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Kinetics of the Alcoholysis of Acetyl Chloride in Ethanol

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The rate of alcoholysis of acetyl chloride in ethanol has been measured at temperatures from +35 to −40°C by conductometric and titrimetric methods, which gave consistent results. The reaction was found to obey the Arrhenius equation. In the titrimetric method, the value of the ratio of the products of the concurrent hydrolysis and alcoholysis reactions was required and was determined in a 50 volume per cent ethanol-water mixture at different temperatures.

Although the kinetics of the hydrolysis and alcoholysis reactions of acyl chlorides has been investigated extensively (for recent reviews, see, *e.g.*, Kivinen[1,2] and Minato[3]) the alcoholysis of aliphatic acyl halides in pure alcohols has been studied only in a few cases.[4] The reason is without doubt the high rates of the reactions, as a result of which conventional kinetic methods do not yield reliable results. The only attempt to measure the rate of alcoholysis of acetyl chloride in ethanol seems to be that made by Kivinen,[4] but his method gave only an approximate value for the half-life of the reaction at 0°C. The present authors[5] developed nearly twenty years ago a titrimetric method by which the rate in question was measured at temperatures from 35 to 0°C. For comparison and for extension of the temperature range, the rate has now been measured conductometrically at temperatures from 0 to −40°C. Both of the employed methods are described in the following.

EXPERIMENTAL

Materials. Acetyl chloride (E. Merck AG) was distilled before use (b.p. 51.1°C/760 torr). Ethanol (Grade Aa, Oy Alkoholiliike Ab) was dried by the method of Lund and Bjerrum[6] (b.p. 78.2°C/760 torr; it was found to contain 0.014 weight per cent water by Karl Fischer titration).

Preliminary experiments. The heat of reaction was found to warm the reaction mixture appreciably if the initial concentration of acetyl chloride was of the magnitude usual in kinetic experiments. The temperature rose about 5.2° when 1 ml of acetyl chloride was mixed with 100 ml of ethanol in a Dewar flask, about 3.2° when the mixture was kept in a glass reaction flask immersed in a water thermostat, and about 2.2° when the glass flask containing the mixture was continuously shaken in the thermostat. A ratio of acetyl chloride and ethanol smaller than 1:1000 was therefore used in the actual kinetic experiments. The maximal increase of temperature was then found to be less than 0.2° (about 20 sec after mixing at 15°C).

Because of the low initial concentration of acetyl chloride, the usual method of taking samples from the reaction mixture and adding them to water [7] was not appropriate for the kinetic measurements. The alcoholysis reaction was therefore arrested by adding an equal volume of water to the reaction mixture. In these conditions, however, the remaining acetyl chloride does not hydrolyse completely, but part of it reacts with ethanol. The ratio of the products of the concurrent hydrolysis and alcoholysis reactions had therefore to be determined.

Determination of the product ratio. The ratio was determined by adding about 0.1 vol. per cent acetyl chloride dissolved in a small volume of dioxane to a 50 vol. per cent ethanol-water mixture (prepared by mixing equal volumes of ethanol and water) and titrating the mixture after complete reaction with a standard sodium hydroxide solution employing a mixture of phenol red and bromothymolbenzein in the ratio of 3:2 as indicator. This indicator was found to be suitable when the titration mixture contained about 30 % ethanol at the end point.[8] The chloride ion was then titrated with standard silver nitrate solution by the method of Fajans using fluorescein as indicator. One group of experiments was performed by adding acetyl chloride to a thermostated ethanol-water mixture, and another group by adding separately thermostated water and acetyl chloride to thermostated ethanol. In the last-mentioned conditions, which correspond to those in the kinetic measurements, the temperature rose about 10°.

If the observed base consumption is b and the silver nitrate consumption c equivalents, the fraction μ of acetyl chloride that has reacted with ethanol is, if the acetyl chloride was pure,

$$\mu = (2c - b)/c \tag{1}$$

Table 1. The uncorrected and corrected fractions of alcoholysis μ and m (eqn. (1) and (2)) for the concurrent alcoholysis and hydrolysis reactions of acetyl chloride in 50 vol. per cent ethanol-water mixtures at different temperatures (see text).

Temperature °C	μ	u	m	m (average)
15	0.231 (3)	0.986 (2)	0.234 ± 0.002	0.234 ± 0.002 (3)
15 + 10	0.226 (41)	0.993 (3)	0.228 ± 0.002	0.230 ± 0.002 (66)
	0.233 (25)		0.233 ± 0.003	
35	0.224 (8)	0.986 (2)	0.227 ± 0.006	0.227 ± 0.006 (8)
0 + 10	0.237 (7)	0.980 (4)	0.242 ± 0.003	0.233 ± 0.002 (39)
10	0.253 (6)	0.997 (4)	0.254 ± 0.002	
	0.223 (7)	0.991 (3)	0.225 ± 0.006	
	0.224 (6)	0.970 (4)	0.231 ± 0.014	
	0.222 (6)	0.977 (4)	0.227 ± 0.006	
	0.220 (7)	0.989 (4)	0.222 ± 0.003	
10 + 10	0.256 (5)	1.004 (4)	0.255 ± 0.008	0.247 ± 0.003 (57)
	0.289 (4)	1.007 (3)	0.287 ± 0.004	
	0.262 (6)	0.990 (3)	0.265 ± 0.007	
	0.294 (5)	0.996 (3)	0.295 ± 0.008	
	0.231 (7)	0.991 (4)	0.233 ± 0.006	
	0.213 (5)	0.991 (4)	0.215 ± 0.007	
	0.239 (6)	0.999 (4)	0.239 ± 0.004	
	0.222 (4)	0.998 (4)	0.222 ± 0.005	
20	0.234 (6)	0.960 (2)	0.244 ± 0.004	
	0.230 (9)	0.983 (2)	0.234 ± 0.005	

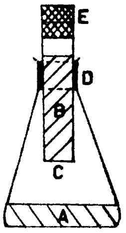

Fig. 1. The apparatus employed to arrest the reaction. A is the reaction mixture, B a measured volume of water in a wide glass tube, C a piece of waterproof paper, D and E stoppers.

because both the hydrolysis and alcoholysis reactions produce hydrogen chloride but only the first-mentioned reaction acetic acid; ethyl acetate formed in the last-mentioned reaction does not hydrolyse under these conditions. Because even freshly distilled acetyl chloride usually is partly hydrolysed during the manipulations, the quality of every acetyl chloride sample was tested by adding a sample of it to ethanol and analysing the mixture for acid and chloride after complete reaction. The experimental purity u calculated from eqn. (1) was found to vary between 0.960 and 1.007. When it is taken into account that the actual amount of acetyl chloride in the sample is equivalent to only uc, the fraction m that has reacted with ethanol is not μ but

$$m = (2c - b)/uc = \mu/u \tag{2}$$

The determined fractions of alcoholysis and the standard errors of the means are given in Table 1. The numbers in parentheses are the numbers of experiments. It is seen that the values of m at different temperatures do not differ significantly. Therefore, the value 0.230 was employed for the fraction of alcoholysis in the kinetic experiments at the temperatures 15, 25, and 35°C (experiments performed by one of the authors (E. K. E.)) and the value 0.240 at the temperatures 0, 10, and 20°C (experiments performed by Mr. E. Kalkas).

Titrimetric method. A conical flask containing an accurately measured volume of ethanol (50 ml) was placed in a thermostat. About 0.05 ml of acetyl chloride was added quickly from a syringe and the mixture was thoroughly shaken. After the chosen reaction time, exactly the same volume of water (50 ml) was added quickly to and shaken vigorously with the reaction mixture. To effect as rapid a mixing as possible, the apparatus shown in Fig. 1 was employed. When the stopper E is removed rapidly, the water in the tube B falls into and is quickly mixed with the reaction mixture A. The stopper D has holes to allow air to escape from the reaction flask. The reaction mixture is titrated first with standard sodium hydroxide solution and then with standard silver nitrate solution.

As ethanol was present in great excess, the integrated first-order rate equation was employed in the calculation of the rate coefficient k. If a and $(a - x)$ are the concentrations of acetyl chloride at the beginning of the reaction and at time t, V the volume of the reaction mixture, and the other symbols have the same meanings as above, then a is obtained from the expression $uc = aV$ and the experimental number of base equivalents is the sum $b = c + (1 - m)(a - x)V + (1 - u)c = (2 - u)c + (1 - m)(a - x)V$, where c is the found number of equivalents of silver nitrate, $(1 - m)(a - x)V$ the amount of acetic acid formed by hydrolysis after the addition of water, and $(1 - u)c$ the amount of acetic acid present before the reaction was started. The equation for k is thus

$$k = \frac{1}{t}\ln\frac{a}{a - x} = \frac{1}{t}\ln\frac{(1 - m)uc}{b - (2 - u)c} \tag{3}$$

For illustration, experimental data for the alcoholysis of acetyl chloride in ethanol at 20°C are given in Table 2. $m = 0.240$, $u = 0.990$ (4 experiments), $c_{\text{NaOH}} = 0.03966$ mole/l, $c_{\text{NaOH}}/c_{\text{AgNO}_3} = 0.9276$.

Conductometric method. The rates at temperatures below 0°C were measured by a conductometric method described earlier[9] but employing a Philips PR 9501 conducto-

Table 2.

t (s)	$V_{\mathrm{AgNO_3}}$ (ml)	$V_{\mathrm{NaOH}} \times \dfrac{c_{\mathrm{NaOH}}}{c_{\mathrm{AgNO_3}}}$ (ml)	k ($\mathrm{s^{-1}}$)
7.40	22.82	30.45	0.114
8.15	17.35	23.05	0.105
8.85	30.08	38.80	0.112
9.05	15.92	20.97	0.099
9.50	25.09	32.13	0.108
9.50	32.53	41.24	0.113
10.05	14.50	18.66	0.100
10.40	27.31	34.14	0.110
10.55	19.56	24.45	0.108
11.50	25.44	31.39	0.105
12.35	25.65	30.95	0.109
13.05	40.80	48.05	0.115
13.55	21.19	25.17	0.106
14.35	18.76	22.32	0.100

meter. A calibration curve was constructed after alcoholysing various amounts of acetyl chloride in ethanol and measuring the conductances of the solutions and titrating samples of the solutions potentiometrically with a standard silver nitrate solution.

RESULTS AND DISCUSSION

Concurrent alcoholysis and hydrolysis of acetyl chloride in 50 vol. per cent ethanol-water. The measured fractions of alcoholysis (Table 1) can be used to calculate the ratio of the rate coeffients of concurrent alcoholysis and hydrolysis reactions, if it can be assumed 1) that the products are formed in the rate-determining stage of the reaction and 2) if the order of the reaction in respect of each reacting species is known. If the orders of the reaction in respect of acetyl chloride, ethanol, and water are 1, α, and β, respectively, the rate equations for the alcoholysis and hydrolysis reactions are

$$-(\mathrm{d}c_{\mathrm{AcCl}}/\mathrm{d}t)_{\mathrm{a}} = k_{\mathrm{a}}\, c_{\mathrm{AcCl}}\, c_{\mathrm{EtOH}}{}^{\alpha} \tag{4}$$

$$-(\mathrm{d}c_{\mathrm{AcCl}}/\mathrm{d}t)_{\mathrm{h}} = k_{\mathrm{h}}\, c_{\mathrm{AcCl}}\, c_{\mathrm{H_2O}}{}^{\beta} \tag{5}$$

where the subscripts a and h refer to alcoholysis and hydrolysis, respectively. From (4) and (5) one gets

$$\frac{(\mathrm{d}c_{\mathrm{AcCl}})_{\mathrm{a}}}{(\mathrm{d}c_{\mathrm{AcCl}})_{\mathrm{h}}} = \frac{k_{\mathrm{a}}}{k_{\mathrm{h}}} \times \frac{c_{\mathrm{EtOH}}{}^{\alpha}}{c_{\mathrm{H_2O}}{}^{\beta}} \tag{6}$$

Because the concentrations of ethanol and water may be considered to be constant in the experiments, the ratio of the rates of alcoholysis and hydrolysis must be constant and the same as the ratio $m/(1 - m)$, where m is the experimentally determined fraction of acetyl chloride that has been alcoholysed (eqn. (2)). If it is further assumed 3) that $\alpha = \beta = 1$, one gets

$$\frac{k_{\mathrm{h}}}{k_{\mathrm{a}}} = \frac{c_{\mathrm{EtOH}}}{c_{\mathrm{H_2O}}} \times \frac{1 - m}{m} \tag{7}$$

By substituting in eqn. (7) the data $c_{\mathrm{EtOH}} = 50 \times 0.789/46.07V$ mole/l, $c_{\mathrm{H_2O}} = 50 \times 0.998/18.02V$ mole/l, and $m = 0.236 \pm 0.001$ for 50 vol. per cent ethanol-water, one gets the value 1.00 ± 0.01 for $k_{\mathrm{h}}/k_{\mathrm{a}}$. The second-order rate coefficients of hydrolysis and alcoholysis of acetyl chloride in 50 vol. per cent ethanol-water may thus be considered to be equal within the limits of experimental error. This result may be compared with that of Oliver Ruiz and Galbis Muñoz[10] who found by a different method the corresponding ratios 1.05,

Table 3. The rate coefficients for the alcoholysis of acetyl chloride in ethanol at different temperatures. Titrimetric method. Initial concentration of acetyl chloride about 0.02 mole/l.

Temperature °C	k s^{-1}	Number of runs
35	0.309 ± 0.014	4
25	0.147 ± 0.016	5
20	0.107 ± 0.0014	14
15	0.0691 ± 0.0011	12
10	0.0465 ± 0.0006	28
0.1	0.0191 ± 0.0002	19

Table 4. The rate coefficients for the alcoholysis of acetyl chloride in ethanol at different temperatures. Conductometric method.

Temperature °C	$c_{\mathrm{H_2O}}$ mole/l	c_{AcCl} mole/l	10^3k (s^{-1})	
			mean of a run	average
0.00	≈0.006	0.0055	17.8 ± 0.16	18.3
		0.0078	18.8 ± 0.22	
−10.00	≈0.006	0.0015	7.71 ± 0.013	
		0.0040	7.50 ± 0.015	
		0.0059	7.28 ± 0.030	7.26
		0.0074	7.21 ± 0.034	
		0.0125	7.29 ± 0.020	
		0.0212	7.08 ± 0.046	
		0.0057*	7.15 ± 0.021	
		0.0116**	6.97 ± 0.042	
	0.134	0.0077	7.56 ± 0.024	
	0.230	0.0085	7.64 ± 0.011	
−20.37	≈0.006	0.0097	2.49 ± 0.007	2.53
		0.0101	2.58 ± 0.015	
−30.08	≈0.006	0.0056	1.01 ± 0.006	1.01
		0.0070	1.00 ± 0.007	
−40.10	≈0.006	0.0080	0.292 ± 0.0027	0.297
		0.0112	0.301 ± 0.0018	

* In a solution 0.0059 M in both hydrogen chloride and acetic acid.
** In a solution 0.0116 M in both hydrogen chloride and acetic acid.

1.12, and 1.18 for solutions containing more ethanol at the temperatures 2, 15, and 28°C, respectively.

The kinetics of the alcoholysis of acetyl chloride in ethanol. The values of the determined rate coefficients are given in Tables 3 and 4. It is seen that the titrimetric and conductometric methods gave the same value for the rate coefficient at 0°C within the limits of experimental error. The value is also in satisfactory agreement with the preliminary value, 30 sec, reported by Kivinen[4] for the half-life of the reaction. A small addition of water to ethanol is found to increase the rate (Table 4). It may, however, be concluded that the low concentration of water in the ethanol used in the kinetic experiments does not affect the rate significantly. Somewhat lower values are obtained for the rate coefficient if the initial concentration of acetyl chloride is increased or if hydrogen chloride and acetic acid are initially present in the reaction mixture (Table 4). This effect is not large, however, and is partly eliminated when approximately equal initial concentrations of acetyl chloride are used in the actual runs.

The effect of temperature is investigated by fitting the equation[11]

$$\log k = (A/T) + B \log T + C \tag{8}$$

to the data obtained separately by the titrimetric method and by the conductometric method and to all of the data together. The parameter B is not found to differ from zero within the limits of experimental error (the values found by a least squares calculation were -16 ± 14, $+3 \pm 19$, and $+6 \pm 4$, respectively). The Arrhenius equation was therefore fitted to the three sets of data and similar values were obtained for the activation energy E (13.3 ± 0.17, 12.9 ± 0.18, and 13.23 ± 0.09 kcal/mole) and for the frequency factor A (in s^{-1}; $\log A = 8.9 \pm 0.13$, 8.6 ± 0.16, and 8.87 ± 0.07).

The kinetic data for acetyl chloride and several other acyl chlorides are given in Table 5. The values for acetyl chloride are seen to be similar to those for pivaloyl chloride and *p*-nitrobenzoyl chloride, the alcoholysis reactions of which have been concluded to take place by a bimolecular mechanism,[4] and differ from those for *p*-methoxybenzoyl chloride, which undergoes alcoholysis by a unimolecular S_N1 mechanism.[1] Whether the bimolecular mechanism is a direct S_N2-type displacement reaction or whether a tetrahedral intermediate is formed (an addition-elimination mechanism) cannot be decided on the basis of the present data, but, besides other facts, the structural effects,

Table 5. Kinetic data for the alcoholysis of acyl chlorides in ethanol at 25°C.

Acyl chloride	10^3k s^{-1}	E kcal/mole	$\log A$ (A in s^{-1})	Ref.
Acetyl chloride	147	13.23	8.87	
Pivaloyl chloride	18.1	13.15	7.90	4
p-Nitrobenzoyl chloride	11.4	12.75	7.40	1
Benzoyl chloride	1.14	15.25	8.05	1
p-Methoxybenzoyl chloride	0.949	19.10	10.98	1
Ethyl chloroformate	0.0211	16.04	7.08	2

the low activation energy (compare with, *e.g.*, the data for the neutral hydrolyses of α-haloalkyl esters [9,11]), and the oxygen exchange reaction accompanying the hydrolysis of benzoyl chloride [12] seem to indicate that the last-mentioned mechanism or that proposed by Minato [3] with two tetrahedral intermediates is the actual mechanism.

It is noteworthy that, in contrast to the neutral hydrolysis of carboxylic esters,[11,13] to many displacement reactions of chlorine at saturated carbon atoms, and to the methanolysis of *tert*-butyl chloride in methanol (for references, see Ref. 11), the Arrhenius' activation energy for the alcoholysis of acetyl chloride was not found to vary with temperature. A negative value for dE/dT was reported by Archer and Hudson [14] for the hydrolysis of benzoyl chloride in 61.05 weight per cent acetone-water, but this value hardly exceeds the experimental error. The observed independence of E on T in the case of the alcoholysis of acetyl chloride in ethanol may be due to a small difference in polarity between the initial and transition states, because negative values of dE/dT are usually connected with highly polarised transition states.[11]

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