br, CH_2CH_3), 3.00–4.10 (7 H, br, CO_2CH_3 and CH_2), 7.10–8.00 (15 H, m, H Ar); MS, *m/z* (relative intensity) 481 (M^+, 10), 365 (M − 116, 100), 262 (24), 183 (33), 116 (12), 108 (32), 88 (26), 60 (37).

8b (R = CO_2Et): 91.5% yield; mp 124–125 °C; IR 1710, 1660 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 1.13 (3 H, t, CH_2CH_3), 3.50 (3 H, s, CH_3), 4.06 (2 H, q, CH_2), 7.15–7.95 (15 H, m, H Ar); MS, *m/z* (relative intensity) 438 (M^+, 14), 365 (M − 73, 100), 262 (31), 183 (35), 108 (15).

[Bis(dimethyldithiocarbamyl)methylene]triphenylphosphorane (9a). (A) Potassium *tert*-butoxide (1.12 g, 10 mmol) was added to a suspension of methyltriphenylphosphonium bromide (3.57 g, 10 mmol) in DME (45 mL) under magnetic stirring and nitrogen atmosphere at room temperature. The solution soon turned light yellow, and the color became more intense with time. Stirring was continued for 3 h. Then a solution of dimethylthiocarbamoyl disulfide (1.20 g, 5 mmol) and benzaldehyde (2.12 g, 2 mmol) in DME (15 mL) was added, and the solution was heated at reflux for 3.5 h. The solvent was removed in vacuo, and the residue was washed with acetone (10 mL) and water (5 mL), affording a light yellow solid (1.0 g, 38.5% yield). A sample recrystallized from benzene had mp 233–235 °C: IR 1490, 1370, 1245, 980, 755, 710, 695, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (12 H, br, CH_3), 7.30–8.10 (15 H, m, H Ar); MS *m/z*, (relative intensity) 514 (M^+, 0.2), 426 (M − 88, 2), 294 (4), 293 (3), 262 (6), 183 (18), 108 (10), 88 (100).

(B) Sodium hydride (80% dispersion in mineral oil 0.15 g, 5 mmol) was added to a suspension of **3a** (1.31 g, 2.5 mmol) and dimethylthiocarbamoyl disulfide (0.60 g, 2.5 mmol) in anhydrous DME (45 mL) under stirring and nitrogen atmosphere at room temperature. Stirring was continued for 1 h; then the mixture was heated at reflux for 1.5 h, turning into an almost complete solution, which was concentrated to 20 mL and cooled. The separated solid was filtered and washed with water (5 mL). Yellow crystals were left, mp 235–236 °C, identified as **9a** by comparison with a sample from A (0.72 g, 56.2% yield; part of **9a** remained in DME solution).

9b was similarly obtained from **3d** and diethylthiocarbamoyl disulfide. **9b**: yellow crystals; mp 139–141 °C; 66.5% yield; ^1H NMR ($CDCl_3$) δ 1.05 (12 H, br, CH_3), 3.75 (8 H, br, CH_2), 7.25–8.15 (15 H, m, H Ar).

Acknowledgment. I am very grateful to Dr. Alberto Griffini for GC–MS spectroscopic analysis and to Leonardo Scaglioni for recording ^1H NMR spectra. This work was made possible by support of the Italian National Research Council, Rome (CNR, Progetto Finalizzato Chimica Fine e Secondaria).

Registry No. **1a**, 3020-28-8; **1b**, 1034-49-7; **1c**, 5293-84-5; **2**, 72140-17-1; **3a**, 110637-62-2; **3b**, 110637-63-3; **3c**, 110637-64-4; **3d**, 110637-65-5; **3e**, 110637-66-6; **3f**, 110637-67-7; **3g**, 110637-68-8; **3h**, 110637-69-9; **3i**, 110637-70-2; **3l**, 110637-71-3; **4**, 110637-72-4; **5**, 110637-73-5; **6**, 68089-86-1; (*E*)-**7a**, 23846-99-3; (*Z*)-**7a**, 110637-74-6; (*E*)-**7b**, 110637-75-7; (*Z*)-**7b**, 110637-76-8; (*E*)-**7c**, 110637-77-9; (*Z*)-**7c**, 110637-78-0; (*E*)-**7d**, 110637-79-1; (*Z*)-**7d**, 110637-80-4; **8a** (R′ = Me), 110637-83-7; **8a** (R′ = Et), 110637-84-8; **8a** (R = CO_2Et), 110637-85-9; **8b** (R′ = Me), 110637-86-0; **8b** (R′ = Et), 110637-87-1; **8b** (R = CO_2Et), 110637-88-2; **9a**, 110637-81-5; **9b**, 110637-82-6; $Ph_3P{=}CHCOMe$, 1439-36-7; $Ph_3P{=}CHCO_2Me$, 2605-67-6; EtO_2CSSCO_2Et, 6365-90-8; MeSSMe, 624-92-0; EtSSEt, 110-81-6; sodium diethyldithiocarbamate, 148-18-5; piperidinium *N,N*-pentamethylenethiocarbamate, 98-77-1; potassium *O*-ethyl thiocarbonate, 35832-93-0; potassium *O*-ethyl xanthate, 140-89-6; potassium thioacetate, 10387-40-3; potassium thiocyanate, 333-20-0; sodium thiobenzoate, 51066-54-7; thiobenzoic acid, 98-91-9; sodium thiophenoxide, 930-69-8; benzaldehyde, 100-52-7; methyltriphenylphosphonium iodide, 2065-66-9; diphenyl disulfide, 882-33-7; sodium thioethoxide, 811-51-8; ethyl disulfide, 110-81-6; dibenzyl disulfide, 150-60-7; styrene, 100-42-5; thiophenol, 108-98-5; triphenyl[(phenylthio)methyl]phosphonium chloride, 13884-92-9; dimethylthiocarbamoyl disulfide, 137-26-8; triphenylphosphine, 603-35-0; 4-chlorobenzaldehyde, 104-88-1; 2,4-dichlorobenzaldehyde, 874-42-0; 3-pyridinecarboxaldehyde, 500-22-1; methyltriphenylphosphonium bromide, 1779-49-3; diethylthiocarbamoyl disulfide, 97-77-8; triphenylphosphine oxide, 791-28-6; methyl dimethyldithiocarbamate, 3735-92-0.

Mechanistic Studies on the Basic Hydrolysis of 2,2,2-Trichloro-1-arylethanones

César Zucco,* Claudio F. Lima, Marcos C. Rezende, Jose F. Vianna, and Faruk Nome*

Departamento de Química, Universidade Federal de Santa Catarina, 88.001 Florianopolis, SC, Brazil

Received May 4, 1987

The basic hydrolysis of 2,2,2-trichloro-1-phenylethanone (**1a**), 2,2,2-trichloro-1-(*p*-methoxyphenyl)ethanone (**1b**), and 2,2,2-trichloro-1-(*p*-chlorophenyl)ethanone (**1c**) has been studied in the pH range 5.5–13.2. In all cases the reaction products were chloroform and the corresponding benzoate. The reaction is first order toward both the ethanone and hydroxide ion and proceeds via an addition–elimination-type mechanism. The initial addition step forms the corresponding ethanone hydrates, which, depending on the pH, will form the mono- and dianionic intermediates, the elimination of CCl_3 from the mono- and/or dianionic species being the rate-limiting step of the reaction.

Introduction

Organic reactions in which the trichloromethyl is a leaving group have long been known, the haloform reaction being a classical example found in any textbook of organic chemistry.[1] In spite of this, systematic studies on the leaving group ability of the CCl_3 group, as compared to other more common groups, are scarce.

We have been interested for some years in exploiting the trichloromethyl as a leaving group in synthetic transformations and in investigating in detail the mechanisms involved in these reactions.[2-5] As an example, 1,1-diaryl-2,2,2-trichloroethanols undergo a base-catalyzed oxidative cleavage to yield chloroform and the corresponding benzophenone derivatives. This elimination proceeds via

---

[1] March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 575.

[2] Nome, F.; Erbs, W.; Correia, V. R. *J. Org. Chem.* **1982**, *46*, 3802.

[3] Nome, F.; Schwingel, E. W.; Ionescu, L. G. *J. Org. Chem.* **1980**, *45*, 705.

[4] Lins, H. S.; Nome, F.; Rezende, M. C.; de Souza, I. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1521.

[5] Uieara, M.; Zucco, C.; Zanette, D.; Rezende, M. C.; Nome, F. *J. Chem. Soc., Perkin Trans. 2* **1987**, 463.

0022-3263/87/1952-5356$01.50/0

a $(ElcB)_R$ mechanism.[3] The decomposition of 1-aryl-2,2,2-trihaloethanols in basic medium follows the same mechanism, a reaction which results in the formation of the haloform and the corresponding benzaldehyde.[4] When the trichloromethyl is adjacent to a carbonyl group, as in the 1-aryl-2,2,2-trichloroethanones **1**, the reaction with alcohols results in the formation of the corresponding benzoate esters, while treatment of **1** with ethylamine in dry dioxane yields the amides ArCONHEt in high yields.[5] The reaction of **1** with alcohols proceeds via a hemiketal intermediate, and the overall mechanism is an addition–elimination process, the reactivity of the alcohols decreasing in the order MeOH > EtOH > *n*-PrOH > *n*-BuOH.[5] The reaction of the trichloroethanones **1** with hydroxide ion has long been known to form the corresponding benzoates,[6] but the detailed mechanism of this conversion has not been studied yet. As was the case for the alcoholysis of **1**, the tetrahedral intermediate formed by the addition of OH^- to the carbonyl group should be relatively stable, the trichloromethyl being a comparatively poor leaving group.

The mechanism of the basic decomposition of 2,2,2-trichloro-1-arylethanones **1** is the subject of the present work.

Experimental Section

The trichloroethanones **1a** and **1c** were prepared by chlorination of the corresponding acetophenones, following previously reported procedures:[7-9] 2,2,2-trichloro-1-phenylethanone (**1a**) had bp 142 °C (25 mmHg) [lit.[10] bp 145 °C (25 mmHg)], and 2,2,2-trichloro-1-(*p*-chlorophenyl)ethanone (**1c**) had bp 177 °C (40 mmHg) [lit.[10] bp 181 °C (40 mmHg)]. Compound **1b**, 2,2,2-trichloro-1-(*p*-methoxyphenyl)ethanone, had mp 33–34 °C (lit.[11] 33–34.5 °C) and was prepared by oxidation of the corresponding 2,2,2-trichloro-1-(*p*-methoxyphenyl)ethanol with pyridinium chlorochromate (PCC)[12] in a similar way as that described for oxidation of alcohols. All the ethanones were further characterized by their IR and NMR spectra and their purity confirmed by GLC.

All reacting solutions were prepared with deionized, distilled, and degassed water. The pH of these solutions were controlled by buffers which were found not to cause any rate influence. At pH values above 12, the hydroxide ion concentration was directly determined by titration.

Stock solutions of the ethanones were prepared with dry acetonitrile and added to the reaction mixture contained in a 10-mm path length cell, when thermally equilibrated, in the thermostated cell compartment of a Shimadzu UV 210A spectrophotometer for slower runs. Faster reactions ($t_{1/2}$ > 20 s) were followed by a Photophysics 1705 stopped-flow instrument.

Rates of degradation of the ethanones were determined by following the appearance of the corresponding carboxylic acids (in their salt forms) at 230, 246, and 235 nm respectively for compounds **1a**, **1b**, and **1c**.

Scheme I

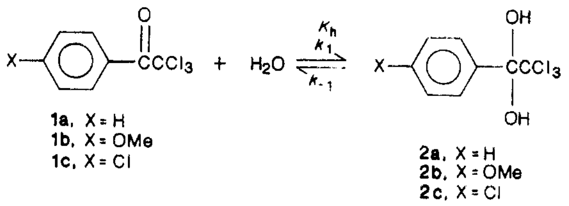

Table I. Observed First-Order Rate Constants for the Hydration of 2,2,2-Trichloro-1-phenylethanone as a Function of Temperature and Acid Concentration

		k_{obsd}, s^{-1}		
pH	[HCl], M	at 5.0 °C	at 10.0 °C	at 25.0 °C
4.42		0.157	0.230	0.540
4.23				0.537
3.00		0.160	0.231	0.531
	0.01	0.156		0.535
	0.10	0.158	0.240	0.542
	0.25	0.153		
	0.50	0.152	0.243	0.540
	1.00	0.157	0.240	0.543
	2.00	0.158	0.239	
	3.00	0.154	0.231	0.538

The temperature for the kinetic measurements was kept at 25.0 ± 0.1 °C. Reactions were monitored up to 90% completion. Reported values for observed first-order rate constants were calculated by a generalized least-squares method[13,14] from the relationship ln $(A_\infty - A_t)$ versus time, and they are weighted averages of two to four runs where the standard deviations were not accepted to be greater than 3%.

Chloroform was identified as a reaction product with a C.G. 370 gas chromatograph which employed an OV-17 column.

Results and Discussion

Addition of 1-phenyl-2,2,2-trichloroethanone (**1a**) to aqueous acid solutions (pH 4.42 to 3 M HCl) caused a decrease in the absorbance of the π–π^* band of **1a** at 258.5 nm. When the resulting solution was analyzed by GLC a single peak was observed, which corresponded to the starting ethanone. These observations are consistent with the equilibrium depicted in Scheme I.

Table I contains the kinetic data obtained for the hydration of **1a** at 5.0, 10.0, and 25.0 °C. As can be seen, the reaction is independent of the acid concentration at all temperatures.

The hydration constants K_h for the trichloroethanones **1** may be calculated with the aid of eq 1, where a_1, a_2, and

$$K_h = (a_1 - a_{1,2})/(a_{1,2} - a_2) \qquad (1)$$

$a_{1,2}$ are the absorbances for the π–π^* band of the ethanone **1**, the hydrate **2**, and the equilibrium mixture of **1** and **2**, respectively, using similar assumptions to those described previously for the alcoholysis of compounds **1**.[5] For the trichloroethanones **1a**, **1b**, and **1c** the estimated values were 1.53 ± 10%, 0.218 ± 10%, and 5.64 ± 10%, respectively, and represent an average of 15 determinations.

Using the data in Table I and the value of the hydration constant for compound **1a**, values of $k_1 = 0.33\ s^{-1}$ and $k_{-1} = 0.21\ s^{-1}$ for the forward and reverse hydration steps at 25 °C were obtained. From pH 4.42 to 3 M HCl, there was no evidence of specific acid catalysis in the hydration of ketone **1a**. The absence of specific acid catalysis is probably due to the strong electron-withdrawing effect of the trichloromethyl group upon the adjacent carbonyl.

The reaction was no longer reversible when the ethanone **1a** was added to aqueous solutions in the pH range 5.5–13.2. In this case chloroform and sodium benzoate were identified as hydrolysis products of the phenyltrichloroethanones. The same behavior was observed for the ethanones **1b** and **1c**. The variations of the observed constants for the basic hydrolysis of compound **1a** with the pH values of the medium is shown in Figure 1. Identical

---

(6) Boyer, W. M.; Bernstein, R. B.; Brown, T. L.; Dibeler, V. H. *J. Am. Chem. Soc.* **1951**, *73*, 770.

(7) Cohen, G.; Wolosinski, H. T.; Scheurer, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 3952.

(8) Aston, J. G.; Newkirk, J. D.; Dorsky, J.; Jenkins, D. M. *J. Am. Chem. Soc.* **1942**, *64*, 1413.

(9) Adams, R.; Woller, C. R. *Organic Syntheses*; Wiley: New York, 1976; Collect. Vol. I, p 109.

(10) *Beilstein Handbuch der Organischen Chemie*; Springer-Verlag: Berlin, 1925; Vol. 7, p 152.

(11) *Beilstein Handbuch der Organischem Chemie*; Springer-Verlag: Berlin, 1948; Vol. 8 (II), p 86.

(12) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(13) Deming, W. *Statistical Adjustment of Data*; Dover: New York, 1964.

(14) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96–103, 162–167.

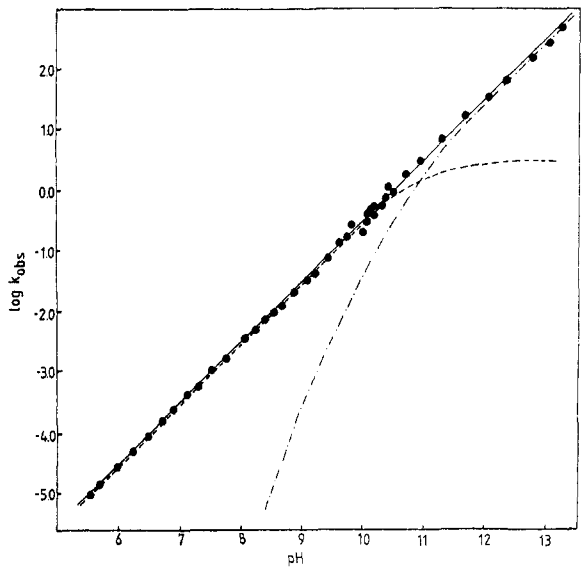

Figure 1. Experimental rate constants for the hydrolysis of **1a** (●) as a function of pH at 25.0 °C. The full line was calculated by means of eq 5. The separate contributions of k' and k'' are indicated by --- and ----, respectively.

pH rate profiles were observed for ketones **1b** and **1c**, the experimental results being included as supplementary material. For all ethanones, a first-order dependence of the observed rate constants on the hydroxide concentration is observed.

In basic solutions, addition of hydroxide ion to form a tetrahedral intermediate should be much faster than the formation of the hydrate at low pH values. Unfortunately we could not measure the hydration constants for this process because the ensuing elimination of the trichloromethyl group took place at a substantial rate, thus precluding the determination of K_h.

In our view a mechanism similar to the classical $B_{AC}2$ process, where the hydroxide addition is the rate-determining step is not operative in this case. In fact, such a mechanism may be rejected on the ground of the following considerations: First, as shown in Figure 1, the decomposition of the phenylethanone **1a** obeys a first-order dependence on OH^- even in slightly acidic solutions (pH 5.5–7.0), where the initial addition step was slow enough to be followed, and was clearly several orders of magnitude faster than the elimination step. It is reasonable to suggest that this situation should not be reversed in more basic solutions and that the addition step should also be much faster than the decomposition of the tetrahedral intermediate. These conclusions are reinforced by a ρ value of 0.8, which can be estimated from the experimental data for the hydrolysis of compounds **1**. This value is clearly lower than expected for $B_{AC}2$-type mechanisms ($\rho = 2.54$[15] for the basic hydrolysis of ethyl benzoates).

A mechanistic possibility which accounts for the above results, is depicted in Scheme II.

For the discussion of this mechanism we must in the first place evaluate constants K_1 and K_2. This can be done if we estimate pK_a values for the hydrate **2** and for the monoanion **3**, $pK_a(\mathbf{2})$ and $pK_a(\mathbf{3})$ (eq 2 and 3), respectively.

$$pK_1 = pK_a(\mathbf{2}) - pK_w \qquad (2)$$

$$pK_2 = pK_a(\mathbf{3}) - pK_w \qquad (3)$$

Scheme II

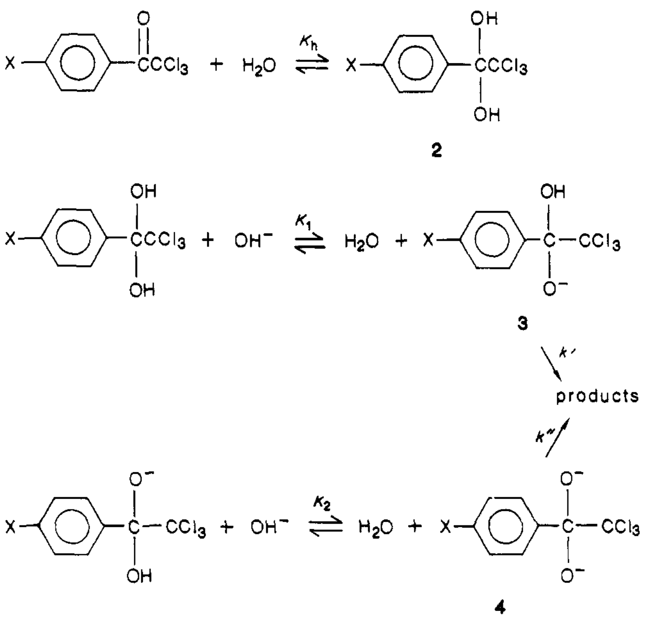

Table II. Estimated pK_a of Trichloro Hydrates 2 and 3 and Trifluoro Hydrates 11, Calculated with Equation 4[a]

X	pK_a hydrate 11 calcd	hydrate 11 obsd[b]	hydrate 2 calcd
p-MeO	10.24	10.18	10.11
p-Me	10.13	10.15	
H	9.94	10.00	9.81
p-Cl			9.55
m-Br	9.50	9.51	
m-NO$_2$	9.15	9.18	

[a] pK_a values for $CH_3CH(OH)_2$ (pK_a (**5**) = 13.57,[17] CCl_3CH_2OH (pK_a(**6**) = 12.24),[21,22] CH_3CH_2OH (pK_a(**7**) = 15.9),[21,22] $C_6H_5CH_2OH$ (pK_a(**8**) = 15.4),[23] and CH_3OH (pK_a(**9**) = 15.5)[21,22] were used in eq 4. Values for compounds **11** were calculated by using the pK_a value for CF_3CH_2OH (pK_a (**11**) = 12.37)[21,22] instead of pK_a(**6**) in eq 4. [b] Taken from ref 18.

The pK_a values of **2** and **3** may be estimated with a reasonable degree of accuracy from extrathermodynamic arguments. Starting from the pK_a value of 13.57 for the parent compound $CH_3CH(OH)_2$[16] and applying to alcohols the ΔpK_a method utilized in the prediction of pK_a values for organic acids and bases,[17] we may estimate the pK_a of hydrates **2** with the aid of eq 4, where the numbers in

$$pK_a(\mathbf{2}) = pK_a(\mathbf{5}) + pK_a(\mathbf{6}) - pK_a(\mathbf{7}) + pK_a(\mathbf{8}) - pK_a(\mathbf{9}) - \rho\sigma \qquad (4)$$

parentheses stand for the alcohols for which pK_a values are listed in Table II and σ is the Hammett substituent constant. A ρ value of 1.11 was used in eq 4, corresponding to the ionization of the hydrates of 1-aryl-2,2,2-trifluoroethanones **11**.[18] The estimated pK_a values of the hydrates **2** are given in Table II. The validity of our treatment is illustrated by the estimated pK_a values of the hydrates of 2,2,2-trifluoro-1-phenylethanone **11**, obtained by our method, which are also listed in Table II. As can be seen, the difference between the estimated and the experimental values[18] is never larger than 0.06 pK_a unit.

---

(15) Johnson, C. D. *The Hammett Equation*; Cambridge University: Cambridge, 1973; p 8.

(16) Bell, R. P.; Anwood, D. P. *Trans. Faraday Soc.* **1962**, *58*, 1557.

(17) *pKa Predictions for Organic Acids and Bases*; Chapman and Hall: London, 1981.

(18) Stewart, R.; Vander Linden, R. *Can. J. Chem.* **1960**, *38*, 399.

Table III. Values of Constants K_h, K_1, K_2, k', and k'' for Para-Substituted Trichloroethanones 1

	K_h	K_1, M^{-1}	K_2, M^{-1}	k', s^{-1}	k'', s^{-1}
X = H	1.53	1.55×10^4	6.17×10^{-3}	0.75	1.20×10^6
X = Cl	5.64	2.82×10^4	1.12×10^{-2}	0.43	1.00×10^6
X = MeO	0.218	7.76×10^3	3.09×10^{-3}	2.85	1.30×10^6

From the pK_a values of hydrates **2** we may obtain pK_a values for the corresponding monoanions **3**, by addition of 6.4 units to the values listed in Table II. This corresponds to the assumption that the difference between the pKa values of **3** and **2** is the same as that between the values of HCO_3^- and H_2CO_3.[19,20] Thus we arrive at values of 16.21, 16.51, and 15.95 for the dissociation of monoanions **3**, where X = H, *p*-MeO, and *p*-Cl, respectively.

By means of eq 2 and 3, where $pK_w = 14$, one may obtain the values for pK_1 and pK_2 and consequently for K_1 and K_2. These values are listed in Table III.

Equation 5, derived from Scheme II, relates the observed rate constant, k_{obsd}, to the hydroxide ion concentration, incorporating K_h, K_1, and K_2, besides the rate-limiting constants k' and k''.

$$k_{obsd} = \frac{k'K_1K_h[OH^-] + k''K_1K_2K_h[OH^-]^2}{1 + K_h(1 + K_1[OH^-] + K_1K_2[OH^-]^2} \qquad (5)$$

The validity of eq 5 is substantiated by the excellent agreement between the experimental data and the theoretical curve (calculated by eq 5), employing the values of K_h, K_1, and K_2 given in Table III (Figure 1). The rate constants k' and k'' also listed in Table III were obtained by best fit of eq 5 to observed rate constants. Figure 1 also include theoretical curves corresponding to the separate contributions of monoanion **3** and dianion **4** to the overall rate constant. It is clear that neither of these species by itself is capable of describing the data in the whole pH range employed. This behavior is indicative that forms **3** and **4** are reacting intermediates in solution. In the low pH range, the reaction proceeds mainly through the monoanion **3**, but as the basicity of the medium increase, the more reactive dianion **4** becomes the major contributor toward products. The values of k' and k'' in Table III show that the dianionic species **4** is on the average 10^6 times more reactive than the monoanion **3**. Both k' and k'' increase with the electron-donating ability of the aryl substituent, in accord with the previously reported substituent effect on the basic decomposition of 2,2,2-trichloro-1-arylethanols.[4] It is also apparent that the ratio k''/k' decreases in the order X = Cl > H > OMe, an observation which points to a smaller sensitivity of the dianion **4** to substituent effects. This is probably due to the strong effect of the two alkoxide groups on carbon 1, which provides enough driving force for the decomposition to proceed without significant contributions from the substituents.

In conclusion, the reaction proceeds through an addition–elimination process in which the elimination of the CCl_3 group from either the monoanionic or dianionic species is the rate-determining step, the contribution of each species being dependent on pH (Scheme II).

In continuation to our mechanistic studies involving the CCl_3 group adjacent to a carbonyl, we are currently investigating the mechanisms for the hydration and aminolysis of the title compounds.

Acknowledgment. We are grateful to CNPq and FINEP (Brazil) for financial support.

Registry No. **1a**, 2902-69-4; **1b**, 36458-91-0; **1c**, 27704-37-6; **2a**, 110374-87-3; **2a** (1^- ion), 110374-90-8; **2a** (2^- ion), 110374-92-0; **2b**, 110374-86-2; **2b** (1^- ion), 110374-89-5; **2b** (2^- ion), 110374-93-1; **2c**, 110374-88-4; **2c** (1^- ion), 110374-91-9; **2c** (2^- ion), 110374-94-2; **11** (X = *p*-MeO, 110374-82-8; **11** (X = *p*-Me), 110374-83-9; **11** (X = H), 56893-91-5; **11** (X = *m*-Br), 110374-84-0; **11** (X = *m*-NO_2), 110374-85-1; 2,2,2-trichloro-1-(*p*-methoxyphenyl)ethanol, 14337-31-6.

Supplementary Material Available: Figures of first-order rate constants for the hydrolysis of compounds **1b** and **1c** as a function of pH (3 pages). Ordering information is given on any current masthead page.

---

(19) Kurz, J. L. *J. Am. Chem. Soc.* **1963**, *85*, 987.

(20) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Chapman and Hall: London, 1973; p 40.

(21) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1959**, *81*, 1050.

(22) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 975.

(23) Takahashi, S.; Cohen, L. A.; Miller, H. K.; Peake, E. G. *J. Org. Chem.* **1971**, *36*, 1205.