ate amounts of unsaturated hydrocarbons appears to have no effect. (b) It is desirable that solvents have a low viscosity and density to facilitate settling of the KH particles. KH has a crystal density of 1.43 g cm^{-3}.

(35) (a) Available from the Hamilton Co., Whittier, Calif. (b) When using a flat-tipped needle, it is necessary to puncture the rubber-sleeve stopper with a regular needle first.

(36) Occasionally short induction periods have been observed especially with samples of KH that have been exposed to the atmosphere repeatedly. In such cases slower metalation (1 hr) has occurred.

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Kinetics and Mechanism for Hydrolysis of Substituted α,α-Dichlorotoluenes

B. Colina, M. G. Rotaeche, E. Guerrero, A. Malpica, M. Calzadilla,* and J. Baumrucker*

Escuela de Quimica, Facultad de Ciencias, Universidad Central, Caracas, Venezuela

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The rate of hydrolysis of α,α-dichlorotoluene and the corresponding *p*-chloro- and *p*-methyl derivatives in aqueous solution is independent of pH over the range 2–11. The reactivity of these substrates is very sensitive to the nature of polar substituents: the relative rates of hydrolysis of the *p*-chloro, unsubstituted, and *p*-methyl compounds is 0.6:1:78. Hydrolysis of these substrates exhibits values of entropy of activation in the range −8 to −13 eu. Salt effects on the rate of hydrolysis of α,α-dichlorotoluenes are small but hydrolysis is markedly retarded by addition of dioxane. Rate constants measured in 50% aqueous dioxane are 600–1000 times as small as those measured for the same substrates in water. Hydrolysis of these substrates is also subject to inhibition by both cationic and anionic surfactants: diminutions in rate between 10- and 100-fold are observed in the presence of 0.05 *M* surfactants. These data corroborate a mechanism of hydrolysis involving rate-determining unimolecular carbon–chlorine bond cleavage.

Mechanism and catalysis for hydrolysis of acetals and ketals[1-3] and related species[4,5] have been vigorously studied. As a consequence, a substantial body of experimental information is available on which to base conclusions concerning mechanism and to found predictions concerning the behavior of novel compounds in the same class. In contrast, rather little study of the hydrolysis of α,α-dichlorotoluenes has been undertaken, although there is substantial reason to believe that these reactions occur with rate-determining unimolecular cleavage of a carbon–chlorine bond.[6-8] However, little information is available concerning structure–reactivity relations, solvent effects, salt effects, and effects of ionic surfactants for these reactions. We report here results of an investigation of the kinetics of hydrolysis of substituted α,α-dichlorotoluenes in aqueous solution and other media designed to provide such information.

Experimental Section

Materials. α,α-Dichlorotoluene, *p*-methyl-α,α-dichlorotoluene, and *p*, α, α-trichlorotoluene were synthesized from the appropriate benzaldehydes and phosphorus pentachloride as previously described.[9] Ir and pmr spectra revealed no detectable impurities in these preparations. 1,4-Dioxane was obtained from the Eastman-Kodak Co. and was purified by distillation and passage through a column of neutral aluminum oxide (M. Woelm). Sodium dodecyl sulfate was obtained from the British Drug Houses Ltd., and was purified as previously described.[10] Dodecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide were purified samples donated by the Department of Chemistry, Indiana University. All other reagents were of the best grade commercially available. Distilled water was employed throughout.

Kinetic Measurements. Hydrolysis of substituted α,α-dichlorotoluenes was followed spectrophotometrically by monitoring the appearance of the appropriate benzaldehyde as a function of time. Substrate concentrations near 10^{-4} *M* were employed. All measurements were made with a Zeiss PMQ II spectrophotometer equipped with a cell holder through which water from a thermostated bath was continuously circulated. First-order rate constants were calculated from semilogarithmic plots of the difference between infinite time optical density and optical density at specific times against time. Excellent first-order behavior was observed for all reactions studied. Except for those reaction mixtures containing ionic surfactants, for which additional electrolytes were not added, ionic strength was maintained constant at 0.5 through addition of calculated quantities of KCl. Values of pH were measured employing a Radiometer PHM 26 pH meter.

Activation parameters were calculated from rate constants measured at 20, 30, 40, and 50°. In accord with previous observations,[7] the energy of activation was found to be dependent on temperature and each value was calculated from the following expression[7]

$$E_{act}^{obsd} = [RT_aT_b/(T_b - T_a)] \ln (k_b/k_a) \qquad (1)$$

in which k_a and k_b refer to rate constants measured at T_a and T_b, respectively. These values of the energy of activation were subsequently refined using the best value of E_0 and c, obtained by the method of least squares, in which c is the temperature dependence of the activation energy, dE/dT, and E_0 is defined by

$$E_{act}^{obsd} = E_0 + c(T_a + T_b)/2 \qquad (2)$$

Values of entropy of activation were then calculated from

$$\ln k_a = \ln (k/h) + \ln (T_a + T_b)/2 + 1 + \Delta S^*/R - E_{act}/RT_a \qquad (3)$$

in which k and h are the Boltzman and Planck constants, respectively.

Equilibrium constants for the association of the α,α-dichlorotoluenes with micelles formed from ionic surfactants were estimated from the dependence of rate of hydrolysis on surfactant concentration employing the following expression[11]

$$1/(k_a - k_{obsd}) = 1/(k_a - k_m) + 1/(k_a - k_m)[N/K(C_d - \text{cmc})] \qquad (4)$$

in which k_a is the rate constant observed in aqueous solution, k_{obsd} is the rate constant observed at each surfactant concentration, k_m is the rate constant observed at saturating concentrations of surfactant, N is the aggregation number of the micelle, C_d is the concentration of surfactant, cmc is the critical micelle concentration, and K is the equilibrium constant of interest. A value of N equal to 70 was employed in the calculations.

Results

First-order rate constants for hydrolysis of α,α-dichlorotoluene and the *p*-methyl and *p*-chloro derivatives in aqueous solution at 30° and ionic strength 0.5 were mea-

Table I
First-Order Rate Constants for Hydrolysis of α,α-Dichlorotoluenes at 30° as a Function of the Volume Per Cent Dioxane in Water–Dioxane Mixtures[a]

Volume per cent dioxane	Substituent p-Methyl	 Hydrogen	 p-Chloro
None	13.0	0.17	0.11
5		0.10	
10	5.0	0.045	0.035
15		0.025	
20	2.0	0.015	0.010
30	0.7	0.005	0.003
40	0.08		0.0008
50	0.012	0.00026	0.0016

[a] All rate constants have units of $\min^{-1}$.

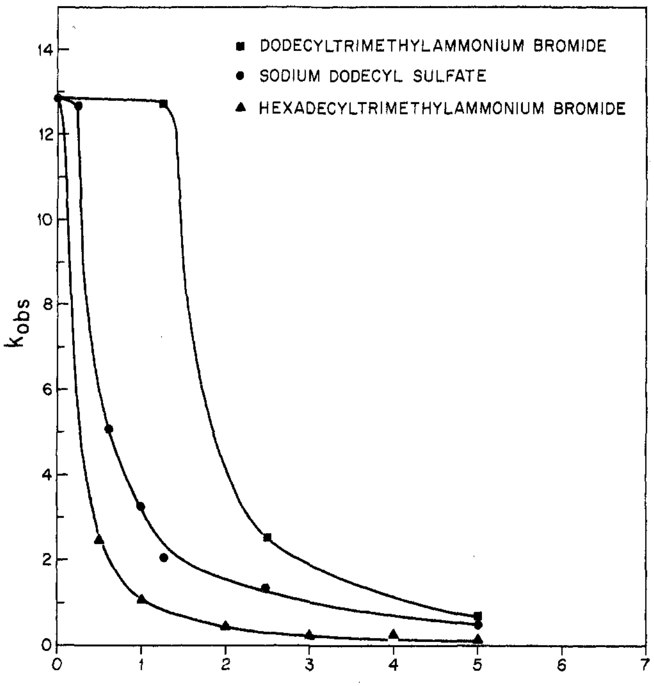


Figure 1. First-order rate constants for hydrolysis of p-methyl-α,α-dichlorotoluene plotted as a function of the concentration of sodium dedecyl sulfate, dodecyltrimethylammonium bromide, and hexadecyltrimethylammonium bromide. All reactions were carried out at 30°; ionic strength was not maintained constant.

Table II
The Effect of Ionic Surfactants on the Rate of Hydrolysis of Substituted α,α-Dichlorotoluenes[a]

Surfactant	Concn, M	Substituent p-Chloro	 Hydrogen	 p-Methyl
Sodium dodecyl sulfate	0.0	0.11	0.17	12.9
	0.005	0.099	0.12	12.7
	0.01	0.043	0.068	3.3
	0.02	0.012	0.037	1.4[c]
	0.04	0.006	0.028[b]	
	0.05	0.0045	0.016	0.5
Dodecyltrimethylammonium bromide	0.0	0.11	0.17	12.9
	0.006	0.10		
	0.012	0.09	0.14[d]	
	0.025	0.008	0.025[b]	2.6
	0.04	0.0049	0.019	
	0.05	0.0034	0.014	0.7
Hexadecyltrimethylammonium bromide	0.0	0.11	0.17	12.9
	0.005	0.089	0.047	2.5
	0.01	0.0036	0.024	1.1
	0.02	0.0036	0.014	0.5
	0.03	0.0021	0.011	0.3
	0.04	0.0011	0.007	0.3
	0.05	0.0010	0.006	0.2

[a] Rate constants have units of $\min^{-1}$ and were measured at 30°. [b] 0.03 M. [c] 0.025 M. [d] 0.01 M.

sured as a function of pH over the pH range 2–10. In each case, the rate of hydrolysis was observed to be pH independent over the range studied, in accord with previous observations.[6,8] The rate of hydrolysis increases markedly with increasing electron donation from the polar substituent; first-order rate constants measured under these conditions are 0.165, 0.11, and 12.9 $\min^{-1}$ for the unsubstituted, p-chloro-, and p-methyl compounds, respectively. Note that the introduction of the mildly electron releasing p-methyl substituent increases the rate of hydrolysis at 30° about 78-fold. On the other hand, the p-chloro substituent has only a small rate-decreasing effect. Hammett plots constructed employing either σ or σ^+ substituent constants are curved.

First-order rate constants for hydrolysis of the α,α-dichlorotoluenes in aqueous dioxane solutions are collected as a function of the volume per cent of dioxane in Table I. In each case, the rate decreases rapidly with increasing dioxane concentration. In 50% aqueous dioxane, rate decreases for the hydrolysis of the p-chloro, unsubstituted, and p-methyl compounds are 680-, 640-, and 1080-fold, respectively, in comparison to rates in water. The data are well-correlated by the equation of Winstein and Grunwald:[12] $\log k/k_0 = mY$. In each case, values of m near 1.3 were obtained.

Hydrolysis of α,α-dichlorotoluenes is markedly inhibited by ionic surfactants, both cationic and anionic. In Figure 1, first-order rate constants for the hydrolysis of p-methyl-α,α-dichlorotoluene are plotted as a function of the concentration of sodium dodecyl sulfate, dodecyltrimethylammonium bromide, and hexadecyltrimethylammonium bromide. Comparable data were obtained with the other substrates. Note that each surfactant is an inhibitor for the hydrolysis reaction. The rates become essentially constant at high surfactant concentrations, reflecting complete incorporation of the substrate into the micellar pseudophase. At saturating concentrations of surfactant, rate decreases in the range of 10–100-fold are observed, depending on the nature of the surfactant and substrate. Quantitative data for all substrates studied are collected in Table II.

From the dependence of rate constant on surfactant concentration, approximate equilibrium constants for association of the α,α-dichlorotoluenes with sodium dodecyl sulfate and hexadecyltrimethylammonium bromide micelles were calculated as described above: p-chloro, 42,000 M^{-1}; unsubstituted, 31,000 and 56,000 M^{-1}; p-methyl, 60,000 and 116,000 M^{-1}, respectively. Thus, the equilibrium constants for association of the α,α-dichlorotoluenes are uniformly larger with the more hydrophobic cationic micelles than with the anionic ones.

Values of the entropy of activation for hydrolysis of p-chloro, unsubstituted, and p-methyl-α,α-dichlorotoluenes at 30° were measured as described above. Results obtained are, p-chloro, −7.7 eu; unsubstituted, −11.3 eu; p-methyl, −12.9 eu. Results are considered to be accurate to within ±1.5 eu. These values are consistent with those previously measured for the unsubstituted compound in aqueous ethanol solutions.[7] Clearly, the trend of the values of entropy of activation is contrary to the trend in reactivity. Thus, the greater reactivity of the p-methyl compared to the p-

Table III
Rate Constants for the Hydrolysis of Substituted α,α-Dichlorotoluenes in Aqueous Solution and in the Presence of 0.05 M Hexadecyltrimethylammonium Bromide as a Function of the Concentration of Added Salts[a]

	Additions					
Substrate	None	0.8 M KCl	0.8 M KNO_3	0.05 M HTAB[b]	0.05 M HTAB + 0.8 M KCl	0.05 M HTAB + 0.8 M KNO_3
p-Methyl	12.9	9.0[c]	18.0	0.22	0.10	0.22
Hydrogen	0.17	0.19	0.23	0.006	0.008	0.008
p-Chloro	0.11	0.05	0.075	0.001	0.0003	0.0017[d]

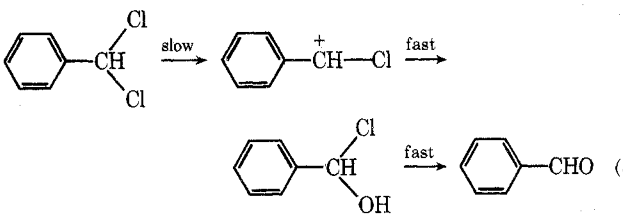
[a] All rate constants have units of $\min^{-1}$ and were measured at 30°. [b] Hexadecyltrimethylammonium bromide. [c] 1.0 M KCl. [d] 0.08 M KNO_3.

chloro substrate is a consequence of a lower energy of activation, not a more positive ΔS^*.

Effects of the concentration of salts on the rate of hydrolysis of the α,α-dichlorotoluenes were measured in aqueous solution and in the presence of 0.05 M hexadecyltrimethylammonium bromide. Results are collected in Table III. In all cases, the effects are small. Changes that are observed show no clear trends in terms of nature of the polar substituent or nature of the salt.

Discussion

The most compelling evidence for rate-determining carbon–chlorine bond cleavage for the hydrolysis of α,α-dichlorotoluenes (eq 5) is provided by the work of Tanabe



(5)

and Ido who demonstrated that (i) hydrolysis of α,α-dichlorotoluene in water is pH independent over the range 0–14; (ii) that chloride is a more effective inhibitor than azide or sulfate for the reaction; and (iii) that hydrolysis proceeds more rapidly than exchange of chloride ion into the substrate.[6] This conclusion is supported by the observation that electron-donating polar substituents increase the rate of hydrolysis in aqueous ethanol mixtures[8] although it did not prove possible to correlate the rate constants with a linear free energy relationship.

Results reported in this manuscript corroborate this conclusion. For the three substrates studied, rate constants independent of pH have been observed over the range investigated, confirming the absence of detectable acid or base catalysis. The effect of polar substituents on rate provides strong evidence for a carbonium ion mechanism. Specifically, the striking rate-promoting effect of the *p*-methyl substituent, in both water and 50% dioxane, argues for an electron-deficient center in the transition state. The evidence is less compelling in the case of the *p*-chloro compound, which is only slightly less reactive than the unsubstituted derivative. The effect of methyl group substitution on reactivity is more pronounced than in the case of acid-catalyzed hydrolysis of benzaldehyde acetals[13-17] for which rate-determining carbonium ion formation has been established.[1-3]

The powerful inhibition of hydrolysis of α,α-dichlorotoluenes by dioxane (Table I) provides additional evidence in favor of rate-determining carbonium ion formation for these reactions. Since the transition state is more polar than the ground state, it follows that less polar solvents will inhibit the reaction. The large value of m derived from use of the equation of Winstein and Grunwald suggests that the transition state has considerable polar character. That is, rupture of the carbon–chlorine bond may be nearly complete in the transition state.

The marked inhibition of hydrolysis of α,α-dichlorotoluenes by ionic surfactants, independent of charge (Figure 1, Table II), is also consistent with a carbonium ion mechanism. It is known that the micellar surface is substantially less polar than is the bulk phase[18,19] and hence, according to the argument presented above, incorporation of the substrates onto this surface should retard the reaction. That the effect observed is predominantly a result of the lowered polarity at the micellar surface rather than electrostatic interactions is established both by the fact that inhibition is independent of the nature of the micellar surface charge and is little affected by the addition of salts (Table III) which results in an increase in the extent of micellar charge neutralization. The inhibition of hydrolysis of α,α-dichlorotoluenes by sodium dodecyl sulfate is in marked contrast to catalysis of hydrolysis of acetals and ortho esters elicited by the same surfactant.[14,16,19,20] The distinctive behavior is undoubtedly the consequence of the cationic nature of the transition state for hydrolysis of acetals and ortho esters, on the one hand, and the zwitterionic nature of the transition state for hydrolysis of the α,α-dichlorotoluenes, on the other.[17]

There is some reason to believe that the carbonium ion derived from the α,α-dichlorotoluenes is not highly selective in its reactions with nucleophiles. The small salt effects observed in this work suggest that it is difficult to trap this carbonium ion with chloride ion or nitrate ion. Moreover, Tanabe and Ido found little effect on the rate of hydrolysis of α,α-dichlorotoluene following addition of azide, sulfate, piperidine, or thiophenol.[6] These results suggest that the carbonium ion reacts with the first nucleophile that it encounters, usually water. In contrast, it is quite possible to trap the more stable carbonium ion formed in the hydrolysis of ortho esters.[21]

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Registry No.—α,α-Dichlorotoluene, 98-87-3; *p*-methyl-α,α-dichlorotoluene, 23063-36-7; *p*,α,α-trichlorotoluene, 13940-94-8; sodium dodecyl sulfate, 151-21-3; dodecyltrimethylammonium bromide, 1119-94-4; hexadecyltrimethylammionium bromide, 57-09-0.

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