488. *The Kinetics and Mechanisms of Some Colour Reactions of Aromatic Nitro-compounds at Low Temperatures. Part II.* 2 : 4 : 6-Trinitroanisole.*

By J. B. Ainscough and E. F. Caldin.

When sodium ethoxide is added to 2 : 4 : 6-trinitroanisole in dilute (*ca.* 10^{-5}M) solution in ethanol at room temperature, a yellow colour is at once produced. At lower temperatures, the rate of the process can be measured, and it is found that there are two colour-producing reactions : (i) a " fast " reaction, whose product is probably a charge-transfer complex, and (ii) a " slow " reaction, which probably produces an addition compound in which OEt is covalently bound to the benzene nucleus. Rate constants have been measured over a range of temperatures, and energies of activation and frequency factors calculated. Both the products are decolorised by acids, and the rates of decolorisation with various aliphatic acids have been measured. It is found that the product of the " fast " reaction is decolorised by the undissociated acids as well as by hydrogen ions, a Brønsted relation being obeyed; on the other hand, with the product of the " slow " reaction hydrogen ions alone are effective.

When a dilute solution ($\sim 10^{-5}$M) of 2 : 4 : 6-trinitroanisole in ethanol is treated with sodium ethoxide, a yellow solution is formed, which is completely decolorised by acids. Both reactions are very rapid at room temperature. This behaviour of trinitroanisole is superficially similar to that of *pp'p''*-trinitrotriphenylmethane,[1] of 2 : 4 : 6-trinitrotoluene,[2] and of *s*-trinitrobenzene.[2] The rates of the reactions can be measured at low temperatures,

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* Part I, *Proc. Roy. Soc.*, 1955, *A*, **228**, 263.

[1] Caldin and Trickett, *Trans. Faraday Soc.*, 1953, **49**, 772.

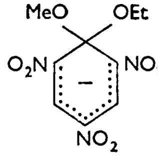
[2] Caldin and Long, Part I, *Proc. Roy. Soc.*, 1955, *A*, **228**, 263; see also Parts III and IV (following papers).

and have been investigated by the methods already developed.[1,2] The colour changes are completely reversible; it is therefore unlikely that nucleophilic replacement of NO_2 by OEt is involved.

Reactions between 2 : 4 : 6-*Trinitroanisole and Ethoxide Ion*.—This reaction would not be expected to proceed by a proton-transfer mechanism such as that attributed to trinitrotriphenylmethane [1] and trinitrotoluene,[2] since it is unlikely that 2 : 4 : 6-trinitroanisole (T.N.A.) can lose a proton in this way. The reaction must therefore be supposed to proceed by an addition mechanism, as proposed for trinitrobenzene.[2] Two such mechanisms are possible. The addition product may be a charge-transfer complex (I) of the type discussed by Mulliken,[3] involving resonance between two structures differing by the transfer of an electron, or it may be an addition compound (II) in which the ethoxy-group is attached by a covalent bond to the same carbon atom as the methoxy-group; the negative charge will be distributed by resonance. This structure was suggested by Meisenheimer,[4] who isolated as solids the products of reaction of 2 : 4 : 6-trinitroanisole with potassium ethoxide and of 2 : 4 : 6-trinitrophenetole with potassium methoxide. On decomposing each of these specimens with dilute sulphuric acid, he obtained a mixture containing trinitrophenetole, and concluded that both specimens consisted of the potassium salt of the anion (II). Hammick and Foster [5] have recently found the infrared spectra of the two products to be identical; and Foster reports that the visible spectra are also identical.[6] The visible spectra of the solutions produced by adding ethoxide to trinitroanisole in ethanol, and by adding methoxide to trinitrophenetole in methanol, are also identical.[7] Jackson and Earle,[8] while criticising Meisenheimer's work in respect of certain points of technique (without really invalidating it), obtained somewhat similar evidence by preparing the addition product of 2 : 4 : 6-trinitroanisole and sodium *iso*pentyloxide, decomposing it with dilute hydrochloric acid, and from the products isolating both *iso*pentyl picrate and trinitroanisole, as would be expected from a substance of structure similar to (II). Such addition products as (II) are fairly generally accepted today as intermediate in both electrophilic and nucleophilic aromatic substitution.

$$(\text{T.N.A.,OEt}^-) \leftrightarrow (\text{T.N.A.}^-\text{,OEt})$$

(I)



(II)

Actually, both of the two possible addition products appear to be formed from trinitroanisole and ethoxide, for the kinetics at different temperatures of the forward reaction show that two reactions are occurring. If the rate is measured at, say, 0°, the optical density reaches a considerable value almost immediately after mixing, and then increases relatively slowly. At a lower temperature the rate of the initial reaction can be measured. By choosing suitable temperature ranges, the rates of both the "fast" and the "slow" reactions can be determined (see p. 2533). They are both of the first order with respect to both reactants, and lead to 1 : 1 addition products.

The kinetics of the "fast" reaction at —60° to —80° have been shown to agree with the scheme (T.N.A., OEt is some addition product) :

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

Since ethoxide is in large excess, we have two opposed first-order reactions. If the optical density at time t is D, and at equilibrium D_e, then for a given kinetic run a plot of

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[3] Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.
[4] Meisenheimer, *Annalen*, 1902, **323**, 205.
[5] Hammick and Foster, *J.*, 1954, 2153.
[6] Foster, *Nature*, 1955, **175**, 746.
[7] Foster, personal communication.
[8] Jackson and Earle, *Amer. Chem. J.*, 1903, **29**, 89.

log ($D_e - D$) against time is linear, and the numerical value of the slope s depends on the ethoxide concentration b according to the equation[2] $2{\cdot}303s = k_{-1} + bk_1$. We can thus determine k_1 from the slope of a plot of s against b, and k_{-1} from the intercept. Their ratio k_1/k_{-1} gives the equilibrium constant $K = [(\mathrm{T.N.A., OEt})^-]/[\mathrm{T.N.A.}][\mathrm{OEt}^-]$ and from results at several temperatures we can find the corresponding energies of activation and " frequency factors " for the two " fast " reactions.

The results for the " slow " reaction, measured at temperatures from −20° to +10°, can be analysed to a scheme similar to (1)—except that the equilibrium lies so far to the right that k_{-1} and K have not been measured—if we assume for the moment that the slow reaction is between trinitroanisole and OEt⁻, *i.e.*, that the " fast " and the " slow " reaction are concurrent. However, the experimental plots of s against b are curved (Fig. 4). This may be attributed partly to (i) a salt effect, which is observed on adding a neutral salt and would no doubt be caused also by sodium ethoxide, and partly to (ii) the fact that initially some of the trinitroanisole (of the order of 10%) will be present in the form of the addition product of the " fast " reaction, which will always be effectively at equilibrium, and that this proportion will decrease with time as the " slow " reaction goes effectively to completion. The two effects are difficult to estimate with enough accuracy to apply corrections to the s–b plot ; but k_1 may be determined from the *initial* slope of the plot, at $b = 0$, where both effects are zero. The main rate and equilibrium parameters are summarised in Table 1, with the estimated limits of error.

There is also the possibility, however, that the " slow " and the " fast " reaction are consecutive. The reaction scheme would then involve the slow transformation of the addition product 1 of the " fast " reaction into the other addition product 2 :

$$\mathrm{T.N.A.} + \mathrm{OEt}^- \overset{\text{Fast}}{\rightleftharpoons} \text{Addition product 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Addition product 1} \xrightarrow[k_5]{\text{Slow}} \text{Addition product 2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The rate constant observed for the " slow " reaction would then be equal to $k_5K/(1 + Kb)$, which would give a curved plot of s against b, though of less than the observed curvature. The initial slope of the s–b plot would give Kk_5 as the observed rate constant. The observed energy of activation would then be equal to $E_5 + \Delta H$, and the observed value of $\ln A$ would be equal to $\ln A_5 + \Delta S^\circ/\boldsymbol{R}$. Here K, ΔH, and ΔS° refer to the " fast " reaction (1), and k_5, E_5, and A_5 to the slow transformation (2). From the data in Table 1, this would give $E_5 = 17{\cdot}5 \pm 0{\cdot}8$ kcal. mole⁻¹, and $\log_{10} A_5 = 13{\cdot}4 \pm 0{\cdot}8$ (l. mole⁻¹ sec.⁻¹), implying an entropy of activation of about 11 cal. deg.⁻¹ mole⁻¹. These are not impossible values, and on the present evidence it does not seems possible to decide between the alternatives of concurrent or consecutive reactions.

TABLE 1.

	" Fast " reaction	" Slow " reaction
$\log_{10} k_1$ at −80° (l. sec.⁻¹ mole⁻¹)	−1·09	−4·8 (calc.)
E_1 (kcal. mole⁻¹)	10·4 ± 0·3	13·1 ± 0·2
$\log_{10} A_1$ (l. mole⁻¹ sec.⁻¹)	10·7 ± 0·3	10·9 ± 0·2
E_{-1} (kcal. mole⁻¹)	13·7 ± 0·3	—
$\log_{10} A_{-1}$ (sec.⁻¹)	12·3 ± 0·3	—
$\log_{10} K$ (l. mole⁻¹)	2·07 at −80°	Large at 0°
ΔH (kcal. mole⁻¹)	−3·3 ± 0·6	—
ΔS° (cal. deg.⁻¹ mole⁻¹)	−7·5 ± 3	—

Trinitroanisole–Toluene Complex.—Since substances such as trinitrobenzene form complexes with aromatic hydrocarbons,[9] toluene might form such complexes with trinitroanisole. Since many of the reaction mixtures contained about 1% of toluene by volume (to facilitate solution of trinitroanisole), this possibility was investigated. It was found that addition of toluene did affect the kinetics of the " fast " reaction, but not of the " slow " one. A change of the rate of the " fast " reaction was observed also when benzene, or

[9] Bier, Thesis, Amsterdam, 1954.

especially 2-methylnaphthalene, was used instead of toluene; but with *cyclo*hexane no effect was observed. The effects of these hydrocarbons on the rate lie in the same order as the equilibrium constants of their complexes with trinitrobenzene.[9] The kinetics agreed with the supposition that a complex is formed between trinitroanisole and toluene, that this equilibrium is rapidly set up and always maintained, and that in the "fast" reaction ethoxide reacts concurrently with the complex and with free trinitroanisole, at different rates, to form the addition product, which is the only species that absorbs visible light. The reaction scheme for the "fast" reaction between trinitroanisole and ethoxide thus consists of (1), the complex ion being coloured, accompanied by

$$\text{T.N.A.} + \text{Toluene} \overset{\text{Fast}}{\rightleftharpoons} \underset{\text{(colourless)}}{(\text{T.N.A., Toluene})} \quad . \; . \; . \; . \; . \quad (3)$$

$$(\text{T.N.A., Toluene}) + \text{OEt}^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{\text{(coloured)}}{(\text{T.N.A., OEt})^-} + \text{Toluene} \quad . \; . \quad (4)$$

By varying the concentration of toluene as well as of ethoxide and trinitroanisole, it was possible to evaluate k_{-4} and find a maximum value for k_4, and hence for the equilibrium constant $K_h = (\text{T.N.A., Toluene})/(\text{T.N.A.})(\text{Toluene})$. The detailed kinetics (see p. 2533) show that if $k_1 > k_4$ addition of toluene should retard the reaction at one ethoxide concentration while accelerating it at another; this was experimentally verified. The results showed that K_h was less than about 2 l. mole^{-1} at —60° and —80°. This implies that the proportion of trinitroanisole present as the toluene complex in the usual 1% toluene solvent is not more than about one-fifth. The energy of activation E_{-4} for the reverse of reaction (3) was found to be $9{\cdot}2 \pm 0{\cdot}8$ kcal. mole^{-1}, and the corresponding value of $\log_{10} A_{-4}$ was $7{\cdot}5 \pm 0{\cdot}7$ (l. mole^{-1} sec.$^{-1}$), markedly lower than $\log_{10} A_{-1}$.

The derivation of the rate constants for the "fast" reaction takes account of this complex-formation. It does not affect the "slow" reaction, whose rate was found to be independent of the toluene concentration in the range used. It has not been detected with any of the other nitro-compounds studied in this series of papers.

Reactions of Weak Acids with Additon Products of "Fast" and "Slow" Reactions.—The reaction occurring when the addition product of the "fast" reaction is decolorised by acids has been studied at —70° with trimethylacetic, acetic, β-chloropropionic, and chloroacetic acids, at constant ionic strength and buffer ratio. (It is noteworthy that this reaction is slow enough to be measured, while the corresponding reaction of free ethoxide ion with acetic acid is effectively instantaneous under comparable conditions, as experiments with indicators have shown.) It is possible to derive accurate values for the velocity constant k_2 for the reactions between the unchanged acids and the addition product, which may be written

$$(\text{T.N.A., OEt})^- + \text{HA} \xrightarrow{k_2} \text{T.N.A.} + \text{HOEt} + \text{A}^- \quad . \; . \; . \; . \quad (5)$$

and also approximate values for the velocity constant k_3 for the reaction between hydrogen ion and addition product, which may be written :

$$(\text{T.N.A., OEt})^- + \text{EtOH}_2^+ \xrightarrow{k_3} \text{T.N.A.} + 2\text{HOEt} \quad . \; . \; . \; . \quad (6)$$

Reaction (5) is no doubt subject to a primary salt effect, hence the use of solutions of constant ionic strength.

A logarithmic relation of the Brønsted type has been found to hold between $\log_{10} k_2$ and $\log_{10} K_a$, where K_a is the dissociation constant of the acid (see Fig. 3). The values of k_2 and K_a both refer to the same solvent (ethanol), but whereas the rates are measured at —70° the dissociation constants refer to 25°; however, the available data on the variation of dissociation constants with temperature suggest that the relative values of $\log_{10} K_a$ will not be greatly different at —70°. The exponent α in the Brønsted equation $k_2 = GK_a^{\alpha}$ is given by the slope of the best line through the four points for the carboxylic acids as 0·56.

The results for the hydrogen ion also agree closely with this relation. The fact that the Brønsted equation is obeyed confirms the expectation that the rate-determining steps in reactions (5) and (6) are proton-transfers.[10]

For the corresponding reaction between acids and the product of the "slow" reaction, which could be followed at +10°, the rate was found to depend only on the concentration of hydrogen ion, the undissociated acids having no effect. The exponent α in the Brønsted equation is thus effectively unity. This differs greatly from the value 0·56 for the previous reaction, and suggests that the mechanisms of the two reactions are radically different. This is not surprising if the two coloured species have different structures.

Nature of the Coloured Addition Products, and Mechanisms of Reaction.—It remains to assign one of the two possible structures (I) and (II)—representing respectively an addition compound and a charge-transfer complex—to each of the two coloured species whose reactions we have described. Either structure would account for the colour, the high extinction coefficients ($\sim 10^4$ l. mole^{-1} cm.$^{-1}$), and the general rate–concentration relations for each of the two sets of reactions.

It seems clear that the product of the "slow" reaction is the addition compound of structure (II), since the absorption spectrum of the product at room temperature is identical with that of the product of reaction of trinitrophenetole with methoxide. The product of the "fast" reaction must then be a charge-transfer complex.

Reactions in which no covalent bond is joined or broken are uncommon in chemical kinetics, and it is hoped to consider in a later paper the interpretation of the energies of activation of such reactions, in the light of the results given in this series of papers. It is of interest that the energy of activation E_1 for the "slow" reaction, in which a covalent bond is formed, is decidedly greater than that of the "fast" charge-transfer reaction (13·1 and 10·4 kcal. mole^{-1}, respectively); and that the reaction with acids is much slower for the addition compound than for the charge-transfer complex, as well as having a different Brønsted exponent.

EXPERIMENTAL

Materials.—2 : 4 : 6-Trinitroanisole, prepared by Jackson and Earle's method,[8] had m. p. 67° (lit., 68°). Carboxylic acids were purified by crystallisation, vacuum-distillation, or fractional freezing; titrations agreed closely with the theoretical values for pure acids (99·6% or better), and the f. p.s or b. p.s were as follows: acetic acid, m. p. 16·5° (lit., 16·6°); chloroacetic acid, m. p. 63° (lit., 61·5—63°); β-chloropropionic acid, m. p. 40—40·5° (lit., 41°); trimethylacetic acid, m. p. 35° (lit., 35·3—35·5°). Toluene was prepared by refluxing B.D.H. sulphur-free toluene over sodium and distilling it as required. 2-Methylnaphthalene was recrystallised three times, distilled *in vacuo*, and recrystallised to constant m. p., 34·6—34·8° (lit., 34·44°). Ethanol was dried by Lund and Bjerrum's method;[11] it was always freshly distilled as required. Its water content after manipulation was determined at intervals by Smith's method;[12] it was in the region of 0·2% by vol., an amount which would effect only a negligible change in the ethoxide-ion concentration.[2]

Stock solutions of trinitroanisole in ethanol or in toluene–ethanol (1 : 2 by vol.) could be kept satisfactorily. Solutions of sodium ethoxide and of the carboxylic acids were made up in ethanol as required, and titrated with standard aqueous sulphuric acid or sodium hydroxide.

Thermostat and Reaction Cell.—These were designed so that the reactions could be followed photometrically. They were similar to those described by Caldin and Trickett,[1] but smaller, since lower temperatures were to be used; the optical path in the reaction vessel proper was 7 cm. The bath liquid was an acetone–ethanol mixture. For temperatures down to −70°, solid carbon dioxide in a glass cooling-tower was used as refrigerant. Below this temperature, liquid nitrogen was used; it was contained in a double-walled cylindrical brass vessel with a gap of 2 mm. between the walls;[13] the rate of cooling could be controlled by altering the pressure in the annular space. The level of the liquid nitrogen was automatically kept constant by a manometric device operating a relay which caused liquid nitrogen to be pumped from a storage vessel. The temperature of the bath was measured by a 5-junction thermocouple, calibrated at

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[10] Bell, "Acid-Base Catalysis," Oxford Univ. Press, 1941, Chap. 7.

[11] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[12] Smith, *J.*, 1927, 1284.

[13] Egerton and Ubbelohde, *Trans. Faraday Soc.*, 1930, **26**, 236.

the f. p.s of mercury, chlorobenzene (−45·21°), chloroform (−63·50°), and carbon disulphide (−111·52°), and at the sublimation point of carbon dioxide (−78·40°); no changes were observed on recalibration at intervals over two years. The temperature inside the reaction cell was found, by experiments with a bare thermocouple, to be slightly higher than that of the bath liquid, and a correction was applied to the measured temperature, amounting to 0·12° at −100° and 0·85° at −115°, the lowest temperature used. The uncertainty in the temperature is about ± 0·1°.

Photoelectric Photometer.—This was similar to that used by Caldin and Long;[2] the uncertainty in the measured optical density is about ± 1% if the optical density is above 0·1. An Ilford gelatine filter 623 has been used throughout; it transmits in the region 470—520 mμ, and all the stable coloured species have absorption maxima in the region of 500 mμ. Absorption spectra of solutions were determined by means of a Unicam S.P. 500 spectrophotometer. Unfortunately, this could only be used at room temperature, so that it was not possible to measure the absorption spectrum of the product of the "fast" reaction. The results are shown in Fig.1.

Experimental Procedures.—These were in general similar to those described by Caldin and Long.[2] The only modification occurred in preparing solutions of the coloured species for reaction with acids. The nature of the coloured species depends on the temperature, and therefore an ethanol solution of sodium ethoxide was first brought nearly to the required temperature in the reaction cell, and the trinitroanisole solution then added to it. The buffer ratio and ionic strength were adjusted by adding appropriate solutions by means of calibrated graduated pipettes. The acid solution was kept separate in the siphon tube of the apparatus and added when all was ready for the run.

Methods of determining Rate Constants.—The determination of rate constants from the experimental first-order plots of $\log_{10}(D_e - D)$ against time has been described by Caldin and Long[2] for the simple case where no corrections need be applied for salt effects or for the small amount (usually 1% by vol.) of toluene in the solvent. We adopt the same symbols as those authors.

It was convenient to use concentrations of trinitroanisole (d) of the order of 10^{-5}M, and of ethoxide (b) in the region 0·01—0·1M, so that ethoxide was always in large excess. Similarly, in the reactions with weak acids, the acid was in large excess. Straight lines were always obtained on plotting $\log(D_e - D)$ against time t, or on using the Guggenheim method[14] for first-order reactions.

(i) *Rate constants for the reactions between ethoxide ion and trinitroanisole.* (a) "Fast" reaction in absence of toluene. At −60° and below, the rate of this reaction is convenient for measurement, and the rate of the "slow" reaction is negligible. When the solvent is pure ethanol, the numerical values s of the slopes of the first-order plots at a given temperature are related linearly to the ethoxide concentrations b in the runs. From a plot of s against b we can find k_1 and k_{-1} for reaction (1) by using an equation similar to that used by Caldin and Long, *viz.*,

$$2{\cdot}303s = \mathrm{d}[\log_{10}(D_e - D)]/\mathrm{d}T = k_{-1} + k_1 b \qquad . \quad . \quad . \quad . \quad . \quad (7)$$

The slope of the plot of s against b gives k_1 and the intercept k_{-1}; their ratio $k_1/k\ _1$ is equal to the conventional equilibrium constant K. The fact that the s–b plot is linear indicates that the product of reaction is a 1 : 1 addition product.[15]

(b) "Fast" reaction in presence of toluene. The observations agree with the assumptions that a 1 : 1 complex is formed between trinitroanisole and toluene, that its formation and dissociation are so rapid that it is always at its equilibrium concentration, and that ethoxide reacts concurrently with this complex and with trinitroanisole, at different rates, to form the trinitroanisole–ethoxide addition complex, which is the only absorbing species (cf. equations 1, 3, and 4). Let the equilibrium constant for the trinitroanisole–toluene complex-formation (reaction 3) be K_h, the concentration at time t of this complex be y, that of the ethoxide complex x, and the toluene concentration z. On writing $\mathrm{d}x/\mathrm{d}t$ from equations (1), (3), and (4), and substituting $D = x\varepsilon l$, we find that the plot of $\log_{10}(D_e - D)$ against time will be linear, and the numerical value of the slope s will be given by :

$$2{\cdot}303s = (k_{-1} + zk_{-4}) + b(k_1 + K_h z k_4)/(1 + K_h z) \qquad . \quad . \quad . \quad . \quad . \quad (8)$$

If a series of runs is carried out at constant toluene concentration z but varying base concentration b, the plot of s against b should be linear, with slope numerically equal to

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

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

$0{\cdot}4343(k_1 + K_h z k_4)/(1 + K_h z)$ and intercept $0{\cdot}4343(k_{-1} + zk_{-4})$. From the values of the slope and intercept at several values of z we can find k_4, k_{-4}, and K_h. Differentiating with respect to z, we obtain :

$$2{\cdot}303\, \mathrm{d}s/\mathrm{d}z = k_4 + bK_h(k_4 - k_1)/(1 + K_h z)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If $k_1 > k_4$, the second term may be greater or less than the first according to the value of b; at low base concentration, increase of z will accelerate the reaction, while at higher base concentration it will retard it. This has been observed (Fig. 2).

(c) "Slow" reaction. Here the rate has been found to be independent of the toluene concentration up to 6% by vol., and since all runs were done at a concentration of 1% the rates may be taken to refer to pure ethanol. There is, however, a correction to be applied because of the equilibrium referred to under (i) (a) (p. 2533). The slope of the first-order plot will be lower than would be expected if there were no "fast" reaction, by a factor $1/(1 + Kb)$. Plots of s against b should therefore be curved, and this is observed. The effect could be allowed for if we had an accurate value of K; unfortunately, we have only values extrapolated from the results at much lower temperatures, and the correction cannot be made accurately. The correction, however, although in the right direction, is not enough to account entirely for the deviations of the s–b plots from linearity.

FIG. 1. *Absorption spectra of the coloured solutions produced by adding sodium ethoxide to* (*A*) 2 : 4 : 6-*trinitroanisole,* (*B*) 2 : 4 : 6-*trinitrobenzene,* (*C*) 2 : 4 : 6-*trinitrotoluene, in ethanol at room temperature.*

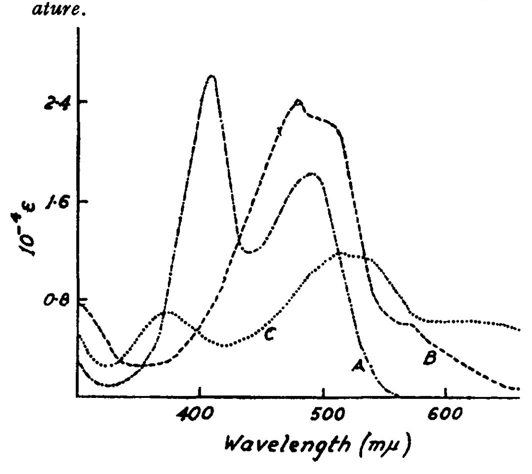
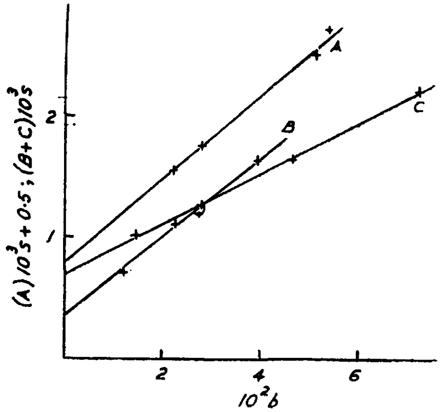


FIG. 2. *Plots of the slope s of first-order kinetic plots against ethoxide concentration b, for the "fast" reaction between ethoxide and trinitroanisole at* −80°.



(Toluene concns. : *A*, 0; *B*, 0·0964M; *C*, 0·61M. Limits of error are indicated by the lengths of the lines.)

There is also an appreciable salt effect. No weak electrolytes are involved, so we need only consider a primary salt effect. As the back reaction is negligible in this particular reaction, the rate constant at constant ethoxide concentration is proportional to s. The relation between s and the ionic strength μ should therefore obey the general equation [16]

$$\log s = \log s_0 + \alpha' z_A z_B \sqrt{\mu} + \alpha'' \mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Here z_A and z_B are the charges on the reactants, μ is the ionic strength, and α', α'' are constants. In the present reaction, one of the reactants is uncharged, so that $z_A z_B = 0$ and the equation becomes

$$\log (s/s_0) = \alpha'' \mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Experiments on the effect of adding lithium iodide, all other concentrations being kept constant, gave results agreeing with this equation, with $\alpha'' \sim 5$ (μ in moles/l.). The sign and order of magnitude of the effect agree with those required to account for the remaining deviations of the s–b plots from linearity. Unfortunately, the constant α'' commonly depends on the salt

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[16] Bell, *op. cit.*, ref. 10, Chap. 2.

added, so we cannot correct for the salt effect by simply using equation (11) with $\alpha'' = 5$. Nor would it be satisfactory to add a neutral salt to keep the ionic strength constant in a series of runs in which the ethoxide concentration varies, since α'' would then vary with the ratio of ethoxide to lithium iodide. In these circumstances it was decided to fit equations to the curved plots and deduce the slopes at zero ethoxide concentration, both corrections then being zero. These slopes give k_1 directly.

(ii) *Rate constants for the reactions between acids and trinitroanisole–ethoxide addition products.* When an acid, such as acetic acid, is added to a solution of the coloured addition product of the reaction between trinitroanisole and ethoxide, the rate of reaction may in the general case contain four terms, corresponding to (i) unimolecular decomposition (equation 1); (ii) reaction with toluene (eqn. 4); (iii) reaction with undissociated acid HA (eqn. 5); and reaction with hydrogen ions (eqn. 6). The kinetics will be of first order with respect to trinitroanisole, and the slope s'' of a first-order plot of $\log_{10} D$ against time will be given in this general case by

$$2{\cdot}303s'' = k_{-1} + zk_{-4} + k_2[\mathrm{HA}] + k_3[\mathrm{H}^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where $[\mathrm{H}^+]$ stands for the concentration of hydrogen ions, which are no doubt solvated, *e.g.*, $\mathrm{EtOH_2}^+$. The first two terms can be found from experiments on the reaction (1). To find k_2 and k_3, rates are measured in solutions of constant buffer ratio, in which $[\mathrm{H}^+]$ is constant. A plot of s'' against [HA] then gives k_2 from its slope. From its intercept and a knowledge of the first two terms, we can find $k_3[\mathrm{H}^+]$, so that if we know $[\mathrm{H}^+]$ we can find k_3 also.

RESULTS

(a) *"Fast" Reaction between Ethoxide Ion and Trinitroanisole* (−60° *to* −80°).—This was investigated at low temperatures, such that the extent of the "slow" reaction was always negligible.

Order of reaction. The reaction is shown to be of first order with respect to ethoxide ion by the linear plots of s against ethoxide concentration. The order with respect to trinitroanisole was found by measuring initial rates at four initial concentrations d, at constant toluene concentration, and nearly constant concentrations b of ethoxide. Table 2, in which concentrations are given in moles/l., shows that $(\mathrm{d}D/\mathrm{d}t)/bd$ is nearly constant for these runs, so that the rate is of the first order with respect to trinitroanisole. The last three runs recorded in this Table show that the rate depends also on the toluene concentration.

TABLE 2.

Temp.	10^4d	10^3b	[Toluene]	$10^4(\mathrm{d}D/\mathrm{d}T)$ (sec.$^{-1}$)	$10^{-3}(\mathrm{d}D/\mathrm{d}T)/bd$
−80°	0·968	2·96	0·965	6·59	2·30
	1·01	3·10	0·965	6·72	2·15
	1·31	2·96	0·965	8·77	2·26
	2·75	3·10	0·965	19·65	2·31
−78·4	0·56	2·46	0·193	2·01	1·47
	1·10	2·46	0·386	5·77	2·14
	1·38	2·46	0·772	8·46	2·49

Rates in pure ethanol and in presence of toluene, at −60° *and* −80°. First-order plots covering at least half the reaction were obtained by using Guggenheim's method,[14] at −60° and −80°, three different toluene concentrations and a range of ethoxide concentrations being used at each temperature. The results are given in Table 3, which shows the slopes s of the observed first-order plots, and also the slopes of the plots of s against b. The experimental uncertainties attached to the values of s, etc., are estimated *limits* of error. Corrections for the change in concentration of the solutions by contraction on cooling have been applied throughout. The plots of s against b for −80° are shown in Fig. 2.

The runs at zero toluene concentration give k_1 and k_{-1} directly on use of equation (6). The ratio k_1/k_{-1} gives K. The values are given in Table 4. The accuracy with which they fit the data may be seen by comparing the values of s calculated from them with the observed values (see Table 3).

The energies of activation and frequency factors calculated from the results at these two temperatures are:

$E_1 = 10{\cdot}4 \pm 0{\cdot}3$ kcal. mole^{-1} $\qquad \log_{10} A_1 = 10{\cdot}7 \pm 0{\cdot}3$ (l. sec.$^{-1}$ mole^{-1})
$E_{-1} = 13{\cdot}7 \pm 0{\cdot}3$ kcal. mole^{-1} $\qquad \log_{10} A_{-1} = 12{\cdot}3 \pm 0{\cdot}3$ (sec.$^{-1}$)
$E_{-4} = 9{\cdot}2 \pm 0{\cdot}8$ kcal. mole^{-1} $\qquad \log_{10} A_{-4} = 7{\cdot}5 \pm 0{\cdot}7$ (l. sec.$^{-1}$ mole^{-1})

The heat-content change and standard-entropy change for the fast addition reaction between trinitroanisole and ethoxide are therefore :

$$\Delta H = -3{\cdot}3 \pm 0{\cdot}6 \text{ kcal. mole}^{-1} \qquad \Delta S^\circ = -7{\cdot}5 \pm 3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Separate measurements of the equilibrium constant in this reaction were not made because the simultaneous occurrence of the " slow " reaction would lead to uncertainty in the measurement of equilibrium densities.

Rates in presence of hydrocarbons other than toluene. The results are shown in Table 5. The temperature was −60°.

TABLE 3. *" Fast " reaction in ethanol and ethanol–toluene.*

Temp.	10^5d (mole/l.)	10^3b (mole/l.)	[Toluene] (mole/l.)	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.$^{-1}$)
−60·0°	1·41	4·33	—	10·6 ± 0·3	10·5	$(4{\cdot}48 \pm 0{\cdot}16)10^{-1}$	$(8{\cdot}50 \pm 0{\cdot}20)10^{-3}$
	7·07	8·66	—	12·9 ± 0·3	12·4		
	1·45	21·0	—	17·3 ± 0·3	17·8		
	1·45	52·5	—	31·7 ± 0·8	31·8		
	2·69	3·45	$9{\cdot}44 \times 10^{-2}$	10·5 ± 0·3	10·4	$(4{\cdot}05 \pm 0{\cdot}15)10^{-1}$	$(9{\cdot}00 \pm 0{\cdot}30)10^{-3}$
	2·69	6·89	$9{\cdot}44 \times 10^{-2}$	11·9 ± 0·3	11·8		
	2·69	10·4	$9{\cdot}44 \times 10^{-2}$	12·8 ± 0·3	13·1		
	2·69	17·3	$9{\cdot}44 \times 10^{-2}$	16·0 ± 0·3	16·0		
	2·69	24·2	$9{\cdot}44 \times 10^{-2}$	19·0 ± 0·4	18·9		
	2·55	4·71	$6{\cdot}27 \times 10^{-1}$	12·4 ± 0·3	12·3	$(1{\cdot}43 \pm 0{\cdot}27)10^{-1}$	$(11{\cdot}65 \pm 0{\cdot}25)10^{-3}$
	2·55	14·2	$6{\cdot}27 \times 10^{-1}$	13·6 ± 0·4	13·6		
	2·55	23·6	$6{\cdot}27 \times 10^{-1}$	14·9 ± 0·2	14·9		
	2·55	28·3	$6{\cdot}27 \times 10^{-1}$	16·1 ± 0·4	15·6		
−80·0°	1·44	21·8	—	1·09 ± 0·03	1·06	$(3{\cdot}54 \pm 0{\cdot}08)10^{-2}$	$(2{\cdot}99 \pm 0{\cdot}15)10^{-4}$
	3·21	50·9	—	2·02 ± 0·05	2·10		
	1·49	53·5	—	2·22 ± 0·06	2·19		
	2·75	11·2	$9{\cdot}64 \times 10^{-2}$	0·72 ± 0·02	0·71	$(3{\cdot}44 \pm 0{\cdot}13)10^{-2}$	$(3{\cdot}25 \pm 0{\cdot}07)10^{-4}$
	2·75	22·5	$9{\cdot}64 \times 10^{-2}$	1·11 ± 0·03	1·10		
	2·75	28·1	$9{\cdot}64 \times 10^{-2}$	1·26 ± 0·04	1·29		
	2·75	39·3	$9{\cdot}64 \times 10^{-2}$	1·65 ± 0·04	1·64		
	2·61	14·4	$6{\cdot}40 \times 10^{-1}$	1·03 ± 0·03	0·95	$(2{\cdot}18 \pm 0{\cdot}05)10^{-2}$	$(6{\cdot}35 \pm 0{\cdot}25)10^{-4}$
	2·61	23·3	$6{\cdot}40 \times 10^{-1}$	1·12 ± 0·03	1·14		
	2·61	46·5	$6{\cdot}40 \times 10^{-1}$	1·65 ± 0·04	1·65		
	2·61	72·2	$6{\cdot}40 \times 10^{-1}$	2·22 ± 0·05	2·21		

TABLE 4. *Rate constants for " fast " reaction.*

Temp.	10^2k_1 (l. sec.$^{-1}$ mole^{-1})	10^4k_{-1} (sec.$^{-1}$)	K (l. mole^{-1})	k_4 (l. sec.$^{-1}$ mole^{-1})	10^3k_{-4} (l. sec.$^{-1}$ mole^{-1})	K_h (l. mole^{-1})
−60°	103 ± 4	196 ± 5	52 ± 4	<0·78	11·5 ± 1·7	<1·6
−80	8·15 ± 0·2	6·9 ± 0·3	118 ± 8	<0·09	1·21 ± 0·14	<1·9

TABLE 5. *Effect of various hydrocarbons on " fast " reaction.*

[Hydrocarbon] (mole/l.)	10^5d (mole/l.)	10^3b (mole/l.)	10^2s (sec.$^{-1}$)	[Hydrocarbon] (mole/l.)	10^5d (mole/l.)	10^3b (mole/l.)	10^2s (sec.$^{-1}$)
			Benzene				
—	7·26	7·21	1·21 ± 0·03	$6{\cdot}79 \times 10^{-1}$	7·26	7·21	1·10 ± 0·03
$3{\cdot}40 \times 10^{-1}$	7·26	7·21	1·18 ± 0·03	$10{\cdot}2 \times 10^{-1}$	7·26	7·21	0·97 ± 0·02
			2-Methylnaphthalene				
—	7·29	6·01	1·18 ± 0·03	$6{\cdot}51 \times 10^{-2}$	7·29	6·01	1·09 ± 0·02
$2{\cdot}17 \times 10^{-2}$	7·29	6·01	1·14 ± 0·03	$2{\cdot}73 \times 10^{-1}$	7·29	6·01	0·98 ± 0·02
			*cyclo*Hexane				
—	6·88	2·07	0·87 ± 0·02	$6{\cdot}66 \times 10^{-1}$	6·88	2·07	0·88 ± 0·02
$3{\cdot}33 \times 10^{-1}$	6·88	2·07	0·85 ± 0·02				

(b) *Reaction between Acids and the Product of the " Fast " Reaction* (−70°).—Kinetic runs were carried out with a series of carboxylic acids at −70°, at constant ionic strength and buffer ratio. Linear first-order plots were obtained. The results are shown in Table 6. Here b = initial ethoxide concentration, c = concentration of acid added, $(c - b)$ = acid concentration in the resulting solution, $r = (c - b)/b$ = buffer ratio of the resulting solution, h = concentration of lithium iodide (added to adjust the ionic strength), μ = ionic strength, and s'' = slope of first-order plot.

TABLE 6. *Reaction between weak acids and product of "fast" reaction at* —70°.

Acid	10^3c (mole/l.)	10^3b (mole/l.)	10^3h (mole/l.)	r	$10^3\mu$ (mole/l.)	$10^3s''$, obs. (sec.$^{-1}$)	$10^3s''$, calc. (sec.$^{-1}$)
Trimethylacetic ...	3·28	1·64	3·36	1·00	5·00	2·23 ± 0·06	2·23
	5·18	2·59	2·41	1·00	5·00	2·57 ± 0·06	2·50
	6·82	3·41	1·59	1·00	5·00	2·60 ± 0·05	2·65
	8·86	4·43	0·57	1·00	5·00	2·85 ± 0·06	2·89
Acetic	3·12	1·56	3·44	1·00	5·00	2·50 ± 0·06	2·50
	6·24	3·12	1·88	1·00	5·00	3·15 ± 0·09	3·17
	8·62	4·31	0·69	1·00	5·00	3·72 ± 0·09	3·68
	10·5	5·25	—	1·00	5·25	4·11 ± 0·08	4·09
β-Chloropropionic	2·80	1·40	3·60	1·00	5·00	3·50 ± 0·08	3·46
	4·01	2·01	2·99	1·00	5·00	3·98 ± 0·10	3·99
	5·93	2·97	2·03	1·00	5·00	4·86 ± 0·10	4·83
	7·64	3·82	1·18	1·00	5·00	5·54 ± 0·13	5·56
Chloroacetic	3·04	1·52	3·48	1·00	5·00	14·3 ± 0·4	14·6
	3·55	1·78	3·22	1·00	5·00	16·6 ± 0·5	15·8
	4·68	2·34	2·66	1·00	5·00	17·3 ± 0·4	18·0
	6·08	3·04	1·96	1·00	5·00	21·0 ± 0·6	21·0
	10·9	5·43	—	1·00	5·43	31·0 ± 0·8	30·7

From these data, linear plots of s'' against the acid concentration [HA] = $(c - b)$ were obtained. The agreement of the best lines with the observed points is shown by the last two columns of Table 6. Values of k_2 were found directly from the slopes of these plots. The intercept (cf. equation 12) gives $k_{-1} + zk_{-4} + k_3[H^+]$. The first two terms in this expression are known from the results on the forward reaction (above) to amount to $10^{-3}(4{\cdot}26 \pm 0{\cdot}16)$ sec.$^{-1}$. The third term $k_3[H^+]$ may thus be found from the intercept. To find k_3, we need to know $[H^+]$. The dissociation constants K_a of the acids in ethanol have not been measured at low temperatures, but reliable measurements have been made for acetic and chloroacetic acids at 25°,[17] and in the absence of better data these have been used as approximations. Values of $[H^+]$ have then been calculated by using activity coefficients calculated from the Debye–Hückel equation with the appropriate values of the dielectric constants.[18] For the other two acids, we have assumed that the change in pK on passing from water to ethanol is the same as for acetic and monochloroacetic acids, which show nearly the same change in pK.[19] The resulting values of k_3 can only be very approximate. The results for k_2 and k_3 are given in Table 7.

TABLE 7. *Rate constants for reaction of acids with product of fast reaction, at* —70°.

Acid	k_2 (l. mole^{-1} sec.$^{-1}$)	$10^{-6}k_3$ (l. mole^{-1} sec.$^{-1}$)	K_a at 25° (mole l.$^{-1}$)
Trimethylacetic	0·54 ± 0·04	—	$2{\cdot}1 \times 10^{-11}$
Acetic	1·00 ± 0·04	—	$3{\cdot}7 \times 10^{-11}$
β-Chloropropionic	1·97 ± 0·08	2·8 ± 0·9	$1{\cdot}84 \times 10^{-10}$
Chloroacetic	9·5 ± 0·3	2·5 ± 0·2	$3{\cdot}0 \times 10^{-9}$

The Brønsted plot of $\log_{10} k_2$ at −70° against $\log_{10} K_a$ (at 25°) for the four acids is shown in Fig. 3. The best straight line through the points is represented by the equation $\log_{10} k_2 = 5{\cdot}73 + 0{\cdot}56 \log_{10} K_a$. The value of k_3 also agrees with this line. If we take the pK of ethanol in ethanol[20] as 19·14, and its concentration as 17 mole/l., the predicted rate constant for hydrogen ion is $2{\cdot}6 \times 10^6$ l. mole^{-1} sec.$^{-1}$, which agrees closely with the values given in Table 7. In view of the extrapolation, the change of charge type, and the use of dissociation constants at 25°, the agreement is striking, and no doubt partly fortuitous. For the solvent considered as an uncharged acid, the predicted rate is about 10^{-5} l. mole^{-1} sec.$^{-1}$, which is less by a factor of about 400 than the observed values. This implies that in the absence of added acid the only effective decolorisation reaction is the unimolecular break-up of addition product, *i.e.*, the reverse of reaction (1).

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

[18] Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312.

[19] Goldschmidt, *Z. phys. Chem.*, 1916, **91**, 46.

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

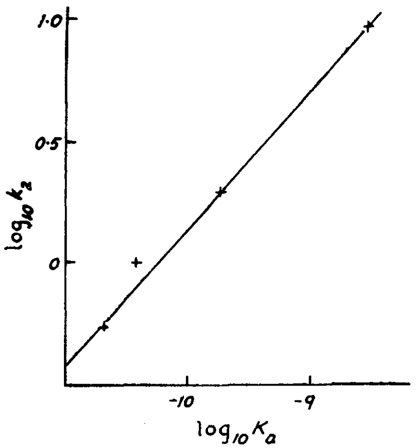
(c) *"Slow" Reaction between Ethoxide Ion and Trinitroanisole* (+10° *to* −20°).—*Order of reaction.* As with the "fast" reaction, first-order dependence on the concentration of ethoxide ion b is shown by linear plots of s against b. The order with respect to trinitroanisole was also found to be unity, by the method of initial rates. The results are shown in Table 8, which shows that $(\mathrm{d}D/\mathrm{d}t)/bd$ is constant. As will be seen, it was necessary to keep the ionic strength constant; in these runs it was $7{\cdot}23 \times 10^{-4}$M. The toluene concentration was 0·096M, and the temperature −30°.

TABLE 8.

10^5d (mole/l.)	10^4b (mole/l.)	$10^4(\mathrm{d}D/\mathrm{d}T)$ (sec.$^{-1}$)	$10^{-3}(\mathrm{d}D/\mathrm{d}T)/bd$	10^5d (mole/l.)	10^4b (mole/l.)	$10^4(\mathrm{d}D/\mathrm{d}T)$ (sec.$^{-1}$)	$10^{-3}(\mathrm{d}D/\mathrm{d}T)/bd$
4·95	7·23	2·60	7·27	9·90	7·23	4·98	6·96
7·43	7·23	3·94	7·34	12·4	7·23	6·58	7·34

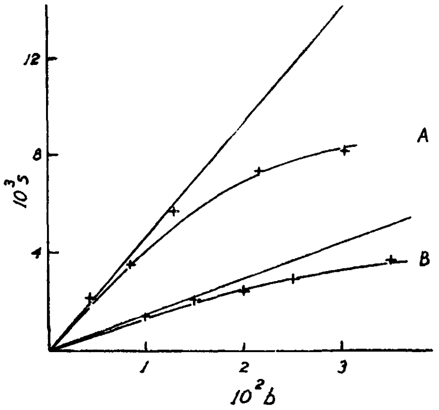
Effect of toluene concentration. This was found to be within experimental error up to a concentration of 0·5M (6% by vol.).

FIG. 3. *Plot of* $\log_{10} k_2$ *at* −70° *against* $\log_{10} K_a$ *at* 25° *for the reaction between carboxylic acids and the product of the "fast" reaction between ethoxide and trinitroanisole.*



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

FIG. 4. *Plots of* s *against ethoxide concn.* b *for the "slow" reaction between ethoxide and trinitroanisole,* (*A*) *at* −10°, (*B*) *at* −20°.



(The initial slopes are also shown. Limits of error are indicated by the lengths of the lines.)

Salt effect. The reaction shows a marked negative salt effect. A series of runs at 0° with added lithium iodide up to about 0·006M, at constant ethoxide concentration (0·0068M), gave results represented approximately by the equation $\log_{10} s = \log_{10} s_0 - 5\mu$.

Runs at varying concentrations of ethoxide. Series of runs with varying concentrations of ethoxide, without added salt, were done at +10°, 0°, −10°, and −20°. The results are given in Table 9. The plots of s against b at a given temperature were all curved (Fig. 4). The

TABLE 9. *"Slow" reaction.*

Temp.	10^6d (mole/l.)	10^3b (mole/l.)	10^3s (sec.$^{-1}$)	Limiting slope of s–b plot (l. mole^{-1} sec.$^{-1}$)	Temp.	10^6d (mole/l.)	10^3b (mole/l.)	10^3s (sec.$^{-1}$)	Limiting slope of s–b plot (l. mole^{-1} sec.$^{-1}$)
+10·0°	9·24	1·75	4·77 + 0·08	2·76	−10·0°	9·43	4·30	1·94 ± 0·03	$0{\cdot}47_4$
	9·24	3·50	9·30 ± 0·14			9·43	8·60	3·51 ± 0·06	
	9·24	5·25	14·1 ± 0·3			9·43	12·9	5·70 ± 0·08	
	9·24	7·00	18·5 ± 0·4			9·43	21·5	7·38 ± 0·11	
	9·24	8·75	23·2 ± 0·7			9·43	30·1	8·28 ± 0·16	
0·0	9·34	1·03	0·830 ± 0·013	1·23	−20·0	9·53	10·0	1·35 ± 0·03	$0{\cdot}17_9$
	9·34	2·65	3·22 ± 0·06			9·53	15·0	2·02 ± 0·05	
	9·34	5·30	6·16 ± 0·10			9·53	20·0	2·43 ± 0·04	
	9·34	10·6	11·6 ± 0·2			9·53	25·1	2·90 ± 0·05	
	9·34	15·9	15·4 ± 0·2			9·53	35·1	3·67 ± 0·05	

curvature is ascribed to a combination of the salt effect and the effect of the equilibrium set up by the " fast " reaction, as mentioned on p. 2533. For reasons there given, it was decided to fit equations to the curves and deduce their limiting slopes at zero ethoxide concentration. This was made easier by the fact that the curves must pass very close to the origin, since separate experiments in which equilibrium was attained showed that K is very large ($>$15,000), so that k_{-1} and hence the intercept will be very small. The " best " values of the limiting slopes were calculated by fitting equations of the type $x = ay + by^2 + cy^3$ to the plots by a least-squares method. These values are given in Table 9, and for two temperatures they are shown in Fig. 4. The values of k_1 derived from the limiting slopes are given in Table 10. It is difficult to assign uncertainties to these values; they are probably in the region of 2—3%.

TABLE 10. *Rate constants for " slow " reaction.*

Temp.	+10·0°	0·0°	−10·0°	−20·0°
k_1 (l. mole^{-1} sec.$^{-1}$)	6·36	2·83	1·09	0·41
k_1, calc. (l. mole^{-1} sec.$^{-1}$)	6·31	2·76	1·10	0·41

The Arrhenius plot derived from these data gives :

$$E_1 = 13{\cdot}1 \pm 0{\cdot}2 \text{ kcal. mole}^{-1} \qquad \log_{10} A_1 = 10{\cdot}9 \pm 0{\cdot}2 \text{ (l. mole}^{-1}\text{ sec.}^{-1})$$

These values of E and A give the values of k_1, calc., shown in Table 10.

(d) *Reaction between Acids and the Product of the " Slow " Reaction* (+10°).—This reaction was investigated at +10°, acetic and monochloroacetic acids being used. The ionic strength was kept constant by adding lithium iodide, since there was found to be a marked positive salt effect. It is known from the results given in the preceding section (c) that there is no appreciable reaction in absence of added acid. With each acid, a series of runs at constant buffer ratio r gave constant values of s'', indicating that the rate depended on [H$^+$] only and not on [HA] : *i.e.*, $2{\cdot}303s'' = k_3[\text{H}^+]$. The results are given in Table 11. Some runs with acetic acid and different buffer ratios, summarised in Table 12, confirmed the result; the last two columns show the observed value of s'' and that calculated on the assumption that the rate is proportional to [H$^+$]. This corresponds to a Brønsted exponent of unity.

An approximate value for k_3 may be calculated from the results in Table 11, by the method used in section (b) above. From the runs with acetic acid, we find $k_3 \sim 8 \times 10^6$ l. mole^{-1} sec.$^{-1}$, and from the runs with chloroacetic acid, 4×10^6 l. mole^{-1} sec.$^{-1}$. The agreement is satisfactory in view of the approximations involved, especially in using values of K_a at 25°.

TABLE 11. *Reaction between weak acids and product of " slow " reaction at* +10°.

Ionic strength = 0·005M. Initial acid concn. = c. Initial ethoxide concn. = b. Buffer ratio = r = $(c - b)/b$.

Acid	10^3c (mole l.$^{-1}$)	10^3b (mole l.$^{-1}$)	r	$10^3s''$ (sec.$^{-1}$)	Acid	10^3c (mole l.$^{-1}$)	10^2b (mole l.$^{-1}$)	r	$10^3s''$ (sec.$^{-1}$)
$CH_3{\cdot}CO_2H$ ...	8·27	0·75	10·0	1·33 ± 0·03	$CH_2Cl{\cdot}CO_2H$	3·33	1·67	1·00	10·4 ± 0·4
	13·5	1·22	10·0	1·43 ± 0·03		4·66	2·33	1·00	9·88 ± 0·2
	23·9	2·17	10·0	1·41 ± 0·03		7·69	3·89	1·00	9·86 ± 0·2
	26·9	2·44	10·0	1·41 ± 0·03		9·78	4·89	1·00	9·94 ± 0·2
	47·8	4·34	10·0	1·41 ± 0·03					

TABLE 12. *Effect of buffer ratio.*

Temperature = + 10°. Ionic strength = 0·001M. Acetate buffers.

r		5·11	6·56	9·15	15·1
$10^3s''$ (sec.$^{-1}$)	obs.	0·75 ± 0·005	0·96 ± 0·02	1·33 ± 0·04	2·45 ± 0·06
	calc.	0·75	0·95	1·33	2·19

The results imply that undissociated acetic and chloroacetic acids react much more slowly with the product of the " slow " reaction than with that of the " fast." The same is true of hydrogen ion; the rates of the two reactions are of the same order at +10° and −70° respectively.

We thank the Department of Scientific and Industrial Research for a maintenance grant (to J. B. A.) during the tenure of which the work described in this and the two following papers was carried out.

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[*Received, November 28th,* 1955.]