

anhydrides of molecular weight 854 (by osmometry).

3,3,7,7-Tetramethyl azelaic anhydride. 3,3,7,7-Tetramethyl azelaic acid was treated as described above. Vacuum distillation gave a partly crystalline fraction, b.p. 70–160°/0.05 mm. The crystals were dried on filter paper and sublimed at 40–42°/0.05 mm to give *monomeric 3,3,7,7-tetramethyl azelaic anhydride* (1.5 g=3.5%), m.p. 59°. (Found: C 68.69; H 9.79. Mol.wt. 221 (by osmometry in chloroform). Calc. for C₁₃H₂₂O₃: C 68.99; H 9.80. Mol.wt. 226). IR absorptions in CCl₄: 1745 and 1790 cm⁻¹. ¹H chemical shifts: 1.0, 2.4 ppm (methyl and α -methylene). Neither the dimer nor other cyclic anhydrides from tetramethyl azelaic acid were found in the fraction.

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Kinetics of the Hydrolysis of α -Chlorobenzyl Esters

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The uncatalysed hydrolysis of α -haloalkyl carboxylates has been investigated previously. It was found to proceed either by the mechanism of the neutral ester hydrolysis (*e.g.* chloromethyl formate,¹ chloromethyl chloroacetate,² and chloromethyl dichloroacetate³), by the

S_N1 mechanism (*e.g.* α -chloroethyl acetate,¹ α,β -dichloro-*sec.*-propyl acetate,⁴ and α -chloro-*sec.*-propyl acetate⁵), or by the S_N1,2 mechanism (*e.g.* chloromethyl acetate¹ and chloromethyl benzoate⁶). These reactions may also occur concurrently, as was found to be the case in the hydrolysis of bromomethyl chloroacetate.⁷ The aim of this work was to enlarge the knowledge of the hydrolysis of the α -haloalkyl esters of carboxylic acids so as to embrace also those esters in which the α -carbon carries a phenyl or a hexachlorocyclohexyl group.

Materials. The α -chlorobenzyl esters of formic, acetic, trichloroacetic, and trifluoroacetic acids as well as hexachlorocyclohexylchloromethyl trifluoroacetate were prepared by chlorinating the corresponding benzyl esters.⁸ When solvent mixtures were prepared, acetone (E. Merck A. G., guaranteed reagent) was used as received but dioxane (BDH) was purified using the method described by Hess and Frahm.⁹ The symbol *p* vol. “%” employed in the following denotes 100 ml of the solvent mixture containing (100–*p*) g of water.

Determination of rate coefficients. The rate coefficients of the hydrolysis of the α -chlorobenzyl and of the hexachlorocyclohexylchloromethyl trifluoroacetate were determined by a conductometric method employing a Philips PR 9501 conductometer. The dependence of conductance on concentration was not linear, and was therefore determined experimentally. The fraction of α -chlorobenzyl acetate used in the kinetic experiments contained benzoyl chloride as an active impurity.⁸ The rates of hydrolysis of this impurity were determined separately under the same experimental conditions and taken into account when calculating the rate coefficients for α -chlorobenzyl acetate. The low hydrolysis rates of benzyl trifluoroacetate were determined by a gas chromatographic method. The rate coefficients for the hydrolysis of these esters and the derived activation parameters are collected in Tables 1 and 2.

The values of the thermodynamic functions of activation presented in Table 1 show that in the hydrolysis of the α -chlorobenzyl esters of trifluoro- and trichloroacetic acids the enthalpy of activation is about 10 kcal mol⁻¹ and the entropy of activation 30–40 cal mol⁻¹K⁻¹ lower than the corresponding values for the hydrolysis of the α -chlorobenzyl esters of formic and acetic acids. It is evident that the reaction of the former esters proceeds by the mechanism of a neutral ester

Table 1. Kinetic data for the hydrolysis of α -chlorobenzyl esters $\text{RCOOCHCl}(\text{C}_6\text{H}_5)$.

R	Solvent	25°C	10^3k (s^{-1})		ΔH^\ddagger kcal mol $^{-1}$	$-\Delta S^\ddagger$ cal mol $^{-1}$ K $^{-1}$	
			35°C	45°C			
CH ₃	60 % D ^a		84.4 ± 0.45				
				34.9 ± 0.35			
				35.2 ± 0.26			
				36.5 ± 0.25			
				33.4 ± 0.42			
	75 %	5.42 ± 0.018	14.4 ± 0.20	33.9 ± 0.12	16.77 ± 0.12	12.7 ± 0.4	
		5.28 ± 0.022	13.6 ± 0.09	33.6 ± 0.16			
	80 " % " A ^b	3.55 ± 0.028	8.74 ± 0.053	20.2 ± 0.08	15.90 ± 0.19	16.4 ± 0.6	
		3.52 ± 0.014	8.41 ± 0.045	20.5 ± 0.08			
	85 %			6.58 ± 0.032			
90 %			7.18 ± 0.061				
			1.70 ± 0.022				
H	60 %	8.17 ± 0.056	20.5 ± 0.20	51.0 ± 0.21			
		8.06 ± 0.063	20.4 ± 0.08	47.2 ± 0.38	16.39 ± 0.07	13.1 ± 0.2	
	70 %			49.5 ± 0.49			
				14.1 ± 0.08			
				15.3 ± 0.18			
80 %			3.34 ± 0.022				
CF ₃	90 %	34.4 ± 0.17	43.0 ± 0.68	(^c)	4.82 ± 0.29	49.2 ± 1.0	
		34.3 ± 0.15	42.8 ± 0.58				
	95 %	6.72 ± 0.10					
		6.64 ± 0.11					
	98 %	0.53 ± 0.04					
CCl ₃	90 %	1.18 ± 0.010	1.92 ± 0.024		7.12	48.1	
			1.69 ± 0.014				
			1.78 ± 0.014				

^a60 wt. % dioxane-water mixture, ^b80 vol. " % " acetone-water mixture. ^c $k = (16.6 \pm 0.11) \times 10^{-3} \text{ s}^{-1}$ at 4.52°C, $k = (23.5 \pm 0.18) \times 10^{-3} \text{ s}^{-1}$, and $k = (23.8 \pm 0.18) \times 10^{-3} \text{ s}^{-1}$ at 15.09°C.

hydrolysis ($\text{B}_{\text{AC}3}$), as is usual for the hydrolysis of trihalocarboxylic esters,⁵ and the hydrolysis of the latter takes place by the nucleophilic displacement of the α -halogen atom of the alkyl component. In the latter case the carbonium ion formed is stabilized by resonance involving the phenyl group. Because the hydrolysis of α -chloroethyl acetate¹ has been found to take place by the $\text{S}_{\text{N}}1$ mechanism, it is to be expected that the hydrolysis of these esters also occurs by this mechanism. The hydrolysis of chloromethyl formate¹ has been found to take place by the mechanism of the neutral ester hydrolysis. The rate coefficient for the hydrolysis of α -chlorobenzyl formate proceeding by the $\text{B}_{\text{AC}3}$ mechanism can be estimated as about 10^{-7} s^{-1} , and so would not affect the ex-

perimentally determined rate coefficient ($8.1 \times 10^{-3} \text{ s}^{-1}$). When the estimation was made, it was assumed that the rate coefficients of the hydrolysis of chloromethyl formate¹ and chloromethyl dichloroacetate³ are similarly dependent on the composition of the solvent mixture, and further, that when the hydrogen in the methyl group was substituted by a phenyl group the effect is the same in both α -chlorobenzyl formate and trifluoroacetate.

In the hydrolysis of α -chlorobenzyl formate and acetate, the retarding effect of the organic solvent component on the reaction rate is of the same order of magnitude as in the hydrolysis of α -chloroalkyl acetates ($\text{S}_{\text{N}}1$) in acetone-water mixtures.^{1,4,5} In the hydrolysis of the α -chlorobenzyl and benzyl esters of trifluoroacetic acid,

Table 2. Kinetic data for the hydrolysis of benzyl trifluoroacetate and hexachlorocyclohexylchloromethyl trifluoroacetate $\text{CF}_3\text{COOR}'$ in P vol. "% acetone-water mixtures.

R'	P vol. "%	$^{\circ}\text{C}$	10^3k (s^{-1})
$\text{CH}_2(\text{C}_6\text{H}_5)$	80	25	0.0128 ± 0.00055
	85	25	0.0060 ± 0.00010
	90	25	0.0017 ± 0.00004
$\text{CHCl}(\text{C}_6\text{H}_2\text{Cl}_6)$	98	25	43–33
		35	49–42

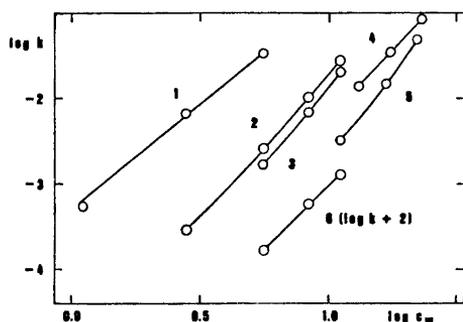


Fig. 1. Plots of $\log k$ versus $\log c_w$ (c_w is the molarity of water in the solvent mixture) for the hydrolyses of the following esters in acetone-water mixtures. 1. α -Chlorobenzyl trifluoroacetate. 2. α -Chloro-*sec*-propylacetate.⁵ 3. α -Chlorobenzyl acetate. 5. α -Chlorobenzyl formate. 6. Benzyl trifluoroacetate. 4. α -Chlorobenzyl acetate in dioxane-water mixtures.

however, this effect is somewhat smaller (Fig. 1), and is measured at a different temperature. The variation may be due to different reaction mechanisms.

The rate coefficients calculated for the hydrolysis of hexachlorocyclohexylchloromethyl trifluoroacetate decrease in value as the reaction proceeds, even though the nonlinear relationship between the conductance and the concentration has been taken into account (Table 2). The decreasing value of the rate coefficient may be the consequence of several hydrolyses proceeding at different rates. The reacting ester is a mixture of several isomers and conformers.⁸ The small effect of the temperature on the hydrolysis rate implies that the reaction takes place by the neutral ester hydrolysis ($\text{B}_{\text{AC}}3$) mechanism. This

is in agreement with the rate coefficient for the hydrolysis of hexachlorocyclohexylchloromethyl trifluoroacetate being one hundred times greater than that for the hydrolysis of α -chlorobenzyl trifluoroacetate.

When the rate coefficients of the hydrolysis of α -chlorobenzyl and benzyl trifluoroacetates are compared, it is seen that the chlorine at the α -position increases the rate of reaction 2×10^4 -fold in a 90% acetone-water mixture, which is, when expressed with this accuracy, the same ratio as is found for aliphatic esters of trifluoroacetic acid.^{10,11}

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