330. *Reactions of Aromatic Nitro-compounds in Alkaline Media. Part I. The Formation of Complexes of Methyl Picrate in Methanolic Sodium Methoxide.*

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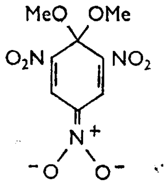
The reaction between methyl picrate (2,4,6-trinitroanisole) and sodium methoxide in methanol solution leads to a 1 : 1 complex which is responsible for the red colour of the solutions [$\lambda_{\text{max.}}$ 4100 Å (ε 24,200), 4860 Å (ε 16,300), and 2500 Å (ε 8700)] at low concentrations of base. The equilibrium constant ([Complex]/[Methyl picrate][OMe^-]) has a value of 7700 l. $mole^{-1}$. The formation of the complex is measurably slow, and this supports the view that it is due to covalent interaction between nitro-compound and base. At high concentrations of base the absorption spectrum assumes a different shape, which suggests the formation of a second complex the concentration of which is governed by a higher power of the concentration of methoxide.

Reactions of aromatic nitro-compounds with bases have in the past received attention on several accounts. First, the formation of highly coloured solutions has long been known [1–3] and solid products can sometimes be isolated.[2] The interpretation of the colour (and, later, of the absorption spectrum [4]) in relation to possible structures of a complex, or complexes, has remained a subject of interest for over 80 years. Structural formulations which have survived to the present day include the addition complex which, for the interaction of methyl picrate (PicOMe) and methoxide ions, is written as (I) (it being understood that in the mesomeric structure the net negative charge is shared between the three nitro-groups). We shall follow general usage in referring to (I) as a Meisenheimer complex, but note that Meisenheimer's formula [5] actually included the addition of the alkali-metal cation to an oxygen atom of the *p*-nitro-group. Alternatively, it has been suggested that the colour is due to an anion formed by removal of a proton from the aromatic ring,[6,7] or from a side-chain if this contains a potentially acidic hydrogen atom.[8] Another possibility arises solely from the high electron affinity of a polynitro-compound, which may lead either to complete electron transfer from the base [9] or to a charge-transfer interaction in which the ground state of the complex is weakly polar and the wave function of the excited state corresponds to more extensive charge transfer.[10] Since all these proposals are, at least to some extent, supported by



(I)

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[1] Hepp, *Annalen*, 1882, **215**, 345.
[2] Lobry de Bruyn, *Rec. Trav. chim.*, 1895, **14**, 89, 150.
[3] Lobry de Bruyn, *Rec. Trav. chim.*, 1890, **9**, 208; 1894, **13**, 122, 126; 1901, **20**, 120.
[4] Foster, *Nature*, 1959, **183**, 1042.
[5] Meisenheimer, *Annalen*, 1902, **323**, 205.
[6] Pollitt and Saunders, *Proc. Chem. Soc.*, 1962, 176.
[7] Baliah and Ramakrishnan, *Rec. Trav. chim.*, 1959, **78**, 783; 1960, **79**, 1150.
[8] *E.g.*, Lewis and Seaborg, *J. Amer. Chem. Soc.*, 1940, **62**, 2122; Briegleb and Delle, *Z. Elektrochem.*, 1960, **64**, 347; Ainscough and Caldin, *J.*, 1956, 2546; Slough, *Trans. Faraday Soc.*, 1961, **57**, 366.
[9] Miller and Wynne-Jones, *Nature*, 1960, **186**, 149.
[10] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801; *Rec. Trav. chim.*, 1956, **75**, 845.

experiment, it is prudent to assume that more than one of them will maintain its place in a complete scheme of things. One should therefore approach the study of any particular system without preconception as to the structures involved, and one must not transfer conclusions from one system to another without supporting evidence.

A second aspect of interest is the occurrence of nucleophilic aromatic substitution reactions [11] in systems of this type.[12] A third group of investigations has taken advantage of the colour formation, and used aromatic nitro-compounds as indicators in the determination of the acidity function H_- for basic solvent systems,[13] on the assumption that the coloured species are formed by proton loss, generally from an amino-group.

The investigation of which the present Paper is Part I aims to connect these different aspects of the same problem. Almost at the outset of our experiments we became aware of the effect of light on certain complexes,[14] and a study of photochemical reactions has been related to measurements of absorption spectra, the quantitative study of equilibria, and the kinetics of complex-formation, and to rates of solvolytic reactions in the absence of light. The reactions of aromatic polynitro-compounds have been studied in dilute solution in either water or methanol, using sodium hydroxide or methoxide, respectively, as the added base. Most of the substrates studied were derivatives of 1,3,5-trinitrobenzene, including (in addition to the parent compound) the hydroxy-, methoxy-, amino-, and dimethylamino-derivatives. For the sake of clarity, in order not to blur differences in behaviour between different systems, the work is arranged in several Parts.

Solutions of methyl picrate in methanolic sodium methoxide represent a convenient starting point. In contrast to other systems, replacement of the substituent group by base does not, in this case, lead to a different product, so that one general complication is avoided. Furthermore, there is fairly conclusive infrared-spectroscopic evidence [15] (based on the study of many alkyl picrate complexes with alkoxides) that (I) is the structure of the anion in the crystalline complex. There must be a strong presumption that no change in structure occurs on dissolution. This hypothesis has been partly confirmed by the observation of only a single methyl resonance (apart from the solvent signal) in the nuclear magnetic resonance spectrum of the complex in acetonitrile, the intensity of the signal being twice that observed for methyl picrate in the same solvent.[16] However, in view of the fact that the ultraviolet spectra of the systems PicOEt + OEt^- in ethanol and PicOMe + OMe^- in methanol (which cannot contain the same complex) are indistinguishable (Fig. 1), the identity of the electronic spectra of the systems PicOEt + OMe^- and PicOMe + OEt^- is inconclusive in this respect.[17] Solutions of methyl picrate in methanolic sodium methoxide are quite stable, provided that light is excluded. The complication of abstraction of a proton from the side-chain is improbable even for the most basic media used.

Throughout this series the term " complex " is used to describe any reversibly formed product of reaction between nitro-compound and base. It is intended to have no structural implication, and it need not signify an associative reaction product.

EXPERIMENTAL

Methyl alcohol (Analar; 500 ml.) was refluxed with magnesium turnings (2·5 g.) and mercuric chloride (0·1 g.), and distilled, a middle fraction being retained.[18] A stock solution of sodium

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[11] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

[12] Holleman and van Haeften, *Rec. Trav. chim.*, 1921, **40**, 67.

[13] (*a*) Ridd, *Chem. and Ind.*, 1957, 1268; (*b*) Stewart, O'Donnell, Cram, and Rickborn, *Tetrahedron*, 1962, **18**, 1917, and references therein; (*c*) Lambert and Schaal, *Compt. rend.*, 1962, **255**, 2256.

[14] Gold and Rochester, *Proc. Chem. Soc.*, 1960, 403.

[15] Dyall, *J.*, 1960, 5160; see also Foster and Hammick, *J.*, 1954, 2153.

[16] Crampton and Gold, unpublished results.

[17] Cf. Foster, *Nature*, 1955, **176**, 746.

[18] Reverdin, *Org. Synth.*, 1927, **7**, 28.

methoxide in methanol was prepared by mixing freshly cut pieces of sodium in AnalaR methanol for about 10 sec. and then transferring them as quickly as possible to the purified methanol which was refluxed while being protected by a soda-lime tube. The solution, being slightly cloudy, was filtered through sintered glass (No. 4) under nitrogen, and diluted with purified methanol as required. The concentration was established by titration of samples diluted with water against aqueous hydrochloric acid which had been related to anhydrous sodium carbonate as standard.

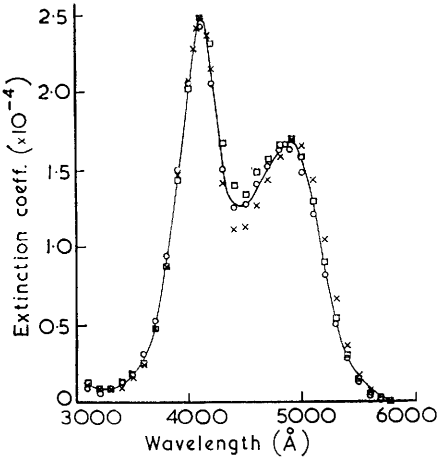

FIG. 1. Absorption spectra of methyl and ethyl picrate in alcoholic alkoxide solutions. ○ PicOMe in MeOH + 0·128M-NaOMe; □ PicOEt in MeOH + 0·075M-NaOMe; × PicOEt in EtOH + 0·046M-NaOEt.

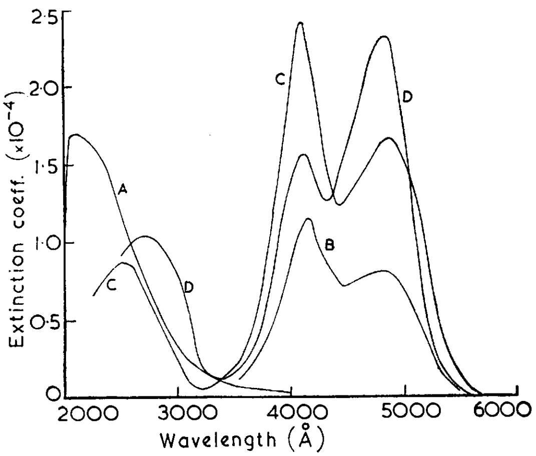

FIG. 2. Typical absorption spectra for the system methyl picrate–sodium methoxide in methanol. [NaOMe]: A, 0; B, $2 \cdot 1 \times 10^{-4}$M; C, 0·128M; D, 2·57M.

Ethyl alcohol (AnalaR) was used without purification.

Methyl and ethyl picrate were crystallised from ethyl alcohol to constant m. p. (68 and 78°, respectively), and dried in a vacuum desiccator.

Dependence of light-absorption of methyl picrate ($3 \cdot 43 \times 10^{-5}$M) on concentration of sodium methoxide, for selected wavelengths.

	Optical density						Optical density				
[NaOMe] (M)	at 4100 Å	at 4800 Å	$10^3 k_{obs}$* (sec.$^{-1}$)	α †	$10^{-3} K_1$	[NaOMe] (M)	at 4100 Å	at 4800 Å	$10^3 k_{obs}$* (sec.$^{-1}$)	α †	$10^{-3} K_1$
0·000082	0·290	—	—	0·349	7·7	0·128	0·830	0·559	—	1·000	—
0·000205	0·491	—	—	0·591	7·9	1·54	0·826	0·585	—	—	—
0·000246	0·504	—	1·21	0·607	6·9	2·05	0·736	0·602	—	—	—
0·000410	0·630	—	2·38	0·759	8·2	2·38	0·670	0·694	—	—	—
0·000815	0·688	—	—	0·828	6·2	2·57	0·533	0·780	—	—	—
0·00122	0·713	—	—	0·859	3·1	2·80	0·560	0·812	—	—	—
0·0051	0·829	0·550	—	0·999	—						

* First-order rate constant for attainment of equilibrium. † Fraction of methyl picrate converted into first complex (calc. as $D_{4100}/0 \cdot 830$).

(Value calculated on the assumption that methyl picrate does not absorb at this wavelength, and that a negligible concentration of the second complex is present.)

Absorption spectra were measured on a Beckman DU quartz spectrophotometer, a pair of matched 1-cm. cells in a thermostatted cell housing at 25° being used (Figs. 1 and 2, and Table). The first-order rate of attainment of equilibrium was followed in two cases by observation of the optical density at 4100 Å as a function of time (Fig. 3).

DISCUSSION

On addition of sodium methoxide to a solution of methyl picrate (at a stoicheiometric concentration, $a = 3{\cdot}45 \times 10^{-5}$M) in methanol, two new absorption bands with maxima at 4100 and 4860 Å appear (Fig. 2). On increasing the concentration of base (which always exceeded that of methyl picrate), the two maxima increase together. The absorption intensity of the stronger band at 4100 Å tends to a maximum value which is reached at a methoxide concentration of $5{\cdot}1 \times 10^{-3}$M and remains constant thereafter for at least a 25-fold increase in concentration. At very much higher methoxide concentrations (1·5—2·8M) the absorption intensity at 4100 Å decreases, and this is associated with an increase in absorption at 4800 Å. The appearance of the spectrum agrees with that reported in in the presence of ethanolic sodium ethoxide.[4]

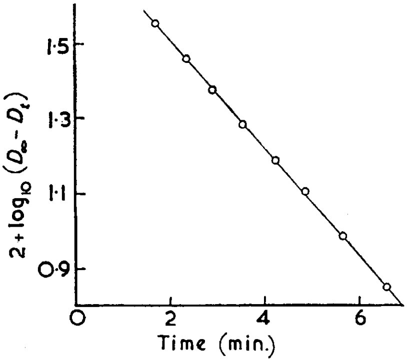

FIG. 3. Rate of attainment of equilibrium (first complex) for methyl picrate ($3{\cdot}43 \times 10^{-5}$M) and methanolic sodium methoxide ($4{\cdot}1 \times 10^{-4}$M).

The constancy of the absorption intensity at 4100 Å over a wide range of methoxide concentrations indicates the stoicheiometric completeness of the first equilibrium reaction at that stage. Consequently the fraction of methyl picrate (α) converted into this product can be evaluated at lower methoxide concentrations from the optical density at 4100 Å. The dependence of α on the stoicheiometric methoxide concentration b indicates that methyl picrate and methoxide interact in a molar ratio of 1 : 1, *i.e.*, corresponding to:

$$\text{PicOMe} + \text{OMe}^- \underset{-1}{\overset{1}{\rightleftharpoons}} \text{A} \qquad \text{(equilibrium constant } K_1\text{)}$$

$$\alpha(1-\alpha) \qquad (b - a\alpha) \qquad a\alpha$$

From the equilibrium concentrations indicated, we obtain

$$K_1 = \alpha/\{(b - a\alpha)(1-\alpha)\}.$$

Values of K_1 calculated from this expression are given in the Table. The best value obtained graphically is $K_1 = 7{\cdot}7 \times 10^3$ l. mole^{-1}.

The change in the absorption spectrum at the very much higher methoxide concentrations is attributed to a second complex formed by further reaction between the first complex and methoxide, the degree of conversion depending steeply on the stoicheiometric methoxide concentration. From the available data (Table) the relationship between the extent of conversion into the second complex and the methoxide concentration cannot be unambiguously deduced. If the assumption is made (which appears reasonable from the shape of the spectra) that the second complex has no light-absorption at all at 4100 Å, the concentration of the complex can be calculated, and the corresponding ratio of the concentration of second to first complex is found to be proportional to a high power (*ca.* third or fourth) of the concentration of sodium methiodide. This species may be identical with the 1 : 2 complex isolated by Jackson and Earle.[19] If one assumes the second complex to have some absorption at 4100 Å, this concentration-dependence becomes even steeper. The high power of methoxide cannot be taken to imply that the second complex is the result of an interaction of methyl picrate with four or five methoxide ions, but is more reasonably interpreted as being due to a high-power concentration-dependence of the appropriate acidity function of sodium methoxide solutions for the further reaction of the first complex. In fact, over this particular range of concentrations of sodium methoxide, the H_- function deduced by Ridd from the indicator behaviour of 2,4-dinitroaniline and 2,4-dinitrodiphenylamine [13a] exhibits a concentration-dependence very similar to that required by our data. On this basis the second complex is likely to involve two methoxide ions per methyl picrate molecule.

For the higher methoxide concentrations listed in the Table the spectra of solutions that were kept in the dark were invariant with time. For the least-basic media, however, the spectrum of the first complex was not produced immediately on mixing the solutions, and the rate of attainment of the equilibrium could be followed by observing the growth of the absorption maximum at 4100 Å. The reaction was of first order (Fig. 3) and, using the simplification $a \ll b$, we can express the observed rate constant as

$$k_{\text{obs}} = k_1 b + k_{-1} = k_1(b + K_1^{-1})$$

and obtain rough values for k_1 (4 l. mole^{-1} sec.$^{-1}$) and k_{-1} (5×10^{-4} sec.$^{-1}$). Our value of k_1 (for reaction with sodium methoxide in methanol at 25°) can be compared with a value of 6·36 l. mole^{-1} sec.$^{-1}$ deduced by Ainscough and Caldin [20] for the "slow" reaction of methyl picrate with ethanolic sodium ethoxide at 10°. (These workers also observed a more rapid reaction on mixing, the "fast" reaction, which was tentatively ascribed to the formation of a charge-transfer complex.) It is clear that Ainscough and Caldin's system must eventually lead to the ethoxide complex of ethyl picrate.[21] However, a consideration of the behaviour of methyl picrate in methanolic sodium methoxide and of ethyl picrate in ethanolic sodium ethoxide, in particular our value of the equilibrium constant K_1 in the former case, makes it unlikely that the methoxide–ethoxide replacement would interfere with measurements of the "slow" reaction. From the kinetic order Ainscough and Caldin formulated the absorbing species formed in the "slow" reaction as a 1 : 1 complex, and also considered it to be a Meisenheimer complex. The constant k_1 in our system is many orders of magnitude smaller than a diffusion-controlled process would require, and this strengthens the view that a covalency change occurs during the formation of the complex A, such as would be required if A is a Meisenheimer complex (I).

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[19] Jackson and Earle, *Amer. Chem. J.*, 1903, **29**, 89.
[20] Ainscough and Caldin, *J.*, 1956, 2528.
[21] Jackson and Boos, *Amer. Chem. J.*, 1898, **20**, 449.