

331. Reactions of Aromatic Nitro-compounds in Alkaline Media. Part II.¹ The Interaction of 1,3,5-Trinitrobenzene and Methanolic Sodium Methoxide.

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1,3,5-Trinitrobenzene and sodium methoxide in methanol rapidly form a 1:1 complex with an absorption spectrum resembling that of the corresponding complex of methyl picrate but with a much smaller equilibrium constant of formation ($K_1 = 15$ l. mole⁻¹ at 28°). The solutions are not stable but fade. The principal products (ca. 90%) of the reaction are 3,5-dinitroanisole and nitrite ions. The reaction is of first order in the concentration of the complex which is not, however, considered to be an intermediate. The differences in behaviour between methyl picrate and trinitrobenzene are attributed mainly to steric effects.

SOLUTIONS of 1,3,5-trinitrobenzene (TNB) in methanolic sodium methoxide present a more complicated case than those of methyl picrate¹ in that they are not stable. Their colour gradually fades and, as is well known, the main products are 3,5-dinitroanisole and nitrite.² The substitution of a nitro-group by methoxide indicates that attachment of a methoxide group to the 1-position is a further possibility for the modes of interaction of an aromatic nitro-compound and methoxide ions, even though the equilibrium concentration of the corresponding complex need not be large. The present Paper examines the kinetics of this nucleophilic substitution reaction, as well as the absorption spectrum, stoichiometry, and thermodynamic stability of the complex present in the coloured solutions.

EXPERIMENTAL

Solutions were prepared as in Part I,¹ the trinitrobenzene used being a commercial sample which was crystallised repeatedly from ethyl alcohol to constant m. p. (122—123°). Absorption spectra were measured on a Unicam S.P. 500 spectrophotometer at an ambient temperature of ca. 28°. For kinetic measurements the reaction vessels were protected from light by metal foil and thermostatted at 40°. Samples were removed for spectrophotometry. Initial optical densities were found by extrapolation to zero time (Fig. 1). Results are summarised in Table 1. Nitrite analyses were carried out spectrophotometrically following Rider and Mellon's

TABLE 1.

Summary of values of D_0 and k at various methoxide concentrations.

	D_0	D_0	10^4k	10^4k		D_0	D_0	10^4k	10^4k
[NaOMe]	(4800 Å)	(4800 Å)	(sec. ⁻¹)	(sec. ⁻¹)	[NaOMe]	(4800 Å)	(4800 Å)	(sec. ⁻¹)	(sec. ⁻¹)
(M)	(exptl.)	(calc.) *	(exptl.)	(calc.) †	(M)	(exptl.)	(calc.) *	(exptl.)	(calc.) †
0.0053	0.086	0.087	0.38	0.40	0.040	0.437	0.439	2.00	1.86
0.0106	0.162	0.162	0.72	0.74	0.120	0.727	0.746	3.03	2.92
0.0158	0.217	0.226	1.07	1.01	0.203	0.879	0.883	3.27	3.32
0.0211	0.285	0.283	1.21	1.25	0.40	0.931	0.990	3.57	3.66
0.0264	0.324	0.332	1.42	1.45	0.84	1.059	1.068	2.87	3.86

* Calc. from equation (4), with K_1 (at 28°) = 15.4 l. mole⁻¹, ϵ_A (4500 Å) = 19,500. † Calc. from equation (8), with K_1 (at 40°) = 20.8 l. mole⁻¹, $k_2 = 4.1 \times 10^{-4}$ sec.⁻¹.

method.³ The procedure was calibrated against a specimen of AnalaR sodium nitrite, the nitrite content of which had been established by titration.⁴ In all experiments the initial stoichiometric concentration of the trinitrobenzene was 5.9×10^{-5} M.

The rate of methanolysis of 1,3,5-trinitrobenzene at 0° was measured by Holleman and van Haeften,² and a reactivity of similar order of magnitude to that in the present work was

¹ Part I, preceding paper.

² Lobry de Bruyn, *Rec. Trav. chim.*, 1890, **9**, 208; Holleman and van Haeften, *Rec. Trav. chim.*, 1921, **40**, 67; Reverdin, *Org. Synth.*, 1927, **7**, 28.

³ Rider and Mellon, *Analyt. Chem.*, 1946, **18**, 96.

⁴ Kolthoff and Belcher, "Volumetric Analysis," Vol. III, Interscience, New York, 1957, p. 69.

deduced. Their result was wrongly interpreted by Bunnett and Zahler⁵ who quote an impossibly large rate constant of $1.6 \text{ l. mole}^{-1} \text{ min.}^{-1}$.

DISCUSSION

At the concentrations studied (TNB, $5.9 \times 10^{-5} \text{ M}$; sodium methoxide, 0.0053—0.84M) a red solution is formed immediately on mixing the reagents, and there is no indication of a build-up of the concentration of the coloured species. On the contrary, the solutions immediately begin to fade. This reaction is sufficiently slow to allow the appearance of the spectrum to be measured by observations taken soon after mixing, but the values of extinction coefficients at selected wavelengths were obtained more reliably by examination of the time-variation of the absorption, and extrapolation to zero time (Fig. 1).

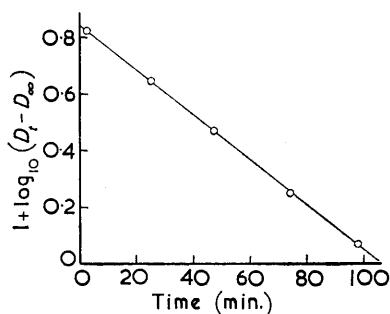


FIG. 1. Specimen run for evaluation of D_0 and rate constant. ($[\text{NaOMe}] = 0.12 \text{ M}$; observations at 4500 \AA).

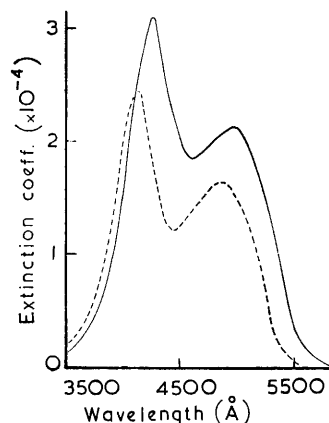
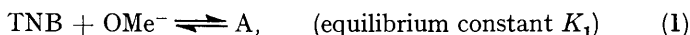


FIG. 2. Absorption spectrum of 1 : 1 complexes of sodium methoxide with trinitrobenzene.

Full line, trinitrobenzene complex. Broken line, comparison spectrum of methyl picrate complex with methoxide.

The stoichiometry of the complex was deduced from the extrapolated D_0 values by the following analysis which is a specific form of the Benesi-Hildebrand treatment.⁶ On the assumption that the complex formation is represented by the equation



we have

$$[\text{TNB}]_{\text{stoich}} = [\text{TNB}] + [\text{A}], \quad (2)$$

and

$$[\text{A}] = K_1[\text{TNB}][\text{OMe}^-]. \quad (3)$$

[The possible addition or elimination of a solvent molecule in reaction (1) is not explicitly included since it would have no verifiable consequences in the following treatment.] Trinitrobenzene itself has negligible absorption at 4500 \AA ; the optical density at that wavelength would therefore be entirely due to the complex A. Hence, for a cell of 1-cm. path-length, $D_0 = \epsilon_A[\text{A}]$, whence, by combination with equations (2) and (3), and rearrangement, we obtain

$$D_0^{-1} = (K_1 \epsilon_A [\text{TNB}]_{\text{stoich}} [\text{OMe}^-])^{-1} + (\epsilon_A [\text{TNB}]_{\text{stoich}})^{-1}. \quad (4)$$

It follows that a graph of D_0^{-1} against $[\text{OMe}^-]^{-1}$ will be linear for the stoichiometry indicated by equation (1). This was confirmed, and from the slope and intercept of the

⁵ Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

⁶ Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

graph the following values (at *ca.* 28°) were calculated: $K_1 = 15.4 \text{ l. mole}^{-1}$; $\epsilon_A(4500) = 19,500$. The same result is conveyed by the agreement between experimental and calculated values of D_0 given in Table 1. Combining this value of ϵ_A with the general shape of the spectrum of the complex, measured rapidly immediately after mixing, the following extinction coefficients are obtained for the two absorption maxima: $\epsilon_A(4250) = 31,200$; $\epsilon_A(4950) = 21,100$; the complete spectrum is recorded in Fig. 2. The absolute intensity of the spectrum (though not its shape) is subject to any error in the evaluation of $\epsilon_A(4500)$.

The rate of decrease in the absorption intensity at 4500 Å reflects the change in [A]. The rate constant, k , evaluated from the slope of graphs such as that in Fig. 1 is given by

$$k = -d \ln (D_\infty - D)/dt = -d \ln [A]/dt. \quad (5)$$

We define a constant k_2 for the rate of formation of product (P) by the equation

$$d[P]/dt = k_2[A]. \quad (6)$$

If it is assumed that TNB and A are rapidly interconvertible and that the starting product is stored in no other form, this rate is also given by

$$d[P]/dt = -d([A] + [\text{TNB}])/dt, \quad (7)$$

and, by combination of equations (3), (5), (6), and (7),

$$k = K_1 k_2 [\text{OMe}^-] / (1 + K_1 [\text{OMe}^-]). \quad (8)$$

A rearranged form of this equation,

$$[\text{OMe}^-]/k = [\text{OMe}^-]/k_2 + (K_1 k_2)^{-1},$$

was tested graphically, and from the slope the value of the rate constant k_2 (at 40°) was found to be $4.1 \times 10^{-4} \text{ sec.}^{-1}$, which, when combined with the intercept, yields a value of 20.8 l. mole⁻¹ for the equilibrium constant K_1 at 40°. This result is consistent with that obtained from the Benesi-Hildebrand plot (15.4 l. mole⁻¹) at a slightly lower temperature (28°). The correctness of equation (8) and of the graphically determined parameters is demonstrated by the agreement between the experimental and calculated values of k in Table 1.

It is known that 3,5-dinitroanisole can be prepared from trinitrobenzene and sodium methoxide.² In order to check how quantitative this reaction was under our conditions, a series of reaction mixtures were allowed to react to completion and the final solutions were analysed for nitrite. The amount of nitrite detected was 90% of the value expected for the replacement of one nitro-group per molecule of trinitrobenzene present initially and showed no regular variation with the concentration of methoxide in the solution (Table 2). The final absorption spectrum of the solution had maxima at 2450 Å (ϵ 16,800)

TABLE 2.

Number of nitrite ions produced in reaction per molecule of trinitrobenzene present initially.

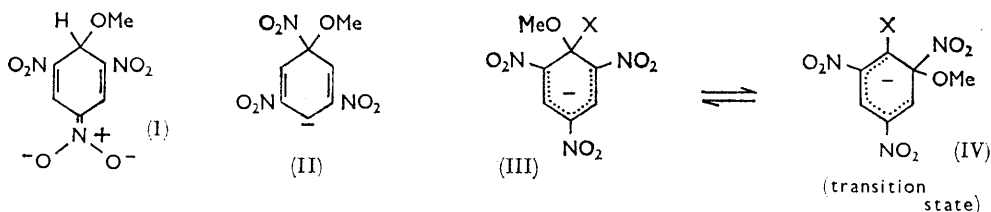
10[NaOMe]	1.06	1.58	2.11	2.64	20.3	84.0
[NO ₂ ⁻] _∞ /[TNB] ₀	0.94	0.88	0.89	0.91	0.89	0.92

and 3350 Å (ϵ 3400), and a minimum at 3056 Å (ϵ 2330), where the extinction coefficients are based on a product concentration of $5.9 \times 10^{-3} \text{ M}$. The positions of the maxima and minimum coincide almost exactly with those of a spectrum of 3,5-dinitroanisole in aqueous solution (2500, 3400, and 3050 Å, respectively) given by Kortüm,⁷ but the extinction coefficients match up less well (15,100, 1300, and 2900, respectively). In addition, the product spectrum has a broad absorption maximum centred at 4800 Å (ϵ 1700) the origin

⁷ Kortüm, *Z. phys. Chem.*, 1939, **42b**, 65.

of which is not known. The measurements leave no doubt that the main cause of the fading reaction is the nucleophilic displacement of one nitro-group per molecule, with *ca.* 10% of unidentified side-reactions. Poorer yields have been reported for this reaction under preparative conditions.⁸ It seems probable that this is due to the vigorous method employed, and that the superior yields achieved with sodium carbonate and sodium hydrogen carbonate⁸ are made possible by the low methoxide concentrations which such solutions would contain as a consequence of solvolysis of the salt, although a more specific role of the carbonate ion remains an alternative explanation.⁸ The balance of product under our conditions may contain some methyl picrate (which is stable under the experimental conditions used¹) which could be formed by oxidation of a complex of structure (I) (with resonance contributions from the analogous forms with the negative charge on the other nitro-groups). It is, however, clear from the appearance of the final spectrum that methyl picrate is not the only product of the side-reactions.

Qualitatively, the behaviour of trinitrobenzene closely resembles that of methyl picrate. The spectra in Fig. 2 indicate a far-reaching similarity between the complexes in the two cases, and, accordingly, structure (I)⁹ is accepted for the 1 : 1 complex of trinitrobenzene. However, there are larger quantitative differences, *viz.*, the equilibrium constant of formation of the complex is roughly 500 times greater for methyl picrate, the methanolysis of trinitrobenzene is much faster (by an unascertained factor in view of the extreme slowness of the reaction of methyl picrate), and the rate of formation of 1 : 1 complex is also faster for trinitrobenzene. The explanation of the difference in equilibrium constants may be partly electronic and partly steric in origin. The inductive effect of a methoxyl group would reinforce the withdrawal of electrons from the carbon atom to which it is attached and thereby promote the attachment of a nucleophilic methoxyl group. Complex-formation in methyl picrate may also relieve steric strain between the methoxyl group and the two flanking nitro-groups by allowing the methoxyl group to bend out of the plane of the aromatic ring, and this may be more important. No such relief operates in the case of trinitrobenzene, where a hydrogen atom is similarly bent away from its aromatic position.



The lower reactivity of methyl picrate in the substitution reaction may be a direct consequence of the order of stability of the complexes. The fact that the rate of the reaction in the case of trinitrobenzene is proportional to the concentration of the coloured complex A does not imply that A must be an intermediate in this reaction. Indeed, if A had the formula (I), such a path would be highly improbable. What the kinetic order implies is that the transition state of the reaction has the same stoichiometric composition ($\pm n$ solvent molecules) as the complex A. A structure best represented by formula (II) and its analogues is both compatible with this requirement and chemically reasonable. The low reactivity (*i.e.*, low concentration of the corresponding transition state for methyl picrate) therefore arises because the high stability of structure (I) of Part I¹ leaves an inadequate concentration of free methyl picrate to react with methoxide ions at the nitro-group. Put another way, the reaction velocity is controlled by the value of the equilibrium constant for the hypothetical reaction (III) \rightleftharpoons (IV) (and its analogue for the *p*-position relative

⁸ Izzo, *J. Org. Chem.*, 1959, **24**, 2026.

⁹ Foster, *Nature*, 1959, **183**, 1042.

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to the group X).^{*} Factors due to the group X which favour the stability of the complex A, on the left-hand side of this equation, must reduce the concentration of transition states.

Our finding that the attainment of equilibrium for complex-formation is too rapid for observation by ordinary techniques is paralleled by Ainscough and Caldin's results for ethanolic sodium ethoxide solutions.¹⁰ These authors report that only a "fast" reaction (similar in speed to the "fast" reaction of methyl picrate) occurs with trinitrobenzene. However, our spectrum of the methoxide complex of trinitrobenzene differs considerably from Ainscough and Caldin's spectrum of the corresponding ethoxide complex,¹¹ although, in the case of methyl picrate, our results (for the 1 : 1 complex) agree very well¹¹ with theirs for ethoxide. A similar point has already been made by Foster.⁹ It appears that the occurrence of solvolysis, the effects of which we were careful to minimise in the absorption measurements, is partly responsible for the deviation of Ainscough and Caldin's methyl picrate-ethoxide result. In view of the close similarity between the spectra in Fig. 2 we agree with Foster⁹ that the "fast" reaction between trinitrobenzene and methoxide ion generates the same type of complex (I) as the "slow" reaction in the case of methyl picrate. This interpretation differs from that of Ainscough and Caldin who inferred that both "fast" reactions led to charge-transfer complexes and that a Meisenheimer complex was not formed from trinitrobenzene. Our description of the situation is thus that the equilibrium constant for 1 : 1-complex formation (*i.e.*, k_1/k_{-1}) is several hundred times greater for methyl picrate than for trinitrobenzene, whereas k_1 itself must be much greater in the case of trinitrobenzene. This difference in rates was not measurable by our technique. Ainscough and Caldin's system suggests a ratio of the order of 10^3 to 10^4 . The implication is that the rate constant k_{-1} for methyl picrate is several powers of ten smaller than k_{-1} for trinitrobenzene, a conclusion which again is intelligible only if a steric effect of the flanking nitro-groups is of paramount importance in methyl picrate. Whatever interpretation is adopted, the results imply that the methoxyl group in methyl picrate reduces k_1 and increases K_1 relative to the values for trinitrobenzene. The steric interpretation requires that, for the methyl picrate system, steric strain is greatest in the transition state of methoxide addition; smaller in the parent molecule, and least in the complex. Acid catalysis of the discharge of the colour of solutions of the 1 : 1 complexes^{10,11} is intelligible in terms of protonation of a nitro-group, the loss of methoxide being either concerted (for general acid catalysis) or subsequent to the establishment of a protonation equilibrium (specific hydrogen-ion catalysis).

The occurrence of methanolysis also offers an explanation for Kharasch, Brown, and McNab's report¹² of hydrogen exchange between trinitrobenzene and sodium hydroxide (0.02M) in ethan[²H]ol after 68 hours at 110°. They observed a decrease in the deuterium content of the alcohol, and attributed this to replacement of nuclear protons. The conclusion seems surprising since Ketelaar, Bier, and Vlaar found¹³ that no exchange occurs with 8N-sodium hydroxide. It is now clear that trinitrobenzene would undergo solvolysis under the conditions used by Kharasch *et al.* In the presence of sodium hydroxide some of the dinitroanisole formed may go on to form 3,5-dinitrophenol which would incorporate deuterium not only in the hydroxyl groups but also in the nucleus. Alternatively, the deuterium may be taken up by the by-products of the reaction under these conditions.⁸

The formation of complexes between trinitrobenzene and amines has recently been discussed in some detail.¹⁴ The structural possibilities with amines are more varied than

* Formulæ such as (III) and (IV) are a convenient notation for the arrangement of nuclei represented by them, but they should not be allowed to obscure the fact that the net negative charge will whenever possible reside on the oxygen atoms of the nitro-groups.

¹⁰ Ainscough and Caldin, *J.*, 1956, 2540.

¹¹ Ainscough and Caldin, *J.*, 1956, 2528.

¹² Kharasch, Brown, and McNab, *J. Org. Chem.*, 1937—1938, 2, 36.

¹³ Ketelaar, Bier, and Vlaar, *Rec. Trav. chim.*, 1954, 73, 37.

¹⁴ Foster and Mackie, (a) *Tetrahedron*, 1961, 16, 119; (b) *ibid.*, 1962, 18, 161; (c) *J.*, 1962, 3843, and references therein.

with methoxide ion as base. Some of these obviously have no relevance to our simpler system. However, Miller and Wynne-Jones¹⁵ noted the appearance of an electron spin resonance in certain amine solutions, pointing to the formation of an odd-electron species, and some of our alkoxide solutions were therefore examined by this method. To check our procedure we repeated, and were able to confirm, Miller and Wynne-Jones's measurements for trinitrobenzene–diethylamine, both in the presence and in the absence of added acetone.¹⁵ This spectrum is generated during the course of a slow reaction¹⁵ (possibly photochemical in nature¹⁶), and its significance in connection with complex-formation has been questioned.¹⁴ By contrast, we obtained no spectrum from solutions of trinitrobenzene in methanolic sodium methoxide or ethanolic sodium ethoxide; also, a spectrum was not given by methyl picrate in the former system. These negative results are required by our interpretation. On addition of acetone to the methoxide solution of trinitrobenzene a distinct spectrum (with more detail than the spectra with diethylamine) appears. Spectra were likewise obtained by similar additions of ethyl methyl ketone, diethyl ketone, or cyclohexanone, their appearance depending markedly on the ketone added.¹⁷

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¹⁵ Miller and Wynne-Jones, *Nature*, 1960, **186**, 149.

¹⁶ Lagercrantz and Yhland, *Acta Chem. Scand.*, 1962, **16**, 1043, 1799.

¹⁷ Gold and Rochester, unpublished results.
