488. *The Kinetics of the Reaction between Hydrofluoric Acid and the Anion of* 2,4,6-*Trinitrotoluene in Ethanol, from* −90° *to* −50°.

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The reaction between hydrofluoric acid and the anion of 2,4,6-trinitrotoluene in ethanol has been studied kinetically from −90° to −50°. The rate of the reaction depends on the concentration of undissociated acid and also on that of hydrogen ions. The rate constants have been determined. That for hydrogen fluoride is about six times, and for ethoxonium ions about 30 times, smaller than would be predicted from the Brønsted plot for carboxylic acids. The Arrhenius plots are linear within experimental error.

Evidence for quantum-mechanical tunnelling in a proton-transfer reaction in solution was first found by Bell, Fendley, and Hulett,[1] who compared the kinetics of proton- and deuteron-transfer in the bromination of 2-ethoxycarbonylcyclopentanone. Their conclusions have been confirmed by measurements which show that the Arrhenius plot for this proton-transfer deviates from linearity as the temperature is decreased to −20°.[2] The largest deviations from classical behaviour were found when the group to which the proton was transferred (from carbon) was the fluoride ion. It seemed to us worthwhile to investigate other reactions involving the transfer of protons between carbon and fluorine. A reaction that can be studied over a suitable temperature range is that between a weak acid and the anion of 2,4,6-trinitrotoluene (T.N.T.); the reactions with acetic and monochloroacetic acid have been studied,[3] and we now report results with hydrofluoric acid. The reaction is believed to involve the proton transfer (1) as its rate-determining step:[4]

$$\mathrm{HF} + (\mathrm{T.N.T.})^- \longrightarrow \mathrm{T.N.T.} + \mathrm{F}^- \qquad . \; . \; . \; . \; . \quad (1)$$

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[1] Bell, Fendley, and Hulett, *Proc. Roy. Soc.*, 1956, *A*, **235**, 453.

[2] Hulett, *Proc. Roy. Soc.*, 1959, *A*, **251**, 274.

[3] Ainscough and Caldin, *J.*, 1960, 2407.

[4] Caldin and G. Long, *Proc. Roy. Soc.*, 1955, *A*, **226**, 263.

At low temperatures, therefore, it might show a decrease in energy of activation, as Bell's calculations suggest.[5]

In this paper we report measurements of the rate of reaction of hydrofluoric acid with the T.N.T. anion from −90° to −50°. We hope later to report measurements on the same reaction in the region of 0°, using a low-temperature fast-reaction apparatus described elsewhere.

The solvent was ethanol containing 0·9% by weight of toluene (0·8% by vol.). The ionic strength was kept small (below 0·002 g.-ion/l.) so that the rates should be related in a simple manner to the concentrations. The Brønsted–Bjerrum equation predicts that there will be no primary salt effect at low concentrations; none the less, the ionic strength was kept constant in each series of runs (except at −60°) by addition of lithium iodide.

EXPERIMENTAL

Materials.—2,4,6-Trinitrotoluene was recrystallised to constant m. p. (81°) from ethanol. Hydrofluoric acid was B.D.H. "AnalaR" 40% aqueous acid. Toluene was refluxed over sodium and fractionally distilled as required; b. p. 110·4°/760 mm. Ethanol was dried by the method of Lund and Bjerrum [6] and distilled as required; the average water content, after manipulations similar to those in starting a kinetic run, was found by Smith's method [7] to be 0·09 ± 0·02% (mean of 3 determinations). Since water is added along with hydrofluoric acid, the total water content of the solvent during a run is $0{\cdot}09 + 2{\cdot}9c$, where c is the molar concentration of hydrofluoric acid. As c is usually in the region of 0·01N, the water content is normally near 0·12%; the maximum is about 0·2%.

Solutions.—Sodium ethoxide in ethanol was prepared as described previously [4] and estimated by titrating with standard acid. T.N.T. in ethanol–toluene was made fresh each day. Hydrofluoric acid solution was prepared from the aqueous acid and freshly-distilled ethanol in a polythene bottle. It was titrated with sodium hydroxide (phenolphthalein indicator). The rate of corrosion of glass by ethanolic hydrogen fluoride was determined; the loss of this acid during a normal kinetic run is of the order of 0·1%. It appears that ethanolic hydrogen fluoride is stable at room temperature as regards esterification.[8]

Thermostat and Photometer.—These are described elsewhere in the preceding paper. Temperatures are accurate to ±0·03°. An Ilford filter (623) was used; this has a maximum transmission at 495 mμ, corresponding to the absorption peak of the T.N.T. anion.[4]

Experimental Procedures.—In general these were similar to those described in earlier papers.[4,9] The solution of the anion of T.N.T., which is formed only slowly at low temperatures, was prepared as follows. Appropriate amounts of ethanol, sodium ethoxide solution, and lithium iodide solution were pipetted into the reaction cell, and cooling was begun; when the required temperature had been reached, 1 ml. was added of a solution prepared by mixing 1 ml. of an appropriate T.N.T. solution with 1 ml. of sodium ethoxide solution at room temperature. Hydrofluoric acid solution (1 or 2 ml.) was placed in the siphon tube. Density corrections were applied to the concentrations.[10] The maximum uncertainties in the concentrations of hydrogen fluoride, sodium ethoxide, and lithium iodide were respectively ±2%, 2%, and 1·2%. These give a maximum uncertainty of ±3·5% in the buffer ratio.

Analysis of kinetics.

The methods of analysis are in general similar to those in previous papers,[4,9] and the same symbols will be used. The main difference is that reaction with hydrogen ions, as well as with undissociated acid, has to be taken into account.

Rate Equation.—The results of each individual run were treated by Guggenheim's method.[11]

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[5] Bell, "Acid-Base Catalysis," Clarendon Press, 1941, chap. 8; *Trans. Faraday Soc.*, 1959, **55**, 1.
[6] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.
[7] Smith, *J.*, 1927, 1284.
[8] Meslans, *Compt. rend.*, 1892, **115**, 1080.
[9] Ainscough and Caldin, *J.*, 1956, 2528.
[10] Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312.
[11] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

The concentration of T.N.T. is small compared with that of acid, and linear plots were always obtained. The complete equation for the slope s'' of such a plot may be derived on the assumption that concurrent reactions proceed between the T.N.T. anion and (*a*) the solvent, with first-order rate constant k°_{-1}, (*b*) the undissociated hydrogen fluoride molecules, with second-order rate constant k_2, (*c*) ethoxonium ions $\mathrm{EtOH_2^+}$, with second-order rate constant $k_{3\mathrm{E}}$, and (on account of the water unavoidably present) hydroxonium ions $\mathrm{H_3O^+}$, with rate constant $k_{3\mathrm{H}}$. The equation for s'' for an individual run is then given by the following equation, in which k°_{-1} is known from previous work:[4]

$$2{\cdot}303s'' = k^\circ_{-1} + k_2(\mathrm{HF}) + k_{3\mathrm{E}}(\mathrm{EtOH_2^+}) + k_{3\mathrm{H}}(\mathrm{H_3O^+}) \quad . \quad . \quad . \quad (2)$$

We assume that concentrations can be used in place of activities; this is reasonable, as the ionic strength does not exceed 0·002 g.-ion/l.; it has been shown that hydrogen chloride in ethanol obeys the Debye–Hückel law up to this concentration,[12] and that the activity coefficients of hydrogen chloride and sodium ethoxide in ethanol are equal even at much higher concentrations.[13] We write for the equilibria concerned in the dissociation of hydrogen fluoride in ethanol containing a little water:

$$K_\mathrm{H} = (\mathrm{H_3O^+})(\mathrm{F^-})/(\mathrm{HF})(\mathrm{H_2O}) \text{ and } K^\circ_\mathrm{E} = (\mathrm{EtOH_2^+})(\mathrm{F^-})/(\mathrm{HF})$$

The formal initial ethoxide concentration when the reaction mixture is formed is denoted by b, and the formal concentration of added acid by c. The fraction of hydrogen fluoride dissociated is assumed to be small. The initial reaction $\mathrm{HF + OEt^- \longrightarrow F^- + EtOH}$ is assumed to be rapid and complete. Then in the reaction mixture $(\mathrm{HF}) = (c - b)$ and $(\mathrm{F^-}) = b$. (The possibility of formation of $\mathrm{HF_2^-}$ is considered later.) We then obtain from equation (2)

$$2{\cdot}303s'' = k^\circ_{-1} + k_2(c - b) + [k_{3\mathrm{E}}K^\circ_\mathrm{E} + k_{3\mathrm{H}}K_\mathrm{H}(\mathrm{H_2O})](c - b)/b \quad . \quad . \quad (3)$$

For convenience, we write

$$k'_3 = [k_{3\mathrm{E}}K^\circ_\mathrm{E} + k_{3\mathrm{H}}K_\mathrm{H}(\mathrm{H_2O})] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and so obtain

$$2{\cdot}303s'' = k^\circ_{-1} + k_2(c - b) + k'_3(c - b)/b \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

All the observed results can be fitted to this equation, as follows.

(i) *Runs at constant buffer ratio* $r = (c - b)/b$. Plots of s'' against $(c - b)$ at constant buffer ratio are linear, up to acid concentrations of about 0·025M; the slopes give values of k_2. When the runs are repeated with different buffer ratios, the plots are parallel. When the intercepts are plotted against the buffer ratio, the slope of the plot gives, according to equation (5), a value of k'_3.

(ii) *Runs at constant fluoride concentration* b *and varying acid concentration* $(c - b)$. Plots of s'' against $(c - b)$, for a set of runs in which b is kept constant, are linear. The slope q of such a plot is, according to equation (5), $0{\cdot}434(k_2 + k_3'/b)$. When the values of q for sets of runs with different values of b are plotted against $1/b$, the plot is linear; according to equation (5), the intercept gives $0{\cdot}434k_2$, and the slope $0{\cdot}434k'_3$.

Evidence on the Rôle of the $\mathrm{HF_2^-}$ *Ion.*—It is necessary to enquire whether the concentrations of the kinetically-active species might be altered by formation of the ion $\mathrm{HF_2^-}$ according to the equilibrium:

$$\mathrm{HF + F^- = HF_2^-};\ K_2 = (\mathrm{HF_2^-})/(\mathrm{HF})(\mathrm{F^-}) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The complete kinetic equation becomes very complex if this equilibrium is introduced, but can be simplified if, as an approximation, it is assumed that the total hydrogen-ion concentration is much less than b. It can then be shown that, in equation (5) which describes the kinetics, the first and the third term remain unchanged, but the coefficient of $(c - b)$ in the second term becomes, instead of k_2,

$$k_2 - \{(k_2K_2/r')(c - b)/[1 + K_2(c - b)] - k_3'K_2(r' - 1)\} \quad . \quad . \quad . \quad (7)$$

where r' is the apparent buffer ratio, $(c - b)/b$, which is no longer exactly equal to $(\mathrm{HF})/(\mathrm{F^-})$. If we plot s'' against $(c - b)$, at constant apparent buffer ratio r', the slope of the plot will

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[12] Woolcock and Hartley, *Phil. Mag.*, 1928, **5**, 1133.

[13] Danner, *J. Amer. Chem. Soc.*, 1922 ,**44**, 2822.

decrease with increase of $(c - b)$; if we plot s'' against r' at constant $(c - b)$, the slope will increase with increase of r'. Neither of these effects has been observed, within the experimental error. Moreover, assuming the derived values of k_2 and k_3', we can calculate the value of K_2 which would produce a detectable variation in the apparent value of k_2, say 10%; K_2 would have to be of the order of 100 l. mole^{-1}. There are no experimental determinations of K_2 in ethanol; but in water, it is 3·86 ± 0·2 l. mole^{-1} at 25° and decreases slightly with decrease of temperature,[14] and it is unlikely to be very different in ethanol. We conclude that the formation of HF_2^- is probably not extensive enough to influence the kinetic scheme.

Results

First-order Rate Constants from Kinetic Runs.—The results of the individual runs are summarised in Table 1. Here d = T.N.T. concentration; b = formal initial ethoxide concentration = fluoride concentration in the resulting solution; c = formal initial concentration of

TABLE 1.*

Temp.	10^5d	10^4b	10^4c	10^4h	$10^4(c - b)$	r'	$10^4\mu$	$10^4s''$, obs. (sec.$^{-1}$)	$10^4s''$, calc. (sec.$^{-1}$)
−49·99°	1·06	3·19	19·2	16·81	16·0	5	20	36·5 ± 0·5	34·9
±0·03°	1·06	6·4	38·4	13·6	32·0	5	20	56·6 ± 1·0	57·3
	1·02	1·6	9·6	18·4	8·0	5	20	22·6 ± 0·6	23·7
	1·02	4·26	25·56	15·74	21·3	5	20	42·8 ± 1·0	42·3
	1·34	0·87	9·59	19·13	8·72	10	20	28·9 ± 0·7	29·3
	1·34	3·49	38·4	16·51	34·9	10	20	66·8 ± 1·2	67·1
	1·91	2·55	28·0	17·45	25·5	10	20	53·9 ± 1·0	53·5
	1·91	1·27	14·0	18·73	12·7	10	20	35·5 ± 1·0	35·1
−59·98°	1·47	6·17	24·5	0·0	18·2	2·9	6·17	13·1 ± 0·3	13·0
±0·03°	1·44	6·17	47·9	0·0	41·7	6·8	6·17	26·8 ± 0·8	25·4
	1·44	6·17	103·9	0·0	97·7	15·8	6·17	55·3 ± 1·5	54·9
	1·57	6·17	69·3	0·0	63·1	10·2	6·17	36·5 ± 1·0	36·8
	1·51	6·17	55·8	0·0	49·6	8·0	6·17	26·3 ± 0·9	29·6
	1·51	6·17	54·5	0·0	48·3	7·8	6·17	29·8 ± 1·0	29·0
	1·53	2·59	51·1	0·0	48·5	18·7	2·59	40·7 ± 1	36·6
	1·53	2·59	25·6	0·0	23·1	8·9	2·59	20·5 ± 0·5	20·5
	1·37	2·59	99·8	0·0	97·2	37·5	2·59	67·0 ± 2·0	67·5
	1·37	2·59	66·5	0·0	63·9	24·7	2·59	48·5 ± 1·5	46·3
	1·41	2·59	60·6	0·0	58·0	22·4	2·59	38·2 ± 1	42·6
	1·41	2·59	30·3	0·0	27·7	10·7	2·59	21·6 ± 0·6	23·4
−69·98°	2·15	16·81	184·8	3·19	168	10	20	30 ± 1	28·0
±0·03°	1·43	6·30	69·51	15·68	63·2	10	20	11·7 ± 0·3	10·7
	1·43	12·63	139·0	7·37	126·4	10	20	20·8 ± 0·5	21·1
	1·91	9·54	104·9	10·46	95·4	10	20	15·2 ± 0·3	16·0
	1·61	13·09	143·9	6·91	130·8	10	20	19·6 ± 0·6	21·8
	1·61	4·36	47·98	15·64	43·6	10	20	7·9 ± 0·2	7·5
	1·80	6·66	139·8	13·34	133·1	20	20	21·9 ± 0·7	22·3
	1·49	1·66	34·95	18·34	33·3	20	20	8·1 ± 0·2	7·8
	1·75	10·93	229·5	9·07	218·6	20	20	35·9 ± 1	34·8
	1·75	5·00	104·9	15·0	99·9	20	20	17·5 ± 0·6	17·4
	1·91	8·60	180·5	11·4	171·9	20	20	27·1 ± 0·9	28·0
−79·98°	1·34	6·35	132·6	13·65	126·2	20	20	6·9 ± 0·2	6·65
±0·03°	1·34	9·48	199·0	10·52	189·5	20	20	9·4 ± 0·3	9·37
	1·60	12·63	265·2	7·37	252·6	20	20	15·5 ± 0·5	12·1
	1·66	15·70	329·8	4·3	314·1	20	20	20·5 ± 0·6	14·8
	1·14	15·70	329·8	4·3	314·1	20	20	21·1 ± 0·6	14·8
	1·62	14·41	302·6	5·59	288·2	20	20	18·0 ± 0·5	13·7
	1·90	9·96	209·2	10·04	199·2	20	20	9·7 ± 0·2	9·79
	1·90	2·49	52·3	17·51	49·8	20	20	3·5 ± 0·1	3·38
	2·08	4·05	85·0	13·95	80·9	20	20	4·4 ± 0·2	4·70
−89·96°	3·58	5·36	112·6	14·64	107·2	20	20	1·64 ± 0·06	1·68
±0·03°	3·09	12·75	267·7	7·25	255·0	20	20	3·65 ± 0·1	3·43
	3·09	18·01	378·3	1·19	360·3	20	20	7·27 ± 0·2	4·67
	2·72	2·8	58·94	17·2	56·1	20	20	1·18 ± 0·03	1·08
	2·52	10·68	224·2	9·32	213·5	20	20	2·76 ± 0·1	2·94

* All concentrations are in moles per litre.

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[14] Broene and de Vries, *J. Amer. Chem. Soc.*, 1947, **69**, 1644.

hydrofluoric acid; $(c - b)$ = concentration of hydrogen fluoride in the resulting solution; r' = apparent buffer ratio = $(c - b)/b$; h = concentration of lithium iodide; μ = ionic strength; s'' = slope of first-order plot (decadic logarithms). The values of s'' calculated from the derived values of the rate constants k_2 and k'_3 (see below) are given in the last column for comparison with the observed values. The rate constant of an individual run could be determined with a precision of $\pm 3\%$ (as was shown by least-squares analysis of six runs); and it was reproducible with the same precision.

Derivation of Rate Constants for Hydrogen Fluoride and for Hydrogen Ions.—All the following calculations of slopes and intercepts were carried out by least-squares methods, and the uncertainties cited are standard deviations. The precision of the experimental results can be judged by comparing the values of s'', calculated from the final values of k_2 and k'_3, with the experimental values (see Table 1).

Results at $-50°$, $-70°$, $-80°$, *and* $-90°$. At each of these temperatures, the rate constant k_2 for hydrogen fluoride was obtained from the slope of a plot of s'' against $(c - b)$ at constant buffer ratio, as described above. The change in buffer ratio due to production of fluoride ion in the reaction was kept below 5% in nearly all the runs, by using buffer ratios not greater than 20. The plot was linear up to a value of $(c - b)$ of about 0·02M, and only this part of the plot was considered; above this concentration the rate increased more rapidly with $(c - b)$. At $-50°$ and $-70°$, two buffer ratios were used, giving parallel lines, and it was possible to plot the intercept against the buffer ratio, especially since the intercept at zero buffer ratio is k°_{-1} which is already known;[4] the slope of such a plot gives k'_3. At $-80°$ and $-90°$, the intercept is not much greater than the experimental error, and only one set of runs at the maximum buffer ratio[19] was carried out; at these temperatures k°_{-1} is negligible. The results are summarised in Table 2.

TABLE 2.

Temp.	$-50°$		$-70°$		$-80°$	$-90°$
Buffer ratio, r'	5	10	10	20	20	20
Slope of plot of s'' against $(c - b)$	1·40 $\pm 0·08$	1·42 $\pm 0·08$	0·165 $\pm 0·016$	0·147 $\pm 0·006$	0·0429 $\pm 0·0019$	0·0118 $\pm 0·0015$
10^4 [Intercept of plot of s'' against $(c - b)$]	$12·5 \pm 1·6$	$17·7 \pm 0·5$	$0·27 \pm 1·8$	$2·7 \pm 0·9$	$1·24 \pm 0·27$	$0·42 \pm 0·27$
Slope of plot of intercept against r'	$(1·8 \pm 0·2) \times 10^{-4}$		$(1·35 \pm 0·5) \times 10^{-5}$		—	—
k_2 (l. mole^{-1} sec.$^{-1}$)	$3·50 \pm 0·18$		$(3·59 \pm 0·21) \times 10^{-1}$		$10^{-2} \times (9·88 \pm 0·44)$	$10^{-2} \times (2·72 \pm 0·35)$
k'_3 (sec.$^{-1}$)	$(4·1 \pm 0·5) \times 10^{-4}$		$(3·1 \pm 1·2) \times 10^{-5}$		$10^{-5} \times (1·4 \pm 0·3)$	$10^{-6} \times (4·8 \pm 3·2)$

Results at $-60°$. At this temperature we have two sets of runs, each at a constant fluoride concentration b. The plots of s'' against $(c - b)$ are linear; the values of their slopes (q) and intercepts are given in Table 3.

TABLE 3

$10^4 b$ (mole l.$^{-1}$)	2·59	6·17
Slope (q) (l. mole^{-1} sec.$^{-1}$)	$0·63 \pm 0·07$	$0·53 \pm 0·03$
10^4 (intercept) (sec.$^{-1}$)	6 ± 4	$3·3 \pm 2·6$

The slope q is related to $1/b$ by a line, whose intercept (equal to $0·434k_2$, as shown above) is $0·46 \pm 0·04$ and whose slope (equal to $0·434k'_3$) is $10^{-5} \times (3·3 \pm 0·3)$. (The uncertainties given here are, exceptionally, maximum values estimated from the graphs.) These figures give, for $-60°$,

$$k_2 = 1·1 \pm 0·1 \text{ l. mole}^{-1}\text{ sec.}^{-1},\ k'_3 = 10^{-5}\,(7·5 \pm 0·8)\text{ sec.}^{-1}.$$

Summary of Results for k_2 and k'_3 at all Temperatures.—The results are collected in Table 4. Included in that Table are the values of the rate constants calculated from the Arrhenius equation with the parameters given later.

The Effect of Water, and the Values of $k_{3\mathrm{E}}$ and $k_{3\mathrm{H}}$.—At $-60°$, four runs were performed to determine the effect of water on the rate. The results are summarised in Table 5. The lowest

TABLE 4.

				log k_2		log k'_3	
Temp.	k_2	k'_3	$10^3/T$	obs.	calc.	obs.	calc.
−50·0°	3·25 ± 0·18	(4·1 ± 0·5) × 10^{-4}	4·481	0·512 ± 0·024	0·502	$\bar{4}$·613 ± 0·06	$\bar{4}$·42
−60·0°	1·110 ± 0·10	(7·5 ± 0·8) × 10^{-5}	4·691	0·045 ± 0·038	0·054	$\bar{5}$·876 ± 0·05	$\bar{4}$·03
−70·0°	(3·59 ± 0·21) × 10^{-1}	(3·1 ± 1·2) × 10^{-5}	4·922	$\bar{1}$·555 ± 0·026	$\bar{1}$·563	$\bar{5}$·491 ± 0·21	$\bar{5}$·60
−80·0°	(9·88 ± 0·44) × 10^{-2}	(1·4 ± 0·3) × 10^{-5}	5·176	$\bar{2}$·995 ± 0·020	$\bar{1}$·020	$\bar{5}$·146 ± 0·1	$\bar{5}$·12
−90·0°	(2·72 ± 0·35) × 10^{-2}	(4·8 ± 3·2) × 10^{-6}	5·457	$\bar{2}$·435 ± 0·059	$\bar{2}$·420	$\bar{6}$·681 ± 0·48	$\bar{6}$·60

water concentration is that in purified ethanol. The initial concentrations of the other constituents were the same in all four runs, *viz.*, (in moles/l.), $10^5d = 1{\cdot}61$, $10^4b = 4{\cdot}37$, $10^4c = 48{\cdot}1$; the buffer ratio $(c - b)/b$ is 10·0.

TABLE 5.

Water concn. (mole l.$^{-1}$)	0·08 ± 0·005	0·33 ± 0·03	0·60 ± 0·03	1·16 ± 0·03
$10^4s''$, obs. (sec.$^{-1}$)	29·4 ± 0·6	31·3 ± 0·7	31·8 ± 0·7	37·0 ± 1·0
,, calc. (sec.$^{-1}$)	29·1	30·6	32·4	36·1

A straight line fitted to these results has the following equation:

$$10^4s'' = (6{\cdot}6 \pm 1{\cdot}2)(H_2O) + (28{\cdot}7 \pm 0{\cdot}6) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

(The values given in the last line of Table 5 are derived from this equation.) This may be compared with equation (3). Comparing the coefficients of (H_2O), we find for −60°:

$$K_{3H}K_H = 10^{-4}(1{\cdot}5 \pm 0{\cdot}3) \text{ l. mole}^{-1}\text{ sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Comparing now the constant terms in equations (3) and (8), and using the value previously determined [4] for k°_{-1} (6×10^{-5} sec.$^{-1}$), and the value found in this present work for k_2, we obtain for −60°:

$$k_{3E}K^\circ_E = 10^{-4}(1{\cdot}3 \pm 0{\cdot}7) \text{ sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

These values imply that for normal runs at −60°, with $(H_2O) \sim 0{\cdot}08$ mole/l., the term $k_{3H}K_H(H_2O)$ is about 10^{-5} sec.$^{-1}$, and is only about 10% of $k_{3E}K^\circ_E$. Thus

$$k_{3E}K^\circ_E \sim 0{\cdot}9k'_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

This implies that about 90% of the protons that react with the T.N.T. anion are solvated by ethanol rather than by water. In assessing this conclusion, however, it should be remembered that part of the change in rate on adding water may be due to a medium effect, which cannot be studied in isolation.

Assuming the conclusion to be correct, we can derive some approximate values for k_{3E} and k_{3H} at −60°. We can find k_{3E} from equation (10), if we assume the value of K°_E given in the next section ($1{\cdot}5 \times 10^{-9}$ mole/l.) to be of the right order of magnitude at −60°; the result is $k_{3E} \sim 10^5$ l. mole^{-1} sec.$^{-1}$. (This will be too large if the estimate of K°_E is too small; see Discussion.) To find k_{3H} from equation (9), we require a value of K_H. We note that $K_H = K^\circ_E K/(\text{EtOH})$, where K is the equilibrium constant for the reaction $H_3O^+ + EtOH = EtOH_2^+ + H_2O$ in ethanol. Here K depends on the relative acid strengths of H_3O^+ and $EtOH_2^+$ in ethanol; there are no determinations of these, but it has been shown that the acid strengths of water and ethanol molecules in ethanol are of the same order,[15, 16] and if we assume that the same is true of H_3O^+ and $EtOH_2^+$, then $K \sim 1$. Then k_{3H} will be of the order of 10^6 l. mole^{-1} sec.$^{-1}$.

Brønsted Relation.—The rates with hydrogen fluoride and $EtOH_2^+$ may be compared with those for the four carboxylic acids previously studied at 78·5°.[4] The rate constant for hydrogen

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[15] Caldin and G. Long, *J.*, 1954, 3741.

[16] Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1959, **81**, 1050.

fluoride (k_2) at this temperature can be calculated from the Arrhenius equations given below. An approximate value for $EtOH_2^+$ (k_{3E}) is obtained by assuming equation (11) to be correct at −78·5° as well as at −60°. Dissociation constants for the four carboxylic acids in ethanol at 25° are available.[17] The dissociation constant of $EtOH_2^+$ in ethanol is obtained by assuming that the concentration of ethanol molecules in ethanol is 17 moles/l. The dissociation constant of hydrogen fluoride has been measured only in water at 25°. To estimate the value in ethanol, $K°_E$, it is assumed that, on passing from water to ethanol, pK increases by 5·56; this is the mean of the corresponding increases for the four carboxylic acids, which all lie in the range 5·56 ± 0·2. The result is $K°_E = 1{\cdot}5 \times 10^{-9}$ mole/l. (This, however, may be too small; see Discussion.)

In order to take into account the statistical difference between the three types of acid concerned, we have plotted $\log_{10}(k/p)$ against $\log_{10}(qK/p)$, where p is the number of equivalent protons detachable from the acid and q is the number of equivalent positions at which the corresponding base may accept a proton; k is the rate constant at −78·5°, and K is the dissociation constant in ethanol at 25°. The data are summarised in Table 6. The six points as a whole do not lie on a good straight line. The best straight line representing all six points, calculated by the method of least squares, has a slope of 0·43 ± 0·04. The best straight line for the four carboxylic acids alone has a slope of 0·56 ± 0·04. The rate constant for hydrogen fluoride is 5 times smaller than would be predicted from this line, and that for $EtOH_2^+$ is 30 times smaller. Hydrofluoric acid shows deviations up to a factor of 3 in other reactions,[18] and the solvated proton up to a factor of 30.[19]

TABLE 6.

Acid	Acetic	Glycollic	Monochloro-acetic	Dichloro-acetic	Hydro-fluoric	$EtOH_2^+$
$\log_{10} K$ at 25°	−10·43	−9·49	−8·52	−6·96	−8·83	+1·23
$\log_{10} k$ at −78·5°	−0·96	−0·43	+0·21	+0·95	−0·90	+4
	±0·02	±0·02	±0·04	±0·04	±0·02	
p	1	1	1	1	1	2
q	2	2	2	2	1	1
$\log_{10}(k/p)$	−0·96	−0·43	+0·21	+0·95	−0·90	+3·7
$\log_{10}(qK/p)$	−10·13	−9·19	−8·22	−6·66	−8·83	+0·93

Temperature-variation of Rate Constants.—The plots of $\log_{10} k_2$ (for the reaction of hydrogen fluoride, and of $\log_{10} k'_3$ (for the overall reaction with hydrogen ions), against $1/T$, are linear within experimental error. The best straight lines and the standard deviations are: $\log_{10} k_2 = -10^3 \times (2{\cdot}133 \pm 0{\cdot}025)/T + (10{\cdot}06 \pm 0{\cdot}12)$ and $\log_{10} k'_3 = -10^3 \times (1{\cdot}87 \pm 0{\cdot}21)/T + (4{\cdot}8 \pm 1{\cdot}0)$. The corresponding values of the Arrhenius activation energy E in the equation $k = A\exp(-E/\boldsymbol{R}T)$ are $9{\cdot}8 \pm 0{\cdot}1_2$ and $8{\cdot}2 \pm 1$ kcal./mole, respectively. For hydrogen fluoride, the value of (A in l. mole^{-1} sec.$^{-1}$) is given by $\log_{10} A = 10{\cdot}0_6 \pm 0{\cdot}1_2$. For hydrogen ion, the difficulty arises that k'_3 is a composite constant, and accurate values for the temperature variation of k_{3E} and k_{3H} separately cannot be given. We obtain the order of magnitude of E and A for the ion $EtOH_2^+$ by assuming that at all temperatures equation (11) is valid and that $K°_E$ has the same value; this gives $E = 8{\cdot}2$ kcal./mole and $\log_{10} A \sim 13{\cdot}6$ (l. mole^{-1} sec.$^{-1}$). These values are tabulated in Table 7, along with those for other acids taken from previous work.[3,4] Values for the entropy of activation ΔS,* calculated from $A = \exp(\boldsymbol{k}T/\boldsymbol{h})\exp(\Delta S^*/\boldsymbol{R})$, are also given. It is seen that the values of E and A for hydrogen fluoride are similar to those for other uncharged acids. For $EtOH_2^+$, the value given for E is similar, while that for

TABLE 7.

Acid	E (kcal./mole)	$\log_{10}A$ (l. mole^{-1} sec.$^{-1}$)	ΔS^* (cal. deg.$^{-1}$ mole^{-1})
Hydrogen fluoride	$9{\cdot}8_2 \pm 0{\cdot}1_2$	$10{\cdot}0_6 \pm 0{\cdot}1_2$	−13·8 ± 0·5
$EtOH_2^+$	(8·2)	(13·6)	+3 ± 5
Acetic	$9{\cdot}3_5 \pm 0{\cdot}0_8$	$9{\cdot}5_0 \pm 0{\cdot}0_7$	−16·1 ± 0·4
Monochloroacetic	$8{\cdot}5_2 \pm 0{\cdot}1_3$	$9{\cdot}6_9 \pm 0{\cdot}1_5$	−14·7 ± 0·7
Glycollic	9·6 ± 0·2	10·3 ± 0·2	−12·4 ± 1
Dichloroacetic	8·5 ± 0·2	10·5 ± 0·3	−11·4 ± 1·4

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[17] Minnick and Kilpatrick, *J. Phys. Chem.*, 1939, **43**, 259.

[18] Bell and McCoubrey, *Proc. Roy. Soc.*, 1956, *A*, **234**, 192.

[19] Bell, ref. 5, p. 93.

A is considerably larger, as would be expected for a reaction between oppositely-charged ions compared with a reaction between an ion and an uncharged molecule.

DISCUSSION

Hydrogen Fluoride.—In the range −90° to −50°, the undissociated acid shows no special peculiarities compared with other uncharged acids, as regards either the Brønsted relation (Table 6) or the parameters of the Arrhenius equation (Table 7). The Arrhenius plot is linear within experimental error, showing no deviation attributable to quantum-mechanical tunnelling. The maximum curvature, in the direction of decrease of E with decrease of temperature, compatible with the measured rates and the standard deviations, corresponds to $\Delta C_p^* = \mathrm{d}(\Delta H^*)/\mathrm{d}T = 80$ cal. deg.$^{-1}$ mole^{-1}; the maximum curvature in the opposite direction corresponds to $\Delta C_p^* = -40$ cal. deg.$^{-1}$ mole^{-1}. We might expect that the increase of solvation in the reaction [4] would lead to a negative value of ΔC_p^*. Various reactions are known [20,21] in which ΔC_p^* has appreciable negative values, in the range 0 to −70 cal. deg.$^{-1}$ mole^{-1}. A positive value of ΔC_p^*, however, could be interpreted only in terms of tunnelling.

Hydrogen Ions.—It is noteworthy that in analysing the kinetics it has been necessary to take account of hydrogen ions, although their contribution to the kinetics was found to be negligible in earlier work with other acids, including monochloroacetic, whose strength in water is comparable with that of hydrofluoric acid. This suggests that the dissociation constant of hydrofluoric acid decreases less than those of carboxylic acids on passing from water to ethanol. The estimate given above for K°_E will then be too small, and hence that for k_{3E} will be too large.

Comparison of Acids.—The Arrhenius energy of activation is surprisingly constant over the whole series of acids; it lies within the range of 9 ± 1 kcal./mole, while the rate constant varies (at −78·5°) from about 10^{-6} l. mole^{-1} sec.$^{-1}$ for ethanol, through 10 for dichloroacetic acid,[4] to about 10^4 for $EtOH_2^+$—a total range of about 10^{10}. This is the more remarkable when it is considered in terms of the Brønsted relation and its interpretation by means of potential-energy curves.[22] On this interpretation we should expect changes in E to be related to changes in the free energy of activation ΔG^* by the relation $\Delta E = \alpha\Delta(\Delta G^*) = \alpha \boldsymbol{R}T(\Delta \ln k)$, where α is the exponent of the Brønsted relation. With $\alpha = 0{\cdot}56$, this gives, for the above range of rates at −78·5°, $\Delta E \sim 5$ kcal./mole. The fact that the observed variation in E is much smaller than this may constitute further evidence that the observed E is considerably larger than the energy required to detach the proton from the acid.[4,23]

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[20] Moelwyn-Hughes, " The Kinetics of Reactions in Solution," 2nd edn., Clarendon Press, 1947, p. 67.

[21] Hyne and Robertson, *Canad. J. Chem.*, 1955, **33**, 1544; 1957, **35**, 623; Hamilton and Robertson, *ibid.*, 1959, **37**, 966.

[22] Bell, ref. 5, chap. 8.

[23] Caldin, *J.*, 1959, 3345.