679. *A Non-linear Arrhenius Plot for the Proton-transfer Reaction between Acetic Acid and the Anion of 2,4,6-Trinitrotoluene in Ethanol at Low Temperatures.*

By E. F. CALDIN and E. HARBRON.

The rate of the proton-transfer reaction between acetic acid and the coloured anion of 2,4,6-trinitrotoluene has been measured at a series of temperatures down to −114·5°. The rates at −110° and −114·5° are considerably faster than would be expected from the results at temperatures from +20° to −90°, which give a linear Arrhenius plot. The deviations are in the direction to be expected if quantum-mechanical tunnelling of the proton is occurring. Alternative explanations are considered and found unsatisfactory. The results can be fitted fairly well to Bell's equations for a parabolic energy barrier.

IT was reported in a recent paper[1] that the Arrhenius plot for the proton-transfer reaction between undissociated acetic acid and the anion of 2,4,6-trinitrotoluene [$C_6H_2(NO_2)_3{\cdot}CH_2^- + HA \longrightarrow C_6H_2(NO_2)_3{\cdot}CH_3 + A^-$] is linear within experimental error from +20° to −100°. The solvent was ethanol containing 1% of toluene by volume. We have now been able to extend the temperature range downwards, with the aid of an improved cryostat,[2] and have made new measurements with greater accuracy at −50°, −60°, −70°, −90°, −100°, −110°, and −114·5°. Between −90° and +20°, the Arrhenius plot is a straight line within the experimental error; at the lowest temperatures,

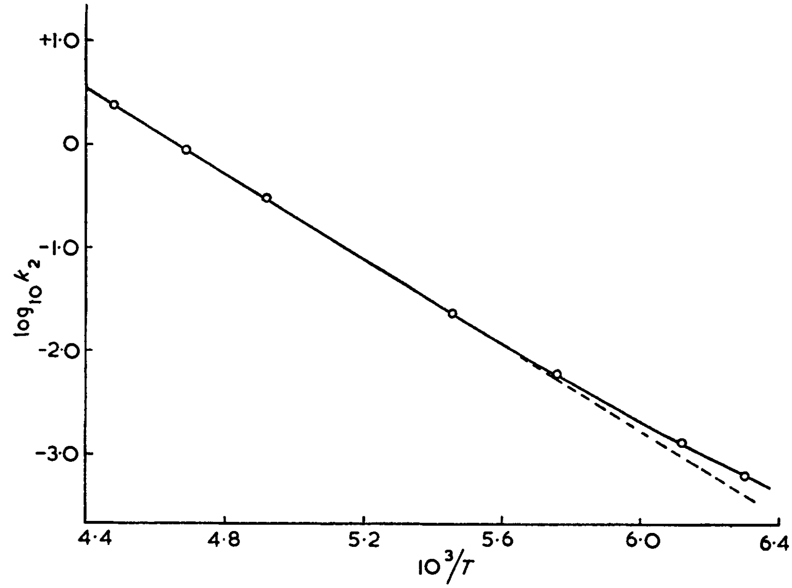

FIG. 1. Arrhenius plot for acetic acid: log k_2 against $1/T$. The standard deviations are too small to show on this scale. The straight line is the best line through the points from −50° to −90°. The point for +20° lies well on the straight line but is omitted so as to permit a scale large enough to show the divergence at low temperatures.

---

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

[2] Caldin and Jackson, *J.*, 1960, 2411.

however, we have found considerable deviations from this line. The observed rate constant at −114·5° is 45% faster than that calculated; this is nearly 40 times the standard deviation of ±1·2%. The Arrhenius plot is shown in Fig. 1, and the deviations from linearity may be seen in Fig. 2 and compared with the standard deviations there shown. The numerical data are given in Table 3.

The rate of the corresponding reaction with monochloroacetic acid has also been re-measured at several temperatures (−70°, −90°, −105°, and −114·5°), and the Arrhenius plot found to be linear over the whole range, except that at the lowest temperature there is a positive deviation of 13%, compared with a standard deviation of ±2·5%. These results are given in Table 7.

Interpretation.—We attribute the deviations from the linear Arrhenius relation to quantum-mechanical tunnelling. This explanation has been adopted[3] for the similar Arrhenius plot found for the fluoride-catalysed bromination of ethyl 2-oxocyclopentane-carboxylate in aqueous solution, and has been confirmed for this reaction by the deuterium isotope effect.[4,5] Before we consider this interpretation quantitatively, however, there are several other hypotheses to be considered.

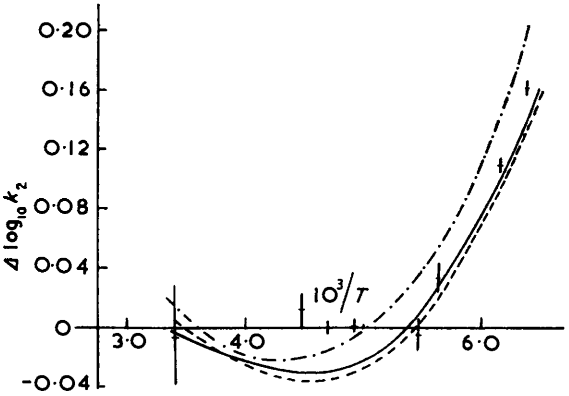

FIG. 2. Deviations from linear Arrhenius plot, for acetic acid. Short vertical lines: [log k_2 (obs.) − log k_2 (Arrh)]. Curves: calculated values of [log k_2(qmt) − log k_2 (Arrh)] for various values of barrier height (E_{qmt}) and width ($2a$), according to Bell's equations for a parabolic barrier.

Full curve E_{qmt} = 10·05 kcal. mole^{-1}; a = 0·84 Å.
— — — — E_{qmt} = 10·10 kcal. mole^{-1}; a = 0·83 Å.
—·—·— E_{qmt} = 10·10 kcal. mole^{-1}; a = 0·81 Å.

(*a*) *A change in the reaction mechanism at the lowest temperatures.* The rate–concentration relations are the same at all temperatures, and the rate-determining step throughout the temperature range is a reaction between the coloured species and the undissociated acid HA. The possibility that some different coloured species might be present at the lowest temperature has been examined by determining absorption spectra at −70°, −85°, and −115° (by Dr. R. Foster and Mr. R. K. Mackie, see Experimental section); there was no evidence for a new species at −115°. The hypothesis that a different product might be formed in the reaction at the lowest temperatures has likewise been rendered very unlikely by some experiments which indicate that the original trinitrotoluene is quantitatively regenerated at the end of the reaction (see Experimental section).

---

[3] Hulett, *Proc. Roy. Soc.*, 1959, *A*, **251**, 274.
[4] Bell, Fendley, and Hulett, *Proc. Roy. Soc.*, 1956, *A*, **235**, 453.
[5] Bell, " The Proton in Chemistry," London, Methuen, 1959, Chap. 11.

(*b*) *Variation of the enthalpy of activation with temperature.* Curved Arrhenius plots have been observed for many reactions [6] and analysed in terms of the equation:

$$\log k = -A/T + B \log T + C.$$

This implies a linear dependence of ΔH^* on temperature, with $\Delta C_p^* = B\boldsymbol{R}$. The main factor determining ΔC_p^* for our reactions will be the change in solvation on formation of the transition state. The entropy of activation is negative ($\Delta S^* = -16{\cdot}5$ cal. deg.$^{-1}$ mole^{-1} for the reaction with acetic acid); this indicates that solvent molecules are partly " frozen " when the transition state is formed, so that ΔC_p^* should be negative. This would give rise to a curvature of the Arrhenius plot in the opposite direction to that observed. Moreover, the results give a nearly linear Arrhenius plot down to about −90°, and a relatively sharp bend in the curve at lower temperatures, so that they cannot be fitted to an equation such as the above with a constant ΔC_p^*. The following equation,

$$\log k = -2159{\cdot}9/T - 1{\cdot}072 \log T + 12{\cdot}5686,$$

gives values of the rate constant agreeing within 2% with those observed down to −90°, but the discrepancies at −100°, −110°, and −114·5° are 14%, 39%, and 59%, respectively. We conclude that the variation of ΔH^* due to the changes of solvation does not account for our results.

(*c*) *A change in the structure of the solvent.* At low temperatures this might affect the Arrhenius plot. In water, for instance, decrease of temperature results in a more ordered structure, and so might lead to a less negative value of ΔS^* and a larger A factor for reactions in which the formation of the transition state involves the orientation of solvent molecules. Such effects have been invoked to account for the negative deviations from the linear Arrhenius plot below 0° for the solvent-catalysed bromination of ethyl 2-oxocyclopentanecarboxylate in aqueous 5·2M-sodium bromide.[3] Only negative deviations could be accounted for in this way, however. Moreover, the great differences observed between the deviations with acetic acid and those with monochloroacetic acid could not be explained, since the effect should be a function of solvent and temperature only.

Quantum-mechanical Tunnelling.—The reaction of the trinitrobenzyl anion with acetic acid gives an Arrhenius plot of the form to be expected if quantum-mechanical tunnelling occurs.[7-9] We have therefore applied Bell's equations, which refer to tunnelling through a parabolic barrier,[10] to our results. These equations contain the height (E_{qmt}) and width ($2a$) of the energy barrier. Since neither of these is independently known, the values have been adjusted by trial and error to give the best fit between the calculated curve and the observed points on the Arrhenius plot. Values of a were chosen to fit the curvature at the lower temperatures (which is very sensitive to a), and those of E_{qmt} were then adjusted to give the correct shape at the higher temperatures. The results are shown in Table 4, where the observed and calculated values of the rate constant k_2 are compared, and in Fig. 2, where the calculated deviations from the linear Arrhenius plot are shown, along with the observed deviations, for various values of a and E_{qmt}. The calculated values of k_2, with $E_{\text{qmt}} = 10{\cdot}10$ kcal. mole^{-1} and $a = 0{\cdot}83$ Å, reproduce the observed values within about 10% over the whole range of temperature. As it appears that Bell's model may overestimate the effects of tunnelling at low temperatures,[8] this agreement is probably as

---

[6] Laughton and Robertson, *Canad. J. Chem.*, 1955, **33**, 1207; Hyne and Robertson, *ibid.*, p. 1544; Robertson, *ibid.*, 1957, **351**, 613; Robertson, Heppolette, and Scott, *ibid.*, 1959, **37**, 803; La Mer and Miller, *J. Amer. Chem. Soc.*, 1935, **57**, 2674; Moelwyn-Hughes, *Z. phys. Chem.*, 1934, **26**, 281; *Proc. Roy. Soc.*, 1940, *A*, **175**, 118; " Kinetics of Reactions in Solution," Cambridge, 1947, p. 67; McKinly-McKee and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247; Gold, *ibid.*, 1948, **44**, 506; Bensley and Kohnstam, *J.*, 1956, 287.

[7] Bell, " Acid-base Catalysis," Oxford, 1941, Chap. 8.

[8] Johnston and Rapp, *J. Amer. Chem. Soc.*, 1961, **83**, 1.

[9] Johnston, " Advances in Chemical Physics," 1961, Vol. III, p. 131.

[10] Bell, *Trans. Faraday Soc.*, 1959, **55**, 1.

good as can be expected over so long a temperature range as from +20° to −115°. The value of E_{qmt} can be specified within about ±0·05 kcal. mole^{-1}, and that of a within about ±0·01 Å. The ratio of the observed Arrhenius activation energy E_A at the higher temperatures (9·38 ± 0·03 kcal. mole^{-1}) to the barrier height E_{qmt} is 0·93. This is considerably larger than that found[4] for the fluoride-catalysed bromination of ethyl 2-oxocyclopentanecarboxylate (0·81), as would be expected from the much lower temperature at which the effects of tunnelling become observable.

The results with monochloroacetic acid cannot be analysed in the same way, since they show only a much smaller deviation at the lowest temperature. We might expect that the barrier-width would be very similar to that for acetic acid, so that the smaller deviations would be attributable to a lower barrier-height, corresponding to the smaller value of the Arrhenius activation energy ($E_A = 8{\cdot}23 \pm 0{\cdot}01$ kcal. mole^{-1}). This appears to be the case; if we assume $a = 0{\cdot}83$ Å and $E_A/E_{qmt} = 0{\cdot}93$, as for acetic acid, we find fairly good agreement between the observed and the calculated values over the whole temperature range (Table 7).

We conclude that the observed Arrhenius plots are fairly well accounted for by the hypothesis of quantum-mechanical tunnelling. The agreement might well be improved if more accurate computations such as those of Johnston and Rapp[8] were made. The alternative hypotheses, on the other hand, must be rejected. The values calculated for E_{qmt} and a are collected in Table 1.

The Dimensions of the Energy Barrier.—(*a*) *Height.* In the above calculations it has been assumed that the observed energy of activation depends only on the energy required to move the proton; other contributions[11] have been neglected. It is probably justifiable to disregard the contributions of repulsion[12] and of electrostatic interactions; but the energy associated with changes of solvation may be considerable, and such changes do occur in this reaction, as is shown by the considerable entropy of activation. It is therefore possible that the value given for the height of the energy barrier E_{qmt} is too high.

TABLE 1.

Values of E (kcal. mole^{-1}) and a (Å).

Acid	E_A	E_{qmt}	E_A/E_{qmt}	a
Acetic	9·38 ± 0·03	10·10	0·93	0·83
Monochloroacetic	8·23 ± 0·01	8·86	0·93	0·83

(*b*) *Width.* The calculations have assumed that the energy barrier is parabolic, with a width $2a$ at the base. As the barrier is no doubt bell-shaped, rather than parabolic, the width is probably[4] nearer $3a$; this would make it about 2·5 Å. However, calculations by Johnston and Rapp[8] suggest that Bell's calculations overestimate the effects of tunnelling at low temperatures for a given value of a, so the derived value of a will be too large. If too high a value has been assumed for E_{qmt}, the result will again be that the calculated value of a is too large. Thus the true barrier width is somewhere below 2·5 Å. This is all that can be concluded from the kinetic results. Another estimate can be made as follows. The distance d travelled by the proton during the transfer from oxygen to carbon is given by $d = r_{C-O} - 2(r_H + r_C + r_O)$, where r_H, r_C, and r_O are the normal covalent radii of the atoms H, C, and O, and r_{C-O} is the distance apart of the oxygen and carbon atoms when interaction becomes appreciable. This distance r_{C-O} may be taken as the sum of the van der Waals radii of carbon and oxygen, 3·5 Å; the other distances may be taken as $r_H = 0{\cdot}35$ Å, $r_C = 0{\cdot}77$ Å, and $r_O = 0{\cdot}74$ Å. We then obtain, for the true barrier-width d, 1·3 Å. This is lower than the original estimate of 2·5 Å, as would be expected.

Our *general conclusion* is that the deviations from the linear Arrhenius plot are due to quantum-mechanical tunnelling and can to a first approximation be fitted to Bell's equations for a parabolic barrier.

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

[12] Bell, *Trans. Faraday Soc.*, 1944, **37**, 493.

EXPERIMENTAL

Materials.—2,4,6-Trinitrotoluene, carboxylic acids, toluene, and ethanol were purified as in previous work. Stock solutions of trinitrotoluene in ethanol–toluene were not kept longer than one week, since they gradually became coloured, and then gave smaller rate constants (see below).

Apparatus.—The low-temperature thermostat has already been described.[2] Two different photometers were used, each incorporating a photomultiplier (R.C.A. 931A) as detector. One embodied a circuit, modified from that of Ashmore, Levitt, and Thrush,[13] which produced a response proportional to the optical density. The other, used in most of the work, had a response proportional to the light intensity, and was based on an unpublished circuit due to Dr. F. W. Trowse, to whom we are much indebted. The two photometers gave results which agreed well (see Tables 2 and 6). They were of comparable accuracy, the uncertainty being about ±1% in the optical density; the second photometer was the more stable and reliable of the two. An Ilford 623 filter was used, as in previous work.

Temperature was measured by means of a platinum resistance thermometer placed in the thermostat bath.[2] The temperature of the bath is known to about ±0·03°. The temperature in the reaction cell is slightly higher than that in the bath, by an amount which depends on the liquid in the cell, presumably because the viscosity determines the rate of circulation by the stirrer. The temperature differences were determined, under reaction conditions, by means of a thermocouple; the correction is 0·48° (reproducible to about 0·02°) at −115°, dropping to 0·33° at −110°, 0·22° at −100°, 0·18 at −90°, and 0·06° at −50°. All temperatures quoted are corrected. At the higher temperatures they are accurate to about ±0·03°, while at −115° the uncertainty is about 0·05°. Corrections for the change of density with temperature have been applied to all concentrations; the correction amounts to 15% at −115°.[14]

Experimental Procedures.—These have been described in earlier papers.[15–17] The solvent is ethanol containing 1% by volume of toluene, as in earlier work. A few experiments in which the ethanol was outgassed by evacuation at room temperature had shown no detectable change in the rate. The concentration of trinitrotoluene was always less than 1% of the concentration of acid, and so first-order plots were obtained. For fast runs, the end-point was observed and $\log_{10} D$ plotted against time (D = optical density); otherwise the method of Guggenheim was used.

Experimental Errors.—The maximum uncertainty in the concentration of acid is about ±2%. Most of the runs gave first-order plots in which over 90% of the points lay on the straight line within experimental error; the limits of error estimated by drawing lines of maximum and minimum slope were usually about ±3%, and the standard deviation of each mean value of the rate constant k_2 is less than this. The uncertainty in the temperature at −115° (0·05°) corresponds to about 1% in k_2; it is smaller at higher temperatures.

Determination of Rate Constants.—The general equation for the slope s'' of the first-order plot, when the acid HA is in large excess, is:

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

If we denote the formal initial ethoxide concentration by b, and the formal initial concentration of added acid by c, and write $(\mathrm{H}^+) = K_a(\mathrm{HA})/(\mathrm{A}^-)$, where K_a is the dissociation constant of HA, we obtain:

$$2{\cdot}303s'' = k^0_{-1} + k_2(c - b) + k_3K_a(c - b)/b. \qquad (2)$$

Previous work [15] has shown that the term k^0_{-1}, due to reaction with the solvent, is negligible; stability tests on solutions of the anion over periods comparable with the reaction time have confirmed this. The term $k_3K_a(c - b)/b$, due to reaction with hydrogen ion, can also be written k_3K_ar, when r is the buffer ratio. This term will be negligible if it can be shown either (i) that variation of b (and so r) at constant $(c - b)$ has no effect on the observed value of $s''/(c - b)$, or

---

[13] Ashmore, Levitt, and Thrush, *Trans. Faraday Soc.*, 1956, **52**, 830.
[14] Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312.
[15] Caldin and Long, *Proc. Roy. Soc.*, 1955, *A*, **228**, 263.
[16] Ainscough and Caldin, *J.*, 1956, 2528.
[17] Caldin and Jackson, *J.*, 1960, 2413.

(ii) that, when $(c - b)$ is varied at constant r, the plot of s'' against $(c - b)$ passes through the origin. The results show that for each acid the term is negligible (see below).

Equation (2) thus reduces to:

$$2{\cdot}303s'' = k_2(c - b). \qquad (3)$$

The plots of s'' against $(c - b)$ could all be reasonably represented by straight lines through the origin. The slopes of these lines, giving k_2, have been determined by the method of least squares. The standard deviations are ± 2—3%. With acetic acid at some of the higher temperatures—but not at $-110°$ or at $-114{\cdot}5°$—it would be possible to represent the plots by straight lines with positive intercepts, and the rate constants would then be a few per cent lower. We have not adopted this procedure, because of the preceding considerations in favour of a negligible intercept. Our general conclusions would in any case be unchanged.

RESULTS

The Absorption Spectrum of the Coloured Species at Low Temperatures.—To test the possibility that at the lowest temperature the coloured solution contains some new species, the absorption spectrum of the solution in the range 340—580 mμ was examined at $-70°$, $-85°$, and $-115°$ ($\pm 3°$), with the help of an Optica CF4R double-beam recording spectrophotometer and a vacuum-jacketed cell. All three absorption curves were very similar, with maxima at about 350, 430, and 490—500 mμ. The curves at $-85°$ and $-115°$ were almost identical. We are much indebted to Dr. R. Foster and Mr. R. K. Mackie, of Queen's College, University of St. Andrews, Dundee, who made these measurements for us.

Results with Acetic Acid.—*Product of the reaction.* To show quantitatively that the trinitrobenzyl anion is entirely converted into trinitrotoluene, the following experiments were performed.

(*a*) Optical density. A known volume (v_A ml.) of a solution of trinitrotoluene in ethanol–toluene was treated with a known volume of ethanolic ethoxide solution (about 0·01M) and diluted to a known volume (V_A ml.) with ethanol; the optical density (D_A) of the resulting purple solution, relative to the pure solvent, was then measured at 495 and at 500 mμ by means of a Unicam spectrophotometer. A similar solution was then made up, from v_x ml. of the trinitrotoluene solution; acetic acid was added to decolorise this solution, then sufficient ethoxide to regenerate the colour; the total volume (V_x ml.) and the optical density D_x of the resulting solution were measured. The reaction producing the coloured anion is about 95% complete in each solution.[15] If all the trinitrotoluene is regenerated by the addition of acetic acid, the final optical density will be given by $D_x = D_A(V_A/V_x)\ (v_x/v_A)$. At 20° this relation was found to be obeyed within 1—3%. When the decolorisation by acetic acid was carried out at $-115°$, the agreement was within 3%. The experimental uncertainty in each optical density is about $\pm 1{\cdot}5\%$. Thus within the experimental error the results are in accordance with the quantitative production of trinitrotoluene, both at 20° and at $-115°$.

(*b*) Infrared spectrum. Several attempts were made to obtain the infrared spectrum of the final product of the reaction, after evaporation of the solvent and redissolution of the residue in chloroform. The spectrum was in general similar to that of pure trinitrotoluene in chloroform as regards the number, positions, and relative intensities of the main peaks, apart from some minor changes of shape, but showed some subsidiary peaks attributable to a C=O stretching frequency, presumably due to residual acetic acid. These subsidiary peaks were greatly reduced by pumping off the solvent under a vacuum, though they were not entirely removed even after 8 hours' pumping. At the least, however, the results show that no species other than trinitrotoluene is produced in any quantity, and confirm the optical-density experiments quoted above.

Rate constants. The results of the individual kinetic runs are given in Table 2.

The contribution of hydrogen ions to the reaction at $-110°$ is shown to be negligible by the fact that a 20-fold variation of b (and hence of buffer ratio r) at constant acid concentration $(c - b)$ has no effect on $s''/(c - b)$ (cf. equation 2 above).

Values of the second-order constant k_2 (l. mole^{-1} sec.$^{-1}$) can therefore be calculated for each run by equation 3. Mean values, with standard deviations, are shown in the second column of Table 3. The value for 20° is that given by Caldin and Long.[15] Values of s'' for each run

TABLE 2.

Results for the kinetic runs with acetic acid.

d = Concn. of trinitrotoluene; b = formal initial concn. of ethoxide; c = formal initial concn. of acid; $(c - b)$ = actual concn. of acid; $r = (c - b)/b$ = buffer ratio; s'' (obs.) = observed slope of first-order plot in sec.$^{-1}$ (decadic logarithms); s'' (calc.) = slope calculated from mean k_2 (Table 3). Concns. are in mole l.$^{-1}$; temp. in °c.

Temp.	10^3c	10^4b	10^5d	$10^3(c - b)$	r	$10^4s''$ (obs.)	$10^4s''$ (calc.)	$s''/(c - b)$
$-49{\cdot}9_4$°	3·30	3·29	1·05	2·97	9·03	29·9 ± 1·0	31·2	1·05 ± 0·03
	3·96	3·16	1·05	3·64	11·52	40·7 ± 1·5	38·2	
	4·95	3·16	1·05	4·63	14·65	45·9 ± 0·9	48·6	
	6·06	3·16	1·05	5·74	18·13	64·7 ± 3·0	60·3	
	8·40	3·16	1·05	8·08	25·57	81·7 ± 1·0	84·8	
$-59{\cdot}9_0$	3·33	3·33	1·06	3·00	9·01	14·0 ± 0·6	11·5	(3·82 ± 0·09) $\times 10^{-1}$
	4·55	6·66	1·06	3·88	5·83	16·7 ± 0·8	14·8	
	7·42	6·66	1·06	6·75	10·14	25·5 ± 0·7	25·8	
	10·08	2·90	1·06	9·79	33·76	37·0 ± 1·1	37·4	
	17·62	2·90	1·06	17·33	59·75	69·1 ± 5·0	66·2	
$-69{\cdot}8_6$	5·96	2·56	1·07	5·70	22·3	7·76 ± 0·31	7·30	(1·28 ± 0·02) $\times 10^{-1}$
	10·56	2·56	1·07	10·30	40·2	13·2 ± 0·4	13·2	
	14·28	2·56	1·07	14·02	54·8	17·4 ± 0·8	17·9	
	18·04	7·13	1·07	17·33	24·3	21·7 ± 1·0	22·2	
	27·75	7·13	1·07	27·04	37·9	33·7 ± 0·6	34·6	
$-89{\cdot}8_8$	14·6	11·13	1·09	13·4	12·0	14·2 ± 1·1	13·6	(1·01 ± 0·02) $\times 10^{-2}$
	23·9	4·16	1·09	23·5	56·5	23·3 ± 0·9	23·7	
	27·2	4·01	1·09	26·8	66·8	27·1 ± 0·6	27·1	
	48·2	10·23	1·09	47·2	46·1	46·6 ± 0·8	47·7	
	10^2c	10^4b	10^5d	$10^2(c - b)$	r	$10^5s''$ (obs.)	$10^5s''$ (calc.)	$s''/(c - b)$
$-99{\cdot}6_6$	2·39	4·20	1·10	2·35	56·0	6·68 ± 0·29	6·09	(2·59 ± 0·06) $\times 10^{-3}$
	3·46	8·12	1·10	3·68	45·3	9·60 ± 0·44	9·53	
	4·83	8·14	1·10	4·75	58·4	12·3 ± 0·4	12·3	
	4·96	4·20	1·10	4·92	117	13·1 ± 0·5	12·7	
	7·26	4·39	1·10	7·22	164	18·1 ± 1·0	18·7	
	8·25	6·53	1·10	8·18	125	18·8 ± 0·5	21·2	
$-109{\cdot}7_2$	5·56	32·2	1·12	5·24	16·3	2·97 ± 0·10 *	3·02	(5·77 ± 0·10) $\times 10^{-4}$
	5·57	6·12	1·12	5·51	90·0	3·00 ± 0·11 *	3·18	
	5·73	2·04	1·12	5·71	280	3·07 ± 0·15 *	3·29	
	5·74	1·57	1·12	5·72	364	3·60 ± 0·11 *	3·30	
	5·82	3·59	1·12	5·78	161	3·21 ± 0·17 *	3·34	
	5·90	1·51	1·12	5·88	389	3·42 ± 0·10 *	3·39	
	6·18	3·59	1·12	6·14	171	3·46 ± 0·20 *	3·54	
	10·31	3·24	1·12	10·28	317	6·55 ± 0·20 *	5·93	
	10·59	6·04	1·12	10·53	174	6·79 ± 0·11 *	6·08	
	11·41	4·24	1·12	11·37	268	6·33 ± 0·30	6·56	
	13·62	4·74	1·12	13·57	286	7·84 ± 0·21	7·83	
	15·77	2·76	1·12	15·74	570	8·57 ± 0·10 *	9·08	
	18·57	1·46	1·12	18·56	1271	10·33 ± 0·40 *	10·71	
$-114{\cdot}4_9$	10·36	4·57	1·12	10·31	226	2·78 ± 0·11	2·81	(2·73 ± 0·03) $\times 10^{-4}$
	11·60	4·16	1·12	11·56	278	3·16 ± 0·10	3·16	
	12·55	4·16	1·12	13·51	325	3·33 ± 0·10	3·42	
	15·12	6·73	1·12	15·05	224	4·10 ± 0·18	4·11	
	17·64	6·73	1·12	17·57	261	4·98 ± 0·18	4·80	

* Results obtained by using logarithmic photometer.

TABLE 3.

Rate constants for the reaction between acetic acid and the trinitrobenzyl anion.

Temp. in °c; k_2 in l. mole^{-1} sec.$^{-1}$.

Temp.	k_2 (obs.)	log k_2 (obs.)	log k_2 (Arrh)	[log k_2 (obs.) − log k_2 (Arrh)]
$+20{\cdot}0$°	10^2(3·60 ± 0·30)	+2·556 ± 0·035	+2·562	−0·006
$-49{\cdot}9_4$	2·42 ± 0·09	+0·384 ± 0·012	+0·372	+0·012
$-59{\cdot}9_0$	10^{-1}(8·80 ± 0·20)	−0·056 ± 0·004	−0·056	0·000
$-69{\cdot}8_6$	10^{-1}(2·95 ± 0·05)	−0·530 ± 0·007	−0·528	−0·002
$-89{\cdot}8_8$	10^{-2}(2·33 ± 0·05)	−1·633 ± 0·010	−1·628	−0·005
$-99{\cdot}6_6$	10^{-3}(5·96 ± 0·14)	−2·225 ± 0·010	−2·258	+0·033
$-109{\cdot}7_2$	10^{-3}(1·33 ± 0·02)	−2·876 ± 0·006	−2·985	+0·109
$-114{\cdot}4_9$	10^{-4}(6·29 ± 0·07)	−3·201 ± 0·005	−3·362	+0·161

have been calculated from these mean values, and are given as s'' (calc.) in the penultimate column of Table 2, for comparison with the observed values.

Arrhenius plot. The plot of log k_2 against $1/T$ is shown in Fig. 1. The line shown was calculated by the method of least squares as the best straight line through the points from +20° to −90°, and has the equation:

$$\log k_2\,(\text{Arrh}) = (9{\cdot}55 \pm 0{\cdot}03) - (2048{\cdot}6 \pm 5{\cdot}4)/T. \qquad (4)$$

The corresponding values of the Arrhenius parameters, and their standard deviations, are:

$$E_{\text{A}} = 9{\cdot}38 \pm 0{\cdot}03 \text{ kcal mole}^{-1};\ \log A = 9{\cdot}55 \pm 0{\cdot}03\ (A \text{ in l. mole}^{-1} \text{ sec.}^{-1});$$
$$\Delta S = -16{\cdot}5 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ at } 25°.$$

Comparison with earlier results. At this point a comparison may be made with the results published by Ainscough and Caldin,[1] which extend down to −99·9°. Their individual rate constants are a few per cent smaller than ours; the actual discrepancies at −50°, −60°, −70°, −80°, and −90° are 9%, 1%, 8%, 5%, and 5%, respectively. These small discrepancies are probably explicable in the same way as those noted later for monochloroacetic acid. Before comparing the Arrhenius parameters, it is necessary to recalculate those of Ainscough and Caldin, since they used an incorrect value of the rate constant k_2 at −60°. The correct value calculated from their values of s'' is 0·860 l. mole^{-1} sec.$^{-1}$, not 0·822 as given in their paper. The following equation is then obtained by the method of least squares:

$$\log k_2\,(\text{Arrh.}) = 9{\cdot}565 - 2056{\cdot}1/T, \qquad (5)$$

whence $E_{\text{A}} = 9{\cdot}41$ kcal. mole^{-1} and $\log A = 9{\cdot}57$. These values agree within the experimental error with those found from the present work.

Deviations from linear Arrhenius plot. These are shown in Fig. 2, where the short vertical lines represent [log k_2 (obs.) − log k_2 (Arrh)], with the standard deviation for k_2 (obs.). Here k_2 (Arrh) has been calculated for each temperature from equation 4, *i.e.*, on the assumption of a linear Arrhenius plot. The results are shown in Table 3.

Quantum-mechanical tunnelling. Calculations of k_2 have been made, with the help of Bell's equations [10] for a parabolic barrier, for various values of the barrier height (E_{qmt}) and width ($2a$). The resulting theoretical values, denoted by k_2(qmt), are shown in Table 4, where they may be compared with k_2 (obs.). The agreement between the observed and theoretical values may also be judged from Fig. 2, where the curves represent

$$[\log k_2\,(\text{qmt}) - \log k_2\,(\text{Arrh})].$$

TABLE 4.

Values of k_2 calculated for quantum-mechanical tunnelling, compared with observed values for the reaction between acetic acid and the trinitrobenzyl anion.

k_2 in l. mole^{-1} sec.$^{-1}$.

	k_2 (qmt)				
E_{qmt} (kcal. mole^{-1})	10·10	10·10	10·05	10·03	
a (Å)	0·81	0·83	0·84	0·85	k_2 (obs.)
Temp.					
+20°	$3{\cdot}77 \times 10^2$	$3{\cdot}69 \times 10^2$	$3{\cdot}61 \times 10^2$	$3{\cdot}61 \times 10^2$	$10^2(3{\cdot}60 \pm 0{\cdot}30)$
$-49{\cdot}9_4$	2·26	2·16	2·20	2·20	$2{\cdot}42 \pm 0{\cdot}07$
$-59{\cdot}9_0$	$8{\cdot}50 \times 10^{-1}$	$8{\cdot}09 \times 10^{-1}$	$8{\cdot}23 \times 10^{-1}$	$8{\cdot}23 \times 10^{-1}$	$10^{-1}(8{\cdot}80 \pm 0{\cdot}20)$
$-69{\cdot}8_6$	$2{\cdot}92 \times 10^{-1}$	$2{\cdot}77 \times 10^{-1}$	$2{\cdot}82 \times 10^{-1}$	$2{\cdot}82 \times 10^{-1}$	$10^{-1}(2{\cdot}95 \pm 0{\cdot}05)$
$-89{\cdot}8_8$	$2{\cdot}54 \times 10^{-2}$	$2{\cdot}35 \times 10^{-2}$	$2{\cdot}39 \times 10^{-2}$	$2{\cdot}38 \times 10^{-2}$	$10^{-2}(2{\cdot}33 \pm 0{\cdot}05)$
$-99{\cdot}6_6$	$6{\cdot}56 \times 10^{-3}$	$5{\cdot}94 \times 10^{-3}$	$6{\cdot}03 \times 10^{-3}$	$5{\cdot}98 \times 10^{-3}$	$10^{-3}(5{\cdot}96 \pm 0{\cdot}14)$
$-109{\cdot}7_2$	$1{\cdot}45 \times 10^{-3}$	$1{\cdot}27 \times 10^{-3}$	$1{\cdot}28 \times 10^{-3}$	$1{\cdot}25 \times 10^{-3}$	$10^{-3}(1{\cdot}33 \pm 0{\cdot}02)$
$-114{\cdot}4_9$	$6{\cdot}92 \times 10^{-4}$	$5{\cdot}89 \times 10^{-4}$	$5{\cdot}90 \times 10^{-4}$	$5{\cdot}66 \times 10^{-4}$	$10^{-4}(6{\cdot}29 \pm 0{\cdot}07)$

Results with Monochloroacetic Acid.—Previous work with monochloroacetic acid [1] had given an Arrhenius plot which was linear down to −115°, the lowest temperature at which the former apparatus could be used. This result has been checked carefully with the new apparatus, since it would rule out the possibility that the curvature of the Arrhenius plot for the reaction with acetic acid is due to a change in the structure of the solvent. On the main issue our results confirm the earlier work, but there are some minor differences.

TABLE 5.

Effect of varying buffer ratio in the reaction between the trinitrobenzyl anion and monochloroacetic acid.

Temp. $-89{\cdot}8_8$°. Symbols as in Table 2. Concns. in mole l.$^{-1}$; s'' in sec.$^{-1}$.

$10^3(c-b)$	10^4b	r	$10^4s''$	$10s''/(c-b)$	$10^3(c-b)$	10^4b	r	$10^4s''$	$10s''/(c-b)$
1·72	0·70	24·8	3·52 ± 0·05	2·05 ± 0·03	1·85	0·99	18·6	3·88 ± 0·20	2·10 ± 0·10
1·72	1·03	16·7	3·95 ± 0·08	2·30 ± 0·04	1·92	1·69	11·5	3·97 ± 0·21	2·07 ± 0·05
1·72	0·57	30·2	3·49 ± 0·05	2·03 ± 0·03	1·71	1·71	10·0	3·47 ± 0·10	2·03 ± 0·04
1·75	18·55	0·94	3·51 ± 0·13	2·01 ± 0·07					

Reproducibility. Some difficulty was at first experienced in obtaining closely reproducible results at −115°, but this was overcome by recrystallisation of the acid and trinitrotoluene. Two different samples of monochloroacetic acid were used, with concordant results.

Effect of buffer ratio. In Table 1 of the previous paper,[1] results were reported for a series of runs (by E. Harbron) at −90·03° in which the buffer ratio r was varied by altering b about 30-fold, and no trend in $s''/(c-b)$ was found. It was concluded that reaction with hydrogen ions was negligible. In deriving the rate constants, the readings of the logarithmic photometer had been wrongly interpreted; we have therefore recalculated these rate constants (Table 5). The changes are not great, and the general conclusion is the same. We have also corrected the temperature; in the former paper it was wrongly assumed that the difference of temperature between cell and bath would be the same for ethanol solutions as for the light petroleum used by Caldin and Jackson [2] in their calibration. These corrections do not affect the rest of the results reported in earlier papers.

That the reaction with hydrogen ion is negligible is shown also by the results given below for −114·5°, where a 12-fold variation of b has no effect on the value of $s''/(c-b)$; and at −105°, where a set of runs at constant buffer ratio gives a plot of s'' against $(c-b)$ that shows no intercept (cf. equation 2 above).

Rate constants. The results of our individual kinetic runs are given in Table 6. The symbols have the same meanings as in Table 2. The mean values of k_2, calculated by equation 3, are given with their standard deviations in the second column of Table 7. The value for 20° is that given by Caldin and Long.[15]

Arrhenius plot. The Arrhenius plot is linear within experimental error from +20° to −105°, but there is a small positive deviation at −114·5°. The best straight line calculated by the method of least squares from the rate constants at +20°, −70°, −90°, and −105° has the equation:

$$\log k_2\ (\text{Arrh}) = (9{\cdot}483 \pm 0{\cdot}008) - (1798{\cdot}5 \pm 1{\cdot}6)/T. \qquad (6)$$

The values of k_2 (Arrh) are compared with the observed values of k_2 in Table 7. From the fifth column it may be seen that the values agree within the experimental error, except at −114·5°, where the discrepancy is 13% compared with the standard deviation of 2·5%. The Arrhenius parameters calculated from equation 6, with their standard deviations, are:

$$E_A = 8{\cdot}23 \pm 0{\cdot}01 \text{ kcal. mole}^{-1};\ \log A = 9{\cdot}48 \pm 0{\cdot}01\ (A \text{ in l. mole}^{-1} \text{ sec.}^{-1});$$
$$\Delta S^* = -16{\cdot}8 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ at } 25°.$$

Comparison with earlier results. These Arrhenius parameters agree within experimental error with those given by Caldin and Long,[15] which were calculated from results at +20° and −78·5° only and have relatively large limits of error ($E = 8{\cdot}3 \pm 0{\cdot}2$, $\log A = 9{\cdot}4 \pm 0{\cdot}15$). They differ by slightly more than the experimental error from the values reported by Ainscough and Caldin,[1] whose values with their standard deviations were $E = 8{\cdot}52 \pm 0{\cdot}13$, $\log A = 9{\cdot}69 \pm 0{\cdot}15$. The discrepancies, with the sums of the standard deviations, are $\delta E = 0{\cdot}29 \pm 0{\cdot}14$, $\delta \log A = 0{\cdot}21 \pm 0{\cdot}16$. Moreover, in the earlier work no deviation from the Arrhenius plot was observed at −114°.

TABLE 6.

Results for the kinetic runs with monochloroacetic acid.

Concns. in mole l.$^{-1}$; s'' in sec.$^{-1}$.

Temp.	10^3c	10^4b	10^5d	$10^8(c-b)$	r	$10^4s''$ (obs.)	$10^4s''$ (calc.)	$s''/(c-b)$
$-69{\cdot}8_6$°	1·38	2·09	1·07	1·17	5·60	22·6 ± 0·7	21·9	1·87 ± 0·06
	2·28	5·69	1·07	1·71	3·00	33·4 ± 1·3	32·0	
	2·66	5·69	1·07	2·09	3·67	42·1 ± 2·4	39·1	
	2·50	1·63	1·07	2·34	14·4	40·9 ± 1·6	43·8	
	3·36	5·69	1·07	2·79	4·90	48·7 ± 0·8	52·2	
$-89{\cdot}8_8$	1·79	0·70	1·09	1·72	24·8	3·52 ± 0·05 *	3·51	(2·04 ± 0·03) * × 10^{-1}
	1·82	1·03	1·09	1·72	16·7	3·95 ± 0·08 *	3·51	
	1·78	0·57	1·09	1·72	30·2	3·49 ± 0·05 *	3·51	
	1·92	18·55 †	1·09	1·75	0·94	3·51 ± 0·13 *	3·57	
	1·95	0·99	1·09	1·85	18·6	3·88 ± 0·20 *	3·77	
	2·09	1·69	1·09	1·92	11·5	3·97 ± 0·21 *	3·92	
	2·43	0·86	1·09	2·34	27·2	4·67 ± 0·20 *	4·77	
	3·06	1·32	1·09	2·93	22·0	5·47 ± 0·18 *	5·98	
	3·45	1·55	1·09	3·39	21·9	6·63 ± 0·14 *	6·92	
	1·88	1·71	1·09	1·71	10·0	3·47 ± 0·10	3·52	(2·06 ± 0·04) × 10^{-1}
	2·83	2·56	1·09	2·57	10·0	5·25 ± 0·17	5·29	
	3·81	3·42	1·09	3·47	10·0	6·48 ± 0·15	7·15	
	4·51	8·78	1·09	3·63	4·13	7·83 ± 0·15	7·48	
	5·62	5·13	1·09	5·11	9·96	11·03 ± 0·60	10·5	
	6·28	1·72	1·09	6·11	35·5	12·00 ± 0·40	12·6	
$-104{\cdot}7_3$	10·63	6·62	1·10	9·97	15·1	2·75 ± 0·08	2·75	(2·76 ± 0·04) × 10^{-2}
	27·92	17·43	1·10	26·18	15·0	7·40 ± 0·22	7·23	
	53·26	33·1	1·10	49·95	15·1	13·8 ± 0·4	13·9	
	57·14	35·6	1·10	53·58	15·0	14·2 ± 0·5	14·8	
						$10^5s''$ (obs.)	$10^5s''$ (calc.)	
$-114{\cdot}4_9$	6·88	7·96	1·12	6·08	7·64	4·88 ± 0·10	4·21	(6·93 ± 0·18) × 10^{-3}
	8·83	5·96	1·12	8·23	13·8	5·60 ± 0·20	5·70	
	11·01	7·96	1·12	10·21	12·8	8·15 ± 0·09	7·08	
	13·4	7·44	1·12	12·7	17·0	9·90 ± 0·20	8·80	
	16·8	7·96	1·12	16·0	20·1	11·0 ± 0·5	11·1	
	19·85	10·5	1·12	18·8	17·9	11·9 ± 0·4	13·0	
	23·2	38·5	1·12	19·3	5·01	12·3 ± 0·3	13·4	
	22·0	10·3	1·12	21·0	20·3	17·9 ± 0·4 ‡	14·6	
	23·1	19·3	1·12	21·2	9·95	13·5 ± 0·3	14·7	
	22·3	10·5	1·12	21·3	20·2	13·0 ± 0·5	14·8	
	23·2	7·42	1·12	22·4	30·2	15·3 ± 0·3	15·5	
	25·1	22·9	1·12	22·9	9·98	15·4 ± 0·4	15·9	
	29·6	3·17	1·12	29·3	92·5	20·3 ± 0·6	20·3	

* Results obtained with logarithmic photometer. † Sodium monochloroacetate added (to 16·9 × 10^{-4}M). ‡ 1·1% of water added; not included in mean value of $s''/(c-b)$.

TABLE 7.

Rate constants for the reaction between monochloroacetic acid and the trinitrobenzyl anion.

k_2 in l. mole^{-1} sec.$^{-1}$.

Temp.	k_2 (obs.)	log k_2 (obs.)	log k_2 (Arrh)	log k_2 (obs.) — log k_2 (Arrh)	log k_2 (qmt)	log k_2 (obs.) — log k_2 (qmt)
+20·0°	10^3(2·23 ± 0·07)	+3·348 ± 0·013	+3·348	0·000	+3·348	0·000
$-69{\cdot}8_6$	4·31 ± 0·14	+0·634 ± 0·014	+0·636	−0·001	+0·617	+0·017
$-89{\cdot}8_8$	10^{-1}(4·72 ± 0·09)	−0·326 ± 0·008	−0·330	+0·004	−0·330	+0·004
$-104{\cdot}7_3$	10^{-2}(6·36 ± 0·09)	−1·197 ± 0·006	−1·195	−0·002	−1·158	−0·039
$-114{\cdot}4_9$	10^{-2}(1·60 ± 0·04)	−1·796 ± 0·011	−1·848	+0·052	−1·768	−0·028

To account for these discrepancies, we have considered the possibility of an error in temperature in the work of Ainscough and Caldin, who used a thermocouple. The error calculated for −114° would be 3·3°, and for −70° it would be 2·2°. These are improbably high, especially in view of the good agreement between the two sets of results with acetic acid (above). The most likely reason for the discrepancies is that in the earlier work the stock solution of trinitrotoluene was not made up fresh every week, as in the present work; the solution used for the runs at −114°, as an extreme example, was 14 weeks old. Solutions of trinitrotoluene in ethanol gradually become yellow, and after some weeks give an appreciably lower rate constant. A run at −90° with a solution three weeks old gave a rate constant 6% lower than that for a fresh solution; with a solution 14 weeks old, the difference was 45%. This effect is sufficient to explain all the discrepancies.

Quantum-mechanical tunnelling. Calculations of k_2 (qmt) have been made with the values of a and E_A/E_{qmt} that gave the best fit for acetic acid ($a = 0{\cdot}83$ Å, $E_{qmt} = E_A/0{\cdot}93 = 8{\cdot}23/0{\cdot}93 = 8{\cdot}86$ kcal. mole^{-1}). The results are shown in the last two columns of Table 7. The agreement between the observed and the calculated values of k_2 is fairly good. A larger value of a would probably give a slightly better fit.

We thank D.S.I.R. for a research studentship awarded to E. H.

Department of Physical Chemistry,
The University, Leeds, 2.

[*Received, November 8th,* 1961.]