# Kinetics and Mechanism of the Carboxylic Acid Catalysed Ethanolysis of p-Chlorophenyl Isocyanate in Diethyl Ether

By Steven A. Lammiman and Rosemary S. Satchell,* Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W.8

The kinetics of carboxylic acid catalysis of the ethanolysis of p-chlorophenyl isocyanate in diethyl ether at 25° have been investigated. The results suggest that an intermediate 1 : 1-acid–ethanol adduct is rapidly formed. and that this intermediate then attacks the isocyanate in a slow step. Equilibrium constants for intermediate formation and rate constants for its reaction with the isocyanate have been deduced. Whereas the values of the former are independent of the acid's strength, the latter are inversely dependent on it. It is argued that the intermediate has a cyclic structure. and that the probable mechanism of the slow step is a simultaneous attack by the intermediate on the carbon and nitrogen atoms of the isocyanate with the formation of a cyclic transition state. This mechanism is analogous to that for the corresponding reaction of ketens. The dimerisation of carboxylic acid catalysts and their interaction with ethanol in ether have been studied using i.r. spectroscopy.

FOLLOWING our earlier kinetic study of the spontaneous alcoholysis of p-chlorophenyl isocyanate [reaction (1)] in ether solution [1] we have now examined the catalysis

$$ClC_6H_4NCO + ROH \longrightarrow ClC_6H_4NHCO_2R \quad (1)$$
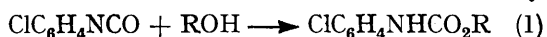
of this process by carboxylic acids. It has been necessary to look also at the dimerisation of these acids in ether and at their ability to form complexes with alcohols. There have been several previous studies of the acid catalysis of the reaction between isocyanates and alcohols, but only one involved catalysis by a hydrogen acid (hydrogen chloride).[2] The others have involved catalysis by a variety of metal compounds.[3]

[1] S. A. Lammiman and R. S. Satchell, J.C.S. Perkin II, 1972, 2300.

[2] J. J. Tazuma and H. K. Latourette, Amer. Chem. Soc., Div. Paint, Plastics, and Printing Ink Chem., paper no. 35, Amer. Chem. Soc. meeting, Atlantic City, September 1956 (see A. Farkas and G. A. Mills, Adv. Catalysis, 1962, 13, 393).

[3] E.g., S. G. Entelis and O. V. Nesterov, Kinetika i. Kataliz, 1966, 7, 464; S. G. Entelis, O. V. Nesterov, and V. B. Zabrodin, ibid., p. 627; O. V. Nesterov, V. B. Zabrodin, Yu. N. Chirkov, and S. G. Entelis, ibid., p. 805.

The mechanism of the spontaneous alcoholysis of isocyanates [1] proved to be very similar to that of the alcoholysis of ketens [4] and we have been concerned in particular to see how far this similarity extends to the carboxylic acid catalysis.

EXPERIMENTAL

Materials.—The purification of diethyl ether, *p*-chlorophenyl isocyanate, and ethanol have been previously described.[1] AnalaR benzoic acid and reagent grade 3-chloropropionic acid were purified by recrystallisation and pumping dry under vacuum. AnalaR monochloroacetic acid was crushed in a dry atmosphere, and dried by pumping under vacuum (24 h). The m.p.s agreed with literature values. Reagent grade dichloroacetic and n-butyric acids were refluxed with a small amount of the corresponding anhydride, and then fractionally distilled under nitrogen. Their b.p.s were 106° at 37 mmHg and 164° at 760 mmHg, respectively.

Reaction Mixtures and Kinetic Arrangements.—The general procedures followed were the same as those used previously.[1] Stock solutions of the carboxylic acids were made up by weight. The progress of the reactions were followed by measuring the absorbance at 293 nm. The reference sample contained the same concentration of alcohol and of acid as the reaction mixture.

In all the reaction mixtures both the alcohol and the acid were present in at least a 10-fold excess of the isocyanate ([RNCO] *ca.* 10^{-3} mol dm^{-3}); this arrangement led to a pseudo-first-order loss of the isocyanate [equation (2)]. The observed first-order rate constant (k_{obs}) was obtained

$$-\mathrm{d[RNCO]}/\mathrm{d}t = k_{obs}\mathrm{[RNCO]} \qquad (2)$$

from a plot of log ($D_\infty - D_t$) against *t*, where D_t and D_∞ were the absorbances at time *t* and ∞ respectively. Plots were rectilinear over several half-lives and values of k_{obs} were reproducible normally to within $\pm 5\%$. Tests were made to check if isocyanate is consumed by reaction (3). Fortunately, at the concentrations used, reaction (3) is very slow and can be ignored.

$$\mathrm{R^1NCO + R^2CO_2H \longrightarrow R^1NHCO{\cdot}O{\cdot}COR^2} \qquad (3)$$

Products.—For each acid, preparative scale reactions were carried out with concentration conditions similar to those used in the kinetic runs. The product urethanes were always obtained in high (>95%) yields and their m.p.s agreed with literature values. U.v. spectra in ether solution showed that the yields in the kinetic runs were close to 100%.

Acid Dimerisation.—The dimerisation of the various carboxylic acids in ether solution was determined by measuring the increasing departure from Beer's law of the i.r. absorption due to the monomer as the stoicheiometric acid concentration is raised.[5] The carbonyl absorption band centred around 1700 cm^{-1} was used. Measurements were made with a Perkin-Elmer 325 i.r. spectrophotometer. A cell of variable pathlength was used to compensate for solvent absorption, and throughout an experiment the apparatus was flushed with dried air. The extinction coefficients of the monomers were obtained from the low concentration regions where Beer's law is obeyed. At higher acid concentrations the monomer concentration was

calculated from the observed absorbance after any necessary allowance had been made for overlap with the dimer band, which occurs *ca.* 30 cm^{-1} away on the long wavelength side. It was assumed that the dimer band like the monomer band is completely symmetrical.

Interaction between Ethanol and the Carboxylic Acids.—Adduct formation between ethanol and a carboxylic acid in ether solution would be expected to shift the carbonyl absorption. The carbonyl bands were examined for a fixed acid concentration (at which the acid was essentially monomeric) over a wide range of ethanol concentrations. As the ethanol concentration was increased the bands broadened and new maxima appeared at lower frequencies. At the lower ethanol concentrations an isosbestic point was seen, but this disappeared at high ethanol concentrations. The change in the magnitude of the absorbance at a given wavelength was small, and it was not possible to determine either the stoicheiometry of any adduct formed, or its association constant. We believe, however, that the spectral changes, and in particular the existence of an isosbestic point at the lower ethanol concentrations, is evidence for adduct formation and that at the concentrations used in the kinetic experiments only one such adduct is formed in significant amounts.

RESULTS AND DISCUSSION

Dimerisation of Carboxylic Acids in Ether.—The carbonyl absorption of 3-chloropropionic acid lies at 1743

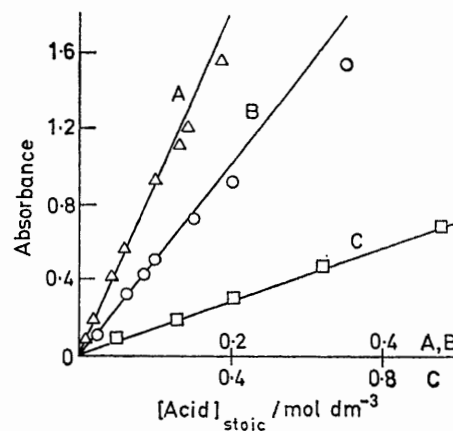FIGURE 1   Test of Beer's law for carboxylic acids in ether: A, benzoic acid; B, n-butyric acid; C, chloroacetic acid

cm^{-1} and obeys Beer's law accurately up to 0·4 mol dm^{-3}. We conclude that this acid is predominantly monomeric up to this concentration. Monochloroacetic acid shows three absorption bands in the carbonyl region at 1737, 1760, and 1790 cm^{-1}, respectively. The absorbance at each wavelength obeys Beer's law accurately up to 0·7 mol dm^{-3} (see *e.g.* Figure 1). We conclude that this acid is also predominantly monomeric at such concentrations. At low concentrations benzoic acid shows an absorption at 1725 cm^{-1} (attributed to the monomer) which obeys Beer's law up to 0·1 mol dm^{-3}, whereafter deviations occur (Figure 1). At high acid concentrations a new band appears at 1695 cm^{-1}, which we attribute to the dimer.

[4] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1968, 897.

[5] D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 1965, **61**, 1199.

The plot of (absorbance)^2 at 1725 cm^{-1} *versus* the absorbance at 1695 cm^{-1} is a straight line, as would be expected for a monomer–dimer equilibrium (4). If [M], [D], and [S] represent the monomer, dimer, and stoicheiometric

$$2 \text{ RCO}_2\text{H} \underset{}{\overset{K_2}{\rightleftharpoons}} (\text{RCO}_2\text{H})_2 \qquad (4)$$

acid concentrations respectively, then the dimerisation constant $K_2 = [\text{D}]/[\text{M}]^2 = ([\text{S}] - [\text{M}])/2[\text{M}]^2$. Hence

TABLE 1

Dimerisation of benzoic acid and n-butyric acid in diethyl ether at 30°. $K_2 = ([\text{S}] - [\text{M}])/2[\text{M}]^2$

[S] mol dm^{-3}	[M] mol dm^{-3}	[S] − [M] mol dm^{-3}	K_2 dm^3 mol^{-1}
Benzoic acid			
0·188	0·176	0·012	0·19
0·142	0·136	0·006	0·16
0·132	0·126	0·006	0·19
n-Butyric acid			
0·551	0·430	0·121	0·33
0·440	0·362	0·078	0·30
0·402	0·320	0·082	0·40
0·348	0·304	0·044	0·24
0·297	0·244	0·053	0·44
0·229	0·200	0·029	0·36
0·200	0·184	0·016	0·24
			Av. 0·34 ± 0·08

K_2 can be calculated, since [M] can be calculated for any value of [S] (see Experimental section). Our derived K_2 values are reasonably constant (Table 1).

n-Butyric acid behaves very like benzoic acid. It has its monomer absorption at 1738 cm^{-1}, and the dimer

solvent ether molecules will stabilise the monomer *via* a hydrogen bond.

Kinetics of the Carboxylic Acid Catalysed Ethanolysis.— The observed first-order rate constant (k_{obs}) is, in general,
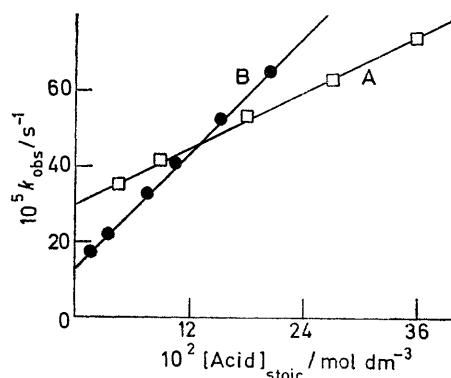

FIGURE 2 Dependence of k_{obs} on [Acid]$_{stoic}$: A, chloroacetic acid with [EtOH]$_{stoic}$ = 1·23 mol dm^{-3}; B, 3-chlororopionic acid with [EtOH]$_{stoic}$ = 0·847 mol dm^{-3}

made up of two parts, (i) a term k_s due to the spontaneous reaction and (ii) a term k_c due to the acid catalysis, *i.e.* $k_{obs} = k_s + k_c$. With [CHCl$_2$CO$_2$H] < 0·5 mol dm^{-3} and [EtOH] = 1·7 mol dm^{-3} no catalysis is observed, but with the other acids k_{obs} increases with acid concentration at fixed alcohol concentration (Tables 2—5). For each catalyst, at any fixed value of [EtOH]$_{stoic}$, a plot of k_{obs} against [Acid]$_{stoic}$ is a straight

TABLE 2

n-Butyric acid catalysis of the ethanolysis of p-chlorophenyl isocyanate in diethyl ether at 25°

For definitions of symbols and method of calculation see text. $K_5 = 1·7$ mol^{-1} dm^3 and K_D (dimerisation constant) for ethanol[1] = 0·71 mol dm^{-3} were used in the calculations. Values of k_s were taken from data for the spontaneous reaction.[1] [EtOH]$_{free}$ represents the total free alcohol concentration

[EtOH]$_{stoic}$ mol dm^{-3}	[Acid]$_{stoic}$ mol dm^{-3}	$10^5 k_{obs}$ s^{-1}	[EtOH]$_{free}$ mol dm^{-3}	[(1)] mol dm^{-3}	$10^5 k_s$ s^{-1}	$10^5 k_c$ s^{-1}
0·118	0·0214	4·08	0·115	0·00313	0·09	3·99
0·118	0·129	25·3	0·101	0·0171	0·1	25·2
0·118	0·173	33·8	0·096	0·0220	0·1	33·7
0·118	0·346	55·3	0·080	0·0380		55·3
0·847	0·0263	30·2	0·835	0·0120	12·3	17·9
0·847	0·105	76·7	0·800	0·0470	11·1	65·6
0·847	0·211	133·0	0·755	0·0923	9·7	123·3
0·847	0·248	149·3	0·739	0·108	8·7	140·6
1·71	0·0363	88·5	1·69	0·0209	55·7	32·8
1·71	0·0821	118·0	1·66	0·0469	53·7	64·3
1·71	0·145	163·0	1·63	0·0825	51·7	111·3
0·132	0·0868	19·5	0·119	0·0130	0·1	19·4
0·530	0·0868	49·5	0·498	0·0316	3·6	45·9
0·866	0·0868	70·0	0·827	0·0394	12·0	58·0
1·054	0·0868	78·2	1·012	0·0424	19·1	59·1
1·227	0·0868	87·8	1·182	0·0447	26·3	61·5
1·544	0·0868	109·5	1·496	0·0482	42·6	66·9
0·101	0·346	48·7	0·068	0·0332		48·7
0·187	0·346	80·2	0·131	0·0557	0·2	80·0
0·277	0·346	108·5	0·202	0·0753	0·4	108·1
0·692	0·346	215·0	0·559	0·133	4·7	210·3

absorption at 1713 cm^{-1}. The derived K_2 values are again reasonably constant (Table 1).

The relative sequence of the values of K_2 is the same as has been reported for other solvents.[5] The values are 1000—2000 times smaller than the values in benzene and in o-dichlorobenzene. This is sensible since the

line (*e.g.* see Figure 2), although there is some indication that when [Acid]$_{stoic}$ > [EtOH]$_{stoic}$ the plots begin to curve. Provided [EtOH]$_{stoic}$ > [Acid]$_{stoic}$ the reaction order in catalyst is therefore unity. The intercepts in Figure 2, when [Acid]$_{stoic}$ = 0, equal k_s for the relevant value[1] of [EtOH]$_{stoic}$.

TABLE 3

Benzoic acid catalysis of the ethanolysis of p-chlorophenyl isocyanate in diethyl ether at 25°

As Table 2. Calculations based on $K_5 = 1.5$ mol^{-1} dm^3 and $K_D = 0.71$ mol^{-1} dm^3

[EtOH]$_\text{stoic}$	[Acid]$_\text{stoic}$	$10^5 k_\text{obs}$	[EtOH]$_\text{free}$	[(I)]	$10^5 k_s$	$10^5 k_c$
mol dm^{-3}	mol dm^{-3}	s^{-1}	mol dm^{-3}	mol dm^{-3}	s^{-1}	s^{-1}
0.138	0.0310	4.05	0.133	0.00455	0.14	3.91
0.138	0.0620	7.68	0.129	0.00885	0.11	7.57
0.138	0.0845	11.0	0.126	0.0119	0.1	10.9
0.138	0.169	21.0	0.116	0.0223	0.1	20.9
1.70	0.133	123.2	1.63	0.0715	51.7	71.5
1.70	0.166	142.2	1.61	0.0889	50.3	91.9
1.70	0.207	164.0	1.59	0.110	49.0	115.0
0.138	0.0382	5.08	0.132	0.00558	0.13	4.95
0.175	0.0382	5.90	0.168	0.00665	0.22	5.68
0.362	0.0382	10.7	0.351	0.0106	1.5	9.2
0.758	0.0382	22.0	0.758	0.0161	6.8	15.2
0.138	0.0684	8.65	0.128	0.00974	0.11	8.54
0.197	0.0684	11.2	0.184	0.0127	0.3	10.9
0.748	0.0684	35.8	0.721	0.0273	8.5	27.3
1.106	0.0684	49.8	1.074	0.0320	21.6	28.2
1.409	0.0684	67.7	1.374	0.0349	35.6	32.1

TABLE 4

3-Chloropropionic acid catalysis of the ethanolysis of p-chlorophenyl isocyanate in diethyl ether at 25°

As Table 2. Calculations based on $K_5 = 2.1$ mol^{-1} dm^3 and $K_D = 0.71$ mol^{-1} dm^3

[EtOH]$_\text{stoic}$	[Acid]$_\text{stoic}$	$10^5 k_\text{obs}$	[EtOH]$_\text{free}$	[(I)]	$10^5 k_s$	$10^5 k_c$
mol dm^{-3}	mol dm^{-3}	s^{-1}	mol dm^{-3}	mol dm^{-3}	s^{-1}	s^{-1}
0.341	0.0161	3.82	0.335	0.00551	1.32	2.50
0.341	0.0434	9.38	0.326	0.0146	1.25	8.13
0.341	0.130	24.5	0.299	0.0419	1.0	23.5
0.847	0.0174	17.5	0.838	0.00885	12.4	5.1
0.847	0.0348	22.0	0.829	0.0176	12.1	9.9
0.847	0.154	52.5	0.771	0.0761	10.1	42.4
0.847	0.204	65.0	0.747	0.0996	9.3	55.7
1.70	0.0965	85.8	1.64	0.0599	52.4	33.4
1.70	0.161	104.2	1.60	0.0992	49.5	54.7
0.374	0.0434	10.0	0.359	0.0154	1.5	8.5
0.847	0.0434	24.0	0.825	0.0220	11.9	12.1
1.038	0.0434	31.8	1.014	0.0235	19.2	12.6
1.208	0.0434	39.8	1.183	0.0247	26.3	13.5
1.372	0.0434	48.7	1.346	0.0256	34.1	14.6
0.370	0.0869	17.6	0.340	0.0300	1.4	16.2
0.538	0.0869	24.0	0.502	0.0361	3.7	20.3
0.847	0.0869	35.3	0.803	0.0436	11.2	24.1
1.039	0.0869	45.2	0.992	0.0468	18.3	26.9
1.200	0.0869	54.0	1.151	0.0490	24.9	29.1
1.369	0.0869	62.8	1.318	0.0509	32.7	30.1

TABLE 5

Monochloroacetic acid catalysis of the ethanolysis of p-chlorophenyl isocyanate in diethyl ether at 25°

As Table 2. Calculations based on $K_5 = 1.5$ mol^{-1} dm^3 and $K_D = 0.71$ mol^{-1} dm^3

[EtOH]$_\text{stoic}$	[Acid]$_\text{stoic}$	$10^5 k_\text{obs}$	[EtOH]$_\text{free}$	[(I)]	$10^5 k_s$	$10^5 k_c$
mol dm^{-3}	mol dm^{-3}	s^{-1}	mol dm^{-3}	mol dm^{-3}	s^{-1}	s^{-1}
0.510	0.0801	12.7	0.483	0.0265	3.3	9.4
0.510	0.584	56.5	0.348	0.162	1.4	55.1
0.510	0.876	74.3	0.292	0.219	1.0	73.3
1.23	0.0898	41.5	1.19	0.0436	26.7	14.8
1.23	0.180	53.5	1.14	0.0860	24.4	29.1
1.23	0.270	63.2	1.10	0.127	22.7	40.5
1.23	0.359	74.3	1.06	0.167	21.0	53.3
1.70	0.0449	62.8	1.68	0.0244	55.0	7.8
1.70	0.270	91.7	1.56	0.143	46.4	45.3
1.70	0.359	103.8	1.51	0.189	43.2	60.6
0.0681	0.0801	1.97	0.0618	0.00632	0.01	1.96
0.182	0.0801	4.30	0.168	0.0139	0.21	4.09
0.294	0.0801	7.05	0.275	0.0193	0.83	6.22
0.510	0.0801	12.7	0.483	0.0265	3.3	9.4
0.849	0.0801	23.7	0.815	0.0337	11.7	12.0
1.37	0.0801	46.7	1.33	0.0404	33.3	13.4

At any fixed value of $[\text{Acid}]_{\text{stoic}}$, plots of k_c (i.e. $k_{\text{obs}} - k_s$) against $[\text{EtOH}]_{\text{stoic}}$ {or $[(\text{EtOH})_M]_{\text{stoic}}$ where $[(\text{EtOH})_M]_{\text{stoic}}$ represents the concentration of the ethanol monomer [1] based on the stoicheiometric ethanol concentration} are curves which approach a limiting value for k_c at high ethanol concentrations. The limiting value depends on the value of $[\text{Acid}]_{\text{stoic}}$. Our results indicate therefore that at high acid, and particularly at high alcohol, concentrations the catalytic velocity begins to level out. This suggests that an acid–alcohol intermediate, say (I), is formed which subsequently reacts with the isocyanate. Such a mechanism [(5) and (6)] is supported qualitatively by the

$$\text{EtOH} + \text{R}^2\text{CO}_2\text{H} \xrightleftharpoons{K_5} \text{(I)} \quad \text{Fast} \quad (5)$$

$$\text{(I)} + \text{R}^1\text{NCO} \xrightarrow{k_6}$$
$$\text{R}^1\text{NHCO}_2\text{Et} + \text{R}^2\text{CO}_2\text{H} \quad \text{Slow} \quad (6)$$
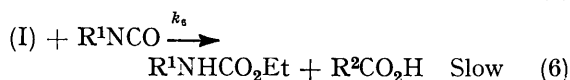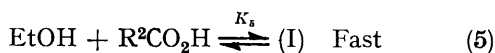
i.r. spectra of mixtures of carboxylic acids and ethanol in ether (see Experimental section).

ments at constant $[\text{EtOH}]_{\text{stoic}}$, and with $[\text{Acid}]_{\text{stoic}} \ll [\text{EtOH}]_{\text{stoic}}$ (under which conditions $[\text{EtOH}]_M$ and k_s can easily be obtained without much error from $[\text{EtOH}]_{\text{stoic}}$) equation (11) predicts that a plot of k_c against $[\text{Acid}]_{\text{stoic}}$ should be a straight line, as found (see Figure 2 remembering that k_s is constant for a given alcohol concentration). The slope will be $k_6 K_5 [(\text{EtOH})_M]_{\text{free}}/\{1 + K_5[(\text{EtOH})_M]_{\text{free}}\} \fallingdotseq k_6 K_5[(\text{EtOH})_M]_{\text{stoic}}/\{1 + K_5[(\text{EtOH})_M]_{\text{stoic}}\}$.

The 1 : 1 composition assumed for (I) is supported by the following consideration. At low alcohol concentrations equation (11) approximates to (12). And under such conditions plots of k_c against $[(\text{EtOH})_M]_{\text{stoic}}$ at

$$k_c \fallingdotseq k_6 K_5[(\text{EtOH})_M]_{\text{free}}[\text{Acid}]_{\text{stoic}} \quad (12)$$

constant $[\text{Acid}]_{\text{stoic}}$ are indeed straight lines whereas similar plots against $[(\text{EtOH})_M]^2_{\text{stoic}}$ are curves. This strongly suggests that the intermediate (I) contains only one, and not two, molecules of ethanol. Also the slope of the plot of k_c against $[(\text{EtOH})_M]_{\text{stoic}}$ at low $[(\text{EtOH})_M]_{\text{stoic}}$ values will be ca. $k_6 K_5[\text{Acid}]_{\text{stoic}}$. Thus an approximate

TABLE 6

Comparison of the values of K_5 and k_6 in diethyl ether at 25° with other constants

K_a is the acid dissociation constant in water at 25°; K_{12} is the equilibrium constant for 1 SnCl_4 : 2 acid adduct formation in o-dichlorobenzene [6] at 28°; k_{cat} is the catalytic rate constant for ethanolysis of dimethylketen at 25°; K_2 is the dimerisation constant for the acid in ether at 30° (Table 1)

Acid	$\dfrac{K_5 \,*}{\text{mol}^{-1}\,\text{dm}^3}$	$\dfrac{10^3 k_6 \,*}{\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}}$	$\dfrac{K_a}{\text{mol dm}^{-3}}$	$\dfrac{K_{12}}{\text{mol}^{-1}\,\text{dm}^3}$	$\dfrac{k_{\text{cat}}}{\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}}$	$\dfrac{K_2}{\text{mol}^{-1}\,\text{dm}^3}$
n-Butyric	1·7	14·3 ± 0·9	1·5 × 10^{-5}	82		0·3
Benzoic	1·5	9·4 ± 0·7	6·3 × 10^{-5}	52	8·6	0·2
3-Chloropropionic	2·1	5·5 ± 0·2	7·9 × 10^{-5}	1·8	5·5 †	
Chloroacetic	1·5	3·3 ± 0·2	1·4 × 10^{-3}	0·14	4·2	

* Values of K_5 and k_6 are based on our total data and not just the data in Tables 2—5. Further data are available in S. A. Lammiman, Ph.D. Thesis, London, 1974. † In ref. 4 this is given as 2-chloropropionic acid, but in P. J. Lillford, Ph.D. Thesis, London, 1968, it is named as β-chloropropionic acid.

The rate equation corresponding to scheme (5) to (6) is (7) and the total rate of loss of isocyanate will be

$$- \text{d}[\text{R}^1\text{NCO}]/\text{d}t = k_6[(\text{I})][\text{R}^1\text{NCO}] = k_c[\text{R}^1\text{NCO}] \quad (7)$$

given by equation (8).

$$-(\text{d}[\text{R}^1\text{NCO}]/\text{d}t)_{\text{Total}} = k_5[\text{R}^1\text{NCO}] + k_6[(\text{I})][\text{R}^1\text{NCO}] \quad (8)$$

Hence $\quad k_{\text{obs}} = k_s + k_6[(\text{I})] = k_s + k_c \quad (9)$

It can be shown that equation (10) applies. Substitution of $[(\text{I})]$ in (9) gives equation (11), where k_s represents

$$[(\text{I})] = \frac{K_5[(\text{EtOH})_M]_{\text{free}}[\text{Acid}]_{\text{stoic}}}{\{1 + K_5[(\text{EtOH})_M]_{\text{free}}\}} \quad (10)$$

the spontaneous contribution of the free ethanol. For a fixed value of $[\text{Acid}]_{\text{stoic}}$ when $[(\text{EtOH})_M]_{\text{free}}$ is large,

$$k_{\text{obs}} - k_s = k_c = \frac{k_6 K_5[(\text{EtOH})_M]_{\text{free}}[\text{Acid}]_{\text{stoic}}}{1 + K_5[(\text{EtOH})_M]_{\text{free}}} \quad (11)$$

equation (11) predicts that k_c reaches a limiting value ($k_6[\text{Acid}]_{\text{stoic}}$) as found. Hence a very approximate value of k_6 can be calculated. For a series of experi-

* It can easily be shown that a mechanism based on an intermediate complex formed between catalyst and isocyanate, rather than alcohol, is incompatible with the results.

value for $k_6 K_5$ can be obtained. Combination of this value with the values of $k_6 K_5[(\text{EtOH})_M]_{\text{stoic}}/\{1 + K_5[(\text{EtOH})_M]_{\text{stoic}}\}$ obtainable from Figure 2 (see above) leads to an approximate estimate of K_5.

Improved values for K_5 for the different acids, and a more exact fit of the data to equation (9), were obtained as follows. For the conditions of each run we calculated (i) $[(\text{EtOH})_M]_{\text{free}}$ from $[\text{EtOH}]_{\text{stoic}}$, (ii) $[(\text{I})]$ from equation (10) using the approximate value of K_5, and (iii) $[\text{EtOH}]_{\text{free}} = \{[\text{EtOH}]_{\text{stoic}} - [(\text{I})]\}$. Steps (i)—(iii) were repeated until constant values were obtained. The value of k_s was then found [1] from the final value of $[\text{EtOH}]_{\text{free}}$. Using such data from all the runs for a given acid a graph of k_c versus $[(\text{I})]$ was plotted. For each acid this plot was a good straight line. This result strongly supports our general interpretation.* The whole iterative process was then repeated for each acid choosing different values for K_5. For each acid the value of K_5 that gave the smallest standard deviation for $k_6 = k_c/[(\text{I})]$ was selected as the best value. The corresponding value of k_6 was then calculated. These values for the different catalysts are summarised in Table 6. Figure 3 shows the plots of k_c versus $[(\text{I})]$

[6] D. P. N. Satchell and J. L. Wardell, Trans. Faraday Soc., 1965, 61, 1132.

using the best values for K_5. *Typical sample data* are in Tables 2—5.

Equilibrium Constants for Adduct Formation between Ethanol and the Catalysts.—Our values of K_5 (see Table 6) show very little variation for the different acids, and are in the sequence 3-chloropropionic > n-butyric >

FIGURE 3 Dependence of k_c on $[(I)]$: A, 3-chloropropionic acid; B, chloroacetic acid; C, benzoic acid; D, butyric acid

chloroacetic $\rightleftharpoons$ benzoic. Since the K_a values for the acids change by a factor of 100 in a quite different sequence (chloroacetic $\gg$ 3-chloropropionic > benzoic $\gg$

in a slow step *via* a cyclic transition state (IV) with carbon–oxygen bond formation dominant. On this basis the total amount of intermediates (II) + (III) is still likely to increase with the acid strength. However, we have used concentration conditions where much intermediate is formed, and have evidence for only o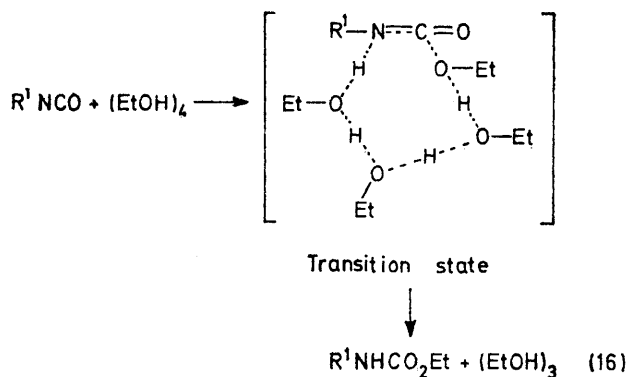ne major type of intermediate, and its amount is *not* related to the acid strength. This suggests that a modification of Lillford and Satchell's views is necessary.

Since carboxylic acids form cyclic dimers, the possibility exists that the intermediate is also cyclic, as in equilibrium (15). In (15) a balance between the proton donating power of the acid and the basicity of its carbonyl oxygen atom will operate.

The likely sequence of the carbonyl oxygen atom's basicity can be deduced from the equilibrium constants for 1 : 2-adduct formation between $SnCl_4$ and carboxylic acids in *o*-dichlorobenzene [6] (Table 6). The sequence is n-butyric > benzoic > 3-chloropropionic > chloroacetic. If in K_5 this sequence is balanced against the sequence of K_a values, then we could well finish with largely constant K_5 values. It is interesting that the K_5 values are numerically greater than the corresponding acid dimerisation constants (Table 6).

Support for the cyclic structure (V) may also be found in the i.r. spectral data. The position of the carbonyl absorption band of the carboxylic acid monomers in ether is shifted by *ca.* 5 cm^{-1} to a lower frequency compared with its position in *o*-dichlorobenzene.[5,7] In ether the acid monomer will be hydrogen bonded to the

(13)

(II)   (III)

(IV)

n-butyric), it follows that proton transfer from the acid is not dominant in the formation of the intermediate (I). Lillford and Satchell [4] found that the efficiency of carboxylic acids as catalysts for the addition of ethanol to dimethylketen in ether (a chemically similar system to the present) is inversely proportional to the carboxylic acid strength. Lillford and Satchell, who also interpreted their results in terms of a (low concentration) alcohol–acid intermediate, therefore proposed that this intermediate is formed initially by protonation of the alcohol by the acid (II), but can rearrange to (III) as in reaction (13); intermediate (III) then attacks the keten

[7] J. L. Wardell, Ph.D. Thesis, London, 1965, p. 115.

solvent. If the intermediate is hydrogen bonded as in (III) then very little change in the position of the peaks would be expected on the addition of ethanol to the acids. In fact the new peaks observed on the addition

(15)

(V)

of ethanol appear at frequencies very close to those of the dimeric acids. This suggests that the acid's carbonyl group is involved in the bonding between the acid and

ethanol. Since the hydrogen bond between the acid's hydroxylic oxygen atom and ethanol's oxygen atom is

(VI)

likely to be a stronger bond we are again led to the conclusion that the adduct formed is cyclic.

Transition state

$$R^1NHCO_2Et + (EtOH)_3 \quad (16)$$

Mechanism of the Acid Catalysed Ethanolysis.—For the spontaneous alcoholysis [1] no reaction of alcohol monomer was detected. At low total ethanol concentrations dimer and tetramer both contribute to the reaction, but at high total concentrations the tetramer dominates, although present in very much lower concentration than the dimer. This result and the probability that the tetramer

is cyclic, and free of solvent molecules, whereas the dimer has an open structure co-ordinated to a solvent molecule (VI) suggested that the alcohol polymer attacks the isocyanate in a one-step process (16) involving a cyclic transition state. The lower reactivity of the dimer was attributed to the need for displacement of the solvent molecule before an analogous transition state can form. With cyclic intermediates the opening up of the ring to form a larger one is all that is involved.

Under acid catalysis the rate constant (k_6) for reaction of the proposed cyclic acid–alcohol intermediate with the isocyanate is inversely proportional to the acid strength (see Table 6). This suggests that, although a simultaneous attack on the N=C double bond by the alcoholic oxygen atom and by the acid proton is necessary (otherwise attacking species capable of providing such twofold attack *via* a cyclic transition state would not prove so essential as they do), nevertheless it is the formation of the new oxygen–carbon bond which is energetically dominant. It is likely that the stronger the acid the lower will be the electron density on the alcohol oxygen atom in the acid–alcohol intermediate and the greater the activation energy in the formation of the transition state. The catalytic step can be represented as (17). Our general conclusions are in essential agreement with those of Lillford and Satchell for the analogous keten alcoholysis, although we have here been able to conduct a fuller analysis and have uncovered more clearly the factors which underlie the inverse dependence of catalytic

Transition state

$$R^1NHCO_2Et + R^2CO_2H \quad (17)$$

ability on acid strength which is common to both reactions. What is becoming very clear is that heterolytic additions to ketens and to isocyanates probably have virtually identical mechanisms.