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Kinetics of the Acid-Base Catalyzed Hydration of 1,3-Dichloroacetone in the Presence of Triton X-100 Reversed Micelles in Carbon Tetrachloride

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The kinetics of the reversible hydration of 1,3-dichloroacetone catalyzed by hydrochloric acid or by imidazole buffer solubilized by the reversed micelles of the nonionic surfactant Triton X-100 in carbon tetrachloride have been studied spectrophotometrically. Rate and equilibrium constants, kinetic isotope effects, and activation parameters have been determined as a function of the [water]/[surfactant] molar ratio. The rate constants were found to be similar to those obtained in the presence of the reversed micelles of the anionic surfactant Aerosol-OT but higher (by factors from 4 to 327) than those for the same reaction in aqueous dioxane. On the basis of the obtained data, transition-state structures for the acid- or base-catalyzed reactions are suggested that clearly show the catalytic role (acid-base) played by the surfactant. The observed rate enhancement is attributed to this participation of the detergent which entails differences between the structures of the transition states for the micelle-mediated reactions and those in aqueous dioxane.

Introduction

Few reactions have been comparatively studied in the presence of differently charged reversed micelles.[1-4] This type of study is important, however, because it should help delineate the role of the hydrophilic groups of the surfactant in the observed catalysis. The addition of water to carbonyl compounds is an interesting reaction because it is the simplest example of the addition of nucleophiles to a CO group. Besides, it has been shown that the hydration of some metabolically important substrates (e.g., glyceraldehyde 3-phosphate, dihydroxyacetone phosphate) is an important step along the catalytic pathways of certain enzymes.[5] A study of this reaction in the presence of reversed micelles is, therefore, biologically relevant since these species are used as models for enzymes and membranes.[4]

The hydration of 1,3-dichloroacetone (DCA) is given by eq 1, where k_h and k_d represent the rate constants for hydration and dehydration, respectively. Hydration of

$$(ClCH_2)_2CO + H_2O \underset{k_d}{\overset{k_h}{\rightleftharpoons}} (ClCH_2)_2C(OH)_2 \qquad (1)$$

DCA by water or solutions of perchloric acid, imidazole, and *N*-methylimidazole solubilized by bis(2-ethylhexyl)sodium sulfosuccinate (Aerosol-OT or AOT) reversed micelles in CCl_4 and in hexane has been previously investigated.[6-8] Recently we studied the reaction of the same ketone with Triton X-100 solubilized water (TX-100, $C_8H_{17}C_6H_4(OCH_2CH_2)_{9.5}OH$) in CCl_4 and compared the results to those obtained by using AOT.[9] We now report on the acid- and base-catalyzed reactions in the presence of the nonionic reversed micelles. From the obtained rate and equilibrium constants, kinetic isotope effects, and activation parameters possible structures for the reaction transition states are discussed, showing the catalytic role (acid-base) of the surfactant.

Experimental Section

Procedures for drying the solvent (Merck) and for the purification of DCA (Fluka), imidazole (Aldrich), and the nonionic surfactant (Rhom & Haas) are given elsewhere.[7,9] Hydrochloric acid (Merck, Titrisol), DCl (Aldrich, 20% in D_2O), and deuterium oxide (Aldrich, 99.8% D) were used as received. Glass double distilled water was used throughout.

Deuterated TX-100 ($C_8H_{17}C_6H_4(OCH_2CH_2)_{9.5}OD$) and imidazole-*d* were prepared by reacting each substrate with excess D_2O followed by drying in vacuo. This process was repeated three times, and the percent of deuteration of the exchangeable protons (50% for TX-100 and 95% for imidazole) was determined by ^1H NMR (Varian T-60).[10]

The drying of the surfactant and the preparation of the stock solutions were carried out as before.[9] All runs were carried out at an ionic strength of 0.2, adjusted with NaCl. The reaction was followed by monitoring the disappearance of the carbonyl group of DCA at 307 nm, using a Zeiss PM6KS spectrophotometer equipped with a thermostated cell holder. Observed rate constants, k_{obsd}, were obtained from the absorbance-time data using a Burroughs B6900 computer. The relative standard deviations were <3%. The constants k_h and k_d and the equilibrium constant for hydration, K_h, were calculated from k_{obsd} and the values of the initial absorbance and that at equilibrium as given in earlier reports.[6-9]

Results

(1) Catalysis by Hydrochloric Acid. In studying the catalysis by the micelle-solubilized acid, measurements were carried out at a fixed R value (R = [water]/[TX-100])

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(1) Reversed micelles are detergent aggregates in nonpolar solvents. Reactions catalyzed by these species usually take place in the central part or "core" of the aggregate. The term "water pool" refers to a droplet of water surrounded by a monolayer of the surfactant molecules.[2-4]

(2) Menger, F. M. *Pure Appl. Chem.* **1979**, *51*, 999.

(3) Kitahara, A. *Adv. Colloid Interface Sci.* 1980, *12*, 109.

(4) Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley: New York, 1982.

(5) Trentham, D. R.; McMurray, C. H.; Pagson, C. I.; *Biochem. J.* **1969**, *114*, 19. Reynolds, S. J.; Yates, D. W.; Pagson, C. I. *Ibid.* 1971, *122*, 285.

(6) El Seoud, O. A.; da Silva, M. J.; Barbur, L. P., Martins, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 331.

(7) El Seoud, O. A.; da Silva, M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 127.

(8) El Seoud, O. A.; Vieira, R. C.; Farah, J. P. S. *J. Org. Chem.* **1981**, *46*, 1231.

(9) El Seoud, O. A.; Vidotti, G. J. *J. Org. Chem.* **1982**, *47*, 3984.

(10) The deuteration of compounds containing acidic hydrogen atoms, e.g., alcohols, acids, and imidazole, is usually carried out under strongly acidic or strongly basic conditions.[11] These procedures could have not been applied to the deuteration of Triton X-100 because they would have contaminated the detergent with acidic or basic impurities whose removal would be, at best, tedious.[12] Therefore, the highly purified neat detergent was reacted with excess D_2O, followed by removal of the exchanged D_2O. It is possible that the hydration of the ether oxygen atoms of the detergent[3] diminshed the availability of the added D_2O for exchange with the terminal OH group.

(11) Tsing-Lien, C.; Yu-Chih, W. *Sci. Rep. Natl. Tsing Hua Univ., Ser. A* **1957**, *4*, 451; *Chem. Abstr.* **1957**, *42*, 7236h. Vaughan, W. R.; Anderson, M. V., Jr.; Blanchard, H. S.; McCane, D. I.; Meyer, W. L. *J. Org. Chem.* **1955**, *20*, 819. More O'Ferrall, R. A.; Kwok, W. K.; Miller, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 5553. Garfinkel, D.; Edsall, J. T. *J. Am. Chem. Soc.* **1958**, *80*, 3807.

(12) Vidotti, G. J. M.Sc. Thesis, University of São Paulo, 1982.

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Table I. Catalytic Rate Constants for Hydration (k_h) and Dehydration (k_d), Equlibrium Constants for Hydration (K_h), and Activation Parameters for the Reaction in the Presence of Micelle-Solubilized Hydrochloric Acid[a]

R	k_h, M^{-1} s^{-1}	k_d, M^{-1} s^{-1}	K_h	activation parameters[b,c]					
				$\Delta H^\ddagger$		$\Delta S^\ddagger$		$\Delta G^\ddagger$	
				h	d	h	d	h	d
2.63	3.82	3.81	1.0	9.9	18.1	-21.4	+6.4	16.3	16.2
5.26	6.09	4.20	1.45	7.3	14.5	-28.8	-5.1	15.9	16.0
7.89	7.53	4.49	1.68	3.9	12.7	-39.4	-10.7	15.6	15.9
10.53	8.58	4.73	1.81						

[a] [TX-100] = 0.38 M, at 25 °C, and ionic strength = 0.2 M. [b] The values of $\Delta H^\ddagger$ and $\Delta G^\ddagger$ are in kcal mol^{-1}, and those of $\Delta S^\ddagger$ are in cal mol^{-1} K^{-1}. The subscripts h and d refer to hydration, and dehydration, respectively. The values of $\Delta S^\ddagger$ were corrected to a reference state of 1 M acid. [c] Values based on three rate constant measurements of 5 °C intervals from 15 to 25 °C. Water solubility problems precluded the study of a wider temperature range and the determination of the activation parameters for the reaction at R = 10.53.

Table II. Rate and Equilibrium Constants and Activation Parameters for the Imidazole-Catalyzed Hydration of DCA in the Micellar Pseudophase[a]

R	10^2k_h, M^{-1} s^{-1}	10^2k_d, M^{-1} s^{-1}	K_h	activation parameters[b,c]					
				$\Delta H^\ddagger$		$\Delta S^\ddagger$		$\Delta G^\ddagger$	
				h	d	h	d	h	d
2.63	1.86	1.12	1.66	8.0	13.6	-37.3	-19.2	19.1	19.3
5.26	5.12	2.21	2.32	6.6	12.4	-40.7	-22.2	18.7	19.0
7.89	7.73	3.30	2.34	5.5	10.4	-43.4	-28.1	18.4	18.8
10.53	9.74	4.21	2.31						

[a] [TX-100] = 0.38 M, at 25 °C, and ionic strength = 0.2 M. [b] Units are kcal mol^{-1} for $\Delta H^\ddagger$ and $\Delta G^\ddagger$ and cal mol^{-1} K^{-1} for $\Delta S^\ddagger$. The latter was corrected to a reference state of 1 M imidazole free base. The subscripts h and d refer to hydration and dehydration, respectively. [c] Values based on three rate constant measurements at 5 °C intervals from 15 to 25 °C. See footnote *c* of Table I.

as a function of increasing acid concentration. This experiment was then repeated at several water or D_2O concentrations. The catalytic constants for the hydration by water (k_h^H, k_d^H) and D_2O (k_h^D, k_d^D) were determined from plots of the corresponding first-order rate constants vs. the "effective" acid concentrations in the water pool. The latter values were calculated on the basis of the work of Fendler et al.[13] in which the pK_a values of acid–base indicators were determined in the presence of the reversed micelles of a similar nonionic detergent (Igepal CO-530, $C_9H_{19}C_6H_4(OCH_2CH_2)_6OH$). Their data showed that the ether oxygen atoms of the surfactant compete for the protons and that under conditions comparable to those used here the micelle decreased the pK_a of the indicator by two units.[14] The linearity of these plots is shown in Figure 1A, and the obtained constants are given in Table I, along with the corresponding activation parameters. The latter were calculated from the rate constants obtained at a single acid concentration (4.17 × 10^{-4} M). Since the reaction is clearly first order with respect to the acid, the activation entropies for a reference state of 1 M acid were obtained by adding $-R$ ln [acid] to $\Delta S^\ddagger$.[15,16] The values of k_h, k_d, and K_h increase as a function of increasing R. On the other hand, water solubilization in the reversed micelle decreases both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ almost in a compensating way so that $\Delta G^\ddagger$ was found to decrease only slowly as R was increased. The kinetic isotope effects (k^H/k^D or K^H/K^D) were obtained from experiments at a single acid concentration (4.17 × 10^{-4} M) and were found to be independent of R. They were 1.91 ± 0.01, 1.85 ± 0.03, and 1.05 ± 0.05 for k_h, k_d, and K_h, respectively.

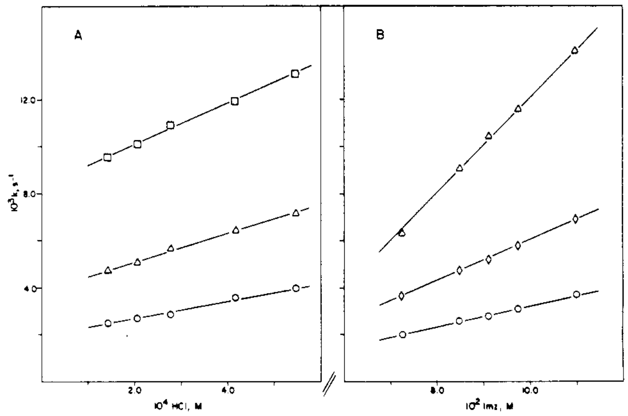

Figure 1. Catalytic plots for the HCl-catalyzed hydration (A) at different R values: ○, k_d (R = 2.63); △, k_h (R = 5.26); □, k_h (R = 10.53). Part B is that for the Imz-catalyzed reaction: ○, k_d (R = 2.63); ◇, k_d (R = 5.26); △, k_h (R = 5.26).

(2) Catalysis by Imidazole (Imz). The hydration of DCA catalyzed by TX-100-solubilized imidazole was studied as a function of the concentration of the imidazole buffer, at a fixed pH of 7.160 and at the same R values used in the acid-catalyzed reaction. Plots of k_h or k_d vs. [Imz] present as a free base were strictly linear, as shown in part B of Figure 1. The intercepts of the plots (corresponding to the uncatalyzed reactions) were practically the same as the rate constants in the absence of imidazole (k_0), showing that there is no catalysis by the OH^- ion. The rate equation is, therefore, given by eq 2.

$$k_{obsd} = k_0 + k_{Imz}[Imz] \qquad (2)$$

Table II shows the obtained constants as a function of increasing the value of R. The activation parameters shown in the table were obtained from the data at a single Imz concentration of 0.05 M (free base) and the values of $\Delta S^\ddagger$ were corrected to a reference state of 1 M imidazole by the addition of $-R$ ln [Imz]. As in the case of the acid-catalyzed reaction the values of k_h, k_d, and K_h increase, whereas $\Delta H^\ddagger$ and $\Delta S^\ddagger$ decrease (more or less in a compensating way) as a function of increasing R. The isotope effects were obtained at a single [Imz] of 0.05 M and were found to be independent of the value of R. They were 2.38

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[13] Nome, F.; Chang, S. A.; Fendler, J. H. *J. Colloid Interface Sci.* **1976**, *56*, 146.

[14] In other words, $pH_{wp} = pH_{st} + 2$ where pH_{wp} and pH_{st} denote the effective pH in the water pool and that which was mesured by a pH meter before solubilizing the acid solution in the micelle, respectively.

[15] Bell, R. P.; Sörensen, P. E. *J. Chem. Soc., Perkin Trans. 2* 1972, 1740.

[16] Sörensen, P. E. *Acta Chem. Scand.* 1976, 673.

± 0.02, 2.0 ± 0.1, and 1.20 ± 0.07 for k_h, k_d, and K_h, respectively.

Discussion

There are two possible sites in which the hydration reaction may occur, the bulk solvent and the micellar pseudophase. Any contribution from the former reaction to the observed rate constants can be ruled out in the following manner. In addition to the very low solubility of water in the solvent used, all other reagents are much more soluble in water than in CCl_4, i.e., they are predominantly located within the domain of the reversed micelle. More significantly, no detectable hydration was observed in the absence of TX-100 when the CCl_4 was preequilibrated with either aqueous acid (0.1 M HCl) or base (0.1 M Imz, pH 7.160). This clearly implies that the observed reaction occurs wholly inside the reversed micelle. One of the main objectives of the present work was to compare the data with those obtained in the presence of AOT and thus shed some light on the catalytic role played by the head groups of the detergent. First we examine the acid-catalyzed reaction where no breaks in the k vs. [acid] graphs were obtained in the present case. It is now believed[17] that the origin of these breaks[7] lies in the ion exchange between the H_3O^+ in the water pool and the counterion (Na^+) of AOT. No such process is possible in the present case, although the detergent itself can be protonated.[13] Because of this basic nature of the micellar interior of TX-100, we think that the catalytic rate constants are, in fact, larger than the ones reported in Table I. The effective pH values used here were based on the data of a detergent containing six oxyethylene units so that one expects that TX-100 should decrease the effective acidity even more (larger number of oxyethylene groups).[18]

Another interesting difference between the present reaction and that in AOT[7] or in water–dioxane[19] is that the kinetic orders with respect to water are positive.[20] The hydration reaction itself is, of course, associated with positive kinetic orders, but it is the dehydration of the acid catalyst (in going from the reactants to the transition state) which is responsible for the observed overall negative orders.[19,21] When the micelle-catalyzed reaction is analyzed, the change in the hydration of the surfactant has to be also considered.[22] AOT forms strong hydrogen bonds with the associated water molecules[2,3] which are not expected to be perturbed in going to the transition state. That is, the important effect will be that due to the dehydration of the acid catalyst, resulting in negative kinetic orders.[23] TX-100 associates with water less strongly than AOT[25,26] so that its hydration can, at least in principle, increase in going to the transition state. Moreover, it is expected that the hydration of the protonated ether oxygens of the surfactant is less than that of the H_3O^+ ion. Both factors can be used to explain the difference between the kinetic orders for the reaction occurring in AOT or in water–dioxane and that in TX-100.

The important feature of the imidazole-catalyzed reaction is that it is first order in imidazole concentration. The corresponding rate equation in aqueous dioxane is given by eq 3,[27] where the second Imz molecule is acting as a general base for the one which is catalyzing the water attack. The rate equation for the micellar reaction (eq 2) can be explained by assuming that the imidazole molecule in the micellar core either is monomeric or else is H bonded to any ether oxygen atom of the surfactant. The latter is, therefore, acting as a general base, substituting the second Imz molecule of eq 3. Of these possibilities the second seems more plausible since imidazole, which is not soluble in CCl_4, can be easily solubilized by the dry surfactant. Additionaly, several spectroscopic studies have clearly shown the H-bonding abilities of both imidazole and TX-100.[25,26,28,29] If our idea were correct, then the last term of eq 2 is a third order one whose rate constant can be obtained by dividing the rate constants of Table II by the micellar concentration of TX-100.[30] Aggregation numbers for Triton X-100 reversed micelles in the presence of water are not available, but a recent study on the effect of water on the aggregation of $C_{12}H_{25}(OCH_2CH_2)_4OH$ in decane showed that values between 50 (R = 2.63) and 80 (R = 10.53) can be used as conservative lower limits for the aggregation number N.[31] The catalytic constants will, therefore, range from 3.32 to 27.8 $M^{-2}\ s^{-1}$ and from 2.0 to 12.03 $M^{-2}\ s^{-1}$ for hydration and dehydration, respectively. Other interesting points of this reaction are that the value of K_h is independent of R (except for the first entry of Table II) and that the kinetic orders with respect to the solubilized water are higher than those for the acid-catalyzed reaction (1.49 and 0.98 for hydration and dehydration, respectively).

Compared to the hydration in aqueous dioxane the TX-100 reversed micelle enhances the rates of both acid and base-catalyzed reactions. For example, at R = 7.89 the micelle increases the rates of hydration by factors of 7 and 327 and those of dehydration by factors of 4 and 139 for the HCl- and Imz-catalyzed reactions, respectively.[19,27] As argued before, these factors are most likely to be lower limits for the true micellar rate enhancement. To analyze the reason for the observed catalysis, we recall that the water in the micellar core is H bonded to the oxygen atoms of the surfactant and that at least one water molecule is necessary to hydrate each ether oxygen atom.[25,26] That is,

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(17) El Seoud, O. A.; Chinelatto, A. M.; Shimizu, M. J. *J. Colloid Interface Sci.* **1982**, *88*, 420.

(18) The magnitude of this effect per oxyethylene group can, in principle, be determined by studying the pK_a of indicators as a function of increasing number of oxyethylene units in the nonionic detergent. Unfortunately, this has not been done so that we are in no position to estimate the additional decrease in the effective acidity due to the presence of the extra three to four oxyethylene groups.

(19) Bell, R. P.; Gritchlow, J. E. *Proc. R. Soc. London, Ser. A* **1971**, A325, 35.

(20) The kinetic orders with respect to water were obtained from the slopes of the plots of log k vs. log [H_2O]. The values were 0.58 and 0.15 for hydration and dehydration, respectively. The corresponding values for the reaction in AOT were −0.25 and −0.69[7] and those for the reaction in water-dioxane were $\sim$−0.8 and $\sim$−1.5.[19]

(21) Bell, R. P.; Millington, J. P.; Pink, J. M. *Proc. R. Soc. London, Ser. A* **1968**, *303*, 1.

(22) There is evidence that the water molecule which is being added to DCA is hydrogen bonded to the sulfonate group of AOT, most likely via another water molecule.[8]

(23) The occurrence of ion exchange with AOT is not in conflict with the preceding phrase because protonated AOT is also a strong acid. Studying DCA hydration in aqueous dioxane, Bell and Jensen showed that the catalytic power varied only slightly within the group of strong acids: HCl, HBr, $C_6H_5SO_3H$, CH_3SO_3H, and $HClO_4$.[24]

(24) Bell, R. P.; Jensen, M. B. *Proc. R. Soc. London, Ser. A* **1961**, *261*, 38.

(25) Polo, F.; Ray, A.; Němethy, G. *J. Am. Chem. Soc.* **1973**, *95*, 6164. Tanford, C.; Nozaki, Y.; Rohde, M. F. *J. Phys. Chem.* **1977**, *81*, 1555. Yoshioda, H. *J. Colloid Interface Sci.* **1978**, *63*, 378.

(26) Gentile, F. P.; Ricci, F.; Podo, F. *Gazz. Chim. Ital.* **1976**, *106*, 423. Christenson, H.; Friberg, S. C.; Larsen, D. W. *J. Phys. Chem.* **1980**, *84*, 3633.

(27) Cordes, E. H.; Childres, M. *J. Org. Chem.* **1964**, *29*, 968.

(28) Grimmett, M. *Adv. Heterocyl. Chem.* **1970**, *12*, 103.

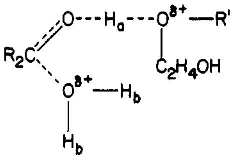
(29) Balasubramanian, D. J. *J. Indian Chem. Soc.* **1981**, *53*, 633.

(30) These are obtained from the equation $C_M = C_D - \mathrm{cmc}/N$ where C_M, C_D, cmc, and N refer to the micellar concentration, that of the detergent, the critical micelle concentration, and the aggregation number, respectively.

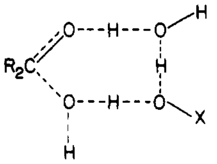
(31) Ravey, J. C.; Buzier, M.; Picot, C. *J. Colloid Interface Sci.* **1984**, *97*, 9.

(32) Corkill, J. M.; Goodman, J. F.; Wyer, J. *Trans. Faraday Soc.* **1969**, *65*, 9.

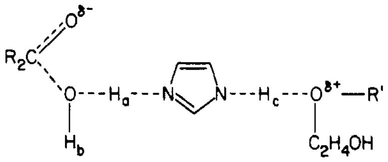
all the water in the core is associated with the surfactant, even at the largest *R* used. The kinetic isotope effects are, in fact, less than what they should be because the OH group of the detergent was only partially deuterated and will exchange with the D_2O in the pool.[26,28] A correction of 14% has been used before,[9] making the isotope effects 2.17 (k_h) and 2.11 (k_d) for the HCl-catalyzed reaction and 2.71 (k_h) and 2.88 (k_d) for the Imz-catalyzed reaction. Except for the third value, which is a borderline case, these figures indicate that a small number of protons (possibly two) contribute to the observed isotope effects.[9,33] This is also in agreement with the kinetic orders with respect to the solubilized water. On the basis of the preceding discussion, we suggest structure A as a reasonable model for the acid-catalyzed reaction, showing the participation of any protonated ether oxygen (via proton H_a), where R = $ClCH_2$ and R′ represents TX-100. Note that protons H_b are probably H bonded to the detergent. For comparison we include transition-state B suggested for the reaction in aqueous dioxane, where XOH is the acid catalyst.[19] For the Imz-catalyzed reaction we suggest transition-state C which is similar to that suggested for the imidazole-catalyzed reaction in aqueous dioxane[27] except that TX-100 is substituting the second Imz molecule as a general base.[34] The observed kinetic isotope effects are similar to those obtained in the aqueous solvent and may be accounted for in terms of transition-state C provided one assumes that either H_a or H_c is asymmetrically placed.[33] The fact that the isotope effects were found to be independent of R is interesting and is similar to that observed for DCA hydration by TX-100-solubilized water.[9] This suggests that the structures of the transition states show no detectable change as a function of increasing R. On the other hand, the kinetic isotope effects for DCA hydration by AOT-solubilized water showed noticeable dependence on R, reflecting a much stronger surfactant–water interaction.[8] This decreases rapidly as a function of increasing R, a fact which was used to explain the participation of more water molecules in the reaction at higher *R* values.[8] Additional evidence for the role of the surfactant could have been obtained from a comparison of the activation parameters for the reaction in the micellar pseudophase[8,9] to those in aqueous solvents. Unfortunately, this is not feasible due to the lack of data for the acid–base catalyzed reactions in the latter case. In summary, the observed micellar catalysis is likely to be due to the participation of the surfactant as acid–base catalyst and to the differences between the structures of the transition states for the reaction in the micelle and those in a reference solvent (e.g., in water–dioxane).



transition-state A



transition-state B



transition-state C

The monotonic decrease of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as a function of increasing *R* can be explained in terms of the accompanied decrease in the water–TX-100 association as follows. It is known that the mobilities of both the water molecules and the surfactant oxyethylene segments increase as a function of increasing R, due to the diminished surfactant–water interactions.[26,32] The variation of $\Delta H^{\ddagger}$ can be attributed to an increased stabilization of the charged transition state since the water is becoming progressively more able to efficiently participate in the solvation process. Concomitantly, this enhanced solvation will contribute to more loss of freedom of the water molecules which explains the behavior of $\Delta S^{\ddagger}$.

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Registry No. $(ClCH_2)_2CO$, 534-07-6; $(ClCH_2)_2C(OH)_2$, 82598-72-9; H_2O, 7732-18-5; CCl_4, 56-23-5; HCl, 7647-01-0; D_2O, 7789-20-0; Imz, 288-32-4; TX-100, 9002-93-1; deuterated TX-100, 93085-29-1; imidazole-*d*, 6128-12-7.

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(33) Albery, W. J. In "Proton-Transfer Reactions"; Caldin, E., Gold, V., Eds.; Chapman & Hall: London, 1975.

(34) Another alternative involves the attack of water on a tetrahedral intermediate formed from DCA and the anion of Imz. This can be ruled out since the intermediate should be less reactive than the starting material.[35] Moreover, the rate constant for the DCA hydration catalyzed by 2,4,6-trimethylpyridine (which obviously cannot act as a nucleophilic catalyst) lies on the same Brönsted plot along with that of Imz.[24]

(35) Jencks, W. P.; Carriuolo, J. *J. Biol. Chem.* **1959**, *234*, 1280.