

Effect of Water on the Kinetics of the Neutral Ester Methanolysis and Ethanolysis

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The kinetic behaviour of the neutral methanolysis and ethanolysis of chloromethyl trichloroacetate in water/methanol and water/ethanol solutions has been studied. Minor amounts of water in the alcohol solutions were found to accelerate the rates of the reactions. Added water decreased ΔH^\ddagger , whereas its effect on the ΔS^\ddagger values was less significant. In contrast to the minima in ΔC_p^\ddagger as observed for the neutral ester hydrolysis in water-rich aqueous methanol, ΔC_p^\ddagger for the present methanolysis remained almost unchanged. This is in accord with the structural differences between water-rich and methanol-rich solvent systems.

Koskikallio^{1,2} has previously studied the spontaneous decomposition of acetic anhydride in water(W)/methanol(MeOH) and in W/ethanol (EtOH) solutions over the whole compositional profile from water to alcohol. The first-order rate coefficients for the total reactions and for both the hydrolysis and alcoholysis reactions separately were shown to increase at the beginning with increasing water content. In the case of the alcoholysis reactions, the rate coefficients were found to go through a maximum at some mole fraction, x_{ROH} (R = Me or Et) of alcohol in the water-rich part of the compositional profile.

The purpose of this work was to study solvent effects caused by minor amounts of water in the neutral methanolysis of chloromethyl trichloroacetate over a wide temperature range. The data obtained were compared to the rate effects in the neutral ester hydrolysis,³ caused by methanol in the most water-rich solutions, in terms of changes in the activation enthalpy, ΔH^\ddagger , activation entropy, ΔS^\ddagger and the heat capacity of activation, $\Delta C_p^\ddagger = d\Delta H^\ddagger/dT$. The data for the neutral ethanolysis of chloromethyl trichloroacetate in W/EtOH solutions were also included.⁴

Experimental

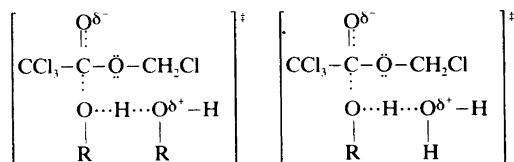
Chloromethyl trichloroacetate⁵ and the reaction solutions were prepared as described.⁶ Methanol (E. Merck AG, *getrocknet, pro analysi*) was used as received. Ethanol (Oy Alko Ab, Aa 99.5%) was poured through a column filled with molecular sieves. By Karl Fischer's water titration, the water content of methanol and of dried ethanol was found to be less than 0.01 and 0.1%, respectively. The initial ester concentrations were about 10^{-4} M. The temperature was stable within 0.01 K.

The reactions were followed conductometrically⁷ by measuring the concentration of hydrogen chloride. The rate coefficients were calculated by Guggenheim's method,⁸ their standard deviations being, in general, less than 0.05%. The thermodynamic activation parameters were calculated from an extended Arrhenius equation, $\ln k = A + B/T + C \ln T + DT + \dots$, in its three-parameter form using the method of Clarke and Glew⁹ after an orthogonalization procedure. The calculated data for the neutral methanolysis of chloromethyl trichloroacetate at 298.15 K are

given in Table 1. The data,⁴ recalculated using the Arrhenius eqn., for the neutral ethanolysis of the same ester are shown in Table 2.

Discussion

As previously proposed, the neutral methanolysis of chloromethyl trichloroacetate in methanol takes place by the $B_{AC}3$ mechanism.⁶ The rate determining step is the nucleophilic addition of methanol to the carbonyl group of the ester; the other methanol molecule acts as a general base catalyst. The neutral ester ethanolysis also presumably proceeds by the $B_{AC}3$ mechanism. In the present study, small amounts of water were added to methanol and ethanol. Both water and the alcohols may act as acids and bases, but water accepts the proton more easily; the distribution constant $K = a(H_3O^+) a(ROH)/[a(ROH_2^+) a(H_2O)]$ of protons between alcohol and water at 298 K being 137 in methanol¹⁰ and 210 in ethanol¹¹. The alcoholysis of chloromethyl trichloroacetate is not expected to be accompanied significantly by simultaneous ester hydrolysis in either methanolysis or ethanolysis reactions due to the small water concentrations present. This conclusion is supported by the data for the decomposition of acetic anhydride in aqueous alcohol solutions^{1,2} where, for example, the rate coefficient for methanolysis is 25 times higher than is found for hydrolysis in W/MeOH solutions at x_{MeOH} 0.96. The possible transition state structures for the rate determining step for the alcoholysis of chloromethyl trichloroacetate in W/ROH solutions are shown below. As the water concentration increases, the water molecules appear better able to compete with the alcohol mol-



ecules in the role of general base catalysts. The water molecule, when acting in this capacity, improves the ability of the oxygen atom of the alcohol molecule immediately involved in the reaction to attack the ester function. Furthermore, based on Raman difference spectroscopy,¹³ it seems that when water is added to methanol, the methanol – methanol interactions remain almost unchanged until $x_{MeOH} < 0.7$. In contrast to this, there are many kinds of evidence of the enhancement of hydrogen bonds among the water molecules when small amounts of a monohydric alcohol are added to water.¹⁴

The consideration above is in accord with the rate increases observed for the neutral methanolysis and ethanolysis of chloromethyl trichloroacetate in W/ROH solutions (Tables 1 and 2). This is opposite to the rate lowering effect caused by organic cosolvents such as methanol in neutral ester hydrolysis³ in water-rich aqueous solutions or acetonitrile in neutral ester methanolysis⁵ in its methanol solutions. The rate increase caused by water in ethanol, $[k(x_{EtOH} 0.96)/k(x_{EtOH} 1.00) \sim 4]$, exceeded that which was found in methanol, $[k(x_{MeOH} 0.96)/k(x_{MeOH} 1.00) \sim 2.5]$, as could be expected on the basis of the proton distribution constants as mentioned above. Because the nucleophilic addition of ethanol to the carbonyl group of the ester may be sterically a more difficult process than the addition of methanol and

Table 1. Temperature range, T , number of data points, N , first-order rate coefficients, k , activation enthalpies, ΔH^\ddagger , activation entropies, ΔS^\ddagger and the heat capacities of activation, ΔC_p^\ddagger for the neutral methanolysis of chloromethyl trichloroacetate in water/methanol solutions at mole fraction of methanol x_{MeOH} at 298.15 K.

x_{MeOH}	T/K	N	$k/10^{-3} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$-\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	$-\Delta C_p^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$
1.000	273–328	11	2.673	27.41(3)	202.2(1)	99(4)
0.995	273–328	10	3.121	26.98(4)	202.4(1)	77(5)
0.990	273–328	14	3.625	26.47(5)	202.9(2)	101(6)
0.985	273–328	13	4.150	26.19(7)	202.7(2)	112(9)
0.980	273–328	13	4.624	26.19(6)	201.8(2)	86(7)
0.970	273–328	12	5.652	25.58(6)	202.2(2)	94(7)
0.960	273–318	19	6.775	25.28(14)	201.7(5)	146(18)

water, it is also possible that the decomposition of chloromethyl trichloroacetate even at x_{EtOH} 0.96 includes a contribution of the neutral ester hydrolysis. On the other hand, the relative rates, 750, 1 and 0.1 for the decomposition of chloromethyl trichloroacetate in water,⁶ methanol and ethanol, respectively, are in accord with the order of solvent polarity which evidently is of importance for reactions where a polar transition state results from a neutral initial state. This rate order is also in accord with the increasing steric hindrance which is involved in the rate determining step of the $B_{AC}3$ mechanism when the reaction changes from hydrolysis to ethanolysis.

As shown in Fig. 1A, water first caused a decrease in ΔH^\ddagger for the neutral methanolysis of chloromethyl trichloroacetate whereas its effect on the ΔS^\ddagger values was less significant. Thus, in the case of methanolysis in the W/MeOH solutions studied (Table 1; Fig. 1A) ΔS^\ddagger at 298.15 K remained almost unchanged. In the case of ethanolysis (Table 2; Fig. 1A), ΔS^\ddagger went through a clear minimum at $x_{\text{EtOH}} \sim 0.975$. If the present data for the neutral ester alcoholysis in alcohol-rich solutions (Fig. 1A) are compared with the available data for the neutral ester hydrolysis in water-rich methanol solutions³ (Fig. 1B) it seems that water in alcohol is more effective than methanol in water in reducing ΔH^\ddagger values. Thus, at 298.15 K in the range from 1.00 to 0.96 for x_{ROH} , ΔH^\ddagger decreased by 1.8 and 6 kJ mol⁻¹ for methanolysis and ethanolysis of chloromethyl tri-

chloroacetate, respectively (Fig. 1A). In the hydrolyses of methyl trifluoroacetate and chloromethyl dichloroacetate in aqueous methanol (Fig. 1B), the decreases in ΔH^\ddagger were only about 0.1 and 0.8 kJ mol⁻¹, respectively, when x_{MeOH} went from 0.00 to 0.04. On the other hand, ΔS^\ddagger for the neutral ester hydrolysis³ was found to decrease almost continuously from water to moderately concentrated methanol solutions.

The changes in ΔH^\ddagger and ΔS^\ddagger with solvent composition are certainly connected with changes in solvent structure. The heat capacity of activation is, however, a more sensitive indicator of solvent effects for solvolytic reactions. In accord with the maximal water structure caused by methanol in water-rich MeOH/W solutions, there is a minimum in ΔC_p^\ddagger at x_w 0.95 and 0.843 for the neutral hydrolysis of chloromethyl dichloroacetate [$\Delta\Delta C_p^\ddagger = \Delta C_p^\ddagger(\text{minimum}) - \Delta C_p^\ddagger(\text{water}) = -62 \text{ J mol}^{-1} \text{ K}^{-1}$] and methyl trifluoroacetate [$\Delta\Delta C_p^\ddagger = -79 \text{ J mol}^{-1} \text{ K}^{-1}$], respectively.³ As shown in Table 1, ΔC_p^\ddagger for the neutral methanolysis of chloromethyl trichloroacetate changed only slightly with increasing water content in methanol. The interpretation of this behaviour is that the addition of water to methanol has only a negligible influence on the structure of liquid methanol. This conclusion is supported by the recent data from Raman difference spectroscopy¹³ which indicate that the decomposition of the structure of liquid methanol in the methanol-rich domain only starts at x_{MeOH} about 0.7. This interpretation

Table 2. Temperature range, T , number of data points, N , first-order rate coefficients, k , activation enthalpies, ΔH^\ddagger and activation entropies, ΔS^\ddagger for the neutral ethanolysis of chloromethyl trichloroacetate in water/ethanol solutions at mole fraction of ethanol x_{EtOH} at 298.15 K.^a

x_{EtOH}	T/K	N	$k/10^{-4} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$-\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$
1.00 ^b	278–348	16	2.676	31.3(3)	208.5(10)
0.998	298–328	8	2.661	30.5(2)	210.9(7)
0.990	298–328	8	4.790	27.2(3)	217.2(8)
0.980	298–328	8	6.827	26.3(3)	217.3(11)
0.978	298–328	8	7.492	25.4(3)	219.4(10)
0.975	298–328	8	8.125	24.9(3)	220.5(11)
0.970	298–328	8	9.198	25.1(3)	218.9(9)
0.965	298–328	8	10.21	25.3(3)	217.3(8)
0.950	298–328	8	13.86	24.6(2)	217.3(6)
0.925	298–328	8	20.07	24.7(3)	213.6(8)
0.900	298–328	8	27.02	24.5(4)	211.8(12)

^aRecalculated from the data in Ref. 4. ^bThis work.

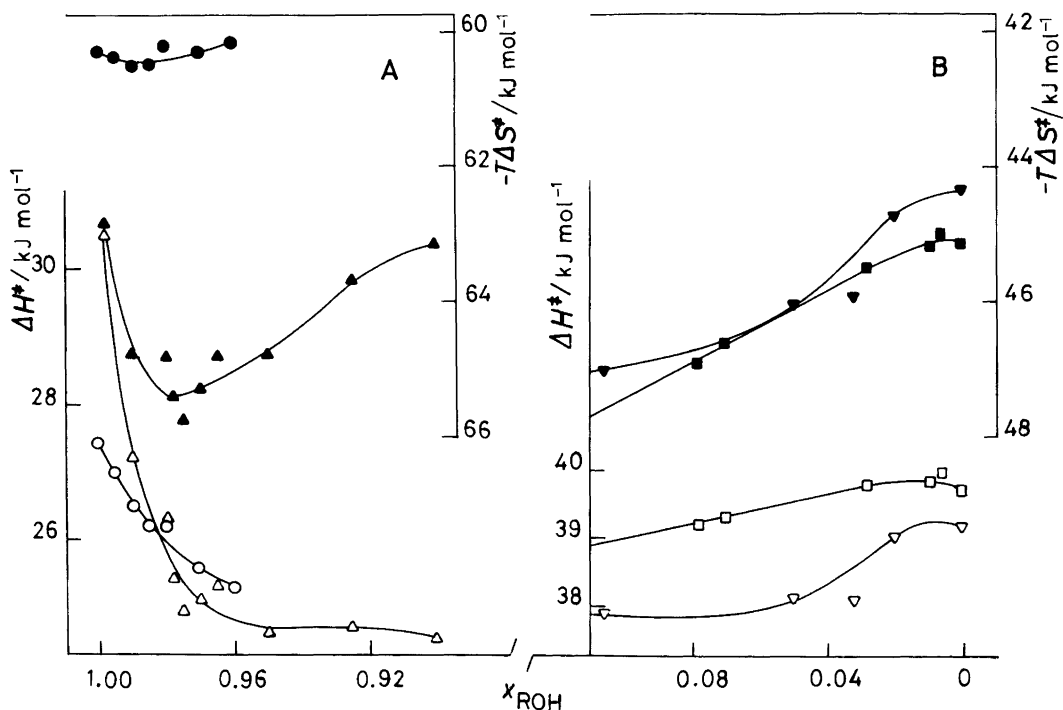


Fig. 1. Plots of ΔH^\ddagger (open symbols) and $T\Delta S^\ddagger$ (blackened symbols) for the neutral methanolysis (○) and ethanolysis (△) of chloromethyl trichloroacetate in water/methanol (R = Me) and water/ethanol (R = Et) solutions (A) and for the neutral hydrolysis of methyl trifluoroacetate (□) and chloromethyl dichloroacetate (▽) in methanol/water solutions (B) at 298.15 K.

is also in accord with the lack of a strong hydrogen-bonded network structure in liquid methanol, typical for the structure of liquid water. The rough estimations of ΔC_p^\ddagger for the neutral ethanolysis of chloromethyl trichloroacetate in W/EtOH solutions seem to indicate that, in this case, ΔC_p^\ddagger goes from the value $-61 \pm 32 \text{ J mol}^{-1} \text{ K}^{-1}$ in ethanol to the minimum value, about $-170 \text{ J mol}^{-1} \text{ K}^{-1}$ at $x_{\text{EtOH}} 0.975$; that is, at the solvent composition where ΔS^\ddagger also shows its minimum. In the case of ethanolysis, the possible contribution of the simultaneous neutral ester hydrolysis should also be borne in mind.

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