489. *The Kinetics and Mechanisms of Some Colour Reactions of Aromatic Nitro-compounds at Low Temperatures. Part III.** s-*Trinitrobenzene.*

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s-Trinitrobenzene (T.N.B.) when treated with sodium ethoxide in dilute ethanol solution gives a reddish-brown solution. When treated with an acid such as acetic acid (HA), this solution is completely decolorised :

$$\text{T.N.B.} + \text{OEt}^- \rightleftharpoons \text{Coloured product} \xrightarrow{\text{HA}} \text{T.N.B.}$$

The first reaction has been studied between $-70°$ and $-100°$; the rate constants and Arrhenius parameters for the forward and the back reaction have been determined, and hence the equilibrium constant. The rate of decolorisation has been studied at $-80°$ with a series of acids; the results obey the Brønsted relation. The rate with acetic acid has been measured between $-50°$ and $-80°$, and the Arrhenius parameters for the reaction with acetic acid and with hydrogen ion have been determined. The nature of the coloured product is discussed; it is considered to be an addition product, probably a charge-transfer complex.

THE reactions have been investigated by methods similar to those of the preceding paper. Some preliminary results were given in Part I.[1]

The Reaction between s-*Trinitrobenzene and Ethoxide Ion.*—This reaction must proceed by some kind of addition mechanism; a proton-transfer mechanism is ruled out both on general grounds and by the experimental demonstration that trinitrobenzene does not exchange with OD^- in D_2O at room temperature.[2] A red, solid, crystallisable addition product has been reported.[3] The reaction may be represented by equation (1) (cf. eqn. 1, preceding paper). The reaction, the rate of which can be conveniently measured in the range $-70°$ to $-100°$, is of first order with respect to each reactant. Since ethoxide is in large excess, each kinetic run gives a linear plot of log $(D_e - D)$ against time, D_e and D being optical densities at equilibrium and at time t, respectively. The slope of this plot is linearly related to the ethoxide concentration; this shows that a 1 : 1-complex is formed, and allows k_1 and k_{-1} to be determined. The reaction is the fastest studied in this series of papers. It is faster by a factor of the order of 10^6 than the nucleophilic displacement of NO_2 by OEt^-, which has been measured at 25° by Holleman and van Haeften.[4] It does not show a salt effect, nor is its rate affected by small additions of hydrocarbons such as toluene (up to 5%), unlike the corresponding reaction of 2 : 4 : 6-trinitroanisole (preceding paper). The equilibrium constant is large and the values for it are therefore not very accurate. The results, given in detail later, may be summarised as in Table 1.

$$\text{T.N.B.} + \text{OEt}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{T.N.B., OEt})^- \quad . \quad . \quad . \quad . \quad (1)$$

TABLE 1.

$\log_{10} k_1$ at $-80°$ (l. mole^{-1} sec.$^{-1}$)	0·04	$\log_{10} A_{-1}$ (sec.$^{-1}$)	9·9 ± 0·3
E_1 (kcal. mole^{-1})	11·7 ± 0·1	$\log_{10} K$ at $-80°$ (l. mole^{-1})	*ca.* 3·3
$\log_{10} A_1$ (l. mole^{-1} sec.$^{-1}$)	13·3 ± 0·2	ΔH (kcal. mole^{-1})	0·3 ± 0·3
E_{-1} (kcal. mole^{-1})	11·4 ± 0·3	$\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})	16·5 ± 1·5

The considerable positive value of $\Delta S°$, which at first sight is surprising for an addition reaction with its accompanying loss of translational and rotational degrees of freedom,

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* Part II, preceding paper.

[1] Caldin and Long, *Proc. Roy. Soc.*, 1955, *A*, **228**, 263.

[2] Ketelaar, Bier, and Vlaar, *Rec. Trav. chim.*, 1954, **73**, 37.

[3] Lobry de Bruyn and van Leent, *ibid.*, 1895, **14**, 150.

[4] Holleman and van Haeften, *ibid.*, 1921, **40**, 67.

has been attributed[1] to desolvation, resulting from the delocalisation of charge that will take place on forming an addition product in which the charge formerly localised on the oxygen atom of the ethoxy-group is partly distributed over the nitro-groups of the trinitrobenzene. The value of A_1 corresponds to an entropy of activation of 10·5 cal. deg.$^{-1}$ mole^{-1}; this implies that more than half the desolvation occurs in forming the transition state. The fact that neither the values of E_1 nor those of A_1 differ greatly for the reactions of trinitrobenzene and trinitrotoluene has already been commented upon[1] (cf. also the following paper). Further interpretation of the Arrhenius parameters is deferred to a later paper.

Reactions of Weak Acids with the Addition Product.—The reaction in which the coloured addition product is decolorised with acids has been studied (*a*) with acetic acid from $-50°$ to $-80°$, and (*b*) with a series of similar acids at $-80°$. It was found that reaction occurred both with uncharged acid and with hydrogen ion, as in the case of trinitroanisole (cf. equations 5 and 6 of the preceding paper):

$$(\text{T.N.B., OEt})^- + \text{HA} \xrightarrow{k_2} \text{T.N.B.} + \text{HOEt} + \text{A}^- \quad . \quad . \quad . \quad (2)$$

$$(\text{T.N.B., OEt})^- + \text{EtOH}_2^+ \xrightarrow{k_3} \text{T.N.B.} + 2\text{HOEt} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From the results with acetic acid it was possible to derive values of the constants k_2 for acetic acid and k_3 for hydrogen ion (and also more accurate values of k_{-1}) at four temperatures, and hence the Arrhenius parameters for these reactions:

Acetic acid: $E_2 = 11{\cdot}9 \pm 0{\cdot}5$ kcal. mole^{-1} $\log_{10} A_2 = 11{\cdot}8 \pm 0{\cdot}5$ l. mole^{-1} sec.$^{-1}$

Hydrogen ion: $E_3 = 11{\cdot}2 \pm 0{\cdot}6$ kcal. mole^{-1} $\log_{10} A_3 = 18{\cdot}4 \pm 0{\cdot}7$ l. mole^{-1} sec.$^{-1}$

The reliability of the value of E_3 is subject to the limitation that it depends on the assumption that K_a, which is used in estimating k_3, does not vary appreciably with temperature in the range used. None the less, it is striking that the energies of activation for acetic acid and for hydrogen ion are very similar, although the values of $\Delta G°$ for the two reactions at $-80°$ will differ by about 12 kcal. mole^{-1}, whereas on a simple potential-energy picture[5] we should expect $\Delta E = \alpha\Delta G°$. It is possible that part of the explanation is that the energy required to remove a proton from the acid is not the whole of the activation energy, to which solvation changes also contribute.

The large value of A_3 is to be expected for a reaction between ions. A_2 is near the "normal" value for bimolecular reaction, despite the considerable increase in solvation that must occur when the negative charge becomes concentrated on the acetate anion; this is presumably because the reaction (2) produces an additional molecule and so leads to an increased number of translational and rotational degrees of freedom.

The results with a series of acids at $-80°$ showed that for reaction (2) the rate constants k_2 of the undissociated acids are related to the dissociation constants K_a of the acids by a relation of the Brønsted type, $k_2 = GK_a^{\alpha}$, where α is a constant. (In the absence of data on K_a in ethanol at $-80°$, values at 25° were used.) The rate constant k_3 for the hydrogen ion agrees fairly well with the same equation. These results show that the rate-determining steps in reactions (2) and (3) are proton-transfers. The exponent α has the value 0·67.

Nature of the Coloured Addition Product.—The kinetics of reaction (1) are compatible with the formation of either of the two kinds of addition product (I) and (II) distinguished in the preceding paper. As only one reaction has been observed, we cannot identify the product by the same arguments as were there used for the products of trinitroanisole. There are, however, certain analogies between the present reaction and the "fast" reaction between ethoxide and trinitroanisole. The two reactions are among the fastest of the series with different nitro-compounds, and have fairly similar energies of activation. The rates of the reverse reactions (k_{-1}) are similar. The reactions of both coloured products with acids obey a relation of the Brønsted type, which covers both undissociated acids and hydrogen ion. The Brønsted exponents are similar (0·56 and 0·67). These analogies do

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[5] Bell, "Acid-Base Catalysis," Oxford Univ. Press, 1941, Chap. 8.

not amount to proof, but coupled with the lack of evidence for an addition compound they suggest that the coloured product is a charge-transfer complex, analogous to those formed by trinitrobenzene with hydrocarbons and amines.[6]

EXPERIMENTAL

s-Trinitrobenzene was recrystallised from ethanol–benzene to constant m. p., 121° (lit., 121—122°). The purification of other materials, the apparatus and experimental procedures, and the methods of deriving rate constants have been described in the preceding paper or in that of Caldin and Long.[1] The plots of $(D_e - D)$ against time, or the corresponding plots obtained by using Guggenheim's method,[7] were always linear, indicating first-order kinetics with respect to trinitrobenzene,[1] whose concentration was always negligible compared with that of the other reactant. The solvent was ethanol containing 1% of toluene by volume, added to prevent crystallisation from the relatively concentrated solutions during cooling before mixing with the ethoxide solution. The rate was unaltered when the toluene concentration was increased to 3% or 6%.

Results.—(a) *Reaction between ethoxide ion and trinitrobenzene.* The rate of this reaction (1) has been measured with a series of concentrations of ethoxide (b) at −70°, −80°, −90°, and −100°. The slopes s of these graphs of $\log_{10}(D_e - D)$ against time, at a given temperature, give a straight line when plotted against b. This shows that the reaction is of first order with respect to ethoxide concentration, that it is not complicated by salt effects, and that it gives rise to a 1 : 1 complex.[8] The slope of such an s–b plot gives k_1 and the intercept gives k_{-1}.

TABLE 2. *Reaction between ethoxide and* s-*trinitrobenzene.*

Temp.	10^5d (mole l.$^{-1}$)	10^3b (mole l.$^{-1}$)	10^3s, obs. (sec.$^{-1}$)	10^3s, calc. (sec.$^{-1}$)	Slope of s–b plot (l. mole^{-1} sec.$^{-1}$)	Intercept of s–b plot (sec.$^{-1}$)
−70·0°	1·84	1·50	3·87 ± 0·08	3·80	2·03 ± 0·05	(8·5 ± 1·5)10^{-4}
	1·84	2·19	4·85 ± 0·15	5·35		
	1·84	3·15	7·20 ± 0·18	7·20		
	1·84	4·38	10·0 ± 0·3	9·55		
	1·84	7·15	15·8 ± 0·6	15·4		
−80·0	1·86	2·21	1·07 ± 0·03	1·25	(4·80 ± 0·16)10^{-1}	(2 ± 2)10^{-4}
	1·86	3·99	2·22 ± 0·04	2·14		
	1·86	9·75	3·44 ± 0·07	4·82		
	1·86	9·97	4·78 ± 0·10	4·95		
	1·86	13·8	6·88 ± 0·16	6·82		
	1·86	25·7	12·9 ± 0·3	12·6		
	1·86	48·3	23·4 ± 0·6	23·4		
−90·0	1·88	12·2	0·99 ± 0·02	1·00	(8·15 ± 0·10)10^{-2}	(4 ± 4)10^{-5}
	1·88	24·3	1·89 ± 0·06	1·98		
	1·88	46·3	3·81 ± 0·09	3·78		
	1·88	63·9	5·37 ± 0·10	5·22		
	1·88	85·0	6·88 ± 0·10	6·95		
−99·9	0·905	36·7	0·50 ± 0·01	0·50	(1·38 ± 0·04)10^{-2}	<3 × 10^{-5}
	0·905	65·9	0·95 ± 0·02	0·91		
	0·905	98·9	1·38 ± 0·04	1·37		
	1·79	148	2·04 ± 0·04	2·04		
	0·905	225	3·06 ± 0·07	3·11		

TABLE 3. *Rate constants from the reaction between* T.N.B. *and* OEt .

Temp.	k_1 (l. mole^{-1} sec.$^{-1}$) : obs.	calc.	k_{-1}, obs. (sec.$^{-1}$)	Temp.	k_1 (l. mole^{-1} sec.$^{-1}$) : obs.	calc.	k_{-1}, obs. (sec.$^{-1}$)
−99·9°	(3·18 ± 0·09)10^{-2}	3·24 × 10^{-2}	$\not>$7 × 10^{-5}	−80·0°	1·11 ± 0·04	1·05	(5 ± 5)10^{-4}
−90·0	(1·88 ± 0·02)10^{-1}	2·00 × 10^{-1}	(9 ± 9)10^{-5}	−70·0	4·68 ± 0·11	4·78	(2·0 ± 0·4)10^{-3}

The intercepts are here very small and correspondingly inaccurate. The experimental results are given in Table 2. The limits of error estimated from the graphs are indicated. The derived values of k_1 and k_{-1}, with their limits of error, are given in Table 3. The accuracy with which

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[6] Bier, Thesis, Amsterdam, 1954.

[7] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

[8] Foster, Hammick, and Wardley, *J.*, 1953, 3817.

they fit the experimental data may be seen by comparing the values of s calculated from them with the observed values (see Table 2, under heading " s, calc."). Corrections for the change in concentration of the solutions by contraction on cooling have been applied throughout.

The parameters of the Arrhenius equation for the forward equation, obtained by plotting the values of $\log_{10} k_1$ given in Table 3 against $1/T$, are :

$$E_1 = 11{\cdot}7 \pm 0{\cdot}1 \text{ kcal. mole}^{-1}; \quad \log_{10} A_1 = 13{\cdot}3 \pm 0{\cdot}2 \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

The values of k_{-1} given in Table 3 are too inaccurate to be treated in this way; but values of k_{-1} at −80°, −70°, −60°, and −50° are available from the results described later on the reaction of acetic acid with the coloured addition product, and from them we find :

$$E_{-1} = 11{\cdot}4 \pm 0{\cdot}3 \text{ kcal. mole}^{-1}; \quad \log_{10} A_{-1} = 9{\cdot}9 \pm 0{\cdot}3 \text{ sec.}^{-1}$$

These results on k_{-1} also allow us to calculate the values of the equilibrium constant K at −80°, −90°, and −99·9°, for which the values of k_{-1} given in Table 3 are too inaccurate. K had been determined from equilibrium densities at 25° by Caldin and Long,[1] and values at 20° and 0° have been determined by the same method. The collected values of K are given in Table 4.

TABLE 4. *Equilibrium constant for the* T.N.B.–OEt⁻ *reaction.*

Temp.	25·0°	20·0°	0·0°	−70·0°	−80·0°	−90·0°	−99·9°
$10^{-3}K$	2·4 ± 0·3	1·8 ± 0·3	1·7 ± 0·3	1·5 ± 0·3	2·2 ± 0·5	1·9 ± 0·4	2·1 ± 0·4

It is evident that K is nearly independent of temperature. A plot of log K against $1/T$ is rather scattered, giving $\Delta H \simeq 0 \pm 0{\cdot}6$ kcal. mole⁻¹. More precise values of ΔH and $\Delta S°$ are obtained by combining the values given for E_1 and E_{-1}, and of A_1 and A_{-1}; we then obtain :

$$\Delta H = 0{\cdot}3 \pm 0{\cdot}3 \text{ kcal. mole}^{-1}; \quad \Delta S° = 16{\cdot}5 \pm 1{\cdot}5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

(b) *Reaction between acetic acid and the coloured addition product.* Linear first-order plots were obtained at −50°, −60°, −70°, and −80°. The rate varied with the buffer ratio, so that hydrogen ions must be involved. The reaction also showed a marked salt effect; presumably this was mainly the primary salt effect on the reaction between the positive hydrogen ion and the negative addition product. The ionic strength was therefore kept constant, by addition of lithium iodide. The complete expression for the numerical value s'' of the slope of the first-order plot will be (cf. eqn. 12, preceding paper) :

$$2{\cdot}303s'' = k_{-1} + k_2[\text{HA}] + k_3[\text{H}^+] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The usual procedure has been to carry out at each temperature two sets of runs, each at constant buffer ratio and constant ionic strength. The slope of a plot of s'' against acid concentration gives k_2, by equation (4). The intercept gives $(k_{-1} + k_3[\text{H}^+])$, in which $[\text{H}^+]$ may be roughly estimated, as in the preceding paper, from the dissociation constant of the acid in ethanol at 25° by use of activity coefficients calculated from the Debye–Hückel equation. From the two sets of runs, at different buffer ratios, we can then calculate k_{-1} and k_3. A different procedure was adopted for the runs at −70°. One set of runs was carried out at constant buffer ratio and ionic strength, and varying acid concentration; and in the second set the acid concentration and ionic strength were kept constant and the buffer ratio was varied. The plot of s'' against acid concentration for the second set has intercept $(k_{-1} + k_2[\text{HA}])$, and together with the slope and intercept for the first set this gives enough data for the determination of k_{-1}, k_2, and k_3.

The results of the kinetic runs are shown in Table 5. Here b = initial ethoxide concentration, c = concentration of acid added, $(c - b)$ = acid concentration in the resulting solution, g = concentration of sodium acetate added, $r = (c - b)/(b + g)$ = buffer ratio of the resulting solution, h = concentration of lithium iodide, and μ = ionic strength.

From these results, linear plots of s'' against the acid concentration $(c - b)$ were obtained; the agreement of the best lines with the experimental observations is seen by comparing the last two columns of Table 5. The derived values of k_{-1}, k_2, and k_3 are shown in Table 6, with their estimated limits of error.

The energies of activation and frequency factors calculated from Arrhenius plots of log k_{-1}, log k_2, and log k_3 against $1/T$ are :

E_{-1} = 11·4 ± 0·3 kcal. mole^{-1} log$_{10}$ A_{-1} = 9·9 ± 0·3 sec.$^{-1}$

E_2 = 11·9 ± 0·5 kcal. mole^{-1} log$_{10}$ A_2 = 11·8 ± 0·5 l. mole^{-1} sec.$^{-1}$

E_3 = 11·2 ± 0·6 kcal. mole^{-1} log$_{10}$ A_3 = 18·4 ± 0·7 l. mole^{-1} sec.$^{-1}$

These values give the "calculated" values of the rate constants shown in Table 6. The value given for E_3 depends on the assumption that the equilibrium constant of the acid is approximately constant over the temperature range concerned; this limits its reliability.

(c) *Reaction between other acids and the coloured addition product.* The reaction was studied, at −80°, with three other weak acids. Since k_{-1} is already known from the results with acetic acid, only one set of runs at constant buffer ratio and ionic strength is necessary for each acid.

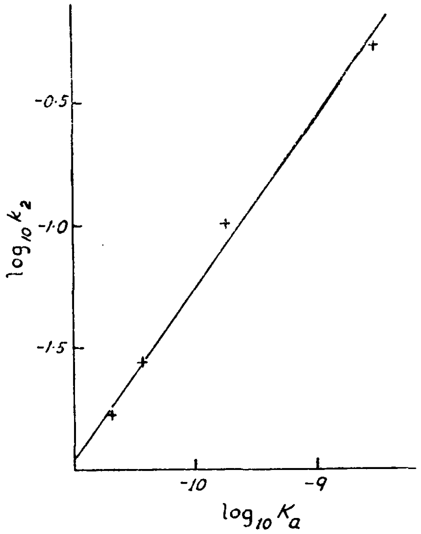
TABLE 5. *Reaction between coloured addition product and acetic acid.*

	10^3c	10^4b	10^4g	10^4h		$10^4\mu$	$10^3s''$ (sec.$^{-1}$)	
Temp.	(mole l.$^{-1}$)				r	(mole l.$^{-1}$)	obs.	calc.
−50·0°	1·84	3·68	—	7·98	4·00	11·64	18·4 ± 0·3	18·35
	2·55	5·13	—	6·52	3·98	11·65	18·8 ± 0·3	18·8
	3·35	6·72	—	4·93	4·00	11·65	19·0 ± 0·3	19·2
	4·58	9·16	—	2·48	4·00	11·64	19·9 ± 0·4	19·9
	5·58	11·18	—	0·46	3·99	11·64	21·1 ± 0·4	20·5
	2·79	2·15	—	9·50	11·95	11·65	23·0 ± 0·5	23·1
	5·58	4·29	—	7·37	12·00	11·66	25·0 ± 0·6	24·9
	5·80	4·47	—	7·18	11·98	11·65	25·2 ± 0·4	25·1
	7·23	5·55	—	6·09	12·00	11·64	26·1 ± 0·6	26·0
	10·2	7·86	—	3·79	12·01	11·64	27·8 ± 0·6	27·9
−60·0	3·82	6·34	—	5·25	5·01	11·61	5·57 ± 0·08	5·57
	4·37	7·28	—	4·37	5·00	11·65	5·78 ± 0·08	5·72
	5·44	9·04	—	2·62	5·01	11·66	6·00 ± 0·07	6·00
	6·43	10·74	—	0·92	4·99	11·66	6·30 ± 0·08	6·28
	6·99	11·65	—	—	5·00	11·65	6·50 ± 0·10	6·42
	2·51	1·93	—	9·72	12·01	11·65	6·37 ± 0·09	6·37
	7·01	5·41	—	6·24	11·98	11·65	7·77 ± 0·13	7·67
	8·00	6·15	—	5·50	12·00	11·65	8·00 ± 0·11	7·97
	10·4	7·98	—	3·67	11·98	11·65	8·69 ± 0·12	8·66
	13·9	10·67	—	0·99	12·00	11·66	9·60 ± 0·15	9·67
−70·0	14·8	4·47	7·53	—	12·0	12·00	2·16 ± 0·07	2·16
	14·8	4·47	3·02	4·54	19·2	12·03	2·41 ± 0·07	2·35
	14·8	4·47	1·51	6·05	24·1	12·03	2·33 ± 0·07	2·47
	14·8	4·47	0·60	6·96	28·4	12·03	2·57 ± 0·07	2·58
	14·8	4·47	—	7·56	32·2	12·03	2·67 ± 0·08	2·68
	5·51	3·66	—	7·98	14·0	11·64	1·90 ± 0·04	1·91
	9·95	6·64	—	4·99	14·0	11·65	2·07 ± 0·04	2·07
	10·9	7·31	—	4·34	14·0	11·65	2·02 ± 0·04	2·09
	12·4	8·26	—	3·37	14·0	11·63	2·20 ± 0·05	2·14
	15·2	10·15	—	1·50	14·0	11·65	2·24 ± 0·04	2·24
−80·0	3·54	2·73	—	8·92	12·0	11·65	0·387 ± 0·007	0·387
	6·03	4·66	—	6·99	12·0	11·65	0·410 ± 0·006	0·416
	8·61	6·62	—	5·02	12·0	11·64	0·440 ± 0·007	0·444
	12·0	9·21	—	2·44	12·0	11·65	0·465 ± 0·008	0·475
	15·4	11·84	—	—	12·0	11·84	0·518 ± 0·008	0·517
	6·03	2·89	—	8·75	19·9	11·64	0·511 ± 0·007	0·509
	8·61	4·09	—	7·55	20·0	11·64	0·543 ± 0·010	0·536
	9·39	4·46	—	7·17	20·0	11·63	0·588 ± 0·012	0·545
	16·6	7·87	—	3·77	20·0	11·64	0·628 ± 0·010	0·626
	20·1	9·57	—	2·07	20·0	11·64	0·655 ± 0·014	0·664

TABLE 6.

	10^3k_{-1} (sec.$^{-1}$)		10^2k_2 (l. mole^{-1} sec.$^{-1}$)		$10^{-6}k_3$ (l. mole^{-1} sec.$^{-1}$)	
Temp.	obs.	calc.	obs.	calc.	obs.	calc.
−50°	35·$_2$ ± 1	33·9	161 ± 15	166	21 ± 3	22
−60	8·6 ± 0·8	10·2	74 ± 5	49	6·7 ± 1·7	7·4
−70	3·1 ± 0·4	2·69	8·3 ± 1	12·3	1·1 ± 0·3	1·8
−80	0·5 ± 0·1	0·63	2·7 ± 0·3	2·7	0·47 ± 0·15	0·44

The results of the kinetic runs are given in Table 7. Linear plots of s'' against acid concentration were again obtained; the agreement of the best straight lines with the observed points is shown by comparing the calculated and observed values of s'' in Table 7. Values of k_{-1}, k_2, and k_3 were derived as for acetic acid, the values of K_a adopted in the previous paper being taken. The values of k_3 can only be very approximate. The calculated results for the four acids at $-80°$ are in Table 8. The values of k_{-1} derived from the several acids agree satisfactorily. The agreement between the values of k_3 is also satisfactory in view of the approximations.



Plot of $\log_{10} k_2$ *at* $-80°$ *against* $\log_{10} K_a$ *at 25° for the reaction between weak acids and the coloured product of the reaction between* s-*trinitrobenzene and ethoxide.*

(Estimated limits of error are indicated by the lengths of the lines.)

Table 7. *Reaction between various acids and the coloured addition product* (temp. —80°).

10^3c	10^4b (mole l.$^{-1}$)	10^4h	$10^4\mu$ (mole l.$^{-1}$)	10^4s (sec.$^{-1}$) obs.	calc.
		Trimethylacetic acid (r = 15·0)			
2·66	1·66	9·99	11·65	2·49 ± 0·04	2·51
5·12	3·20	8·45	11·65	2·68 ± 0·05	2·67
8·31	5·20	6·44	11·64	2·92 ± 0·06	2·88
15·8	9·87	1·78	11·65	3·33 ± 0·07	3·38
		β-Chloropropionic acid (r = 10·0)			
2·20	2·00	9·64	11·64	4·85 ± 0·09	4·82
3·14	2·90	8·74	11·64	5·26 ± 0·08	5·22
5·88	5·34	6·30	11·65	6·07 ± 0·14	6·29
6·29	5·72	5·92	11·64	6·48 ± 0·14	6·44
7·63	6·94	4·70	11·64	7·24 ± 0·16	7·01
		Chloroacetic acid (r = 10·0)			
1·61	1·46	10·18	11·64	85·2 ± 1·6	85·2
2·79	2·55	9·09	11·64	88·0 ± 2·0	87·8
4·95	4·50	7·14	11·64	92·4 ± 2·4	92·5
8·30	7·54	4·10	11·64	100·0 ± 2·4	99·8

Table 8. *Rate constants from the reaction of various weak acids with the coloured addition product at —80°.*

Acid	10^4k_{-1} (sec.$^{-1}$)	10^2k_2 (l. mole^{-1} sec.$^{-1}$)	K_a at 25° (mole l.$^{-1}$)	$10^{-5}k_3$ (l. mole^{-1} sec.$^{-1}$)
Trimethylacetic	5·0 ± 1·2	1·7 ± 0·2	2·1 × 10^{-11}	<2·8
Acetic	5·0 ± 1·2	2·7 ± 0·3	3·74 × 10^{-11}	4·7 ± 1·5
β-Chloropropionic	5·0 ± 1·2	10 ± 1	1·84 × 10^{-10}	1·5 ± 0·7
Chloroacetic	5·0 ± 1·2	55 ± 9	3·0 × 10^{-9}	4·1 ± 0·1

The graph of $\log_{10} k_2$ at $-80°$ against $\log_{10} K_a$ at 25° is shown in the figure. The best straight line at $-80°$ through the points is represented by the equation $\log_{10} k_2 = 5·49 + 0·67 \log_{10} K_a$. For hydrogen ion, this equation predicts a value for the rate constant of 2×10^6 l. mole^{-1} sec.$^{-1}$, the p*K* of ethanol in ethanol[9] being taken as 19·14 and its concentration as 17 moles $l.^{-1}$. This is within a power of 10 of the experimental values given in Table 8, and in view of the extrapolation and approximations the agreement is adequate. For the solvent considered as an uncharged acid, the predicted rate constant is 5×10^{-8} l. mole $sec.^{-1}$, which is much less than the experimental value of k_{-1}, *viz.*, 5×10^{-4} l. $mole^{-1}$ $sec.^{-1}$. This implies that in the absence of added acid the only decolorisation reaction that need be considered is the unimolecular decomposition of the addition product, *i.e.*, the reverse of reaction (1).

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[9] Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2832.