Effects of Anionic Micelles on the Intramolecular General-base-catalysed Hydrazinolysis and Hydrolysis of Phenyl Salicylate. Evidence for a Porous Cluster Micelle

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The hydrazinolysis of phenyl salicylate has been studied in the presence and absence of micelles of sodium dodecyl sulphate (SDS) at 30 °C. The nucleophilic reaction of hydrazine with ionized phenyl salicylate (PS^-) involves intramolecular general-base catalysis while the probable intramolecular general-acid catalysis could not be detected in the reaction of non-ionized phenyl salicylate (PSH) with hydrazine. Kinetic data for both hydrolysis and hydrazinolysis of phenyl salicylate are explained in terms of the pseudophase model of micelles. The rate constants for hydrolysis and hydrazinolysis of PS^- in micellar pseudophase are either insignificant or significantly smaller compared with the corresponding rate constants in aqueous pseudophase. This is attributed largely to considerably low water activity in the specific micellar environment where micellar bound PS^- molecules exist. The micellar bound reactants (PSH and PS^-) and products (non-ionized and ionized phenol and *N*-hydrazinylsalicylamide) appear to exist in the micellar environments of different water activity. The rate constants, k_{obs}, increase *ca.* fivefold with increased [NaOH] from 0.001 to 0.040 mol dm^{-3} at 0.2 mol dm^{-3} SDS and 0.08 mol dm^{-3} NH_2NH_2. This is attributed to an increase in $[PS^-]$ with increase in [NaOH]. These observations favour the porous cluster micellar structure. The values of k_{obs} remain unchanged with increased concentration of 1,4-diazabicyclo[2.2.2]octane from 0.06 to 0.60 mol dm^{-3} at 0.3 mol dm^{-3} SDS, 0.05 mol dm^{-3} NaOH, and 37 °C. This shows that the presence of SDS micelles does not change the reaction mechanism of aqueous pseudophase hydrolysis and aminolysis of PS^-.

Although normal micelles do not conform to a complete or perfect model for a biological membrane, it does display certain characteristics of such membranes. Perhaps because of this and other related reasons, a significant amount of systematic kinetic work has been carried out on the effects of micelles on organic reactions during past two decades.[1] However, the crux of the matter which is concerned with the micellar structure seems to be still largely unresolved. The '2-state' Hartley model of micelle appears to be an oversimplified picture of the real micellar structure. Although the rough-surfaced character of the micellar surface has been proposed and supported by a few workers,[2] more convincing evidence for a porous cluster micellar structure comes from a series of papers by Menger *et al.*[3-5] and others.[6] In terms of the porous cluster micellar model, the micellar pseudophase is regarded as a microenvironment in which medium characteristics such as polarity, water activity, hydrophobicity, *etc.* change continuously with increased distance from the surface of the micelle to its centre.

One of the referees * has suggested that the dynamic model of a micelle is preferable. In considering solute–micelle interactions it would be reasonable to think of solute as associated with, say, non-polar surfactant chains which, from time to time, will be exposed to the aqueous environment.

Most of the studies on the effects of micelles on the rates of organic reactions are concerned with hydrolysis of esters, activated aromatic compounds and a few amides.[1,7-9] Micellar effects upon the rates of aminolysis of esters and activated amides have not been extensively studied. Bunton and co-workers studied the effects of micelles upon the reaction of the tri-(*p*-methoxyphenyl)methyl cation with aliphatic amines[10] and aromatic nucleophilic substitution by both aliphatic and aromatic emines.[11] The kinetics of aminolysis of carboxylic esters in the presence of micelles were studied by Behme *et al.*[12] The lack of the studies on micellar effects upon the aminolysis of esters of both aromatic and aliphatic carboxylic acids is largely due to the fact that these reactions generally require the buffers of amine nucleophiles. The presence of the buffer components into the micellar solutions complicates the kinetic treatment of the observed data because micelles affect the apparent pK_a of the buffer by differential micellar incorporation of buffer components. The studies on the kinetics of hydrolysis of phenyl and alkyl salicylates revealed that the rates of these reactions were independent of $[^-OH]$ within the range 0.002–0.060 mol dm^{-3}.[13,14] Because of these characteristics, the aminolysis of these salicylate esters were studied with and without the buffers of amine nucleophiles.[15,16] Since these reactions do not require buffers of amine nucleophiles, we decided to study the effects of micelles on these reactions. Recently, we studied the effects of SDS micelles upon the rates of the reactions of phenyl salicylate with propylamine and 1-aminopropan-2-ol and methyl salicylate with hydroxylamine, hydrazine, and dimethylamine.[17] The observed data support the porous cluster micellar structure and are explained in terms of pseudophase model of micelle. In these and related studies,[18] we did not explore the effect of different [NaOH] upon hydrolysis and aminolysis of phenyl salicylate. Although most of the organic reactions follow same reaction mechanism in both aqueous and micellar pseudophases, Broxton *et al.*[19] have presented evidence for the occurrence of different reaction mechanisms in aqueous and micellar pseudophases for the basic hydrolysis of diazepam.

The present study was aimed at to explore the effects of [NaOH] upon the hydrolysis and hydrazinolysis of phenyl salicylate and to check whether the presence of SDS micelles

* I thank the referee for suggesting this point.

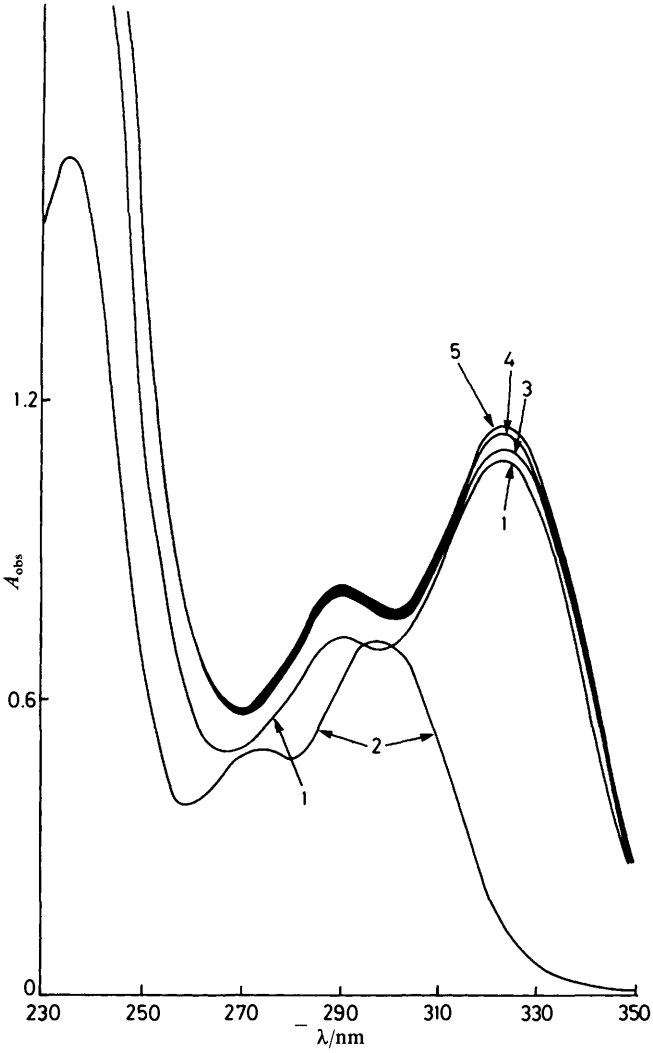


Figure 1. Spectra of the products of hydrazinolysis of phenyl salicylate in the absence of SDS (1, 2) and in the presence of SDS (3, 4, and 5). *Conditions:* [Phenyl Salicylate]$_0$ = 2 × 10^{-4}, [NH_2NH_2] = 0.08 mol dm^{-3}, 30 °C, MeCN = 1% and pH > 11 for 1; pH < 2 for 2; [SDS]$_T$ = 0.14 mol dm^{-3}, pH > 11 and [NH_2NH_2] = 0.06 mol dm^{-3} for 3, [NH_2NH_2] = 0.08 mol dm^{-3} for 4 and [NH_2NH_2] = 0.10 mol dm^{-3} for 5. All the spectra were scanned after more than 11 half-lives of the reactions.

changes the aqueous reaction mechanism. The results and the probable explanations are described in this paper.

Experimental

Materials.—Reagent-grade chemicals such as 1,4-diazabicyclo[2.2.2]octane, phenyl salicylate and hydrazine hydrate were obtained from BDH and sodium dodecyl sulphate (SDS) was obtained from Aldrich. All other chemicals used were also of reagent grade. Sodium dodecyl sulphate was recrystallized according to the published procedure.[20] Glass-distilled water was used throughout. Stock solutions of phenyl salicylate were prepared frequently in acetonitrile.

Kinetic Measurements.—The rates of hydrolysis and hydrazinolysis of phenyl salicylate in the alkaline medium were studied spectrophotometrically by monitoring the decrease in absorbance (A_{obs}^{350}) at 350 nm. However, the kinetic runs carried out at 0.2 mol dm^{-3} SDS, 0.08 mol dm^{-3} NH_2NH_2 and <0.005 mol dm^{-3} NaOH, the change in the absorbances at 350 nm within the period t = 0 to t = ∞ became considerably low and this change became almost zero at 0.001 mol dm^{-3} NaOH. Hence under such experimental conditions, the kinetic treatment of the observed data became somewhat unreliable. A significant change in A_{obs} values within the period of t = 0 and t = ∞ was noted at 330 nm under such experimental conditions. Therefore, the reaction rates of the kinetic runs at 0.2 mol dm^{-3} SDS, 0.08 mol dm^{-3} NH_2NH_2 and ≤0.005 mol dm^{-3} NaOH were studied by monitoring the increase in A_{obs} at 330 nm. In a typical kinetic run, the reaction mixture containing required amounts of hydrazine, sodium hydroxide and SDS was equilibrated at 30 °C (using thermostatted water bath) for a few minutes. The reaction was then initiated by adding 0.05 cm^3 (using a 50 mm^3 Hamilton syringe) of 0.02 mol dm^{-3} phenyl salicylate solution prepared in acetonitrile. The total volume of the reaction mixture in each kinetic run, except at 7.5 × 10^{-3} mol dm^{-3} NaOH, was 5 cm^3 which contained 1%, v/v, acetonitrile. The total volume of the reaction mixture, in each kinetic run, was maintained at 10 cm^3 for the kinetic runs carried out at 7.5 × 10^{-3} mol dm^{-3} NaOH and at different [SDS]$_T$. In these kinetic runs, the reactions were initiated by adding 0.1 cm^3 of 0.02 mol dm^{-3} phenyl salicylate using a 1.0 cm^3 graduated pipette. The change in absorbance with the progress of the reaction was recorded using Beckman Model 35 UV–VIS spectrophotometer. The details of the kinetic procedure and data analysis were the same as described elsewhere.[13]

The values of pH of the reaction mixtures were recorded to within 3–6 minutes exposure of electrode to the solution because a prolonged exposure of electrode to the solutions containing SDS revealed a slow but steady drift of the pH readings. Such observations were also noted by Bunton and Wolfe[21] with a combination electrode. A Philips digital pH meter model PW 9409 with a combination electrode was used for pH measurements. The pH of the reaction mixture, for each kinetic run, was found to be constant during the course of the reaction.

The rates of the hydrazinolysis of phenyl salicylate, in the absence of SDS, were studied for buffered solutions of hydrazine. The buffer solutions of desired pH were prepared just a few minutes before the start of the kinetic runs.

Product Characterization.—The cleavage of an ester, in the amine buffers, might involve either nucleophilic catalysis or general acid–base catalysis by buffer components. Recently, we have presented spectral evidence to support the theory that the cleavage of phenyl salicylate, in the buffers of primary and secondary amines, involves amines acting as nucleophiles.[16] In order to characterize the products of the cleavage of phenyl salicylate in the presence of hydrazine and SDS, we carried out the following spectra studies. The cleavage of phenyl salicylate, in a reaction mixture containing 2 × 10^{-4} mol dm^{-3} phenyl salicylate, 0.002 mol dm^{-3} NaOH and 0.08 mol dm^{-3} NH_2NH_2·H_2O, was allowed to progress for 15 min (which is *ca.* 10 half-lives of the reaction). The spectrum of the products was then quickly recorded as shown in Figure 1. A sufficient known amount of HCl (using stock solution of *ca.* 11 mol dm^{-3} HCl) was then added to the reaction mixture to make it acidic (pH < 2). The spectrum of the acidified reaction products was quickly recorded as shown in Figure 1. These spectra are similar to those obtained for propylaminolysis of phenyl salicylate under similar experimental conditions.[16] The spectra of the products of the reaction mixtures containing 2 × 10^{-4} mol dm^{-3} phenyl salicylate, 0.14 mol dm^{-3} SDS, 0.05 mol dm^{-3} NaOH and varying concentrations of NH_2NH_2 are also shown in Figure 1. These spectra are identical with the spectrum of the products of hydrazinolysis of phenyl salicylate carried out in the absence of SDS under essentially similar experimental conditions (Figure

Table 1. Molar extinction coefficients (ε) at different wavelengths.[a]

Compound	ε_{350}/dm^3 mol^{-1} cm^{-1}	ε_{330}/dm^3 mol^{-1} cm^{-1}	ε_{290}/dm^3 mol^{-1} cm^{-1}
o-$HOC_6H_4CO_2Ph$	(0)	500 (300)	1 800 (1 050)
o-$^-OC_6H_4CO_2Ph$	5 950 (5 650)	5 975 (5 700)	920 (780)
o-$HOC_6H_4CONHNH_2$	0	300	3 182
o-$^-OC_6H_4CONHNH_2$	1 300	5 050	1 296
o-$HOC_6H_4CO_2H$	(0)	200	2 690 (2 630)
o-$^-OC_6H_4CO_2^-$	(0)	200	3 250 (3 170)
PhOH	(0)	(0)	(0)
PhO^-	(0)	(0)	(2 350)

[a] Ionic strength < 0.05 mol dm^{-3}, values in parentheses were obtained at ionic strength 1.0 mol dm^{-3}, aqueous solutions contained 1% CH_3CN.

Table 2. Apparent nucleophilic second-order rate constants (k_n) for hydrazinolysis of phenyl salicylate in the absence of SDS.[a]

pH	k_n/10^{-3} dm^3 mol^{-1} s^{-1}	$[Am]_T$[b] range/ mol dm^{-3}	No. of runs
7.77 ± 0.01[c]	4.66 ± 0.06[c]	0.06–0.36	6
8.13 ± 0.01	8.78 ± 0.15	0.03–0.18	6
8.50 ± 0.02	19.2 ± 0.6	0.03–0.18	6
8.90 ± 0.01	24.9 ± 0.6	0.03–0.18	6

[a] $[Phenyl\ Salicylate]_0 = 1.6 \times 10^{-4}$ mol dm^{-3}, ionic strength 1.0 mol dm^{-3}, 30 °C, λ = 340 nm, reaction mixture for each kinetic run contained 0.8% CH_3CN. [b] Total hydrazine buffer concentration range. [c] Error limits are standard deviations.

1). This shows that the presence of SDS does not affect the spectrum of products under alkaline medium.

If hydrazine were acting as a general base, then the expected products of the cleavage of phenyl salicylate would be salicylate and phenolate ions at pH ≥ 11. Both non-ionized and ionized salicyclic acid and phenol do not show the detectable absorption at 350 m, (Table 1). The significant absorption of products of hydrazinolysis of phenyl salicylate at pH > 11 indicates that the products formed are due to nucleophilic catalysis rather than general-base catalysis by hydrazine. Furthermore, the possibility of the hydrazine acting as general-base catalyst, in the presence and absence of SDS, may be ruled out as sterically less hindered tertiary amines such as 1,4-diazabicyclo[2.2.2]-octane did not show detectable catalysis in the cleavage of phenyl salicylate in either the presence or absence of SDS.

Results

Molar Extinction Coefficients of Ionized and Non-ionized Reactants and Products of Hydrolysis and Hydrazinolysis of Phenyl Salicylate at Different Wavelengths.—Both the reactant (phenyl salicylate) and its hydrolysis and aminolysis products contain the easily ionizable phenolic group. The binding constants of non-ionized and ionized molecules with anionic micelles are expected to be quite different from each other. In order to find out the probable locations of reactants and products inside the micelles, the molar extinction coefficients of the reactant and products at different wavelengths are required. We determined these molar extinction coefficients in the absence of SDS and the results are summarized in Table 1.

Hydrazinolysis of Phenyl Salicylate in the Absence of SDS.—The reaction rates of hydrazinolysis of phenyl salicylate were studied at different pH (7.77–8.90) and 30 °C. The ionic strength of the reaction medium was kept constant at 1.0 mol dm^{-3} using aqueous KCl. At constant pH, the observed pseudo-first-order rate constants (k_{obs}) obeyed equation (1) where $[Am]_T$ is the

$$k_{obs} - k_o = k_n[Am]_T \quad (1)$$

total concentration of hydrazine buffer and k_n is the apparent nucleophilic second-order rate constant. The values of buffer-independent rate constants (k_o) at different pH were obtained from the relationship: $k_o = kK_a/(a_H + K_a)$ with $k = 3.6 \times 10^{-4}$ s^{-1} [16] and the ionization constant of phenyl salicylate, $K_a = 5.67 \times 10^{-10}$ mol dm^{-3}.[13] The rate constants, k_n, were calculated from equation (1) using the least-squares technique and the results obtained are summarized in Table 2. The fitting of the observed data to equation (1) is evident from the standard deviations associated with k_n (Table 2).

Hydrolysis of Phenyl Salicylate in the Presence of SDS.—The effects of the concentration of SDS on the rates of hydrolysis were studied at 7.5×10^{-3} mol dm^{-3}, 0.06 mol dm^{-3} NaOH, and 30 °C. The total concentration of SDS ($[SDS]_T$) was varied from 0.02 to 0.20 mol dm^{-3} at 7.5×10^{-3} mol dm^{-3} NaOH, and from 0.02 to 0.40 mol dm^{-3} at 0.06 mol dm^{-3} NaOH. The observed data such as k_{obs}, ε_{app} (apparent molar extinction coefficient) and A_{obs} ($t = \infty$) (absorbance at $t = \infty$) are summarized in Tables 3 and 4.

Effect of $[SDS]_T$ *upon Hydrazinolysis of Phenyl Salicylate.*—The rates of hydrazinolysis of phenyl salicylate were studied within the total hydrazine concentration, $[Am]_T$, range 0.02–0.10 mol dm^{-3} at different $[SDS]_T$, 0.05 mol dm^{-3} NaOH and 30 °C. Similar observations were obtained at 7.5×10^{-3} mol dm^{-3} NaOH. The observed rate constants (k_{obs}) obtained at constant $[SDS]_T$, revealed a reasonably good fit to equation (1) where k_o and k_n were considered as unknown parameters. The least-squares-calculated values of k_o and k_n are shown in Table 5 (for $[NaOH] = 7.5 \times 10^{-3}$ mol dm^{-3}) and Table 6 (for [NaOH] = 0.05 mol dm^{-3}). The fitting of the observed data to equation (1) is evident from some representative plots of Figure 2 and standard deviations associated with the calculated parameters k_o and k_n. The average values of pH and calculated parameters, A_{obs} ($t = 0$) (absorbance at $t = 0$) and A_{obs} ($t = \infty$) (absorbance at $t = \infty$) are also summarized in Tables 5 and 6.

Effect of [NaOH] *upon Hydrazinolysis of Phenyl Salicylate.*—The effect of [NaOH] upon the rates of reaction of phenyl salicylate with NH_2NH_2 was studied within the [NaOH] range 0.001–0.040 mol dm^{-3} at 30 °C, 0.2 mol dm^{-3} SDS, and 0.08 mol dm^{-3} NH_2NH_2. The calculated parameters such as k_{obs}, A_{obs} ($t = 0$), and A_{obs} ($t = \infty$) are shown in Table 7.

Cleavage of Phenyl Salicylate in the Presence of 1,4-*Diazabicyclo*[2.2.2]*octane* (*DABCO*) *in* 0.3 *mol dm*$^{-3}$ *SDS.*—A few kinetic runs were carried out to study the effect of varying the concentration of DABCO upon the cleavage of phenyl salicylate in the presence of 0.3 mol dm^{-3} SDS at 37 °C. The

Table 3. Effect of [SDS] on observed pseudo first-order rate constant (k_{obs}) for hydrolysis of phenyl salicylate at 7.5 × 10^{-3} mol dm^{-3} NaOH.[a]

$[SDS]_T$/mol dm^{-3}	k_{obs}[b]/10^{-4} s^{-1}	ε_{app}[b]/dm^3 mol^{-1} cm^{-1}	A_∞^{350}[b]	A_{obs}^{350} (t = 0)[c]	pH	R[d]	Y[e]
0.0	4.80 ± 0.02[f]	6 451 ± 11[f]	0.013 ± 0.002[f]	1.290	11.41	1.0	0.0
0.02	4.17 ± 0.02	5 724 ± 12	0.010 ± 0.002	1.145	11.48	0.89	0.124
0.04	3.62 ± 0.01	5194 ± 2	0.018 ± 0.001	1.039	11.53	0.81	0.235
0.07	3.09 ± 0.01	4 873 ± 5	0.023 ± 0.001	0.975	11.56	0.76	0.316
0.10	2.65 ± 0.01	4 552 ± 73	0.015 ± 0.002	0.910	11.54	0.71	0.408
0.10	2.73 ± 0.01	4 427 ± 11	0.009 ± 0.002	0.885	11.52	0.69	0.449
0.14	2.17 ± 0.02	4 036 ± 12	0.016 ± 0.002	0.807	11.54	0.63	0.587
0.20	1.72 ± 0.00	3 902 ± 21	0.053 ± 0.004	0.780	11.36	0.60	0.667

[a] [Phenyl Salicylate]$_0$ = 2 × 10^{-4} mol dm^{-3}, 30 °C, λ = 350 nm, reaction mixture for each kinetic run contained 1% CH_3CN. [b] Calculated from the relationship: $A_{obs}^{350} = \varepsilon_{app}[X]_0 \exp(-k_{obs}t) + A_\infty^{350}$ where A_{obs}^{350} represents observed absorbance at time t, ε_{app} is the apparent molar extinction coefficient, $[X]_0$ = 2 × 10^{-4} mol dm^{-3} and A_∞^{350} is absorbance at $t = \infty$. [c] Estimated absorbance at t = 0, *i.e.* A_{obs}^{350} (t = 0) = $\varepsilon_{app}[X]_0$. [d] $R = A_{obs}^{350}$ (t = 0)/1.290. [e] $Y = (1 - R)/R$. [f] Error limits are standard deviations.

Table 4. Effect of [SDS] on observed pseudo-first-order rate constant (k_{obs}) for the hydrolysis of phenyl salicylate at 0.06 mol dm^{-3} NaOH.[a]

$[SDS]_T$/mol dm^{-3}	k_{obs}[b]/10^{-4} s^{-1}	ε_{app}[b]	A_∞^{350}[b]	A_{obs}^{350} (t = 0)[c]
0.0	5.11 ± 0.03[d]	6 051 ± 14[d]	0.003 ± 0.002[d]	1.210
0.02	4.35 ± 0.03	5 970 ± 15	0.002 ± 0.003	1.194
0.04	4.15 ± 0.02	6 008 ± 10	0.004 ± 0.002	1.202
0.10	3.34 ± 0.02	5 928 ± 12	0.018 ± 0.002	1.186
0.14	3.02 ± 0.02	6 013 ± 14	0.017 ± 0.003	1.203
0.20	2.38 ± 0.01	6 099 ± 11	0.029 ± 0.002	1.220
0.30	1.81 ± 0.02	6 187 ± 28	0.052 ± 0.006	1.237
0.40	1.33 ± 0.02	6 343 ± 26	0.065 ± 0.005	1.269

[a,b,c] Notations have the same meanings as in Table 3. [d] Error limits are standard deviations

Table 5. Effect of [SDS] on the apparent nucleophilic second-order rate constants (k_n) for hydrazinolysis of phenyl salicylate at 7.5 × 10^{-3} mol dm^{-3} NaOH.[a]

$[SDS]_T$/mol dm^{-3}	$k_o/10^{-4}$ s^{-1}	$k_n/10^{-3}$ dm^3 mol^{-1} s^{-1}	A_{obs}^{350} ($t = \infty$)[b]	A_{obs}^{350} (t = 0)[c]	pH[d]	$[Am]_T$[e] range/ mol dm^{-3}	R[f]	Y[g]
0.02	4.49 ± 0.44[h]	109 ± 1[h]	0.301 ± 0.014[b]	1.178 ± 0.026[h]	11.44 ± 0.04[h]	0.02–0.10	0.91	0.099
0.04	4.99 ± 0.95	95.4 ± 1.4	0.298 ± 0.011	1.068 ± 0.024	11.48 ± 0.03	0.02–0.10	0.83	0.205
0.07	4.43 ± 0.47	81.3 ± 0.7	0.303 ± 0.003	0.965 ± 0.008	11.47 ± 0.04	0.02–0.10	0.75	0.333
0.10	3.74 ± 0.27	69.7 ± 0.4	0.308 ± 0.004	0.909 ± 0.009	11.49 ± 0.04	0.02–0.10	0.71	0.408
0.14	2.10 ± 0.91	62.1 ± 1.4	0.302 ± 0.012	0.833 ± 0.012	11.43 ± 0.04	0.02–0.10	0.65	0.538
0.20	1.76 ± 0.49	46.7 ± 0.7	0.357 ± 0.018	0.811 ± 0.002	11.33 ± 0.05	0.02–0.10	0.63	0.587

[a] [Phenyl Salicylate]$_0$ = 2 × 10^{-4} mol dm^{-3}, 30 °C, λ = 350 nm, reaction mixture for each kinetic run contained 1% CH_3CN, at a constant $[SDS]_T$, five kinetic runs were carried out at five different concentrations of hydrazine ($[Am]_T$). [b] Average of five A_{obs}^{350} ($t = \infty$) obtained at five $[Am]_T$. [c] Average of five A_{obs}^{350} (t = 0) obtained at five $[Am]_T$. [d] Average of five pH obtained at five $[Am]_T$. [e] Total hydrazine concentration range. [f] $R = A_{obs}^{350}$ (t = 0)/1.290. [g] $Y = (1 - R)/R$. [h] Error limits are standard deviations.

Table 6. Effect of [SDS] on the apparent nucleophilic second-order rate constants, k_n, for hydrazinolysis of phenyl salicylate at 0.05 mol dm^{-3} NaOH.[a]

$[SDS]_T$/mol dm^{-3}	$k_o/10^{-4}$ s^{-1}	$k_n/10^{-3}$ dm^3 mol^{-1} s^{-1}	A_{obs}^{350} ($t = \infty$)[b]	A_{obs}^{350} (t = 0)[c]	$[Am]_T$ range[d]/ mol dm^{-3}
0.02	5.60 ± 1.54	98.0 ± 2.3	0.257 ± 0.013	1.169 ± 0.027	0.02–0.10
0.04	6.10 ± 2.26	91.1 ± 3.4	0.258 ± 0.014	1.158 ± 0.021	0.02–0.10
0.07	4.93 ± 1.30	88.2 ± 2.0	0.262 ± 0.011	1.141 ± 0.024	0.02–0.10
0.10	4.06 ± 0.81	79.2 ± 1.2	0.268 ± 0.015	1.148 ± 0.021	0.02–0.10
0.14	3.92 ± 0.36	69.6 ± 0.5	0.275 ± 0.009	1.166 ± 0.018	0.02–0.10
0.20	3.80 ± 0.62	58.3 ± 0.9	0.284 ± 0.014	1.213 ± 0.039	0.02–0.10
0.30	2.35 ± 0.67	43.2 ± 1.0	0.295 ± 0.012	1.249 ± 0.026	0.02–0.10

[a,b,c] Notations as in Table 5. [d] Total hydrazine concentration range. [e] Error limits are standard deviations.

observed data, k_{obs}, A_{obs} (t = 0) and A_{obs} ($t = \infty$) are shown in Table 8. It is evident from Table 8 that the rate constants (k_{obs}) are independent of the total concentration of DABCO.

Discussion

Hydrazinolysis of Phenyl Salicylate in the Absence of SDS.—The general rate law for the reaction of phenyl salicylate with

Table 7. Effect of [NaOH] on observed pseudo-first-order rate constants, k_{obs}, for hydrazinolysis of phenyl salicylate at 0.2 mol dm^{-3} SDS.[a]

[NaOH]/mol dm^{-3}	k_{obs}[b]/10^{-3} s^{-1}	A_{obs}^{330} (t = 0)[b]	A_{obs}^{350} (t = ∞)[c]	pH	pH[d]
0.001	0.930 ± 0.019[e]	0.432 ± 0.002[e]		10.65	9.98
0.002	1.35 ± 0.03	0.509 ± 0.002		10.97	10.40
0.003	1.78 ± 0.02	0.572 ± 0.00		11.12	10.63
0.004	2.29 ± 0.05	0.629 ± 0.002		11.21	10.83
0.005	2.59 ± 0.07	0.709 ± 0.002		11.26	11.04
0.006	3.10 ± 0.07		0.267 ± 0.003[e]		
0.010	4.02 ± 0.04		0.269 ± 0.002	11.53	11.38
0.020	4.64 ± 0.04		0.260 ± 0.002	11.79	
0.030	4.69 ± 0.03		0.256 ± 0.003	11.96	11.91
0.040	4.64 ± 0.06		0.247 ± 0.002	12.09	12.06

[a] [Phenyl Salicylate]$_0$ = 2 × 10^{-4} mol dm^{-3}, 30 °C, reaction mixture for each kinetic run contained 1% CH_3CN, $[NH_2NH_2]_T$ = 0.08 mol dm^{-3}. [b] These parameters were obtained from the relationship: $A_{obs}^{350} = \varepsilon_{app}[X]_0\,[1 - \exp(-k_{obs}t)] + A_{obs}^{330}$ (t = 0) where $[X]_0$ = 2 × 10^{-4} mol dm^{-3} and ε_{app} is the apparent molar extinction coefficient. [c] Obtained from $A_{obs}^{350} = \varepsilon_{app}[X]_0 \exp(-k_{obs}t) + A_{obs}^{350}$ (t = ∞). [d] Obtained in the absence of SDS. [e] Error limits are standard deviations.

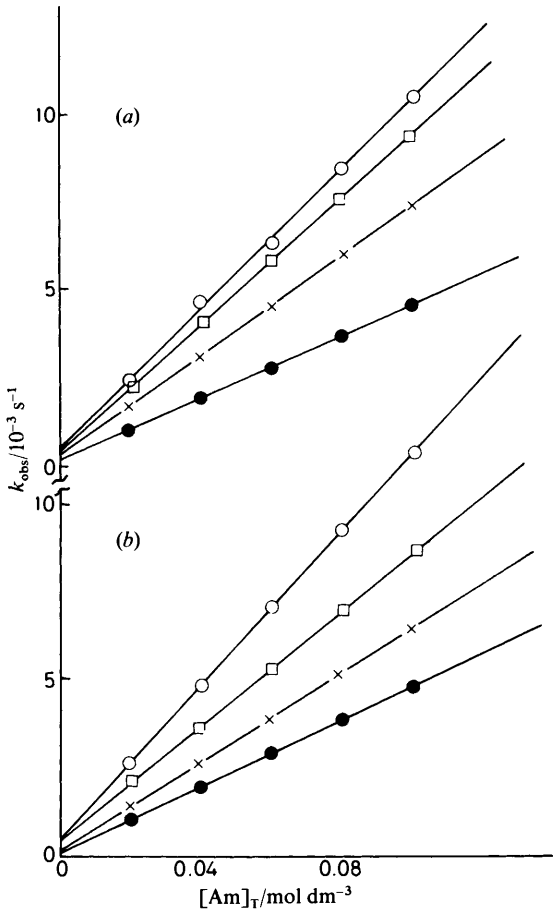


Figure 2. Plots showing the dependence of k_{obs} upon the total hydrazine concentration ([Am]$_T$) at 0.02 mol dm^{-3} SDS for (○), 0.07 SDS for (□), 0.14 SDS for (×) and 0.2 SDS for (●) in the presence of 7.5 × 10^{-3} mol dm^{-3} NaOH and 0.02 mol dm^{-3} SDS for (○), 0.07 mol dm^{-3} SDS for (□), 0.14 mol dm^{-3} SDS for (×) and 0.30 mol dm^{-3} SDS for (●) in the presence of 0.05 mol dm^{-3} NaOH. The solid lines are drawn through the least squares calculated points. [NaOH] = (*a*) 0.05; (*b*) 7.5 × 10^{-3} mol dm^{-3}.

hydrazine, within the pH range of 7.77–8.90, may be given as equation (2) where $[Sub]_T$ is the total concentration of phenyl

$$\text{rate} = k_0[Sub]_T + k_1[PS^-][NH_2NH_2] + k_2[PSH][NH_2NH_2] \quad (2)$$

salicylate and $[NH_2NH_2]$, [PSH], and $[PS^-]$ represent the concentration of non-protonated hydrazine and non-ionized and ionized phenyl salicylate, respectively. The observed rate law (rate = $k_{obs}[Sub]_T$) and equations (1) and (2) yield equation (3) where $Q = (a_H + K_a)(a_H + K'_a)$ and K'_a is the

$$k_nQ = k_1K_aK'_a + k_2K'_a a_H \quad (3)$$

ionization constant of monoprotonated hydrazine. The other probable kinetic terms such as $k_3[PSH][NH_2NH_2][^-OH]$ and $k_4[PS^-][NH_2NH_2][^-OH]$ were ignored on the basis of information described elsewhere.[21] The least-squares technique was used to calculate $k_1K_aK'_a$ and $k_2K'_a$ from equation (3) and the calculated respective values are (3.37 ± 0.70) × 10^{-19} mol dm^{-3} s^{-1} and (9.69 ± 0.74) × 10^{-11} s^{-1}. The fitting of the observed data to equation (3) is evident from the standard deviations associated with the calculated vaues of $k_1K_aK'_a$ and $k_2K'_a$. The rate constants, k_1 and k_2, were calculated from the values of $k_1K_aK'_a$ and $k_2K'_a$, respectively, with K_a = 5.67 × 10^{-10} mol dm^{-3} and K'_a = 7.08 × 10^{-9} mol dm^{-3}.[22] The calculated values of k_1 and k_2 are (83.9 ± 17.5) × 10^{-3} dm^3 mol^{-1} s^{-1} and (13.7 ± 1.1) × 10^{-3} dm^{-3} mol^{-1} s^{-1}, respectively. The calculated value of k_1 is associated with a considerably high standard deviation. The statistically more reliable value of k_1 (=0.111 dm^3 mol^{-1} s^{-1})[16] was obtained by carrying out kinetic runs under such experimental conditions in which the k_2 term was negligible compared with the k_1 term in equation (2). The use of the value of k_1 as 0.111 dm^3 mol^{-1} s^{-1} resulted in k_2 as (12.4 ± 1.2) × 10^{-3} dm^3 mol^{-1} s^{-1} which is only *ca.* 9% smaller than that of 13.7 × 10^{-3} dm^3 mol^{-1} s^{-1}.

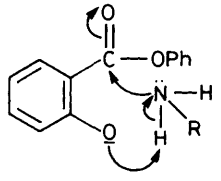
It is interesting to note that the rate constant k_1 is nearly 6–8 times larger than k_2. In terms of a purely polar effect of the substituents, *o*-O$^-$ and *o*-OH, one would expect k_2 to be larger than k_1 since the observed values of the nucleophilic second-order rate constants (k_{OH}) for the reactions of $^-$OH with methyl benzoate, methyl *o*-methoxybenzoate, methyl *p*-methoxybenzoate, ionized methyl salicylate and ionized methyl *p*-hydroxybenzoate are 0.125 dm^3 mol^{-1} s^{-1} (30 °C, ionic strength, μ = 1.0 mol dm^{-3}),[23] 0.031 dm^3 mol^{-1} s^{-1} (35 °C, μ = 2.0 mol dm^{-3}),[24] 0.032 dm^3 mol^{-1} s^{-1} (32 °C, μ = 2.0 mol dm^{-3}),[25] 6.65 × 10^{-4} dm^3 mol^{-1} s^{-1} (35 °C, μ = 2.0 mol dm^{-3}),[24] and 17.1 × 10^{-4} dm^3 mol^{-1} s^{-1} (32 °C, μ = 2.0 mol dm^{-3}),[26] respectively. Similarly, Bender *et al.*[27] obtained a *ca.* eightfold larger reactivity of imidazole toward non-ionized 5-nitrophenyl 5-nitrosalicylate compared with the ionized form. Thus, the observed value of k_1/k_2 (≥6) cannot be explained in terms of the polar effect of *o*-substituents. Recently, we concluded that the reactions of ionized phenyl salicylate (PS^-) with primary

Table 8. Effect of [DABCO] on observed pseudo first-order rate constant (k_{obs}) for the cleavage of phenyl salicylate in the presence of 0.3 mol dm^{-3} SDS.[a]

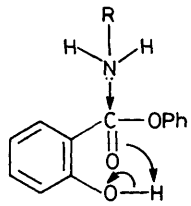
$[DABCO]_T$[b]/mol dm^{-3}	k_{obs}[c]/10^{-4} s^{-1}	A_{obs}^{350} ($t = \infty$)[c]	ε_{app}[c]/dm^3 mol^{-1} cm^{-1}	A_{obs}^{350} ($t = 0$)[d]
0.06	3.53 ± 0.04[e]	0.050 ± 0.003[e]	5 811 ± 20[e]	1.162
0.24	3.74 ± 0.04	0.057 ± 0.003	6 154 ± 19	1.231
0.42	3.78 ± 0.04	0.062 ± 0.003	6 128 ± 21	1.226
0.60	3.66 ± 0.05	0.081 ± 0.004	6 349 ± 29	1.270

[a] [Phenyl Salicylate]$_0$ = 2 × 10^{-4} mol dm^{-3}, 0.05 mol dm^{-3} NaOH, 37 °C, reaction mixture for each kinetic run contained 1% CH_3CN. [b] Total concentration of diazabicyclo[2.2.2]octane. [c] Calculated from the relationship: $A_{obs}^{350} = \varepsilon_{app}[X]_0 \exp(-k_{obs}t) + A_{obs}^{350}$ ($t = \infty$) where $[X]_0$ = 2 × 10^{-4} mol dm^{-3}. [d] A_{obs}^{350} ($t = 0$) = $\varepsilon_{app}[X]_0$. [e] Error limits are standard deviations.

and secondary amines involve intramolecular general-base catalysis (TS1).[16] Such catalysis has been shown to increase the rate of hydrolysis of PS^- by a factor of *ca.* 10^4–10^6.[14] The probable occurrence of the reaction mechanism involving intramolecular general-acid catalysis (TS2) has been ruled out



TS1



TS2

as discussed elsewhere.[28] The hydrazinolysis of PS^-, undoubtedly, involves intramolecular general-base catalysis similar to TS1. If the mechanism TS2 is considered to be operative, then the value of k_2 would be expected to be much larger than k_1 because the nucleophilic attack by NH_2NH_2 at carbonyl carbon would be greatly retarded by the polar effect of o-O^- in the absence of intramolecular general-base catalysis. Thus, the ratio k_1/k_2 of *ca.* 6–8 unequivocally confirms the occurrence of TS1.

A sceptic might think that both mechanisms, TS1 and TS2, could operate simultaneously in these reactions. The significant and effective occurrence of TS2 may be ruled out based on the observations that only a *ca.* 1.2–1.7 times greater reactivity of imidazole with *p*-nitrophenyl 5-nitrosalicylate and *p*-nitrophenyl salicylate compared with the corresponding *o*-methoxy esters was observed.[27] Capon and Ghost[29] also observed a *ca.* twofold increase in the reactivity of imidazole with non-ionized phenyl salicylate (PSH) compared with phenyl *o*-methoxybenzoate. Such a small increase (≤ twofold) in the reactivity could be attributed to the difference in the steric requirements of *o*-OH and *o*-OMe groups. The second-order rate constants for the reactions of PSH with primary and secondary amines displayed a Brønsted plot with slope and intercept of 0.82 and −7.68 dm^3 mol^{-1} min^{-1}, respectively.[28] Although a few observed data points were concluded not to be very reliable, the rate constant for imidazole appeared to fall on the same Brønsted plot.[28] The observed rate constant, k_2 (= 0.0137 dm^3 mol^{-1} s^{-1}) for hydrazine incorporates a *ca.* eightfold positive deviation from this Brønsted plot, which may be attributed to the α-effect. These observations do not appear to favour the effective occurrence of TS2 along with TS1.

Hydrolysis of Phenyl Salicylate in the Presence of SDS.—The increase in the total concentration of SDS ($[SDS]_T$), at a constant [NaOH], resulted in a decrease in k_{obs} as shown in Tables 3 and 4. The observed values of A_{obs}^{350} ($t = 0$) are independent of $[SDS]_T$ at 0.06 mol dm^{-3} NaOH while a decrease in A_{obs}^{350} ($t = 0$) with increased $[SDS]_T$ could be observed at 7.5 × 10^{-3} mol dm^{-3} NaOH (Tables 3 and 4). The observed values of A_{obs}^{350} ($t = 0$) obtained in the absence of SDS, are essentially same at 0.06 and 7.5 × 10^{-3} mol dm^{-3} NaOH within the limits of experimental uncertainty. Under such experimental conditions, phenyl salicylate is expected to exist as the 100% ionized form (PS^-). The non-ionized phenyl salicylate (PSH) does not absorb at 350 nm (Table 1). Thus, the ratio $[A_{obs}^{350}\ (t = 0)]_{SDS}/[A_{obs}^{350}\ (t = 0)]_{H_2O}$ at 7.5 × 10^{-3} mol dm^{-3} NaOH, where $[A_{obs}^{350}\ (t = 0)]_{SDS}$ and $[A_{obs}^{350}\ (t = 0)]_{H_2O}$ represent the initial absorbance at a constant $[SDS]_T$ and at $[SDS]_T = 0$, respectively, gives the measure of the fraction of $[PS^-]$ into the reaction mixture. These results, as shown in Table 3, indicate the presence of only *ca.* 60% PS^- at 7.5 × 10^{-3} mol dm^{-3} NaOH and 0.20 mol dm^{-3} SDS. The pH of the reaction mixture did not appear to change significantly with increased $[SDS]_T$ at 7.5 × 10^{-3} mol dm^{-3} NaOH (Table 3) and it remained ≥ 11.36. The measured pH of a reaction mixture is believed to be that of the aqueous pseudophase. The pK_a of PSH is 9.25 and salicylate molecules would be almost completely ionized in an aqueous solution of pH ≥ 11. This shows that entire PSH molecules exist in the micellar pseudophase at different $[SDS]_T$.

It may be worth mentioning here that the calculation of the fraction of $[PS^-]$ from the ratio $[A_{obs}^{350}\ (t = 0)]_{SDS}/[A_{obs}^{350}\ (t = 0)]_{H_2O}$ involves the assumption that no PS^- species are associated with the micelles or that molar extinction coefficient for PS^-, $\varepsilon_{350}^{PS^-}$, is the same in the micelles and in the aqueous environment. We studied the cleavage of PS^- in different mixed aqueous organic solvents in which acetonitrile, methanol, ethanol, propanol, and ethane-1,2-diol were considered as organic cosolvents. The change in the contents of organic cosolvents from 10–90% v/v, did not produce a detectable change in the values of ε^{PS^-} within the wavelength range 280–350 nm. Similar observations were obtained in mixed solvents containing different alkanols and acetonitrile. These results suggest that $\varepsilon_{350}^{PS^-}$ is most likely same in the micelles and in aqueous pseudophase. The observed pseudo-first-order rate constants (k_{obs}) for hydrolysis of ionized methyl salicylate were found to be unchanged[25] while those for hydrolysis of PS^- were decreased by a factor of four (Table 4) within the $[SDS]_T$ range 0.0–0.4 mol dm^{-3}. These reactions were carried out at constant $[^-OH]$ under which the concentrations of non-ionized salicylate esters were almost zero. These observations are difficult to explain if PS^- molecules are not associated with micelles.

The hydrolytic cleavage of phenyl salicylate may be easily discussed in terms of micellar pseudophase model[30] in the presence of SDS. The assumptions involved in this model and its advantages and disadvantages are critically discussed by Bunton.[1f,31] The reaction scheme for hydrolysis of phenyl salicylate, in the presence of SDS micelles, may be given as shown in Scheme 1, where the subscripts W and M represent the aqueous pseudophase and micellar pseudophase, respectively,

and D_n is the micellized SDS. Although an equilibrium process [equation (4)] is more favourable than the K_1 equilibrium

$$PS^-_W + D_n \overset{K_1}{\rightleftharpoons} PS^-_M \overset{\pm H^+}{\underset{K_a^M}{\rightleftharpoons}} PSH_M$$

$$OH^-_W + D_n \overset{K_{OH}}{\rightleftharpoons} OH^-_M$$

$$PS^-_W \xrightarrow{k^h_W} \text{Product(s)}$$

$$PS^-_M \xrightarrow{k^h_M} \text{Product(s)}$$

Scheme 1.

$$PSH_W + D_n \overset{K_2}{\rightleftharpoons} PSH_M \qquad (4)$$

(Scheme 1), we did not consider it because the concentration of PSH_W ($[PSH_W]$) appeared to be negligible under the experimental conditions imposed. It has been convincingly ascertained that the hydrolysis of PS^- involves intramolecular general-base catalysis while the hydrolysis of PSH does not involve the kinetically indistinguishable intramolecular general-acid catalysis.[13,14,27,29] The intramolecular general-base catalysis has been shown to increase the rate hydrolysis of PS^-_W by a factor of *ca.* 10^6 compared with that of an analogous substrate where such catalysis would not be expected.[14] We assume that the same mechanism is operating in the hydrolysis of both PS^-_W and PS^-_M. These conclusions reveal that the rate constants for hydrolysis of PSH_M and PSH_W may be neglected compared with k^h_M and k^h_W, respectively.

The observed rate law (rate = $k_{obs}[Sub]_T$) and Scheme 1 gives rise to equation (5) where $K_S^{app} = ([PS^-_M] + [PSH_M])/$

$$k_{obs} = \frac{k^h_W + k^h_M f_M^{PS^-} K_S^{app}[D_n]}{1 + K_S^{app}[D_n]} \qquad (5)$$

$[PS^-_W][D_n]$ with $[D_n] = [SDS]_T - cmc$ (critical micelle concentration), $f_M^{PS^-} = K_a^M/(a_H^M + K_a^M)$, and K_a^M and a_H^M are the ionization constant of PSH and activity of proton in the micellar pseudophase. It is evident from Table 3 that the observed pH of the reaction mixtures remained essentially unchanged (within the limits of experimental uncertainty) in the $[SDS]_T$ range 0.0–0.20 mol dm^{-3} at 7.5 10^{-3} mol dm^{-3} NaOH. It may therefore be assumed that $f_M^{PS^-}$ would remain constant within the $[SDS]_T$ range 0.02–0.20 mol dm^{-3} at 7.5 × 10^{-3} mol dm^{-3} NaOH. Bunton and Wolfe[21] also did not observe any appreciable change in pH of the solutions containing 0.01 mol dm^{-3} HCl and varying concentrations of cetyltrimethylammonium bromide (CTABr).

The observed data (Table 3) were treated with equation (5) considering $k^h_M f_M^{PS^-}$ and K_S^{app} as two unknown parameters and cmc = 0.008.[32] The non-linear least-squares-calculated values of $k^h_M f_M^{PS^-}$ and K_S^{app} are (1.8 ± 3.6) × 10^{-5} s^{-1} and 9.8 ± 1.5 dm^3 mol^{-1}, respectively. A nearly 200% standard deviation associated with the calculated value of $k^h_M f_M^{PS^-}$ indicates that the contribution of $k^h_M f_M^{PS^-}$ compared with k^h_W is not statistically different from zero. The maximum contribution of $k^h_M f_M^{PS^-} K_S^{app}[D_n]$ turned out to be *ca.* 7%.

An alternative data treatment using equation (6) was also

$$\frac{1}{k^h_W - k_{obs}} = \frac{1}{k^h_W - k^h_M f_M^{PS^-}} + \frac{1}{(k^h_W - k^h_M f_M^{PS^-})K_S^{app}[D_n]} \qquad (6)$$

carried out and the least-squares-calculated values of $(k^h_W - k^h_M f_M^{PS^-})^{-1}$ and $[(k^h_W - k^h_M f_M^{PS^-})K_S^{app}]^{-1}$ are 2 609 ± 390 s and 164 ± 11 mol dm^{-3}, respectively. These calculated values yielded $k^h_M f_M^{PS^-}$ and K_S^{app} as 9.7 × 10^{-5} s^{-1} and 15.9 dm^3 mol^{-1}, respectively. Although equation (6) is being commonly used, partly because the data treatment with the non-linear equation (5) is perhaps more difficult than that with an alternative linear equation (6), we consider equation (5) to be more appropriate for data treatment due to the following reason. The statistical reliability of $k^h_W - k_{obs}$ or $k_{obs} - k^h_W$ seems to decrease as $[D_n] \longrightarrow 0$. But $(k^h_W - k_{obs})^{-1}$ or $(k_{obs} - k^h_W)^{-1} \longrightarrow \infty$ as $[D_n] \longrightarrow 0$. Thus, the data treatment with equation (6) suffers from the disadvantages of placing a very high emphasis on the values of k^h_W and k_{obs} as $[D_n] \longrightarrow 0$ and being very sensitive to errors when k_{obs} is nearly equal to k^h_W.

The observed values of A^{350}_{obs} ($t = 0$) at 0.06 mol dm^{-3} NaOH and within the $[SDS]_T$ range of 0.02–0.40 mol dm^{-3} (Table 4) indicate the non-existence of $[PSH]_T$ ($[PSH]_T = [PSH_M] + [PSH_W]$) in the reaction mixtures and hence $f_M^{PS^-} = 1$. The observed data (Table 4) were also treated with equation (5). The least-squares-calculated values of k^h_M and K_S^{app} are (13.5 ± 8.1) × 10^{-5} s^{-1} and 11.0 ± 5.5 dm^3 mol^{-1}, respectively, when the data treatment involved the observed data points within the $[SDS]_T$ range 0.02–0.20 mol dm^{-3}. But the respective values of k^h_M and K_S^{app} were turned out to be (3.4 ± 8.2) × 10^{-5} s^{-1} and 6.9 ± 2.6 dm^3 mol^{-1} for $[SDS]_T$ range 0.02–0.30 mol dm^{-3} and (−2.6 ± 6.7) × 10^{-5} s^{-1} and 5.5 ± 1.5 dm^3 mol^{-1} for $[SDS]_T$ range 0.02–0.40 mol dm^{-3}. This change in the calculated values of k^h_M and K_S^{app} (or K_1) with change in the range of the observed data for kinetic treatment is probably the consequence of the breakdown of the assumptions, involved in the simple pseudophase model for the micelle, at relatively high $[SDS]_T$. There is evidence that, at high detergent concentration, a phase transition of a micellar structure such as from spherical to rod-shaped and then to liquid crystalline phase takes place.[1c] Under such structural transitions of micelle, the validity of equation (5) does not exist. We therefore consider the kinetic treatment, using equation (5), of the observed data within the $[SDS]_T$ range 0.02–0.20 or 0.02–0.30 mol dm^{-3} as more reliable. The calculated values of k^h_M involve considerably high standard deviations and the maximum contribution of $k^h_M K_S^{app}[D_n]$ compared with k^h_W is < 40 or < 15%.

It is apparent that the contribution of $k^h_M f_M^{PS^-} K_S^{app}[D_n]$ compared with k^h_W [in equation (5)] is insignificant in both 7.5 × 10^{-3} and 0.06 mol dm^{-3} NaOH. Thus, the assumption that $k^h_M f_M^{PS^-} K_S^{app}[D_n] < k^h_W$ reduces equation (5) to (7). The

$$\frac{k^h_W - k_{obs}}{k_{obs}} = K_S^{app}[SDS]_T - cmc\ K_S^{app} \qquad (7)$$

least-squares-calculated values of K_S^{app} and cmc K_S^{app} are 9.1 ± 0.2 dm^3 mol^{-1} and 0.070 ± 0.036 at 7.5 × 10^{-3} mol dm^{-3} NaOH and 5.9 ± 0.3 dm^3 mol^{-1} and 0.025 ± 0.057 at 0.06 mol dm^{-3} NaOH, respectively. Although the calculated values of cmc K_S^{app} are not very reliable (because of the large standard deviations associated with them), these values were used to calculate the cmc as 0.008 and 0.004 mol dm^{-3} at 7.5 × 10^{-3} 0.06 mol dm^{-3} NaOH, respectively. These calculated cmc values are comparable to the literature value(s).[1c,32] The fitting of the observed data to equation (7) is evident from the plots of Figure 3 where solid lines are drawn through the calculated points. The observed point at 0.4 mol dm^{-3} SDS was not included in the least-squares calculation of K_S^{app} and cmc K_S^{app} because of its significant positive deviation from the linear plot. This deviation may be attributed to the micellar structural change from spherical to perhaps rod-shaped.

The calculated value of K_S^{app} at 7.5 × 10^{-3} mol dm^{-3} NaOH is *ca.* 1.5 times larger than that at 0.06 mol dm^{-3} NaOH. The

decrease of K_S^{app} with increase of [NaOH] may be explained as follows. By definition equation (9) may be derived from Scheme

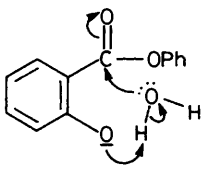
$$K_S^{app} = \frac{[PS_M^-] + [PSH_M]}{[PS_W^-][D_n]} \quad (8)$$

1 and equation (8).* The value of a_H^M will decrease with increase

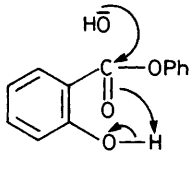
$$K_S^{app} = K_1 + \frac{K_1 a_H^M}{K_a^M} \quad (9)$$

of [NaOH] at a constant $[SDS]_T$. We also noted earlier at a_H^M is almost independent of $[SDS]_T$ within the range *ca.* 0.02–0.20 mol dm^{-3} at 7.5×10^{-3} mol dm^{-3} NaOH. It is, therefore, apparent from equation (9) that K_S^{app} should increase with decrease of [NaOH]. The observed values of A_{obs}^{350} ($t = 0$) (Table 4) reveal the absence of $[PSH]_T$ into the reaction mixtures at 0.06 mol dm^{-3} NaOH and $[SDS]_T$ range 0.02–0.40 mol dm^{-3}. Under such conditions, equation (8) indicates that $K_S^{app} = K_1$. Thus, the value of K_1 may be considered as 5.9 dm^3 mol^{-1} (K_S^{app} at 0.06 mol dm^{-3} NaOH).

Significantly larger rates of hydrolysis of salicylate esters compared with those of 2-methoxy analogues could be attributed to either one of the kinetically indistinguishable mechanisms TS3 and TS4. But these reactions have been shown, although by



TS3



TS4

indirect evidence, to involve mechanisms TS3.[14,27,29] The change from pure aqueous to mixed aqueous solvents does not generally change the reaction mechanism of an organic reaction. But the presence of micelles[19] and pure apolar solvents[33,34] have been shown to change the aqueous reaction mechanism of a few reactions. In order to find out if there is a change from TS3 to TS4 for the micelle-mediated reactions, we studied the effect of the presence of different concentrations of 1,4-diazabicyclo[2.2.2]octane (DABCO) in 0.3 mol dm^{-3} SDS and 37 °C. The observed rate constants, k_{obs}, did not reveal the detectable reactivity of DABCO toward PS_M^- and PSH_M (Table 8). The observed values of A_{obs}^{350} ($t = 0$) (Table 8) indicate the absence of $[PSH]_T$ into the reaction medium. The average value of k_{obs} $(3.7 \pm 0.1) \times 10^{-4}$ s^{-1}, obtained within the [DABCO] range 0.06–0.60 mol dm^{-3}, is similar to k_{obs} (3.8×10^{-4} s^{-1})[25] obtained in the absence of DABCO under similar experimental conditions. The absence of reactivity of DABCO toward PS_M^- can not be attributed solely to the probable lack of binding of DABCO with micelles of SDS. If the hydroxide ions could reach to the anionic micellar region where PS_M^- molecules exist, then it would be difficult to believe that neutral and relatively less hydrophilic DABCO molecules could not reach to the same micellar region even at [DABCO]:[$^-$OH] ratios of 1.2–12. We conclude that the lack of reactivity of DABCO toward PS_M^- indicates that the mechanisms of hydrolysis of phenyl salicylate remains the same in both aqueous and SDS micellar pseudophases.

The rate constants (k_{obs}) for hydrolysis of phenyl salicylate in the presence of SDS at 30 °C obeyed equation (7). Assuming that the k_{obs}, obtained in the presence of DABCO, 0.05 and 0.3 mol dm^{-3} NaOH and SDS, respectively, at 37 °C, would also obey equation (7), the value of K_S^{app} ($= K_1$ in 0.05 mol dm^{-3} NaOH) turns out to be 4.8 dm^3 mol^{-1}. The value of K_1 (4.8 dm^3 mol^{-1}) at 37 °C is slightly smaller than that (5.9 dm^3 mol^{-1}) at 30 °C. This is conceivable for the reason that the increase in temperature decreases the micellar solubility of the substrate.[11] The binding constant K_1 is *ca.* 2.5 times smaller than the binding constant of aniline with SDS micelles at 25 °C.[11c]

Although the calculated values of k_M^h at 0.06 and 7.5×10^{-3} mol dm^{-3} NaOH are not very reliable, they do, however, reflect the fact that k_W^h is more than four times larger than k_M^h. Since the hydrolysis of the phenyl salicylate involves PS^- and the water molecules, it is apparent that the hydrolysis of PS_M^- involves a micellar region where the water concentration is considerably reduced. It has been elegantly concluded by Cordes[35] that at ionic micellar surface, the concentration of charged groups is 3–5 mol dm^{-3}, the polarity is considerably reduced (relative permittivity is *ca.* 35) and the activity of water remains unchanged compared to the aqueous pseudophase. We have concluded elsewhere[18] that these factors cannot explain ≥ fourfold decrease of k_M^h compared with k_W^h. Furthermore, the rate constant, k_W^h has been found to be decreased by a factor of *ca.* two and 2.5 in the mixed aqueous solvents containing 40%, v/v, 1,4-dioxane[25] (relative permittivity = 44 at 25 °C)[36] and 84%, v/v, acetonitrile[37] (relative permittivity > 37 at 25 °C),[38] respectively. The k_{obs}–% content of organic cosolvent profiles are distinctly different from each other in these two mixed solvent systems.

It seems reasonable to conclude that the reaction between PS_M^- and H_2O does not occur at the surface of the micelle. The PS_M^- molecules are presumably dragged a little deeper inside the micellar pseudophase where the water concentration is considerably decreased and the hydrophobicity of the environment is considerably increased due to the exposure of the large number of methylene units of SDS monomers. There are sufficient water molecules, even in this region, essentially to solvate the anionic and cationic charges of the medium. The PSH_M molecules exist either in the same region as the PS_M^- molecules, or they are dragged into a relatively more hydrophobic micellar region. These observations are in favour of the porous cluster micellar structure. The assumption, involved in a porous cluster micelle, is that some of the water molecules penetrate deep inside the micellar core to fill the voids. Unlike the '2-state' Hartley micellar model, the porous cluster micellar model does not predict a well-defined 2-state of the micelle such as hydrophilic Stern layer and hydrophobic micellar core.

Effect of SDS on Hydrazinolysis of Phenyl Salicylate.—The increase in $[SDS]_T$, at a constant [NaOH] and 30 °C, resulted in a decrease in the nucleophilic second-order rate constant for the reactions of hydrazine with phenyl salicylate (Tables 5 and 6). These observations may be explained in terms of the pseudophase model of micelle. Along with other assumptions made in this model, the most crucial one is that the micellar binding of both the reactants, phenyl salicylate and hydrazine, is independent of either. Even the micellar incorporation of $^-$OH does not presumably affect the binding constant for PS^- with micelle. We consider the validity of these assumptions for the following reasons. The hydrazine-independent rate constants (k_o) (Tables 5 and 6) are essentially similar (within the limits of experimental uncertainties) to the corresponding rate constants, k_o (Tables 3 and 4), obtained in the absence of hydrazine under almost similar experimental conditions. The observed values of A_{obs}^{350} ($t = 0$) at both 7.5×10^{-3} and 0.05 mol dm^{-3} NaOH (Tables 5 and 6) and pH at 7.5×10^{-3} mol dm^{-3} NaOH (Table

* If K_S^{app} is defined as $K_S^{app} = ([PS_M^-] + [PSH_M])/([PS_W^-] + [PSH_W])[D_n]$ then it may be shown that $K_S^{app} = (K_1 K_a^W + K_2 a_H^W)/(a_H^W + K_a^W)$, where $K_2 = [PSH_M]/[PSH_W][D_n]$ and $K_a^W = [PS_W^-]a_H^W/[PSH_W]$.

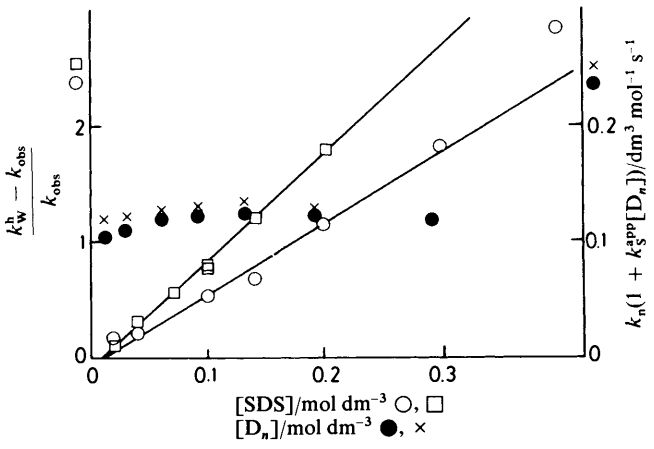


Figure 3. Dependence of k_n $(1 + K_S^{app}[D_n])$ upon $[D_n]$ for the hydrazinolysis of phenyl salicylate at 7.5 × 10^{-3} mol dm^{-3} NaOH for (×) and 0.05 mol dm^{-3} NaOH for (●). Plots of $(k_W^h - k_{obs})/k_{obs}$ *versus* $[SDS]_T$ for hydrolysis of phenyl salicylate at 7.5 × 10^{-3} mol dm^{-3} NaOH for (□) and 0.06 mol dm^{-3} NaOH for (○).

5) are similar to the corresponding values of A_{obs}^{350} $(t = 0)$ (Tables 3 and 4) and pH (Table 3) obtained in the absence of hydrazine. The complete reaction scheme for these reactions may be shown by Schemes 1 and 2 where N represents hydrazine.

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

$$PS_W^- + N_W \xrightarrow{k_W^n} \text{Product(s)}$$

$$PS_M^- + N_M \xrightarrow{k_M^{ns}} \text{Product(s)}$$

Scheme 2.

We have neglected the following reaction steps in Scheme 2 for the following reasons. Since the concentration of PSH_W is nearly zero under the experimental conditions imposed and k_W^n

$$PSH_W + N_W \xrightarrow{k_W^{n,PSH}} \text{Product(s)}$$

$$PSH_M + N_M \xrightarrow{k_M^{n,PSH}} \text{Product(s)}$$

$[\equiv k_1$, equation (2)] is *ca.* 6–8 times larger than $k_W^{n,PSH}$ $[k_2$, equation (2)], therefore the contribution of the $k_W^{n,PSH}$ step should be negligible compared with that of the k_W^n step (Scheme 2). The observed values of A_{obs}^{350} $(t = 0)$ (Table 6) indicate that $[PSH_M] = 0$ at 0.05 mol dm^{-3} NaOH and the maximum fraction of non-ionized phenyl salicylate is *ca.* 40%, obtained at 0.2 mol dm^{-3} SDS (Table 5). If we assume that the effect of anionic micelles does not change the ratio of $k_W^n/k_W^{n,PSH}$, *i.e.*, $k_W^n/k_W^{n,PSH} \simeq k_M^n/k_M^{n,PSH}$, then the contribution of $k_M^{n,PSH}$ step may be neglected compared with that of the k_M^n step. Furthermore, some PSH_M molecules may be expected to be dragged deeper than the PS_M^- molecules inside the micelles and hence would lie in a micellar region of relatively low water activity. The water activity is believed to decrease with increased distance from the exterior surface to the centre of a spherical micelle in the porous cluster micellar model. The existence of some of the PSH_M molecules in a region of water activity lower than that of the PS_M^- molecules would lead to $k_M^n/k_M^{n,PSH} > k_W^n/k_W^{n,PSH}$ and consequently the $k_M^{n,PSH}$ step may be neglected in comparison with the k_M^n step.

The observed rate law (rate = $k_{obs}[Sub]_T$) and Scheme 1 and 2 give rise to equation (10) where $K_N = [N_M]/[N_W][D_n]$, $[N_M]$

$$k_{obs} = \frac{k_W^h + k_M^h f_M^{PS^-} K_S^{app}[D_n]}{1 + K_S^{app}[D_n]} + \frac{(k_W^n + k_M^{ns} K_N K_S^{app} f_M^{PS^-}[D_n])[Am]_T}{(1 + K_S^{app}[D_n])(1 + K_N[D_n])} \quad (10)$$

and $[N_W]$ represent the concentration of hydrazine in micellar and aqueous pseudophase, respectively, and $[Am]_T = [N_M] + [N_W]$. The magnitude of a second-order rate constant depends upon the choice of the concentration units of the reacting species involved. The micellar pseudophase constitutes a typical reaction environment in which there is a continuous decrease and increase of water activity and hydrophobicity of the medium, respectively, with increasing distance from the shear surface to the centre of the spherical micelle. It is therefore very difficult to ascertain the volume element for any micelle-mediated chemical reaction. To avoid this problem, Bunton *et al.*[39] have defined the second-order rate constant, k_M^{ns}, for micelle-mediated bimolecular reactions, in terms of the mole ratio of micelle-bound reactant to micellized surfactant. Thus, the rate of hydrazinolysis of phenyl salicylate, v, in micellar pseudophase, may be defined as equation (11) where $m_N^s = [N_M]/[D_n]$.

$$v = k_M^{ns}[PS_M^-]m_N^s \quad (11)$$

Equation (10) is similar to the rearranged form of equation (1) with

$$k_n = \frac{k_W^n + k_M^{ns} K_N K_S^{app} f_M^{PS^-}[D_n]}{(1 + K_S^{app}[D_n])(1 + K_N[D_n])} \quad (12)$$

The plots of k_n $(1 + K_S^{app}[D_n])$ *versus* $[D_n]$ are as shown in Figure 3. The values of K_S^{app} used at 0.05 and 7.5 × 10^{-3} mol dm^{-3} NaOH were those obtained at 0.06 mol dm^{-3} (K_S^{app} = 5.9 dm^3 mol^{-1}) and 7.5 × 10^{-3} mol dm^{-3} NaOH (K_S^{app} = 9.1 dm^3 mol^{-1}), respectively, in the absence of hydrazine. It is evident from these plots that the values of k_n $(1 + K_S^{app}[D_n])$ are essentially independent of $[D_n]$ within the $[SDS]_T$ range of the present study. The intercepts of the plots are not different from k_W^n (0.111 dm^3 mol^{-1} s^{-1}). These observations may be ascribed to either one of the following possibilities: (i) $K_N = 0$, (ii) $k_W^n \gg k_M^{ns} K_S^{app} f_M^{PS^-}[D_n]$ and $1 \gg K_N[D_n]$, and (iii) $k_W^n \simeq k_M^{ns} K_S^{app} f_M^{PS^-}$. The first possibility that $K_N = 0$ does not seem to be correct because it means that hydrazine molecules do not bind with SDS micelles. Hydroxide ion is presumably more hydrophilic than hydrazine and also anions are less effectively bound by anionic micelles compared with the corresponding neutral molecules. The present study reveals the presence of hydroxide ions into the micelles and therefore it does not seem to be correct that $K_N = 0$. Recently, we found kinetically that K_N = 3.8 dm^3 mol^{-1} in the hydrazinolysis of methyl salicylate.[17] The value of K_N of 3.8 dm^3 mol^{-1} rules out the possibility that $1 \gg K_N[D_n]$ at $[D_n] > 0.1$ mol dm^{-3}. The third possibility appears to be the most reasonable one.

The assumption that $k_W^n \simeq k_M\ ^{ns}K_S^{app} f_M^{PS^-}$ gives a value of k_M^{ns} of 19 × 10^{-3} s^{-1} at 0.05 mol dm^{-3} NaOH ($f_M^{PS^-}$ = 1 at 0.05 mol dm^{-3} NaOH). If we consider the density of the micellar pseudophase as 1 g cm^{-3},[1f] then the molar volume of SDS micelles would be 0.288 dm^3. Thus, the value of the micellar second-order rate constant, k_M^n, in terms of molarity concentration units may be given as: $k_M^n = 0.288\ k_M^{ns}$ = 5.47 × 10^{-3} dm^3 mol^{-1} s^{-1}. This value of k_M^n may be considered as its upper limit for the reason that only a certain volume fraction of the total volume of micellar pseudophase constitutes the reaction medium for the micelle-mediated reactions. Although the ratio k_W^n/k_M^n of >18 is not very reliable because of the large uncertainty of the presumed density (1 g cm^{-3}) of the micellar

Table 9. Fractions of ionized phenyl salicylate (F^{PS^-}) *N*-hydrazinylsalicylamide, F^{HDS^-}, and phenol, F^{PhO^-}, at different [NaOH] in the presence of 0.2 mol dm^{-3} SDS and 0.08 mol dm^{-3} NH_2NH_2.

[NaOH]/mol dm^{-3}	A_{obs}^{350} (t = 0)	A_{obs}^{350} (t = ∞)	A_{obs}^{330} (t = ∞)	A_{obs}^{290} (t = ∞)	F^{PS^-}	$F_{350}^{HDS^-}$	$F_{330}^{HDS^-}$	F^{PhO^-}	K_S^{app}/mol dm^{-3}	Y
0.001	0.204	0.231	0.930	0.444	0.17	0.89	0.92	0.32	44.5	4.83
0.001	0.204	0.231	0.930	0.472	0.17	0.89	0.92	0.38	44.5	4.83
0.002	0.330	0.246	0.976	0.532	0.28	0.95	0.96	0.55	29.1	2.61
0.003	0.407	0.250	0.986	0.614	0.34	0.96	0.97	0.72	20.8	1.92
0.004	0.515	0.260			0.43	1.00			15.0	1.31
0.005	0.597	0.264			0.50	1.02			12.6	0.99
0.006	0.664	0.267			0.55	1.03			9.7	0.79
0.010	0.838	0.269	1.000	0.752	0.70	1.03	0.99	1.05	6.3	0.42
0.020	1.045	0.260			0.87	1.00			4.8	0.14
0.030	1.111	0.256			0.93	0.98			4.6	0.07
0.040	1.098	0.247			0.92	0.95			4.8	0.08

pseudophase, it is conceivable if we assume that the reaction between PS_M^- and N_M occurred in the micellar region where water concentration was considerably reduced compared with $[H_2O]$ of aqueous pseudophase. The presence of 70%, v/v, propan-1-ol, in the mixed aqueous solvents, resulted in a decrease, by a factor of 3.6, in the value of k_W^n.[40]

Effect of [NaOH] *on the Hydrazinolysis of Phenyl Salicylate in the Presence of SDS.*—The non-ionized phenyl salicylate (PSH) does not absorb whereas the ionized form (PS^-) absorbs strongly at 350 nm (Table 1). The observed values of A_{obs}^{350} (t = 0) (Table 7) appeared to increase with increased [NaOH] at 0.2 mol dm^{-3} SDS. The fractions of ionized phenyl salicylate ($[PS^-]/([PSH] + [PS^-])$ at different [NaOH] were calculated from A_{obs}^{350} (t = 0) as described in the Appendix and the results are shown in Table 9. The pH of the reaction mixture was found to be 10.65 at 0.001 mol dm^{-3} NaOH (Table 7). Phenyl salicylate (pK_a 9.25) would be completely ionized in aqueous solution pH 10.65. It is therefore apparent that, at 0.001 mol dm^{-3} NaOH, all of the PSH molecules will have entered into the micelles and occupied the specific micellar region where [NaOH] is seemingly zero. If we assume that at 0.001 mol dm^{-3} NaOH, the concentration of the micellized ^-OH ions is zero, the apparent binding constant, K_S^{app}, would be *ca.* 21 dm^3 mol^{-1}. This is however, an underestimated value of K_S^{app} because we do not have any evidence to support that at 0.001 mol dm^{-3} NaOH, the micellar incorporation of ^-OH ions at 0.2 mol dm^{-3} SDS does not occur at all.

From Figure 3 it can be seen that equation (13) is valid for the

$$k_n = \frac{k_W^n}{1 + K_S^{app}[D_n]} \qquad (13)$$

hydrazinolysis of phenyl salicylate under varying $[D_n]$ at 0.05 and 7.5 × 10^{-3} mol dm^{-3} NaOH. Equation (13) may be also considered to be applicable for hydrazinolysis of phenyl salicylate within the [NaOH] range 0.001–0.040 mol dm^{-3} at 0.2 mol dm^{-3} SDS and 0.08 mol dm^{-3} NH_2NH_2. Rearrangement of equation (13) produces equation (14) where $[NH_2NH_2]$ =

$$K_S^{app} = \frac{k_W^n[NH_2NH_2] - k_{obs}}{k_{obs}[D_n]} \qquad (14)$$

0.08 mol dm^{-3} and $k_{obs} = k_n [NH_2NH_2]$. The hydrazine-independent first-order rate constants (k_o) were neglected compared with $k_n [NH_2NH_2]$ at 0.08 mol dm^{-3} NH_2NH_2 which seemed to be reasonable for the reason that the contributions due to k_o term to k_{obs} were *ca.* 8 and 5% at 0.05 and 7.5 × 10^{-3} mol dm^{-3} NaOH, respectively, under similar experimental conditions (Tables 5 and 6). The values of k_{obs} (Table 7) at different [NaOH] were used to calculate K_S^{app} from

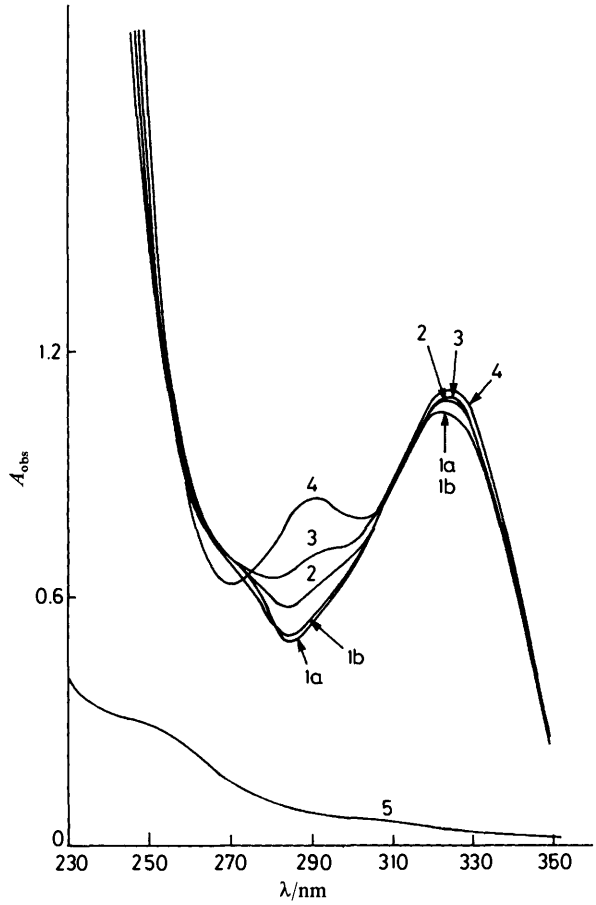


Figure 4. Representative spectral scans of the products of hydrazinolysis of phenyl salicylate at different [NaOH] in the presence of 0.2 mol dm^{-3} SDS. *Conditions:* $[Phenyl\ salicylate]_0$ = 2 × 10^{-4}, MeCN = 1% $[NH_2NH_2]$ = 0.08 and [NaOH] = 0.001 mol dm^{-3} for (**1a**) (t = 180 min) and (**1b**) (t = 105 min); [NaOH] = 0.002 for 2 (t = 92 min), [NaOH] = 0.003 for 3 (t = 78 min), and [NaOH] = 0.010 mol dm^{-3} for 4 (t = 26 min) where t represents the time at which the spectra were scanned from the start of the reaction. Spectrum 5 was obtained for the solution containing 0.001 and 0.2 mol dm^{-3} NaOH and SDS, respectively.

equation (14) with k_W^n = 0.111 dm^3 mol^{-1} s^{-1}. These results as summarized in Table 9 reveal an increase in K_S^{app} with decreased [NaOH] which is in accordance with equation (9). The value of K_S^{app} turned out to be independent of [NaOH] at ⩾ 0.02 mol dm^{-3} NaOH which indicates that under these conditions, K_S^{app} = K_1. The limiting value of K_S^{app} of 4.8 dm^3 mol^{-1} may be compared with that of K_1 (=5.9 dm^3 mol^{-1}) obtained in the absence of NH_2NH_2 at 0.06 mol dm^{-3} NaOH.

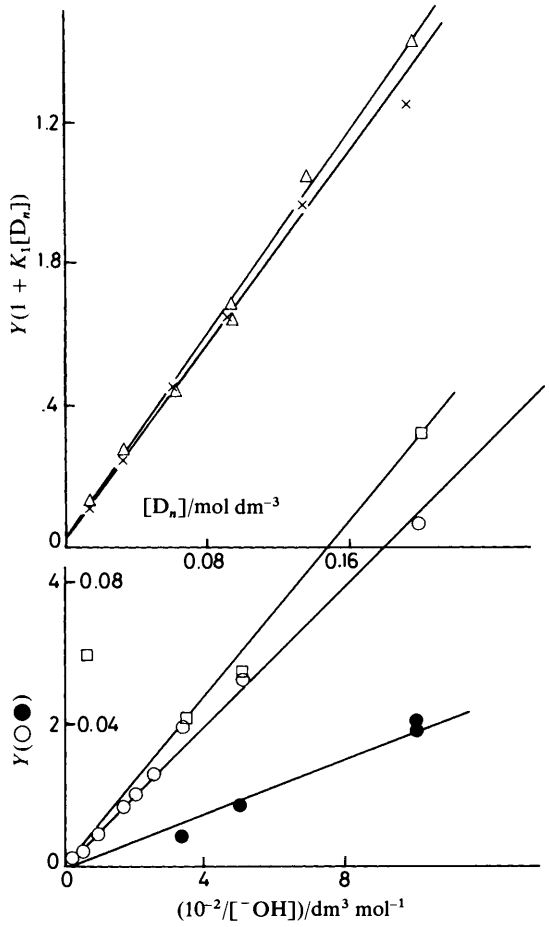


Figure 5. Plots showing the mole ratio (Y) of non-ionized and ionized phenyl salicylate, *N*-hydrazinylsalicylamide and phenol *versus* $1/[^-OH]$ in the presence of 0.2 mol dm^{-3} SDS and 0.08 mol dm^{-3} NH_2NH_2. Phenyl salicylate (○), *N*-hydrazinylsalicylamide (□) and phenol (●). Plots of $Y(1 + K_1[D_n])$ *versus* $[D_n]$ for phenyl salicylate at a constant [NaOH] of 7.5×10^{-3} mol dm^{-3} and in the absence of NH_2NH_2 (△) as well as in the presence of NH_2NH_2 (×).

The UV spectra of the products of hydrazinolysis of phenyl salicylate carried out at 0.001, 0.002, 0.003, and 0.01 mol dm^{-3} NaOH in the presence of 0.2 mol dm^{-3} SDS are shown in Figure 4. The spectrum at 0.01 mol dm^{-3} NaOH is similar to that obtained in the absence of SDS under similar experimental conditions (Figure 1). But the spectra at 0.001–0.010 mol dm^{-3} NaOH are distinctly different from each other at wavelength (λ) < 310 nm. These spectral changes may be easily explained in terms of different sites occupied by the products, phenol and *N*-hydrazinylsalicylamide, in the micellar pseudophase. The molar extinction coefficients of both non-ionized and ionized phenol are zero at $\lambda \geqslant 310$ nm (Table 1). Thus, the spectra (Figure 4) at $\lambda \geqslant 310$ nm are only due to the presence of ionized and non-ionized *N*-hydrazinylsalicylamide. However, at 290 nm, the molar extinction coefficients of non-ionized and ionized phenol are zero and 2 350 dm^3 mol^{-1}, respectively. Therefore, the increase in absorbance at 290 nm (Figure 4) with increase in [NaOH] is the consequence of the increased fraction of the product phenolate ion. As described in the Appendix, the observed absorbance values of the product mixtures at 350, 330, and 290 nm and that of the reactant (phenyl salicylate) at 350 nm were used to calculate the fraction of ionized *N*-hydrazinylsalicylamide, phenol, and phenyl salicylate at different [NaOH]. These results are shown in Table 9.

It is interesting to note that the fraction of ionized *N*-hydrazinylsalicylamide, phenol, and phenyl salicylate are 0.86, 0.31, and 0.19, respectively at 0.001 mol dm^{-3} NaOH (Table 9). These results cannot be attributed to the difference in pK_a of these species since the aqueous pK_a of phenyl salicylate is presumably smaller than that of *N*-hydrazinylsalicylamide [$\sigma_I(OPh) > \sigma_I(NH_2NH_2)$ and $\sigma_R^\circ(OPh) > \sigma_R^\circ(NH_2)$ or $\sigma_R^\circ(NMe_2)$].[41] The pK_a of phenyl salicylate is 0.36 pK units smaller than that of methyl salicylate[15] which is consistent with $\sigma_I(OPh) > \sigma_I(OMe)$ and $\sigma_R^\circ(OPh) > \sigma_R^\circ(OMe)$.[41] *N*-Hydrazinylsalicylamide is apparently less hydrophobic than phenyl salicylate and hence the former is expected to exist in a relatively more hydrophilic region of the micellar pseudophase. We propose that micellar bound *N*-hydrazinylsalicylamide molecules exist in the exterior surface of micelle where the water activity and polarity of the medium are not very different from that of the aqueous pseudophase. Recently, we have shown that the micelle-bound ionized methyl salicylate molecules exist in the extreme outer surface of the SDS micellar pseudophase where rate of its hydrolysis could not be affected by the presence of SDS.

Although the aqueous pK_a of phenol (10)[42] is larger than that of phenyl salicylate (9.25), the larger values of the fraction of ionized phenol than those of phenyl salicylate, under identical experimental conditions, demonstrate the presence of micelle-bound phenol in a relatively more hydrophilic micellar region. This is conceivable in terms of the hydrophobicity of phenol and phenyl salicylate. These observations indicate that the hydrophobicity of the species involved in the reaction varies in the order, phenyl salicylate > phenol ⩾ *N*-hydrazinylsalicylamide. The difference in the hydrophobic requirements of phenol and *N*-hydrazinylsalicylamide cannot be ascertained readily from these observations because of the difference in pK_a of phenol and *N*-hydrazinylsalicylamide. However, these observations also seem to be consistent with the notion that the reacting species occupy the same micellar region and the different values of the fractions of ionized phenyl salicylate, phenol, and *N*-hydrazinylsalicylamide may be attributed to the difference in the values of K_S^{app} of these species. If this is correct then K_S^{app} (phenyl salicylate) > K_S^{app} (phenol) > K_S^{app} (*N*-hydrazinylsalicylamide). But we are reluctant to favour this alternative explanation for the observed data due to the reasons described elsewhere.[17]

The mole ratio (Y) of non-ionized and ionized phenyl salicylate may be given as equations (15) or (16) where K_1 = $[PS_W^-]/[PS_W^-][D_n]$, $K_2 = [PSH_M]/[PSH_W][D_n]$, $K_w^W = [^-OH_W][H_W^+]$, $K_a^W = [PS_W^-][H_W^+]/[PSH_W]$ and $[^-OH_T] = [^-OH_M] + [^-OH_W]$. The value of Y at different $[^-OH]_T$ were calculated as described in the Appendix. Equation (16) reveals that a plot of Y *versus* $1/[^-OH]_T$ at a constant $[D_n]$ should be linear. Such a plot as shown in Figure 5 is essentially linear. This shows that the pseudophase model of the micelle which is the basis for the proposed reaction Schemes 1 and 2, is apparently correct for the present system. The linearity of the plot of Figure 5 also indicates the presence of $[PS_M^-]$ even at 0.001 mol dm^{-3} NaOH.

$$Y = \frac{[PSH_W] + [PSH_M]}{[PS_W^-] + [PS_M^-]} \quad (15)$$

$$Y = \frac{K_w^W(1 + K_2[D_n])(1 + K_{OH}[D_n])}{K_a^W(1 + K_1[D_n])[^-OH]_T} \quad (16)$$

The values of Y at 0.001, 0.002, and 0.003 mol dm^{-3} NaOH were also calculated for products, phenol and *N*-hydrazinylsalicylamide, at 0.2 mol dm^{-3} SDS (Appendix). Although three-data-point linear plots are not very reliable, these Y values show a linear dependence with $1/[^-OH_T]$ as shown in Figure 5.

As described in the Appendix, the values of Y were

determined at different $[D_n]$ from the observed values of A_{obs}^{350} ($t = 0$) obtained in the absence and presence of hydrazine at 7.5×10^{-3} mol dm^{-3} NaOH (Tables 3 and 5). Equation (16) indicates that, at a constant $[^-OH]_T$ and provided $1 \gg K_{OH}[D_n]$, the plot of $Y(1 + K_1[D_n])$ *versus* $[D_n]$ should be linear with slope and intercept of $K_2K_w^W/K_a^W[^-OH]_T$ and $K_w^W/K_a^W[^-OH]_T$, respectively. Such plots as shown in Figure 5 (using $K_1 = 5.9$ dm^3 mol^{-1}) are linear. The least-squares-calculated values of $K_2K_w^W/K_a^W[^-OH]_T$ and $K_w^W/K_a^W[^-OH]_T$ are $(2.1 \pm 3.2) \times 10^{-2}$ and 7.3 ± 0.3 dm^3 mol^{-1} in the absence of NH_2NH_2 and $(1.7 \pm 1.7) \times 10^{-2}$ and 7.0 ± 0.2 dm^3 mol^{-1} in the presence of NH_2NH_2, respectively. The considerably large standard deviations ($\geqslant 100\%$) associated with the values of the intercepts indicate that the contribution due to $K_w^W/K_a^W[^-OH]_T$ is negligible compared with $K_2K_w^W/K_a^W[^-OH]_T$ toward $Y(1 + K_1[D_n])$. The calculated value of $K_w^W/K_a^W[^-OH]_T$, at 7.5×10^{-3} mol dm^{-3} NaOH, is 3.4×10^{-3} which is *ca.* 32 times smaller than the lowest observed value of $Y(1 + K_1[D_n])$. The calculated values of $K_2K_w^W/K_a^W[^-OH]_T$ were used to calculate K_2 as 2.15×10^3 dm^3 mol^{-1} in the absence and 2.06×10^3 dm^3 mol^{-1} in the presence of NH_2NH_2 using $K_w^W = 1.449 \times 10^{-14}$ mol^2 dm^{-6},[43] $K_a^W = 5.67 \times 10^{-10}$ mol dm^{-3} and $[^-OH]_T = 7.5 \times 10^{-3}$ mol dm^{-3}. The nearly 350-fold larger value of K_2, compared with K_1 may be attributed largely to electrostatic requirement of the binding.

Appendix

(*a*) *Calculation of the Fractions of Ionized Phenyl Salicylate* (*PS*$^-$), N-*Hydrazinylsalicylamide* (*HDS*$^-$), *and Phenol* (*PhO*$^-$) *in the Presence of SDS.*

The observed absorbance at 350 nm at $t = 0$ $[A_{obs}^{350}(t = 0)]$ is the sum of absorptions due to non-ionized phenyl salicylate (PSH) and PS$^-$. The molar extinction coefficient of PSH at 350 nm is zero (Table 1) and hence

$$A_{obs}^{350}(t = 0) = \varepsilon_{350}^{PS^-}[PS^-]_0 \quad \text{(i)}$$

where $\varepsilon_{350}^{PS^-}$ is the molar extinction coefficient of PS$^-$ at 350 nm and $[PS^-]_0$ is the molar concentration of PS$^-$ at $t = 0$. The observed values of A_{obs}^{350} ($t = 0$) at 0.2 mol dm^{-3} SDS and at different [NaOH] are shown in Table 9. These values were used to calculate the fractions of $[PS^-]_0$, F^{PS^-} ($[PS^-]_0/[X]_0$ where $[X]_0$ is the initial concentration phenyl salicylate) using equation (ii). These results are shown in Table 9.

$$F^{PS^-} = A_{obs}^{350}(t = 0)/\varepsilon_{350}^{PS^-}[X]_0 \quad \text{(ii)}$$

The observed absorbance at $t = \infty$ (*i.e.* the time, $t \geqslant 9$ half-lives of the reaction, $A_{obs}(t = \infty)$, may be given as equation (iii)

$$A_{obs}(t = \infty) = \varepsilon^{HDS^-}[HDS^-] + \varepsilon^{HDSH}[HDSH] + \varepsilon^{PhO^-}[PhO^-] + \varepsilon^{PhOH}[PhOH] \quad \text{(iii)}$$

where HDSH and PhOH represent non-ionized *N*-hydrazinyl-salicylamide and phenol, respectively. The molar extinction coefficients of HDSH (ε^{HDSH}), PhOH (ε^{PHOH}) and PhO$^-$ (ε^{PhO^-}) are equal to zero at 350 nm (Table 1) and therefore, at 350 nm, equation (iii) is reduced to equation (iv) where $F_{350}^{HDS^-} =$

$$F_{350}^{HDS^-} = A_{obs}^{350}(t = \infty)/\varepsilon_{350}^{HDS^-}[X]_0 \quad \text{(iv)}$$

$[HDS^-]_\infty/[X]_0$. The values of $\varepsilon_{350}^{HDS^-}$ (Table 1) and A_{obs}^{350} ($t = \infty$) (Table 9) were used to calculate $F_{350}^{HDS^-}$ from equation (iv). These results are shown in Table 9.

It is evident from Table 1 that $\varepsilon_{330}^{PhO^-} = \varepsilon_{330}^{PhOH} = 0$ and hence, at 330 nm, equation (iii) is reduced to equation (v). The values of

$$F_{330}^{HDS^-} = [A_{obs}^{330}(t = \infty) - \varepsilon_{330}^{HDSH}[X]_0]/(\varepsilon_{330}^{HDS^-} - \varepsilon_{330}^{HDSH})[X]_0 \quad \text{(v)}$$

A_{obs}^{330} ($t = \infty$) at different [NaOH] were obtained from the spectra of the products as shown in Figure 4 and are listed in Table 9. The values of $F_{330}^{HDS^-}$ were calculated from equation (v) using known values of ε_{330}^{HDSH} and $\varepsilon_{330}^{HDS^-}$ (Table 1). These results are also shown in Table 9.

The values of A_{obs}^{290} ($t = \infty$) at 0.2 mol dm^{-3} SDS and different [NaOH] were obtained from the spectra of the products of Figure 4 and are summarized in Table 9. The value of ε_{290}^{PhOH} is zero (Table 1) and hence the fraction of PhO$^-$, F^{PhO^-}, was calculated from equation (vi). The average values of $F_{350}^{HDS^-}$,

$$F^{PhO^-} = \{A_{obs}^{290}(t = \infty) - [\varepsilon_{290}^{HDS^-}F^{HDS^-} + (1 - F^{HDS^-})\varepsilon_{290}^{HDSD})][X]_0\}/\varepsilon_{290}^{PhO^-}[X]_0 \quad \text{(vi)}$$

$F_{330}^{HDS^-}$ and F_{350}^{HDSH}, F_{330}^{HDSH} were used to calculate F^{PhO^-} from equation (vi). These results are shown in Table 9.

(*b*) *Calculation of the Mole Ratio of Non-ionized and Ionized Phenyl Salicylate.*—In the presence of SDS micelles, the mole ratio (Y) of PSH and PS$^-$ may be defined as equation (vii).

$$Y = \frac{[PSH_M] + [PSH_W]}{[PS_M^-] + [PS_W^-]} \quad \text{(vii)}$$

Equation (i) may be rewritten as equation (viii). Equation (ix)

$$A_{obs}^{350}(t = 0) = \varepsilon_{350}^{PS^-}([PS_M^-]_0 + [PS_W^-]_0) \quad \text{(viii)}$$

can be easily derived from equations (vii) and (viii). The values of Y at different [NaOH] were calculated from equation (ix)

$$Y = \frac{\varepsilon_{350}^{PS^-}[X]_0 - A_{obs}^{350}(t = 0)}{A_{obs}^{350}(t = 0)} \quad \text{(ix)}$$

using the values of $A_{obs}^{350}(t = 0)$ as listed in Table 9. These results are summarized in Table 9. The values of Y were also determined at different $[SDS]_T$ using $A_{obs}^{350}(t = 0)$ obtained in the absence and presence of hydrazine at 7.5×10^{-3} mol dm^{-3} NaOH. These results are shown in Tables 3 and 5.

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