied by Fluka or Aldrich and were of highest commercially available purity. The stock solutions of phenyl salicylate were prepared in acetonitrile.

Kinetic Measurements. Ionized phenyl salicylate (PS^-) absorbs strongly while hydrolysis and aminolysis products of PS^- absorb weakly at 350 nm in both the absence and the presence of cetyltrimethylammonium bromide (CTABr) micelles. Thus, the spectrophotometric technique was conveniently used to monitor the disappearance of reactant (PS^-) as a function of time at 350 nm. The details of the kinetic procedure, data analysis, and product characterization are the same as described elsewhere.[10]

Results and Discussion

The effects of total concentration of amine ($[Am]_T$ where Am = piperidine and *n*-butylamine) on the rates of reactions of PS^- with Am were studied at three different $[Am]_T$ ranging from 0.04 to 0.10 M for piperidine (Pip) and *n*-butylamine (n-$BuNH_2$) at 0.02 M NaOH, 35 °C, and constant total concentrations of CTABr ($[CTABr]_T$)

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Table 1. Effects of $[\mathrm{CTABr}]_T$ on k_n^{obs} for the Nucleophilic Reactions of PS^- with Ppiperidine and *n*-Butylamine at a Constant $[\mathrm{NaBr}]^a$

	[NaBr]									
	0.005 M		0.02 M		0.04 M		0.1 M		0.5 M	
$10^4[C]_T{}^b$	$10^3k_n{}^{obs}$	$10^3k_n{}^{calcd}$	$10^3k_n{}^{obs}$	$10^3k_n{}^{calcd}$	$10^3k_n{}^{obs}$	$10^3k_n{}^{calcd}$	$10^3k_n{}^{obs}$	$10^3k_n{}^{calcd}$	$10^3k_n{}^{obs}$	$10^3k_n{}^{calcd}$
Piperidine										
0.2	312 ± 17^c		294 ± 2^c		294 ± 8^c					
0.4	304 ± 5		296 ± 2		293 ± 1					
0.6	308 ± 9		288 ± 3		284 ± 10					
0.8	293 ± 6		271 ± 4	275^d	276 ± 4	277^d				
1.0	283 ± 10	278^d	253 ± 5	252	260 ± 4	257				
1.2	265 ± 9	246	244 ± 7	232	236 ± 5	240				
1.4	243 ± 11	221	224 ± 6	216	224 ± 4	225				
2.0	175 ± 3	169	185 ± 8	179	197 ± 5	190	209 ± 1^c	219^d	236 ± 3^c	247^d
3.0	113 ± 1	123	140 ± 11	140	155 ± 4	152	202 ± 13	190	223 ± 10	229
4.0	86.4 ± 0.2	97.9	110 ± 3	116	131 ± 3	128	174 ± 2	168	211 ± 3	213
5.0	67.5 ± 2.7	81.7	95.5 ± 1.1	99.0	109 ± 3	110	153 ± 4	151	204 ± 2	200
7.0	50.7 ± 1.3	62.3	67.8 ± 1.6	78.0	84.8 ± 1.8	88.4	120 ± 4	126	182 ± 2	178
10.0	38.5 ± 1.5	47.1	51.7 ± 1.9	60.4	63.5 ± 1.6	69.3	96.5 ± 7.6	102	157 ± 3	154
20.0	28.3 ± 1.9	28.6	33.6 ± 2.0	37.5	38.8 ± 3.3	43.7	61.2 ± 3.6	65.1	110 ± 4	107
60.0	24.6 ± 0.5	15.8	24.8 ± 0.6	20.6	25.5 ± 1.5	24.4	33.1 ± 1.3	33.0	54.2 ± 3.7	55.2
100.0	23.3 ± 0.7	13.2	23.3 ± 0.6	17.1	23.3 ± 0.8	20.3	27.0 ± 1.3	25.5	40.1 ± 3.7	41.1
200.0	21.4 ± 0.0	11.2	21.4 ± 0.0	14.4	21.4 ± 0.3	17.2	22.7 ± 1.2	19.7	28.4 ± 1.6	29.3
n-Butylamine										
0.2	62.9 ± 1.4		62.2 ± 1.0		60.2 ± 0.8					
0.4	65.1 ± 1.9		63.0 ± 3.4		59.2 ± 1.2					
0.6	65.1 ± 0.9		61.2 ± 0.5		62.1 ± 4.0					
0.8	65.5 ± 1.5		61.5 ± 2.7		55.2 ± 1.1	58.3				
1.0	63.2 ± 2.3	59.4	60.2 ± 2.2	55.2	56.7 ± 1.8	55.6				
1.2	57.1 ± 2.1	53.7	56.4 ± 3.2	52.0	55.1 ± 2.1	53.2				
1.4	55.3 ± 3.2	49.2	54.2 ± 3.5	49.2	55.7 ± 1.2	51.0				
2.0	40.6 ± 0.5	39.9	44.5 ± 1.8	42.8	46.7 ± 1.4	45.6	54.2 ± 2.3	50.3	54.3 ± 2.7	54.5
3.0	30.5 ± 1.6	31.3	34.5 ± 0.9	35.6	41.0 ± 1.1	39.1	48.1 ± 1.7	45.8	52.8 ± 2.5	52.0
4.0	22.9 ± 0.8	26.6	28.9 ± 1.0	31.0	33.6 ± 1.5	34.6	41.9 ± 0.6	42.1	51.6 ± 1.9	49.7
5.0	20.3 ± 2.0	23.5	24.8 ± 0.3	27.8	29.7 ± 1.4	31.2	39.0 ± 1.8	39.1	47.9 ± 3.0	47.7
7.0	16.3 ± 1.2	19.8	20.2 ± 0.3	23.5	24.8 ± 1.8	26.6	33.5 ± 0.8	34.5	43.6 ± 1.6	44.1
10.0	14.6 ± 0.4	16.8	16.9 ± 1.7	19.9	19.9 ± 0.9	22.4	27.9 ± 0.3	29.8	39.6 ± 0.8	39.9
20.0	13.2 ± 0.8	13.2	14.1 ± 0.5	15.0	15.2 ± 1.3	16.4	19.7 ± 0.9	21.7	30.0 ± 0.4	30.7
60.0	13.5 ± 0.4	10.7	13.3 ± 0.5	11.3	12.5 ± 0.3	11.6	14.2 ± 1.2	14.0	17.6 ± 1.1	18.4
100.0	12.6 ± 0.2	10.2	12.2 ± 0.5	10.5	11.8 ± 0.3	10.5	13.2 ± 0.2	12.1	14.6 ± 0.8	14.5
200.0	12.0 ± 0.4	9.84	12.3 ± 0.6	9.88	10.9 ± 0.3	9.69	11.3 ± 0.4	10.6	11.9 ± 0.3	11.2

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ M, $[\mathrm{NaOH}] = 0.02$ M, 35 °C, $\lambda = 350$ nm, aqueous solvent for each kinetic run contained 2% v/v CH_3CN. [b] $[C]_T = [\mathrm{CTABr}]_T$. [c] Error limits are standard deviations. [d] Calculated from eq 6 using $k^n{}_W$ and calculated parameters $k^{ns}{}_MK_N$ and K_S, listed in Table 3.

and NaBr. Pseudo-first-order rate constants (k_{obs}) for aminolysis of PS^- obeyed eq 3,

$$k_{obs} - k_0 = k_n{}^{obs}[\mathrm{Am}]_T \tag{3}$$

where k_0 represents pseudo-first-order rate constants for the hydrolysis of PS^-. The values of k_0 at different $[\mathrm{CTABr}]_T$ were obtained from the literature.[11] The nucleophilic second-order rate constants ($k_n{}^{obs}$) were calculated from eq 3 using the linear least-squares technique, and these values of $k_n{}^{obs}$ at different [NaBr] and $[\mathrm{CTABr}]_T$ for Pip and *n*-$BuNH_2$ are summarized in Table 1. The reliable fitting of observed data to eq 3 is evident from the standard deviations associated with $k_n{}^{obs}$ as shown in Table 1.

A few kinetic runs were also carried out within the $[\mathrm{Am}]_T$ range of 0.04−0.10 M at 0.1 M NaBr and at a constant $[\mathrm{CTABr}]_T$ in the absence of NaOH. The observed data obeyed eq 3, and the least-squares calculated values of $k_n{}^{obs}$ at different $[\mathrm{CTABr}]_T$ are summarized in Table 2. The values of $k_n{}^{obs}$ at $[\mathrm{NaOH}] = 0$ slightly decreased (nearly 5−15%) compared to the corresponding $k_n{}^{obs}$ at $[\mathrm{NaOH}] = 0.02$ M for Pip, but the values of $k_n{}^{obs}$ for *n*-butylamine remained almost unchanged with the change in [NaOH] from 0 to 0.02 M (Tables 1 and 2). These observation and the evidence presented in an earlier report indicate a near absence of protonated

Table 2. Effects of $[\mathrm{CTABr}]_T$ on $k_n{}^{obs}$ for the Nucleophilic Reactions of PS^- with Piperidine and *n*-Butylamine at 0.1 M NaBr in the Absence of NaOH^a

	piperidine		*n*-butylamine	
$10^4[\mathrm{CTABr}]_T$ (M)	$10^3k_n{}^{obs}$ ($M^{-1}\ s^{-1}$)	$10^3k_n{}^{calcd\ b}$ ($M^{-1}\ s^{-1}$)	$10^3k_n{}^{obs}$ ($M^{-1}\ s^{-1}$)	$10^3k_n{}^{calcd\ b}$ ($M^{-1}\ s^{-1}$)
2	198 ± 2^c	201	51.6 ± 5.9^c	48.6
3	165 ± 6	169	45.1 ± 0.8	43.6
4	150 ± 4	147	40.1 ± 2.9	39.6
5	131 ± 5	130	33.2 ± 1.8	36.5
7	105 ± 10	107	32.9 ± 4.3	31.7
10	91.1 ± 4.4	85.6	27.7 ± 0.3	26.9
20	57.3 ± 5.1	55.3	15.5 ± 0.3	19.2
60	29.7 ± 2.3	30.5	10.7 ± 1.1	12.0
100	24.5 ± 2.3	25.1	11.6 ± 1.0	10.3
200	18.3 ± 2.2	20.8	10.7 ± 0.9	8.89

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ M, 35 °C, $\lambda = 350$ nm, aqueous solvent for each kinetic run contained 2% v/v CH_3CN. [b] Calculated from eq 6 using $k^n{}_W$ and calculated parameters $k^{ns}{}_MK_N$ and K_S, listed in Table 3. [c] Error limits are standard deviations.

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amine ($PipH^+$ and n-$BuNH_3^+$) in the presence of 0.02 M NaOH.

Experimental procedures as described elsewhere[11] were used to affirm that the concentration of nonionized phenyl salicylate (PSH) was not present in the reaction mixtures at a detectable level under the experimental conditions of the present study. The decrease in k_n^{obs} with the increase in $[CTABr]_T$ can be explained in terms of the pseudophase model of micelle.[12] The assumptions and the weaknesses involved in the pseudophase model of micelle are critically discussed by a few investigators.[13,14]

In terms of the pseudophase model of micelle, the reaction scheme for aminolysis of ionized phenyl salicylate (PS^-) in the presence of CTABr micelles (D_n) may be shown by the following:

$$PS^-_W + D_n \overset{K_S}{\rightleftharpoons} PS^-_M$$

$$N_W + D_n \overset{K_N}{\rightleftharpoons} N_M$$

$$PS^-_W + N_W \xrightarrow{k^n_W} \text{Products } (P_1 + P_2)$$

$$PS^-_M + N_M \xrightarrow{k^n_M} \text{Products } (P_1 + P_2)$$

$$PS^-_W \xrightarrow{k^h_W\,(H_2O_W)} \text{Products } (P_3 + P_2)$$

$$PS^-_M \xrightarrow{k^h_M\,(H_2O_M)} \text{Products } (P_3 + P_2)$$

where N represents the amine nucleophile and all other symbols have their usual meanings.[11] The observed rate law (rate = $k_{obs}[PS^-]_T$ where $[PS^-]_T = [PS^-_W] + [PS^-_M]$ and subscripts W and M refer to aqueous pseudophase and micellar pseudophase, respectively) and the above equations can lead to eq 4,

$$k_{obs} = \frac{k^h_W + k^h_M K_S[D_n]}{1 + K_S[D_n]} + \frac{(k^n_W + k^{ns}_M K_N K_S[D_n])[Am]_T}{(1 + K_S[D_n])(1 + K_N[D_n])} \quad (4)$$

where $[Am]_T = [N_W] + [N_M]$ and $k^{ns}_M = k^n_M/V_M$ (V_M is the micellar molar volume in M^{-1}).[13]

Comparison of eqs 3 and 4 gives eq 5.

$$k_n^{obs} = \frac{(k^n_W + k^{ns}_M K_N K_S[D_n])}{(1 + K_S[D_n])(1 + K_N[D_n])} \quad (5)$$

It has been concluded elsewhere[11] that $1 \gg K_N[D_n]$ under the present reaction conditions, and the application of this inequality reduced eq 5 to eq 6.

$$k_n^{obs} = \frac{(k^n_W + k^{ns}_M K_N K_S[D_n])}{(1 + K_S[D_n])} \quad (6)$$

Table 3. Calculated Parameters $k^{ns}_M K_N$ and K_S from Equation 6

[NaBr] (M)	10^5(cmc) (M)	$10^3 k^n_W$ ($M^{-1}\ s^{-1}$)	$10^3 k^{ns}_M K_N$ ($M^{-1}\ s^{-1}$)	K_S (M^{-1})	K_S^{calcd} [a] (M^{-1})
			Piperidine		
0.005[b]	8.5	308	9.21 ± 6.48[c]	7526 ± 777[c]	7386
0.020	6.5	295	11.7 ± 3.7	5157 ± 282	5520
0.040	6.5	294	14.0 ± 2.2	4348 ± 135	4130
0.100	4.0	294	13.7 ± 4.3	2275 ± 132	2352
0.500	0.0	294	16.4 ± 3.8	1024 ± 47	608
0.100[d]	4.0	294	16.4 ± 1.9	3137 ± 89	
			n-Butylamine		
0.005	8.5	64.7	9.46 ± 1.68	7082 ± 1009	7031
0.020	6.5	62.0	9.27 ± 1.81	4252 ± 591	4410
0.040	6.5	60.5	8.84 ± 1.31	3000 ± 287	2945
0.100	4.0	60.5	8.93 ± 1.34	1536 ± 140	1475
0.500	0.0	60.5	7.27 ± 0.78	634 ± 29	341
0.100[d]	4.0	60.5	7.45 ± 1.55	1799 ± 188	

[a] Calculated from eq 2 (with [KBr] replaced by [NaBr]) as described in the text. [b] [NaOH] = 0.02 M. [c] Error limits are standard deviations. [d] [NaOH] = 0.0 M.

The occurrence of ion exchange processes in the presence of ionic micelles appears to be an ubiquitous feature of micelle-mediated reacting systems. The possible ion exchange processes in the present reacting system are Br^-/OH^-, OH^-/PS^- and Br^-/PS^-. However, the ion exchange Br^-/OH^- cannot be detected in the present kinetic system because such an ion exchange cannot bring any change in k_{obs} or k_n^{obs}. The ion exchange OH^-/PS^- also has been shown to be kinetically unimportant.[7] The ion exchange Br^-/PS^- may be considered to be relatively effective, especially at high values of [NaBr], despite the fact that the difference in hydrophobicity of PS^- and Br^- is very large. The change in K_S with the increase in $[CTABr]_T$ (from 2×10^{-5} to 0.02 M) at a constant [NaBr] may be considered to be insignificant because of the large difference in hydrophobicity of PS^- and Br^-. Thus, the observed data (k_n^{obs} versus $[CTABr]_T$) at a constant [NaBr] were used to calculate $k^{ns}_M K_N$ and K_S from eq 6 considering k^n_W as known parameter.

The values of k^n_W were obtained by carrying out experiments under similar reaction conditions in the absence of micelles. The values of cmc (summarized in Table 3) under different kinetic conditions were obtained by both Broxton[15] and iterative[16] techniques. The nonlinear least-squares calculated values of $k^{ns}_M K_N$ and K_S at different [NaBr] for both piperidine and n-butylamine are summarized in Table 3. The nature of fitting of the observed data to eq 6 is evident from the values of k_n^{calcd} (Tables 1 and 2) and from standard deviations associated with the calculated parameters $k^{ns}_M K_N$ and K_S (Table 3).

The values of k_n^{calcd} show definite negative deviations from the corresponding k_n^{obs} values at $[CTABr]_T \geq 0.006$ M at [NaBr] < 0.1 M (Tables 1 and 2). The respective residual errors $\{RE = 100(k_n^{obs} - k_n^{calcd})/k_n^{obs}\}$ at 0.01 and 0.02 M CTABr are 43 and 48 at 0.005 M NaBr, 27 and 33 at 0.02 M NaBr, 13 and 20 at 0.04 M NaBr, 6 and 13 at 0.1 M NaBr, and −2 and −3 at 0.5 M NaBr for piperidine. Similarly, the respective values of RE at 0.01 and 0.02 M CTABr are 19 and 18 at 0.005 M NaBr, 14 and 20 at 0.02 M NaBr, 11 and 11 at 0.04 M NaBr, 8 and 6 at 0.1 M NaBr, and 1 and 6 at 0.5 M NaBr for n-butylamine. These results show that the values of RE at 0.01 and 0.02 M CTABr decrease with the increase in [NaBr] from 0.005 to 0.04 M for piperidine and from 0.005 to 0.02 M for n-butylamine. Although it is not possible

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to give definite reason(s) for these results, the most probable reason may be explained as follows. It seems that the micellar surface is not homogeneous in terms of polarity and distribution of solubilizate molecules. Hydrophilic amines such as piperidine and *n*-butylamine remain in a more polar region while the relatively less hydrophilic anions, PS^-, remain in a less polar region of the micelle. The different average locations of amines (piperidine and *n*-butylamine) and PS^- have been attributed as one of the major factors for the rate of aminolysis of PS^- in micellar pseudophase being slower than that in the aqueous pseudophase.[11] It is known that the addition of electrolytes increases the solubilizing capacity of ionic micelles.[1] Thus, the increase in [NaBr] increases the degree of homogeneity of the micellar surface in terms of distribution of amine and PS^-, and consequently it decreases the values of RE at 0.01 and 0.02 M CTABr.

The calculated values of $k^{ns}{}_{M}K_N$ showed a rather small change with the increase in [NaBr] from 0.005 to 0.5 M for both piperidine and *n*-butylamine (Table 3). However, the values of K_S decreased by nearly 7-fold for piperidine and 11-fold for *n*-butylamine with the increase in [NaBr] from 0.005 to 0.5 M (Table 3). These results show that bromide ions expel PS^- from the micellar pseudophase to the aqueous pseudophase. Similar results were obtained in the methanolysis of PS^- in the presence of CTABr micelles and the inert salt KBr.[7] The values of K_S fit to the empirical nonlinear equation (eq 2) where [KBr] was replaced by [NaBr]. The magnitude of Ψ is the measure of the ability of an ion (such as Br^-) to expel the coion (such as PS^-) from the cationic micellar pseudophase to the aqueous pseudophase. The nonlinear least-squares technique was used to calculate $K_S{}^0$ and Ψ from eq 2, and these respective calculated values are 8324 ± 506 M^{-1} and 25.4 ± 4.7 M^{-1} for piperidine and 8772 ± 398 M^{-1} and 49.5 ± 5.7 M^{-1} for *n*-butylamine. The fitting of K_S values to eq 2 is satisfactory, as evident from the standard deviations associated with the values of $K_S{}^0$ and Ψ and from the $K_s{}^{calcd}$ values listed in Table 3.

The values of $K_S{}^0$ (8324 M^{-1} for piperidine and 8772 M^{-1} for *n*-butylamine) may be compared with the corresponding values of K_S obtained from the kinetic data on the reactions of PS^- with piperidine ($K_S = 8400$ M^{-1}) and *n*-butylamine ($K_S = 8500$ M^{-1}) in the absence of inert salt (NaBr).[11] The values of $k^{ns}{}_{M}K_N$ for *n*-butylamine (13.1×10^{-3} M^{-1} s^{-1}) and for piperidine ($11.0.41 \times 10^{-3}$ M^{-1} s^{-1}) obtained in the absence of NaBr[11] may be compared with the corresponding $k^{ns}{}_{M}K_N$ values summarized in Table 3.

The values of Ψ (25.4 M^{-1} in the presence of piperidine) is not significantly different from Ψ (19−23 M^{-1}) obtained for KBr in mixed aqueous solvent containing 2% v/v CH_3CN and 10% v/v CH_3OH.[7] Although the value of Ψ (49.5 M^{-1}) in the presence of *n*-butylamine is nearly 2-fold larger than Ψ (25.4 M^{-1}) in the presence of piperidine, more data on related systems are needed to comment on these Ψ values, because both piperidine and *n*-butylamine are neutral solubilizates and their CTABr micellar binding affinities are very weak.[17]

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