486. The Kinetics from Room Temperature to about −100° of the Reactions between Certain Acids and the Anion of 2,4,6-Trinitrotoluene, in Ethanol.

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The proton-transfer reactions of the anion of 2,4,6-trinitrotoluene with undissociated acetic acid and monochloroacetic acid in ethanol have been studied kinetically at temperatures down to −100° and −114°, respectively, to see whether they exhibit quantum-mechanical tunnelling. There is no significant deviation either from the Arrhenius or from the Eyring equation between these temperatures and +20°. The two equations represent the results about equally well.

QUANTUM-MECHANICAL tunnelling in proton-transfer should be more easily detected the lower the temperature,[1] and it is therefore of interest to measure the rates of such reactions at temperatures as low as possible. We have determined the rates of the reactions of the anion of 2,4,6-trinitrotoluene (T.N.T.) with acetic acid at −50°, −60°, −70°, −80°, −90°, and −100°, and that of the corresponding reaction with monochloroacetic acid at −70°, −80°, −99°, and −114°. The solvent was ethanol containing 1% by weight of toluene. The rates have already been measured at +20° by a rapid-reaction technique.[2] Thus the temperature ranges over which the rates have been measured are 120° and 134° respectively; and the factors by which the absolute temperature varies are 1·7 and 1·8.

Evidence that these reactions are proton-transfers has already been given,[2] and further support is provided by the report that T.N.T. exchanges with deuterium oxide in presence of pyridine.[3] It has also been shown that *p*-nitrotoluene and 2,4-dinitrotoluene exchange with deuterium oxide in presence of bases,[4] the hydrogen atoms concerned being those of the methylene group; and tritium exchange occurs in presence of ethoxide ion in ethanol containing 10% of water.[5]

Only the undissociated acids (HA) are concerned in the reactions, as was shown by experiments in which the buffer ratio was varied (below). The observed velocity constants therefore refer to the reaction: $TNT^- + HA \longrightarrow TNT + A^-$.

EXPERIMENTAL AND RESULTS

The reactions were followed photometrically. The apparatus, experimental procedures, and methods of determining first-order rate constants have been described in previous papers.[2,6]

[1] Bell, " Acid-base Catalysis," Clarendon Press, 1941, Chap. 8.
[2] Caldin and Long, *Proc. Roy. Soc.*, 1955, *A*, **226**, 263.
[3] Miller and Wynne-Jones, *J.*, 1959, 2375.
[4] Miklukhin, *Zhur. Fiz. Khim.*, 1948, **22**, 1511; *Uspekhi Khimii*, 1948, **17**, 663; N.R.C. translation TT 168 (Ottawa, 1950).
[5] Wilzbach, personal communication.
[6] Ainscough and Caldin, *J.* 1956, 2528.

Temperatures were measured by means of a five-junction thermel calibrated at five temperatures: the f. p.s of mercury, chlorobenzene ($-45 \cdot 21°$), chloroform ($-63 \cdot 50°$), and carbon disulphide ($-111 \cdot 52°$), and the sublimation point of carbon dioxide ($-78 \cdot 40°$); no changes greater than $0 \cdot 1°$ were observed on recalibration after a year. The uncertainty in the temperature is about $\pm 0 \cdot 1°$. For the six runs recorded in Table 1, however, a platinum-resistance thermometer (calibrated at the oxygen, steam, and sulphur points and the triple point of water) was used, and a new reaction cell and photometer to be described in the succeeding paper.

We use the same symbols as in previous papers. The slope s'' of a first-order plot of $\log_{10} D$ (D = optical density) against time is given in the general case by

$$2 \cdot 303 s'' = k^0_{-1} + k_2(\text{HA}) + k_3(\text{H}^+) \qquad \ldots \ldots \quad (1)$$

The term k^0_{-1} is known to be negligible from earlier work.[2]

Effect of Buffer Ratio.—The term $k_3(\text{H}^+)$ was shown to be negligible by the results of a series of six runs with monochloroacetic acid at $-90 \cdot 03°$, in which the buffer ratio was varied from 1 to 30 by adjusting the concentration of monochloroacetate; the values of s'' showed no trend. The numerical data for these runs, for which we are indebted to Mr. E. Harbron, are given in Table 1. Here c is the formal concentration of added acid; b = formal initial ethoxide-ion

TABLE 1.

$10^3(c - b)$ (mole l.$^{-1}$)	$10^4 b$ (mole l.$^{-1}$)	r	$10^4 s''$ (sec.$^{-1}$)	$s''/(c - b)$ (l. mole^{-1} sec.$^{-1}$)	$10^3(c - b)$ (mole l.$^{-1}$)	$10^4 b$ (mole l.$^{-1}$)	r	$10^4 s''$ (sec.$^{-1}$)	$s''/(c - b)$ (l. mole^{-1} sec.$^{-1}$)
1·92	1·69	11·5	2·77	0·144	1·72	1·03	16·7	2·60	0·151
1·85	0·99	18·6	2·43	0·131	1·72	0·57	30·2	2·33	0·136
1·72	0·70	24·8	2·37	0·138	1·75	18·61	0·9	2·45	0·140

TABLE 2. *Acetic acid.*

Temp.	$10^3 c$ (mole l.$^{-1}$)	$10^4 b$ (mole l.$^{-1}$)	$10^4 s''$, obs. (sec.$^{-1}$)	$10^4 s''$, calc. (sec.$^{-1}$)	Slope, $s''/(c - b)$ (l. mole^{-1} sec.$^{-1}$)
$-50 \cdot 0°$	2·39	1·42	20·8 ± 0·4	20·8	
	3·34	1·42	29·3 ± 0·9	29·7	
	4·71	2·51	45·6 ± 1·4	41·6	$(9 \cdot 38 \pm 0 \cdot 18) \times 10^{-1}$
	5·19	1·42	46·4 ± 1·3	47·2	
	8·39	4·44	76·0 ± 1·5	74·6	
$-60 \cdot 0$	0·745	0·786	3·00 ± 0·07	2·99	
	3·56	1·58	14·3 ± 0·6	12·7	
	5·37	1·19	17·8 ± 1·2	19·4	
	6·66	1·70	24·3 ± 0·7	24·1	$(3 \cdot 57 \pm 0 \cdot 08) \times 10^{-1}$
	9·76	0·735	36·0 ± 0·4	35·8	
	11·0	1·40	41·1 ± 1·0	41·1	
	17·8	0·498	66·3 ± 1·3	65·9	
$-70 \cdot 0$	3·03	2·53	4·16 ± 0·08	3·30	
	8·27	2·16	9·83 ± 0·21	9·55	
	11·9	1·63	14·3 ± 0·3	14·1	$(1 \cdot 19 \pm 0 \cdot 02) \times 10^{-1}$
	24·4	0·945	28·6 ± 0·5	28·9	
	27·1	2·65	31·8 ± 0·7	31·8	
$-80 \cdot 0$	2·44	2·27	1·03 ± 0·04	0·93	
	5·35	1·80	2·26 ± 0·12	1·96	
	11·6	2·40	4·58 ± 0·22	4·35	
	23·8	2·40	8·83 ± 0·27	8·62	
	26·9	3·51	9·73 ± 0·37	9·69	$(3 \cdot 66 \pm 0 \cdot 10) \times 10^{-2}$
	31·4	2·21	11·3 ± 0·5	11·4	
	37·6	3·24	13·2 ± 0·5	13·5	
	48·7	3·24	17·6 ± 0·5	17·6	
$-90 \cdot 0$	3·82	3·50	0·428 ± 0·020	0·32	
	8·16	1·72	0·808 ± 0·037	0·76	
	14·7	2·74	1·38 ± 0·11	1·37	$(9 \cdot 64 \pm 0 \cdot 30) \times 10^{-3}$
	24·7	2·74	2·32 ± 0·13	2·33	
	31·5	1·82	3·17 ± 0·15	3·02	
$-99 \cdot 9$	4·69	1·55	* 0·111 ± 0·009	0·098	
	7·33	1·00	0·156 ± 0·006	0·156	$(2 \cdot 16 \pm 0 \cdot 05) \times 10^{-3}$
	8·95	1·23	0·188 ± 0·007	0·191	
	9·64	1·18	0·210 ± 0·005	0·206	

* By method of initial rates.

concentration = monochloroacetate concentration during the run; $(c - b)$ = acid concentration during run; $r = (c - b)/b$ = buffer ratio. These runs show that the kinetic effect of hydrogen ion is negligible. Equation (1) thus becomes:

$$2 \cdot 303 s'' = k_2(\text{HA}) = k_2(c - b) \qquad \qquad \qquad (2)$$

From this equation values of k_2 have been derived.

Rate Constants.—The values of s'' for the runs at various temperatures and concentrations are given in Tables 2 and 3. Plots of these values of s'' against the acid concentration $(c - b)$ give good straight lines passing through the origin; the slopes of these lines are given, with the estimated limits of error, in the last columns of Tables 2 and 3. The derived values of k_2 are given in col. 3 of Table 4. (The values of s'' calculated from these are given for comparison in the penultimate columns of Tables 2 and 3.)

TABLE 3. *Monochloroacetic acid.*

Temp.	$10^3 c$ (mole l.$^{-1}$)	$10^4 b$	$10^4 s''$, obs. (sec.$^{-1}$)	$10^4 s''$, calc. (sec.$^{-1}$)	Slope, $s''/(c - b)$ (l. mole^{-1} sec.$^{-1}$)
$-70 \cdot 0°$	2·00	1·09	26·8 ± 0·5	27·7	
	3·26	1·73	48·5 ± 1·4	46·0	
	4·21	1·73	59·0 ± 1·2	60·0	(1·49 ± 0·04)
	6·32	1·48	92·6 ± 2·1	92·4	
	6·81	1·73	101 ± 2	99·2	
$-80 \cdot 0$	2·54	1·12	12·4 ± 0·3	11·7	
	4·77	1·17	22·2 ± 0·7	22·2	
	5·79	1·10	27·0 ± 0·5	27·2	(4·82 ± 0·07) × 10^{-1}
	7·36	1·17	34·4 ± 0·7	34·7	
	10·2	1·17	48·6 ± 0·8	48·5	
$-99 \cdot 3$	6·78	1·07	3·06 ± 0·11	2·91	
	8·29	1·26	3·46 ± 0·19	3·54	
	13·2	1·53	5·80 ± 0·10	5·69	(4·30 ± 0·10) × 10^{-2}
	18·3	1·50	7·90 ± 0·16	7·89	
	20·2	1·42	8·60 ± 0·17	8·67	
$-114 \cdot 2$	10·8	1·74	0·383 ± 0·025	0·438	
	11·3	1·53	0·488 ± 0·019	0·459	
	16·7	0·73	0·700 ± 0·029	0·674	(4·25 ± 0·13) × 10^{-3}
	20·0	0·61	0·828 ± 0·035	0·848	

The rate constants at $-80°$ are in reasonable agreement with those reported earlier [2] for $-78 \cdot 5°$. It is also satisfactory that the results in Table 1, which were obtained by using a platinum resistance thermometer and a different apparatus from that used for the rest of the

TABLE 4.

(1) Acid	(2) Temp.	(3) k_2, obs. (l. mole^{-1} sec.$^{-1}$)	(4) $\log_{10} k_2$, obs.	(5) $\Delta \log_{10} k_2$	(6) $\Delta \log_{10} (k_2/T)$
CH$_3$·CO$_2$H	+20·0°	$10^2 \times (3\cdot60 \pm 0\cdot3)$	+2·556 ± 0·035	+0·028	±0·000
	−50·0	2·16 ± 0·04	+0·335 ± 0·008	−0·006	−0·009
	−60·0	$10^{-1} \times (8\cdot22 \pm 0\cdot17)$	−0·085 ± 0·009	+0·004	+0·003
	−70·0	$10^{-1} \times (2\cdot73 \pm 0\cdot04)$	−0·564 ± 0·006	−0·003	−0·002
	−80·0	$10^{-2} \times (8\cdot44 \pm 0\cdot24)$	−1·074 ± 0·012	+0·008	+0·010
	−90·0	$10^{-2} \times (2\cdot22 \pm 0\cdot07)$	−1·654 ± 0·015	+0·006	+0·007
	−99·9	$10^{-3} \times (4\cdot98 \pm 0\cdot10)$	−2·303 ± 0·009	−0·005	−0·008
CH$_2$Cl·CO$_2$H ...	+20·0	$10^3 \times (2\cdot23 \pm 0\cdot07)$	+3·348 ± 0·014	+0·003	−0·005
	−70·0	3·44 ± 0·09	+0·537 ± 0·012	+0·003	+0·013
	−80·0	1·11 ± 0·02	+0·045 ± 0·013	−0·014	−0·006
	−99·3	$10^{-2} \times (9\cdot90 \pm 0\cdot23)$	−1·004 ± 0·011	+0·005	+0·005
	−114·2	$10^{-3} \times (9\cdot79 \pm 0\cdot3)$	−2·009 ± 0·014	+0·003	−0·007

work, give a value of k_2 (0·32$_2$ l. mole^{-1} sec.$^{-1}$, with standard deviation ±0·007) which agrees within experimental error with the value interpolated from the data given in Table 4 (0·332 ± 0·007 l. mole^{-1} sec.$^{-1}$). A further set of four runs at $-90 \cdot 03°$ at concentrations similar to those in Table 3, in the new apparatus, gave $k_2 = 0\cdot31_8 \pm 0\cdot007$ l. mole^{-1} sec.$^{-1}$; we are indebted to Mr. Harbron for these runs also.

Arrhenius Plots.—These are nearly linear over the whole range. They are not shown, because the experimental uncertainties are too small to appear in a figure, the temperature-range being so large. The best straight lines through the points, calculated by least squares, and the corresponding values of the Arrhenius parameters A and E, are:

$$\text{Acetic acid:} \qquad \log_{10} k_2 = 9 \cdot 498 - 2043 \cdot 4/T \qquad \ldots \ldots \quad (3)$$

whence $E = 9 \cdot 35 \pm 0 \cdot 08$ kcal./mole, $\log_{10} A = 9 \cdot 50 \pm 0 \cdot 07$ (A in l. mole^{-1} sec.$^{-1}$).

$$\text{Monochloroacetic acid:} \qquad \log_{10} k_2 = 9 \cdot 692 - 1861 \cdot 1/T \qquad \ldots \ldots \quad (4)$$

whence $E = 8 \cdot 52 \pm 0 \cdot 13$ kcal./mole, and $\log_{10} A = 9 \cdot 69 \pm 0 \cdot 15$ (A in l. mole^{-1} sec.$^{-1}$).

The accuracy with which these values of E and A fit the observed values of k_2 is shown by the values of $\Delta \log_{10} k_2$, *i.e.*, [$\log_{10} k_2$ (obs.) $- \log_{10} k_2$ (calc.)], which are given in col. 5 of Table 4. The values of E and A agree within experimental error with those of Caldin and Long,[2] but are more precise.

Eyring Equation.—The temperature-variation of k_2 may also be represented by Eyring's equation, $k_2 = (\boldsymbol{k}T/\boldsymbol{h}) \exp (\Delta S^*/\boldsymbol{R}) \exp (-\Delta H^*/\boldsymbol{R}T)$, according to which we should expect linear plots of $\log_{10} (k_2/T)$ against $1/T$. The best straight lines representing these plots for the present reactions, calculated by least squares, are:

$$\text{Acetic acid:} \qquad \log_{10} (k_2/T) = 6 \cdot 7732 - 1 \cdot 9595 \times 10^3/T \qquad \ldots \ldots \quad (5)$$

$$\text{Monochloroacetic acid:} \quad \log_{10} (k_2/T) = 6 \cdot 9176 - 1 \cdot 7683 \times 10^3/T \qquad \ldots \ldots \quad (6)$$

The accuracy with which these equations fit the data can be judged from col. 6 of Table 4, where values are shown of $\Delta \log_{10} (k_2/T)$, *i.e.* [$\log_{10} (k_2/T)$ (obs.) $- \log_{10} (k_2 T)$ (calc.)].

DISCUSSION

The Arrhenius plots for the two acids show no systematic trends and no significant deviations from linearity. This may be seen by comparing the estimated limits of error given in col. 4 of Table 4 with the deviations in col. 5. The Eyring equation has also been tested, since it is arguable that results covering so long a temperature-range should be analysed in terms of this equation rather than Arrhenius's. The values of ΔH^* and ΔS^* have been assumed to be constant. The deviations, shown in col. 6 of Table 4, again show no systematic trends and no significant deviations from linearity. So far as the accuracy of the experiments allows one to judge, the two equations represent the results about equally well.

It is unfortunate that below $-100°$ the reaction with acetic acid is too slow to be measured accurately with the present apparatus. Some attempts to measure initial rates gave, as the mean of two values of $\log_{10} k_2$ at each temperature, $-2 \cdot 5_4 \pm 0 \cdot 1$ (l. mole^{-1} sec.$^{-1}$) at $-104 \cdot 8°$, and $-2 \cdot 7_5 \pm 0 \cdot 2$ (l. mole^{-1} sec.$^{-1}$) at $-109 \cdot 7°$. For these points the respective deviations $\Delta \log_{10} (k_2/T)$ are $+0 \cdot 10$ and $+0 \cdot 25$, which are comparatively large, and in the right direction for tunnelling, but not significantly larger than the experimental uncertainties. We hope to obtain more accurate values with the aid of the apparatus described in the following paper.

We conclude that there is no satisfactory evidence that quantum-mechanical tunnelling is kinetically significant in the reaction with either acid. The reasons that may be suggested for this result are similar to those suggested for the analogous results for the reaction between T.N.T. and ethoxide ion.[2]

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