197. *Nucleophilic Reactivity. Part I. The Reaction between a Series of Anions and Ethyl Chloroformate.**

By R. F. Hudson and M. Green.

Measurements of the rates of reaction of ethyl chloroformate with a series of anions in 85% aqueous acetone lead to the following rate order: acetoxime $> OH^- > PhO^- > NO_2^- > N_3^- > F^- > H_2O > Br^-$, I^-, CNS^-. The differences in the nucleophilic orders observed for reactions at alkyl and acyl carbon atoms are discussed in terms of the relative importance of the various energy factors involved in the transition states.

It is now well established that nucleophilic reactivity does not follow the order of increasing basicity towards protons, but varies with the nature of the reaction and with the reaction conditions. This is apparent in the classical calculation by Polanyi and Evans,[1] in which the various energy factors determining the activation energy are

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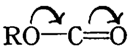
* Cf. *Proc. Chem. Soc.*, 1959, 149.

[1] Polanyi and Evans, *Trans. Faraday Soc.*, 1938, **34**, 11.

considered. McCleary and Hammett [2] drew attention to the rate order $I^- > OH^- > Br^- > Cl^-$ for the reactions of these ions with ethyl toluene-*p*-sulphonate in dioxan–water, which is the reverse of the order of the free energies of the corresponding equilibria. Similar rate orders have been observed in many substitutions and Scott and Swain [3] suggested that this order is characteristic of the nucleophile and holds for all displacements. The rate constant k is then given by $\log (k/k_0) = sn$, where k_0 is the rate in the solvent alone, s is a constant characteristic of the substrate only, and n is the nucleophilicity. In a detailed analysis of the available rate data, Edwards [4] pointed out the limitations of this relation, and proposed an extended equation in terms of the oxidation–reduction potential of the nucleophile, E_r, and the pK_a of the conjugate acid, $\log (k/k_0) = \alpha E_r + \beta pK_a$. He showed that the constant n is proportional to E_r, and Hudson and Harper [5] suggested that this order is characteristic of all S_N2 displacements at a saturated carbon atom.

This raises the general question of the relation between the nucleophilic order and the reaction mechanism. The reactivity orders observed for reactions at unsaturated centres usually differ considerably from the order given by the Scott–Swain equation. For instance Bunnett and Zahler [6] drew up an approximate order for the reactions of 1-chloro-2,4-dinitrobenzene, $SO_3^{2-} > OH^- > PhO > Ph{\cdot}NH_2 > NH_3 > I^- > Br^-$, which was later supplemented by Bunnett and Davis,[7] yielding $PhS^- \gg C_5H_{10}N > MeO^- > PhO^- > OH^-$. However, these orders differ from that observed for *p*-fluoronitrobenzene [8] in that methoxide ions are less reactive than phenylthio-ions. A different reactivity order is also observed for the reactions of diethyl phosphorochloridate in ethanol,[9] as shown by the rate sequence, $F^- > EtO^- > PhO^- > EtOH > PhS^-, AcO^-$. Fried and Miller [10] showed that the typical order towards alkylating agents is reversed in various reactions of fluoro-olefins, *e.g.*, the order $F^- > Cl^- > Br^-$ for the S_N2' reaction, $N^- + CF_2{:}\underset{|}{C}{\cdot}CF_3 \longrightarrow N{\cdot}CF_2{\cdot}\underset{|}{C}{:}CF_2 + F^-$ (where N^- = a nucleophile).

In order to obtain the nucleophilic order for an acyl chloride, the rates of reaction of ethyl chloroformate with a series of anions in 85% aqueous acetone have now been measured. Ethyl chloroformate was chosen because the conjugation  $RO{-}C{=}O$ reduces the reactivity, so that the reactions may be followed conveniently in a solvent of a high water content. The salts are therefore almost completely dissociated, and the observed rate constants may be compared with similar values obtained for alkyl halides in aqueous solvents.

The results presented in the following section are compared in Table 1 with similar results recently obtained for *p*-nitrophenyl acetate.[11]

TABLE 1.

Rate constant, k_2 (in l. $mole^{-1}$ $min.^{-1}$).

Nucleophile	$Cl{\cdot}CO_2Et$	$p-NO_2{\cdot}C_6H_4{\cdot}OAc$	n	E_r	Nucleophile	$Cl{\cdot}CO_2Et$	$p-NO_2{\cdot}C_6H_4{\cdot}OAc$	n	E_r
$Me_2C{:}N{\cdot}O^-$	500,000	3700	—	—	F^-	0·22	0·0010	2·00	—
OH^-.........	167	890	4·20	1·65	I^-	~0	~0	5·04	2·06
OPh^-	50	105	—	1·46	Br^-	~0	~0	3·89	1·51
NO_2^-	31	0·0013	—	1·73	CNS^-	~0	~0	4·77	1·83
N_3^-	17·5	2·2	4·00	1·58					

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[2] McCleary and Hammett, *J. Amer. Chem. Soc.*, 1941, **63**, 2254.
[3] Scott and Swain, *J. Amer. Chem. Soc.*, 1953, **75**, 141.
[4] Edwards, *J. Amer. Chem. Soc.*, 1954, **76**, 1540; 1956, **78**, 1819.
[5] Hudson and Harper, *J.*, 1958, 1356.
[6] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.
[7] Bunnett and Davis, *J. Amer. Chem. Soc.*, 1954, **76**, 3011.
[8] Bevan and Hirst, *J.*, 1956, 254.
[9] Dostrovsky and Halmann, *J.*, 1953, 503.
[10] Fried and Miller, *J. Amer. Chem. Soc.*, 1959, **81**, 2078.
[11] Jencks and Carriuolo, *J. Amer. Chem. Soc.*, 1960, **82**, 1778.

These rate sequences are quite different from the typical S_N2 order represented by the Swain coefficient n or by the oxidation–reduction potential, E_r.

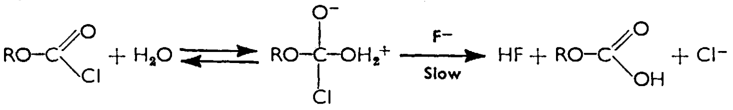
Of the ions which are found to be reactive towards ethyl chloroformate, the phenoxide[12] and the azide ion give rise to stable products: $Cl{\cdot}CO_2Et + PhO^- \longrightarrow PhO{\cdot}CO_2Et + Cl^-$; $Cl{\cdot}CO_2Et + N_3^- \longrightarrow N_3{\cdot}CO_2Et + Cl^-$. In the reaction with azide ions, second-order kinetics were observed and no acid was produced, in agreement with the formation of the acyl azide.[13]

Addition of acetoxime, nitrite, and fluoride ions increased the rate of hydrolysis, and here alternative mechanisms are possible, namely, nucleophilic attack to give an unstable intermediate or general base-catalysis.

Oximes have been shown[14] to give unstable *O*-acylated products with acid chlorides, which rapidly undergo the Beckmann rearrangement:[15] $R{\cdot}COCl + R'_2C{:}N{\cdot}O^- \longrightarrow R{\cdot}CO{\cdot}O{\cdot}N{:}CR'_2 \longrightarrow R{\cdot}CO_2H + R'CN + R'OH$. A similar reaction is assumed to occur with ethyl chloroformate. Nitrite ions produce an intermediate which rapidly nitrosylates α-naphthylamine in aqueous solution:[16] $Cl{\cdot}CO_2R + NO_2^- \longrightarrow ON{\cdot}O{\cdot}CO_2R \longrightarrow RO_2C{\cdot}O^- + NO^+$. The increase in the rate of hydrolysis by fluoride ion is probably produced also by formation of an unstable substitution product, since ethyl fluoroformate was found to hydrolyse *ca.* 30 times faster than the chloroformate, according to the following scheme, which leads to second-order kinetics:

$$Cl{\cdot}CO_2R + F^- \underset{}{\overset{\text{Slow}}{\rightleftharpoons}} F{\cdot}CO_2R \xrightarrow[\text{Fast}]{H_2O} ROH + CO_2 + HF$$

In this case, however, this mechanism cannot be readily differentiated from general base-catalysis, which has been observed for acetic anhydride[17] and certain esters.[18] This involves addition of water in a pre-equilibrium, followed by the catalytic removal of the proton by the fluoride ion in the rate-determining step. Since the removal of a proton from oxygen is very fast, the bond-breaking and proton-removal may proceed simultaneously, as follows:



More complex mechanisms[18] of a similar kind have been proposed, all of which lead to a rate equation that is first order in fluoride ion and in the acylating agent.

In view of the ease of displacement of the chlorine atom by fluoride ions in acetone (p. 1060), and the appreciable reactivity of fluoride ions towards *p*-nitrophenyl acetate,[11] the former mechanism is preferred. It is also noted that the rate of the general base-catalysis observed in the hydrolysis of acetic anhydride is less than the rate of the alternative catalytic mechanism involving nucleophilic substitution at the carbonyl group.[17]

The Nucleophilic Orders for Alkylation and Acylation.—The most interesting features of the rate orders given in Table 1 are: the low reactivities of I^-, Br^-, and CNS^- ions which are highly reactive towards alkylating reagents; the relatively high reactivity of fluoride and nitrite ions; and the high reactivity of acetoxime, compared with hydroxide ion.

The different orders for alkylation and acylation are reflected in the different transition-state structures and reaction mechanisms. Thus, in an S_N2 displacement, repulsion

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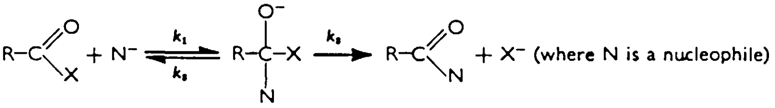
[12] Fatianow, *Z. Chem.*, 1864, 77.
[13] Forster and Fierz, *J.*, 1909, **95**, 81.
[14] Brady and McHugh, *J.*, 1923, **123**, 1190.
[15] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 322.
[16] Lees and Saville, *J.*, 1958, 2262.
[17] Kilpatrick, *J. Amer. Chem. Soc.*, 1928, **50**, 2891; Butler and Gold, *Proc. Chem. Soc.*, 1960, 15.
[18] Jencks and Carriuolo, *J. Amer. Chem. Soc.*, 1961, **83**, 1743.

between the electrons competing for the *p*-orbital forming the reaction co-ordinate reduces the bond energy and tends to localise the charge on the electronegative atoms, *viz.*:

$$N^- + RX \longrightarrow \overset{\delta-}{N}\cdots\overset{\delta+}{R}\cdots\overset{\delta-}{X} \longrightarrow RN + X^-$$

The energy of the bond R-N in the transition state is therefore low compared with that in the ground state. The approach of N^- to RX to within the van der Waals distance involves partial desolvation of the ion, and it follows therefore that in such a system the rate order is more sensitive to changes in solvation energy than to changes in bond energy, as suggested by the rate orders $I^- > Br^- > Cl^- > F^-$ and $RS^- > RO^-$ observed for aqueous solutions. The importance of solvation has recently been proved by the observed change in nucleophilic order with change in solvent.[18]

On the other hand, acylation normally proceeds through a tetrahedral *sp*^{3}-hybridised intermediate:[19]



and the observed rate constant is therefore given by $k_1k_3/(k_2 + k_3)$.

Since the energy of the intermediate is normally considerably greater than that of the ground state, the transition state may be assumed to have a similar structure.[20] In that case, bond formation makes a greater contribution to the activation energy than in bimolecular alkylation, as indicated by the rate orders $F^- > Br^-$ and $HO^- > SCN^-$, given in Table 1.

If the transition state is assumed to have the same energy as the intermediate, the activation energy is given by

$$E^* = \Delta H_N + E_N - D_{C-N} + E_\pi - \Delta H_0 - E_0 \text{ (where N = nucleophile)},$$

where E_π is the π-bond energy of the C=O bond, ΔH_O the solvation energy of the O^- ion, and E_O the electron affinity of oxygen. ΔH_N is the solvation energy of the nucleophile, E_N its electron affinity, and D_{C-N} the dissociation energy of the N-C bond.

In comparing observed and calculated reactivities the corresponding changes in entropy must be considered. The entropies of the halide ions in water, S_N, are known accurately[21] and, since the entropy of the intermediate will be approximately constant, the free energy of the equilibrium is given approximately by:

$$\Delta F^* \approx \Delta H_N + E_N - D_{C-N} + TS_N + [E_\pi - \Delta H_O - E_O].$$

In order to compute values of ΔF^*, the bond dissociation energies given by Cottrell[22] and the most probable electron-affinity values given by Pritchard[23] were used. The solvation energies are those given by Verwey[24] and are close to the alternative values of Latimer, Pitzer, and Slansky.[25] Since there is no satisfactory value available, the solvation energy of the hydroxide ion and of the intermediate oxy-anion were assumed to be the same as the solvation energy of the fluoride ion, in view of the similar radii of fluorine and oxygen. These values are certainly too high, but this does not affect the qualitative conclusions drawn from the data of Table 2. The value of E_π was taken to be the

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[19] Bender, *Chem. Rev.*, 1960, **60**, 53.

[20] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[21] Powell and Latimer, *J. Chem. Phys.*, 1951, **19**, 1139.

[22] Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publns., London, 1958, 173.

[23] Pritchard, *Chem. Rev.*, 1953, **52**, 529.

[24] Verwey, *Rev. Trav. chim.*, 1942, **61**, 127.

[25] Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108.

difference in the dissociation energies of the carbonyl bond in a ketone [22] (179 kcal./mole) and the C–O bond [22] (85·5 kcal./mole).

Although these calculations are approximate in view of the uncertainty in some of the energy terms involved, the values of $-\Delta F^*$, which give measures of the corresponding reactivities, increase in the same order as the observed rate constants, *i.e.*, $HO^- > F^- > Br^-, I^-$.

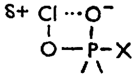
If the structures of the transition state and the intermediate differ appreciably, the observed rate constant will vary with k_3/k_2, *i.e.*, with the relative rates of ionisation of the C–X and the C–N bonds. Since the rates of ionisation of alkyl halides increase in the order [26] $RI \sim RBr > RCl > RF$, k_3/k_2 should increase in the reverse order. This would lead to a high reactivity for the fluoride ion, as observed experimentally. A similar explanation has been advanced by Wiberg [27] to explain the high reactivity of the HO_2^- ion towards anhydrides, and the lack of reactivity towards esters.

TABLE 2.

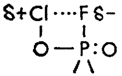
N	D_{C-N}	ΔH_N	S_N	E_N	ΔF^*
F^-	108	122	−2·5	83·5	15·7
Cl^-	81	89·5	13·17	88·2	19·6
Br^-	68	83	19·25	81·6	21·4
I^-	52·6	73·5	26·14	74·6	22·8
HO^-	85·5	(122)	−2·5	54	8·7

(N = nucleophile.)

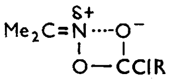
The high reactivities of oximes and other basic oxy-anions, *e.g.*, hydroperoxide and hypochlorite, towards carbonyl [11] and phosphonyl centres [28] have been attributed to specific interactions in the transition state. For instance, Epstein *et al.*[29] suggested bifunctional catalysis for the reaction between the hypochlorite ion and phosphorofluoridates represented by structures (I and II).



(I)



(II)



(III)

A similar explanation (cf. III) could be invoked to explain the high reactivity of oximes with acid chlorides. It should be noted, however, that oximes show a similar enhanced reactivity in general base-catalysis [30] where the above specific interaction is unlikely. This suggests that the high reactivities of these ions are due to differences in the relative importance of solvation, repulsion, and bond-formation energies, compared with the corresponding values for the hydroxide ion, rather than to any specific effect.

EXPERIMENTAL

Purification of Materials.—Acetone (" AnalaR ") was dried ($MgSO_4$) and distilled before use, having b. p. 56·5°. Water-acetone mixtures were made up by volume. " AnalaR " potassium salts were used for measuring the rates of reaction. Acetoxime, phenol, and dianisidine hydrochloride were used as supplied by B.D.H. Ltd. Triethylamine was dried (KOH) and distilled, having b. p. 94·5°.

Measurement of Reaction Rates.—Apparatus was washed with acetone, then with distilled

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[26] Evans, *Trans. Faraday Soc.*, 1946, **42**, 719.

[27] Wiberg, *J. Amer. Chem. Soc.*, 1955, **77**, 2519.

[28] Green and Saville, *J.*, 1956, 3887; Green, Sainsbury, Saville, and Stansfield, *J.*, 1958, 1583; Hackley, Plapinger, Stolberg, and Wagner-Jauregg, *J. Amer. Chem. Soc.*, 1955, **77**, 3651.

[29] Epstein, Bauer, Saxe, and Demek, *J. Amer. Chem. Soc.*, 1956, **78**, 4068.

[30] Bell and Higginson, *Proc. Roy. Soc.*, 1949, *A*, **197**, 141.

water, and dried in a current of warm dry air. The reactions were carried out in 100-ml. glass-stoppered flasks, except for those with fluoride ions and the hydrolysis of ethyl fluoroformate, for which Polythene bottles were used. A conventional thermostat was used for the experiments at 25° ± 0·01°, and a large Dewar flask containing ice–water for experiments at 0° ± 0·05°.

The following methods were used for following the reactions. A known volume of the appropriate solution was allowed to reach thermal equilibrium in the thermostat bath, the requisite quantity of ethyl chloroformate was added from a Lunge–Rey pipette, the mixture shaken vigorously until the solution was complete, and the stop clock started. Aliquot samples were removed at intervals and analysed in one of the following ways.

(i) The sample was run into a large volume of acetone, which served to quench the reaction, and the acid produced was then titrated with triethylamine in toluene to lacmoid.

(ii) The sample was run into an equal volume of carbon tetrachloride contained in a stoppered bottle. The mixture was shaken and an aliquot part of the upper aqueous layer withdrawn and titrated for (*a*) chloride ions by the Volhard method, (*b*) fluoride ions by thorium nitrate solution (sodium alizarinsulphonate as indicator) at pH 4·0, or (*c*) thiosulphate ions iodometrically.

(iii) In some cases the rate was followed by estimating the ethyl chloroformate colorimetrically, by the Schoeneman reaction,[31] involving the reaction with hydrogen peroxide; $HO_2^- + Cl{\cdot}CO_2Et \longrightarrow Cl^- + EtHCO_4 \rightleftharpoons H^+ + EtO{\cdot}CO{\cdot}O_2^-$ (+Dianisidine) $\longrightarrow$ 3,3′-dimethoxydiphenoquinone di-imide. The colour intensity was measured in each case after an interval of 10 min., in a 1 cm. cell, by means of a " Spekker " photometer with an Ilford 1C 601 special violet filter. The calibration curve of intensity against concentration was approximately linear at 10^{-3}—10^{-4}M.

(iv) The rates of some of the faster reactions were measured electrometrically by means of a potentiometric balancing cell previously described;[32] in these experiments, dilute solutions of the chloroformate (~10^{-3}M) were used, and where necessary the reactions were carried out in a 0·01M-buffer containing 0·2M-ammonium nitrate to reduce solution junction potentials.

Evaluation of the Rate Constants.—The rates of solvolysis of ethyl chloroformate and fluoroformate were calculated from the first-order rate expression. The reactions in the presence of added salts, also followed the first-order rate equation when the nucleophile was present in excess, and when the reaction was performed at constant pH in the presence of a feebly ionised reactant. The second-order rate constant k_2 was then calculated from the pseudo-unimolecular rate constant k_1, for the total reaction, the rate constant for the solvolysis alone k_0, and the concentration of nucleophile [N⁻], as follows: $k_2 = (k_1 - k_0)/[N^-]$.

Second-order kinetics were observed for the reactions of hydroxide and azide ions, and k_2 was obtained in these cases from the appropriate second-order rate equation. The correction for the concurrent hydrolysis was neglected since this was less than 1% of the total rate, *i.e.*, within experimental error. The rate of reaction with thiosulphate was followed iodometrically, and approximate rate constants were obtained from the initial part of the reaction, allowances being made for the concurrent hydrolysis.

A summary of the rate constants obtained, with an indication of the method used in each case, is given in Tables 3 and 4.

Preparation of Ethyl Fluoroformate.—(*a*) The action of potassium fluoride on ethyl chloroformate in xylene, benzene, carbon tetrachloride, or methyl ethyl ketone was investigated. A reaction occurred in the ketone but no fluoroformate was isolated. The lack of reaction in the other solvents confirms Saunders and Stacey's observations.[33] (*b*) Hydrogen fluoride was bubbled through ethyl chloroformate at −20°. In a second experiment, the anhydrous liquids were mixed. No product was obtained in either case. (*c*) The action of anhydrous thallous fluoride on ethyl chloroformate[34] was followed, but no fluoroformate was obtained. (*d*) In view of the high rate of reaction between fluoride ions and ethyl chloroformate in aqueous solution (p. 1057), the difficulty which has been experienced in obtaining the fluoroformate is attributed to insolubility of the salt fluoride and the instability of the fluoroformate towards acids and bases. To overcome these difficulties, amides were used as solvents.

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[31] Marsh and Neale, *Chem. and Ind.*, 1956, 494.
[32] Hudson and Wardill, *J.*, 1950, 1729.
[33] Saunders and Stacey, *J.*, 1948, 1773.
[34] Nakanishi, Myers, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 3099.

TABLE 3.

Rate constants for the reactions of nucleophiles with ethyl chloroformate in 85% aqueous acetone (v/v) * at 25°.

$[Cl{\cdot}CO_2Et]$ (M)	Nucleophile	[Nucleophile] (M)	Analyt. method	10^3k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)
0·0710	H_2O	—	Acidity	12·5	
0·100	H_2O	—	Volhard	14·0	
0·0510	Cl^-	0·425	Acidity	13·4	
0·030	Br^-	0·100	,,	13·0	
0·035	Br^-	0·050	,,	13·8	
0·030	CNS^-	0·050	Volhard †	14·0	
0·030	I^-	0·030	Volhard †	13·8	
0·0316	F^-	0·060	Schoeneman	117·0	1·68
0·032	F^-	0·120	,,	205·0	1·60
0·0290	F^-	0·030	,,	62·0	1·63
0·030	F^-	0·030	Volhard	62·2	1·64
0·015	ClO_3^-	0·150	,,	13·8	—
0·030	$S_2O_3^{2-}$	0·030 (pH 7·0)	Iodometry	—	~0·60
0·031	$S_2O_3^{2-}$	0·060 (pH 7·0)	,,	—	~0·56

* 85 volumes of water + 15 volumes of acetone.

† The concentration of iodide and thiocyanate, determined by absorption indicator and colorimetrically, respectively, remained constant throughout the reaction.

TABLE 4.

Rate constants for the reactions of nucleophiles with ethyl chloroformate in 85% aqueous acetone (v/v) * at 0°.

$[Cl{\cdot}CO_2Et]$ (M)	Nucleophile	[Nucleophile] (M)	Anal. method	10^3k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)
0·014	N_3^-	0·0150	Volhard	—	17·5
0·0030	N_3^-	0·0200	,,	348·0	17·3
0·029	NO_2^-	0·0300	,,	970·0	32·2
0·0100	NO_2^-	0·0700	,,	2050	29·3
0·0070	H_2O	—	Acidity	1·70	—
0·0900	H_2O	—	,,	1·56	—
0·0180	H_2O	—	,,	1·60	—
0·0050	HO^-	0·0100	Volhard	—	166·2
0·0035	HO^-	0·0200	,,	—	
0·0110	F^-	0·0350	,,	9·2	0·22
0·0118	F^-	0·0850	,,	22·1	0·24
0·0090	F^-	0·0850	,,	20·8	0·23
0·0124	PhOH †	0·055 (pH 8)	Acidity	—	50·4
0·0116	PhOH †	0·024 (pH 8)	,,	—	49·9
0·0055	$Me_2C{:}N{\cdot}OH$ ‡	0·0278 (pH 7·0)	Potentiometric	140·8	501 × 10^3
0·0055	$Me_2C{:}N{\cdot}OH$ ‡	0·0556 (pH 7·0)	,,	278·0	497 × 10^3
0·0055	$Me_2C{:}N{\cdot}OH$ ‡	0·0250 (pH 6·0)	,,	14·2	503 × 10^3
0·0055	$Me_2C{:}N{\cdot}OH$ ‡	0·0500 (pH 6·0)	,,	26·75	501 × 10^3

* 85 volumes of water plus 15 volumes of acetone. † Results obtained by Dr. G. Loveday using an automatic titrator. ‡ pK_a 12·0.

Ammonium fluoride was dried by azeotropic distillation with carbon tetrachloride, and acetamide over phosphoric oxide. Ethyl chloroformate (1 mole), ammonium fluoride (1 mole), and acetamide (0·5 mole) were stirred together in carbon tetrachloride (500 ml.) for 4 hr. at room temperature. The fluoroformate was then removed *in vacuo* and redistilled through a 12″ Dixon column; it had b. p. 57—58°, n_D^{25} 1·3315 (yield 80%).

The rate of hydrolysis in 85% aqueous acetone was determined at 0° by analysis of the fluoride to give 10^3k_1 46·0, 45·0; 47·0 min.$^{-1}$.

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