Preparation and Kinetics of the Hydrolysis of Trichloromethyl Esters

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The rates of the hydrolyses of trichloromethyl trichloroacetate and trifluorocetate have been measured in aqueous acetonitrile and dioxane solutions of low water content. The rates and activation parameters are found to be identical with those for phosgene. It is proposed that the very fast neutral $B_{AC}3$ ester hydrolysis is followed by a fast decomposition of the initially formed trichloromethanol to phosgene, the hydrolysis of which is the rate-determining stage.

Although the preparation and physical properties of monochloromethyl and dichloromethyl esters are well known, trichloromethyl trichloroacetate seems to be the only trichloromethyl ester of simple aliphatic carboxylic acids the preparation and physical properties of which are known.[1] Elbs and Kratz[2] found that trichloromethyl trichloroacetate, prepared by the electrolysis of an aqueous solution of potassium trichloroacetate, produced phosgene and hydrochloric acid. On that basis Gibson[3] concluded that trichloromethyl esters are, in general, hydrolysed according to eqn. (1). However, the kinetics of the hydrolyses of trichloromethyl esters have not been
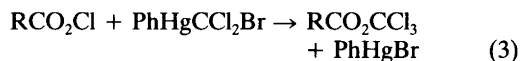
$$RCO_2CCl_3 + H_2O \rightarrow COCl_2 + HCl + RCO_2H \qquad (1)$$

studied. On the other hand, those of 1-monohaloalkyl esters have been thoroughly investigated,[4] although there seems to be only one published kinetic investigation of 1,1-dichloroalkyl esters.[5] Therefore, the preparation of trichloromethyl trifluoroacetate was attempted and the kinetics of the hydrolysis of the trichloromethyl trihaloacetates were studied.

Experimental

Preparation of trichloromethyl esters. Trichloromethyl trichloroacetate was prepared by photochlorination of methyl trichloroacetate.[1] The preparation of trichloromethyl trifluoroacetate was found to be more difficult, largely because of the high volatility of methyl trifluoroacetate (b.p. 43–44 °C), slow rate of chlorination, and the formation of polymers. The chlorination was performed in carbon tetrachloride solution, using, to begin with, a UV-lamp outside the reaction vessel to minimize evaporation. The mixture of methyl trifluoroacetate and its chlorination products obtained was then chlorinated in a Hanovia photochemical reactor. The reaction was followed by NMR spectroscopy. After a total chlorination time of 64 h and after having removed the solvent, a solid product was obtained, the ^1H NMR spectrum of which did not show any signals. Distillation of the product gave several fractions, the best of which was found, by hydrolysis and titration against silver nitrate, to contain 87 % of the ester.

Attempts to prepare trichloromethyl esters by the reaction of an acyl chloride with phosgene [eqn. (2)] or from acetyl hypochlorite bromodichloromethyl(phenyl)mercury [eqn. (3) (cf. Ref. 1) were unsuccessful.

$$Cl_2C{=}O + RCOCl \rightarrow RCO_2CCl_3 \qquad (2)$$

$$RCO_2Cl + PhHgCCl_2Br \rightarrow RCO_2CCl_3 + PhHgBr \qquad (3)$$

Chemicals. 1,4-Dioxane was purified by the method of Hess and Frahm.[6] It was found that

acetonitrile samples of different origin gave greatly varying rate coefficients, evidently because of catalysis by basic impurities. The most reliable (lowest rate coefficients) and reproducible results were obtained when the *purissimum p.a.* grade product supplied by Fluka was used after having been purified by the method of Coetzee.[7] Phosgene was obtained from Fluka as a 20 % solution in toluene. The solvent mixtures were prepared by diluting a known weight of distilled water with the organic solvent component to a known volume in a volumetric flask. The symbol *p* vol. '%' means that 100 ml of the solvent mixture contained $(100-p)$ g of water.

Kinetic measurements. The rates of hydrolysis of the esters were measured either conductimetrically employing a Philips 9501 conductimeter or manometrically by allowing the reaction to take place in a thermostatted reaction vessel fused to a mercury manometer.[5] The methods are based on the premise that carbon dioxide, hydrogen chloride and trihaloacetic acid are the end products of the hydrolysis of trichloromethyl esters [eqn. (4)].

$$RCO_2CCl_3 + 2 H_2O \rightarrow RCO_2^- + CO_2 + 4 H^+ 3 Cl^- \qquad (4)$$
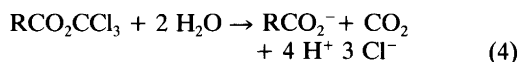
The rate of the hydrolysis of phosgene was measured conductimetrically by the method described earlier.[8] The rate coefficients were calculated by the Guggenheim method.

Results and discussion

The kinetic results for the hydrolysis of trichloromethyl trichloroacetate in acetonitrile–water and 1,4-dioxane–water solutions are given in Tables 1 and 2, respectively. The reaction rate was not found to increase with the addition of acids. The calculated rate coefficients, therefore, represent an uncatalysed hydrolysis, evidently taking place either by the addition–elimination mechanism, $B_{AC}3$, or by an S_N solvolysis of chlorine. These reactions can be recognised by the much lower activation enthalpy and the highly negative activation entropy for the former mechanism.[4] Unfortunately, no data are available for such low water contents as used in the present case, although it is known that solvent composition has marked effects on these quantities. However, the

Table 1. Kinetic data for the hydrolysis of trichloromethyl trichloroacetate in acetonitrile–water solutions: conductometric method.
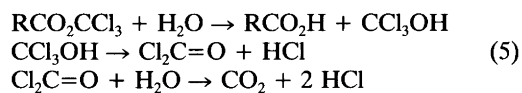
Acetonitrile/ vol. '%'	$T/°C$	$k/10^{-2} \text{ s}^{-1}$	Thermodynamic functions of activation
97	−2.08	4.20(1)	
	3.97	5.31(2)	$\Delta G^\ddagger = 78.23(4) \text{ kJ mol}^{-1}$
	10.07	6.48(1)	$\Delta H^\ddagger = 19.6(6) \text{ kJ mol}^{-1}$
	17.01	8.31(5)	$\Delta S^\ddagger = -197(2) \text{ J mol}^{-1} \text{ K}^{-1}$
	24.99	10.16(9)	
98	−2.08	1.80(1)	
	2.07	1.78(1)	
	5.01	2.28(1)	$\Delta G^\ddagger = 80.50(1) \text{ kJ mol}^{-1}$
	14.96	3.13(1)	$\Delta H^\ddagger = 18.3(2) \text{ kJ mol}^{-1}$
	25.01	4.12(1)	$\Delta S^\ddagger = -209(1) \text{ J mol}^{-1} \text{ K}^{-1}$
		4.14(1)	
99	−2.08	0.366(1)	
	3.97	0.454(1)	
	10.07	0.556(2)	$\Delta G^\ddagger = 84.49(2) \text{ kJ mol}^{-1}$
	17.01	0.673(2)	$\Delta H^\ddagger = 17.2(3) \text{ kJ mol}^{-1}$
	24.99	0.840(1)	$\Delta S^\ddagger = -225(1) \text{ J mol}^{-1} \text{ K}^{-1}$
	35.00	1.075(1)	
	45.00	1.341(3)	

Table 2. Kinetic data for the hydrolysis of trichloromethyl trichloroacetate in 1,4-dioxane–water solutions: manometric method.

Dioxane	$T/°C$	$k/10^{-3}$ s^{-1}	Thermodynamic functions of activation
97	10.00	8.80(7)	
wt %		8.91(10)	
	15.00	10.7(1)	
		11.4(1)	$\Delta G^{\ddagger}$ = 82.67(4) kJ mol^{-1}
	20.00	13.3(1)	$\Delta H^{\ddagger}$ = 29.4(14) kJ mol^{-1}
		13.7(1)	$\Delta S^{\ddagger}$ = −179(5) J mol^{-1} K^{-1}
	25.00	16.8(1)	
		17.9(2)	
		18.0(2)	
99.83	7.1	10.94(9)	
vol '%'		10.96(8)	$\Delta G^{\ddagger}$ = 81.97(9) kJ mol^{-1}
0.005M	15.63	14.9(2)	$\Delta H^{\ddagger}$ = 26.7(19) kJ mol^{-1}
LiCl	25.0	23.5(2)	$\Delta S^{\ddagger}$ = −185(7) J mol^{-1} K^{-1}

exceptionally low activation enthalpies, 17–30 kJ mol^{-1}, and highly negative activation entropies, −180 to −220 J mol^{-1} K^{-1}, without doubt indicate that the rate-determining step of the reaction takes place by the addition–elimination mechanism rather than by the solvolysis of chlorine.

It may be assumed that the hydrolysis of trichloromethyl esters follows the $B_{AC}V3$ mechanism[4] of neutral ester hydrolysis. In the case of trichloromethyl esters the alcohol formed by the hydrolysis is trichloromethanol, which evidently reacts rapidly with water. The mechanism therefore can be written according to eqn. (5).

$$RCO_2CCl_3 + H_2O \rightarrow RCO_2H + CCl_3OH$$
$$CCl_3OH \rightarrow Cl_2C{=}O + HCl \quad\quad (5)$$
$$Cl_2C{=}O + H_2O \rightarrow CO_2 + 2\ HCl$$

As mentioned above, Elbs and Kratz[2] stated that trichloromethyl trichloroacetate is decomposed by water to trichloroacetic acid, phosgene and hydrogen chloride. This is in agreement with the above mechanism, but does not identify the rate-determining step in mechanism (5). It is well known that the hydrolyses of acid chlorides are, in general, fast compared with those of carboxylic esters and Leimu[9] found that the alcoholysis of phosgene in a 2 M solution of 2-chloroethanol in 1,4-dioxane takes place more than·ten times faster than that of acetyl chloride. Therefore it could

be supposed that the first stage of eqn. (5) is rate-determining. However, it can be estimated from the data of Böhme[10] for the hydrolysis of phosgene in solutions of very low water concentration, that its hydrolysis under the conditions of the present work would take place at almost exactly the rate found for trichloromethyl trichloroacetate (Table 2). Furthermore, although trichloromethyl trifluoroacetate could not be prepared in a pure state, the measured rates for its hydrolysis were found to be of the same order as those for trichloroacetate under the same conditions. The most reliable value for its hydrolysis in 99 % acetonitrile–water solution at 25 °C, $(8.9\pm0.2) \times 10^{-3}$ s^{-1}, is almost the same as that found for trichloromethyl trichloroacetate (Table 1), although it should be expected that the first step in (5) would be at least ten times faster for the trichloroacetate.[4]

In order to confirm the above-mentioned conclusions, the hydrolysis of phosgene was studied under the same conditions as those used for the above-mentioned measurements. The results (Table 3) show that the hydrolysis of phosgene does, in fact, take place almost exactly at the same rate as that of trichloromethyl trichloroacetate. Also the derived thermodynamic activation parameters are the same, to within the limits of the experimental accuracy. Therefore, it can be safely concluded that the hydrolyses of trichloromethyl esters of trihaloacetic acids take place

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Table 3. Kinetic data for the hydrolysis of phosgene, $COCl_2$, in acetonitrile–water solutions: conductometric method.

Acetonitrile/ vol. '%'	T/°C	$k/10^{-2}$ s^{-1}	Thermodynamic functions of activation
97	3.92	5.46(1)	$\Delta G^{\ddagger} = 78.12(4)$ kJ mol^{-1}
	9.93	6.80(3)	$\Delta H^{\ddagger} = 19.6(8)$ kJ mol^{-1}
	16.96	8.64(2)	$\Delta S^{\ddagger} = -196(3)$ J mol^{-1} K^{-1}
98	5.14	2.262(7)	$\Delta G^{\ddagger} = 80.51(1)$ kJ mol^{-1}
	12.09	2.836(10)	$\Delta H^{\ddagger} = 18.4(2)$ kJ mol^{-1}
	18.00	3.386(11)	$\Delta S^{\ddagger} = -208.5(2)$ J mol^{-1} K^{-1}
	24.99	4.122(14)	
99	34.84	1.06(3)	

according to mechanism (5), the third step, the hydrolysis of phosgene formed in the first two steps, being rate determining. The hydrolyses of perhalogenated methyl acetates are thus very rapid, their rates of hydrolysis being clearly faster than those of acid chlorides. Thus, the rate coefficients observed for the hydrolyses of acetyl chloride and phosgene in 99 '%' aqueous acetonitrile at 34.48 °C are $(4.59 \pm 0.03) \times 10^{-4}$ and $(1.065 \pm 0.003) \times 10^{-2}$ s^{-1}, respectively.

The above results do not, however, exclude the possibility that phosgene is formed in a one-step reaction (1) rather than in the two steps of mechanism (5). However, this is at variance with the stability of trichloromethyl trichloroacetate in the dry state and does not explain the mechanism of the action of water. The known structural effects in neutral ester hydrolysis are in accordance with mechanism (5).

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