summarized in Tables XI and XII.

Registry No. 1, 18707-60-3; 2, 10544-63-5; 3, 18060-77-0; 4, 3246-27-3; 5, 16491-62-6; 6, 46472-88-2; 7, 2445-93-4; 8, 1552-67-6; 9, 2351-88-4; 10, 2351-90-8; 11, 78217-11-5; 12, 2351-97-5; 13, 6048-09-5; (*E*)-14-2, 22485-82-1; (*Z*)-14-2, 22528-27-4; (*E*)-14-7, 78217-12-6; (*Z*)-14-7, 78217-13-7; (*E*)-14-8, 78217-14-8; (*Z*)-14-8, 78217-15-9; (*E*)-14-9, 78217-16-0; (*Z*)-14-9, 78217-17-1; (*Z*)-14-10, 78217-18-2; (*Z*)-1410, 78217-19-3; (*E*)-14-11, 78217-20-6; (*Z*)-14-11, 78217-21-7; (*E*)-15-2, 78217-22-8; (*Z*)-15-2, 78217-23-9; (*E*)-15-7, 78217-24-0; (*Z*)-15-7, 78217-25-1; (*E*)-15-8, 78217-26-2; (*Z*)-15-8, 78217-27-3; (*E*)-15-9, 78217-28-4; (*Z*)-15-9, 78217-29-5; (*E*)-15-10, 78217-30-8; (*Z*)-15-10, 78217-31-9; (*E*)-15-11, 78217-32-0; (*Z*)-15-11, 78217-33-1; crotonic acid, 3724-65-0; malonic acid, 141-82-2.

Kinetic and Thermodynamic Study of the Base-Catalyzed Oxidative Cleavage of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol

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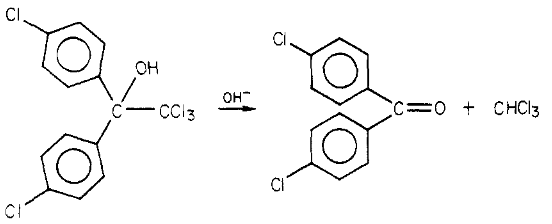
The kinetics and mechanism of the base-catalyzed oxidative cleavage of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (**1a**) and 1,1-diphenyl-2,2,2-trichloroethanol (**1b**) have been studied as a function of base concentration, solvent, and temperature. The pseudo-first-order rate constant for the disappearance of both **1a** and **1b** increases linearly at low base concentration, reaching a plateau at high hydroxide ion concentration. From data obtained in the plateau region values of 18.7 kcal/mol, 21.3 kcal/mol, and 8.8 eu were determined for the free energy, enthalpy, and entropy of activation of **1a**, respectively. The values of the activation parameters for compound **1b** are similar to those described for **1a**. The data obtained are consistent with an ElcB-type mechanism.

It has been recently reported[1] that in the presence of hexadecyltrimethylammonium bromide (CTAB) and hexadecyldimethyl(2-hydroxyethyl)ammonium bromide (CHEDAB) enhancements of 200- and 345-fold of the rate of the base-catalyzed oxidative cleavage of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (**1a**) occurs in aqueous basic solutions (eq 1). Despite the fact that **1a** is a pesticide used on a commercial scale and that it has also been identified as a metabolite in the enzymatic degradation of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT),[2-4] there is not any detailed study available about the stability, kinetics, and mechanism of its oxidation to 4,4'-dichlorobenzophenone (**2a**) in basic solutions.



(1)

Considering that **1a** has a reasonably acidic proton and a not very labile leaving group, it represents an ideal compound for detection of an ElcB type mechanism similar to the "irreversible" first-order carbanion elimination.[5-7] The decomposition of **1a** has many biological implications. Thus, it appeared of interest to study this reaction in order to obtain information about the mechanism of the base-catalyzed oxidative cleavage and of the kinetic and thermodynamic stability of **1a** in aqueous solutions.

Experimental Section

1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (**1a**) was purchased from Chemical Service, and its purity found to be satisfactory by thin-layer chromatographic, UV, and IR analysis. The compound 1,1-diphenyl-2,2,2-trichloroethanol (**1b**) was prepared by a previously described procedure.[8] Methanol was obtained from Merck Chemical Co., and water was deionized and distilled. The pH of the aqueous solutions was adjusted by the addition of NaOH and determined by means of a Methrohm E-350-B pH meter. Stock solutions of **1a** and **1b** (10^{-3} M) were prepared in methanol and kept in the refrigerator, being stable for several weeks. In solutions with pH >11, the concentration of hydroxide ion was directly determined by titration.

Rates of oxidation of **1a** were determined by following (Shimadzu UV-210-A spectrophotometer for the slower runs and Durrum JASCO stopped-flow instrument for the faster ones) the appearance of 4,4'-dichlorobenzophenone (**2a**) at 263 nm in methanol and at 267 nm in water; for compound **1b** the reaction was monitored at 258 nm. The temperature for the kinetic runs was maintained within ±0.1 °C of the desired value by using a water-jacketed cell. Individual pseudo-first-order rate constants, k_{expt} values, were obtained from linear plots of ln $(A_\infty - A_t)$ vs. time. All of these plots were linear for at least 90% of the reaction, and the correlation coefficients were greater than 0.99.

Chloroform was identified with a Varian 2440-D gas chromatograph by using a 2 m × 3.2 mm column packed with squalane. The temperatures of the column, detector, and injection block were 85, 120, and 125 °C, rspectively. A retention time of 80 s was found. Under our experimental conditions the hydrolysis of chloroform to carbon monoxide and formate ($k_2 = 2.3 \times 10^{-5}$ M^{-1} s^{-1} at 20.0 °C[9]) is not observed.

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Table I. Pseudo-First-Order Rate Constants for the Base-Catalyzed Oxidative Cleavage of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol and 1,1-Diphenyl-2,2,2-trichloroethanol in Water at 25.0 °C[a]

1a		1b	
[KOH], M	k_{expt}, s^{-1}	[KOH], M	k_{expt}, s^{-1}
3.18×10^{-5}	8.38×10^{-4}	5.67×10^{-5}	9.76×10^{-4}
1.00×10^{-4}	2.20×10^{-3}	1.01×10^{-4}	1.60×10^{-3}
	2.34×10^{-3}	1.79×10^{-4}	2.70×10^{-3}
1.59×10^{-4}	2.91×10^{-3}	3.19×10^{-4}	4.62×10^{-3}
	3.33×10^{-3}	5.67×10^{-4}	7.45×10^{-3}
2.53×10^{-4}	5.43×10^{-3}	1.00×10^{-3}	9.07×10^{-3}
3.18×10^{-4}	6.81×10^{-3}	2.28×10^{-3}	2.13×10^{-2}
4.01×10^{-4}	8.73×10^{-3}		2.31×10^{-2}
5.05×10^{-4}	1.01×10^{-2}	4.56×10^{-3}	6.93×10^{-2}
6.36×10^{-4}	1.12×10^{-2}	1.00×10^{-2}	9.54×10^{-2}
1.42×10^{-3}	3.22×10^{-2}		1.03×10^{-1}
4.74×10^{-3}	7.47×10^{-2}	2.28×10^{-2}	1.60×10^{-1}
9.48×10^{-3}	8.75×10^{-2}		1.63×10^{-1}
2.37×10^{-2}	1.08×10^{-1}	4.56×10^{-2}	2.25×10^{-1}
4.74×10^{-2}	1.24×10^{-1}		2.40×10^{-1}
7.11×10^{-2}	1.21×10^{-1}	1.00×10^{-1}	2.51×10^{-1}
1.18×10^{-1}	1.20×10^{-1}		2.41×10^{-1}
2.37×10^{-1}	1.19×10^{-1}		2.41×10^{-1}

[a] [1a] = 7.0×10^{-6} M and [1b] = 1.5×10^{-5} M.

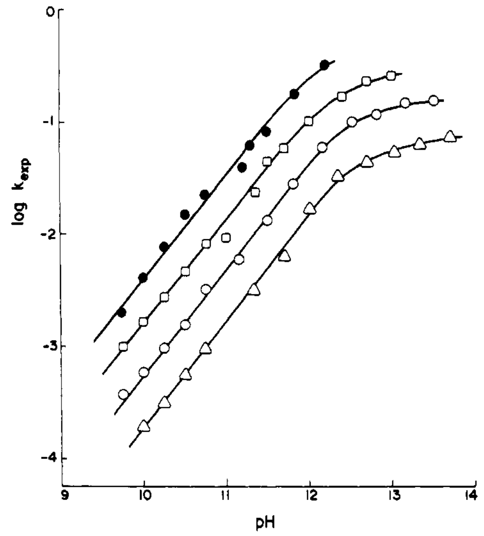


Figure 1. Plot of log k_{expt} against pH for the reaction of 1,1-diphenyl-2,2,2-trichloroethanol with base in water at 15.0 (△), 20.0 (○), 25.0 (□), and 30.0 °C (●).

The energy of activation, E_a, was determined from linear plots of ln k_2 vs. $1/T$, were k_2 represents the experimental first-order constant in the plateau region. The enthalpy of activation (ΔH^*) was obtained by using the relation $\Delta H^* = E_a - RT$, the entropy of activation (ΔS^*) from $\Delta S^* = 2.303R(\log k_2 - \log ek/h - \log T + E_a/2.303RT)$, and the free energy of activation (ΔG^*) from $\Delta G^* = \Delta H^* - T\Delta S^*$.

Table II. Activation Parameters for the Oxidation of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol and 1,1-Diphenyl-2,2,2-trichloroethanol in Water

compd[a]	$\Delta G^\ddagger$, kcal/mol	$\Delta H^\ddagger$, kcal/mol
1a	18.7	21.3
1b	18.1	20.8

[a] $\Delta S^\ddagger$ = 8.8 eu in both cases.

Table III. Pseudo-First-Order Rate Constants for the Base-Catalyzed Oxidative Cleavage of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol in Methanol at 25.0 °C[a]

[KOH], M	k_{expt}, s^{-1}	[KOH], M	k_{expt}, s^{-1}
2.90×10^{-3}	9.30×10^{-4}	1.58×10^{-1}	4.63×10^{-2}
5.90×10^{-3}	1.57×10^{-3}		4.56×10^{-2}
8.90×10^{-3}	3.52×10^{-3}	3.16×10^{-1}	7.57×10^{-2}
1.18×10^{-2}	5.18×10^{-3}	4.74×10^{-1}	9.69×10^{-2}
1.48×10^{-2}	5.24×10^{-3}		1.06×10^{-1}
1.78×10^{-2}	6.20×10^{-3}	6.00×10^{-1}	1.17×10^{-1}
2.07×10^{-2}	8.15×10^{-3}		1.16×10^{-1}
2.37×10^{-2}	9.14×10^{-3}		1.17×10^{-1}
2.67×10^{-2}	1.04×10^{-2}	7.90×10^{-1}	1.43×10^{-1}
4.50×10^{-2}	1.36×10^{-2}	1.03×10^{-1}	1.68×10^{-1}
8.51×10^{-2}	2.25×10^{-2}		1.76×10^{-1}
	2.39×10^{-2}	1.25×10^{-1}	2.00×10^{-1}
	2.43×10^{-2}	1.48×10^{-1}	2.00×10^{-1}

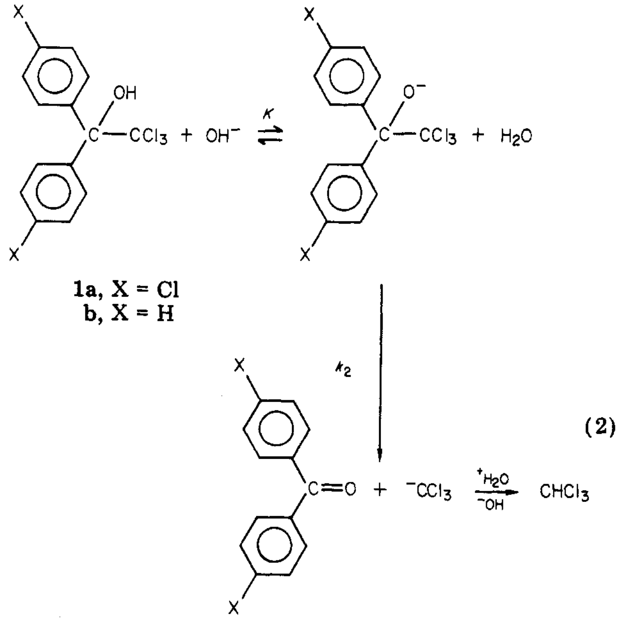
[a] [1a] = 2.0×10^{-5} M.

Results and Discussion

The values of the pseudo-first-order rate constant, k_{expt}, for the oxidation of **1a** and 1,1-diphenyl-2,2,2-trichloroethanol (**1b**) to **2a** and benzophenone (**2b**), respectively, are given in Table I. For both compounds (**1a** and **1b**) an increase in k_{expt} is observed up to a plateau, which is reached at hydroxide ion concentration higher than 0.05 M. The temperature dependence of k_{expt} as a function of hydroxide ion concentration for compound **1b** is illustrated in Figure 1. As can be seen at pH values in the range of 9.5–12 the slope of the lines is 1.0, which indicates a first-order dependence in hydroxide ion of the reaction. At higher pH the value of the slope decreases, reaching a limiting value of zero. The behavior of compound **1a** is identical with that reported for **1b**. The experimental results are consistent with the reaction scheme depicted in eq 2, and accordingly the value of k_{expt} is described by

$$k_{expt} = \frac{k_2K[OH^-]}{1 + K[OH^-]} \tag{3}$$

eq 3, where k_2 represents the first-order rate constant for the formation of benzophenone and K represents the equilibrium constant for the alkoxide ion formation.



1a, X = Cl
b, X = H

(2)

2a, X = Cl
b, X = H

The linear dependence observed at low hydroxide ion concentration (Figure 1) is consistent with eq 3, assuming that 1 ≫ $K[OH^-]$, and the slope of the line corresponds to k_2K. Combining the value of k_2K with k_2 obtained from the limiting value of k_{expt} at high hydroxide ion concentration, K values of 166 and 47 M^{-1} are obtained for compounds **1a** and **1b**, respectively. Values of pK_a of 11.8 and 12.3 can be estimated from the kinetic data for the ionization constant of (**1a** and **1b**), since $pK_a = pK + pK_w$. The pK_a values obtained are the range expected for this type of compound.[10]

The activation parameters for the reaction were calculated from k_2 values determined at several temperatures as already described. The results obtained for the free energy ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), and entropy ($\Delta S^{\ddagger}$) of activation are given in Table II. Considering that for $\Delta S^{\ddagger}$ the initial state is a anion and that the transition state (4) has considerable charge delocalization, water will preferentially solvate the alkoxide rather than the transition state, since the distribution of charge in 4 will make it appear as a large anion to the solvent. This decrease in structuring of the solvent, which results from progress along the reaction coordinate from the reactant to the transition state, is more likely to be responsible for the observed entropy of activation.

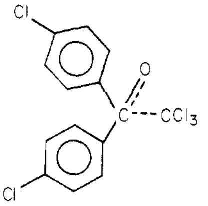

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Table III contains the results obtained for the base-catalyzed oxidative cleavage of **1a** with methanol as the solvent. The observed pseudo∞first-order rate constant increases with hydroxide ion concentration up to a plateau, which is reached with 1.25 M base. The value of k_2 determined from the plateau region with the use of eq 3 was 0.20 s^{-1}. The increase in k_2 with a decrease in polarity of the solvent (k_2 in methanol > k_2 in water) is consistent with the electrostatic theory of Hughes and Ingold, for a reaction in which charge delocalization occurs going from the initial to the transition state.

This elimination is mechanistically similar to the base-catalyzed decomposition of cyanohydrins, but the kinetic analysis is simpler in this case since the pK_a of the trichloromethyl carbanion, which is the leaving group in the oxidative cleavage, is much higher than that of cyanide. Thus, chloroform is formed spontaneously, making the second step of the reaction irreversible for practical purposes. This statement does not mean that the principle of microscopic reversibility is broken in this particular reaction but only that the trichloromethyl carbanion is protonated faster than it reacts with the ketones **2a** and **2b**, in the pH range studied. The described results are consistent with an ElcB-type mechanism, the decomposition of the alkoxide being the rate-limiting step of the reaction.

Table IV. Activation Parameters for the Oxidation of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol in Water, Aqueous Methanol, Methanol, and Ethanol[a]

solvent	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
water	16.3	13.8	−8.2
20% v/v methanol–water	16.6	17.2	+2.0
40% v/v methanol–water	16.9	21.6	+15.5
60% v/v methanol–water	17.4	23.2	+19.5
80% v/v methanol–water	17.9	25.4	+24.9
methanol	18.6	26.1	+25.1
ethanol	16.5	26.3	+32.8

[a] Determined from the temperature dependence of k_2K.

Table IV contains the activation parameters obtained for the reaction of **1a** with base in the region of linear dependence in hydroxide ion in water, water–methanol mixtures, methanol, and ethanol. As can be seen, the enthalpy and entropy of activation have a strong dependence on solvent composition. Since the activation parameters in the region of linear dependence reflect both k_2 and K, it is not possible to compare them directly with the activation parameters in the plateau region (Table II). By use of these parameters as a solvent polarity scale and on the assumption that for the base-catalyzed oxidative cleavage of **1a** in the presence of aqueous micellar solutions of CTAB the values of the enthalpy and entropy of activation are 27.7 kcal/mol and 25.9 eu, respectively, it seems that the microenvironment in the micellar catalyzed reaction resembles that of methanol or ethanol. The result is consistent with the surface polarity estimated by Menger[12] and others[13] and does not agree with that of the Hartley model,[14] which considers the micellar surface as an aqueous salt solution. This observation that the activation parameters for CTAB-catalyzed hydrolysis are more similar to basic methanolysis than to uncatalyzed basic hydrolysis has previously been reported for the reactions of toluanilides.[15]

Our results strongly supports the idea that the decomposition of **1a** leading to the formation of 4,4′-dichlorobenzophenone may proceed via a similar pathway in biological systems. In fact, the kinetic stability of **1a** is such that spontaneous decomposition, as opposite to an enzyme-catalyzed process may be responsible for the appearance of **2a** in vivo.

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Registry No. **1a**, 115-32-2; **1b**, 6795-82-0.

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