Kinetic and equilibrium studies of anilinoalkanesulfonate formation†

Michael R. Crampton,* Peter M. Lowry and Ian J. Smith

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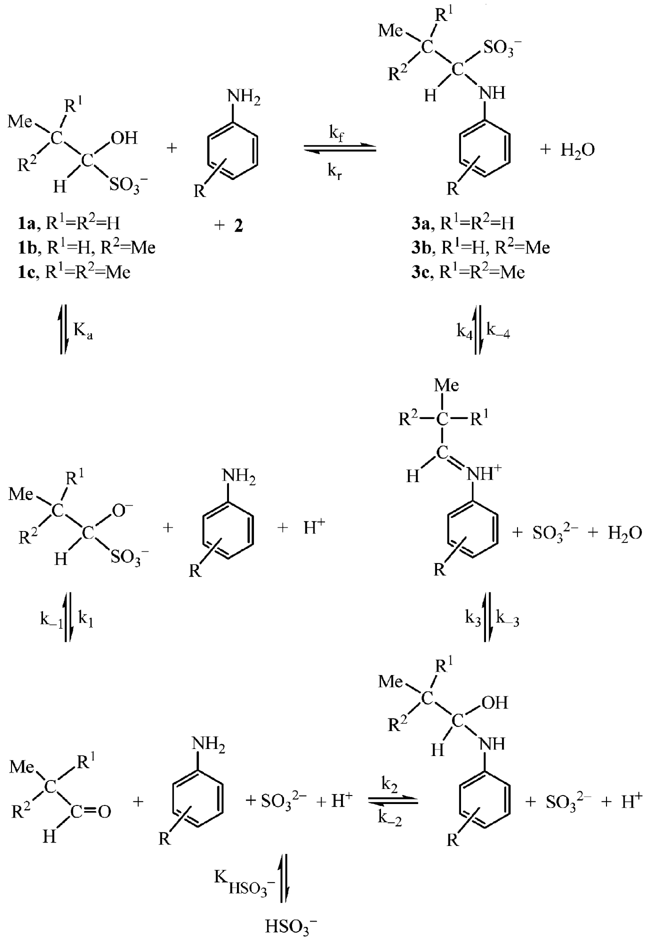
^{1}H NMR studies of the reactions of some hydroxyalkanesulfonates, **1**, with aniline derivatives, **2**, show the formation at equilibrium of anilinoalkanesulfonates, **3**. Kinetic studies in water are consistent with a mechanism involving dissociation of **1** to give the parent aldehyde, which reacts with **2** to give a carbinolamine. Acid-catalysed dehydration of the carbinolamine yields an iminium ion which reacts rapidly with sulfite to give the product **3**. Study of the variation with pH of the rate constants of the reaction indicates a change in the nature of the rate-determining step from carbinolamine formation to carbinolamine dehydration as the pH is increased. Variations in values of rate and equilibrium constants with the nature of **1** and **2** are discussed in terms of electronic and steric effects.

Introduction

The formation of aminoalkanesulfonates either by reaction of amines with hydroxyalkanesulfonates or by reaction of the appropriate imine with bisulfite is well known.[1–3] One mechanistic proposal involved an S_N2 reaction between the amine and protonated hydroxyalkanesulfonate.[4,5] However there is strong evidence against this route,[6] and the accepted mechanism involves reaction with sulfite of the iminium ion formed from the amine and the free aldehyde, present at low concentration in equilibrium with the hydroxyalkanesulfonate.[7]

One reason for the current interest in these compounds is their use in the synthesis of azo-dyes for ink-jet printing.[8–10] A major problem with their use is that the reactions forming them may fail to go to completion or, once formed, the required products may partially revert to reactants. Hence to use these reactions efficiently, quantitative information regarding the kinetics and equilibria of their formation is essential. There is a brief report of the reaction of ammonia with hydroxymethanesulfonate[11] and a fuller study of the formation of anilinomethanesulfonate from aniline and hydroxymethanesulfonate.[7] The latter concluded that the rate-limiting step in the overall reaction is likely to be either carbinolamine formation from amine and aldehyde, or carbinolamine dehydration. However, since this study covered a narrow acidity range, pH 6–8, definite conclusions could not be drawn.

Here we report kinetic and equilibrium results for the reactions in water of hydroxypropanesulfonate, **1a**, with a series of ring-substituted anilines, **2**, to form the corresponding anilinopropanesulfonates, **3a**. Some data for reactions of 2-methylhydroxypropanesulfonate, **1b**, and 2,2-dimethylhydroxypropanesulfonate, **1c**, with aniline are included for comparison. The results are interpreted[7] in terms of Scheme 1. Values of the overall equilibrium constant, K, defined in eqn (1) were measured either using ^{1}H NMR spectroscopy or by combination of values of the rate constants k_f and k_r for the forward and reverse reactions (Scheme 1).



Scheme 1

$$K = \frac{[\mathbf{3}]}{[\mathbf{1}][\mathbf{2}]} = \frac{k_f}{k_r} \tag{1}$$

Measurements here were made over a much larger acidity range, pH 5–10, than previously.[7] The results clearly show that the rate-determining step changes from carbinolamine formation to carbinolamine dehydration as the pH is increased. This work also

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Chemistry Department, Durham University, Durham, DH1 3LE, UK

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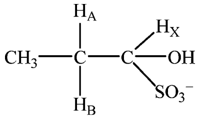
extends from one to four the number of hydroxyalkanesulfonates studied and examines in detail the effects of ring substituents in the anilines.

Results and discussion

^{1}H NMR measurements

The spectrum of **1a**, formed from equimolar propanal and sodium bisulfite in deuterium oxide, shows a doublet of doublets at δ 4.15 attributed to H_x, the α-hydrogen. Due to the chirality of the adjacent carbon atom the β-hydrogens, H_A and H_B give distinct resonances. Shifts and coupling constants are in Table 1. In the presence of aniline, new bands attributed to anilinopropanesulfonate, **3a**, are gradually formed, the change taking several hours. Shifts are given in Table 1, where the H_A, H_B and H_X correspond to that for **1a**. Changes in shift of the aromatic hydrogens of the aniline ring, the methyl hydrogens and of hydrogens labelled H_B were small. However, on reaction, significant changes in the values of shifts for H_X and H_A were observed, and integration after equilibrium had been reached allowed the calculation of a value for the equilibrium constant, *K*, of 70 ± 10 $dm^3\ mol^{-1}$. In a related fashion, new bands observed in the spectra of **1b** and **1c** in the presence of aniline are attributed to the formation of **3b** and **3c**. NMR data and equilibrium constants are in Table 1.



1a

Changes of shift in the spectrum of *N*-methylaniline in the presence of **1a** are relatively small. However, integration of bands due to the *N*-Me hydrogens, at δ 2.65 in the parent and δ 2.82 in the product, in solutions containing various known excesses of **1a** allowed the calculation of a value of 1.1 ± 0.1 $dm^3\ mol^{-1}$ for *K*.

Changes in the spectrum of **1a** in the presence of six ring-substituted anilines are consistent with the formation of the corresponding anilinopropanesulfonates. Values of shifts for H_X (the α-hydrogen) in **1a** and in the products **3a** are listed in Table 2. It should be noted that in all cases spectra recorded with stoichiometric concentrations of **1** and **2** in the range 0.02–0.10 mol dm^{-3} gave no evidence for the presence of species other than the reactants or products **3**. The thermodynamic stabilities of the hydroxyalkanesulfonates, **1**, are high[12,13] so that there was little dissociation to give aldehyde and bisulfite. For **1** in a large excess of **2**, no bands were observed from adducts formed by displacement of both the anilino hydrogens.

Table 2 Chemical shifts of H_X (the α-hydrogen) in **1a** and in adducts **3a** formed with ring-substituted anilines

	δ/ppm	$\Delta\delta^a$/ppm
1a	4.15	0
Ring substituent in **3a**		
H	4.31	+0.16
4-Me	4.19	+0.04
4-Cl	4.24	+0.09
3-Cl	4.28	+0.13
3-CN	4.30	+0.15
3-NO_2	4.34	+0.19
4-NO_2	4.46	+0.31

[a] $\Delta\delta$ = shift in **3a** − shift in **1a**.

Kinetic and equilibrium measurements

Aniline in water shows a strong UV absorbance band at 230 nm ($\varepsilon = 8 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$). In the presence of hydroxyalkanesulfonates, **1**, the absorbance maximum slowly moves to longer wavelength, 240 nm, with increased intensity. Related shifts in absorbance maximum were observed with ring-substituted anilines in the presence of **1**. Spectrophotometric measurements at an appropriate wavelength, usually 250 nm, were used for kinetic studies. With a concentration of **1** in a large excess over that of aniline (which was 1×10^{-4} mol dm^{-3}) a single first-order process was observed, designated k_{obs}. Measurements were made at 25 °C in solutions whose pH was controlled with dilute buffers (0.02–0.04 mol dm^{-3}). As will be shown, the analysis is simplified by working with slight excesses of free sulfite added either in the form of sodium sulfite or sodium bisulfite depending on the pH. The sum of these concentrations will be designated as [sulfite] as indicated in eqn (2).

$$[\text{sulfite}] = [SO_3^{2-}] + [HSO_3^-] \qquad (2)$$

Specimen results for reactions of 4-methylaniline and 3-chloroaniline at pH 8.0 are in Tables 3 and 4, and data for other ring-substituted anilines are provided as ESI in Tables S1–5†. Examination of Table 3 shows that at a constant concentration of **1a** values of k_{obs} depend inversely on the sulfite concentration. Hence values of the product k_{obs}[sulfite] are independent of the free sulfite concentration. Since the formation of **3** from **1** and **2** is an equilibrium process, k_{obs} may be expressed in terms of the overall

Table 1 ^{1}H NMR data[a] at 23 °C for hydroxyalkanesulfonates, **1**, and corresponding anilinoalkanesulfonates, **3**, in D_2O

	δ/ppm				J/Hz				
	H_X	H_A	H_B	Me	J_{AX}	J_{BX}	J_{AB}	$J_{AMe} = J_{BMe}$	$K^a/dm^3\ mol^{-1}$
1a	4.15	1.84	1.53	0.90	3.2	10	15	7.5	—
1b	4.09	2.06	—	0.91, 0.94	5.2	—	—	6.8	—
1c	4.03	—	—	0.97	—	—	—	—	—
3a	4.31	2.02	1.5	0.90	3.2	10	15	7.5	70 ± 10
3b	4.35	2.30	—	0.94, 0.96	4.4	—	—	7	62 ± 10
3c	4.25	—	—	1.03	—	—	—	—	34 ± 10

[a] Values of *K*, defined in eqn (1), determined from NMR integrals for systems at equilibrium. Specimen data in Table 8.

Table 3 Kinetic and equilibrium data for reaction of **1a** with 4-methylaniline[a] in water at 25 °C and pH 8.0

[**1a**]/10^{-3} mol dm^{-3}	[sulfite]/10^{-3} mol dm^{-3}	k_{obs}[b]/10^{-3} s^{-1}	k_{obs}[sulfite]/10^{-6} mol dm^{-3} s^{-1}	ΔAbs[c]	K[d]/dm^3 mol^{-1}
8.0	3.0	3.26	9.8	0.342	63
17	4.0	3.07	12.3	0.509	59
17	5.0	2.22	12.0	0.504	57
34	7.0	3.19	22.3	0.683	60
53	8.0	3.31	26.5	0.764	56
53	13	1.85	24.1	0.780	61
71	10	3.37	33.7	0.823	59
90	11	3.44	37.8	0.866	62
90	20	1.91	38.3	0.860	60

[a] Concentration is 1×10^{-4} mol dm^{-3}. [b] Measured at 255 nm. [c] Change in absorbance accompanying reaction. [d] Calculated as ΔAbs/(ΔAbs$_\infty$ − ΔAbs)[**1a**] with ΔAbs$_\infty$ = 1.02.

forward, k_f, and reverse, k_r, rate constants by eqn (3). Correspondingly, plots of k_{obs}[sulfite] *versus* [**1**] were linear, allowing the values (at a given pH) of k_f[sulfite] and k_r[sulfite] to be determined from the slopes and intercepts respectively. The results in Table 3 give values for the reaction of **1a** with 4-methylaniline at pH 8.0 of k_f[sulfite] 3.7×10^{-4} s^{-1} and k_r[sulfite] 6.4×10^{-6} mol dm^{-3} s^{-1}. Their combination gives a value for K (= k_f[sulfite]/k_r[sulfite]) of 58 dm^3 mol^{-1}. The value of K calculated independently using the absorbance changes accompanying reaction is 60 dm^3 mol^{-1}. Data for the corresponding reaction of 3-chloroaniline are in Table 4. Values obtained are k_f[sulfite] 8.0×10^{-5} s^{-1} and k_r[sulfite] 8.4×10^{-7} mol dm^{-3} s^{-1}, whose combination gives a value for K of 95 dm^3 mol^{-1}, in good agreement with the value of 97 dm^3 mol^{-1} from absorbance measurements.

$$k_{obs}[\text{sulfite}] = k_f[\text{sulfite}][\mathbf{1}] + k_r[\text{sulfite}] \qquad (3)$$

For reactions of **1a** with aniline and five ring-substituted anilines, and for reaction of **1b** with aniline, values of k_f[sulfite] and k_r[sulfite] were determined at several pH values in the range pH 5–10. Representative results for the reaction of **1a** with aniline are given in Table 5 and other results are given as ESI in Tables S6–11†. The results show that when pH ≥ 7, the rate coefficients show little dependence on acidity, while when pH < 7 values show moderate increases with increasing acidity. Nevertheless, values of K determined either from kinetic or absorbance measurements are independent of pH over the range examined. The latter observation is expected since there will be no change in the ionisation state of the reactants **1** and **2** or the product **3** in this pH range.

Reverse reaction

For the reaction of propanal with aniline and sulfite an alternative method was used to evaluate the term k_r[sulfite] relating to the reverse reaction. Thus ^{1}H NMR studies in CD$_3$CN showed that reaction of propanal (0.2 mol dm^{-3}) with equimolar aniline gave the imine **4** in high yield.

Table 4 Kinetic and equilibrium data for reaction of **1a** with 3-chloroaniline[a] in water at 25 °C and pH 8.0

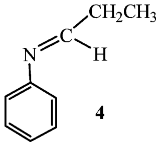
[**1a**]/10^{-3} mol dm^{-3}	[sulfite]/10^{-3} mol dm^{-3}	k_{obs}[b]/10^{-4} s^{-1}	k_{obs}[sulfite]/10^{-6} mol dm^{-3} s^{-1}	ΔAbs[c]	K[d]/dm^3 mol^{-1}
8.0	3.0	4.65	1.40	0.60	100
17	4.0	5.09	2.24	0.87	106
34	7.0	5.49	3.62	1.02	91
53	8.0	6.17	4.95	1.12	92
71	10	6.69	6.56	1.18	97
90	11	7.23	7.95	1.21	96

[a] Concentration is 1×10^{-4} mol dm^{-3}. [b] Measured at 250 nm. [c] Change in absorbance accompanying reaction. [d] Calculated as ΔAbs/(ΔAbs$_\infty$ − ΔAbs)[**1a**] with ΔAbs$_\infty$ = 1.35.

Table 5 Variation with pH of values of rate and equilibrium constants for reaction of **1a** with aniline

pH	k_f[sulfite]/10^{-4} s^{-1}	k_r[sulfite]/10^{-6} mol dm^{-3} s^{-1}	K[a](kinetic)/dm^3 mol^{-1}	K[b](Abs)/dm^3 mol^{-1}
5.2	14	18	77	60
5.9	3.7	4.7	78	52
7.0	1.85	2.2	84	76
7.6	1.40	2.2	64	76
8.0	1.90	2.3	84	71
9.1	0.74	1.0	74	68
10.0	0.88	1.2	73	70

[a] $K = k_f$[sulfite]/k_r[sulfite]. [b] Calculated from changes in absorbance accompanying reaction, as in Tables 3 and 4.



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Bands were observed at δ 7.90 (CH, t, J = 5 Hz), δ 7.03–7.36 (Ar), δ 1.81 (CH_2, m) and δ 1.19 (CH_3, t, J = 7.5 Hz). The reaction was repeated in acetonitrile and a small volume of the solution was mixed with a large excess of aqueous sulfite solution, so that the final stoichiometric concentration of imine was *ca.* 1×10^{-4} mol dm^{-3} with a ratio of [sulfite] : [imine] of greater than ten. UV studies indicated two processes on mixing the imine with sulfite; a fast reaction, too rapid for measurement, giving increased absorption at 250 nm and compatible with initial formation of the anilinopropanesulfonate **3a**, and a slow decomposition with decreasing absorbance at 250 nm. The final spectrum was consistent with the regeneration of aniline. Kinetic measurements showed a first-order process whose rate constant was measured in buffered solution with ionic strength 0.1 mol dm^{-3} using potassium chloride. It should be noted that here the final concentrations of aniline and of hydroxypropanesulfonate, **1a**, are *ca.* 1×10^{-4} mol dm^{-3}, so that in contrast with the earlier data, where concentrations of **1a** are much higher, the reaction flux in the forward direction is negligible compared to the flux in the reverse direction; hence $k_{obs} = k_r$. At each pH studied, values of k_{obs} were measured at six sulfite concentrations in the range 1×10^{-3} mol dm^{-3} to 2×10^{-2} mol dm^{-3}, and values were found to be inversely dependent on [sulfite], so that the term k_{obs}[sulfite] was constant. Values in the pH range 5.8 to 9.9 are shown in Fig. 1. Measurements of k_r[sulfite] showed that values were, within experimental error, independent of ionic strength in the range I = 0.05 to 0.20 mol dm^{-3}.

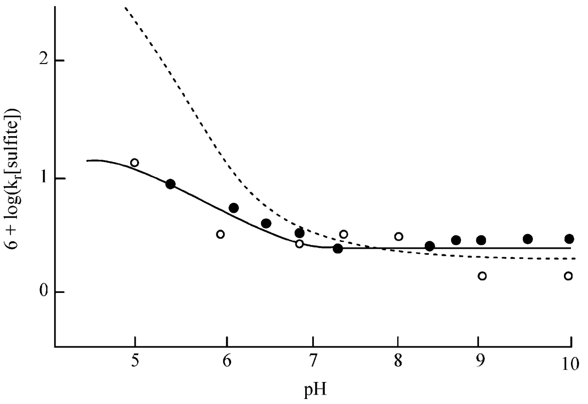


Fig. 1 Variation with pH of values of log(k_r[sulfite]) in the reaction of propanal with aniline and sulfite. Experimental points determined from the equilibration process are shown as ○, and from the reverse reaction as ●. The broken line is calculated from eqn (5) with $k_{-3}/K_4 = 1.6 \times 10^{-6}$ mol dm^{-3} s^{-1} and $K_{HSO_3^-} = 8 \times 10^{-8}$ mol dm^{-3}.

Rate-determining step

The forward reaction has a first-order dependence on the aniline concentration, showing that the k_1 step in Scheme 1, formation of free aldehyde from the hydroxyalkanesulfonate, **1**, is not rate-limiting. Similarly, the inverse dependence on sulfite concentration is not compatible with rate-limiting reaction of sulfite with iminium ions, the k_4 step. Hence carbinolamine formation, k_2, or dehydration, k_3, will be the slow step in the overall reaction. Jencks and co-workers have shown[14–17] that in general in the reactions of carbonyl compounds with amines, carbinolamine dehydration is rate-limiting in alkaline solutions (pH > 7). In the present case the assumption that k_3, the acid-catalysed dehydration of carbinolamine, is rate-limiting and that steps leading to the carbinolamine are at equilibrium, leads[7] to eqn (4). Here K_1 is the equilibrium constant for dissociation of the dianion of **1** to give aldehyde and sulfite, and K_2 is the equilibrium constant for formation of carbinolamine from aldehyde and aniline. Correspondingly, eqn (5) will apply to the reverse reaction.

$$k_f[\text{sulfite}] = k_3K_1K_2K_a\left(\frac{[H^+]+K_{HSO_3^-}}{K_{HSO_3^-}}\right) \tag{4}$$

$$k_r[\text{sulfite}] = \frac{k_{-3}}{K_4}\left(\frac{[H^+]+K_{HSO_3^-}}{K_{HSO_3^-}}\right) \tag{5}$$

In these eqns $K_{HSO_3^-}$ is the acid dissociation constant of hydrogen sulfite,[7,18,19] and its value, 8×10^{-8} mol dm^{-3}, indicates that both the forward and reverse reactions should show a change in dependence on acidity around pH = 7. When $K_{HSO_3^-} > [H^+]$, at higher pH, values should become independent of acidity, and when $[H^+] > K_{HSO_3^-}$, at lower pH, then the logarithms of values should increase linearly with increasing pH. The experimental results in Table 5 and Tables S6–11† show that values of both k_f[sulfite] and k_r[sulfite] do become approximately independent of acidity when pH > 7. Values for the reverse reaction, determined both from the equilibration process and from independent measurements are shown in Fig. 1, where they are compared with the acidity dependence predicted from eqn (5). This shows that while there is acceptable agreement with eqn (5) in alkaline solutions, when pH < 7 experimental values fall below those predicted. It should be noted that the assumption that dehydration of the carbinolamine occurs without acid catalysis predicts an inverse relation with acidity when pH > 7, which is not observed.

The other possibility is that formation of the carbinolamine, the k_2 step, is rate-limiting in the forward direction. At pH values above those where the parent anilines (**2**) are protonated, the k_2 step is not expected to show strong dependence on pH, although weak general acid catalysis is possible.[7,14,16] In the present work we have worked at low buffer concentrations where such effects should be small. The assumption that carbinolamine formation/decomposition is rate-limiting leads to eqns (6) and (7) for the forward and reverse reactions respectively.

$$k_f[\text{sulfite}] = k_2K_1K_a\frac{([H^+]+K_{HSO_3^-})}{[H^+]K_{HSO_3^-}} \tag{6}$$

$$k_r[\text{sulfite}] = \frac{k_{-2}}{K_3K_4}\frac{([H^+]+K_{HSO_3^-})}{[H^+]K_{HSO_3^-}} \tag{7}$$

These expressions predict that when pH > 7, values should show an inverse dependence on acidity, which is not observed experimentally. When pH < 7 values should become independent of acidity.

Table 6 Summary of rate and equilibrium constants for formation of anilinoalkanesulfonates at pH 8.0 and 25 °C in water

Aniline	Hydroxyalkane sulfonate					
R	R^1	R^2	pK_a[a]	k_f[sulfite]/10^{-4} s^{-1}	k_r[sulfite]/10^{-6} dm^3 mol^{-1} s^{-1}	K[b]/dm^3 mol^{-1}
H	H	H	4.60	1.9	2.3	80
4-Me	H	H	5.08	3.6	6.0	60
4-Cl	H	H	4.15	1.1	1.4	81
3-Cl	H	H	3.46	0.79	0.84	94
3-CN	H	H	2.75	0.24	0.21	115
$3\text{-}NO_2$	H	H	2.47	0.18	0.14	133
H	H	Me	4.60	2.0	3.3	60
H	Me	Me	4.60	—	—	34
NMe	H	H	4.85			1.1

[a] Values for anilinium ions, from ref. 20. [b] From data in Tables 1, 3–6 and S1–10.

Overall, our results (Fig. 1) are consistent with the idea that in alkaline solutions, where pH > 7, acid-catalysed carbinolamine dehydration is rate-limiting. As the solutions are made increasingly acidic, in the pH range 7 → 5, carbinolamine formation becomes rate-limiting.

Substituent effects

Values of rate and equilibrium constants measured at pH 8.0 are summarised in Table 6. Hammett plots, *versus* σ^-, show good correlations, with ρ values of -1.47 for the forward reaction and -1.81 for the reverse reaction. At this pH, acid-catalysed carbinolamine dehydration will be rate-limiting and eqn (4) reduces to eqn (8).

$$k_f[\text{sulfite}] = \mathrm{k_3K_1K_2K_a} \tag{8}$$

For the reactions involving hydroxypropanesulfonate, **1a**, values of K_1 and K_a will be invariant. Hence it is values of k_3 and K_2 which may be affected by ring substitution. K_2 is the equilibrium constant for carbinolamine formation, and the data for the corresponding reaction involving formaldehyde[7] show no variation, within experimental error, with ring substitution. Hence it is likely that in the present system the ρ value reflects changes in value of k_3. This step, as shown in Scheme 2, is likely to involve transfer of positive charge in the transition state towards the aniline ring. Hence a negative value of ρ is expected. The value obtained, -1.47, can be compared with a value of $\rho = -2.8$ for protonation of the parent anilines.

For the reverse reaction at this pH the rate-determining step will be hydration of the iminium ion. Eqn (5) reduces to eqn (9) and the observed ρ value will depend on both the k_{-3} step and the K_4 equilibrium, as shown in eqn (10).

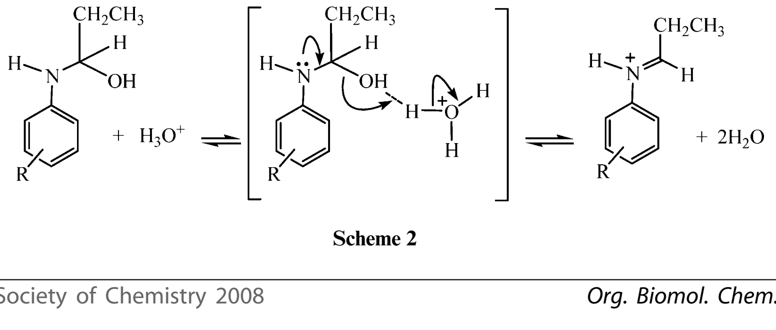
$$k_r[\text{sulfite}] = \frac{k_{-3}}{k_4} \tag{9}$$

$$\rho(\text{observed}) = \rho(k_{-3}\ \text{step}) - \rho(K_4\ \text{process}) \tag{10}$$

The values of ρ for each of those processes will be positive since they both involve reduction of positive charge on the iminium ion. However, that for the equilibrium process is expected to be larger since it involves full neutralisation of charge. Hence overall ρ has a negative value.

The results in Table 6 show that values of K, the overall equilibrium constant for formation of anilinoalkanesulfonates, **3**, from hydroxyalkanesulfonates, **1**, and anilines, **2**, show only small variation. Both electronic and steric factors may be important. In the reactions of hydroxypropanesulfonates, **1a**, with substituted anilines, **2**, the substituent R is remote from the reaction centre so that only electronic factors are involved. Here the values of K change by only a factor of *ca.* 2 as the substituent is changed from 4-Me to $3\text{-}NO_2$, indicating that the electronic effect of the $CHEt(SO_3^-)$ group is rather similar to hydrogen. Interestingly, the value of K for reaction of **1a** with *N*-methylaniline is considerably reduced, even allowing for the statistical factor of two relative to aniline. This is probably a consequence of increased steric repulsion with the ethyl and sulfite groups as the substituent on nitrogen is changed from H to Me.

Increasing methyl substitution in the hydroxyalkanesulfonate from **1a** ($R^1 = R^2 = H$) to **1b** ($R^1 = H, R^2 = Me$) and **1c** ($R^1 = R^2 = Me$) results in small decreases in the value of K. Here both steric effects in the reactants, **1**, and products, **3**, must be considered, and the small decreases observed are likely to indicate that the anilinoalkanesulfonates, **3**, are rather more sterically demanding than the hydroxyalkanesulfonates, **1**. Further evidence that this is the case comes from the knowledge[7] that for the reaction of hydroxymethanesulfonate (formed from formaldehyde) with



Scheme 2

aniline the value of K is 780 dm^3 mol^{-1}, which is a factor of ten larger than for the corresponding reaction of **1a**.

Carbinolamine formation

Our results indicate that as the acidity of the solutions increases the rate-limiting step changes from the dehydration of carbinolamine to its formation. This change is likely to have occurred by pH 5, so that the forward rate term may be expressed as eqn (11).

$$k_f[\text{sulfite}] = \frac{k_2 K_1 K_a}{K_{HSO_3^-}} \tag{11}$$

Values obtained at this pH for reaction with a series of substituted anilines are given in Table 7. Values of K_a, the acid dissociation constant of **1a**, and K_1, the equilibrium constant for dissociation of the dianion into propanol and sulfite, are available,[12,13] allowing values of k_2 to be calculated. The values in Table 8 show a dependence on substituent, $\rho = -1.6$, similar to that shown in the reactions of anilines with formaldehyde, where $\rho = -1.8$. However, values for the formaldehyde reaction are *ca.* 250 times greater than those for reactions involving propanal, consistent with the greater electrophilicity expected for formaldehyde.[7,21,22]

Conclusion

^{1}H NMR studies show that reactions of hydroxyalkanesulfonates **1** derived from propanal, isobutyraldehyde(2-methylpropanal) and trimethylacetaldehyde (2,2-dimethylpropanal) with substituted anilines, **2**, proceed smoothly to equilibrium to yield the corresponding anilinoalkanesulfonates. There is no evidence for the formation of species with anything other than 1 : 1 overall stoichiometry. Kinetic studies in water with **1** in large excess over **2** give a single first-order process, and the results are consistent with the mechanism of Scheme 1. Variation of rate constants with pH indicate that in alkaline solution, pH > 7, the rate-determining step is acid-catalysed dehydration of the carbinolamine followed by rapid reaction with the sulfite of the iminium ion formed in this process. In more acidic solutions the results show that carbinolamine formation becomes rate-limiting. Values of the overall equilibrium constant show relatively little variation with the nature of the ring substituent in the aniline or with the degree of methyl substitution at the β-carbon atom of the parent aldehydes. The results also allow determination of the values of rate constants for carbinolamine formation from the aldehydes and anilines. The results presented will be of interest in industrial processes which use the anilinoalkanesulfonates as intermediates.

Table 7 Values of k_2 calculated from the forward reaction of **1a** at pH 5.0 and 25 °C

Aniline		
R	k_f[sulfite]/10^{-4} s^{-1}	$k_2{}^a$/dm^3 mol^{-1} s^{-1}
4-Me	20	760
H	14	530
4-Cl	5.0	190
3-Cl	3.0	110
3-CN	1.3	50
3-NO$_2$	1.0	38

[a] Calculated from eqn (11) with K_a 2.0×10^{-11} mol dm^{-3}, K_1 0.0105 mol dm^{-3} and $K_{HSO_3^-}$ 8.0×10^{-8} mol dm^{-3}.

Table 8 Specimen calculation of K for reaction of **1b** with **2**, R = H

[**1b**]$_{stoich}$/dm^3 mol^{-1}	[**2**]$_{stoich}$/dm^3 mol^{-1}	[**3b**]$_{eq}$/dm^3 mol^{-1}	K^a/dm^3 mol^{-1}
0.063	0.070	0.041	64
0.054	0.090	0.041	64
0.071	0.053	0.036	60

[a] Calculated as

$$K = \frac{[\mathbf{3b}]_{eq}}{([\mathbf{1b}]_{stoich} - [\mathbf{3b}]_{eq})([\mathbf{2}]_{stoich} - [\mathbf{3b}]_{eq})}$$

using integrals for peaks due to [**1b**] and [**3b**] at equilibrium.

Experimental

Aniline, its substituted derivatives, and aldehydes were the purest available commercially. Solutions of sodium sulfite and sodium hydrogen sulfite were prepared in high purity water and concentrations checked by iodine titration.

^{1}H NMR spectra were measured at 23 ± 1 °C in D$_2$O using a Bruker Avance 400 MHz spectrometer with a 30 degree pulse, 4 second acquisition and 1 second recycle delay, or with a Varian Inova 500 MHz instrument with a 45 degree pulse and 4 second acquisition time. Conditions were chosen to avoid saturation, confirmed by the correspondence of spectra measured on different instruments. Some early measurements were made with a Varian Mercury 200 MHz instrument. Spectra of solutions containing equimolar solutions of aldehydes and sodium hydrogen sulfite confirmed the near-quantitative formation of hydroxyalkanesulfonates, **1**. Changes in spectrum in the presence of aniline and its derivatives showed the formation at equilibrium of anilinoalkanesulfonates, **3**. Values for equilibrium constants, defined in eqn (1), were determined from integrated peak intensities. A specimen calculation for reaction of **1b** with **2**, R = H, is in Table 8.

UV spectra and kinetic measurements were made in water at 25 ± 0.2 °C using a Shimadzu UV-2102 PC spectrometer fitted with a Peltier temperature control, or with Perkin Elmer λ12 or λ2 instruments, for which the temperature was controlled by circulation of thermostatted water. The temperatures of actual reaction solutions were checked regularly. The pH of solutions was controlled using dilute buffers containing borax, phosphate, acetate or bicarbonate, and pH values of reaction solutions were checked using a Jenway 3020 pH meter. First-order rate constants were evaluated using standard methods and are precise to ±5%.

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