

## Kinetics of the Reversible Hydration of 1,3-Dichloroacetone Catalysed by Aerosol-OT-solubilized Acids and Bases in Carbon Tetrachloride

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The kinetics of the reversible hydration of 1,3-dichloroacetone catalysed by Aerosol-OT-solubilized perchloric acid,  $\text{DClO}_4$ , imidazole (Imz), and *N*-methylimidazole (MeImz) have been studied in carbon tetrachloride. Rate constants for acid-catalysed hydration are higher in the presence of the detergent than in acid-dioxan mixtures. The average rate enhancement is 15.6 for perchloric acid catalyst and 14.2 for  $\text{DClO}_4$ . Hydration equilibrium constants are also higher in the presence of Aerosol-OT than in water- or  $\text{D}_2\text{O}$ -dioxan mixtures. Compared with the Imz- and MeImz-catalysed reactions in aqueous dioxan, the surfactant increases the rate constants by factors of 209 and 144. The results are interpreted in terms of the properties of the Aerosol-OT-solubilized water, acids, and bases, as well as of the role played by the hydrophilic groups of the surfactant.

THE mutarotation of tetramethylglucose,<sup>1</sup> the decomposition of Meisenheimer complexes,<sup>2</sup> the aquation of chromium and cobalt complexes,<sup>3</sup> and the aminolysis and hydrolysis of esters<sup>4,5</sup> are examples of reactions catalysed by detergent aggregates in non-aqueous solvents. These aggregates, called reversed or inverted micelles, possess a polar interior or 'core' formed from the hydrophilic groups of the surfactant.<sup>6</sup> Reversed micelles can solubilize large amounts of water, as well as organic and inorganic substances. Solubilization studies show that many of the properties of the substrate are modified upon micellar solubilization,<sup>6-8</sup> this modification being one of the main factors responsible for the observed catalysis.<sup>6,7</sup>

We recently reported<sup>9</sup> a study of the reversible hydration of 1,3-dichloroacetone (DCA) in the presence of bis-2-ethylhexyl sodium sulphosuccinate (Aerosol-OT or AOT) in carbon tetrachloride. The choice of this ketone was due to the availability of rate and equilibrium constants for its hydration (including spontaneous and acid and/or base-catalysed reactions) in water- or  $\text{D}_2\text{O}$ -dioxan mixtures,<sup>10-12</sup> with which our results can be compared. Thus our previous data showed that compared with the reaction in water- or  $\text{D}_2\text{O}$ -dioxan, the surfactant increases both the hydration rates and equilibrium constants. We report here the results of a study of the perchloric acid-, imidazole-, and *N*-methylimidazole-catalysed hydration of DCA in the presence of AOT in the same solvent. The results of this study bear on the role played by the surfactant head-groups and the effects of micellar solubilization on acid-base catalysis.

### EXPERIMENTAL

Carbon tetrachloride (Merck; Uvasol; maximum water content 0.005%) was further dried by storing over type 4A molecular sieve. The latter was activated by heating at 300° for several hours and cooling *in vacuo* over  $\text{P}_2\text{O}_5$ , and was used immediately.<sup>13</sup> AOT (Aldrich; 96%) was purified from the organic and inorganic impurities by dissolving the surfactant (100 g) in anhydrous ethanol (300 ml) and filtering off any suspended solid. Water (200 ml) was then added and the solution was extracted, several times, with light petroleum (b.p. 30–60°). The aqueous ethanol was evaporated to yield pure detergent (80 g). DCA was purified by two vacuum distillations, and its molar absorp-

tivity of  $41.1 \pm 0.1$  at 298 nm is in good agreement with the value reported elsewhere.<sup>11</sup> No hydrate or any other impurity was detected in the <sup>1</sup>H n.m.r. spectrum of a 0.6M solution of the ketone in carbon tetrachloride, immediately after preparation, or after several hours. Imz (Merck; analytical grade) was dried *in vacuo* over phosphorus pentoxide, and MeImz (Aldrich) was distilled from calcium hydride and stored over 4A molecular sieve. Perchloric acid stock solutions were prepared by diluting the AnalR reagent (Baker) with water or  $\text{D}_2\text{O}$ , and were titrated against standardized sodium hydroxide using Bromothymol Blue as indicator. Deuterium oxide (Stohler Isotope Chemicals; 100% D) and doubly distilled water were used throughout.

<sup>1</sup>H N.m.r. measurements were carried out as previously described.<sup>9</sup> The solvent was  $\text{C}_6\text{D}_6\text{-CCl}_4$  (30% v/v) and chemical shifts were measured relative to internal tetramethylsilane. They are accurate to  $\pm 0.1$  Hz.

The distribution coefficients of Imz, MeImz, and perchloric acid between carbon tetrachloride and water ( $\alpha$  = solute concentration in  $\text{CCl}_4$ /solute concentration in water) were determined as follows. Equal volumes of  $\text{CCl}_4$  and the aqueous solution (containing a known concentration of the acid or the diazole) were vigorously shaken for several hours. After complete phase separation at 25°, the solute concentration in the aqueous phase was determined by conductimetric titration using a standardized HCl or NaOH solution. The values of  $\alpha$  were 0.037, <0.01, and <0.0004 for MeImz, Imz, and perchloric acid, respectively. For DCA the value of  $\alpha$  has been found to be 0.49.<sup>9</sup>

Special care was taken to exclude moisture during all stock solution preparations and manipulation. The surfactant was dried at 65° *in vacuo* (ca. 0.1 Torr) over  $\text{P}_2\text{O}_5$  using an Abderhalden drying apparatus. A maximum weight loss of 3% was reached after 6 h of drying. The reagent stock solutions in carbon tetrachloride were: AOT 1.0M, DCA 0.6M, and MeImz 0.2M. Due to the limited solubility of Imz in the solvent, a solution of 0.2M-Imz in 0.1M-AOT was used. The surfactant solution was renewed daily, that of the ketone was renewed weekly.

Kinetic measurements were carried out spectrophotometrically using a Gilford model 240 spectrophotometer equipped with a thermostatted cell holder. The temperature was controlled inside the reaction cell to  $25 \pm 0.05^\circ$ . The kinetic experiments were carried out as previously described,<sup>9</sup> and the hydration was followed by measuring the absorption of the DCA carbonyl group at 316 nm. Good first-order kinetics were observed in all cases. The observed rate constants ( $k_{\text{obs}}$ ) were evaluated from the

absorbance-time data using a Burroughs model 6700 computer. The percentage relative standard deviations (*i.e.* the standard deviation  $\times 100/k_{\text{obs}}$ ) were  $<1.5\%$ . Rate constants for hydration  $k_h$ , dehydration  $k_d$ , and the equilibrium constant for hydration  $K_h$  can be calculated from the initial absorbance ( $A_0$ ) and that at equilibrium ( $A_e$ ) using equations (1)–(3).<sup>11</sup> All three 'constants' are a function

$$K_h = (A_0 - A_e)/A_e \quad (1)$$

$$k_h = k_{\text{obs}}(A_0 - A_e)/A_0 \quad (2)$$

$$k_d = k_{\text{obs}}(A_e/A_0) \quad (3)$$

of the water concentration, and  $k_h$  and  $k_d$  also depend upon the nature and concentration of added catalysts.

## RESULTS

**Catalysis by Perchloric Acid.**—The variation of  $k_{\text{obs}}$ , as a function of the stoichiometric concentration of solubilized  $\text{HClO}_4$  is shown in Figure 1. The plots consist of two intersecting lines with an abrupt increase in the slope at an acid concentration of *ca.* 0.004M. The ratios of the slopes at concentrations below and above the breaks are 0.06 and 0.03 for the perchloric acid- and the  $\text{DClO}_4$ -catalysed reactions, respectively.

In general, measurements were made at a fixed water concentration, increasing the acid concentration. The experiment was then repeated at several other water and  $\text{D}_2\text{O}$  concentrations. The catalytic constants for the

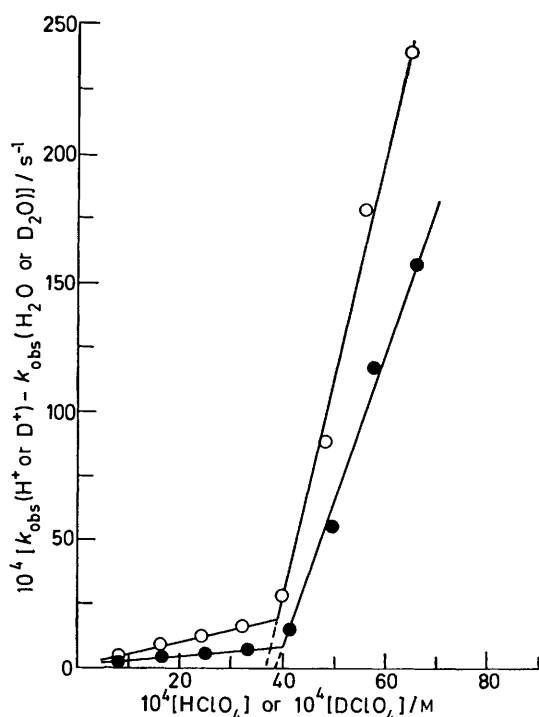


FIGURE 1 Observed rate constants for perchloric acid,  $\circ$ , and  $\text{DClO}_4$ ,  $\bullet$ , catalysis. The acid concentrations are stoichiometric

reaction in the presence of water ( $k_h^{\text{H}}$ ,  $k_d^{\text{H}}$ ) or  $\text{D}_2\text{O}$  ( $k_h^{\text{D}}$ ,  $k_d^{\text{D}}$ ) were determined from plots of the corresponding first-order rate constants *versus* the effective acid concentration in the water pool. These concentrations were calculated from the Henderson–Hasselbalch equation using indicator  $\text{p}K_a^{\text{app}}$

values determined in the presence of 0.4M-AOT in carbon tetrachloride.\* Since the reaction was not sensitive to increasing  $\text{HClO}_4$  or  $\text{DClO}_4$  concentrations below 0.004M, the  $x$ -intercepts of Figure 1 were subtracted from the acid concentrations. The linearity of the catalytic plots, using those 'effective' acid concentrations, is shown in Figure 2

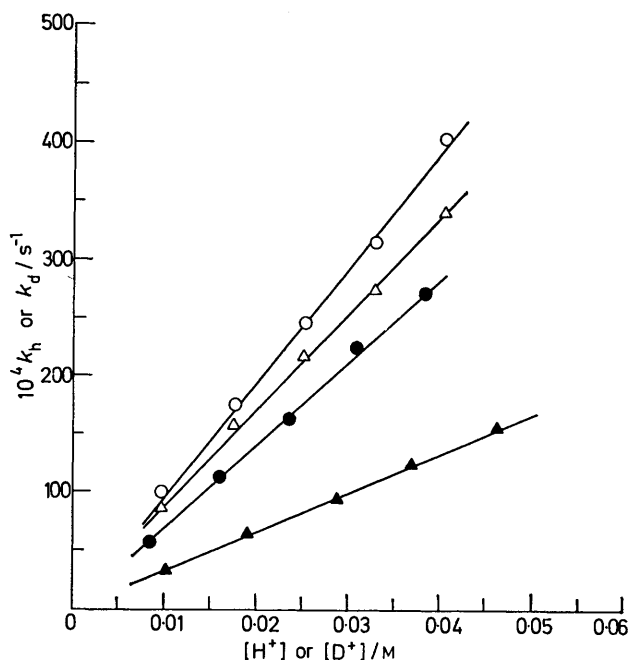


FIGURE 2 Catalytic plots using corrected acid concentrations showing  $\circ$ ,  $k_h^{\text{H}}$  (water 1.667M);  $\triangle$ ,  $k_d^{\text{D}}$  (water 1.667M);  $\bullet$ ,  $k_h^{\text{H}}$  ( $\text{D}_2\text{O}$  1.103M); and  $\blacktriangle$ ,  $k_d^{\text{D}}$  ( $\text{D}_2\text{O}$  2.757M)

and the values of the catalytic rate constants are given in Table 1. The rate constants decrease and the equilibrium constant  $K_h$  increases as a function of increasing water or  $\text{D}_2\text{O}$  concentration. The figures in parentheses refer to the ratios of the rate or equilibrium constants in the presence of the detergent (*i.e.*  $\text{HClO}_4$ : AOT or  $\text{DClO}_4$ : AOT) to those in  $\text{HClO}_4^-$  or  $\text{DClO}_4^-$ -dioxan. The latter constants were obtained from the data of Bell *et al.*<sup>11</sup>

Rate and equilibrium constants were always higher in the presence of AOT than in  $\text{HClO}_4^-$  or  $\text{DClO}_4^-$ -dioxan. The mean value of the ratio  $k_h^{\text{H}}$  (AOT) :  $k_h^{\text{H}}$  (dioxan) is 15.6, that of  $k_d^{\text{D}}$  (AOT) :  $k_d^{\text{D}}$  (dioxan) is 14.2. On the other hand, the ratios of the dehydration rate constants  $k_d^{\text{H}}$  (AOT) :  $k_d^{\text{H}}$  (dioxan) and  $k_d^{\text{D}}$  (AOT) :  $k_d^{\text{D}}$  (dioxan) increase as a function

\* The  $\text{p}K_a^{\text{app}}$  of Thymol Blue was determined spectrophotometrically at  $25^\circ$ , using the Henderson–Hasselbalch equation as follows. A Beer law plot of the acid form of the indicator in the presence of 0.4M-surfactant in  $\text{CCl}_4$  and solubilized perchloric acid (3.95M) was constructed using the indicator absorbance at 415 nm. This linear plot was then used to calculate the concentration of the acid form of Thymol Blue in the presence of AOT and dilute perchloric acid solutions or KCl–HCl buffers. The  $\text{p}K_a^{\text{app}}$  was determined from a graph of  $\log(\text{indicator ratio})$  *versus* pH of the acid or the buffer solutions by taking  $\text{p}K_a^{\text{app}} = \text{pH}$  at  $\log(\text{indicator ratio}) = 0$ . In this anionic micelle, these values are, not surprisingly, less than that in water and also depend on the water : AOT ratio. The  $\text{p}K_a^{\text{app}}$  values in the presence of 0.4M-AOT and 0.555, 1.111, 1.667, 2.222, and 2.778M solubilized water are 0.47, 0.82, 1.02, and 1.30. The partitioning of the indicator between carbon tetrachloride and water was largely in favour of the latter ( $\alpha < 0.003$ ). Details of this work will be given elsewhere.

TABLE I

Catalytic rate and equilibrium constants for acid-catalysed hydration of DCA in the presence of AOT in carbon tetrachloride at 25°<sup>a</sup>

HClO <sub>4</sub> -H <sub>2</sub> O-AOT				DCIO <sub>4</sub> -D <sub>2</sub> O-AOT			
[water]/M	10k <sub>h</sub> <sup>H</sup>	10k <sub>d</sub> <sup>H</sup>	K <sub>h</sub> <sup>H</sup>	[D <sub>2</sub> O]/M	10k <sub>h</sub> <sup>D</sup>	10k <sub>d</sub> <sup>D</sup>	K <sub>h</sub> <sup>D</sup>
0.555	12.95 (16.5)	17.57	0.737 (3.69)	0.551	9.64 (15.8)	13.33	0.723 (1.35)
1.111	10.50 (14.6)	11.00 (7.0)	0.954 (2.50)	1.103	8.03 (14.3)	7.31 (7.2)	1.098 (1.99)
1.667	9.73 (15.0)	8.15 (7.8)	1.194 (2.09)	1.654	6.88 (13.5)	5.22 (7.1)	1.318 (1.89)
2.222	9.15 (15.6)	6.99 (9.7)	1.309 (1.89)	2.206	6.34 (13.8)	4.18 (8.8)	1.517 (1.56)
2.778	8.57 (16.5)	5.69 (10.2)	1.506 (2.01)	2.757	5.62 (13.8)	3.50 (9.8)	1.606 (1.42)

<sup>a</sup> [AOT] 0.4M, all rate constants are in l mol<sup>-1</sup> s<sup>-1</sup>. The figures in parentheses refer to the ratios of the rate or equilibrium constants in the presence of AOT to those in acid-dioxan.

of increasing water or D<sub>2</sub>O concentration. Equilibrium constant ratios generally decrease upon addition of water.

The kinetic order with respect to water ( $n_h^H$ ,  $n_d^H$ ) and D<sub>2</sub>O ( $n_h^D$ ,  $n_d^D$ ) were obtained graphically, plots of log catalytic

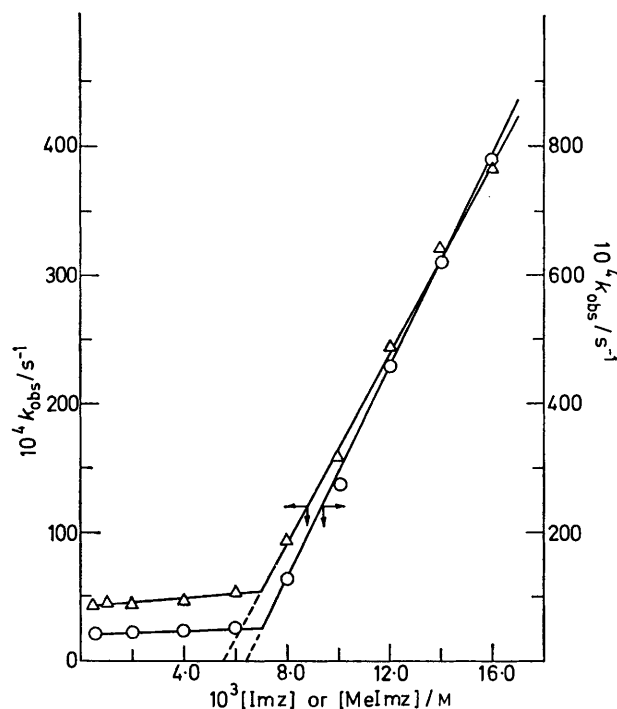


FIGURE 3 Observed rate constants as a function of Imz, O, and MeImz, Δ, in the presence of 0.4M-AOT and 1.389M solubilized water

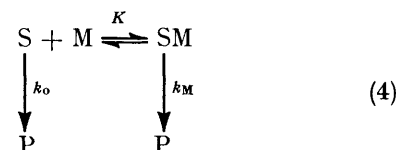
constant against log (water) or log (D<sub>2</sub>O) being effectively linear. The values are  $n_h^H$  -0.25,  $n_d^H$  -0.69,  $n_h^D$  -0.37, and  $n_d^D$  -0.83. All are negative, the dehydration reaction being more sensitive to addition of water.

*Diazole-catalysed Reactions.*—Figure 3 shows plots of  $k_{obs}$ .

versus [Imz] or [MeImz]. The rate constants increase very slowly up to a diazole concentration of 0.007M after which they increase much faster. The ratios of the slopes at concentrations below and above the breaks are 0.02 and 0.05 for the Imz- and MeImz-catalysed reaction, respectively. Catalytic rate constants ( $k_h^{Imz}$ ,  $k_d^{Imz}$ ,  $k_h^{MeImz}$ , and  $k_d^{MeImz}$ ) were obtained from graphs of the observed rate constants against the diazole concentration. The latter was obtained by subtracting the  $x$  intercepts of Figure 3 from the stoichiometric diazole concentration. Table 2 shows the first-order rate constants as a function of the catalyst concentrations. The second-order rate constants are  $k_h^{Imz}$  3.84,  $k_d^{Imz}$  4.36,  $k_h^{MeImz}$  1.94, and  $k_d^{MeImz}$  1.77 l mol<sup>-1</sup> s<sup>-1</sup>. At fixed imidazole and water concentrations, the rate constant decreases with increasing surfactant concentration, as shown in Table 2.

#### DISCUSSION

Micellar catalysis can be represented by equation (4),<sup>6</sup> where S, M, SM, and P represent substrate, micelle, substrate-micelle complex, and product respectively,  $k_o$  and  $k_M$  are rate constants for hydration in the bulk



solvent and in the micelle, and  $K$  is the substrate-micelle association constant. Any contribution from  $k_o$  to the observed rate constants can be ruled out as follows. In addition to the very low solubility of water in the organic solvent ( $3.5 \times 10^{-3}M$  at 24°)<sup>14</sup> all other reagents are more soluble in water than in CCl<sub>4</sub>, *i.e.* they are predominantly located in the micellar water pool. More importantly, in the absence of AOT hydration of DCA was negligible whether the solvent was pre-equilibrated with 0.2M-perchloric acid or 0.5M-diazole

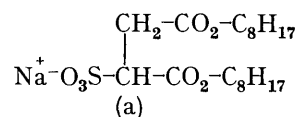
TABLE 2

Rate constants for imidazole- and N-methylimidazole-catalysed hydration of DCA in the presence of AOT reversed micelles in carbon tetrachloride at 25°

Effect of Imz concentration <sup>a</sup>			Effect of MeImz concentration <sup>a</sup>			Effect of AOT concentration	
10 <sup>4</sup> [Imz]/M	10 <sup>4</sup> k <sub>h</sub> /s <sup>-1</sup>	10 <sup>4</sup> k <sub>d</sub> /s <sup>-1</sup>	10 <sup>4</sup> [MeImz]/M	10 <sup>4</sup> k <sub>h</sub> /s <sup>-1</sup>	10 <sup>4</sup> k <sub>d</sub> /s <sup>-1</sup>	[AOT]/M	10 <sup>3</sup> k <sub>obs</sub> /s <sup>-1</sup>
16	62.8	66.9	25	47.5	46.4	0.15	116.1
36	129.0	144.8	45	82.2	75.8	0.20	99.3
56	216.0	240.0	65	125.3	117.8	0.25	71.6
76	298.2	323.4	85	166.9	153.4	0.30	51.3
96	362.0	414.2	105	198.9	184.6	0.35	36.3
						0.40	27.8

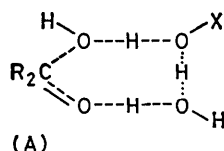
<sup>a</sup> In the presence of 0.4M-AOT and 1.398M solubilized water. In the presence of 0.0036M-Imz and 1.5M micellar water.

solution, *i.e.* the observed hydration is that taking place in the micellar water pool. The break in Figure 1 corresponds to a sudden increase in the activity of the hydronium ion at concentrations  $>0.004M$ . In the presence of  $2.778M$ -water this corresponds to less than one  $H_3O^+$  per micelle.\* Figure 1 is best understood in terms of the structure of the water in the micellar core. It has been shown that the added water first binds to the surfactant head-groups in a tight primary hydration shell followed, at higher water concentrations, by formation of a secondary shell of less strongly attached water.<sup>17,18</sup> At low concentrations, the acid is probably tightly bound to the surfactant sulphonate group.† A subsequent increase in the acid concentration may result in its inclusion in the loose hydration shells, leading to the observed rate enhancement. The effect of the addition of water on the strength of the  $H^+-SO_3^-$  ion-dipole interaction can be inferred from the chemical shifts of proton (a) of AOT. The sharp triplet of this proton shifts to lower fields upon addition of acid.



However, at a fixed acid concentration ( $0.0034M$ ), the magnitude of the shift is dependent upon the total  $D_2O$  concentration. Thus proton (a) shifts 2, 1.4, and 0.8 Hz in the presence of 0.551, 1.103, and 1.654M solubilized  $D_2O$ , respectively.‡ The direction of the shift indicates that the  $D^+$  ion binds to the  $SO_3^-$  group more strongly than the sodium ion. As a function of adding  $D_2O$ , the decrease in the magnitude of the chemical shift variation is consistent with decreased ion-dipole interactions due to an increase in their hydration.

A cyclic transition state of the type (A) where XOH



represents water, a weak acid catalyst or a hydronium ion, has been proposed by Bell and Critchlow for both the spontaneous and acid-catalysed hydration of DCA in water-dioxan.<sup>11</sup>§ Our previous results for DCA

\* The micellar concentration  $M$  is given by  $M = (C_D - \text{c.m.c.})/N$  where  $C_D$  is the total detergent concentration, c.m.c. its critical micelle concentration, and  $N$  is the aggregation number.<sup>6</sup> Values of c.m.c. and  $N$  in carbon tetrachloride are given in ref. 15. Light scattering studies in the presence of  $2.778M$ -water, in several solvents, showed that the value of  $N$  increases by a factor of 2.5.<sup>16</sup> At  $0.4M$ -AOT and  $2.778M$ -water, the micelle concentration is  $0.0076M$ .

† This implies that protons can displace some  $Na^+$  ions from the micellar interface. A similar exchange takes place in anionic micells in water.<sup>19</sup>

‡ On the other hand, simple head-group hydration results in decreased charge neutralization and a larger shift to higher fields.<sup>9</sup>  
§ Transition state (A) has been drawn with the protons symmetrically positioned between the two oxygen atoms, but this does not imply any particular degree of proton transfer.

hydration by AOT-solubilized water are also consistent with the above transition state.<sup>9</sup> Based on structure (A) one might expect that the  $n$  values for the acid catalysis would be *ca.* 2 and 1 for hydration and dehydration, respectively. Indeed, weakly acidic catalysts that are not strongly hydrated in the initial state gave values of  $n_h$  and  $n_d$  of this order.<sup>11</sup> On the other hand,  $HClO_4$ , a strongly hydrated catalyst, exhibited negative values of  $n_h$   $-0.2$  and  $n_d$   $-0.8$ , a result attributed to a decrease in degree of hydration in passing from the initial state to a transition state of type (A).<sup>11</sup> The negative values obtained in the present study thus imply net loss of water in going from the initial state (in which perchloric acid is strongly hydrated) to the transition state. The more negative  $n$  values observed for the  $DClO_4$ -catalysed reaction indicate that it is more strongly hydrated than  $HClO_4$  in the water pool.

The macroscopic and microscopic properties of micellar water are known to be different from those of bulk water.<sup>6,17,18,20</sup> In our system, the hydration of the surfactant head-groups<sup>17</sup> and perchloric acid should result in highly structured micelle-solubilized water. Since the latter is necessarily one of the reactants in the hydration of DCA, its unique properties must surely contribute to the higher reaction rates (even after taking into account the local acid concentration) in the presence of AOT.

The diazole-catalysed reaction also exhibits breaks in the plots of  $k_{obs}$  versus diazole concentration, corresponding to about one diazole molecule per micelle.¶ Imidazole binds reasonably strongly to AOT<sup>22</sup> and its partitioning between water and the organic solvent is more in favour of the former than that of MeImz (see Experimental section). This explains, in part, the higher observed rate constants for the Imz-catalysed reaction.

In water-dioxan, the rate constant is given by equation (5),<sup>12</sup> where the last term reflects the role of a second

$$k_{obs.} = k_1[Imz] + k_2[Imz]^2 \quad (5)$$

imidazole molecule acting as a general base catalyst for the Imz-catalysed water attack. In the presence of AOT, however, the reaction is first order in Imz. Thus the water attack is catalysed either by a free imidazole molecule or by imidazole hydrogen-bonded (through its N-H bond) to the  $SO_3^-$  group. Direct evidence for the formation of the latter bond comes from the observed upfield shift of the N-H proton as a function of increasing AOT concentration in  $CCl_4$ .<sup>5</sup> Although the sulphonate

¶ The  $pK_a^{app}$  of Imz in AOT reversed micelles is not known. A recent study has shown, however, that Imz is preferentially adsorbed at the micellar interface.<sup>21</sup> The  $pK_a^{app}$  of *p*-nitrophenol adsorbed at the AOT reversed micelle interface is 4 units greater than that in bulk water.<sup>21</sup> Because of the similarity of the  $pK_a$  values of the two acids in water, one would expect a similar high  $pK_a^{app}$  for Imz. If all the added diazole were concentrated in the water pool (water concentration  $1.389M$ ), the effective base concentration would be increased by a factor of 40 ( $55.5M/1.389M$ ). From the Henderson-Hasselbalch equation, this increase would be cancelled by an increase of only 1.6 units in  $pK_a^{app}$ . The stoichiometric diazole concentration thus represents a conservative maximum for the effective concentration in the micellar core.

group might conceivably participate through general base catalysis, Table 2 shows that  $k_{\text{obs}}$  decreases linearly as a function of increasing the surfactant concentration. This inverse dependence on [AOT] has also been observed in the Imz-catalysed ester hydrolysis, and can be rationalized in terms of the progressive dilution of the reagents in the micellar core as more detergent is added.<sup>4,5</sup>

The ratios of  $k$  (diazole-AOT) :  $k$  (diazole-dioxan) obtained in the present work are 209 and 144 for Imz and MeImz, respectively. In addition to the enhanced reactivity of the micelle-solubilized water, the rate increase may additionally reflect a favourable diazole orientation due to interaction with the surfactant head-groups.

The type of behaviour shown in Figures 1 and 3, namely that the catalytic constants for both the acid- and base-catalysed reactions depend upon the catalyst concentration range, has not been reported before. Thus in reversed micelle catalysis, a wide range of catalyst concentration has to be covered in order to check for the presence of such breaks.

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