490. *The Kinetics and Mechanisms of Some Colour Reactions of Aromatic Nitro-compounds at Low Temperatures. Part IV.** *2 : 4 : 6-Trinitrotoluene : a Second Reaction with Ethoxide Ion.*

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The early stages of the reaction between ethoxide ion and 2 : 4 : 6-trinitrotoluene in ethanol have been examined. By using relatively high concentrations, it is possible to observe the rapid formation of a brown colour, which passes more slowly into the usual purple. The kinetics of the initial fast reaction have been investigated, and the Arrhenius parameters determined. The mechanism of the reaction is discussed.

THE kinetics at low temperatures of the reaction between sodium ethoxide (10^{-2} to 10^{-1}M) and 2 : 4 : 6-trinitrotoluene (*ca.* 10^{-5}M) in ethanol, producing a purple solution, have been described in Part I of this series.[1] It was there mentioned that in much more concentrated solutions it is possible to detect an initial reaction, which rapidly produces a brown solution, passing over slowly into the usual purple. A plot of optical density against time is shown in the Figure; this refers to 0·25M-sodium ethoxide and 0·0061M-trinitrotoluene in ethanol at $-80°$. The curved part of the plot refers to the formation of the brown solution, containing only a small proportion of the purple species. The linear part gives the initial rate of formation of this species, which gives rise to a much higher optical density at equilibrium.

Evidence has been given that the purple species is an anion derived from trinitrotoluene by loss of a proton, and it has been suggested that the brown species is an addition product of trinitrotoluene with ethoxide.[1] Solid addition products with potassium methoxide and with sodium *n*-butoxide have been described.[2,3] Such an addition product might be either a charge-transfer complex or an addition compound of the type described by Meisenheimer.[4] It is of interest to investigate the kinetics of the formation of this addition product, for comparison with those of the proton transfer, and the results are now described. The reaction producing the brown solution will be called the " fast " reaction, to distinguish it from the " slow " reaction which produces the purple solution.

From results such as those shown in the Figure it is possible to determine the rate constants for the initial "fast" reaction (see p. 2549). The rate–concentration relations would be the same for an addition reaction as for a proton-transfer reaction.[1] It is found that for a given run the plot of log ($D_e - D$) against time is linear, D_e and D being the optical densities at equilibrium and at time t, respectively; this indicates a first-order dependence of the rate on the concentration of trinitrotoluene (T.N.T.). The slopes of these plots, when plotted against the ethoxide concentration, are grouped about lines with

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* Part III, preceding paper.

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

[2] Hantzsch and Kissel, *Ber.*, 1899, **23**, 3137.

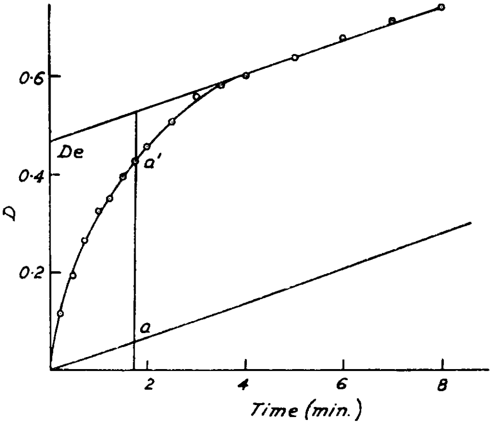
[3] Ryan and O'Riordan, *Proc. Roy. Irish Acad.*, 1919, **34**, *B*, 175.

[4] Meisenheimer, *Annalen*, 1902, **323**, 205.

small slope and large intercept, indicating that an equilibrium is set up in which the concentration of the brown species is small:

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

Because of the low concentration of the coloured species, even at high concentrations of reactants (which make the reaction rather too fast for convenient measurement), the values of k_1 are not very precise; those of k_{-1} are somewhat better. Both k_1 and k_{-1} have been determined at —70°, —80°, and —90°. Below —90°, the reactant solutions were too viscous to mix fast enough. Above —70°, the reaction was too fast to be measured by conventional means; but a few rate measurements were carried out with a rapid-reaction apparatus [5] at about +20°. It has thus been found possible to determine energies of activation and frequency factors with reasonable precision. The results are summarised in Table 1, in the column headed " Fast "; E_1 and A_1 refer to the forward reaction, E_{-1} and A_{-1} to the back reaction. Estimated limits of error are given. The values of the corresponding parameters for the " slow " reaction are given for comparison.



Plot of optical density against time for 0·25M-*sodium ethoxide and* 0·0061M-*trinitrotoluene at* – 80°.

TABLE 1.

	" Fast "	" Slow "
$\log_{10} k_1$ at —80° (l. mole^{-1} sec.$^{-1}$)	—1·7	—3·3
E_1 (kcal. mole^{-1})	12·4 ± 0·3	$13{\cdot}6_4$ ± 0·08
$\log_{10} A_1$ (l. mole^{-1} sec.$^{-1}$)	12·3 ± 0·3	12·0 ± 0·05
E_{-1} (kcal. mole^{-1})	8·2 ± 0·7	10·0 ± 0·5
$\log_{10} A_{-1}$ (sec.$^{-1}$)	7·4 ± 0·6	6·1 ± 0·1
$\log_{10} K$ at —80° (l. mole^{-1})	0·2	1·8
ΔH (kcal. mole^{-1})	4·2 ± 1	3·6 ± 0·4
$\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})	$22{\cdot}_5$ ± 4	27 ± 1·5
Extinction coefficient (l. mole^{-1} cm.$^{-1}$)	$(2 \pm 1)10^3$	$1{\cdot}3 \times 10^4$

It will be seen from Table 1 that the energies of activation E_1 and frequency factors A_1 for the " fast " and the " slow " forward reaction are rather similar. Since the " slow " reaction is believed to be a proton transfer, giving an anion, and the " fast " reaction an addition process, this is rather remarkable. It suggests that the conditions for reaction are fairly similar in the two cases, despite the fact that a covalent C–H bond is broken in one reaction and not in the other. The energy of activation in the proton-transfer reaction would then be due mainly, not to the breaking of the C–H bond, but to the factors common to both the reactions. The largest contribution to E common to both reactions may be the energy required to remove part of the solvent sheath from the reactant molecules to enable them to come together. We hope to return to this matter in a later paper.

[5] Caldin and Trowse, *Discuss. Faraday Soc.*, 1954, **17**, 133.

The large positive standard entropy change for the " fast " reaction is no doubt to be understood in terms of the net desolvation resulting from the partial distribution of the charge over the nitro-groups of trinitrotoluene, which will occur in either of the two possible addition products.[1] The entropy of activation for the forward reaction is +6 cal. deg.$^{-1}$ mole^{-1} and indicates a partial desolvation when the transition state is formed from trinitrotoluene and ethoxide.

The question whether the addition product is a charge-transfer complex or an addition compound cannot be conclusively decided on the present evidence. However, a comparison of the results on the present reaction with those on the " fast " reaction of ethoxide with 2 : 4 : 6-trinitroanisole, which almost certainly gives a charge-transfer complex,[6] and with those on the reaction of ethoxide with *s*-trinitrobenzene, which probably does the same,[7] shows that nearly all the rate and equilibrium parameters fall into regular series. This is shown in Table 2. (The one exception is the value of A_1 for trinitrobenzene; this can be understood, since there might well be steric effects with trinitroanisole and trinitrotoluene that would be absent with trinitrobenzene.) If these regularities are significant, they suggest that the " fast " reaction of trinitrotoluene, like the reactions of trinitroanisole and trinitrobenzene, probably gives rise to a charge-transfer complex.

TABLE 2. *Rate and equilibrium parameters for the reactions of ethoxide with* s-*trinitrobenzene, 2 : 4 : 6-trinitroanisole (" fast " reaction), and 2 : 4 : 6-trinitrotoluene (" fast " reaction).*

	T.N.T. (" fast ")	T.N.B.	T.N.A. (" fast ")		T.N.T. (" fast ")	T.N.B.	T.N.A. (" fast ")
E_1 (kcal. mole^{-1})	12·4	11·7	10·4	A_{-1} (sec.$^{-1}$)	7·4	9·9	12·3
A_1 (l. mole^{-1} sec.$^{-1}$) ...	12·3	13·3	10·7	ΔH (kcal. mole^{-1})	+4·2	+0·3	−3·3
E_{-1} (kcal. mole^{-1})	8·2	11·4	13·7	$\Delta S°_1$ (cal. deg.$^{-1}$ mole^{-1})	+2·2	+16·$_5$	−7·$_5$

It has been assumed so far that the " fast " and the " slow " reaction are concurrent. The possibility that they are consecutive must be considered. The reaction scheme would then be similar to that considered in Part II of this series (equations 1 and 2), *viz.*,

$$\text{T.N.T.} + \text{OEt}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Brown solution} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \text{Purple solution}$$

The observed energy of activation would be $E_5 + \Delta H$; whence from Table 1, $E_5 = 8·2 \pm 1·3$ kcal. mole^{-1}. The observed value of $\log_{10} A$ would be $\log_{10} A_5 + \Delta S°/2·3\boldsymbol{R}$; whence $\log_{10} A_5 = 7·4 \pm 1$ sec.$^{-1}$. This value of E_5 would not be unreasonable, but that of A_5 would be anomalously low, since the formation of the anion in the purple solution would involve a delocalisation of charge, accompanied by desolvation, leading to a positive entropy of activation. It appears therefore that the reactions are probably not consecutive, but concurrent. The results at lower concentrations reported earlier [1] are not affected by the reaction studied in this paper, which would be a negligible side reaction at the lower concentrations.

EXPERIMENTAL

The purification of materials, the apparatus, and the experimental procedures have been described.[1,6] The solvent throughout was ethanol containing 1% by volume of toluene.

Kinetic runs were carried out at −70°, −80°, and −90°. The rate constant for each run was derived from a plot, such as that shown in the Figure, of optical density against time, which shows that the " fast " reaction has progressed far on the way to equilibrium and that the " slow " reaction is in its initial stages. The optical density due to the purple species produced by the " slow " reaction must be allowed for. Since under the conditions of experiment the " slow " reaction gives rise to a linear increase in optical density, it was allowed for by drawing a line through the origin parallel to the linear part of the plot, and taking the length *aa'* as representing the optical density D due to the brown species produced by the " fast " reaction. (D_e is the optical density that would be reached at equilibrium if only the " fast " reaction occurred).

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[6] Ainscough and Caldin, *J.*, 1956, 2528 (Part II).

[7] *Idem, ibid.*, p. 2540 (Part III).

Plots of log (D_e − D) against time were linear. The slopes s of these graphs for various ethoxide concentrations (b) were plotted against b. The plots were more scattered than for the other reactions studied in this series, on account of the high rate of reaction and the small density differences, which had to be read from the curved graph.

The results are shown in Table 3, which gives the slopes of the first-order plots, with the estimated limits of error, at various ethoxide concentrations (b), the T.N.T. concentration (d) being nearly constant; the optical density at equilibrium D_e due to the brown species is also given. The slopes and intercepts of the plots of s against b are given in the last two columns. The derived values of k_1, k_{-1}, and K, with the estimated limits of error, are given in Table 4. Corrections have been applied throughout for the changes in concentration of the solutions by contraction on cooling. An approximate value of k_1 at room temperature, obtained by Dr. G. Long using a rapid-reaction apparatus,[5] is included in Table 4.

TABLE 3. *"Fast" reaction between* 2 : 4 : 6-*trinitrotoluene and ethoxide ion.*

Temp.	10^4d (mole l.$^{-1}$)	10^2b (mole l.$^{-1}$)	D_e	10^3s (sec.$^{-1}$)	Slope of s–b plot (l. mole^{-1} sec.$^{-1}$)	Intercept of s–b plot (sec.$^{-1}$
−70·0°	1·87	2·80	0·136	18·1 ± 0·9	(1·2 ± 0·3)10^{-1}	(1·7 ± 0·2)10^{-2}
	1·87	4·96	0·314	26·3 ± 0·9		
	1·87	5·07	0·269	20·1 ± 1·7		
	1·87	5·78	0·374	23·7 ± 0·6		
	1·87	7·74	0·337	28·7 ± 2·1		
	1·87	11·3	0·628	28·8 ± 0·8		
−80·0	1·89	1·87	0·071	5·23 ± 0·45	(8·3 ± 4·3)10^{-3}	(4·8 ± 0·4)10^{-3}
	1·89	4·57	0·151	5·23 ± 1·33		
	1·89	4·98	0·214	6·55 ± 1·45		
	1·89	8·21	0·364	4·38 ± 0·65		
	1·89	11·5	0·471	6·07 ± 0·60		
	1·89	14·0	0·579	5·70 ± 0·53		
	1·89	15·4	0·672	6·39 ± 0·78		
−90·0	1·91	4·52	0·107	1·73 ± 0·06	(1·4 ± 0·5)10^{-3}	(1·77 ± 0·05)10^{-3}
	1·91	6·51	0·112	1·90 ± 0·08		
	1·91	11·5	0·256	1·86 ± 0·07		
	1·91	12·4	0·378	1·92 ± 0·07		

TABLE 4. *Rate and equilibrium constants for the "fast" reaction between* 2 : 4 : 6-*trinitrotoluene and ethoxide ion.*

Temp.	10^2k_1 (l. mole^{-1} sec.$^{-1}$) obs.	10^2k_1 (l. mole^{-1} sec.$^{-1}$) calc.	10^3k_{-1} (sec.$^{-1}$) obs.	10^3k_{-1} (sec.$^{-1}$) calc.	K (l. mole^{-1})
+19·1°	8·0 × 10^4	9·8 × 10^4	—	—	—
−70·0	28 ± 7	8·3	39 ± 4	34	7·2 ± 2·3
−80·0	1·9 ± 1	1·7	11 ± 1	11·8	1·7 ± 1·0
−90·0	0·33 ± 0·11	0·30	4·1 ± 0·1	3·7	0·8 ± 0·3

The Arrhenius plots of k_1 and k_{-1} against $1/T$ give :

$$E_1 = 12{\cdot}4 \pm 0{\cdot}3 \text{ kcal. mole}^{-1} \qquad \log_{10} A_1 = 12{\cdot}3 \pm 0{\cdot}3 \text{ l. mole}^{-1} \text{ sec.}^{-1}$$
$$E_{-1} = 8{\cdot}2 \pm 0{\cdot}7 \text{ kcal. mole}^{-1} \qquad \log_{10} A_{-1} = 7{\cdot}4 \pm 0{\cdot}6 \text{ sec.}^{-1}$$

The heat of reaction, calculated as $\Delta H = E_1 - E_{-1}$, and the standard entropy of reaction, calculated from $A_1/A_{-1} = \exp(\Delta S^\circ/\boldsymbol{R})$, are therefore :

$$\Delta H = +4{\cdot}2 \pm 1 \text{ kcal. mole}^{-1} \qquad \Delta S^\circ = 22{\cdot}_5 \pm 4 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

The extinction coefficient ε of the brown species has been evaluated by measuring the initial slopes of the plots of density against time, equal to $k_1 \varepsilon lbd$, where l is the length of the optical path, the values of k_1 given in Table 1 being used. The mean value, from the results at −80° and −90°, is $\varepsilon = 10^3 \times (2 \pm 1)$ l. mole^{-1} cm.$^{-1}$.

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