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

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Introduction

Some nonionic detergents aggregate in organic solvents to form reversed or inverted micelles.[1,2] The central part (core) of the micelle contains the oxyethylene groups of the surfactant and is the site of solubilization and chemical reactions. Little attention has been given to catalysis by nonionic reversed micelles, although the results may be easier to rationalize due to the absence of the complicating ion-exchange processes.[3] Additionally, comparing the results of reactions catalyzed by ionic and nonionic reversed micelles may shed some light on the catalytic role of the surfactant hydrophilic groups, leading to a better understanding of reversed micellar catalysis.

We report here on the kinetics of the reversible hydration of 1,3-dichloroacetone (DCA) in the presence of the nonionic surfactant Triton X-100 (TX-100, $p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}(OCH_2CH_2)_{9.5}OH$) reversed micelles in CCl_4. This reaction is particularly suitable because the results can be compared with those of the same reaction in aqueous dioxane[4] and in the presence of reversed micelles of the anionic surfactant Aerosol-OT [AOT, $C_8H_{17}OCOCH_2CH(SO_3^-Na^+)COOC_8H_{17}$).[5]

Results and Discussion

The reaction under investigation is

$$(\mathrm{ClCH_2})_2\mathrm{CO} + \mathrm{H_2O} \underset{k_d}{\overset{k_h}{\rightleftharpoons}} (\mathrm{ClCH_2})_2\mathrm{C(OH)_2}$$

where k_h and k_d refer to the rate constants for hydration and dehydration, respectively. The equilibrium constant for hydration is $K_h = k_h/k_d$, and the results are given in Table I. The figures in parentheses refer to the ratios of the rate or equilibrium constants (water–TX 100 or D_2O–TX 100) to those in water–dioxane or D_2O–dioxane.[4] Rate constants in the presence of the surfactant are higher than those in aqueous dioxane, and the ratio between the rates decrease as a function of increasing the water or D_2O concentration. The values of K_h are also higher, except for the last two entries of Table I. At comparable surfactant concentrations (TX-100 = 0.38 M and AOT = 0.4 M), the rate enhancement by the nonionic one (relative to that in water–dioxane or D_2O–dioxane) is ca. 13 to 25% less than that by AOT.[5] The kinetic isotope effects are independent of the R ratios ($R = [H_2O]/[\text{TX-100}]$), and their values are 2.65 ± 0.1, 2.21 ± 0.02, and 1.20 ± 0.05 for k_h, k_d, and K_h, respectively. The kinetic orders with respect to solubilized water (n_h and n_d) were obtained from the slope of the linear plots of log k_h or log k_d vs. log $[H_2O]$. The values are $n_h = 1$ and $n_d = 0.6$. Contrary to the hydration of DCA in AOT reversed micelles,[5] no breaks were observed in the present kinetic order plots. Activation parameters were obtained from the rate data in the temperature range of 15–25 °C and are shown as a function of solubilized water in Figures 1 and 2.[6] The $\Delta G^{\ddagger}$ values for hydration and dehydration are identical and decrease slowly as a function of increasing R. The small variation in $\Delta G^{\ddagger}$ is the result of a decrease of $\Delta H^{\ddagger}$, which is almost offset by a decrease in $\Delta S^{\ddagger}$. For water concentrations of 1 and 2 M, the values of $\Delta S^{\ddagger}_d$ is positive. To our knowledge, this is the first case for a reversed-micelle-catalyzed bimolecular reaction showing a positive entropy of activation.[7]

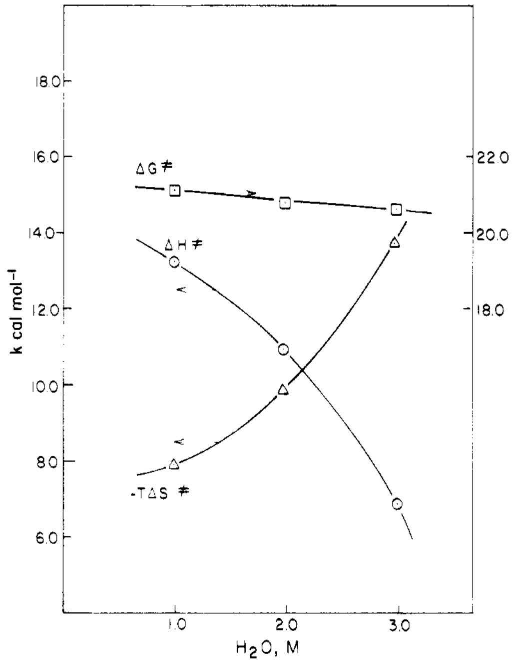

Figure 1. Activation parameters for the hydration of 1,3-dichloroacetone by TX-100-solubilized water.

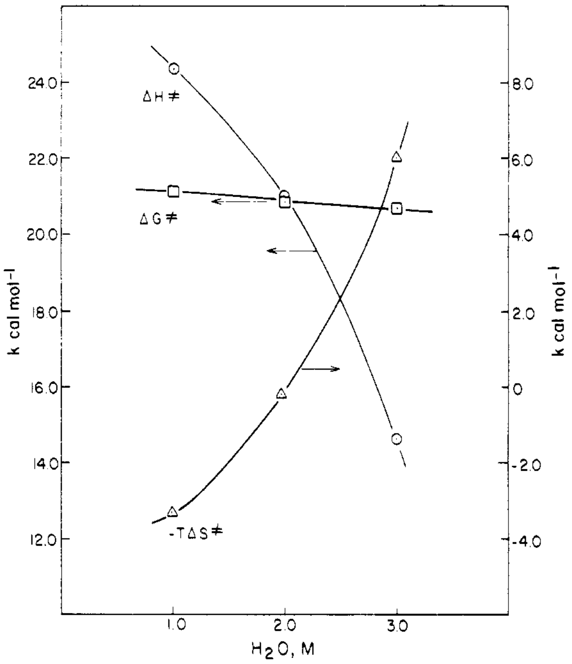

Figure 2. Variation of the activation parameters for the dehydration of 1,3-dichloroacetone as a function of the solubilized water concentration.

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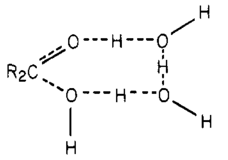
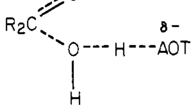
Table I. Rate Constants for Hydration (k_h) and Dehydration (k_d) and Equilibrium Constant for Hydration (K_h) for the Reaction with Micelle-Solubilized Water and D_2O at 25 °C[a]

H_2O, M	$10^4 k_h$, s^{-1}	$10^4 k_d$, s^{-1}	K_h	D_2O, M	$10^4 k_h$, s^{-1}	$10^4 k_d$, s^{-1}	K_h
1.0	18.9 (630)[b]	21.4 (238)[b]	0.88 (2.67)[b]	1.0	6.8 (680)[b]	9.6 (480)[b]	0.71 (1.42)[b]
1.5	27.0 (318)	27.5 (162)	0.98 (1.96)	2.0	12.8 (178)	15.0 (188)	0.85 (0.94)
2.0	34.6 (184)	33.0 (118)	1.05 (1.57)	3.0	20.7 (95)	18.9 (105)	1.09 (0.90)
3.0	52.6 (79)	42.1 (55)	1.25 (1.45)				
4.0	70.8 (44)	51.4 (34)	1.38 (1.31)				

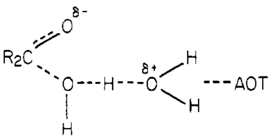
[a] Solvent CCl_4; TX-100 = 0.38 M. [b] The figures in parentheses refer to the ratios of the rate or equilibrium constants for the micellar reaction relative to those in water-dioxane or D_2O-dioxane. The latter values were taken from ref 4.



TS A for the reaction in aqueous dioxane[4]



TS B for the reaction in AOT reversed micelle, at $R = 1.3$[8]



TS C for the reaction in AOT reversed micelle, at $R = 11.1$[8]

Previous results showed no hydration in water-saturated CCl_4; i.e., the observed reaction is that taking place in the micelle.[5] Micellar rate enhancement implies a transition state (TS) whose structure is different from that in water–dioxane. Transition states (A–C) were suggested for the reaction in aqueous dioxane and for that catalyzed by AOT reversed micelles in hexane.[5,8] Note that the structures of the TS suggested for the micellar reaction depend on R. Evidence for this dependence was based on the isotope effect, on the observed sharp breaks in the log k_h, or log k_d, vs. log $[H_2O]$ graphs at $R \simeq 0.25$, and in the plots of $\Delta H^{\ddagger}_h$ or $\Delta S^{\ddagger}_h$ vs. R at values of $R > 1.3$.[8] These breaks were rationalized in terms of a change in the TS structure from B to C as more water is solubilized. No similar behavior was observed in our case, which can be taken to indicate that the number of water molecules in the TS does not change as a function of R. The value of $n_h = 1$ does not necessarily mean that the TS contains one water molecule, because one has to consider the surfactant hydration in the reagent state (RS). Evidence has been given to show the hydration of nonionic surfactants in water[11] and in organic solvents.[12] The activation parameters clearly show this hydration. A comparison of the results shown in Figures 1 and 2 with those for the same reaction in water–dioxane[13] shows that the micellar reaction is accompanied by a sizable increase in $\Delta S^{\ddagger}$. For example, in the presence of 2 M solubilized water, $\Delta S^{\ddagger}_h$ and $\Delta S^{\ddagger}_d$ are higher by 35.6 and 43.2 eu, respectively. This shows that the RS for the micellar reaction is more ordered, probably due to the fact that the water molecules are hydrogen bonded to the surfactant ethereal oxygen atoms.[11,12]

The reported isotope effects are, in fact, less than they should be. This is because the atom fraction of deuterium in the micellar core is less than unity because of the exchange with the OH group of the surfactant.[11,14] Using a partially deuterated TX-100 (50% OD), we observed a rate decrease of 14% relative to the nondeuterated detergent (at 2 M solubilized D_2O). Employing this correction factor, one concludes that the isotope effects are higher than 3.0 and 2.5 for hydration and dehydration, respectively. A TS containing one proton "in flight" (TS B) is usually accompanied by a kinetic isoptope effect between 2 and 2.5.[15] Indeed, TS B for the AOT-catalyzed reaction is accompanied by an isotope effect of 1.9.[8] This value is compared to 3.3 for TS C.[8] Assuming that the TS structure will not change appreciably in going from AOT to TX-100 (both the SO_3^- group and the ethereal oxygen atoms act as a general base for the water attack) and taking into account the similar n_h values, rate enhancement, and the isotope effects,[8] we suggest a TS similar to TS C with the nonionic detergent substituting AOT.

The reasons for the faster micellar reaction (relative to that in aqueous dioxane) and for the obsereved dependence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ on the R ratio will now be discussed. The observed micellar rate enhancement is due to higher entropies of activation, since the corresponding $\Delta H^{\ddagger}$ values are actually greater than those for the reaction in water–dioxane.[13] For example, at a water concentration of 2.0 M $\Delta H^{\ddagger}_h$ and $\Delta H^{\ddagger}_d$ are higher by 6.7 and 9.9 kcal mol^{-1}. Although water is known to be associated in dioxane,[13] ^1H NMR studies show strong water–nonionic surfactant association.[12,14] Consequently, the greater $\Delta H^{\ddagger}$ values for the micellar reaction indicate a surfactant-stabilized RS, probably through hydrogen bonding. Several factors can contribute to the higher $\Delta S^{\ddagger}$ values for the reaction in TX-100. First, the surfactant–water bonding implies a more ordered RS and a smaller variation of the entropy in going to the TS. Compared to TS A, the one suggested for the micellar reaction (TS C) is acyclic and contains one less water molecule. Both factors imply that there will be a smaller loss of freedom in going to the TS; hence, higher $\Delta S^{\ddagger}$ values will be obtained. It is also possible that the formation of a polar transition state (e.g., TS C) induces

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(7) The hydration of DCA in AOT reversed micelles is accompanied by negative $\Delta S^{\ddagger}$ values.[8] Ester aminolysis in reversed micelles is also accompanied by negative entropies of activation.[9] On the other hand, reversed micelle-catalyzed unimolecular decomposition reactions show positive $\Delta S^{\ddagger}$ values.[10]

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disturbances in the structure of the micelle-bonded water, a process which will lead to an increase in the disorder of the system. Although the contribution of this factor is difficult to quantify, its importance is likely to be higher in the case of a nonionic reversed micelle than for an ionic one (e.g., AOT).

The observed decrease in the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as a function of increasing R can be rationalized as follows. ^{1}H NMR studies showed that the mobilities of the water molecules and of the surfactant oxyethylene groups increase as a function of increasing R, due to diminished surfactant–water interactions.[14] The variation of $\Delta H^{\ddagger}$ can be attributed to a decrease in the stabilization of the RS accompanied by an enhanced stabilization of the TS through solvation by the surrounding water molecules (these become more free to form hydrogen bonds as the size of the water pool is increased). Both factors are also responsible for the observed dependence of $\Delta S^{\ddagger}$ on R.

Experimental Section

The drying of the solvent (Merck, Uvasol), the purification of DCA (Fluka), and proofs of its purity were given elsewhere.[5] TX-100 was purified by column chromatography,[16] and its purity was established as given before.[17] The surfactant was dried in vacuo for several days before making up the stock solution (1 M), which was renewed daily. Partially deuterated surfactant was prepared by dissolving D_2O (Aldrich, 99.8% D) in a 1 M surfactant solution in CCl_4, followed by distilling off the solvent. This procedure was repeated twice. ^{1}H NMR peak integration (Varian T-60) showed a 50% deuteration of the OH group.

The reaction was followed by monitoring the disappearance of the carbonyl group of DCA at 307 nm, with a Zeiss PM6KS spectrophotometer. The reaction was initiated by injecting 10 μL of a 0.75 M ketone solution in 0.4 mL of a 0.38 M surfactant solution containing the appropriate concentration of solubilized water or D_2O. Observed rate constants (k_{obsd}) were obtained from the absorbance–time data. The percent relative standard deviations (i.e., the standard deviation $\times$ 100/k_{obsd}) were < 3%. The constants k_h, k_d, and K_h can be calculated from the initial absorbance (A_0) and that at equilibrium (A_e) with the following equations:[4,5]

$$K_h = (A_0 - A_e)/A_e$$

$$k_h = k_{obsd}\,(A_0 - A_e)/A_0$$

$$k_d = k_{obsd}\,(A_e/A_0)$$

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Registry No. D_2O, 7789-20-0; DCA, 534-07-6; Triton X-100, 9002-93-1; aersol-OT, 577-11-7; H_2O, 7732-18-5; $(ClCH_2)_2C(OH)_2$, 82598-72-9.

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Synthesis of 1,4-Cyclohexadienylbis(benzylidene)

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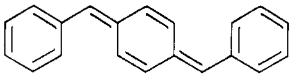
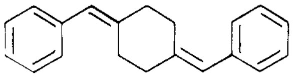
We report the synthesis of 3,6-dibenzylidene-1,4-cyclohexadiene (I), the model compound in our ongoing study of the synthesis and properties of conducting polymers.



I



II

We have pursued the following unsuccessful paths to I:

(a) Sulfuric acid catalyzed dehydration of *p*-benzylbenzohydrol (III). Only the corresponding ether, IV, resulted.

(b) Potassium *tert*-butoxide dehydrobromination of α,α'-diphenyl-α-bromo-*p*-xylene (V).

(c) Wittig reaction[2] between benzyltriphenylphosphonium chloride and 1,4-cyclohexanedione in the presence of phenyllithium and ethyl ether as solvent to give 1,4-dibenzylidenecyclohexane (II) followed by NBS bromination of II followed by dehydrohalogenation in the presence of Zn and NaOH. The product could not be freed of bromine.

(d) Dehydrobromination of 1,4-bis(α-bromobenzyl)-1,4-dibromocyclohexane (VI) gave only 1,4-bis(α-bromobenzylidene)cyclohexane (VII).

Since II was easy to prepare, we explored the dehydrogenation of II as a possible route to I. We first selected chloranil,[3-5] as dehydrogenating agent. Although we could isolate and identify the reduction product, tetrachlorohydroquinone, we could not isolate the corresponding oxidation product I. Use of the stronger agent 2,3-dichloro-5,7-dicyanobenzoquinone[4-7] (DDQ) led to pure I.

Carrying out the Wittig reaction to product II in N,N-dimethylformamide (DMF) as solvent gave a 40% yield of a mixture of I and II. Reaction of this mixture with DDQ also gave pure I.

The ^{1}H NMR spectra show benzylidine protons at 6.4 ppm in I and 6.2 ppm in II. Both compounds have virtually identical UV spectra. There were considerable differences in the infrared spectra of compounds I and II, however. The complexity of the ^{1}H NMR spectra in the regions near 2 and 6 ppm suggests that both I and II were obtained as mixtures of cis–trans isomers.

Experimental Section

1,4-Dibenzylidenecyclohexane (II). A solution of 0.1 mol of phenyllithium in 70/30 cyclohexane/ether was diluted to 150 mL with anhydrous ether under N_2. Benzyltriphenylphosphonium chloride (BTPC; 0.1 mol) was added. The ensuing reaction was exothermic and the mixture turned orange. After 1 h, 0.05 mol of 1,4-cyclohexanedione was added and the mixture heated under reflux for 4 days under N_2. Color gradually changed to a light tan. After cooling and filtering, the solution was washed with aqueous $NaHSO_3$ solution and then several times with water. The organic layer was dried over $MgSO_4$ and evaporated to turbidity. Addition of methanol yielded a white crystalline product, II, in 25% yield: mp 110–112 °C; IR (KRr pellet) 1600, 1665, 3010, 2880 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.4 (s, 8), 6.2 (s, 2), 7.1 (s, 10); UV (cyclohexane) 295 nm, 305, 320.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found C, 92.08; H, 7.90.

Wittig Reaction in DMF. The above reaction was repeated with the modification of diluting the phenyllithium solution with DMF instead of ether. The product, 33%, melted at 107–108 °C and was found to be a mixture of II and I by elemental, IR, and NMR analysis.

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