Kinetics of the Decomposition of 1-Aryl-2,2,2-trihalogenoethanols in Aqueous Base

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The decomposition of several 1-aryl-2,2,2-trichloro- and 1-aryl-2,2,2-tribromo-ethanols in aqueous base is studied. The title compounds yield the corresponding benzaldehydes and the halogenoform with base. The kinetics are compatible with an $(E1cB)_R$ mechanism. Values for the rates of collapse of the intermediate alkoxides and for the pK_a values of all ethanols are estimated. Electron-donating substituents on the ring facilitate decomposition and decrease the acidity of the ethanols. Solvent isotope effects, k_{H_2O}/k_{D_2O}, for the reactions are small. The absence of mandelic acid derivatives among the products, in apparent disagreement with other related studies, is discussed and justified in the light of a scheme which reconciles previous conflicting observations found in the literature.

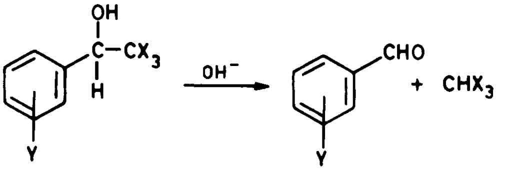
The basic decomposition of 1-aryl-2,2,2-trihalogenoethanols has long been known to afford the corresponding benzaldehydes, the halogenoform, and/or mandelic acid derivatives.[1] The reaction has been exploited in many patents as a method of preparation of these compounds.[2] In addition, 1-aryl-2,2,2-trichloroethanols (**1**) have found application as herbicides.[3] In this respect compounds (**1**) bear some resemblance to the structurally related 1,1-diaryl-2,2,2-trichloroethanols, a group of compounds with herbicidal activity, of which the bis-(*p*-chlorophenyl) analogue (Kelthane, Dicofol) is perhaps the best known.

As part of our studies on the degradation of pesticides and herbicides of the DDT family[4] we had previously reported an investigation on the basic decomposition of Kelthane in water and water–methanol.[5] We now investigate the decomposition of 1-aryl-2,2,2-trichloro- and 1-aryl-2,2,2-tribromo-ethanols in aqueous base. Our interest in this reaction is justified not only by the ever-growing concern with pesticides and their degradation products but also by the fact that, in spite of previous mechanistic studies, there are still some obscure points regarding this reaction. Thus, the literature reports benzaldehyde and mandelic acid derivatives as major products of the treatment of ethanols (**1**) with aqueous base, but there is no comparative study of the supposedly competitive pathways which lead to both products, and the reaction conditions which favour either of them are still unclear. Mechanistic studies on the formation of mandelic acid derivatives from ethanols (**1**)[6] only scarcely mention the parallel formation of the corresponding benzaldehydes and chloroform. This latter process is formally similar to the much better studied basic decomposition of cyanohydrins and bisulphite addition complexes of benzaldehydes. The kinetics of that decomposition, which has not been studied in detail yet, are the subject of this report.

Results and Discussion

The basic decomposition of 1-aryl-2,2,2-trichloro- and 1-aryl-2,2,2-tribromo-ethanols in water, under pseudo-first-order conditions, gave the corresponding benzaldehydes and the halogenoform.

The products were characterized by g.l.c. The conversion was nearly quantitative, as shown by the decomposition of ethanol (**1a**) (1 g) to give benzaldehyde and also by comparison of the initial and final absorbances of reaction mixtures. The formation of mandelic acid derivatives was not detected under our reaction conditions. The trihalogenomethane formed underwent slow hydrolysis with time. This was especially evident when the decomposition of the tribromoethanols (**2**) was followed spectroscopically. After reaching the infinite value A_∞ which corresponded to the total decomposition of the ethanol into benzaldehyde and bromoform, the absorbance started to decay slowly, until it reached a constant value after 6—10 h. That this decay was due to the bromoform hydrolysis was confirmed by following the disappearance of $CHBr_3$ in the reaction mixture with the Fujiwara reagent.[7] The gradual fading out of the red colour of different samples, taken at various times, coincided with the observed absorbance decay. This consecutive reaction ($t_{\frac{1}{2}}$ *ca.* 30 min for [OH$^-$] 0.1M) did not interfere with the decomposition of (**2**), as the first process was much faster ($t_{\frac{1}{2}}$ *ca.* 1—2 min) than the second.



(**1**) X = Cl
(**2**) X = Br
a; Y = H
b; Y = *p*-CH_3
c; Y = *p*-OCH_3
d; Y = *p*-$N(CH_3)_2$
e; Y = *p*-Cl
f; Y = *m*-NO_2
g; Y = *p*-NO_2

Scheme 1.

The observed pseudo-first-order rate constants for ethanols (**1**) and (**2**) at different hydroxide concentrations are given in Table 1. The rate constants increase with increasing concentrations of base, reaching constant values at high [OH$^-$] (Figures 1 and 2). This behaviour is compatible with an $(E1cB)_R$ mechanism as depicted in Scheme 2.

Equation (1)[5] describes the observed pseudo-first-order rate constants k_ψ in terms of the pre-equilibrium constant *K*, the rate constant of decomposition of the alkoxide, k_1, and [OH$^-$].

$$k_\psi = \frac{k_1 K[\mathrm{OH}^-]}{1 + K[\mathrm{OH}^-]} \qquad (1)$$

Table 1. Pseudo-first-order rate constants for the decomposition of 1-aryl-2,2,2-trichloroethanols (**1**) and 1-aryl-2,2,2-tribromoethanols (**2**) in water at 25 °C and different hydroxide concentrations

	$10^4k_\psi{}^a/s^{-1}$						$10^3k_\psi{}^a/s^{-1}$				
$10^3[OH^-]$/M	(**1a**)	(**1b**)	(**1c**)	(**1d**)	(**1e**)	(**1f**)	(**2a**)	(**2b**)	(**2c**)	(**2f**)	(**2g**)
2					0.76					2.31	
3	0.99			0.77		1.16					
4	1.41	1.19	1.31				3.46	3.33	2.17	3.46	2.01
5	1.55	1.27	1.78	1.16	1.35	1.44					
6		1.47					4.62	4.92	4.38	4.03	2.25
8							5.55	6.93	5.33	4.13	2.27
10	1.75	2.11	2.57	2.13	1.52	1.50		10.04			2.70
12			2.69		1.89			11.17		4.15	
15		2.48	2.75		1.91						
18							9.90	16.50		4.17	2.79
20	2.41		3.15		2.03	1.51	10.08	16.90	8.67		
30	3.00	3.34	3.71	4.20	2.40	1.55					
40				5.02		1.60	11.08	23.10	9.37		2.88
60	3.62	4.12		5.77		1.65	11.55	24.70	10.35	4.40	3.20
80	3.98			6.24	2.81	1.60	11.74	28.28	10.83		3.39
100	4.00	4.45	4.71	6.42	2.90		11.85		11.55		3.46
120	4.15	4.54	4.81	6.60	3.04	1.60	12.16	28.80	12.10	4.40	3.68
150	4.17	4.72	4.85	6.72	3.12		12.37	29.40	12.30		3.96
180	4.23	4.88					12.60	30.10	12.60	4.50	
200	4.35	5.00	5.25	6.89	3.25	1.66	12.84	31.00	13.10	4.50	3.95

[a] Deviations smaller than 3%.

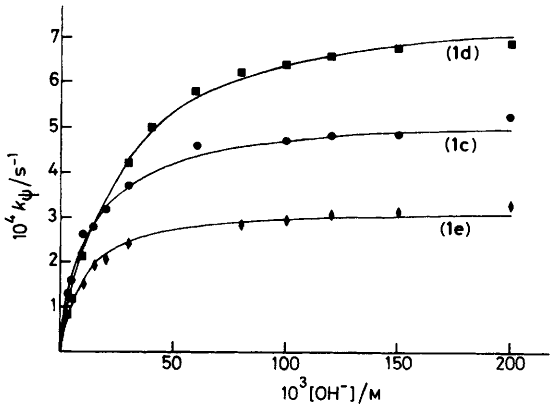


Figure 1. Pseudo-first-order rate constants k_ψ *versus* $[OH^-]$ for the decomposition of trichloroethanols (**1c**, **d**, and **e**) at 25 °C. Curves were drawn from equation (1)

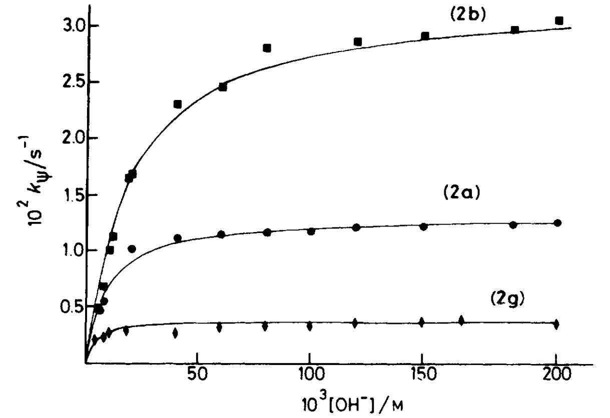


Figure 2. Pseudo-first-order rate constants k_ψ *versus* $[OH^-]$ for the decomposition of tribromoethanols (**2a**, **b**, and **g**) at 25 °C. Curves were drawn from equation (1)

At high hydroxide concentration $K[OH^-] \gg 1$, and k_ψ reduces to the limit constants value k_1. The pre-equilibrium constants K can be used to estimate the pK_a values of ethanols (**1**) or (**2**) by equation (2), where pK_w = 14.

$$pK_a = pK_w + pK \qquad (2)$$

Values of K, k_1, and pK_a for all compounds are given in Table 2. These values were obtained by best fits of equation (1) to the experimental data (see Figures 1 and 2 for examples).

Activation parameters for the reaction in the plateau region ($[OH^-]$ 0.2M) where $k_\psi \approx k_1$ were obtained from Arrhenius plots of ln k_ψ against $1/T$ for all compounds. Values of k_ψ at different temperatures and the resulting activation parameters for ethanols (**1**) and (**2**) are given in Tables 3 and 4, respectively.

An intriguing feature that emerges from inspection of Table 4 is the variation of $\Delta S^\neq$ values when comparing ethanols (**1**) with the tribromo analogues (**2**). This observation, and the change from normal to inverse solvent isotope effects for the two series (see below), could imply different mechanisms of decomposition for the two sets of compounds. If this is the case, to account for the negative values of entropy one is left with little else besides some sort of proton transfer from the solvent to the tribromoalkoxides in the transition state, most probably to the leaving group CBr_3. Although solvent-assisted departure of the tribromomethyl leaving group cannot be dismissed, it is difficult to see why this assistance is brought into play for compounds (**2**) and not for analogues with the poorer leaving group CCl_3.

A second alternative is to assume the same mechanism of decomposition for the two series, in spite of the changes in the entropy values. In fact, when the values of log k_ψ at 25 °C for all 11 compounds studied are plotted against the corresponding values of log k_ψ at 35 °C, all points obtained are found to fall on the same straight line with a correlation coefficient r 0.998 (graph not shown). The assertion that such a plot reveals a true isokinetic relationship for our compounds must be regarded with caution, because of the small range of temperature employed.[8] This plot may, however, be taken as an indication

Table 2. Rate constants k_1, pre-equilibrium constants K, and pK_a values of ethanols (**1**) and (**2**) in water at 25 °C

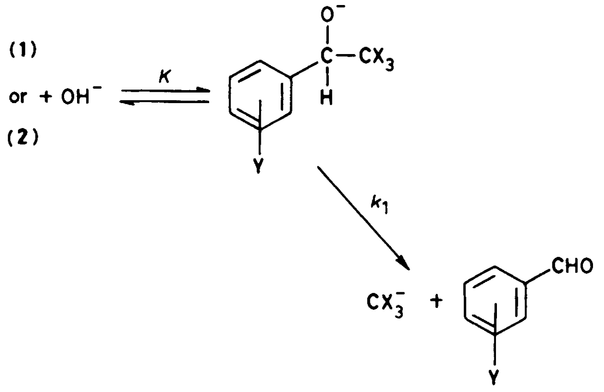
	Ethanols (**1**)						Ethanols (**2**)				
	(1a)	**(1b)**	**(1c)**	**(1d)**	**(1e)**	**(1f)**	**(2a)**	**(2b)**	**(2c)**	**(2f)**	**(2g)**
$k_1{}^a$	4.50	5.25	5.35	8.00	3.25	1.65	13.20	33.00	13.40	4.60	3.80
K^b	75	65	75	38	104	400	110	50	75	400	230
pK_a	12.12	12.19	12.12	12.42	11.99	11.40	11.96	12.30	12.12	11.40	11.70

[a] 10^4 k_1/l mol^{-1} s^{-1} for ethanols (**1**) and 10^3 k_1/l mol^{-1} s^{-1} for ethanols (**2**). [b] l mol^{-1}.

Table 3. Pseudo-first-order rate constants for the decomposition of ethanols (**1**) and (**2**) in aqueous base ([OH$^-$] 0.2M) at different temperatures

	Ethanols (**1**) $10^4k_\psi{}^a$/s^{-1}						Ethanols (**2**) $10^3k_\psi{}^a$/s^{-1}				
Temp. (°C)	**(1a)**	**(1b)**	**(1c)**	**(1d)**	**(1e)**	**(1f)**	**(2a)**	**(2b)**	**(2c)**	**(2f)**	**(2g)**
20							7.60	19.80	7.90	2.80	2.10
25	4.35	5.0	5.25	6.89	3.25	1.66	12.84	31.00	13.10	4.50	3.95
30		10.6	10.81	13.88^b	5.96^d	3.63	21.00	50.00	22.50	7.10	7.10
35	17.36	21.76	21.51	30.89^c	14.74	7.58	34.90	80.50	37.60	11.00	12.10
40	33.46	45.2	41.61	70.83	30.28	15.5					

[a] Deviations smaller than 3%. [b] Run at 29.5 °C. [c] Run at 24.5 °C. [d] Run at 29 °C.



Scheme 2.

Table 4. Activation parameters for the decomposition of ethanols (**1**) and (**2**) in aqueous base ([OH$^-$] 0.2M) at 25 °C in the plateau region

Compound	$E_a{}^a$	$\Delta H^{\neq a}$	$\Delta S^{\neq b}$	$\Delta G^{\neq a}$
(1a)	25.2 ± 0.1	24.6 ± 0.1	8.6 ± 0.2	22.0
(1b)	27.6 ± 0.6	26.6 ± 0.6	15.5 ± 2.1	21.9
(1c)	25.6 ± 0.3	25.0 ± 0.3	10.3 ± 1.0	21.9
(1d)	28.8 ± 0.8	28.2 ± 0.8	21.8 ± 2.5	21.7
(1e)	27.6 ± 0.4	26.9 ± 0.4	16.1 ± 1.2	22.2
(1f)	27.6 ± 0.4	26.9 ± 0.4	14.7 ± 1.3	22.6
(2a)	18.1 ± 0.7	17.6 ± 0.7	−8.2 ± 2.0	20.0
(2b)	16.8 ± 1.0	16.2 ± 1.0	−11.0 ± 3.4	19.5
(2c)	18.7 ± 0.7	18.1 ± 0.7	−6.4 ± 2.3	20.0
(2f)	16.3 ± 0.2	15.8 ± 0.2	−16.4 ± 0.5	20.6
(2g)	20.9 ± 1.0	20.3 ± 1.0	−1.3 ± 3.4	20.7

[a] In kcal mol^{-1}. [b] In cal K^{-1} mol^{-1}.

that the two sets of compounds (**1**) and (**2**) decompose by the same mechanism.

In the transition state of the C–CX$_3$ cleavage process one would expect a greater dispersion of charge with reduced solvation, as compared to the initial alkoxide ground state. The negative entropies of compounds (**2**) suggest on the contrary a ground-state alkoxide ion less solvated than the transition state. A somewhat tenuous argument to rationalize these observations may be derived from the increased steric effects which come into play when the Cl atoms are substituted by Br. Steric shielding of the alkoxide ion by the voluminous CBr$_3$ group might reduce interactions with the solvent. The analysis of the i.r. spectra of some 1-aryl-2,2,2-trichloroethanols (**1**)[9] supports this hypothesis. The hydroxy group of trichloroethanol (**1a**) is unusually inert[6b] and shows less intermolecular hydrogen bonding than 1-phenylethanol.[9] These observations can be accomodated by a steric shielding of the hydroxy group by the trihalogenomethyl substituent, which should be greater for the bigger CBr$_3$ group. In addition, the CCl$_3$ group might itself contribute to the increased solvation of the alkoxides from (**1**), due to weak hydrogen bonds between the water molecules and the Cl atoms. This contribution to the solvation of the alkoxide would be absent for the less electronegative, larger Br atoms. Hydrogen bonding with chlorine atoms in organic halides has been reported, the bond strength decreasing in the order Cl > Br > I.[10] The combination of these two effects would thus reduce the solvation of the tribromoalkoxides, as compared with the trichloro analogues.

Inspection of Table 2 shows that the decomposition of ethanols (**1**) and (**2**) is accelerated by electron-donating substituents on the ring. This effect is best visualized in Figure 3 where Hammett plots for both series of compounds are shown. ρ Values for the k_1 step are −0.58 and −0.81 for the trichloro and tribromo series, respectively. Table 2 also shows that electron-withdrawing substituents tend to decrease pK_a values for all trihalogenoethanols. Plots of pK_a against σ° (graphs not shown) yielded values of −0.72 and −0.69 for the trichloro- and the tribromo-ethanols respectively. In all cases σ° gave better correlations than σ constants. This result had been anticipated by Stewart and Linden,[11] who reported pK_a values for some 1-aryl-2,2,2-trifluoroethanols. Partial insulation of the charge centres from the ring, due to an interposed side-chain carbon atom, may be invoked to rationalize better correlations with σ°.

Comparison of the pK_a values of trichloro- and tribromo-ethanols in Table 2 shows that substitution of chlorine by bromine atoms at C-2 has little effect on the acidity of these compounds. The range of pK_a values is also the same as that reported for 1-aryl-2,2,2-trifluoroethanols[11] and 1,1-diaryl-2,2,2-trichloroethanols.[5] In contrast, the collapse of the intermediate alkoxide is strongly dependent on the nature of the

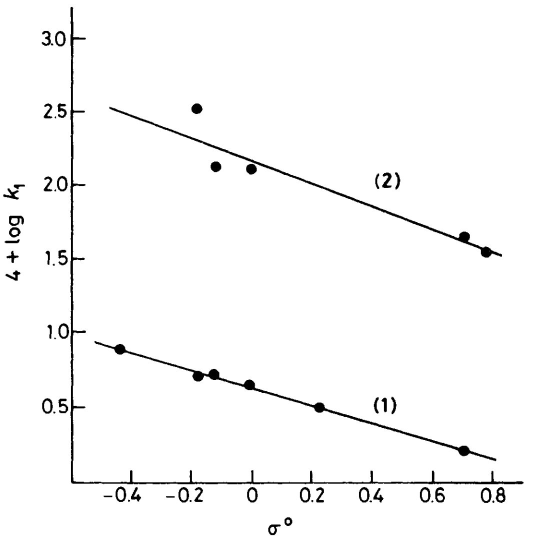


Figure 3. Hammett plots for the rate constants of decomposition of the alkoxide intermediates, k_1, at 25 °C for ethanols (**1**) and (**2**)

groups adjacent to C-1. Thus, basic decomposition of 1-aryl-2,2,2-trifluoroethanols is presumably so slow that equilibrium constants between these compounds and the corresponding alkoxide could be obtained directly in aqueous base by spectroscopic measurements.[11] 1-Aryl-2,2,2-trichloroethanols (**1**) decompose faster than the trifluoroethanols and for the tribromo series (**2**) decomposition is on average 30 times faster than for their trichloro analogues (**1**). Substitution of a hydrogen atom in (**1a**) by a phenyl group[5] causes a 540-fold increase in the decomposition rate constant. These accelerations may be ascribed to the steric relief brought about by breaking the C–CX_3 bond of the alkoxide. In addition, in the case of the phenyl group acceleration, a second effect, namely, the resonance stabilization of the incipient carbonyl group by a second conjugated aryl group may also help decompose the alkoxide. Steric effects, which should play a major role in the last step, would be of minor importance in the ionization of the hydroxy group. The relative constancy of the acidities for the different trihalogenoethanols, combined with the acceleration observed for the last step, seems to indicate that steric effects are a major factor in determining the rate of decomposition of these compounds. Steric factors have been invoked to explain the decarboxylation rates of trihalogenocarboxylate anions, which decrease in the order $Br_3CCO_2^- > Cl_3CCO_2^- > F_3CCO_2^-$.[12] This order, which is also found in the dedeuteriation of halogenoforms,[12] shows that the leaving group ability of a CX_3^- group is not related to the electronegativity of the halogen X but to other factors such as polarizability and *d*-orbital contributions to the stabilization of the anion.[12]

Solvent isotope effects for the decomposition of ethanols (**1a**), (**2a**), and (**2c**) are given in Table 5. Values obtained are all near unity, in agreement with the value of 1.05 observed by Jencks and Young for the breakdown of the dianion intermediate of the *p*-methoxybenzaldehyde–bisulphite addition complex.[13] Small inverse solvent isotope effects were observed for the tribromoethanols (**2a**) and (**2c**). Kinetic runs at higher hydroxide concentrations (0.4 and 0.6M), where ionization of the tribromoethanols should be practically complete in both solvents, yielded essentially constant values of k_{H_2O}/k_{D_2O}. This observation discarded the possibility of a contribution of the pre-equilibrium step to the observed inverse values. The change from normal to inverse isotope effects shown in Table 5 is not easy to explain. It might be tempting to associate it with the changes in activation entropies for the two series. According to the model proposed by Swain *et al.*,[14] inverse solvent isotope effects are to be expected from processes with negative entropies.[15] However, such a correlation is probably an oversimplification, as, for example, data on the hydrolysis of organic halides seem to indicate.[16] All one can say is that our small isotope effects probably originate from solute–solvent interactions and are to be expected from a process where primary effects are absent.

Table 5. Solvent isotope effects for the decomposition of some trihalogenoethanols at 25 °C

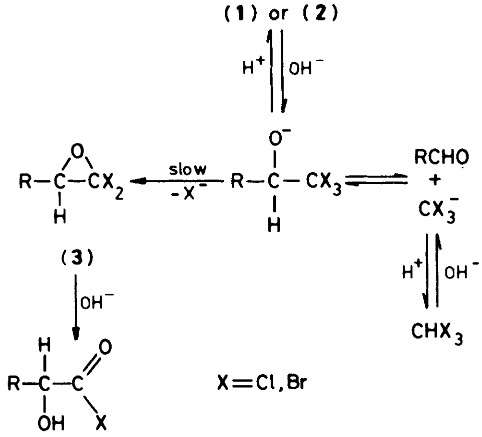
Substrate	k_{H_2O}/k_{D_2O}
(**1a**)	1.09[a]
(**2a**)	0.95,[a] 0.89,[b] 0.94[c]
(**2c**)	0.83,[a] 0.81,[b] 0.84[c]

[a] $[OH^-]$ ($[OD^-]$) 0.2M. [b] $[OH^-]$ ($[OD^-]$) 0.4M. [c] $[OH^-]$ ($[OD^-]$) 0.6M

In all reactions studied in this work, the formation of mandelic acid derivatives was never detected by us. However, preparation of these derivatives by decomposition of ethanols (**1**) in aqueous base is well documented in the literature.[6] The mechanism of formation of these compounds in the presence of CH_3O^-–CH_3OH,[6b] KNH_2–NH_3,[6a] and a variety of nucleophiles[6c] has been studied and a dichloro-epoxide (**3**) postulated as an intermediate in these processes. The apparent discrepancy between our results and the above mentioned studies stems from the different reaction conditions employed. A typical conversion of ethanol (**1a**) into methoxyphenylacetic acid (13.5% yield, 53% recovery of the unchanged ethanol) is achieved at 40 °C by adding over 90 min a four-fold excess of KOH in MeOH to a methanolic solution of the substrate (**1a**).[6b] The same reaction at 0 °C in ethanol–water (4:1) has a half-life of nearly 600 h, as measured by titration of portions of the base during the reaction. On the other hand, under our pseudo-first-order rate conditions, the trichloroethanols (**1a**) should decompose into benzaldehyde and chloroform at 0 °C in aqueous base with a half-life of nearly 22 h, estimated from extrapolation of k_ψ values for (**1a**) at different temperatures in Table 3. If one takes into account the different solvents employed, the same reaction in ethanol–water (4:1) should have an even shorter half-life, as indicated by the decomposition of similarly related 1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethanol in both media.[5]

These considerations show that the decomposition of the alkoxide into benzaldehydes and chloroform is a much faster process than the competing intramolecular displacement of a Cl^- to form a dichloro-epoxide (**3**). Thus, under our experimental conditions the reaction should be essentially complete before any appreciable amount of mandelate is formed. However, when both the substrate and the hydroxide concentrations are increased, abstraction of a proton from the solvent by the trichloromethyl anion formed is no longer a practically irreversible step. An equilibrium is then established between the alkoxide and the products, which allows for the slow, irreversible detour towards mandelic acid derivatives.

Trichloroethanols (**1**) are often prepared by reaction of benzaldehydes with excess of chloroform and base.[6a] Our results show that formation of mandelic acid derivatives from ethanols (**1**) cannot compete kinetically with the formation of benzaldehydes from the breakdown of the intermediate alkoxides. Such acid derivatives can only be formed when an excess of base and the trichloromethane formed guarantee a high, 'permanent' concentration of the alkoxide, which may then slowly produce the acid derivatives.



Scheme 3.

In conclusion, our results stress the importance of steric effects in the basic decomposition of trihalogenoethanols of the DDT family. The leaving-group ability of the trihalogenomethyl groups decreases in the same order as that observed previously, and is not to be correlated with the electronegativity of the halogen substituents. Finally, the conflicting observations found in the literature of different products for the same reaction have a simple, though not previously mentioned, explanation.

Experimental

M.p.s were taken with a Kofler hot-stage apparatus and were not corrected. I.r. spectra were obtained with a Perkin-Elmer 720 spectrophotometer. N.m.r. spectra were recorded on a Varian T-60 instrument. Tetramethylsilane was always used as internal reference. Chromatographic analyses of the products were carried out with a C.G. 370 instrument.

The following compounds were prepared by methods previously described: 1-phenyl-2,2,2-trichloroethanol (**1a**), b.p. 140—142 °C at 10 mmHg, (lit.,[6a] 148—149 °C at 17 mmHg); 1-(*p*-methylphenyl)-2,2,2-trichloroethanol (**1b**), m.p. 61 °C (lit.,[17] 63 °C); 1-(*p*-methoxyphenyl)-2,2,2-trichloroethanol (**1c**), b.p. 155—158 °C at 20 mmHg (lit.,[18] 160—163 °C at 24 mmHg); 1-(*p*-dimethylaminophenyl)-2,2,2-trichloroethanol (**1d**),[19] isolated as the *hydrochloride*, m.p. 168 °C (from water) (Found: C, 39.4; H, 4.3; N, 4.5. $C_{10}H_{13}Cl_4NO$ requires C, 39.3; H, 4.3; N, 4.6%); 1-(*p*-chlorophenyl)-2,2,2-trichloroethanol (**1e**), m.p. 45 °C (lit.,[20] 47—48 °C); 1-(*m*-nitrophenyl)-2,2,2-trichloroethanol (**1f**),[21] m.p. 90 °C (lit.,[22] 92 °C); 1-phenyl-2,2,2-tribromoethanol (**2a**), m.p. 74—75 °C (lit.,[23] 72.5—73 °C); 1-(*p*-methylphenyl)-2,2,2-tribromoethanol (**2b**), m.p. 63—64 °C (lit.,[24] 61—62 °C); 1-(*p*-nitrophenyl)-2,2,2-tribromoethanol (**2g**), m.p. 121—122 °C (lit.,[25] 118—120 °C). All compounds thus prepared were further characterized by their i.r. and n.m.r. spectra. The following new compounds were prepared by reaction of the corresponding benzaldehyde and excess of bromoform in the presence of powdered KOH;[23] 1-(*p*-methoxyphenyl)-2,2,2-tribromoethanol (**2c**), m.p. 78 °C (from light petroleum) (Found: C, 27.8; H, 2.1. $C_9H_9Br_3O_2$ requires C, 27.8; H, 2.3%); $\nu_{max.}$(Nujol) 3 530, 1 610, 1 260, 1 180, 1 060, 1 020, 820, and 750 cm^{-1}; δ($CDCl_3$) 3.8 (3 H, s), 4.8 (1 H, s), 5.2 (1 H, s), 6.81 (2 H, d, *J* 7 Hz), and 7.65 (2 H, d, *J* 7 Hz); 1-(*m*-nitrophenyl)-2,2,2-tribromoethanol (**2f**), m.p. 89—90 °C (from light petroleum) (Found: C, 24.0; H, 1.6; N, 3.4. $C_8H_6Br_3NO_3$ requires C, 23.8; H, 1.5; N, 3.5%); $\nu_{max.}$(KBr) 3 530, 1 520, 1 350, 1 200, 1 080, and 770 cm^{-1}; δ($CDCl_3$) 4.8 (1 H, s), 5.2 (1 H, s), and 7.8—8.1 (4 H, m).

Sodium hydroxide solutions were prepared with deionized water and the hydroxide concentrations determined by titration. Stock solutions of ethanols (**1**) and (**2**) were prepared in methanol (*ca.* 10^{-3}M) and were stable for several weeks in the refrigerator. Sodium deuterioxide solutions were prepared from 99.0% pure deuterium oxide, supplied by Fluorochem Ltd.

Rates of decomposition of the ethanols were determined spectroscopically with a Shimadzu UV-210A spectrophotometer equipped with thermostatted (±0.1 °C) water-jacketted cell compartments, by following the appearance of the corresponding benzaldehydes. Reactions were followed for at least 90% and the linear plots ($r > 0.99$) of $\ln(A_\infty - A_t)$ against time yielded pseudo-first-order rate constants k_ψ with deviations smaller than 3%. Rate deviations due to ionic strength variations were considered negligible. Kinetic runs for compound (**2a**) at constant hydroxide concentration ([OH^-] 2×10^{-2}M) but different ionic strengths (2×10^{-2} and 0.5M), through addition of NaCl, yielded practically the same rate constants within experimental error.

G.l.c. analyses of the products of the reactions were performed for ethanols (**1a** and **c**) (column OV-17; temperature 80 °C) and for the tribromoethanol (**2a**) (column OV-17; temperature 150 °C). Reactions were carried out on a 0.5—1 g scale and the formation of benzaldehydes and the halogenoform was confirmed by analysing ethereal extracts of previously acidified portions of the reaction mixtures.

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