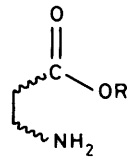
Stereochemical Studies. Part 112.† Geometrical Dependence of Intramolecular Catalysis in the Hydrolysis and Aminolysis of Aryl Esters

Michael I. Page* and David Render
Department of Chemical & Physical Sciences, The Polytechnic, Queensgate, Huddersfield HD1 3DH
Gábor Bernáth
Institute of Pharmaceutical Chemistry, University Medical School, Szeged, PO Box 121, H-6701, Szeged, Hungary

The spontaneous hydrolyses of a series of *p*-nitrophenyl esters of 2-aminocarboxylic acids show rate enhancements of *ca.* 10^3. These can be attributed to intramolecular general base catalysis by the neighbouring amino group, or to hydrogen-bonding/electrostatic stabilisation of the tetrahedral intermediate formed in the kinetically equivalent mechanism of hydroxide ion attack on the ammonium ion ester. The hydrolysis of the esters catalysed by phosphate and carbonate ions shows rate enhancements of 10^3 and 10^2, respectively, attributable to electrostatic/hydrogen-bonding catalysis. Conversely, the aminolysis of the esters with trifluoroethylamine shows a rate enhancement of 10^2 attributable to intramolecular general base catalysis. In all these reactions there is little dependence of the rate enhancement upon the geometrical relationship between the amino and ester functions. These observations support the suggestion that proton transfer/hydrogen bonding requires relatively little loss of entropy.

The geometric relationship between atoms undergoing chemical reaction is of widespread interest. This is particularly the case for enzyme-catalysed reactions, for which there have been several suggestions that the relationship is critical.[1] It appears that the requirement for an optimal arrangement of atoms in an enzyme-catalysed reaction or an intramolecular one is dependent upon the mechanism involved.[2] Reactions involving hydrogen bonding or proton transfer attract attention because, although the importance of a linear hydrogen bond has been emphasised,[3] the energetic cost of deviations from linearity is the subject of controversy. The majority of hydrogen bonds are not linear[4] and half the population in an intermolecular hydrogen-bonded system deviates by 20° or more from linearity.[5]

In an attempt to contribute to the understanding of the geometrical relationship between reaction centres and intramolecular stabilisation sites, we report here studies of acyl-transfer reactions of some esters. The systems studied are of the general type (**1**), containing a suitably placed intramolecular β-amino group which may potentially act as a general base catalyst, as a general acid catalyst in its conjugate acid form, or simply as a hydrogen-bonding or electrostatic stabilising site. By varying the carbon skeleton the geometrical relationship between the catalyst and the reaction site has been examined.



(**1**)

Experimental

Materials.—The syntheses of the esters studied have been previously described; the esters were purified by recrystallisation of the halide salts.[6] Inorganic salts were of AnalaR grade, and freshly boiled deionised water was used throughout.

Kinetics.—The ionic strength was maintained at 0.2M by addition of potassium chloride unless otherwise stated. The reactions were initiated by the addition of 25 μl of a stock solution of the ester to 2.5 cm^3 of the aqueous buffer solution, pre-incubated at 30.0 ± 0.05 °C, with thorough mixing. The disappearance of the substrate was followed spectrophotometrically with a Gilford 240 spectrophotometer. The output from the spectrophotometer was fed into a Solartron data logger equipped with a Facit tape punch, thus enabling voltages proportional to the absorbance to be punched at constant time intervals. Rate constants were calculated from the results with an IBM 1130 or ICL 2960 computer, using a generalised least-squares method which treated the absorbances at time zero and infinity and the first-order rate constant as disposable parameters.[7]

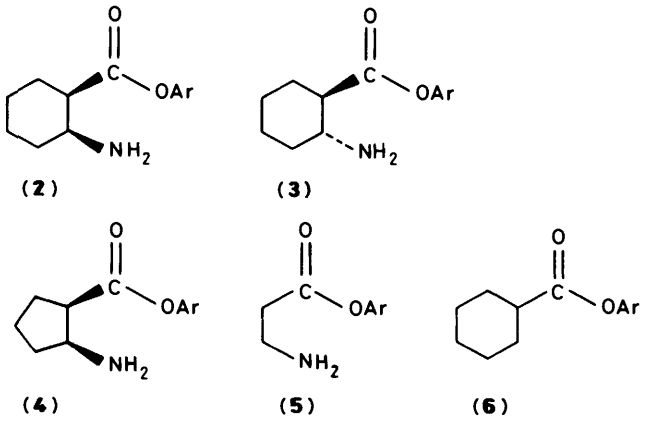
Some kinetic measurements were collected with a Gilford 2600 spectrophotometer which fed the data directly into an Apple II Europlus microcomputer; the calculated parameters were then displayed on a visual display unit while an Epson printer gave a permanent record of calculated and observed absorbances and the calculated rate constants.

Fast reactions were followed by using a Nortech SF-3A stopped-flow spectrophotometer. The signal from the photomultiplier was fed into a Datalab DL901 transient recorder which was automatically triggered and simultaneously triggered the display on a Gould Advance OS-Z50B oscilloscope. The change in absorbance with time was output from the transient recorder to a chart recorder. The slopes and intercepts of linear relationships were determined by a linear least-squares method. The pH of all solutions was checked before and after each kinetic experiment and if it had changed by more than 0.03 the experiment was rejected.

Results and Discussion

The main reactions studied were the hydrolysis and aminolysis of *cis*- and *trans*-*p*-nitrophenyl 2-aminocyclohexanecarboxylate, (**2**) and (**3**), respectively, *cis*-2-aminocyclopentanecarboxylate (**4**), β-alaninate (**5**), and cyclohexanecarboxylate (**6**).

† Part III, H. P. Richter, P. Flegel, F. Fülöp, and G. Bernátt, *Pharmazie*, in the press.



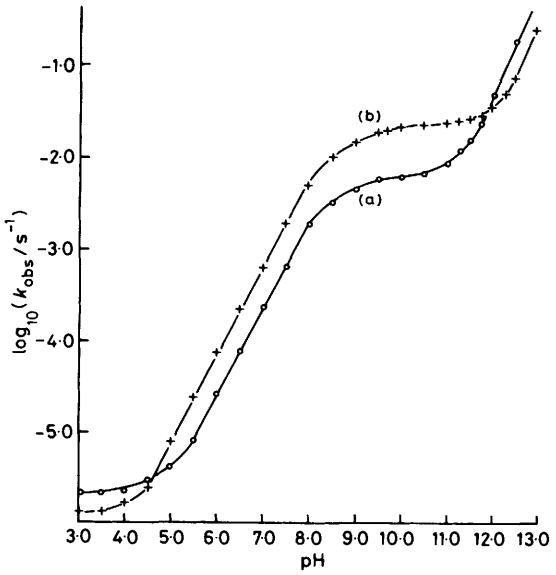


Figure 1. The pH–rate profile for the hydrolyses of (a) *cis*- and (b) *trans*-2-aminocyclohexanecarboxylic acid *p*-nitrophenyl esters at 30 °C and I = 0.2M (KCl) (solid lines are calculated from the constants given in Table 1)

Hydrolysis.—The pH–rate profiles for the hydrolyses of the esters are shown in Figure 1. The pseudo-first-order rate constants, k_{int}, were obtained by extrapolation of the observed rate constants, k_{obs}, to zero buffer concentration. The shape of the pH–rate profile indicates that hydrolysis occurs according to the rate law of equation (1). Below pH 2 the dominant term in

$$\text{rate} = k_H[H^+][ENH_3^+] + k_0^+[ENH_3^+] + k_0[ENH_2] + k_{OH}[ENH_2][OH^-] \quad (1)$$

the hydrolysis of *p*-nitrophenyl cyclohexanecarboxylate is the acid-catalysed reaction, which has a second-order rate constant, k_H. The esters with a protonated amino group (ENH_3^+) do not show this reaction, presumably owing to the retardation brought about by the positively charged amino group. Quaternary α-ammonium groups decrease the rate of acid hydrolysis of esters 2000-fold.[8] Between pH 2 and 4 there is a pH-independent reaction due to the spontaneous hydrolysis of the amino-protonated ester with a first-order rate constant k_0^+. From pH 4 to 11 either the spontaneous hydrolysis of the ester with an unprotonated amino group (ENH_2) occurs, with a pseudo-first-order rate constant k_0, or else the kinetically equivalent hydroxide-ion-catalysed hydrolysis of the ester with a protonated amino group takes place, with a second-order rate

Table 1. Summary of the rate constants for the hydrolysis of *p*-nitrophenyl esters in water at 30 °C and I = 0.2M

Substrate	pK_a[a]	k_0^+[c] / s^{-1}	k_0[d] / s^{-1}	k_0K_a/K_w[e] / l mol^{-1} s^{-1}	k_{OH}[f] / l mol^{-1} s^{-1}
(6)[b]			6.10×10^{-7}		4.50
(2)	8.42	2.11×10^{-6}	6.31×10^{-3}	1.60×10^{3}	2.83
(3)	8.57	1.26×10^{-6}	2.52×10^{-2}	4.53×10^{3}	1.15
(4)	8.36	6.42×10^{-6}	1.55×10^{-2}	4.58×10^{3}	4.82
(5)	9.17	7.63×10^{-6}	1.48×10^{-2}	6.80×10^{2}	15.6

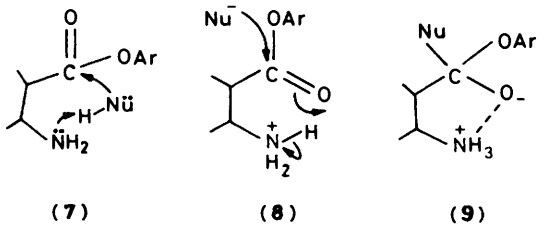
[a] Acid dissociation constant of the alkylammonium group. [b] Second-order rate constant for acid hydrolysis, $k_H = 5.36 \times 10^{-5}$ l mol^{-1} s^{-1}. [c] First-order rate constant for the uncatalysed hydrolysis of the protonated ester; see equation (1) and text. [d] First-order rate constant for the uncatalysed hydrolysis of the unprotonated ester. [e] Calculated second-order rate constant for the hydroxide-ion-catalysed hydrolysis of the protonated ester. [f] Second-order rate constant for the hydroxide-ion-catalysed hydrolysis of the unprotonated ester.

constant k_0K_a/K_w (K_a is the acid dissociation constant of the amino group and K_w the ionisation constant for water). Finally, at high pH, hydroxide-ion-catalysed hydrolysis of the unprotonated amino ester occurs, with a second-order rate constant, k_{OH}. The values for the various rate constants are summarised in Table 1.

There is a slight variation in the magnitude of the rate of hydroxide-ion-catalysed hydrolysis of the *p*-nitrophenyl esters (Table 1). This reaches a maximum difference of 13-fold between the acyclic β-alaninate and the *trans*-2-aminocyclohexanecarboxylate. As both *cis*- and *trans*-2-aminocyclohexanecarboxylates have second-order rate constants smaller than the unsubstituted cyclohexanecarboxylate, the rate differences probably result from a combination of electronic and steric effects. Because of the relatively small differences in rates these will not be discussed further.

The β-ammonium substituent causes a rate increase of up to 10-fold in the rate constant for the spontaneous hydrolysis [k_0^+ *cf.* k_0 for (6)] (Table 1). Again this is the order of magnitude expected for a normal substituent effect and these values will also not be further discussed.

The term in the rate law which is unusual is the rate constant for the spontaneous hydrolysis of the unprotonated amino-esters, k_0, or its kinetic equivalent, the hydroxide-ion-catalysed hydrolysis of the protonated amino ester, k_0K_a/K_w (Table 1). The former rate constants are all about 10^4-fold greater than that for an unsubstituted *p*-nitrophenyl ester. This is far greater than expected for a normal substituent effect and could be taken as evidence for intramolecular general base catalysis by the neighbouring amino group [see (7)]. Intramolecular nucleophilic catalysis is also a possible explanation, but as this would involve the formation of a four-membered ring it is unlikely to occur. However, the rate constants for the kinetically equivalent mechanism of hydroxide-ion attack on the ammonium ion ester are 10^3-fold greater than that for hydroxide-ion attack on an unsubstituted ester. A β-protonated amino group is expected to increase the rate of hydroxide-ion-catalysed hydrolysis by 10-fold, owing to its inductive effect.[9] The observed rate enhancement could therefore suggest intramolecular general acid catalysis by the neighbouring ammonium group [see (8)], or simple electrostatic catalysis by stabilisation of the presumed tetrahedral intermediate [see (9)]. The rate enhancements do not appear to be very sensitive to the geometrical relationship between the amino and ester groups. It makes little difference whether the system is conformationally mobile as in (5) or is held in a more rigid relationship such as that in (2), (3), or (4).



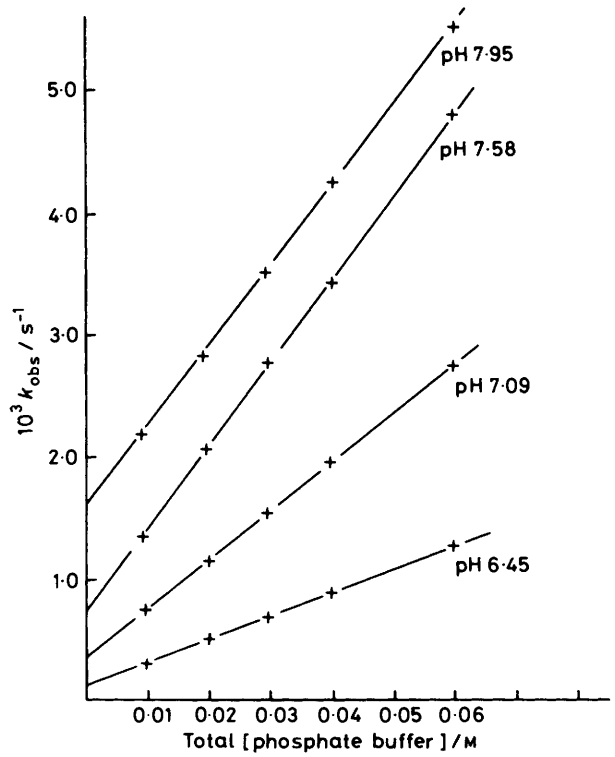


Figure 2. Plot of the observed first-order rate constant for the hydrolysis of *cis*-2-aminocyclohexanecarboxylic acid *p*-nitrophenyl ester as a function of total phosphate buffer concentration at the indicated pH, at 30 °C and I = 0.20M (KCl)

Previous studies on the effect of positively charged nitrogen substituents on the rate of hydrolysis of esters have concluded that the effect is predominantly an electrostatic one.[8-10] There is little difference between the rates of reactions of substrates containing $-\overset{+}{N}HR_2$ and $-\overset{+}{N}R_3$. There have been several reports on the hydrolysis of choline esters in which the positively charged nitrogen is in the alcohol part of the ester.[10,11] One has shown that there is little difference in the rate of hydrolysis of *cis*- and *trans*-esters of 3-trimethylammonionorbornan-2-ol.[12] Cox has recently shown that a neighbouring positively charged nitrogen stabilises an incipient enolate anion electrostatically rather than by a hydrogen-bonding mechanism.[13]

In an attempt .o distinguish between these mechanisms [(7)—(9)] for our systems, it was of interest to see if nucleophiles other than hydroxide or water showed similar rate enhancements. Nucleophiles subject to general base catalysis, *e.g.* amines, may show a rate enhancement if mechanism (7), but not (9), is operative, whereas the reaction of oxyanion nucleophiles will be accelerated for (9) but not (7).

Reaction with Oxyanions.—Oxyanions more basic than acetate catalyse the hydrolysis of *p*-nitrophenyl esters by the nucleophilic mechanism.[14] If electrostatic stabilisation/hydrogen bonding occurs in the tetrahedral intermediate formed by attack of hydroxide ion as in (9), then it would also be expected to occur when other anions attack the ester. The kinetically equivalent mechanism of intramolecular general base catalysis by the amino group as in (7) is not expected to occur with the conjugate acid of the oxyanion if the latter and the oxyanion are present in significant concentrations when used as a buffer.[15]

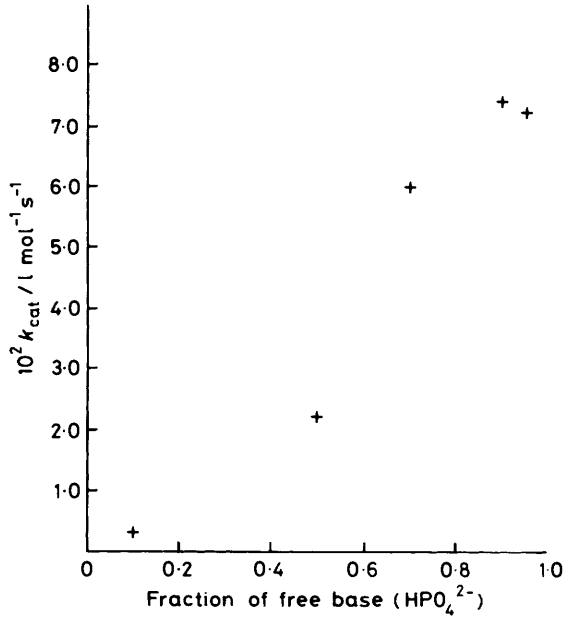


Figure 3. Dependence of the observed catalytic rate constant k_{cat} for the phosphate-buffer-catalysed hydrolysis of *cis*-2-aminocyclohexanecarboxylic acid *p*-nitrophenyl ester on the fraction of free base (HPO_4^{2-})

A plot of the observed pseudo-first-order rate constant as a function of total phosphate buffer concentration at different pH values is given in Figure 2. The slopes of these graphs are designated k_{cat}, and contrasting plots for k_{cat} for phosphate, carbonate, and acetate buffers as a function of the fraction of free base (FFB) in the buffer are shown in Figures 3—5. Catalysis by phosphate buffer becomes more important as the pH increases, whereas the amount of catalysis by carbonate buffer decreases as the pH increases.

Clearly from Figure 5, only acetate ion, and not acetic acid, reacts with the esters. As the pH of the acetate buffers is well below the pK_a of the ammonium ion esters, the intercept at FFB = 1.0 gives the second-order rate constant k_{AcO^-} for the reaction of acetate ion with the ammonium ion ester (ENH_3^+) [equation (2)]. The pH values of the carbonate and phosphate

$$\text{rate} = k_{AcO^-}[AcO^-][ENH_3^+] \qquad (2)$$

buffers used are close to the pK_a of the ammonium group of the ester. A correction must therefore be applied to the observed pseudo-first-order rate constants so that they refer to the same species of substrate. To standardise the rate constants to the conjugate acid of the ester, *i.e.* with the amino group protonated, all rate constants were multiplied by $(K_a + [H^+])/[H^+]$ where K_a is the dissociation constant of the ammonium group. Replotting the values of k_{cat} against the fraction of free base gives the second-order rate constants for carbonate and phosphate dianions reacting with the ammonium ion form of the ester (Table 2).

There are two important observations to make from the data in Table 2. Carbonate ion and phosphate dianion show rate enhancements of 3.7×10^2 to 4.5×10^3 as compared with the

Table 2. Summary of the second-order rate constants (l mol^{-1} s^{-1}) for the catalysed hydrolysis of *p*-nitrophenyl esters in water at 30 °C and I = 0.2M[a]

Substrate	Acetate $k_{ENH_3^+}$	Carbonate $k_{ENH_3^+}$	Phosphate (HPO_4^{2-}) k_{ENH_3}	Trifluoroethylamine k_{ENH_2}	Propylamine k_{ENH_2}
(6)	2.87×10^{-6}	4.97×10^{-3}	5.84×10^{-5}	1.75×10^{-4}	2.72
(2)	4.52×10^{-5}	22.4	8.10×10^{-2}	2.55×10^{-2}	0.456
(3)	6.45×10^{-5}	16.3	3.67×10^{-2}	1.38×10^{-2}	0.175
(4)	1.05×10^{-4}	12.1	2.56×10^{-2}	1.26×10^{-2}	0.148
(5)	5.83×10^{-5}	9.75	1.93×10^{-2}	9.64×10^{-3}	0.125

[a] Rate constants refer to the ester containing the ammonium ion for acetate, carbonate, and phosphate, but to the ester containing the free amine for amine nucleophiles.

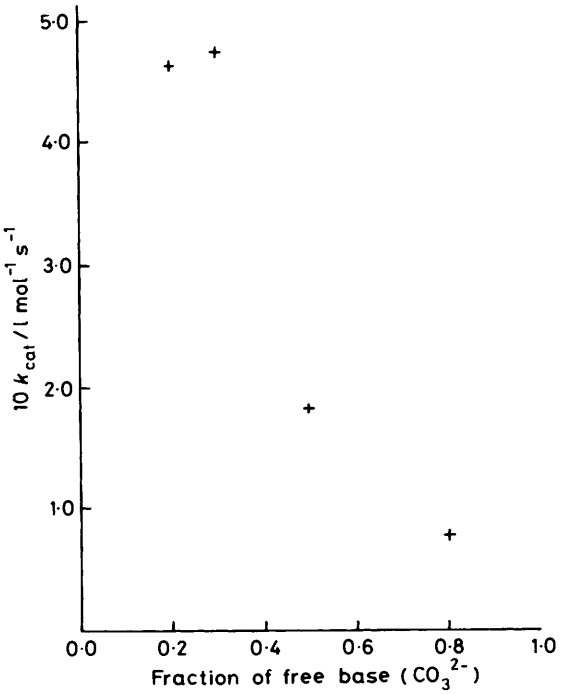


Figure 4. Dependence of the observed catalytic rate constant k_{cat} for the carbonate-buffer-catalysed hydrolysis of *trans*-2-aminocyclohexanecarboxylic acid *p*-nitrophenyl ester on the fraction of free base (CO_3^{2-})

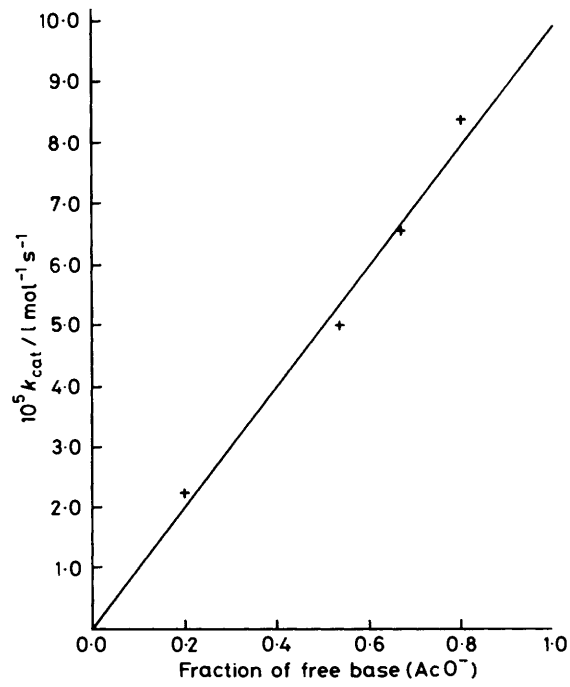


Figure 5. Dependence of the observed catalytic rate constant k_{cat} for the acetate-buffer-catalysed hydrolysis of *cis*-2-aminocyclopentanecarboxylic acid *p*-nitrophenyl ester on the fraction of free base (AcO^-)

unsubstituted ester (**6**). This is indicative of an inductive effect[16] or electrostatic catalysis[9,17] [as (**9**)], but is also not inconsistent with intramolecular hydrogen-bond stabilisation of the tetrahedral intermediate (**9**) or even intramolecular general acid catalysis (**8**). The second important observation is that the rate enhancement shows a very small dependence on the geometrical relationship between the ester and ammonium ion groups. The rate constants for the conformationally mobile acyclic system (**5**) are similar to the analogous ones for the more rigid systems (**2**)—(**4**).

Both these observations are consistent with electrostatic stabilisation. The rate enhancement is of the magnitude expected, and electrostatic interactions between cations and anions do not show strong directional dependences.[18] However, the energetic penalty for deviations from optimum geometry for proton transfer and hydrogen bonding is also generally small.[4-6] We were unfortunately unable to synthesise the quaternary ammonium salt derivatives, the study of which might have allowed a distinction between these mechanisms of stabilisation.

The hydrolysis of esters containing a suitably placed amino group may proceed by intramolecular general base catalysis,[19] and it is shown in the next section that this mechanism can also occur in the aminolysis of β-amino esters.

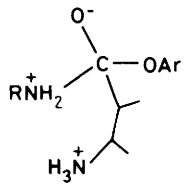
Aminolysis.—The reaction of amines with the β-amino esters presents the opportunity of studying the effects of the ester amino substituent with an electrically neutral nucleophile. However, this type of reaction usually requires base catalysis to remove a proton from the attacking amine.[20] The intramolecular amino group in the ester could carry out this function.

The aminolyses of the esters by trifluoroethylamine and propylamine follow the rate law of equation (3), where ENH_2

$$\text{rate} = k_1[RNH_2][ENH_2] + k_2[RNH_2][ENH_3^+] \quad (3)$$

and ENH_3^+ represent the free base and the protonated forms of the amino ester, respectively. The rate constants were obtained using five different concentrations of amine at three or four different pH values, and are given in Table 2.

The only detectable reaction with propylamine was with the free base form of the amino ester. The second-order rate constants for this reaction are of similar magnitude to that



(10)

observed for the cyclohexanecarboxylate ester lacking an amino group (**6**), and up to an order of magnitude smaller than that previously reported for *p*-nitrophenyl acetate.[21] There is thus no evidence of intramolecular general base catalysis in this reaction.

By contrast the observed second-order rate constants for the reaction of trifluoroethylamine with the amino esters are up to 100-fold greater than that for (**6**) or *p*-nitrophenyl acetate.[21] This rate enhancement is indicative of intramolecular general base catalysis, (**7**).

The aminolysis of esters is subject to general base catalysis with weakly basic amines and when the leaving group alcohol is basic.[22] Thus the aminolysis of *p*-nitrophenyl esters does not generally exhibit general basis catalysis, whereas esters of aliphatic alcohols undergo aminolysis predominantly by a general base-catalysed pathway.[22,23] Conversely, weakly basic amines exhibit general base catalysis even for the more reactive esters. The effective molarity for intramolecular amine general-base-catalysed aminolysis by diamines is small.[20] It was therefore expected that if intramolecular general base catalysis occurs as in (**7**), a rate enhancement may be observed with the reaction of weakly basic amines, but not with basic ones, in their reactions with the amino esters. Conversely, if (**8**) or (**9**) are effective mechanisms of stabilisation, then a term in the rate law proportional to the protonated ammonium ester and free amine should be apparent unless there is relative destabilisation in the tetrahedral intermediate (**10**) due to adjacent positive charges. There is no evidence of a significant term in the rate law consistent with this mechanism.

Again, there is little or no geometric dependence on the rate enhancement for intramolecular general base-catalysed aminolysis. The rate constants for all amino esters reacting with trifluoroethylamine (Table 2) are similar. This is consistent with a previous report involving the aminolysis of acetylimidazole where the base catalyst and the nucleophile were in the same molecule.[20] Catalysis occurs here with the base catalyst in the same molecule as the ester function. It therefore appears that there is little geometrical constraint on intramolecular general base catalysis involving proton transfer between electronegative atoms.[18,20,24]

Acknowledgements

P. R. thanks I.C.I. Organics Division for support. We thank Drs. L Gera and F. Fülöp for the preparations of many of the compounds studied.

References

1 F. M. Menger and D. Y. Williams, *Tetrahedron Lett.*, 1982, **23**, 3879; D. R. Storm and D. E. Koshland, *J. Am. Chem. Soc.*, 1972, **94**, 5805, 5815; D. G. Hoare, *Nature*, 1972, **236**, 1972.
2 M. I. Page and W. P. Jencks, *Proc. Natl. Acad. Sci. USA*, 1971, **68**, 1678; M. I. Page, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 449; *Chem. Soc. Rev.*, 1973, **2**, 295; 'The Chemistry of Enzyme Action,' ed. M. I. Page, Elsevier, Amsterdam, in the press.
3 R. D. Gandour, *Tetrahedron Lett.*, 1974, 295.
4 J. Kroon, J. A. Kanters, J. G. C. M. van Duijneveldt-van de Rijdt, F. B. van Duijneveldt, and J. A. Vliegenhart, *J. Mol. Struct.*, 1975, **24**, 109; G. Ferraris and M. Franchini-Angela, *Acta Crystallogr., Sect. B.*, 1972, **28**, 3572; I. Olovsson and P.-G. Jönsson, in 'The Hydrogen Bond—Recent Developments in Theory and Experiments,' ed. P. Schuster, G. Zundel and C. Zandorfy, North-Holland, Amsterdam, 1976, ch. 8.
5 W. L. Jorgensen and M. Ibrahim, *J. Am. Chem. Soc.*, 1980, **102**, 3309.
6 G. Bernáth, L. Gera, Gy. Göndös, I. Pánovics, and Z. Ecsery, *Acta Chim. Acad. Sci. Hung.*, 1976, **89**, 61; F. Fülöp, G Bernath, P. Sohár, and T. Pelozer, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2043..
7 W. E. Deming, 'Statistical Adjustment of Data,' Dover, New York, 1964; W. E. Wentworth, *J. Chem. Educ.*, 1965, **42**, 96, 162.
8 R. P. Bell and F. J. Lindars, *J. Chem. Soc.*, 1954, 4601.
9 R. P. Bell and B. A. W. Coller, *Trans. Faraday Soc.*, 1964, **60**, 1087; 1965, **61**, 1445.
10 G. Aksnes and J. E. Prue, *J. Chem. Soc.*, 1959, 103; G. Aksnes and P. Froeyen, *Acta. Chem. Scand.*, 1966, **20**, 1451; 1967, **21**, 1507.
11 R. P. Bell and M. Robson, *Trans. Faraday Soc.*, 1964, **60**, 893; A. Agren, U. Hedstein, and B. Jonsson, *Acta Chem. Scand.*, 1961, **15**, 1532.
12 H. Kunz, *Justus Liebigs Ann. Chem.*, 1975, **919**, 1219.
13 B. G. Cox, P. De Maria, A. Fini, and A. F. Hassan, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1351.
14 D. G. Okenfull, T. Riley, and V. Gold, *Chem. Commun.*, 1966, 385.
15 W. P. Jencks and M. Gilchrist, *J. Am. Chem. Soc.*, 1962, **84**, 2910.
16 P. J. Thomas and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1909
17 B. G. Cox, P. De Maria, and A. Fini, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1647; B. M. Dunn and T. C. Bruice, *J. Am. Chem. Soc.*, 1971, **93**, 5725; D. B. Dahlberg, M. A. Kuzenko, Y. Chiang, A. J. Kresge, and M. F. Powell, *ibid.*, 1983, **105**, 5387; R. A. Lazarus and S. J. Benkovic, *ibid.*, 1979, **101**, 4300.
18 M. I. Page in 'The Chemistry of Enzyme Action,' ed. M. I. Page, Elsevier, Amsterdam, 1984, p. 1.
19 A. J. Kirby and G. L. Lloyd, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1748; P. Y. Bruice and T. C. Bruice, *J. Am. Chem. Soc.*, 1974, **96**, 5523; T. C. Bruice and S. J. Benkovic, *ibid.*, 1963, **85**, 1.
20 M. I. Page and W. P. Jencks, *J. Am. Chem. Soc.*, 1972, **94**, 8818.
21 W. P. Jencks and M. Gilchrist, *J. Am. Chem. Soc.*, 1968, **90**, 2622
22 A. C. Satterthwait and W. P. Jencks, *J. Am. Chem. Soc.*, 1974, **96**, 7018.
23 T. C. Bruice and M. F. Maydhi, *J. Am. Chem. Soc.*, 1960, **82**, 3067.
24 M. I. Page, *Chem. Soc. Rev.*, 1973, **2**, 295; J. J. Morris and M. I. Page, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1131.

Received 23*rd September* 1985; *Paper* 5/1646