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SOME STRUCTURAL, EQUILIBRIUM AND KINETIC STUDIES OF AROMATIC NITRO-COMPOUNDS WITH NUCLEOPHILES

by

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ABSTRACT

The interactions of certain aromatic nitro compounds with nucleophiles in protic solvents and in protic dipolar aprotic solvent mixtures have been investigated using the techniques of proton magentic resonance and visible spectroscopy.

Picrate ion reacts with concentrated aqueous sodium sulphite to give an unusual ion carrying five negative charges. This results from the covalent addition of two sulphite molecules to the picrate ion, at ring carbon carrying hydrogen. At low sulphite concentration a 1:1 adduct is produced. The equilibrium constants for the formation of these complexes have been determined. Solvent effects on the formation of 1:1 adduct were examined in water-dimethyl sulphoxide mixtures. With hydroxide ion in aqueous solutions, the major of the picrate ion is to give a 1:2 adduct.

1,2,3,5-Tetranitrobenzene reacts with hydroxide ion or sulphite ion in water, or ethoxide ion in ethanol to form red complexes whose NMR spectra indicate covalent addition of the nucleophile at C_4. The complexes are not stable and replacement of the nitro group at C_2 occurs quickly. The equilibrium and the rate constants for these processes have been measured. In contrast 1,2,4,5-tetranitrobenzene reacts with hydroxide ion to give 2,4,5-trinitrophenol without the production of colour. With ethoxide or sulphite ions coloured species are produced.

1,3-Dimethoxy-4,6-dinitrobenzene reacts with methoxide ion in dimethyl sulphoxide-methanol mixtures to form an adduct whose NMR spectrum indicates methoxide addition at C_1. The equilibrium constants in various solvent compositions have been determined.

Solvent effects on the stability of Meisenheimer complexes formed from 1,3,5-trinitrobenzene and thiolate ions have been investigated in alcohol-water mixtures. The equilibrium constants for formation of the 1:1 adducts are smaller in water than in alcohol but go through a maximum at about 80% alcohol. The equilibrium constants of the 1:2 adducts increase monotonically as the proportion of water is increased and are ca. 10^3 greater in water than in pure alcohol. This greater stability is attributed partly to the good solvation by water of a localised negative charge on the nitro group between the positions of addition.

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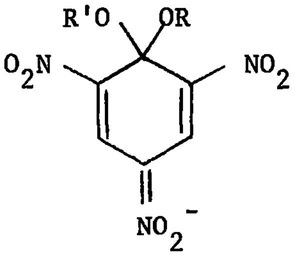
Section III. Interaction of 1,3-dimethoxy-4,6-dinitrobenzene with sodium methoxide in dimethyl sulphoxide mixtures

Section IV. Solvent effects on the stabilities of Meisenheimer-type complexes

CHAPTER 1

INTRODUCTION

Highly coloured σ-complexes formed by the action of nucleophiles on aromatic nitro-compounds were first reported before 1900. Much of the early structural work on these adducts was carried out by Meisenheimer[1] and by Jackson and his co-workers.[2] The early work involved chemical methods of structure determination and indicated the structure (1) for the reaction of picryl ethers with alkoxides. In this quinonoid structure the negative charge is associated with the para nitro-group. Today a structure (2) where the negative charge is delocalized about the ring and the nitro-groups is thought to be more appropriate. It was also suggested[1] that the adduct produced from the interaction of 1,3,5-trinitrobenzene with methoxide ion might be due to attack of methoxide ion on a ring carbon carrying hydrogen to form a covalently-bound adduct (3). In recent years "Meisenheimer Complexes", that is adducts formed by the covalent addition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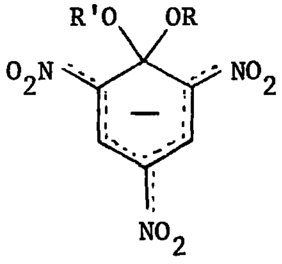
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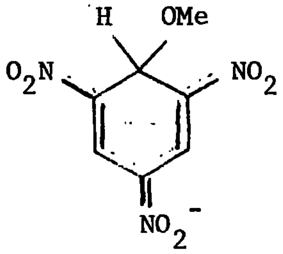
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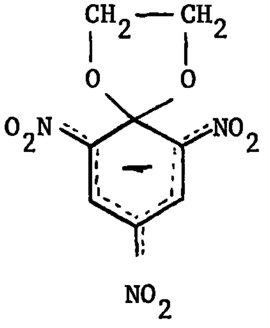
of nucleophiles to activated aromatic species, have been intensively investigated. Several reviews[3-7] have been written about the complexes themselves and on their theoretical importance as reaction intermediates in aromatic nucleophilic substitution reactions. It is therefore neither necessary nor desirable to give a complete survey of the literature. Only the fundamentals and more important recent results will be discussed here. In the first section the structural investigations are considered, most space being devoted to adducts formed from carbonyl compounds and with heteroaromatics; these latter subjects not having been reviewed elsewhere. In the second section of the introduction the factors governing the stabilities of the adducts are considered.

A. STRUCTURAL STUDIES

i) σ-Complexes from Aromatic Nitro-Compounds and Alkoxide

Since Meisenheimer's classical work using chemical methods, a large body of information concerning his formulation has come from spectroscopic studies. I.R., U.V./Visible, N.M.R. spectroscopic techniques and X-ray crystallography have all been used to advantage to study the adducts. The infrared spectra[8,9] of the solid salts produced from picryl ethers and alkoxide show bands typical of ketals and are consistent with an increase in negative charge on the nitro groups on complex formation. Visible spectroscopy has been frequently used to examine the complexes. The identity of the visible spectra of 2,4,6-trinitroanisole in ethanolic potassium ethoxide and 2,4,6-trinitrophenetole in methanolic potassium methoxide was considered[10,11] to be evidence that the same complex (2, R = Me, R' = Et) was produced in each case. However Gold and Rochester[12] showed that this argument is inconclusive. In fact the visible spectra of a variety of complexes where R = R' or R $\neq$ R' are all very similar. In general it is unsatisfactory to make structural assignments on the basis of visible spectra, since the position of addition cannot be unambiguously assigned. If N.M.R. spectra of the adducts can be obtained then these usually give definite information as to the structure of the species produced.

Thus the fact that the solid adduct of 2,4,6-trinitroanisole with potassium methoxide is indeed a Meisenheimer salt is demonstrated by N.M.R. spectroscopy.[13] The spectrum in dimethylsulphoxide (DMSO) shows two bands with intensities representing two and six protons attributed to the ring and methoxyl proton respectively. The resonance due to the ring protons at -8•65 ppm is shifted upfield from its position in the parent compound -9•07 ppm, while that due to methoxyl protons shows a large upfield shift from -4•07 to -3•03 ppm (all chemical shifts are quoted relative to the internal reference TMS). The fact that a single band is observed for six methoxyl protons indicates the equivalence of the methoxyl groups in the complex. The N.M.R. spectrum of the solid adduct of 1,3,5-trinitrobenzene and potassium methoxide in dimethylsulphoxide confirmed the correctness of structure (3). The large upfield shift of the resonance due to the 2-proton from -9•20 to -6•14 ppm is compatible with the change in hybridization from sp^2 to sp^3 at the centre of attack. Several N.M.R. spectral studies have also been made on the interaction of a variety of nitro-compounds containing various alkoxy groups with alkoxide.[14,15] The spectra indicated in each case the formation of σ-complexes. Furthermore, Murto[16] has reported the formation of a spiro Meisenheimer-type complex (4) and later Foster et al[14] confirmed this structure by N.M.R. spectroscopy which shows the anticipated equivalence of the four protons in the dioxolan ring.



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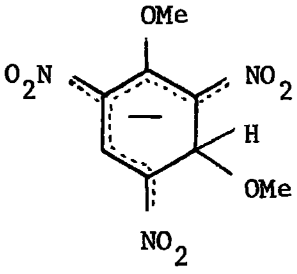

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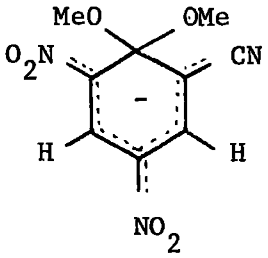
Recent studies by crystallography on picryl ethers and alkoxide adducts[17,18,19] have added further evidence supporting Meisenheimer's structure. They showed, in addition to the equivalence of the alkoxy groups in the complex, that the angle between C_2-C_1-C_6 is 109^o very close to tetrahedral angle required for sp^3 hybridized carbon.

Although Meisenheimer originally discarded the possibility of alkoxide addition to C_3 to form adduct (5), Servis[20] has recently shown by N.M.R. spectroscopy that the initial spectra recorded immediately after addition of concentrated sodium methoxide to solutions of 2,4,6-trinitroanisole in DMSO are due to the formation of adduct (5). However, the spectrum gradually decreases with time and is eventually replaced by the spectrum due to adduct (2) (R = R' = Me) which is thermodynamically more stable. The conversion was found to be catalysed by methanol and methoxide ion. For this reason, Crampton and Gold[21] were unable to detect the formation of adduct (5) by N.M.R. spectroscopy in mixtures of methanol and DMSO.

On this basis, it seems more likely that the fast reaction observed by Ainscough and Caldin,[22] between 2,4,6-trinitroanisole and sodium ethoxide using a stopped-flow technique at low temperatures, is due to the formation of an adduct of structure type (5) and not to a charge-transfer complex as they originally thought. It is evident that addition of methoxide ion to carbon carrying hydrogen is faster than addition to carbon carrying a methoxyl group through the latter yields thermodynamically more stable adducts. This, in fact, is contrary to what would be expected on the basis of Miller's[23] calculation.

Formation of Meisenheimer complexes of greater than 1:1 stoichiometry from 2,4,6-trinitroanisole and 1,3,5-trinitrobenzene in the presence of high concentrations of base has also been reported.[12,15,24-27]

The effect of replacement of one or two nitro groups by cyano groups, on the formation and stability of Meisenheimer complexes, has received attention in recent years. Thus Pollitt and Saunders[28] examined complex formation from 2-cyano-4,6-dinitroanisole and 4-cyano-2,6-dinitroanisole with methoxide ion. More recently the N.M.R. spectra of the complexes (6)[29] and (7)[30] have been obtained. However these complexes were less stable than their picryl analogue(2, R = R' = Me). Evidence for the transitory formation of adducts (8) and (9) has also been reported.[31] Fendler et al[32] have recently investigated the formation of Meisenheimer complexes from the isomeric 2,4,6-dicyano-nitroanisoles with methoxide ion.



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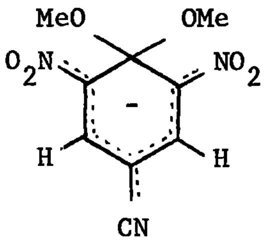

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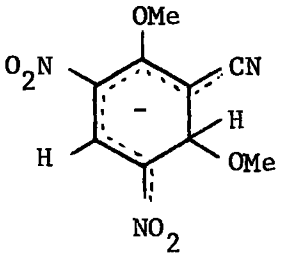

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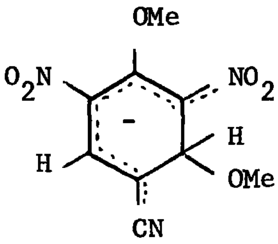

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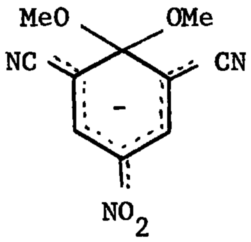
The N.M.R. spectra of the solid products dissolved in DMSO indicated the formation of the adducts (10) and (11). Calorimetric studies have also been made of these interactions and indicate the formation of a transit complex in the reaction leading to (11) although no assignment regarding the structure could be drawn on this basis. However N.M.R. studies leave no doubt that the initial complex formed in solution of 2,4-dicyano-6-nitroanisole in DMSO and sodium methoxide, is in fact adduct (12) and not its isomer. This result indicates the importance of a nitro-group para to



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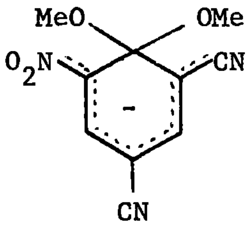

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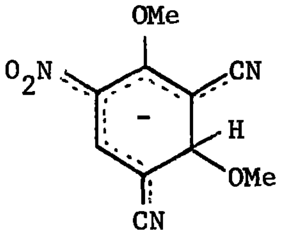

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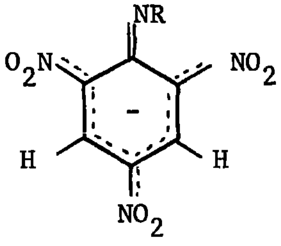
the position of attack in the stabilisation of an adduct. No such transit complexes were observed in the case of 2,6-dicyano-4-nitroanisole.

It has generally been assumed[33-36] that picramide and N-alkyl picramides ionised in basic media by proton loss to form anions (13). However Gold and Rochester[37] who made a detailed equilibrium and kinetic study found evidence for the formation of Meisenheimer complexes such as



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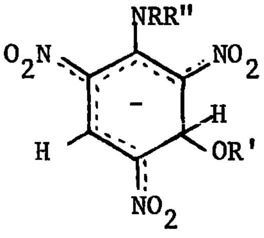

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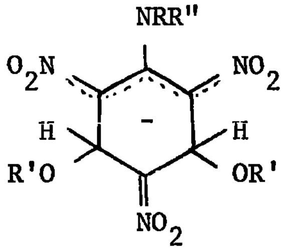

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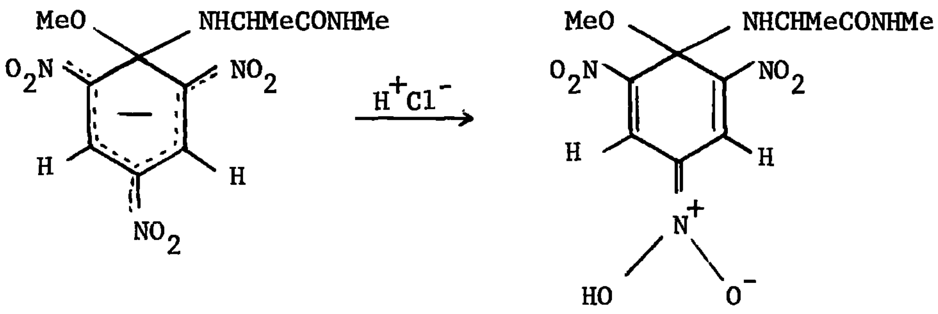
(14) (R = R" = H, R' = Me or R = R' = R" = Me) and (15) (R = R" = Me, R' = Me). More recently these assignments have been confirmed by N.M.R. spectroscopy.[20,21,27,38]

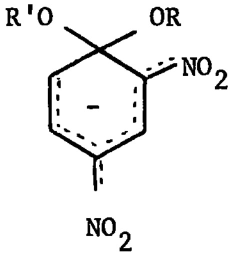
An interesting report has recently been made by Bergman et al[39] that the adduct (16) is produced by addition of potassium methoxide to a solution of the parent compound in methanol and that addition of one equivalent of HCl gives a relatively stable neutral complex (17).



(16) (17)

Benzene rings substituted with only two activating groups are less reactive. However 1,3-dinitrobenzene gives a red solution in methanolic sodium methoxide[40] with absorption maximum at 5160Å ascribed to the adduct at the 4-position. No N.M.R. evidence has yet been obtained for this adduct due to the presence of small quantities of radical anions which obliterate the spectrum. However Foreman and Foster[41] have observed N.M.R.

spectra of adducts from 1-X-3,5-dinitrobenzene (X = CN, CF_3). It is noteworthy that they found evidence only for adducts formed at position para to nitro-groups. Gitis et al[42] found that 2,4- and 2,6-dinitroanisoles give coloured solutions in the presence of base and were able to separate solid products. They proposed the structures (18) and (19). Pollitt and Saunders[28] examined the visible spectra of a variety of 2,4-dinitro-6-X-anisoles and 2,6-dinitro-4-X-anisoles (X = OMe, H, Cl, CO_2, $CONH_2$, CO_2Me , CN) in the presence of base. They argued in favour of formation of adducts



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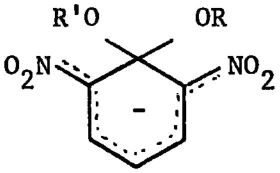

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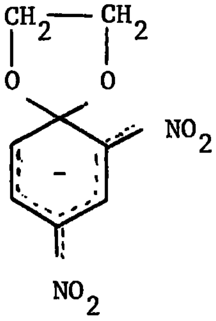
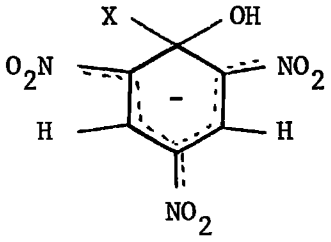


(20)

by addition at C_1. They also interpreted the observation[43] of a red colour in solutions of glycol-2,4-dinitrophenyl ether as the production ofacyclic adduct (20). Recent N.M.R. spectroscopic studies by several groups of workers have confirmed structures (18), (19) and (20).[15,38,44-46] Di-adducts have been suggested to account for the visible spectral change at high alkoxide concentration.[25,47]

ii) σ-Complexes from Aromatic Nitro-Compounds and Hydroxide Ion

Gold and Rochester[48] have examined the reactions of a number of aromatic nitro-compounds with aqueous sodium hydroxide solution using visible spectroscopy. 2,4,6-trinitroanisole was converted rapidly to the picrate ion, presumably via the intermediate (21) (X = OMe). No direct evidence for this intermediate was found. However recently Gaboriaud and Schaal[49] have studied the interaction of a number of 1-X-2,4,6-trinitrobenzene (X = H, Cl, OMe) with fairly concentrated sodium hydroxide solutions using a stopped-flow technique. This enabled visible spectra to be obtained very soon after mixing of components. These spectra were interpreted as indicating the formation of adducts of structure (21). However in view of the results presented later in this thesis it seems possible that the initially formed adducts may have structure (22), although formation of picrate ion must proceed via adducts of type (21).



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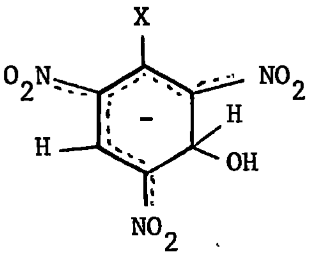
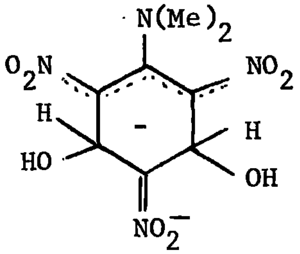


(22)

The equilibrium constant for the formation of an adduct formed from 1,3,5-trinitrobenzene and hydroxide was determined by Gold and Rochester.[48]

They considered that the adduct resulted from the covalently-bound adduct (21) (X = H). N.M.R. evidence for the formation of this adduct in water-dimethylsulphoxide mixtures has been obtained by Fyfe.[50] The ring protons of the adduct absorb at -8•20 and -6•15 ppm while a band at -4•50 ppm was attributed to the hydroxyl proton of the added hydroxide group. This latter absorption was not observed when potassium deuteroxide was used which adds strength to the assignment.

The interaction of picramide and N,N-dimethylpicramide with aqueous sodium hydroxide has been reported by Gold and Rochester.[51] They found that at low concentration of sodium hydroxide, picramide reacts with one hydroxide ion to form a 1:1 adduct and N,N-dimethylpicramide with two hydroxide ions to form a 1:2 complex. A structure (23) was suggested for the latter complex. More recently Crampton and Gold[21] have made a



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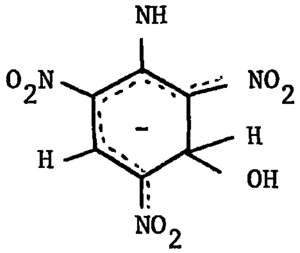

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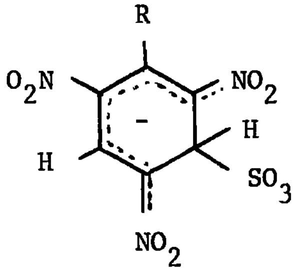
structural study by N.M.R. spectroscopy on reactions of picramide and its N,N-dimethyl derivative with hydroxide ion in water-dimethylsulphoxide mixtures. They found evidence that in the case of picramide the major interaction yielded a product of structure (24) while for N,N-dimethyl picramide-hydroxide solutions, the spectrum confirms the structure (23).

iii) σ-Complexes from Aromatic Nitro-Compounds and Sodium Sulphite

The interaction of 1,3,5-trinitrobenzene and 2,4,6-trinitrotoluene with aqueous sodium sulphite solutions have been known[52] for some time, but no detailed studies concerning the composition, spectral characteristics and extent of formation of the coloured species have been reported until recently. Cuta and Beranek[53] examined the visible spectra of 1,3,5-trinitrobenzene in buffered solutions containing _ca._ 10^{-3}M potassium sulphite and suggested a structure (25) (R = H) to account for the absorption spectrum of the coloured species. At higher concentration of



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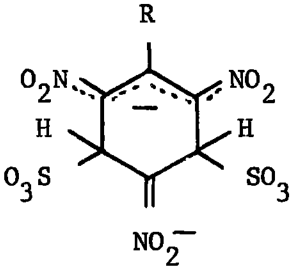


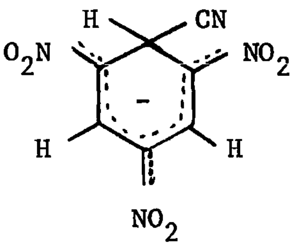
(26)

sodium sulphite the visible spectra decreased and this was attributed to the formation of higher complexes. This speculation was supported by isolation of a dark red crystalline[54] adduct which showed a stoichiometry 1 TNB:2 sodium sulphite, from aqueous solution. However Norris[55] suggested that 1:1 complex in aqueous solution may result from formation of a charge transfer complex.

More recently, Crampton[56] has made a careful structural and equilibrium study by N.M.R. and visible spectroscopy on the interaction of 1,3,5-trinitrobenzene and its derivatives in water and in water-DMSO mixtures. He found strong evidence that at low concentration of sodium sulphite 1:1 complexes (25) (R = H, NH_2, NHMe, NMe_2) are formed by addition of sulphite ion at a ring carbon carrying hydrogen. The formation of 1:2 complex (26) was observed at high concentration of sodium sulphite. It was also found in this latter complex that sulphite addition occurred at two ring carbons carrying hydrogen rather than at the substituted position.

iv) σ-Complexes from Aromatic Nitro-Compounds and CN^- ion

The interaction of aromatic nitro-compounds with cyanide ion to form deep red coloured solutions was known as early as 1882.[57] Meisenheimer[1] attributed these coloured species and the red violet salt obtained by early workers to the formation of σ-complexes. For example the adduct (27)



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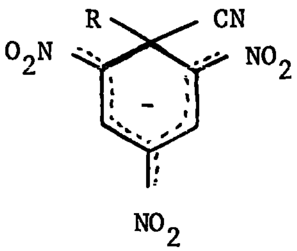


(28)

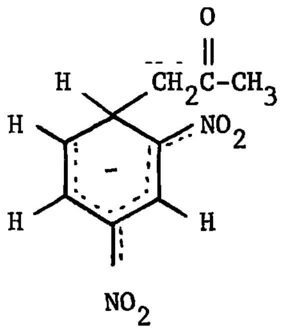
was thought to result from reaction of 1,3,5-trinitrobenzene with cyanide ion.

Although a recent attempt[58] to prepare a solid product by the early method was unsuccessful, the initial visible spectrum of 1,3,5-trinitrobenzene with potassium cyanide in alcohol or acetone is very similar to that of Meisenheimer compounds. Several groups of workers[53,59-61] have studied the reaction of 1,3,5-trinitrobenzene and 1,3-dinitrobenzene with cyanide ion in a variety of solvents by visible and I.R. spectroscopy. The results were ascribed to the formation of a covalent addition adduct. More conclusive evidence confirming the correctness of structure (27) has come from N.M.R. spectroscopy. Thus Buncel et al[62] have found the N.M.R. spectrum produced from solution of 1,3,5-trinitrobenzene in chloroform containing cyanide ion is consistent with the formation of adduct (27). They also showed that addition of cyanide ion to 2,4,6-trinitrotoluene occurred at C_3, an unsubstituted position, whereas with 2,4,6-trinitrobenzoic acid the cyanide addition occurred at C_1 to form adduct (28) ($R = CO_2H$). Norris[63] also found recently that cyanide ion may add to C_1 or C_3 in 2,4,6-trinitroanisole. However the spectra indicated that addition at C_3 predominates and yields the more stable isomer. This in fact is contrary to the 2,4,6-trinitroanisole-methoxide adduct where addition at C_1 results in a more stable adduct than that at C_3. Further evidence has been reported by N.M.R., I.R. and visible spectroscopy confirming the structure of the adduct from 1,3,5-trinitrobenzene and cyanide ion.[64-66]

v) Adducts Formed from Aromatic Nitro-Compounds with Carbanions

The production of intense purple colour when a solution of m-dinitrobenzene in acetone is treated with alkali was first noted by Janovsky and Erb[67] in 1886, and is known now as the Janovsky reaction. Von Bitto[68] found that acetone could be replaced by aldehydes and other ketones. Summaries of the literature have been given by Canback[69] and more recently by Pollitt and Saunders.[70]

On the basis of the electronic spectrum, Canback suggested that the coloured species resulted from acetonate ion addition at C_4 of 1,3-dinitrobenzene to give structure (29). However Zimmermann,[71] has described an apparently similar reaction in which 1,3-dinitrobenzene is dissolved in ethanol, to which the base and the carbanion are added. In this reaction there is an excess of 1,3-dinitrobenzene. More recent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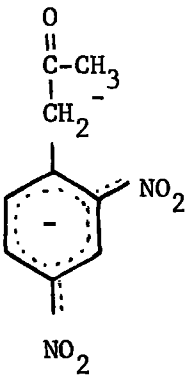
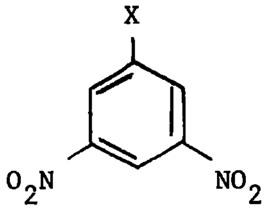

(30)

investigations[70,72] have shown that under this condition the initially formed Janovsky adduct is oxidised by a second molecule of 1,3-dinitrobenzene to yield the conjugate base of 2,4-dinitrobenzylmethyl ketone (30). The detection of 3-nitroaniline among the products was taken as evidence in support of this mechanism.

It is evident that the presence of powerful electronegative groups at the 5-position in 1,3-dinitrobenzene increases the susceptibility of the aromatic ring toward nucleophilic attack. Thus Pollitt and Saunders[70] found that the visible spectra for the Janovsky reaction for 1-X-3,5-dinitrobenzenes (31) (X = electronegative group) have two maxima attributed to the complexes formed by reaction at the 2- and 4-positions respectively. This attribution was confirmed by observation of only a single maximum when a substituent was present at either of the positions of attack.[70,73] Akatsuka[74] was also able to isolate purple crystals from the reaction of (31) (X = SO_3^-, CO_2^-) with acetophenone or acetone in the presence of base. Chemical evidence showed that this resulted from addition at C_4.



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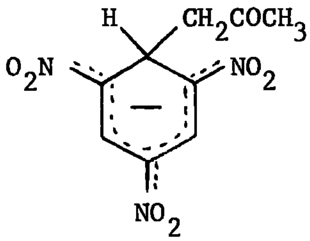

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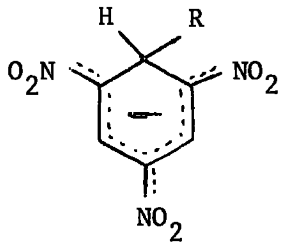


(33)

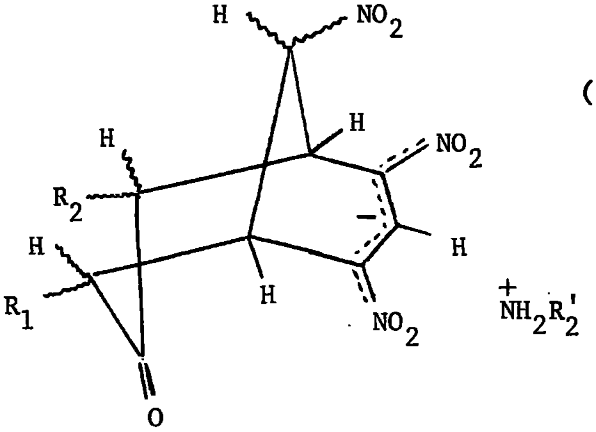
More generally in recent years a variety of aromatic nitro-compounds have been found to give coloured adducts with carbanions generated in solution. Kimura[75] formulated the violet crystalline product formed from 1,3,5-trinitrobenzene and acetone in the presence of base as adduct (32) and this formulation has been supported by chemical evidence. Probably the strongest evidence for structure (32) comes from N.M.R. spectroscopy. Thus Foster and Fyfe[15] found that if the Meisenheimer adduct from 1,3,5-trinitrobenzene and potassium methoxide was dissolved in acetone the bands at -8·66 and -6·33 ppm initially present decreased in intensity with the production of new bands at -8·47 (doublet J = 1 Hz) and -5·20 ppm (triplet J = 9 Hz). These new bands were assigned to adduct (32). The large coupling constant of the triplet at -5·20 ppm results from coupling with the adjacent methylene protons. Similarly it has been shown[76] that the orange colour produced on addition of tertiary amines to 1,3,5-trinitrobenzene in a variety of ketones results from the addition of the conjugate base of the ketones to give structures analogous to (32). Apparently the amine serves the role of proton acceptor:

$$NR_3 + CH_3COCH_3 \rightleftharpoons \overset{+}{H}NR_3 + CH_3COCH_2^-$$

Other 1:1 adducts have been reported[77] to be formed from carbanions generated from aliphatic nitro-compounds (33) (R = CH_2NO_2, $CHMeNO_2$, $CHEtNO_2$, CMe_2NO_2), from propionaldehyde[78] (33) (R = CHMeCHO) from acrylonitrile[79] and from chloroform[80] (33) (R = CCl_3).

Recent research has thrown light on a previously unidentified compound produced from 1,3,5-trinitrobenzene and ketones in presence of primary or secondary amines. Abe[81] isolated this compound from the action of 1,3,5-trinitrobenzene with ketones in the presence of amines or aqueous ammonia and found the I.R. spectrum possessed two absorption bands at 1710 cm^{-1} and 1550 cm^{-1} attributed respectively to the carbonyl and nitro groups. The visible spectrum showed a single absorption at ca.500 mμ. A similar compound was reported[82] from the reaction of 1,3,5-trinitrobenzene with acetone in the presence of diethylamine. Although an N.M.R. spectrum was obtained no assignment of the structure was given. Orugu and Murco[83] who made a kinetic study of the reaction of 1,3,5-trinitrobenzene in acetone by a stopped flow method, observed two reactions. The fast reaction was attributed to a Zwitterionic adduct of diethylamine. The slower reaction gave a product with visible absorption maximum at ca. 516 mμ and a red solid was isolated. Analysis indicated that the product had a stoichiometry of 1,3,5-trinitrobenzene:acetone:amine 1:1:2. The elemental analysis reported by Foster and Fyfe[82] is not consistent with this analysis or with a 1:1:1 adduct.

However, very recently Strauss and Schran[84] have isolated and recrystallised a stable red compound from this reaction and have interpreted the N.M.R. spectrum in terms of the cyclic adduct (34). The proton on the dinitropropenide portion appears as a singlet at -8•52 ppm,



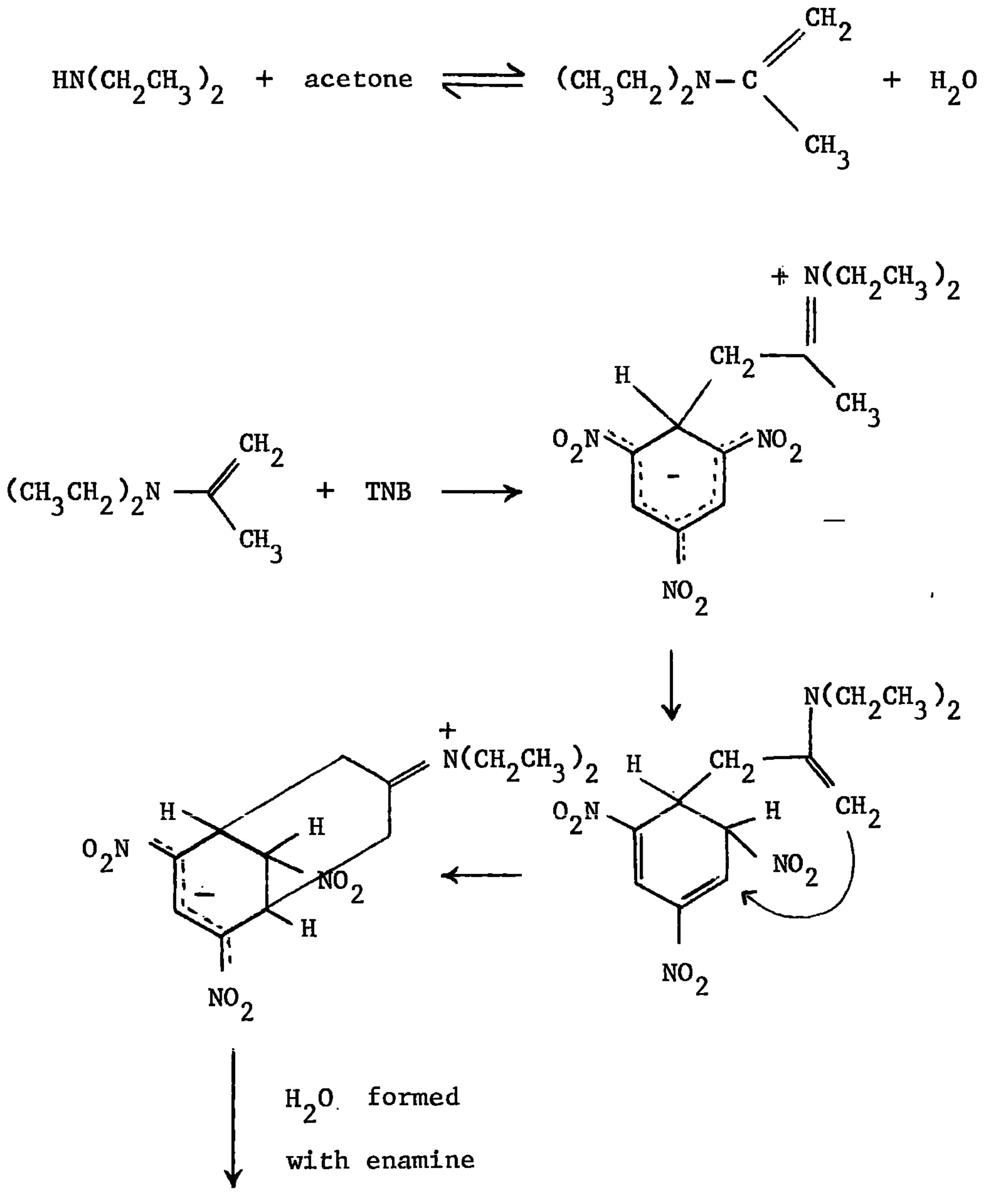
(R_1 = R_2 = H, R' = Et)

(34)

the NH$_2$ protons appear as a broad singlet at -6·84 ppm while the bridge H-CNO$_2$ proton appears as a triplet centred at -5·72 ppm. The splitting (J = 3 c/s) results from coupling with the two bridge-head protons, which appear as a broad doublet at -4·53 ppm. The position of the bridge-proton (-5·72 ppm) is 1·3 ppm downfield from resonance position of nitromethane which indicates that the nitro-group on the one-carbon bridge is directed toward the anionic portions of the molecule. If it were not the bridge protons would occupy a position above the delocalized system, a region of high shielding, and would be expected to appear at higher field than normal nitro compounds.

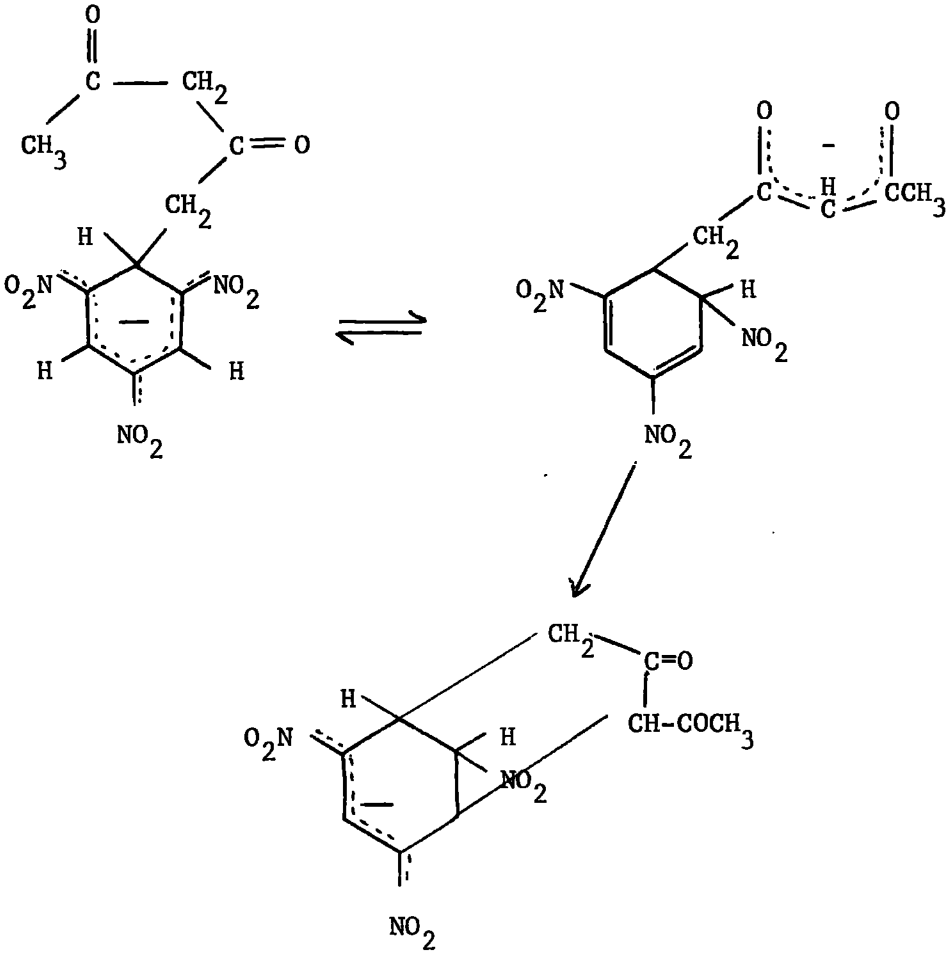
Although the bicyclic structure (34) is obtained from the reaction of acetone, 1,3,5-trinitrobenzene and diethylamine it appears that with triethylamine as base reaction produces only the Meisenheimer type salt (32). However Foster and co-workers[85] found that using more acidic ketones such as acetyl acetone or dibenzyl ketone structures similar to (34) were formed using either the secondary or tertiary amines as base. These complexes presumably arise through cyclization of the initially formed adduct of type (32).

Further study by Foster et al[86] has shown that it may be possible to isolate stereoisomers of structure (34) ($R_1 = R_2 = Ph$). Starting from dibenzyl ketone they were able to prepare what they thought to be two isomers one with trans and the other with cis configuration. The two isomers showed small differences in m.p., I.R. and N.M.R. spectra. Thus the isomer with m.p. 193-5° showed a single N.M.R. band for the two phenyl groups and was thus thought to be the cis isomer while the isomer m.p.175-8° trans gave two distinct phenyl absorptions. Although it was originally thought that the formation of bicyclic anions such as (34) occurred only with 1,3,5-trinitrobenzene and specific ketones it has since been found that the reaction is quite general and occurs with a variety of ketones and ketoesters with various electron deficient benzenes. Thus Strauss et al[87] found that 3,5-dinitrobenzonitrile and methyl-3,5-dinitrobenzoate react with acetone, dicarbomethoxyacetone, ethyl acetoacetate, α-acetyl butyacetone and acetylacetone to give stable adducts analogous to (34). These condensation cyclizations are initiated with primary, secondary or tertiary amines. Strauss argues that two distinct mechanistic pathways are available for production of bicyclic adducts. With acetone and 1,3,5-trinitrobenzene (which give a cyclic adduct with diethylamine but not triethylamine) an enamine intermediate is proposed which reacts as follows:



(34)

with more acidic ketones and esters it is thought that a delocalized carbanion intermediate is involved. Thus with acetylacetone the following scheme is envisaged.

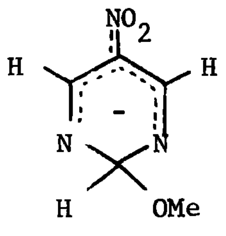


The initially formed adduct undergoes cyclization. It seems improbable that enamine intermediates can be involved since tertiary amine will initiate the reaction.

vi) σ-Complexes from Heteroaromatic Compounds

There has been considerable interest in recent years in the adducts formed from heteroaromatic compounds resulting from the need to identify the intermediates in nucleophilic heteroaromatic substitution reactions. The essential analogies between the nitro- and aza- activated systems have played a major role in the studies so far reported. The polar effect of the aza-group is qualitatively similar to that of the nitro group though it differs from the nitro group in having a lower steric requirement.

The obvious starting point is s-triazine, however due to the very high reactivity of this compound and its methoxy derivative it has not so far been possible to identify adducts from reaction with methoxide. A gradual replacement of the nitro groups by nitrogen has proved more profitable. Biffin et al[88] found that the adduct (35) was produced from



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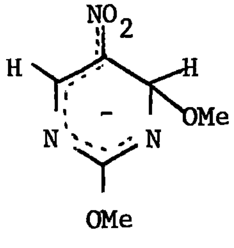

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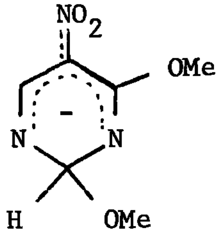
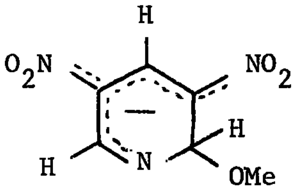


(37)

5-nitro pyrimidine while 2-methoxy-5-nitro-pyrimidine gave adduct (36) and 4-methoxy-5-nitro-pyrimidine gave the adduct (37). Similarly the replacement of a single nitro group by an aza group has been examined.

Thus Fyfe[89] reported the interaction of 3,5-dinitropyridine with the methoxide ion in DMSO studied by visible and N.M.R. spectroscopy. The visible spectra showed an absorption band at ca. 487 mμ. Addition of sodium methoxide to solutions of 3,5-dinitropyridine in DMSO caused the disappearance of the N.M.R. bands at -9•73 and -9•14 ppm due to the ring protons of the parent compound and new bands at -8•62, -8•30 and -6•08 ppm occurring. This spectrum is consistent with structure (38). Although



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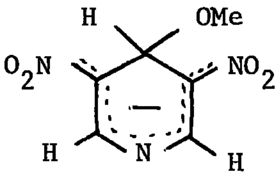
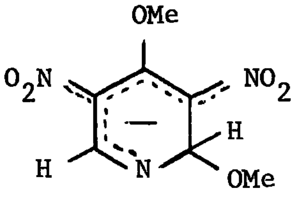


(39)

Fyfe was not able to detect the formation of adduct (39), it has been shown[90] recently by N.M.R. spectroscopy that the initial spectrum of 3,5-dinitropyridine in DMSO and sodium methoxide is due to the formation of adduct (39). However, this adduct is not stable and conversion to (38) occurs. It has been shown previously that in the case of 2,4,6-trinitro-anisole, methoxide addition in DMSO solution, occurs first at C_3 followed by conversion to the more stable adduct (2) (R = R' = Me). Accordingly it would be expected that 4-methoxy-3,5-dinitropyridine would behave in the same way. Confirmation that this is indeed the case has come from N.M.R. spectroscopy study. Thus Biffin[91] et al found the N.M.R. spectrum of the species initially formed on addition of sodium methoxide to a solution of 4-methoxy-3,5-dinitropyridine, is consistent with the formation of adduct (40). However, this adduct is not stable and is gradually replaced by adduct (41). Formation of (42) has also been observed presumably by hydrolysis of the parent compound or by demethylation of the parent compound with methoxide ion. The conversion of adduct (40) to adduct (41) was found to accelerate on addition of methanol. The spectrum due to the formation of adduct (41) is in agreement with that reported by other workers. In contrast to the behaviour of 4-methoxy-3,5-dinitropyridine, 2-methoxy-3,5-dinitropyridine was found to form (43).



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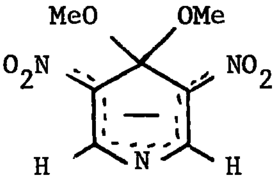

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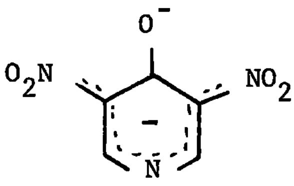

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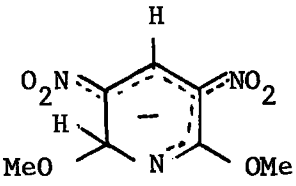

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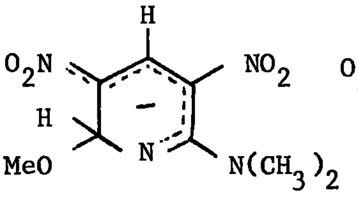

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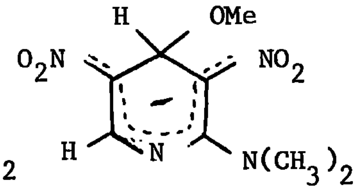
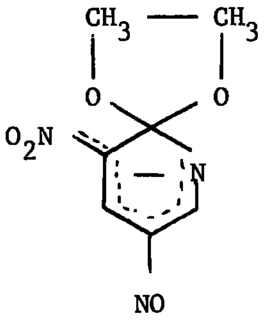


(45)

Fyfe[89] has reported N.M.R. data for the formation of covalent complexes by addition of sodium methoxide to solutions of 2-dimethylamino-3,5-dinitropyridine in DMSO, though he was not able to deduce which of the two isomers (44) or (45) is formed. It is of interest that a spiro-Meisenheimer type complex (46) from an aza aromatic compound has also been reported.[89]



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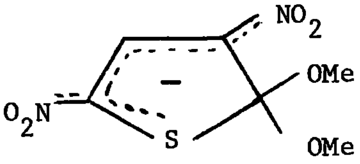


(47)

A complex from 2-methoxy-3,5-dinitrothiophene has been reported.[92] The N.M.R. spectrum is in accord with the structure (47). Apparently this complex is very stable and has a larger equilibrium constant for formation than the adduct from 2,4,6-trinitroanisole with methoxide.

B. STABILITY OF MEISENHEIMER COMPOUNDS

Before the factors governing the stability of Meisenheimer complexes are discussed in this section, a brief outline of the methods used to determine the equilibrium constants is considered. In cases where complex formation occurs at low base concentrations, it can be shown that measurement of optical density at appropriate wavelength allows the equilibrium constant to be determined either directly, if the extinction coefficient of the complex is known, or by the use of Benesi-Hildebrand[93] plots.

However, it has been found that for less reactive substrates such as 1,3-dinitrobenzene and also for the formation of higher complexes from certain aromatic nitro-compounds, significant conversion to complexes occurs only at very high concentrations of base. In these solutions the basicity of the medium can not be adequately described by the stoichiometric concentration of the base ions. Therefore determination of the equilibrium constants for the formation of the complexes in these solutions in terms of ion concentration is subject to error. However, the use of the acidity function concept proves to be useful and gives satisfactory results.

The original concept of the acidity function was proposed by Hammett and Deyrup[94] in the early thirties from a study of acidic media. They defined the acidity function H_o as the measure of the ability of a medium to transfer a proton to a neutral molecule, i.e.

$$B + H^+ \rightleftharpoons BH^+$$

Thus

$$H_o = pK_{BH} - \log_{10} \frac{[BH^+]}{[B]}$$

where pK_{BH^+} is the thermodynamic ionization constant of its conjugate acid in terms of molar concentration referred to ideal dilute solution in water. The acidity function H_o is not the same as the pH, but it does approach it in dilute aqueous solution where the activity coefficient ratio approaches unity. This subject has been reviewed by Paul and Long.[95]

Recently, the concept of the acidity function has been extended to the study of alkaline media. Thus More O'Ferrall and Ridd[96] defined an H_- acidity function in methanolic sodium methoxide as a measure of the ability of a solvent to remove a proton from an electrically neutral weakly acidic molecule.

For example

$$BH + MeO^- \rightleftharpoons B^- + MeOH$$

where

$$H_- = pK_{BH} - \log_{10} \frac{[BH]}{[B^-]}$$

Gold and Rochester[12] found that the conversion of the first complex of 2,4,6-trinitroanisole to higher complex depends on the H_- acidity scale.

Similarly Terrier et al[47] correlated the complex formation of dinitroanisoles with an H_- acidity function.

In part compounds which ionise by base addition rather than by proton loss should be subject to a different dependence on the basicity of the medium. Thus Rochester[97] studied the ionisation of certain aromatic nitro-compounds in methanolic sodium methoxide and defined a $J_{-(M)}$ scale. This measures the ability of the medium to add a molecule of base to a neutral indicator.

For equilibria in methanol such as

$$P + OMe^- \rightleftharpoons A$$

The $J_{-(M)}$ scale is given by

$$J_{-(M)} = p[K_1 . K_{MeOH}] + \log_{10}\frac{[A]}{[P]}$$

where K_1 is the thermodynamic equilibrium constant for the formation of the adduct A with methoxide and K_{MeOH} is the autoprotolysis constant of methanol. From $J_{-(M)}$ scale which ranges from $J_{-M} = 18$ to 23, Rochester was able to determine the equilibrium constants for complex formation from certain aromatic nitro-compounds which were either less reactive or where the formation of higher complexes occurred at high concentration of base.

Kinetic and equilibrium studies for the reaction of aromatic nitro compounds with nucleophiles to form covalent addition complexes indicate that the stability of these complexes depend on the following factors:

I. The Nature of the Parent Compound.

II. The Attacking Nucleophile.

III. The Solvent.

I. The Nature of the Parent Compound

Owing to the increase of negative charge on the formation of Meisenheimer complexes, the stability of these adducts will depend to a large extent on the ability of the parent compound to accommodate this excess negative charge. Therefore the more electronegative the substituents in the ring the greater the stability of the complex. Steric effects and the great importance of a nitro-group para to the the attacked position also contribute to the stability of the adducts.

Some equilibrium constants for the formation of Meisenheimer complexes are collected in Table 1. These show that the stability of the 2,4,6-trinitroanisole-methoxide adduct (addition at C-OMe) is 500 times greater than that of the 1,3,5-trinitrobenzene-methoxide adduct (addition at C-H). It has been suggested[98] that this difference in stability may be due to electronic and steric effects; the electronic effect of the methoxyl group at C_1 will reinforce electron withdrawal from this position and thereby promote attachment of base. Also complex formation in 2,4,6-trinitroanisole was considered to reduce steric strain between the methoxyl group and the flanking nitro-groups, allowing the methoxyl group to bend from the ring plane. No such relief would operate in the case of 1,3,5-trinitrobenzene. More recently crystal structure studies[17-19] have confirmed the steric relief on the formation of adducts from picryl ethers. However, it is found that addition of base at a ring carbon carrying hydrogen is faster than at a ring carbon carrying a methoxyl group.

TABLE 1

Equilibrium Constants for Complex Formation with Sodium Methoxide in Methanol at 25°C

Parent	K_1 $(1.mol^{-1})$ Addition at ring carbon carrying		K_2 $(1.mol^{-1})$	Reference
	H	OMe		
1,3-Dinitrobenzene (a)	5×10^{-7}			40
2,6-Dinitroanisole (b)		5×10^{-3}	10^{-4}	47
2,4-Dinitroanisole (b)		10^{-3}	3×10^{-5}	47
2,4 -Dinitroanisole(a)		3×10^{-4}	10^{-5}	25
1,3,5-Trinitrobenzene	15•4			12
2,4,6-Trinitroanisole		$7{\cdot}7 \times 10^{3}$		98
Picramide	$3{\cdot}8 \times 10^{1}$			37
N,N-Dimethylpicramide	7			37
Picrate ion (a)	3×10^{-4}		$1{\cdot}6 \times 10^{-2}$	25
4-Methoxy-3,5-dinitropyridine		$4{\cdot}7 \times 10^{3}$		99
2,4-Dinitro-1-methoxynaphthalene		$2{\cdot}3 \times 10^{2}$		101

TABLE 1 contd.

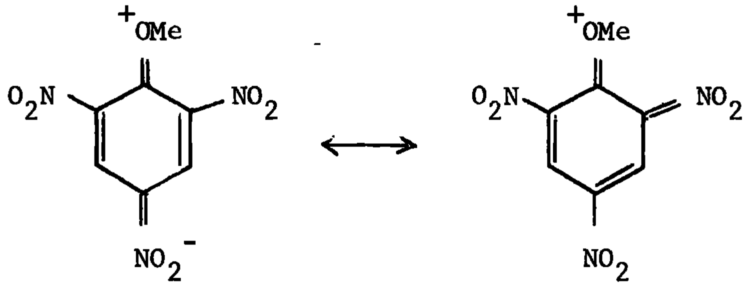
Parent	K_1 (1.mol^{-1}) Addition at ring carbon carrying		K_2 (1.mol^{-1})	Reference
	H	OMe		
2,4-Dinitro-6-cyanoanisole		$1{\cdot}14 \times 10^3$		100
2,6-Dinitro-4-cyanoanisole (c)		$2{\cdot}5$		99
2,4-Dicyano-6-nitroanisole		10		32
2,6-Dicyano-4-nitroanisole		35		32
2,4,6-Trinitroanisole (a)			$1{\cdot}3 \times 10^{-4}$	25
2,4,6-Trinitroanisole		$1{\cdot}7 \times 10^4$		31
2,4-Dinitro-6-cyanoanisole		$2{\cdot}6 \times 10^3$		31
2,6-Dinitro-4-cyanoanisole		$2{\cdot}8 \times 10^2$		31
2,4-Dinitroanisole		5×10^{-5}		102a

(a) Determined via $J_{-(M)}$ acidity function

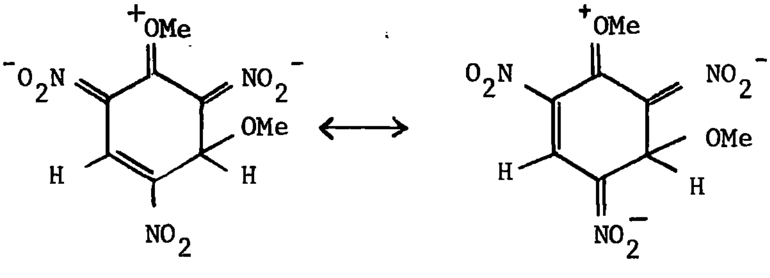
(b) Determined via $H_{-(M)}$ acidity function using potassium methoxide

(c) With lithium methoxide

This implies that the transition state for the formation of the 1,1-complex should be a more sterically strained structure than 2,4,6-trinitroanisole itself. Bernasconi[102] has recently put forward the alternative argument that the greater stability of the 1,1-complex than the 1,3-complex is related to the fact that multiple alkoxy substitution has a large stabilizing effect on an sp^3 substituted carbon atom relative to a non-substituted or little substituted carbon atom as well as relative to an equally substituted sp^2 carbon. This would explain the higher stability of the 1,1-complex of 2,4,6-trinitroanisole compared to the 1,3-complex or the 1,3,5-trinitrobenzene complex. He explained the faster formation of the 1,3-complex relative to 1,1-complex in terms of stabilisation of the parent compound by resonance of the form:



In the 1,3-complex this stabilisation is still possible though this



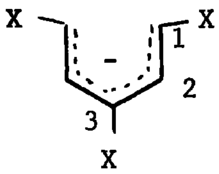
resonance stabilisation can not operate in the case of the 1,1-complex. Thus ground state stabilisation of 2,4,6-trinitroanisole will significantly affect only 1,1-complex formation and reduce its rate compared to 1,3-complex formation.

It appears that the factors involved are more complex than is allowed for by Miller's[23] method of calculation which predicts that the 1,3-complex should be the more thermodynamically stable species and that the 1,1-adduct should be the more rapidly formed.

To summarise, it is generally found that for the addition of alkoxide ion the stability of an adduct is increased (i) by the presence of a para nitro group and (ii) by the presence of an alkoxy group at the position of addition. The factors concerned must however be fairly finely balanced as 2-methoxy-5-nitropyrimidine surprisingly forms an adduct at C_4 (36).

Zollinger et al[100] made a simple HMO calculation which indicated that the negative charge on Meisenheimer adducts is delocalized entirely on the ring substituents, so that any change in the number or the type of these substituents must have considerable effect on the stability of the adduct. This calculation is in accord with the observation of smaller equilibrium constants for the formation of adducts from dinitroanisoles relative to those from 2,4,6-trinitroanisole.

More recently, Haruo Hosoya[103] has reported more sophisticated calculations of the π-electron structure and stabilizing energy for the anion I-V.



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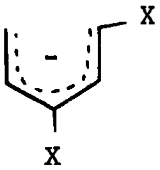
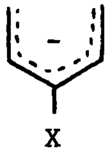


II

III

IV



V

The data for the factors governing the stability of these anions are given in Table 2. These data indicate, contrary to Zollinger's calculation, that considerable net charge resides in the π-electron system of the adducts. It is also interesting to note that the importance of the nitro-group para to the position of attack in the stabilisation of the negative charge.

Replacement of nitro groups by less electronegative groups such as CN, CF_3, CO_2Me and aza groups has a significant effect on the formation and the stability of Meisenheimer complexes. Fendler and co-workers[31,32]

TABLE 2

Electronic properties of several nitropentadienyl anions

	I	II	III	IV	V
Stabilizing energy ev	2•121	1•736	1•11	0•004	0•832
Net charge					
Ring	-0•586	-0•594	-0•669	-0•995	-0•680
1-NO_2	-0•121 (2)	-0•189	-0•165 (2)		
2-NO_2				-0•002 (2)	
3-NO_3	-0•173	-0•217			-0•320

have recently made an intensive study on the formation and decomposition of Meisenheimer complexes and have examined the effect of replacement of one or more nitro groups by cyano groups on the stability of these complexes. They found that replacement of para nitro groups by cyano groups has a much more serious effect on the stability of the complexes than the corresponding replacement of ortho nitro groups. This result indicates the importance of nitro-group para to the position of attack. Further evidence for the great effect of nitro group para to the attacked position has come from N.M.R spectroscopy. Thus Foreman and Foster[41] found the base addition occurs para to nitro group in 1-X-3,5-dinitrobenzene (X = CF_3, CO_2Me, CN). Replacement of two nitro-groups by cyano groups[32] caused a large decrease in the stability of the complexes and the adduct from 2,4-dicyano-6-nitroanisole is less stable that that from 2,6-dicyano-4-nitroanisole.

The equilibrium constants are similar for the formation of complexes from 1,3,5-trinitrobenzene ($2{\cdot}5 \times 10^2$ 1 mol^{-1}) and 2,4,6-trinitroanisole ($2{\cdot}1 \times 10^2$ 1 mol^{-1}) with sodium sulphite in water, where addition occurs in both cases at ring carbon carrying hydrogen. This indicates that the electronic effects of the methoxy group at C_3, the position of addition, are small. The fact that sulphite addition occurs at C_3 rather than C_1 in contrast to methoxide addition has been attributed to the greater steric requirement of the sulphite group compared with a methoxyl group. However, if stabilisation of 1,1-adducts is only effective when two alkoxy groups are present, as argued by Bernasconi,[102b] then the formation of 1,3-adduct is not surprising. The 1,3-adduct will be stabilised by resonance involving electron release from the methoxy group while the 1,1-adduct can not be stabilised by a similar effect.

II. Variation of Reactivity with Attacking Nucleophile

The second factor which governs the stability of Meisenheimer compounds is the nature of the nucleophile. However very little work has been done on this subject since it was last reviewed. In order to compare the reactivity of nucleophiles, it is necessary to study the reactivity of a variety of nucleophiles toward a single substrate in one solvent. Unfortunately, no extensive studies have been made so far, though the available data are given in Table 3.

In fact these equilibrium constants give a measure of thermodynamic affinity of nucleophiles for an aromatic carbon atom. This quantity which has been termed the 'carbon basicity' of the nucleophile will be expected to differ considerably from the Bronsted basicity, thermodynamic affinity for hydrogen, of the nucleophiles. Much of the work on this subject has been done on 1,3,5-trinitrobenzene with a variety of nucleophiles, however, the fact that most of these studies were in different solvents which have a major influence on the nucleophilic reactivity make the comparison between the carbon basicity for these nucleophiles inapplicable. Crampton,[104] made recently measurements in methanol for a variety of sulphur bases. He found that the order of carbon basicity is $EtS^- > OMe^- > PhS^- > PhO^-$. This is contrary to the Bronsted basicity order which indicate $OMe^- > EtS^- > PhO^- > PhS^-$. Data from the table for hydroxide and sulphite indicate that the sulphite ion

TABLE 3

Equilibrium Constants for Formation of Adducts from 1,3,5-Trinitrobenzene with Various Nucleophiles

Nucleophile	Solvent	K_1 ($l.mol^{-1}$)	Reference
OMe^-	Methanol	$1{\cdot}54 \times 10^{1}$	98
EtS^-	"	$3{\cdot}5 \times 10^{3}$	104
PhS^-	"	$1{\cdot}95$	"
PhO^-	"	2×10^{-3}	"
OH^-	Water	$2{\cdot}7$	48
EtO^-	Ethanol	$1{\cdot}21 \times 10^{3}$	102b
$SO_3^=$	Water	$2{\cdot}5 \times 10^{2}$	56
CN^-	Acetone	$1{\cdot}4 \times 10^{5}$	60
CN^-	Chloroform	$3{\cdot}5 \times 10^{5}$	60
CN^-	Methanol	$3{\cdot}9 \times 10^{1}$	65
CN^-	Ethanol	$1{\cdot}26 \times 10^{3}$	"
CN	n-propanol	$1{\cdot}47 \times 10^{3}$	"
CN^-	iso-propanol	1×10^{4}	"
CN^-	n-butanol	2×10^{3}	"
CN^-	t-butanol	5×10^{5}	"
OMe^-	DMSO	c. 10^{9}	104
PhS^-	DMSO	8×10^{4}	104
NHMe	DMSO	2×10^{3}	105
NEt_2	DMSO	$1{\cdot}3 \times 10$	105
NC_5H_{10}	Acetonitrile	6×10^{-2}	106

has a considerably higher carbon basicity than the hydroxide. It is of interest to note that the carbon basicity of the cyanide ion is similar to that of the methoxide ion in methanol and the ethoxide ion in ethanol.

Although no diversity of nucleophilic attack is possible in 1,3,5-trinitrobenzene, it has been found that for substituted derivatives such as 2,4,6-trinitroanisole or 2,4,6-trinitroaniline the mode of interaction may vary on changing the nucleophile. Thus structural measurements show that the thermodynamically stable adducts of 2,4,6-trinitroanisole with OMe^-, N_3^- or NEt_2 result from addition at C_1 while the apparently stable adducts with $SO_3^=$, CN^- or CH_3-$CO.CH_2^-$ are formed at C_3.

III. Solvent Effect

It is generally recognised that basic ions which are strong hydrogen bond acceptors become considerably less solvated on transfer from protic to dipolar aprotic solvents.[107] Accordingly basic ions in dipolar aprotic solvents are less extensively hydrogen bonded and consequently become more reactive nucleophiles than in pure protic solvents. This enhanced reactivity has been observed in the enormous increase in the formation of 1:1 adducts of Meisenheimer complexes in dipolar aprotic solvents relative to protic ones. Thus, 1,3-dinitrobenzene which gives little colour with sodium methoxide in methanol, was found to produce strong colour in dipolar aprotic solvents such as dimethylsulphoxide or dimethylformamide. Crampton and Gold[13] have shown by visible and N.M.R. spectroscopy that dimethylsulphoxide does not change the mode of reaction of the aromatic nitro-compound and base, but increases the efficiency of interaction. Although addition of the conjugate base of the solvent has been reported,[108] it was found that this specific reaction is only significant if acetone was used as a solvent where the acetonate ion is readily produced.

Values for the equilibrium constants for the reaction of 1,3,5-trinitrobenzene with certain nucleophiles have been measured in a variety of solvents and in protic-dipolar aprotic solvent mixtures. Thus Crampton[104] has measured the equilibrium constant for the reaction between 1,3,5-trinitrobenzene and sodium thiophenoxide over the whole composition range of methanol-dimethylsulphoxide mixtures. He found the value of the equilibrium constant increases as the solvent composition changes from protic to dipolar aprotic solvent and obtained a value for K in DMSO 4×10^4 greater than that in methanol. This behaviour of K may be related to changes in the solvent activity coefficients of the species. Thus using Parker's[107] expression, the equilibrium constants for the reaction of 1,3,5-trinitrobenzene with sodium thiophenoxide to give the covalent adduct $[TNB.PhS^-]$ are related by:

$$K_{(MeOH)} = K_{(DMSO)} \frac{{}^{(MeOH)}\gamma^{(DMSO)}_{(complex)}}{{}^{MeOH}\gamma^{DMSO}_{TNB} \quad {}^{MeOH}\gamma^{DMSO}_{PhS^-}}$$

It is expected in these solvents that the activity coefficients for all three species will have non-unit values. However the activity coefficients for 1,3,5-trinitrobenzene and the complex may be considered of the same order, since both are large polarizable molecules and will be better solvated by dimethylsulphoxide than methanol. Therefore, it seems more likely that the observed increase in the value of K, which measures the stability of the adduct, may be due to the increase in the activity coefficient of PhS^- ion with value about 4×10^4. This interpretation may also account for the great increase in the value of the equilibrium constant for the formation of 1,3,5-trinitrobenzene-methoxide adduct in dimethylsulphoxide and it indicates a value 10^8 for the activity coefficient for the methoxide ion. The larger value of the activity coefficient of the methoxide ion than that of the thiophenoxide ion is consistent with the fact that methoxide ion is a strong hydrogen bond acceptor and it will be more activated on transfer from methanol to DMSO than the polarizable thiophenoxide ion.

Norris[60] has determined the equilibrium constants for the reaction between 1,3,5-TNB and cyanide ion in some non aqueous solvents. Although the values showed a considerable change from one solvent to another, he did not relate this behaviour to any solvent properties. Buncel et al[65] have recently measured the equilibrium constant for the formation of the 1,3,5-TNB-CN adduct in alcoholic solvents. The large increase in the value of K in t-butanol (5×10^5 l/mol) compared with that in methanol (40 l/mol) has been attributed to solvation differences of the reactants and the product which may vary considerably from one solvent to another. Thus the cyanide ion is small with relatively localised negative charge and it would be strongly solvated by a polar protic solvent such as methanol. Furthermore the charge on the σ-complex is delocalised and hydrogen bonding between the complex and polar protic solvent is probably fairly weak. On the other hand, the cyanide ion is poorly solvated by t-butanol and hence it becomes more reactive.

It was found that the high value of K in t-butanol is associated with a large enthalpy of reaction (-15 k cal mol^{-1}) and large negative entropy change (-25 cal $deg^{-1}mol^{-1}$) while in methanol the enthalpy change is approximately zero and the entropy is small and positive. It might, therefore, be anticipated that the reaction of cyanide ion with 1,3,5-trinitrobenzene to give σ-complex in weakly interacting solvents should be characterised by a high K, large ΔH and large negative ΔS. Values of ΔH and ΔS of this order of magnitude associated with high values of K - 10^5 $1.mol^{-1}$ have been observed for the formation of the 1,3,5-trinitrobenzene-cyanide complex in chloroform and acetone. The equilibrium constant in other alcohols such as ethanol, n-propanol, n-butanol at 25^o are all in the range 1,000-20,000 1 mol^{-1}. The heats of reaction are -7 ± 1•5 kcal mol^{-1} and the entropy change -9 ± 3 cal deg^{-1} mol^{-1}. They thus show intermediate behaviour between the two extremes of methanol and t-butanol. This indicates that the solvation of CN^- ion is a major factor in Meisenheimer complexes stability. Comparison between the enthalpy and entropy changes for the formation of 1,3,5-trinitrobenzene-cyanide adducts in ethanol and 1,3,5-trinitrobenzene-ethoxide adducts in ethanol indicate that the larger entropy change in the latter case may imply that desolvation of ethoxide ion in the formation of its σ-complex with 1,3,5-trinitrobenzene is greater than with cyanide ion.

It might be expected that the factors which cause a larger increase in the stability of 1:1 adducts in dipolar aprotic solvents will also favour formation of 1:2 adducts. However there is some evidence that 1:2

adducts are not readily formed in dipolar aprotic solvents are better solvated by water. Thus N,N-dimethylpicramide gives a 1:2 adduct with hydroxide ions in water,[51] and 1:2 adduct is readily formed from nitrocompounds and aqueous sodium sulphite.[56]

CHAPTER 2

EXPERIMENTAL

I. Solvents

Water: Distilled water was boiled to remove carbon dioxide and subsequently protected from air.

Methanol: A.R. methyl alcohol was used without purification.

Ethanol: The commercial material was distilled, the middle portion, b.p.78•5^{o}, being collected.

Isopropyl alcohol: The commercial material was used without purification.

Dimethylsulphoxide: Commercial dimethylsulphoxide was refluxed with calcium hydride and fractionated under reduced pressure.

Dioxan: Commercial dioxan was refluxed with sodium metal and distilled.

Acetone: A.R. acetone was used without purification.

Chloroform: The commercial material was used.

II. Solutions of Alkali

Aqueous Sodium Hydroxide: A.R. sodium hydroxide pellets were washed several times with distilled water and the washings were discarded. The remaining solid was dissolved in more distilled water. The concentration of the solution was determined by titration of 1 ml. samples with standard 0•1N hydrochloric acid using phenolphthalein as indicator.

Aqueous Buffer Solution: Borax buffer[109] solutions were prepared from 0•025M borax and 0•1M sodium hydroxide solution in water. The acidities of all buffers were checked before use with a pH meter.

Sodium Methoxide: Freshly cut pieces of sodium metal were washed with A.R. methanol and then dissolved in methanol under reflux in a flask protected from the atmosphere with a soda lime guard tube. Nitrogen was passed through the methyl alcohol before and during the reaction with sodium. Usually a clear solution was obtained. Sometimes the solution was cloudy, however clear solutions were obtained on standing. The concentration of the solution was found by titrating 1 ml. of the sample with 0•1N standard hydrochloric acid using phenolphthalein as indicator.

Sodium Ethoxide and Sodium Isopropoxide: were prepared in a similar manner to sodium methoxide from sodium metal and the appropriate alcohol.

Lithium Methoxide: Lithium metal pieces were dissolved in A.R. methanol, and prepared as for the sodium methoxide preparation.

Aqueous Sodium Sulphite: A.R. anhydrous sodium sulphite was dried in an oven at 140°C. Aqueous solutions of known concentration were made up from the solid and distilled water.

Sodium Thiophenoxide: Commercial ethanthiol was used without purification. Thiolate ions were generated from solutions of ethanthiol in ethyl alcohol by addition of known quantities of sodium ethoxide in ethanol. A sufficient excess of ethanthiol was used to insure a very low residual concentration of ethoxide ions.

Similarly solutions of sodium thiophenoxide, sodium and lithium p-aminothiophenoxide and sodium-p-methylthiophenoxide in ethanol or methanol were prepared by addition of known quantities of the appropriate alkoxide to solutions containing excess of the parent thiols.

III. Aromatic Nitro-Compounds

Picric acid: Commercial picric acid was recrystallised from methanol to constant m.p. 122°C (Lit. 122°C).[110]

1,3,5-Trinitrobenzene: Commercial 1,3,5-trinitrobenzene was recrystallised from methanol to constant m.p. 121°C (Lit. 122•5°).[110]

2,4,7-Trinitrofluorenone: Commercial specimen was used without purification.

Picramide: Was prepared from picryl chloride by the method of Glazer et al.[111] To a solution of picryl chloride (31 gm.) in methanol (200 ml.) was added a 1:1 mixture of 0•88 ammonia and water (120 ml.). The solution turned bright red before precipitating picramide as a yellow solid. When recrystallised from acetic acid crystals of m.p. 191°C were obtained (Lit. m.p. 192°C).[112]

1,2,3,5-Tetranitrobenzene: was prepared by the oxidation of picramide using Holleman's method.[113] To dry picramide (19 gm.) was added 20% of its weight of water. The wet picramide was suspended in 58•4 ml. of nitric acid (d. 1•40) to which nitric acid (d. 1•50) was added in order to correct for the added water. Nitrous vapours prepared by the decomposition of sodium nitrite with sulphuric acid, were introduced into the mixture which had been cooled to -5°. The temperature rose and addition of gas was halted until the temperature again fell to -5°. This procedure was performed three times until an increase in weight amounting to 3 gm. had been achieved. An excess of nitrous gas was used in order to avoid the formation of hexanitro-diphenylamine which might be formed by the action of diazo compound on unchanged picramide. After the third addition of gas the mixture was allowed to stand overnight at room temperature. The crude 1,2,3,5-tetranitrobenzene which separated, was filtered, washed with a little nitric acid (density 1•4), then washed with cold water and finally washed with a little petroleum ether. The product was dried. Yield 17 gm.

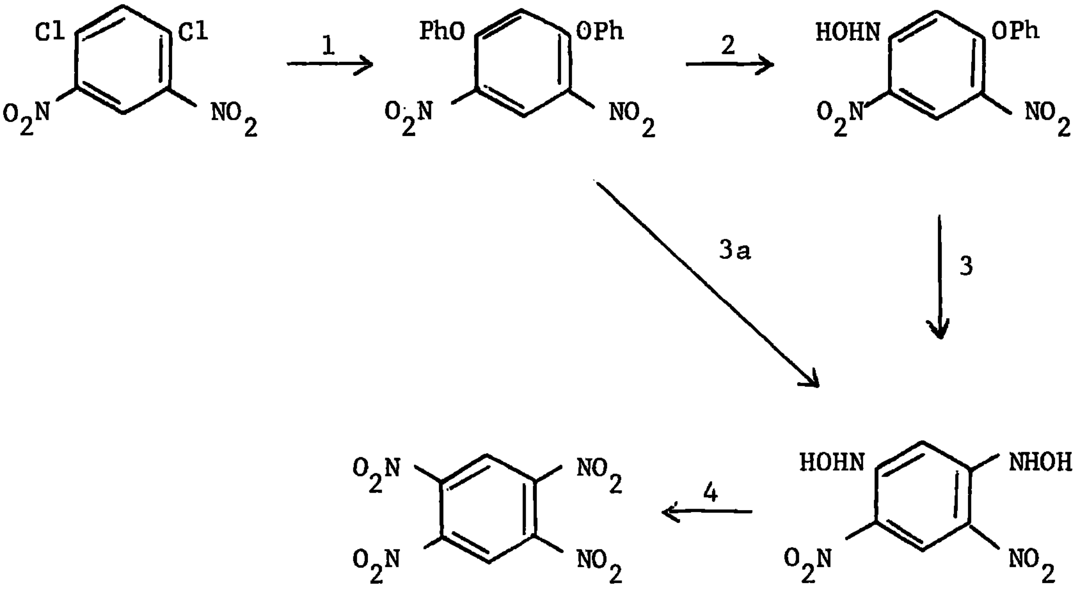
<u>Purification of 1,2,3,5-tetranitrobenzene</u>: 17 gm. of 1,2,3,5-tetranitrobenzene was dissolved in benzene (1 litre) and decanted from the residue. The 1,2,3,5-tetranitrobenzene solution in benzene was shaken vigorously three times with 17 c.c. portions of concentrated sulphuric acid. The acid was removed each time after shaking. The benzene solution was washed twice with cold water to remove the acid. The benzene solution was then dried with calcium chloride and the solvent evaporated off on a water bath until the volume was 200 ml. 1,2,3,5-tetranitrobenzene was obtained and recrystallised from chloroform to constant m.p. 127°C (Lit. 126°C).[114]

As was expected, the N.M.R. spectrum of the obtained crystals dissolved in dioxan or ethanol showed, in addition to the solvent peaks, a single resonance at -9•40 ppm (relative to TMS) due to the two equivalent ring protons.

1,3-Dichloro-4,6-dinitrobenzene: was prepared by the method of T.H. Boyer and R.S. Buriks.[115] To a well stirred solution of potassium nitrate (140 gm., 1•386 mole) in concentrated sulphuric acid (500 ml.) was added m-dichlorobenzene (100 gm., 0•68 mole) in one portion. The temperature of the reaction mixture rose during a few minutes to 135-140°, then dropped slowly to 125°. The stirred mixture was kept at 120-135° for an additional hour. After the reaction mixture had been cooled to about 90° it was poured over 1•5 kgm of crushed ice. The precipitated product was collected by suction filtration, drained well on the funnel, and dissolved in about 1 litre of boiling 95% ethanol. A small amount of insoluble impurity was removed by filtration of the hot solution, and the product was allowed to crystallise at about 0°. The yield of yellow needles was 113 gm., m.p. 103° (Lit. 103-104).[115]

As expected for this compound, the H^1 N.M.R. spectrum in dimethylsulphoxide showed two bands of equal intensity at -8•38 and -8•93 ppm from internal tetramethylsilane.

1,2,4,5-tetranitrobenzene: Borsche and Faske[116] had prepared this compound starting from 1,3-dichloro-4,6-dinitrobenzene in several stages according to the following scheme:



1,3-Diphenoxy-4,6-dinitrobenzene: Sodium metal (4·6 gm.) was dissolved in heated phenol (200 gm.) and 1,3,-dichloro-4,6-dinitrobenzene (23·6 gm.) was gradually added. The reaction mixture was kept on a water bath for one day. Excess phenol was removed by steam distillation and the non-volatile residue was recrystallised from boiling methanol. Yield was 30 gm. of colourless crystals m.p. 128^{o} (Lit. 129^{o}).[116]

In addition to the solvent peaks, the H^{1} NMR spectrum of this compound dissolved in dimethylsulphoxide showed two resonances of equal intensity at -8·9 and -6·3 ppm attributed to ring protons and a multiplet absorption centred at -7·22 ppm attributed to the phenyl groups. These absorptions are consistent with those expected from 1,3-diphenoxy-4,6-dinitrobenzene.

1,Hydroxyl-3-phenoxy-4,6-dinitrobenzene: A solution of hydroxylamine hydrochloride (8 gm.) in alcohol (120 ml.) was mixed with a solution of sodium (2•6 gm.) in alcohol (40 ml.). The resultant solution, while still hot, was added to a solution made up from 1,3-diphenoxy-4,6-dinitrobenzene (11•9 gm.) in alcohol (80 ml.). The deep-green coloured mixture was boiled on a water bath for three hours, becoming brown-yellow during the course of the reaction. On evaporation a red-violet crystalline crust remained behind. This was washed with cold benzene to remove the phenol and afterwards treated with more benzene. The solution was filtered and the filtrate diluted with half its volume of ligroin (60/80 petroleum ether). When the solution was allowed to cool yellow needles, m.p. 115^{o} with decomposition (Lit.116^{o}C)[116] separated out which were the required product. These yellow crystals were, however, unstable. On leaving in the mother liquor for a few days they changed into red coloured crystals with m.p.106^{o} (Lit. 108^{o}C).[116]

1,3-Dihydroxylamino-4,6-dinitrobenzene: Was prepared in two stages. In the first stage a solution of ether 1-hydroxylamino-3-phenoxy-4,6-dinitrobenzene (17•6 gm.) in alcohol (80 c.c.) was boiled for 4 hours with hydroxylamine (90 ml.) solution from hydroxylamine hydrochloride (4 gm.). The resulting mixture was filtered and concentrated by evaporation.

In the second stage, to the residue was added alcohol (80 ml.) and as before was boiled with hydroxylamine solution from hydroxylamine hydrochloride (8 gm.). While still hot the reaction mixture was filtered by suction and left at room temperature to evaporate in a large evaporating dish. After evaporating, the crude product, in a mixture with phenol in a dark crust, was obtained. This mixture was boiled successively with benzene and with alcohol. The benzene dissolved out only the impurities. On addition of water to the alcoholic solution of the product, brown crystals were obtained, m.p. 184°C with expn. (Lit. 189°).[116]

On repeating this preparation, it was found that only a poor yield of 1-hydroxylamine-4,6-dinitro-3-phenoxybenzene was obtained from reaction (2). However it was found that the portion of the product of reaction (2) which was insoluble in benzene contained mainly the 1,3-dihydroxylamine-4,6-dinitrobenzene as was indicated from the m.p. and the H^1 NMR spectrum. Thus it seems likely that the reaction (3a) was the main route to 1,3-dihydroxylamino-4,6-dinitrobenzene.

The H^1 NMR spectra of 1-hydroxylamino-4,6-dinitro-3-phenoxybenzene and 1,3-dihydroxylamino-4,6-dinitrobenzene are shown in Fig.1. The spectrum of the former compound shows two singlets at -6•60 and -8•9 ppm due to the ring protons, a multiplet centred at -7•4 ppm due to the five protons of the phenoxy ring and a band at -11•0 ppm which is attributed to the amino proton of the hydroxylamino group.

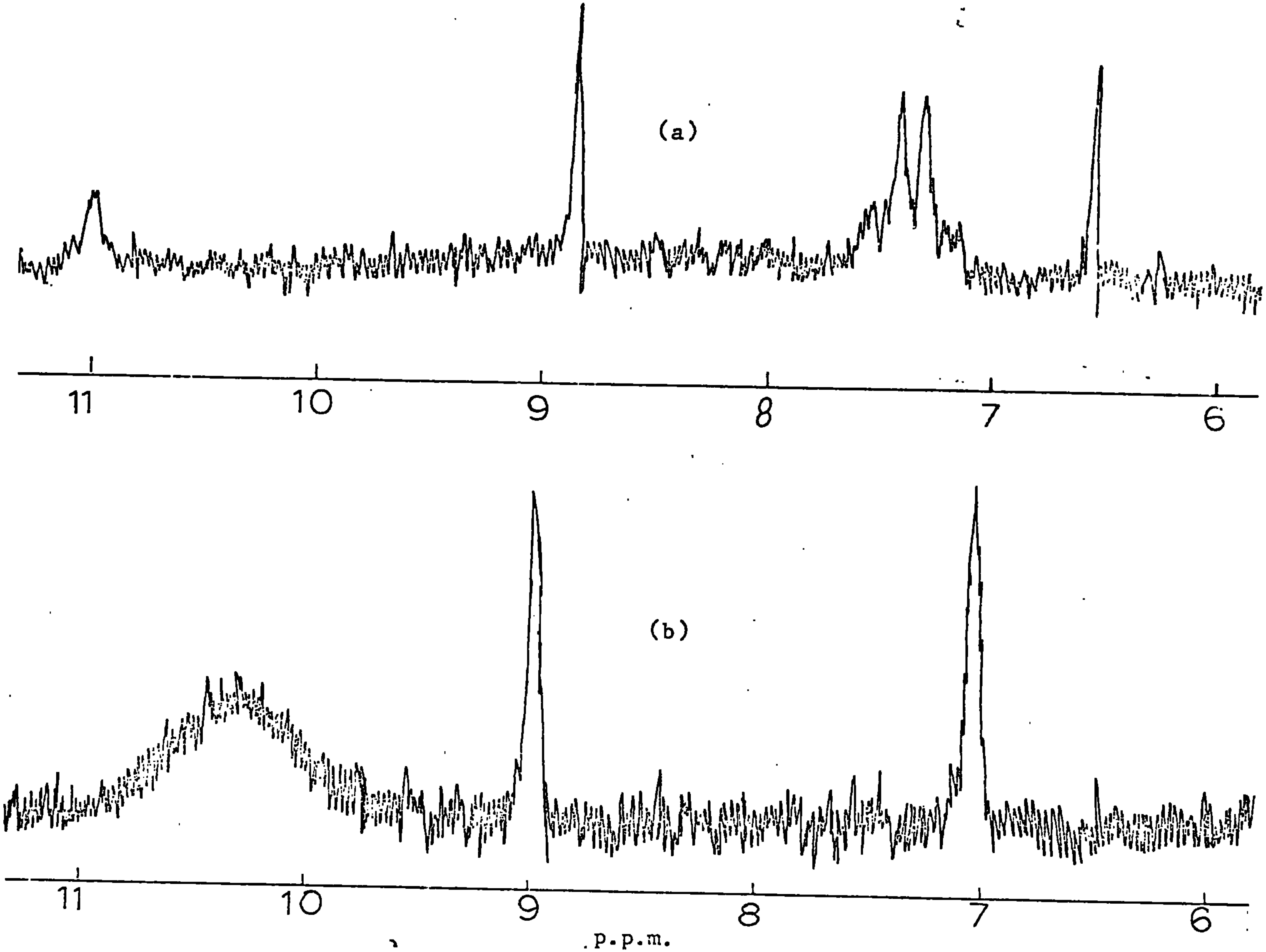


Fig.1. NMR spectra in DMSO of (a) 1-hydroxylamino-4,6-dinitro-3-phenoxybenzene (b) 1,3-dihydroxylamino-4,6-dinitrobenzene (chemical shifts are measured relative to internal TMS).

The latter compound shows two singlets of equal intensity at -7•03 and -9•00 ppm due to the ring protons and a band at -10•3 ppm due to the two amino protons of the hydroxylamino groups. These spectra are consistent with the expected structure of the products.

1,2,4,5-tetranitrobenzene: was prepared by oxidation of 1,3,-dihydroxylamino-4,6-dinitrobenzene which on dissolving in ten times its weight of cold nitric acid (d. 1•52) gave a light green colour. On heating the colour changed through brown to yellow. After 90 minutes on a water bath the reaction mixture was allowed to cool and then poured into water to give light yellow crystals which were the required 1,2,4,5-tetranitrobenzene. Recrystallisation from chloroform yielded a product of m.p. 188°C (Lit.188°C).[116] The ^{1}H NMR spectrum shows a single sharp resonance at -8•82 ppm.

1,3-Dimethoxy-4,6-dinitrobenzene: was prepared by the method of Holleman.[117] To a solution of 1,3-dinitro-4,6-dichlorobenzene (10 gm.) in hot methanol (200 ml.) was gradually added sodium methoxide (20.ml., 5•5M) (2 equivalent). The reaction solution was boiled for one hour. The solid product was filtered off after the solution cooled. Crystallisation from methanol yielded crystals of m.p. 152-154° (Lit. 154-157°).[117] As expected the H^1 NMR spectrum showed two bands of equal intensity at -8•66 and -7•06 ppm (relative to internal reference TMS) due to the two ring protons and a more intense band at -4•12 ppm due to the two equivalent methoxyl groups.

2,4,6-Trinitrophenetole: was prepared from picryl chloride in boiling ethanol to which was added slowly a solution of sodium ethoxide in ethanol (1 equivalent). When the addition was complete water was added and the 2,4,6-trinitrophenetole which separated on cooling was recrystallised from ethanol to give dark yellow crystals, m.p. 78° (Lit. 78•5°).[110]

2,4,5-Trinitrophenol: To a solution of sodium hydroxide was added an equivalent quantity of 1,2,4,5-tetranitrobenzene. The solution was warmed and stirred. The product which was isolated had m.p. 94° (Lit. 96°).[118]

1,3-dinitro-4,6-diaminobenzene: was prepared by method of Boyer and Buriks.[115] Ammonia gas was bubbled into a well-stirred, clear yellow solution of 1,3-dichloro-4,6-dinitrobenzene (30 gm., 0•253 mole) in technical grade ethylene glycol (200 ml.) (heated to 140°) at such a rate that the gas was just absorbed. Within 30 minutes, the colour of the solution changed through orange to deep red. About 1 hour after the start of the reaction an orange crystalline precipitate began to separate. Heating was continued for an additional 2 hours as a slow stream of ammonia gas was bubbled through the reaction mixture. Finally, the reaction mixture was cooled to room temperature, the product was collected by suction filtration, and the finely divided orange-brown crystals were washed with boiling water and boiling ethanol. The yield of dried product was 23 gm., m.p. 300°C.

1,2,4-Trinitrobenzene: was prepared by the oxidation of 2,4-dinitroaniline using the method of William et al.[119] A solution of peroxytrifluoroacetic acid was prepared from 90% hydrogen peroxide (4•5 ml., 0•2 mole), trifluoroacetic anhydride (34 ml., 0•24 mole) and chloroform (50 ml.). The solution was rapidly heated to reflux and 2,4-dinitroaniline (9•2 gm., 0•05 mole) was added in small portions. After the vigorous exothermic reaction was complete, the volatile solvent was removed at reduced pressure. To the residual oil was added ice-water (50 ml.) and the oil crystallised after being scratched with a glass rod. This product was recrystallised from ethanol (25 ml.) to yield 9•3 gm. of yellow crystalline 1,2,4-trinitrobenzene, m.p. 57-59° (Lit. m.p. 61°).[119]

IV. Spectroscopic Measurements

A. Visible Spectra: In view of the strong colours produced as a result of the interaction of aromatic nitro-compounds with nucleophiles, visible spectroscopy was found very useful in studying these reactions for both kinetic and equilibrium purposes. Thus the general shape of the visible spectra were recorded on Unicam SP 800 instrument at room temperature 20 ± 2°. However in certain cases where species produced were unstable at this temperature, spectra were recorded on solutions cooled to near 0°.

Accurate values of the optical density at suitable wavelengths were measured on an SP 500 spectrophotometer fitted with a thermostatted cell compartment. Test solutions (5 or 10 ml.) were prepared from stock solutions of the components by pipette. Stock solutions were prepared as near the time of use as possible and test solutions were made up immediately prior to the measurement.

These measurements allowed the equilibrium constant for a reaction between colourless reactants to give a single coloured product to be determined in the following way:

$$P + Nu \rightleftharpoons A$$

i) If at some stage conversion to complex A was complete then the extinction coefficient of A could be determined using Beer's Law.

$$O.D = \Sigma_A \times [A] \times 1$$

where 1 is the pathlength of the cell used (1 cm). Concentrations of A at various nucleophile concentrations could then be found and the equilibrium constant determined by the law of the mass action

$$K = \frac{[A]}{[P][Nu]} \quad 1.mol^{-1}$$

ii) If the extinction ceofficient of complex A could not be found directly the Benesi-Hildebrand[93] expression

$$\frac{a}{O.D} = \frac{1}{\Sigma_A K_A} \frac{1}{[Nu]} + \frac{1}{\Sigma_A}$$

was used (a = stoichiometric concentration of P). Usually the plot of $\frac{a}{O.D}$ versus $\frac{1}{[Nu]}$ was linear and from the slope and intercept the equilibrium constant and extinction coefficient could be found.

B. Proton Nuclear Magnetic Resonance Spectroscopy:

Two instruments were used, a Perkin-Elmer R10 spectrometer and a Varian A 60 spectrometer. Measurements were usually made at ambient probe temperature ($30^{o}C$). Solutions of concentration 0·1 mole $litre^{-1}$ were required. Internal tetramethylsilane was used as internal reference. However in solutions in water where this reference material was insoluble, dioxan was used. A chemical shift difference of 3·7 ppm between the two standards is assumed.

CHAPTER 3

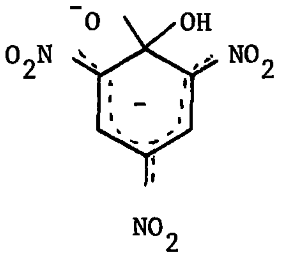
RESULTS AND DISCUSSION

Section I

Interaction of Picric Acid with Aqueous Sodium Sulphite and with Sodium Hydroxide

INTRODUCTION

Owing to its high dissociation constant (pK_a = -0·33),[120] picric acid exists in dilute solutions in water or slightly alkaline media as the picrate ion which has a characteristic visible spectrum with maximum at 3550Å (Σ = 1·4 x 10^4 $l.mol^{-1}cm^{-1}$) and shoulder at 4000Å. However, Abe[121] has reported the replacement of the visible absorption due to the picrate ion by an intense band at 3900Å in solutions containing high concentrations of sodium hydroxide. He ascribed this change in the visible absorption, to the formation of the adduct (I) which results from hydroxide ion addition at C_1.


(I)

More recently, Gold and Rochester[122] have examined the behaviour of picric acid in aqueous sodium hydroxide. They found that the change in the visible spectrum depended on a high power of sodium hydroxide concentration and suggested that the adduct produced probably resulted from the interaction of picrate ion with one or more hydroxide ions.

In this part of the present work the interaction of picric acid with sodium sulphite and sodium hydroxide have been examined by visible and proton nuclear magnetic resonance spectroscopy. The former was used to determine the equilibrium constants while the investigation by the latter technique throws light on the structures of the species formed.

i) Interaction of Picric Acid with Sodium Sulphite

(a) Visible spectroscopic Study

The visible spectra of dilute aqueous solutions of picric acid showed very little absorption in the visible region above 4800Å. However, as the concentration of sodium sulphite was gradually increased, changes occurred in the visible spectrum as shown in Fig.1a. These changes which are indicated by a new absorption at longer wavelength and the occurrence of an isobestic point at 3710Å, suggest an equilibrium between the picrate ion and sodium sulphite presumably through the formation of a complex which will be denoted as complex A. However, before the conversion to complex A was complete, a second interaction occurred and eventually at high sulphite concentration the spectra showed a single absorption in the visible region with a maximum at 3850Å attributed to a complex B resulting from the interaction of complex A with second molecule of sulphite. Spectra of solutions containing only A and B (Fig.1b) showed isobestic points at 3550 and 4160Å.

It has been shown previously[56] that a number of 1-X-2,4,6-trinitrobenzenes(X = H, OMe, NH_2, etc.) react reversibly with aqueous sodium sulphite solution to give 1:1 and 1:2 adducts by addition of one and two sulphite ions at ring carbon carrying hydrogen. Therefore assuming a similar mode of interaction which would involve a picrate ion and respectively one and two molecules of sodium sulphite, thenthe two equilibria mentioned above may be written as follows, neglecting the

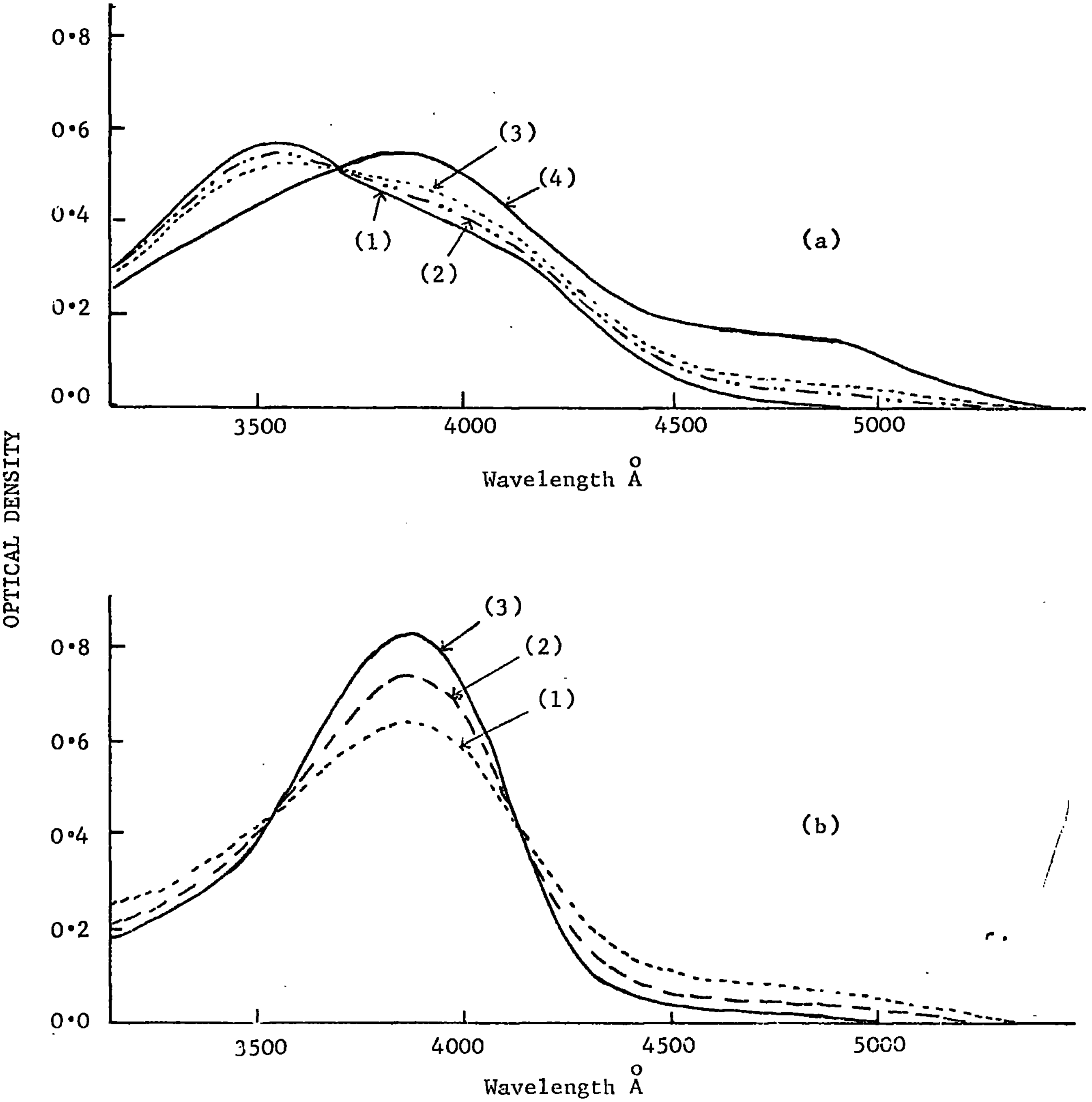


Fig.1. Visible absorption spectra of picric acid (4 x 10^{-5}M) in water containing the following molarities of sodium sulphite (a) 1, 0•00; 2, 0•04; 3, 0•08; 4, calculated spectrum for complete conversion into complex A, (b) 1, 0•20; 2, 0•30; 3, 0•80 corresponds to complete conversion into complex B.

charges of the species A and B.

$$\text{Picrate}^{-} + SO_3^{=} \rightleftharpoons A \qquad K_A$$

$$A + SO_3^{=} \rightleftharpoons B \qquad K_B$$

Independent evidence that complex B results from the addition of two sulphite ions to the picrate ion is presented later. The equilibrium constants K_A and K_B were determined by measurement of the optical densities at 3710, 4160 and 4900Å given in Table 1. The increase in the optical density at 4900Å was mainly due to the formation of complex A, as both the picrate ion and complex B have very little absorption at this wavelength.

However, the measurement of the optical densities at the isobestic points 3710 and 4160Å allowed the extent of the formation of complex B and the free picrate ion to be calculated in the following manner.

Solutions containing only complex A and B showed an isobestic point at 4160Å. Therefore

$$\Sigma_A\ (4160\text{Å}) = \Sigma_B\ (4160\text{Å}) \tag{1}$$

where Σ_A and Σ_B are the extinction coefficients for the complexes A and B respectively. However the optical density at 4160Å for solutions containing A, B and the picrate ion is given by:

$$\mathrm{O.D}(4160\text{Å}) = [\mathrm{P.A}]\ \Sigma_{\mathrm{P.A}}(4160\text{Å}) + [\mathrm{A}] \times \Sigma_{\mathrm{A}}(4160\text{Å}) + [\mathrm{B}] \times \Sigma_{\mathrm{B}}(4160\text{Å}) \qquad (2)$$

And also since the stoichiometric concentration of picrate ion was 4×10^{-5}M, then

$$[\mathrm{P.A}] + [\mathrm{A}] + [\mathrm{B}] = 4 \times 10^{-5} \qquad (3)$$

Therefore, from (1), (2) and (3)

$$\mathrm{O.D}(4160\mathrm{A}) = [\mathrm{P.A}]\left\{ \Sigma_{\mathrm{P.A}}(4160\text{Å}) - \Sigma_{\mathrm{A}}(4160\text{Å}) \right\} + \Sigma_{\mathrm{A}}(4160\text{Å}) \times 4 \times 10^{-5} \qquad (4)$$

Since the optical density at 4160Å for solutions containing only A and B is 0•445 and that due to the picrate ion is 0•32, then

$$\Sigma_{\mathrm{A}}(4160\text{Å}) = \frac{0{\cdot}445}{4 \times 10^{-5}}\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$$

$$\Sigma_{\mathrm{P.A}}(4160\text{Å}) = \frac{0{\cdot}32}{4 \times 10^{-5}}\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$$

Substituting for Σ_{A} and $\Sigma_{\mathrm{P.A}}$ in (4) gives

$$\mathrm{O.D}(4160\mathrm{A}) = [\mathrm{P.A}]\left[\frac{-0{\cdot}125}{4 \times 10^{-5}}\right] + 0{\cdot}445$$

from which the concentration of the picrate ion is given by

$$[\mathrm{P.A}] = \frac{0{\cdot}445 - \mathrm{O.D}(4160\mathring{A})}{0{\cdot}125} \times 4 \times 10^{-5}$$

Similarly, the measurement of the optical density at 3710Å gave the concentration of complex B by the expression

$$[\mathrm{B}] = \frac{\mathrm{O.D}(3710\mathring{A}) - 0{\cdot}518}{0{\cdot}162} \times 4 \times 10^{-5}$$

Once the concentration of the picrate ion and the complex B were known, the concentration of the complex A could be determined by difference. However, in view of the fact that the picrate ion and complex B have little absorption at 4900Å, the concentration of complex A could be found from measurements at this wavelength where the extinction coefficient of complex A was found to be $(3{\cdot}8 \pm 0{\cdot}2) \times 10^{3} M^{-1} cm^{-1}$. The data related to complex A in Table 1 were in fact calculated on this basis. Measurement of the optical densities, relative concentrations of the species and the calculated equilibrium constants are given in Table 1.

However the increase in the values of the equilibrium constants K_A and K_B as the concentration of the sodium sulphite is raised, is similar to that observed by Crampton[56] in the equilibrium constants for the formation of 1:2 adduct produced from the reaction of 1-X-2,4,6-trinitrobenzene (X = H, OMe, NH_2) with sodium sulphite. He ascribed this behaviour to changes in the activity coefficients of the charged species

TABLE 1

Dependence of visible absorption of picric acid (4 x 10^{-5}M) on sodium sulphite concn. in water and calculated eq.const.

$[Na_2SO_3]$	O.D.			Relative Concn.			K_A	K_B
(M)	3710Å	4160Å	4900Å	Picrate	B	A	(l.mole^{-1})	
0·000	0·522	0·320	0·003	1	0	0		-
0·010	0·522	0·323	0·006	0·975	0	0·02	2·05	-
0·015	0·520	0·325	0·008	0·96	0	0·04	2·79	-
0·020	0·520	0·327	0·011	0·945	0	0·055	2·9	-
0·025	0·520	0·330	0·014	0·920	0	0·075	3·25	-
0·030	0·518	0·332	0·017	0·905	0	0·095	3·5	-
0·040	0·518	0·337	0·022	0·865	0	0·13	3·9	-
0·050	0·520	0·343	0·028	0·815	0	0·18	4·4	-
0·060	0·518	0·348	0·034	0·78	0	0·21	4·5	-
0·065	0·518	0·351	0·037	0·75	0	0·24	4·9	-
0·070	0·520	0·356	0·041	0·725	0	0·27	5·3	-
0·080	0·520	0·361	0·046	0·67	0·02	0·30	5·6	1·25
0·085	0·520	0·365	0·048	0·65	0·024	0·32	5·8	1·5
0·090	0·522	0·369	0·052	0·61	0·03	0·35	6·4	1·7
0·095	0·524	0·373	0·058	0·58	0·04	0·37	6·7	1·4
0·10	0·526	0·376	0·063	0·55	0·06	0·39	7·1	1·6
0·15	0·560	0·409	0·075	0·29	0·26	0·48	11	3·6
0·20	0·590	0·432	0·069	0·11	0·44	0·44	20	5·0
0·25	0·630	0·437	0·060	0·06	0·69	0·35	-	7·9
0·30	0·644	0·443	0·045	0·02	0·78	0·25	-	10·5
0·40	0·66	0·445	0·027	0	0·88	0·12	-	18
0·60	0·68	0·445	0·019	0	1	0·06	-	28
0·80	0·68	0·445	0·010	0	1	0	-	-
1·0	0·68	0·445	0·010	0	1	0	-	-

with the ionic strength of the solutions. In the present case, if the complexes A and B are formed by addition of one and two molecules of sulphite ions to the negatively charged picrate ion, then A and B would carry 3 and 5 negative charges respectively. Therefore it would not be expected that the activity coefficient ratios

$$\frac{f(A)}{f(P.A)f(SO_3)} \text{ for complex A and } \frac{f(B)}{f(A)f(SO_3)} \text{ for complex B,}$$

would remain constant with the increasing ionic strength in these solutions. The fact that this behaviour was indeed due to the effect of the ionic strength was shown by the almost constant values obtained for K_A and K_B in solutions made up to constant ionic strength with sodium sulphite. Details of the optical density and the equilibrium constants in these solutions are given in Tables 2 and 3. In addition to that, Crampton[56] has shown recently in a similar system that the activity coefficient of charged species could be satisfactorily represented by Debye-Huckel[123] expression

$$-\log_{10} f_i = \frac{AZ^2 \sqrt{I}}{1 + 1{\cdot}2\sqrt{I}}$$

where $A = 0{\cdot}507 \text{ mol}^{\frac{1}{2}}\ 1^{\frac{1}{2}}$ and I is the ionic strength. This expression has also been applied in the present work in the following way:

The first equilibrium between the picrate ion and sulphite ion to form complex A, could be written in terms of the charges on the species as

TABLE 2

Measurements of the optical densities and the calculated equilibrium constants in solutions of constant ionic strength[a] 0·3

[Na_2SO_3] (M)	O.D.		Relative Concn.			K_A
	4160A	4900A	Picrate	[A]	[B]	l.mole^{-1}
0	0·320	0·003	1	0	0	-
0·01	0·328	0·011	0·94	0·055	0	5·9
0·015	0·330	0·145	0·92	0·08	0	5·9
0·020	0·333	0·018	0·90	0·105	0	5·8
0·025	0·335	0·020	0·88	0·12	0	5·5
0·030	0·337	0·022	0·87	0·13	0	5·0
0·04	0·346	0·030	0·80	0·19	0	5·9
0·05	0·351	0·036	0·76	0·23	0·01	6·1
0·06	0·357	0·043	0·70	0·28	0·02	6·6
0·065	0·359	0·044	0·69	0·29	0·02	6·4
0·07	0·361	0·046	0·67	0·30	0·03	6·4
0·08	0·368	0·053	0·62	0·34	0·04	6·8

[a] Using sodium sulphate as the added salt.

TABLE 3

Measurements of optical densities and calculated eq. constants in solution of constant ionic strength[a] 3

$[Na_2SO_3]$ (M)	O.D.			Relative Concentration			K_A	K_B
	3710Å	4160Å	4900Å	Picrate	[B]	[A]	$l.mole^{-1}$	$l.mole^{-1}$
0	0·522	0·322	0·003	1	0	0	-	-
0·010	0·530	0·356	0·028	0·725	0·075	0·18	25	42
0·015	0·544	0·372	0·038	0·60	0·16	0·24	27	45
0·020	0·555	0·384	0·043	0·51	0·23	0·27	27	43
0·025	0·570	0·395	0·048	0·042	0·32	0·30	28	43
0·030	0·580	0·403	0·049	0·35	0·39	0·30	28·5	43
0·040	0·600	0·416	0·048	0·25	0·51	0·28	28	45
0·050	0·615	0·426	0·046	0·17	0·60	0·27	32	44
0·060	0·625	0·435	0·044	0·10	0·67	0·25	40	44
0·065	0·630	0·438	0·043	0·06	0·70	0·25	-	43
0·070	0·633	0·445	0·040	0	0·72	0·23	-	45
0·080	0·641	0·445	0·037	0	0·77	0·20	-	48
0·085	0·643	0·445	0·036	0	0·78	0·20	-	46
0·090	0·647	0·445	0·035	0	0·81	0·19	-	47
0·095	0·65	0·445	0·034	0	0·83	0·18	-	48
0·100	0·65	0·445	0·032	0	0·83	0·17	-	49
0·15	0·665	0·445	0·024	0	0·92	0·125	-	68
0·20	0·67	0·445	0·018	0	0·96	0·05	-	96
0·25	0·67	0·445	0·015	0	0·96	0·03	-	-
0·30	0·67	0·445	0·013	0	0·96	0·02	-	-
0·40	0·677	0·445	0·010	0	1	0	-	-
0·60	0·677	0·445	0·007	0	1	0	-	-
0·80	0·677	0·445	0·004	0	1	0	-	-
1·000	0·677	0·445	0·007	0	1	0	-	-

[a] using sodium sulphate as the added salt

$$[P.A]^{-1} + [SO_3]^{2-} \rightleftharpoons [A]^{3-}$$

The stoichiometric equilibrium constant for this is given by

$$K_A = \frac{[A]}{[P.A][SO_3]} \qquad (5)$$

and the thermodynamic equilibrium constant is given by

$$K'_A = \frac{[A]}{[P.A][SO_3]} \cdot \frac{f_A}{f_{P.A}\ f_{SO_3}} \qquad (6)$$

From (5) and (6)

$$K'_A = K_A \cdot \frac{f_A}{f_{P.A}\ f_{SO_3^-}}$$

Thus

$$\log_{10} K'_A = \log_{10} K_A + \log_{10} f_A - \log_{10} f_{P.A} - \log_{10} f_{SO_3} \qquad (7)$$

Using Debye-Huckel theory

$$-\log_{10} f_A = \frac{9A\sqrt{I}}{1 + 1{\cdot}2\sqrt{I}}$$

$$-\log_{10} f_{P.A} = \frac{A\sqrt{I}}{1 + 1{\cdot}2\sqrt{I}}$$

$$-\log_{10} f_{SO_3} = \frac{4A\sqrt{I}}{1 + 1{\cdot}2\sqrt{I}}$$

Substitution in equation (7) gives

$$\log_{10} K'_A = \log_{10} K - \frac{4 \times 0{\cdot}507\sqrt{I}}{1 + 1{\cdot}2\sqrt{I}}$$

or

$$\log_{10} K_A = \frac{2{\cdot}028\sqrt{I}}{1 + 1{\cdot}2\sqrt{I}} + \log_{10} K'_A$$

A graph of $\log_{10} K_A$ versus $\frac{\sqrt{I}}{1 + 1{\cdot}2\sqrt{I}}$ was linear for most of its length (Fig.2). The slope was found to be 2•2, very close to that predicted (2•02) theoretically for the formation of triply charged ions from ions carrying respectively one and two charges. Extrapolation to zero ionic strength yielded the thermodynamic equilibrium constant K'_A. A similar plot for $\log_{10} K_B$ was also linear (Fig.3), with slope 6•3, in agreement with that expected (6•1) for the formation of a pentavalent ion from ions carrying three and two charges. These results provide good evidence that the complexes A and B result from the interaction of the picrate ion with respectively one and two molecules of sulphite ion.

(b) H^1 Nuclear Magnetic Resonance Spectra

More light has been thrown on the molecular structure of the higher complex (B) by H^1 N.M.R. measurements of picric acid dissolved in

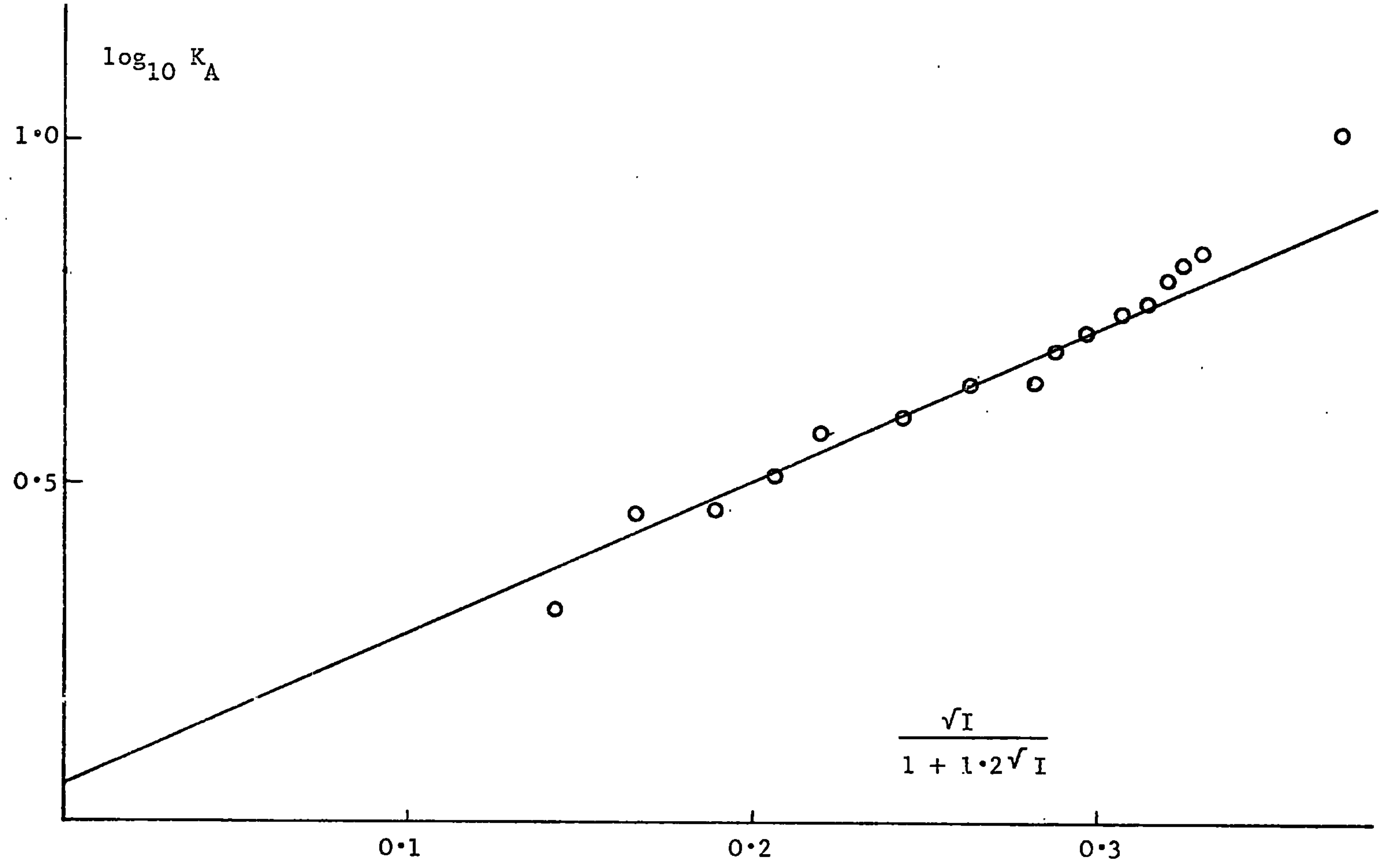


Fig.2. Variation of $\log_{10} K_A$ with the ionic strength for the interaction of picrate ion with sodium sulphite

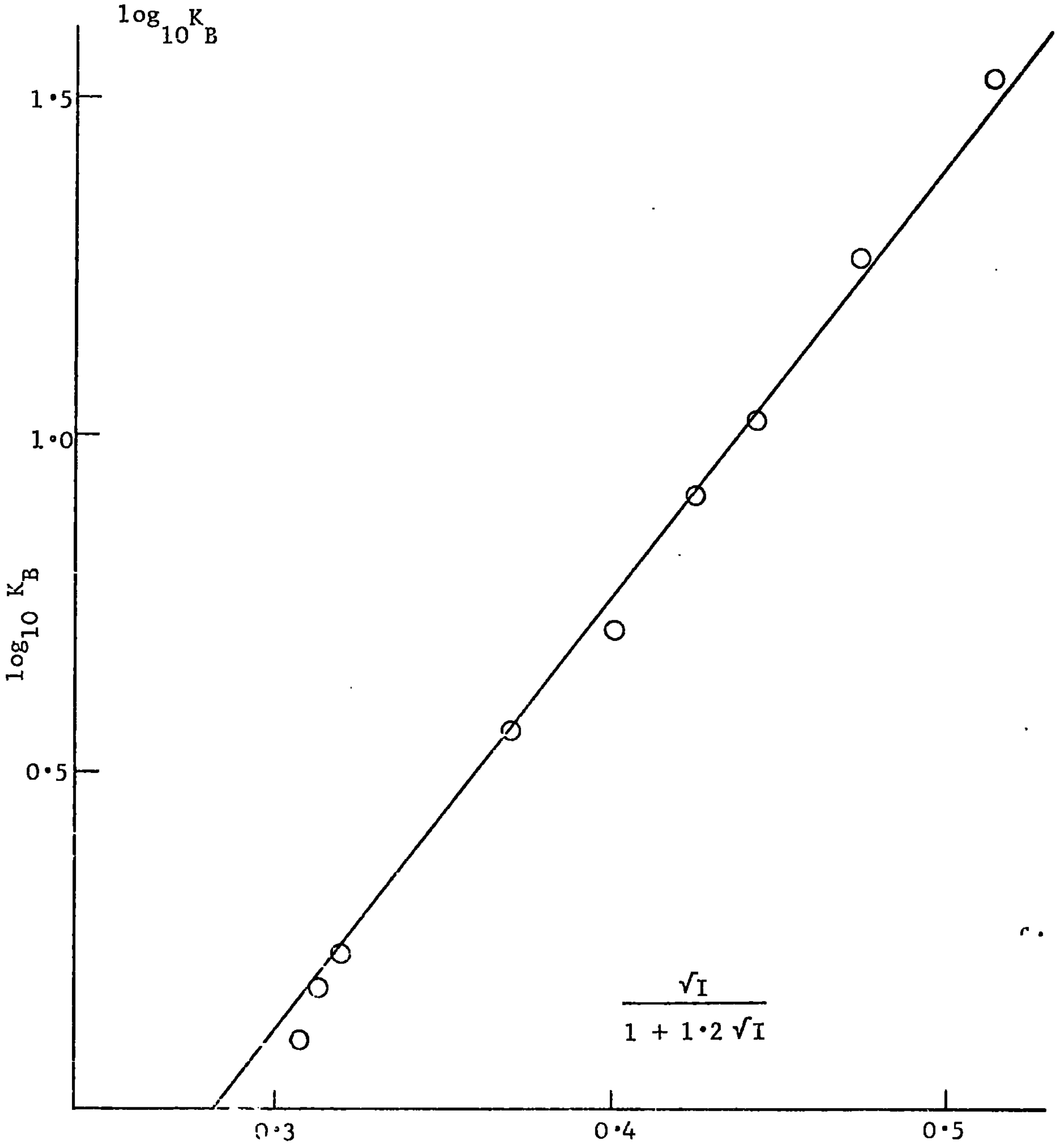
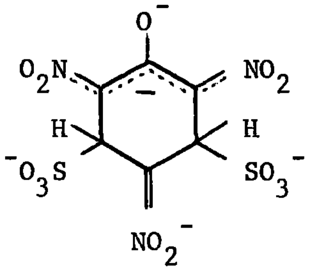
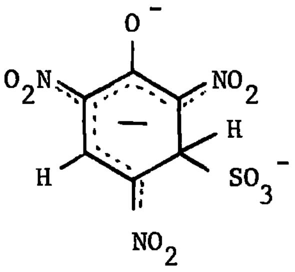


Fig.3. Variation of $\log_{10} K_B$ with the ionic strength.

1-2M-sodium sulphite solutions (Table 7). These spectra showed in addition to the solvent bands, a single sharp resonance at -6·20 ppm (relative to internal tetramethylsilane) attributed to the ring protons of the complex B. This band was shifted considerably to high field from the position of resonance of the ring protons of the picrate ion (-8·70 ppm). This high field shift is consistent with a covalency change at the ring positions carrying hydrogen and is strong evidence that the structure of complex B is (II). The N.M.R. spectrum would in fact be equally in accord with an adduct formed by sulphite addition at three positions (1,3, and 5) or by a bridging sulphite group at the 3- and 5-positions, but these possibilities were rendered unlikely by the equilibrium measurements which indicated that the higher complex involved two sulphite molecules.



(II)



(III)

Attempts to obtain direct evidence for the structure of the lower complex A were unsuccessful. However in view of the structure of complex B, this will probably have structure (III).

These results provide convincing evidence as to the structure of the adducts formed by picric acid with aqueous sodium sulphite solutions and show that they are similar in structure to those formed from other 1-x,2,4,6-trinitrobenzenes and sodium sulphite.[56] It is also of interest to note that the values of K_A and K_B given in Table 4 extrapolated to zero ionic strength are much smaller than the corresponding values for other 1-X-2,4,6-trinitrobenzenes. This resistance of the picrate ion to attack is no doubt due to its initial negative charge.

(c) Effect of Solvent on the Formation of Complexes from Sodium Sulphite and Picrate Ion

Parker[107] has shown that the activities of ions may vary considerably with the change from protic to aprotic solvent. In the present work the effect of changing the solvent from water to dimethyl sulphoxide were examined. Equilibrium constants were determined in solvents containing 20, 40 and 50 volume % dimethylsulphoxide. It was not possible to make measurements in solutions containing a greater proportion of aprotic constituent due to the insolubility of sodium sulphite. The visible spectra in these solutions (Fig.4.) indicate that the major interaction is to produce complex A. However in media containing dimethyl sulphoxide the visible spectrum of complex A varies slightly from that obtained in water. Thus the band at _ca_. 3850Å shows a bathochromic shift while the band at _ca_.4900Å has increased absorption. In addition the spectrum of the picrate ion shows a bathochromic shift and increased

TABLE 4

Equilibrium constants for formation of 1:1 and 1:2 adducts from picrate ion and other 1-X-2,4,6-trinitrobenzenes with aqueous sodium sulphite

Parent	K_A l.mol^{-1}	K_B [b] l.mol^{-1}
Picric acid	$1{\cdot}2 \pm 0{\cdot}3$ [b]	$(1{\cdot}6 \pm 0{\cdot}8) \times 10^{-2}$
1,3,5-trinitrobenzene [a]	$(2{\cdot}5 \pm 0{\cdot}1) \times 10^{2}$	$9{\cdot}2 \pm 1$
2,4,6-trinitroanisole [a]	$(2{\cdot}1 \pm 0{\cdot}3) \times 10^{2}$	$(9 \pm 2) \times 10^{2}$
Picramide [a]	$(1{\cdot}01 \pm 0{\cdot}07) \times 10^{4}$	$(1{\cdot}85 \pm 0{\cdot}15) \times 10^{1}$
N-methylpicramide [a]	$(5{\cdot}4 \pm 0{\cdot}5) \times 10^{4}$	$(1{\cdot}8 \pm 0{\cdot}2) \times 10^{3}$
N,N-dimethylpicramide [a]	$(5{\cdot}4 \pm 0{\cdot}6) \times 10^{4}$	$(6{\cdot}2 \pm 0{\cdot}7) \times 10^{4}$

[a] Reference 56

[b] extrapolated to zero ionic strength

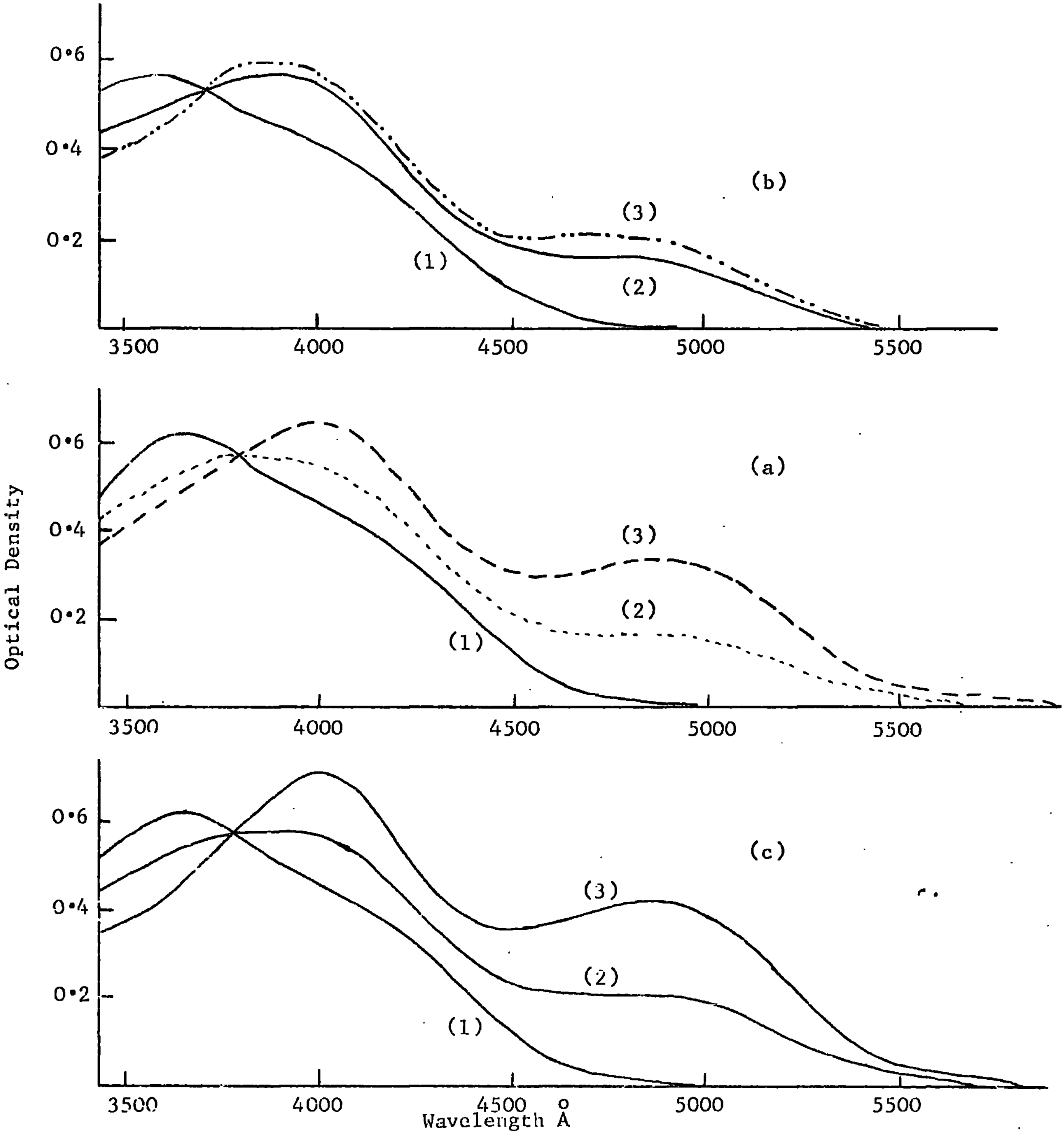


Fig.4. Visible absorption spectra of picric acid (4×10^{-5}M) in a - 4:1 (v/v) water-DMSO with [Na_2SO_3]M:1,000; 2, 0·14; 3, calculated spectrum for complete conversion to complex A, b - 3:2 (v/v) water-DMSO with [Na_2SO_3]M : 1,000; 2, 0·03; 3, 0·11, c - 1:1 (v/v) water-DMSO with [Na_2SO_3]M 1, 0·00 ; 2, 0·02; 3, 0·05.

absorption (Table 6). These changes no doubt reflect changes in solvation of these anions, which being large polarisable species will tend to be better solvated by dimethylsulphoxide than water.

Measurement of optical density at three or two wavelengths allowed the determination of the concentration of the species present in a manner similar to that described for aqueous solutions. Results for the 40/60 (v/v) DMSO/water system are given in Table 5. In each case the value of K_A was found to increase with sodium sulphite concentration. These changes reflect once more the effect of the ionic strength in these solutions. However data of the visible spectra and the values of the equilibrium constants extrapolated to zero ionic strength are given in Table 6. The enhanced value of K_A observed in media containing dimethylsulphoxide probably arises mainly from the increased activity of the sulphite ion, which will not be well solvated by the aprotic solvent. Because of the low solubility of sodium sulphite in these media formation of higher complex B, was not systematically examined.

However, the results in Table 5 indicate that the value of K_B in this solvent system will be smaller than in pure water. This probably results from the poor solvation of the pentavalent complex B by dimethyl sulphoxide.

TABLE 5

Visible absorption of Picric Acid containing sodium sulphite in the solvent system 40/60 DMSO/Water

Na_2SO_3 mole $litre^{-1}$	O.D 4900Å	O.D 4110Å	Relative Concentration			K_A $1.mole^{-1}$	K_B $1.mole^{-1}$
			[Picrate ion]	[A]	[B]		
0	0	0·385	1	-	-	-	-
0·01	0·035	0·41	0·895	0·095	0	10·6	-
0·02	0·080	0·435	0·79	0·215	0	13·5	-
0·03	0·130	0·47	0·64	0·35	0	18·2	-
0·05	0·200	0·515	0·45	0·54	0	24	-
0·07	0·240	0·545	0·32	0·65	0·03	29	-
0·09	0·280	0·58	0·17	0·76	0·07	49	1·0
0·11	0·300	0·545	0·105	0·81	0·085	70	0·95
0·13	0·300	0·61	0·04	0·81	0·15	-	1·4
0·15	0·295	0·615	0·02	0·80	0·18	-	1·5
0·15	0·295	0·62	0	0·80	0·20	-	1·65
0·17	0·290	0·62	0	0·78	0·22	-	1·65
0·20	0·265	0·62	0	0·71	0·29	-	2·05
0·24	0·205	0·62	0	0·55	0·45	-	3·4

TABLE 6

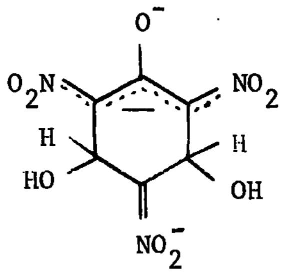
Data for complexes from picrate ion and sodium sulphite in different solvent systems

Solvent	K_A *	K_B *	Complex A		Picrate ion	
	$1.mol^{-1}$	$1.mol^{-1}$	λ_{max} (A)	$10^{-4}\Sigma$	λ_{max} (A)	$10^{-4}\Sigma$
Water	$1{\cdot}2 \pm 0{\cdot}3$	$(1{\cdot}6 \pm 0{\cdot}8) \times 10^{-2}$	3850	1•3	3550	1•4
4:1 Water/DMSO v/v	2	-	3900	1•5	3580	1•45
3:2	5	-	3950	1•7	3620	1•5
1:1	10	-	4000	1•8	3640	1•55

* Extrapolated to zero ionic strength

ii) Interaction of Picric Acid with Sodium Hydroxide

The visible spectrum of picric acid dissolved in concentrated sodium hydroxide solution was very similar to that previously reported.[121] The spectrum also resembles that of complex B formed from the picrate ion and sodium sulphite. This similarity suggests an analogous mode of interaction so that the species present in concentrated sodium hydroxide solutions probably results from interaction of the picrate ion with two molecules of sodium hydroxide to form the diadduct (IV).



(IV)

Strong evidence for this structure also comes from N.M.R. spectroscopy (Table 7). Thus picric acid (0•2M) in water shows a resonance at -8•80 ppm. Addition of 1 equivalent of sodium hydroxide caused a small shift to -8•68 ppm consistent with complete dissociation to the picrate ion. However in 6•0M sodium hydroxide, the spectrum shows in addition to the solvent band a single band at -5•95 ppm. The position of this resonance is that expected for ring protons of structure IV. It is similar to the

TABLE 7

Chemical shifts (relative to internal tetramethylsilane[x]) of the band attributed to ring protons in solutions of picric acid (0•2M) in various media.

Medium	Chemical Shift
Water	-8•80 ppm
Sodium sulphite (0•2M) in water	-8•68 ppm
Sodium hydroxide (0•2M) in water	-8•68 ppm
Sodium sulphite (1•0M) in water	-6•17 ppm
Sodium sulphite (2•0M) in water	-6•18 ppm
Sodium hydroxide (6•0M)in water	-5•95 ppm

[x] measured relative to internal dioxan

A difference of 3•70 ppm between the two standards was assumed.

position (-6•0 ppm) of the resonance of the diadduct formed from N,N-dimethylpicramide and sodium sulphite.[56] This evidence rules out the possibility of hydroxide addition to form adduct (I) suggested by Abe,[121] where there is no covalency change at the ring-carbon atoms carrying hydrogen, so that resonance would be expected at much lower field. The fact that no separate band was observed due to the added hydroxy-protons of (IV) is almost certainly due to their fast exchange with the solvent. There is apparently little tendency for picrate ion to form a 1:1 adduct with hydroxide in water. However close examination of Abe's spectra showed that in solutions containing 2-3M sodium hydroxide there was some absorption above 4500Å due neither to the diadduct nor to the picrate ion, and this may indicate some formation of a 1:1 adduct. This observation was supported in the present work by the visible spectra of picric acid and sodium hydroxide in 50:50% by volume water/dimethyl sulphoxide (Fig.5). This spectrum shows absorption at about 4900Å which is similar to that observed for the 1:1 adduct formed from the picrate ion and sodium sulphite and consistent with the formation of a 1:1 adduct with hydroxide. Previous work indicates that the 1:1 adduct should have greater stability in dimethyl sulphoxide than in water.

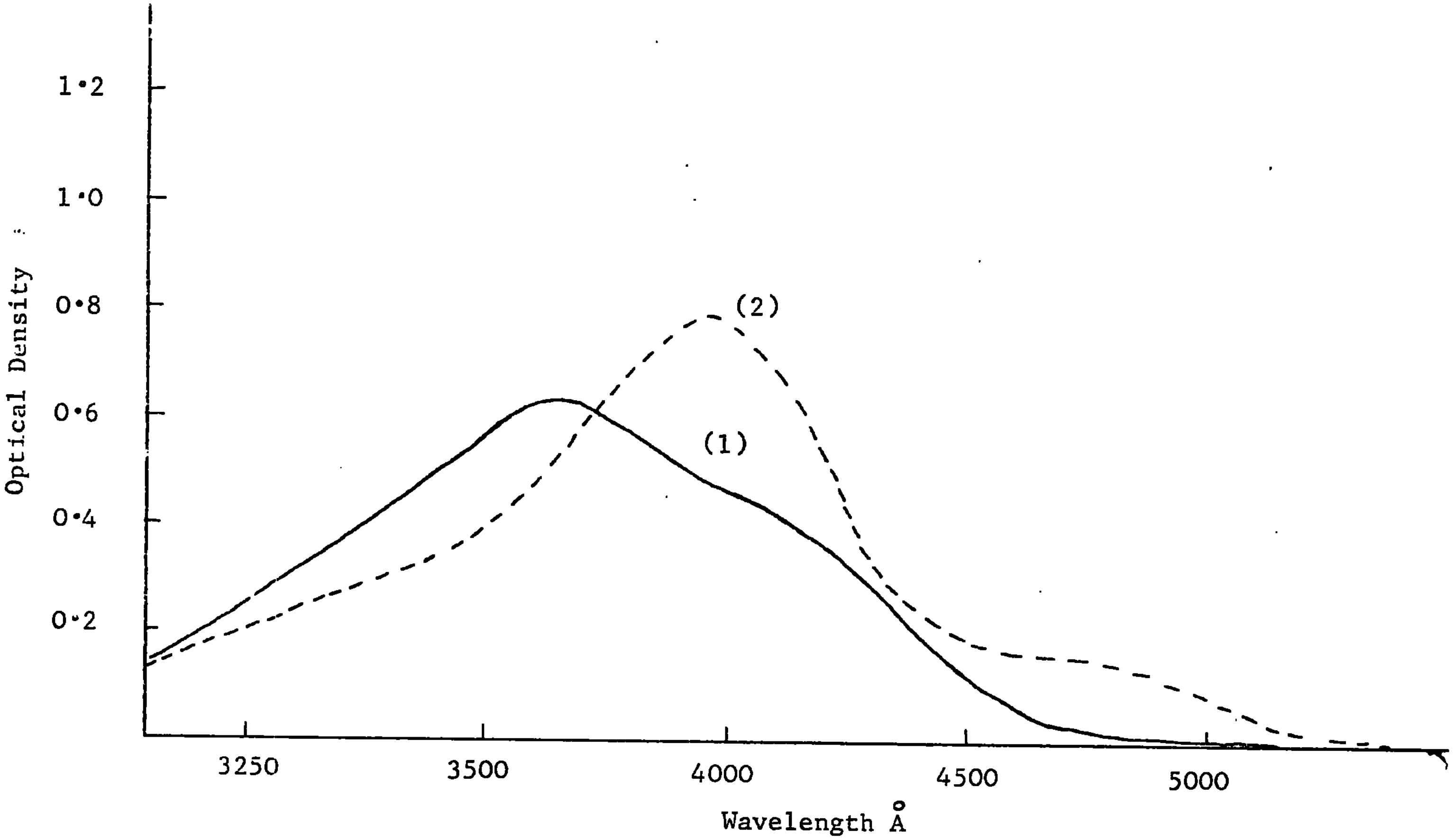


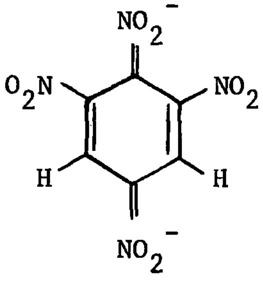
Fig.5. Visible spectra of picric acid (4 x 10^{-5}M) in 1:1 (v/v) water-DMSO with [NaOH]M; 1, 0·00; 2, 0·6.

Section II

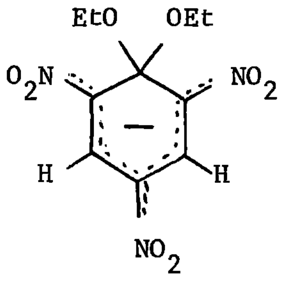
Interaction of 1,2,3,5- and 1,2,4,5-Tetranitrobenzene with some Nucleophiles in Protic Solvents

INTRODUCTION

Most of the work which has been carried out so far on the study of Meisenheimer[1] complexes has been restricted to compounds containing only two or three activating groups. However, Mürto,[125] in a recent report has examined the interaction of 1,2,3,5-tetranitrobenzene with aqueous sodium hydroxide or ethanolic sodium ethoxide solutions. In these solutions he found that the red colour produced, which he attributed to the formation of charge transfer complex (I), was not stable but faded quickly to give either picric acid or 2,4,6-trinitrophenetole according to the base used. In the latter case the product existed in the form of complex (II) in solutions of sodium ethoxide.



(I)



(II)

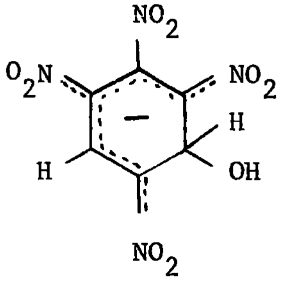
The rate of decomposition for the red species in the former case, was found to be independent of the concentration of hydroxide ion at 0•001-0•005M sodium hydroxide.

However, in view of the well established mechanism[2-7] for the reaction of aromatic nitro-compounds with bases, Murto's[125] interpretation for the red species initially produced in these solutions was not satisfactory. Therefore in the present work, the interaction of 1,2,3,5- and 1,2,4,5-tetranitrobenzene with certain nucleophiles in protic solvents have been examined by visible and proton nuclear magnetic resonance spectroscopy. The main purpose was to investigate and compare the structures and the stabilities of the species formed from the two isomers. It was also hoped, in view of the increasing interest[104] in the carbon basicities[126] (thermodynamic affinity for carbon) of nucleophiles, that the presence of a fourth nitro group might render these compounds susceptible to complex formation with nucleophiles too unreactive to form adducts with other nitro-compounds.

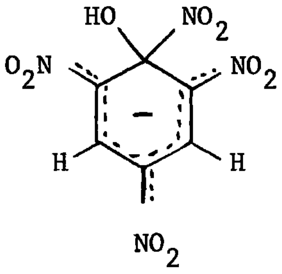
I. Interaction of 1,2,3,5-tetranitrobenzene (1235 TNB) with Hydroxide Ion

A. Structural Study by NMR Spectroscopy

Due to the rapid decomposition of the red species produced in solutions of 1235 TNB and sodium hydroxide the following NMR investigation was made at $0^{o}C$, in order to slow down the rate of decomposition of the red species. The NMR spectrum of 1235 TNB itself in ethanol or dioxan shows a single resonance at -9•40 ppm (relative to internal TMS) due to the two equivalent ring protons at C_4 and C_6. However, when a concentrated solution of 1235 TNB in dioxan was injected by micro syringe into aqueous sodium hydroxide solution (1 equivalent) the NMR spectrum recorded immediately after mixing, showed two sets of doublets, Figure 1, with spin coupling constant 1•5 Hz at -8•30 and -6•15 ppm attributed to the two ring protons. The large high field shift at -6•15 ppm relative to the parent compound (-9•40 ppm) is consistent with the covalent addition of hydroxide ion at C_4 to form adduct III. This spectrum which is similar to those observed for 1:1 adducts formed by base addition to



(III)



(IV)

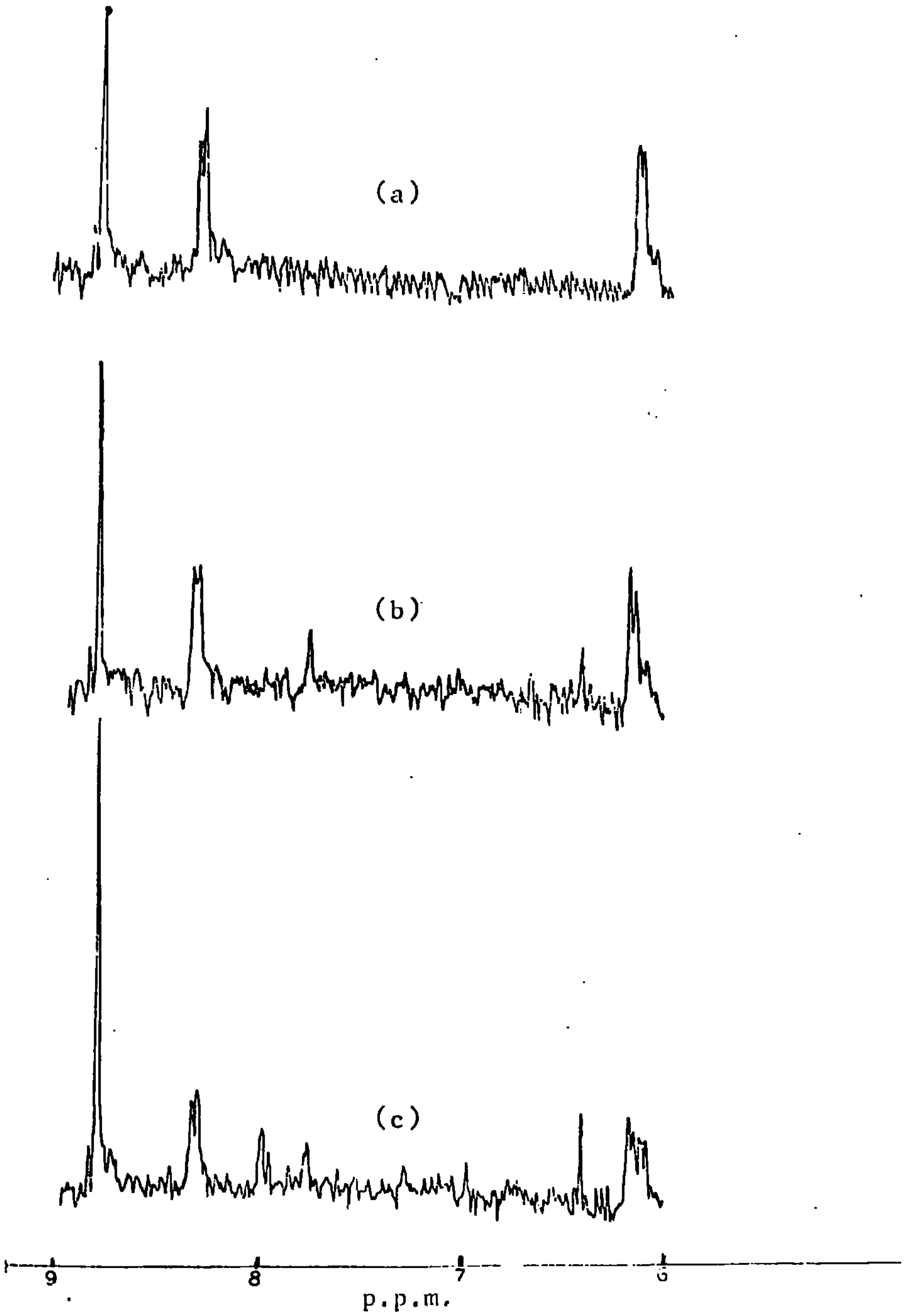


Fig.1. NMR spectra of 1,2,3,5-tetranitrobenzene (0·2M) and 1 equivalent of sodium hydroxide solution (a) soon after mixing (b) after 4 min. (c) after 8 min.

carbon carrying hydrogen of 1-X-2,4,6-trinitrobenzene (X = H, OMe, NH_2, etc.....)[3], excludes the possibility of the formation of adducts such as I or IV. In the latter case if the hydroxide ion addition occured at C_2, the ring hydrogens would be more nearly if not completely equivalent and their NMR absorption would not be expected to change much from the position in the parent compound.

However, these spectra changed with time so that the bands at -8•30 and -6•15 ppm decreased in intensity and a new single band at -8•75 ppm grew at their expense. This new absorption was attributed to the formation of picric acid. Attempts to obtain interpretable spectra in solution containing excess of sodium hydroxide were unsuccessful.

B. Kinetics and Equilibrium Studies

When a small quantity of concentrated solution of 1235 TNB in dioxan was injected into borax buffers (pH 9•2-12) or into dilute sodium hydroxide solution in water, a red colour formed very quickly and faded within a few minutes with production of picric acid. The visible spectra of such solutions, given in Fig.2, are similar to those of 1:1 adducts formed from hydroxide ion or sulphite ion and 1,3,5-trinitrobenzene.[56] Increasing the concentration of hydroxide ion in the range pH 9•2-12 caused an increase in the initial visible absorption without varying the shape of the spectrum and in solutions containing ca. 10^{-3}M hydroxide ion conversion to complex is almost complete. The independence of the spectral

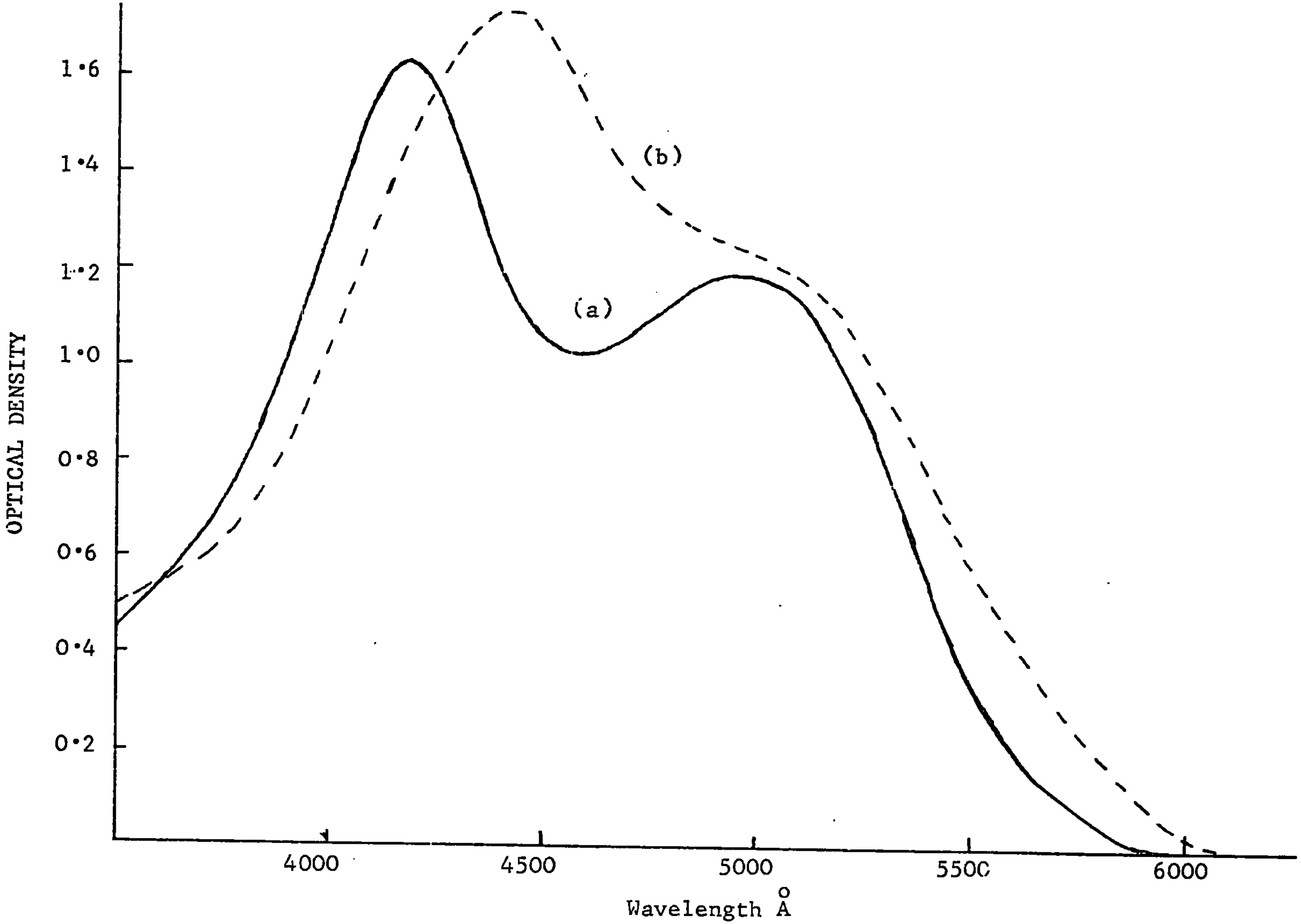


Fig.2. The visible absorption at 0° of 1,2,3,5-tetranitrobenzene ($1 \times 10^{-4}M$) in water containing (a) $5 \times 10^{-3}M$ and (b) 0·2M sodium hydroxide.

shape in these solutions of base concentration indicates production of a single complex whose structure is shown to be (III) from the NMR measurements. However, it was found that in the concentration range 0•01-0•2M hydroxide ion, the maximum shifted toward longer wavelength in the visible spectrum of the 1235 TNB. This change is unlikely to be due to a medium effect and hence it may indicate the formation of a 1:2 complex.

In view of the above results, the reaction between 1235 TNB and hydroxide ion in dilute solutions to form a single adduct which will be denoted as complex A, can be presented by the following equilibrium, neglecting the charge on the complex:

$$\mathrm{TNB} + \mathrm{OH}^- \rightleftharpoons \mathrm{A} \qquad K$$

where K is the equilibrium constant for the formation of complex A. The value of K was determined by measurements of the optical density at 5000Å extrapolated to zero time as shown later. Table 2 gives the values of K calculated at various concentrations of hydroxide ion. These values are in a good agreement with that obtained from a Benesi-Hildebrand[91] plot (Fig.3) which gives K a value of $2{\cdot}4 \times 10^4$ $\mathrm{l.mol^{-1}}$ and the extinction coefficient at 5000Å a value of $9{\cdot}7 \times 10^3$ $\mathrm{M^{-1}cm^{-1}}$.

A kinetic study was made by injecting a known quantity of concentrated 1235 TNB in dioxan into solutions containing various hydroxide ion concentrations previously brought to constant temperature, 22°C. The

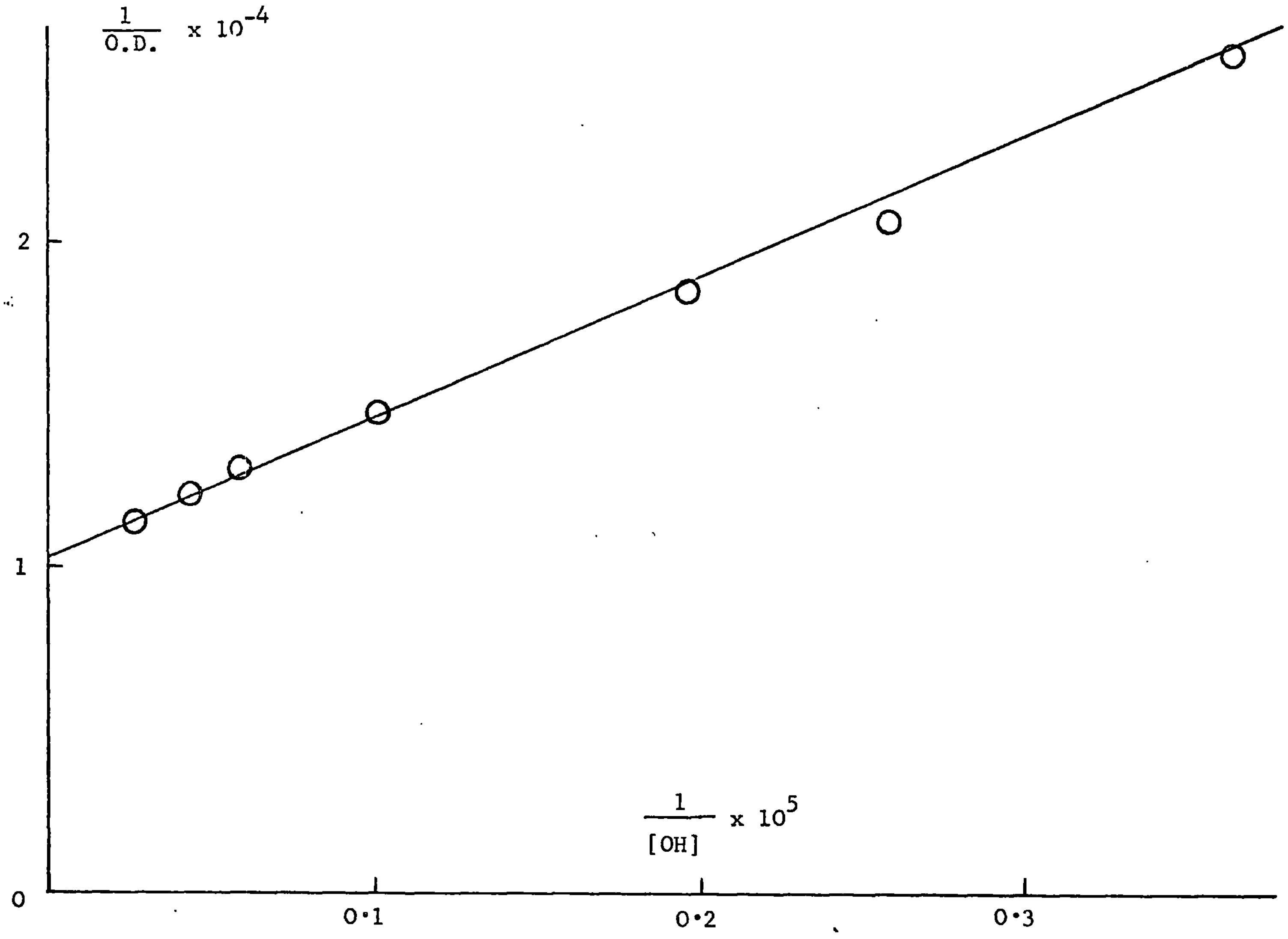


Fig.3. Benesi-Hildebrand plot for 1,2,3,5-tetranitrobenzene (1×10^{-4}M) and sodium hydroxide in water measured at 5000Å.

decomposition of the red species was followed by measurements (at suitable time intervals) of the optical density at 5000Å where the product, picric acid, has a negligible absorption. Such measurements are given in Table 1. In all cases the logarithmic plots of the optical density versus the time indicate that the rate of fading (k_{obs}) is first order in the concentration of the red species. Two such plots are shown in Figure 4. Extrapolation of the above plots to zero time allowed the optical density at time of mixing to be determined. Values of k_{obs}, K and other data for the interaction of 1235 TNB with hydroxide ion are given in Table 2.

Production of picric acid as a result of nucleophilic displacement of nitro group at C_2 by hydroxide ion can not be attributed to direct decomposition of the complex A. It seems more likely that the reaction path involves direct nucleophilic substitution of the nitro group at C_2 by hydroxide ion via intermediate IV. The results in Table 2 show that the rate of fading of complex A varies with the hydroxide concentration at low concentration but becomes constant at concentrations where conversion of 1235 TNB to complex A is complete. This variation can be rationalised in the following way[98]

$$\text{TNB} + \text{OH}^- \xrightarrow{k_2} \text{picric acid}$$

$$\text{TNB} + \text{H}_2\text{O} \xrightarrow{k_w} \text{picric acid}$$

where k_2 is the rate constant for the reaction of 1235 TNB with hydroxide

TABLE 1

Measurements of the decrease in the visible absorption at 5000Å due to the decomposition of complex A at temp. (22 ± 0•2)

[OH]	TIME IN SECONDS													
10^5M	20	30	45	60	80	100	120	140	160	180	210	240	300	360
1•7	0•26	0•25	0•23	0•22	0•20	0•19	0•17	0•16	0•15	0•14	0•125	0•115	0•11	0•085
2•7	0•35	0•34	0•31	0•29	0•265	0•24	0•215	0•21	0•19	0•18	0•125	0•14	0•115	0•09
3•9	0•43	0•41	0•39	0•36	0•32	0•28	0•25	0•23	0•21	0•19	0•155	0•145	0•11	0•085
5•1	0•219	0•46	0•42	0•38	0•35	0•31	0•28	0•25	0•23	0•21	0•17	0•155	0•12	0•09
10	0•60	0•56	0•52	0•48	0•41	0•36	0•33	0•26	0•26	0•23	0•18	0•17	0•12	0•09
17	0•66	0•62	0•55	0•50	0•43	0•37	0•32	0•28	0•245	0•22	0•20	0•15	0•10	0•075
23	0•71	0•66	0•60	0•54	0•47	0•41	0•36	0•31	0•27	0•24	0•18	0•17	0•11	0•08
40	0•76	0•70	0•62	0•55	0•48	0•44	0•37	0•33	0•29	0•26	0•215	0•18	0•12	0•09
200	0•85	0•78	0•70	0•64	0•56	0•49	0•43	0•37	0•32	0•29	0•240	0•19	0•14	0•09
500	0•86	0•79	0•70	0•63	0•55	0•48	0•42	0•36	0•31	0•28	0•23	0•19	0•13	0•09
1000	0•85	0•77	0•70	0•64	0•57	0•50	0•44	0•38	0•34	0•30	0•25	0•20	0•145	0•10

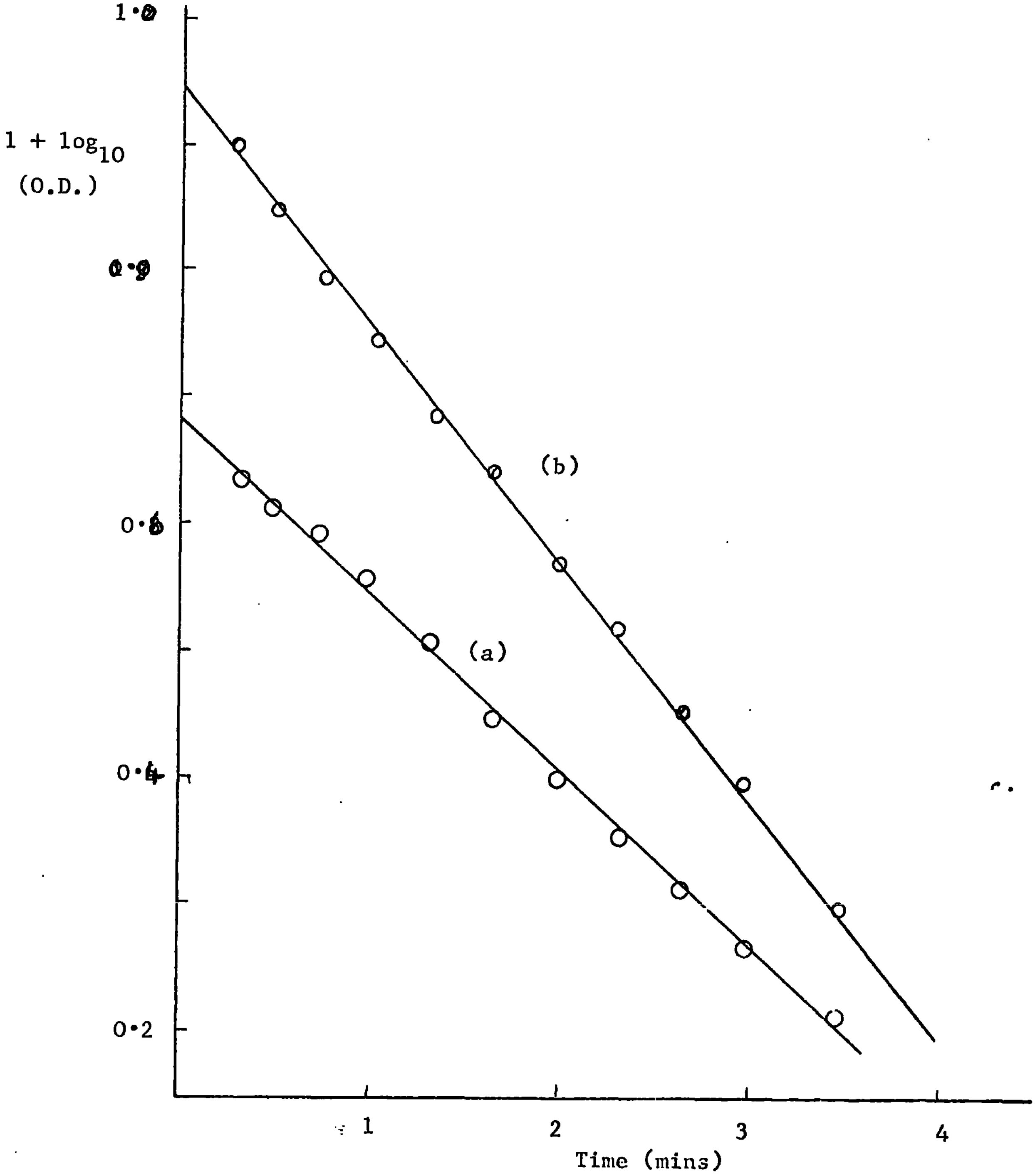


Fig.4. Illustration of the first-order fading reaction of the red complex formed from 1,2,3,5-tetranitrobenzene in aqueous buffers at pH (a) 9·6 and (b) 10·6, measurements at 5000Å.

TABLE 2

Data for the interaction of 1,2,3,5-tetranitrobenzene and hydroxide ion in water at 22°C

10^5 [OH$^-$] M	D_o ^{a}	10^3 k_{obs} (sec^{-1})	Calculated	
			10^{-4} K^b (l.mol^{-1})	$10^{-2}k_2$ (l.mol^{-1}sec^{-1})
1·7	0·28	3·5 ± 0·5	2·4	2·5
2·7	0·39	4·6	2·5	2·5
3·9	0·48	5·0	2·5	2·3
5·1	0·54	5·4	2·5	2·2
10	0·68	6·0	2·4	2·0
17	0·77	6·8	2·3	2·0
23	0·81	6·9	2·2	2·0
40	0·88	7·2	2·4	1·9
200	0·96	7·4	-	1·8
500	0·97	7·5	-	1·8

a) For [1235 TNB] = 1 x 10^{-4}M

b) Calculated assuming D_o = 0·97 for complete conversion to complex.

ion and k_w is the rate constant for the hydrolysis of 1235 TNB in water. The value of k_w was found by measuring the rate of formation of picric acid in neutral or slightly acidic solutions. Measurements were made at 3600Å in neutral water and in solutions at pH = 3 and pH = 4. Plots of $\log_{10}(O.D_\infty)/(O.D_\infty - O.D_t)$ versus time were linear (see Figure 5) indicating that the reaction was first order in 1235 TNB. The values of the rate constants in the three media were $6{\cdot}0 \times 10^{-4}$ sec^{-1} in pH = 3, $6{\cdot}07 \times 10^{-4}$ sec^{-1} in pH = 4 and $6{\cdot}13 \times 10^{-4}$ sec^{-1} in water, showing that the rate of reaction is independent of pH in these solutions.

Since the rate measured is that of the decrease of absorption at 5000Å with time, that is, decrease of concentration of complex A with time, then

$$k_{obs} = -\frac{d\ \ln(O.D_t - O.D_\infty)}{dt} = -\frac{d\ \ln[A]}{dt} \qquad (1)$$

The rate of formation of picric acid is given by

$$\frac{d[P]}{dt} = k_2[TNB][OH^-] + k_w[TNB] \qquad (2)$$

However, 1235 TNB and complex A are in equilibrium, thus

$$K = \frac{[A]}{[TNB][OH^-]} \qquad (3)$$

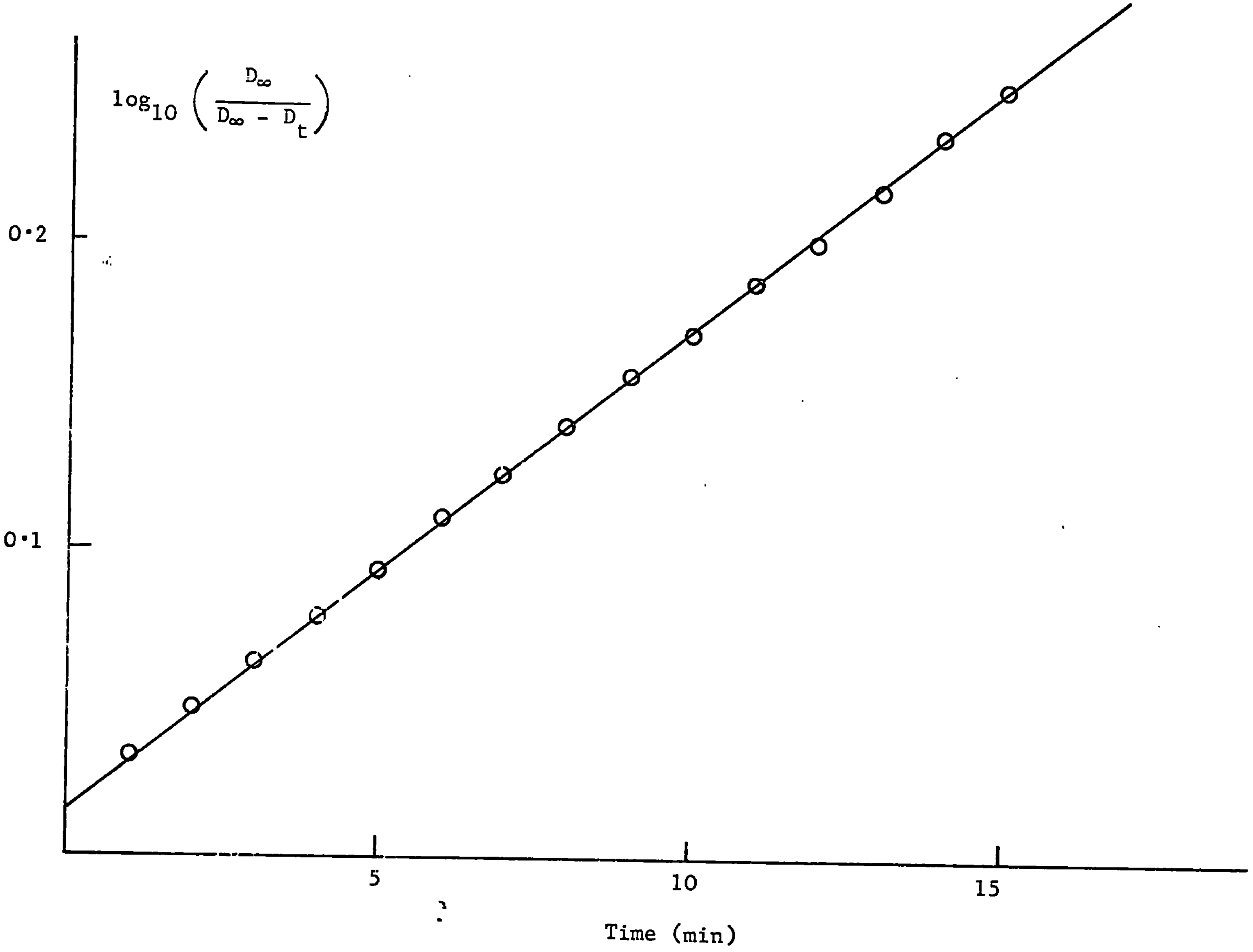


Fig.5. Illustration of the first-order hydrolysis reaction of 1,2,3,5-tetranitrobenzene in water. Measurements at 3600Å.

From (2) and (3)

$$\frac{d[P]}{dt} = k_2 \frac{[A]}{K} + k_w \frac{[A]}{K[OH^-]} \tag{4}$$

The NMR spectra show that no appreciable concentration of the intermediate IV is produced. Thus for material balance

$$\frac{d[P]}{dt} = -\frac{d\{[A] + [TNB]\}}{dt}$$

$$= -\frac{d\left\{[A] + \frac{[A]}{K[OH^-]}\right\}}{dt} \tag{5}$$

Equating the rates of production of picric acid given by (4) and (5) gives

$$\frac{k_2[A]}{K} + \frac{k_w[A]}{K[OH^-]} = -\frac{d\left\{[A] + \frac{[A]}{K[OH^-]}\right\}}{dt} \tag{6}$$

From (1) and (6)

$$\frac{k_2}{K} + \frac{k_w}{K[OH^-]} = k_{obs}\left\{1 + \frac{1}{K[OH^-]}\right\}$$

In this expression k_{obs} is measured from the plots of $\log_{10}$ O.D. versus time. K and k_w were found to be $2{\cdot}4 \times 10^4$ $1.mol^{-1}$ and $6{\cdot}1 \times 10^{-4}$ sec^{-1} respectively and the only non-observable quantity is k_2. Values of k_2

calculated from this expression are given in Table 2. However it is not expected that the value of k_2 would vary with the hydroxide ion concentration at the low concentrations used and the drift in the calculated values is probably not significant.

In solutions containing ca. 1 x 10^{-3}M hydroxide ion, conversion of 1235 TNB to complex A is virtually complete. In these solutions the contribution to the overall rate of decomposition from the neutral hydrolysis will be negligible, therefore

$$V_1 = k_{obs}[A] = \text{rate of fading}$$

and $$V_2 = k_2[TNB][OH^-] = \text{rate of production of picric acid}$$

however $$K = \frac{[A]}{[TNB][OH^-]}$$

Thus $$V_2 = \frac{k_2[A]}{K}$$

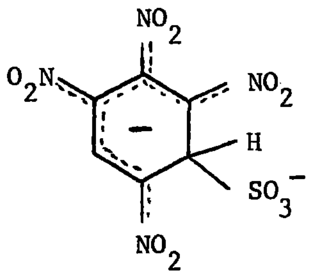
since in this solution $V_1 = V_2$

Then $$k_{obs} = \frac{k_2}{K}$$

The fact that k_2 and K will not be expected to vary greatly with base concentration, explains the constancy of k_{obs}, in the rate of fading in these solutions.

II. Interaction of 1,2,3,5-Tetranitrobenzene with Sulphite Ion

The reaction of 1235-TNB with sodium sulphite was studied by visible spectroscopy in solutions buffered at pH 8 to inhibit interaction of 1235 TNB with hydroxide ion produced by hydrolysis of the sulphite. In solutions containing <u>ca</u>. 0•001M sodium sulphite and 1 x 10^{-4}M 1235 TNB a strong red colour was produced. The visible spectrum recorded at 0°C (Figure 6) shows two distinct absorption maxima at 4430 and 5300Å which is similar but shifted to longer wavelength, to that of the adduct formed by hydroxide addition at a ring carbon carrying hydrogen. This similarity argues for an analogous mode of interaction. Thus the red species produced in these solutions will result from sulphite addition at C_4 to form adduct (V).



(V)

However, as in the case of the hydroxide adduct, the red species formed in dilute aqueous sodium sulphite solutions are not stable, but decompose very quickly with time. The product of the reaction has little absorption above 3000Å and probably results from replacement of the nitro group at C_2 by sulphite ion.

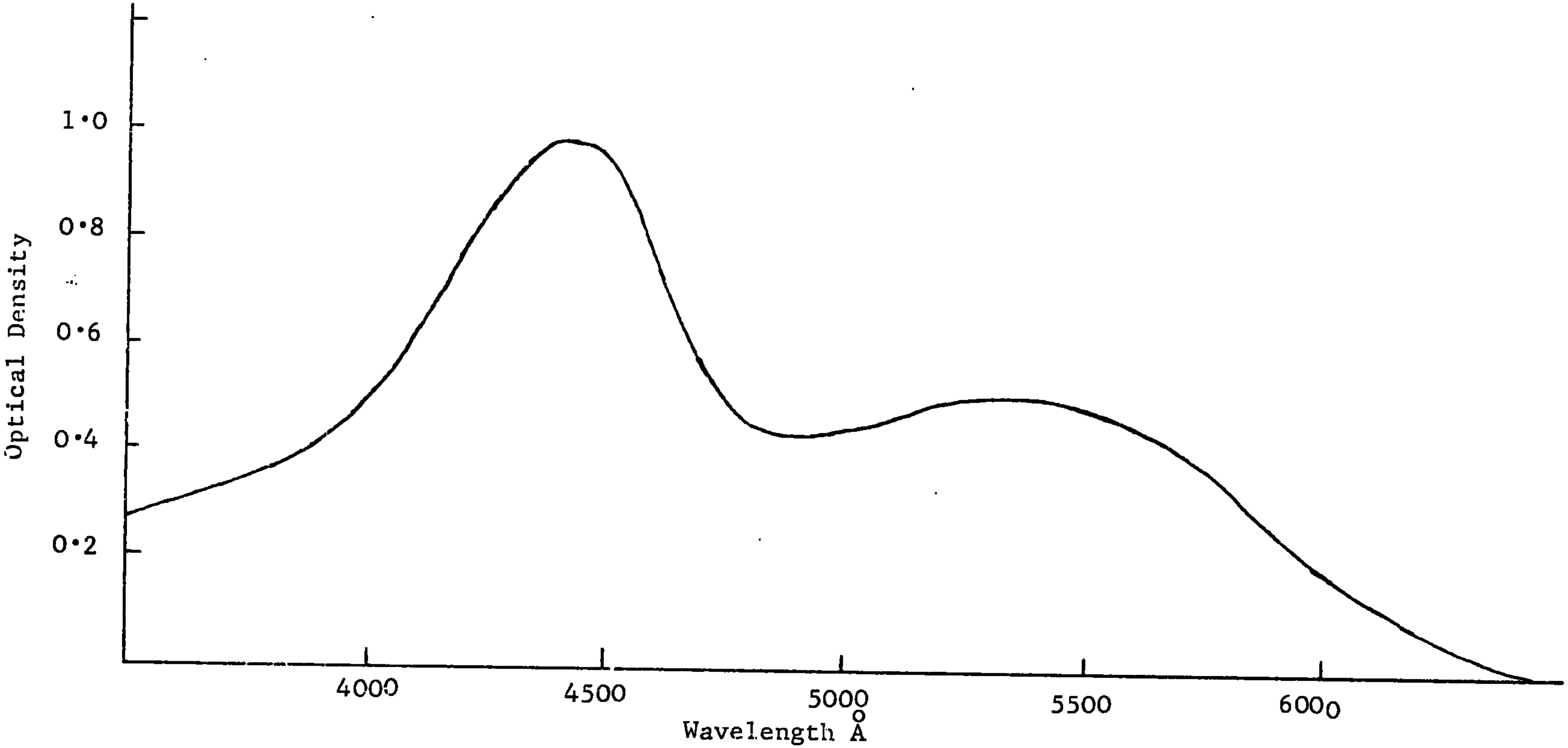


Fig.6. Visible absorption spectra of 1,2,3,5-tetranitrobenzene (1×10^{-4}M) in buffer pH = 8 containing 2×10^{-4}M sodium sulphite.

In view of the high reactivity of 1235 TNB with sulphite ion and the rapid decomposition of the produced species, determination of the equilibrium constant for the formation of the coloured species by the same technique used for the hydroxide complex was not comprehensive. However the few measurements which were made revealed the general picture of this interaction. Measurement of optical density at 5300Å for two runs are given in Table 3 below.

TABLE 3

$[Na_2SO_3]$	Time sec.	15	20	25	30	35	40	45	50
1×10^{-4}	O.D.	0•30	0•18	0•13	0•09	0•06	0•04	0•03	0•02
2×10^{-4}	O.D.	0•38	0•20	0•13	0•09	0•06	0•04	0•03	0•02

Logarithmic plots of the optical density versus time (see Figure 7) indicate that the rate of fading is first order in the concentration of red species. From the slope the rate of fading in these solutions was found to be independent of the sulphite concentration and has a value $7{\cdot}6 \times 10^{-2}$ sec^{-1}. Extrapolation to zero time indicated that in solutions containing 1×10^{-4}M 1235 TNB and 2×10^{-4}M sulphite, complex formation was virtually complete and in a solution containing 1×10^{-4}M sulphite

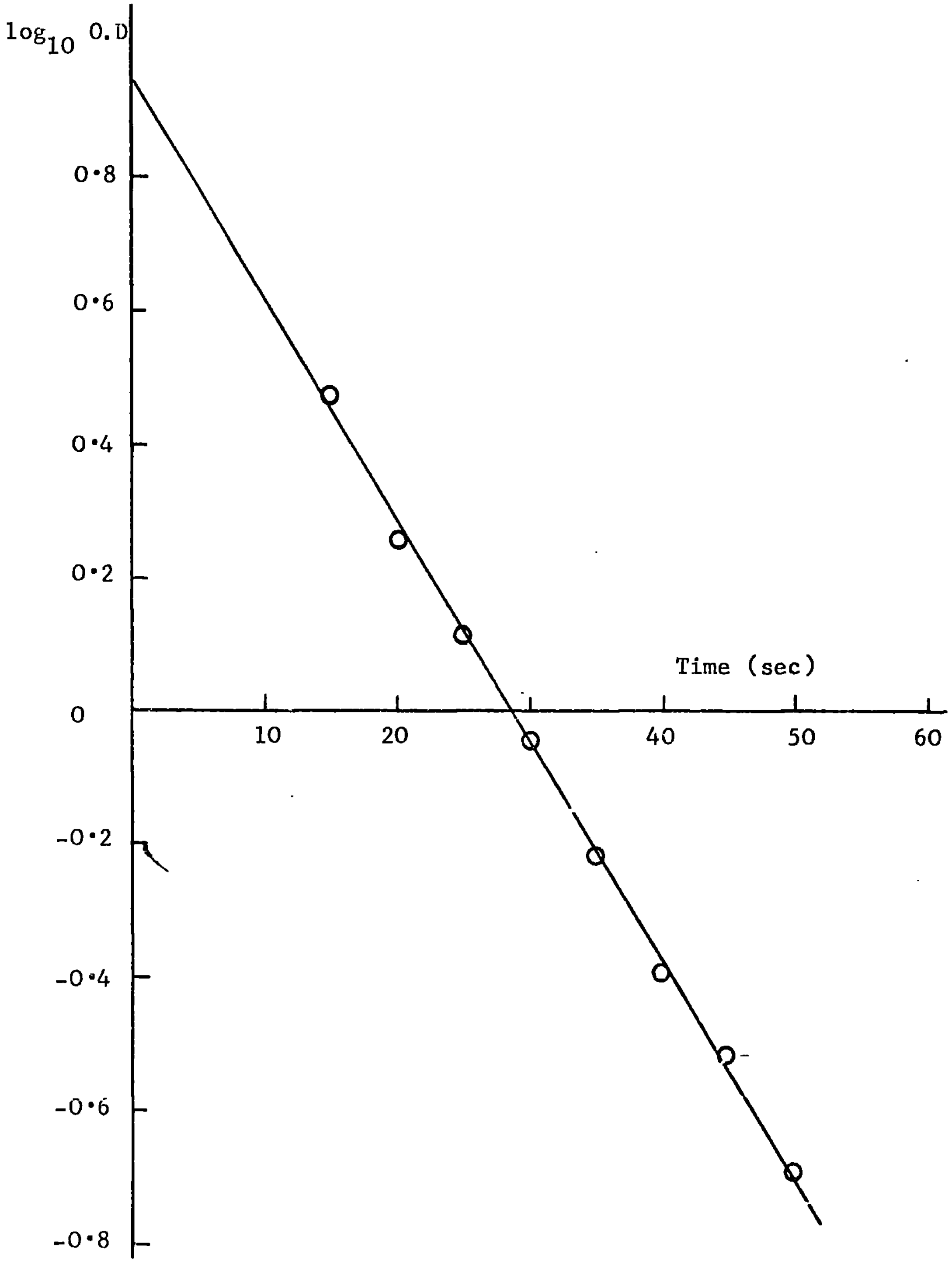


Fig.7. Illustration of the first-order fading reaction of the red complex formed from 1,2,3,5-tetranitrobenzene in aqueous buffer pH = 8 containing 1×10^{-4}M sodium sulphite. Measurements at 5300Å.

about 90% of 1235 TNB was converted to complex. This latter result indicates that the complex can not have greater than 1 sulphite : 1 TNB stoichiometry, and gives a value for the equilibrium constant for the formation of a 1:1 adduct of 1×10^{6} $1.\text{mol}^{-1}$. This is perhaps a minimum value because of the instability of sulphite ion in dilute solution. The constancy of the rate of decomposition in these solutions where the conversion to complex is almost complete, can be explained on a similar basis to that previously given for the constant rate of decomposition of 1235 TNB in the more concentrated hydroxide solutions.

An attempt to investigate this interaction by NMR spectroscopy was unsuccessful due to the fast decomposition of the red species.

III. Interaction of 1,2,3,5-tetranitrobenzene and Ethoxide Ion

The red species formed on the addition of 1235 TNB to ethanolic sodium ethoxide have been investigated by NMR and visible spectroscopy. When 1235 TNB, dissolved in dioxan, was injected into 1 equivalent of sodium ethoxide in ethanol the NMR spectrum initially recorded (Figure 8) showed two sets of doublets (J 1•5 Hz) at -8•60 and -6•30 ppm. With time, these bands gradually decreased in intensity with the simultaneous development of new bands at -8•85 and -8•80 ppm. The singlet at -8•85 ppm is attributed to the formation of adduct (II) and that at -8•80 to the formation of picric acid which may result from the presence of traces of water in the solvent. An alternative mechanism for the formation of picric

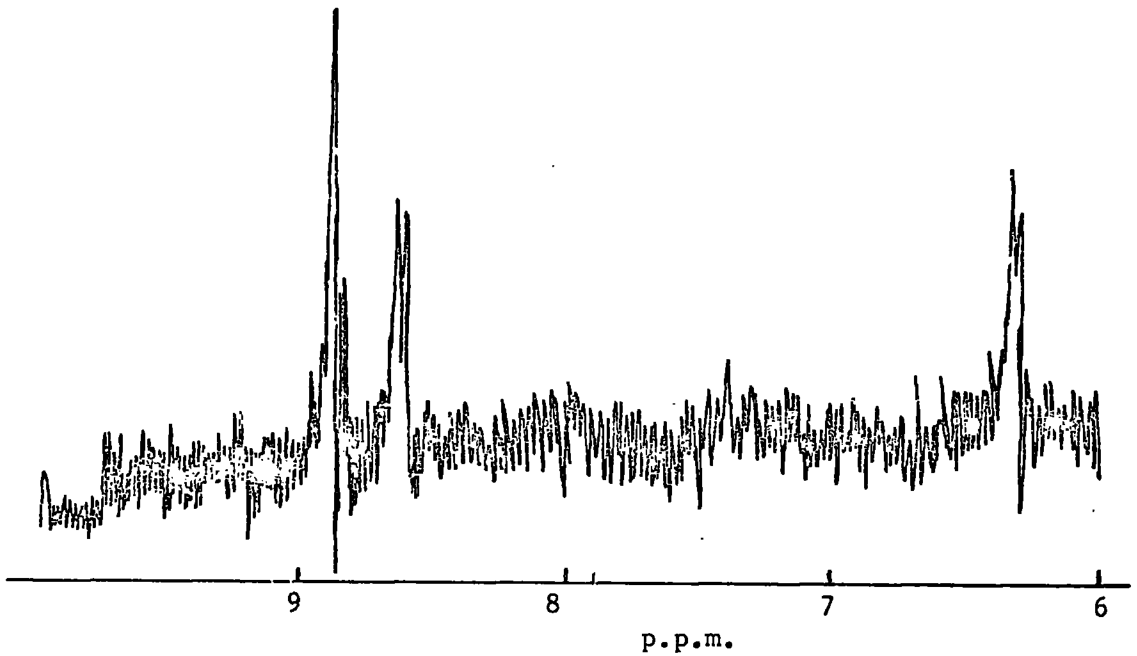
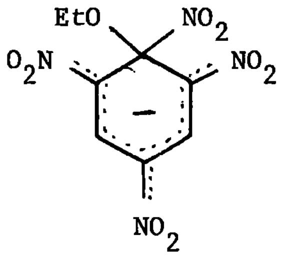


Fig.8. NMR spectrum of 1,2,3,5-tetranitrobenzene (O·2M) in ethanol containing 1 equivalent of sodium ethoxide. (Chemical shifts measured relative to internal TMS).

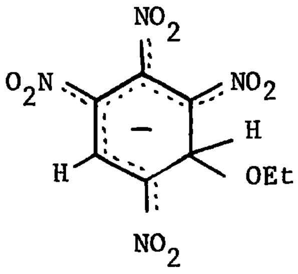
acid is de-ethylation by ethoxide ions of 2,4,6-trinitrophenetole which will be present in small concentration in these solutions.[88,127] However, it seems unlikely that this can be a major path to the production of picric acid in this case as the solutions contain only one equivalent of ethoxide ions. However it was found that in the presence of excess of 1235 TNB a considerable amount of picric acid was formed. It is possible that an electron transfer mechanism operates under this condition, perhaps with transfer occurring between the complex and unchanged 1235 TNB.[128]

There is no doubt that the initial spectrum of the complex is only consistent with a structure in which the nuclear protons in the parent compound have become non-equivalent due to the attachment of an ethoxyl group at a ring carbon atom carrying hydrogen. The large upfield shift at -6•30 ppm relative to the parent compound at -9•4 ppm is attributed to the ring hydrogen at C_4 while the band at -8•60 ppm is attributed to the ring hydrogen at C_6. This arrangement is compatible with the formation of adduct (VII) as the author believes or the formation of adduct (VIII) which could be produced in these solutions via 2,4,6-trinitrophenetole.[21,27] The spectrum is not consistent with (I) or with the formation of adduct (VI) where the two ring protons are nearly equivalent.

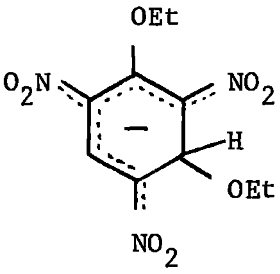
For the sake of completeness and in order to show that the observed initial spectrum is in fact due to the formation of adduct VII and not adduct VIII 2,4,6-trinitrophenetole was prepared and its interaction with



(VI)



(VII)



(VIII)

the ethoxide ion was studied under the same conditions used for 1235 TNB. The NMR spectrum of the neutral molecule in ethanol shows a sharp resonance at -9•00 ppm which shifted to -8•85 ppm on addition of sodium ethoxide (1 eq.). This latter absorption is consistent with the formation of adduct (II). Spectra measured within one minute of mixing show no other bands between -9•00 and -6•00 ppm. This result precludes the possibility that the doublets which have been observed initially in solutions of 1235 TNB in ethanolic sodium ethoxide result from adduct VIII, and add strong evidence confirming the formation of adduct VII. These results indicate that the species initially formed from 1235 TNB has similar structure to the adducts produced in the presence of hydroxide ion.

The visible spectra of the red species initially formed in solution containing 1235 TNB and low concentration of sodium ethoxide show two maxima at 4100 and 4900Å. Though there is no doubt that initially formed adducts will have structure VII while the final adducts will be in the form (II), no change was observed in the position of absorption maxima over the period of time which is thought to be required for transfer from (VII) to (II). This observation indicates that the visible spectra of species (VII) and (II) must be very similar. This shows that precise structural assignment can not be drawn from the results of visible spectroscopy[12] and indicate the importance of NMR spectroscopy in determining structures and in differentiating between adducts which may have similar electronic properties.

In view of the high reactivity of 1235 TNB and the similarity of the visible spectra of the initial and the final adducts, it was not possible to determine the equilibrium constant for the formation of the initial complex by the same method used in the case of hydroxide or sulphite. However it was found that in solutions containing 1×10^{-4}M 1235 TNB and 1×10^{-4}M sodium ethoxide, conversion to complex was nearly complete. This indicates a very large $>10^6$ $1.mol^{-1}$ value for the equilibrium constant for the complex formation.

IV. Interaction of 1,2,3,5-Tetranitrobenzene with Other Nucleophiles

The interaction in water of 1,2,3,5-tetranitrobenzene with a variety of nucleophiles including azide hypochlorite, iodide, phenoxide, thiocyanate and thiosulphate ions were examined. In no case was there evidence of production of complexes with absorption maxima above 4000Å.

V. Interaction of 1,2,4,5-Tetranitrobenzene and Hydroxide Ion

In the borax buffer (9•2-10) or in dilute solutions of sodium hydroxide in water, a yellow colour is gradually formed. Visible spectra showing build-up of the yellow colour are shown in Figure 9. This behaviour is unlikely to be due to the formation of σ-complexes and consequently it suggests that the yellow species is formed through a hydrolysis process in which one nitro-group is replaced by hydroxide ion to give 2,4,5-trinitrophenol. This speculation was confirmed by the separation of a solid product with melting point 94°C which is identical with that of 2,4,5-trinitrophenol . The rate of formation of 2,4,5-trinitrophenol was followed by measurement of optical density at 3700Å as shown in Table 4. Plots of $\log_{10}(O.D - O.D_t)$ versus time were linear which indicate the reaction is first order in 1,2,4,5-tetranitrobenzene. Two such plots are given in Figure 10. Rate constants in buffers of varying pH are given in the table below, indicating the variation of the rate constant in these solutions. A plot of k_{obs} versus [OH] is linear as shown in Figure 11,

10^5 [OH]	1•8	2•6	4•8	6•8	10•7
10 k_{obs}(sec^{-1})	1•15	1•76	2•7	4•0	5•8

which indicates that the reaction is first order in hydroxide ion. The slope gave the bimolecular rate constant for the reaction of 1,2,4,5-tetra-

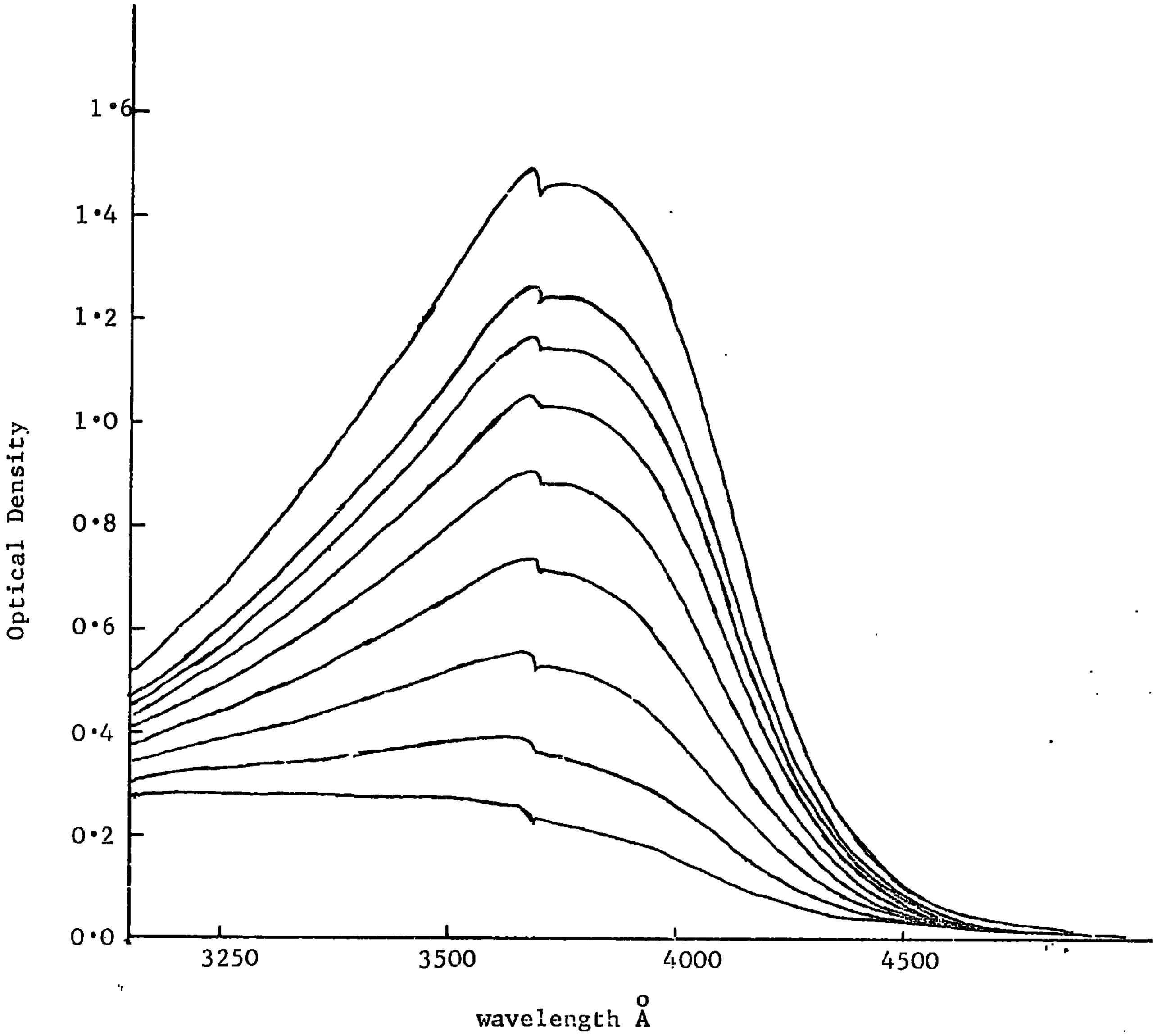


Fig.9. Illustration of the hydrolysis reaction of 1,2,4,5-tetranitrobenzene (5×10^{-5}M) in aqueous pH = 9·2 solution Spectra show the production of 2,4,5-trinitrophenol.

TABLE 4

Measurement of the optical density at 3700Å due to the formation of 2,4,5-trinitrophenetole from 1,2,4,5-tetranitrobenzene (5 x 10^{-5}M) at temperature 23°C

Time min.	10^5 [OH]				
	1·8	2·6	4·8	6·8	10·7
1	0·215	0·228	0·258	0·308	0·35
2	0·262	0·288	0·335	0·40	0·47
3	0·298	0·33	0·392	0·475	0·548
4	0·337	0·368	0·44	0·53	0·604
5	0·353	0·402	0·487	0·571	0·642
6	0·378	0·437	0·52	0·618	0·667
7	0·399	0·468	0·55	0·626	0·683
8	0·422	0·49	0·579	0·652	0·694
9	0·443	0·514	0·60	0·665	0·70
10	0·461	0·534	0·619	0·678	0·708
11	0·479	0·553	0·635	0·69	0·71
12	0·495	0·570	0·648	0·70	0·71
13	0·51	0·59	0·658	0·701	0·717
14	0·522	0·60	0·668	0·71	0·72
15	0·534	0·605	0·675	0·71	0·72
16	0·55	0·62	0·683	0·714	0·72
17	0·56	0·63	0·69	0·72	0·72
18	0·57	0·64	0·698	0·72	0·72
19	0·584	0·65	0·699		
20	0·595	0·658	0·70		
25	0·634	0·677	0·72		
30	0·66	0·695	0·72		
∞	0·72	0·72	0·72		

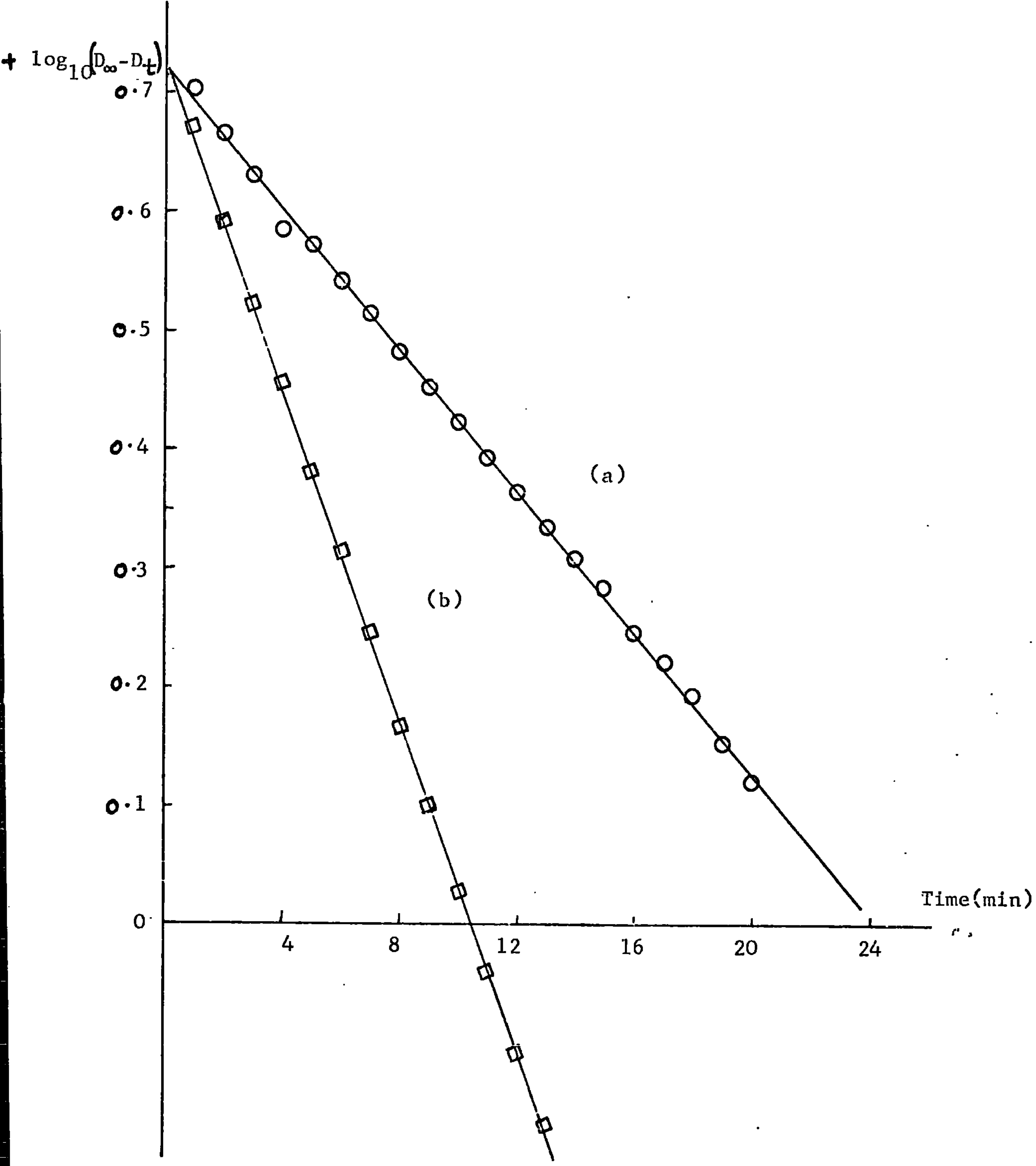


Fig.10. Illustration of the first-order hydrolysis reaction of 1,2,4,5-tetranitrobenzene in aqueous buffers (a) pH = 9·2 and (b) pH = 9·6.

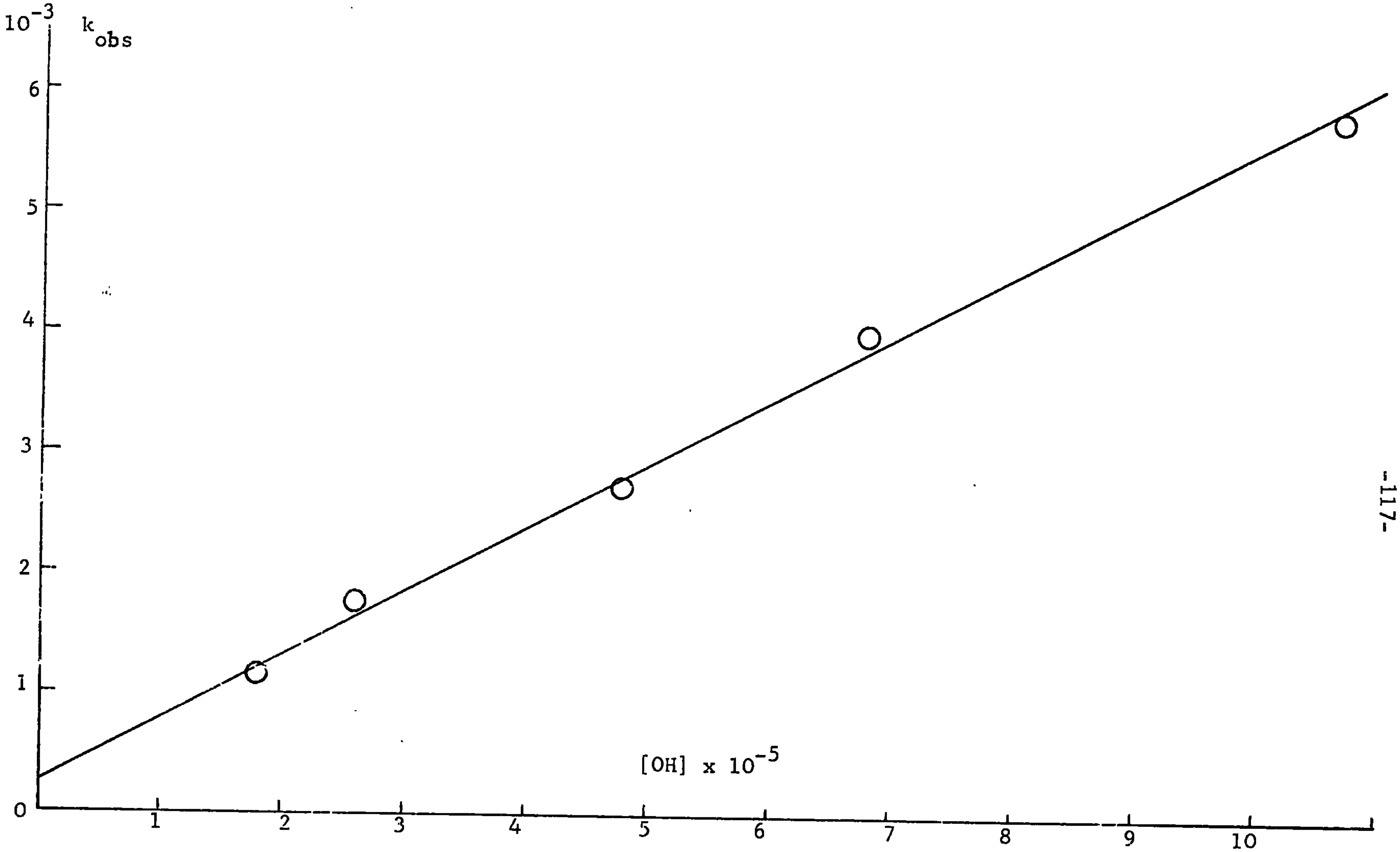


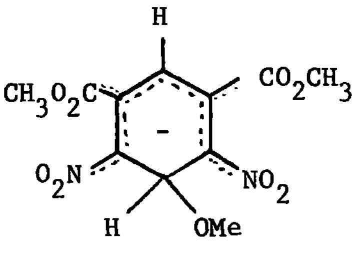
Fig.11. Plot of k_{obs} versus $[OH^-]$ indicating that the reaction ir first order in hydroxide ion.

nitrobenzene with hydroxide ion as 53 $l.mol^{-1}$ sec^{-1}.

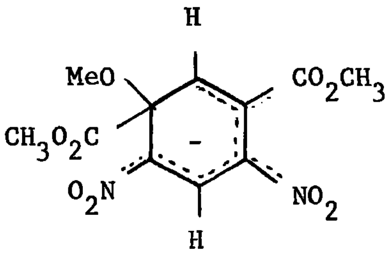
The visible spectrum of 1,2,4,5-tetranitrobenzene in pH = 11 solution recorded at 0°C showed no absorption in the visible region which may be attributed to the formation of a coloured intermediate and the observed spectrum was that due to 2,4,5-trinitrophenol . Assuming that any complex formed would have an extinction coefficient in the region of 1×10^4 M^{-1} cm^{-1} somewhere in the visible spectrum, this allows a maximum value to be put on the equilibrium constant for formation of such a complex. An initial absorption of 0•05 would be detectable, showing that the equilibrium constant for formation of 1:1 complex must have value less than 50 l/mol.

VI. Interaction of 1,2,4,5-Tetranitrobenzene and Sulphite Ion

Addition of 1,2,4,5-tetranitrobenzene, dissolved in dioxan, to aqueous solutions containing 10^{-2}M sodium sulphite resulted in the formation of a transient blue colour. The visible spectrum of this coloured species recorded at near 0°C indicated an absorption maximum at 6500Å. It was found that colour formation was greater in solutions containing dimethyl sulphoxide. It is interesting to compare this result with that from a somewhat similar system activated by four electron withdrawing groups. Thus Pollitt and Saunders[70] have observed a blue colour when sodium methoxide was added to a solution of 1,3-dinitro-4,6-di(methoxycarbonyl)-benzene in dimethylformamide. This colour was not stable but changed to red with time. They suggested that the blue colour may be due to the formation of adduct (IX) which was converted to the more stable

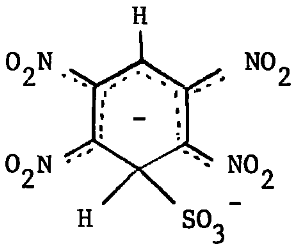


(IX)



(X)

adduct (X). In view of this interpretation it seems possible that the observed blue colour in the present case may be due to the sulphite



(XI)

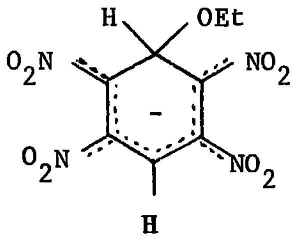
addition to a ring carbon carrying hydrogen to form adduct (XI).

In the absence of quantitative measurements, it is only possible to estimate an equilibrium constant for the formation of adduct (XI) which will have a value of $\sim 10^2$ $1.mol^{-1}$.

In addition it was found that in solutions containing 10^{-1}M sodium sulphite a pink colour λ_{max} 4900Å was initially formed but faded very quickly. This pink colour produced in the more concentrated sulphite solution could be attributed to a diadduct or to a decomposition product. In the absence of NMR spectra no firm assignments can be made.

VII. Interaction of 1,2,4,5-Tetranitrobenzene and Ethoxide Ion

Addition of 1,2,4,5-tetranitrobenzene dissolved in dioxan or ethanol, to dilute solution of sodium ethoxide in ethanol gives a transitory purple colour which fades within one second. The disappearance of this colour is no doubt due to a nucleophilic substitution reaction which destroys the parent compound. The colour was apparent in solutions containing 10^{-1}, 10^{-2} or 10^{-3}M sodium ethoxide and 1×10^{-4}M 1,2,4,5-tetranitrobenzene. In the absence of quantitative measurements, the equilibrium constant for formation of the coloured species can only be estimated. However the observation of the colour in a solution containing 10^{-3}M sodium ethoxide suggest that $K \geqslant 10^{2}$ $1.mol^{-1}$. Following the same line of argument for the interaction of 1,2,4,5-tetranitrobenzene with sodium sulphite, the transitory purple colour produced in the present case may be due to the formation of the adduct XII.



(XII)

Comparison of the stability of the 1:1 adducts formed from 1,2,3,5-, 1,2,4,5-tetranitrobenzene and 1,3,5-trinitrobenzene

Data for the equilibrium constants for the formation of 1:1 adducts from the two tetranitrobenzenes and 1,3,5-trinitrobenzene are given in Table 5.

Despite the uncertainty about the adducts formed from 1,2,4,5-tetranitrobenzene and sodium ethoxide or sodium sulphite, it is clear that the adducts formed from 1,2,3,5-tetranitrobenzene have considerably greater stability than those formed from its isomer. This adds to the increasing evidence[3,31] that the presence of a strongly electron withdrawing group para to the position of addition is of great importance in determination of the stabilities of Meisenheimer complexes. The very great increase observed in the reactivity of 1,2,3,5-tetranitrobenzene relative to 1,3,5-trinitrobenzene is perhaps surprising in view of the fact that the

TABLE 5

Equilibrium constants for formation of 1:1 adducts from poly-nitro-compounds with various nucleophiles

Nitro-compound	$K\ l.mol^{-1}$		
	OH	OEt	SO_3^-
1,2,3,5-tetranitrobenzene	$2{\cdot}4 \times 10^4$	$> 10^6$	$\geqslant 10^6$
1,2,4,5-tetranitrobenzene	< 50	$\geqslant 10^2$	$\sim 10^2$
1,3,5-trinitrobenzene	$2{\cdot}7$ [a]	$2{\cdot}0 \times 10^3$ [b]	$2{\cdot}5 \times 10^2$ [c]

a) Ref.48 b) Ref.6 c) Ref.56

fourth nitro group is meta to the position of addition, so that the electronic effect would not be expected to be very large. However 1,2,3,5-tetranitrobenzene contains three nitro groups at adjacent ring positions which will cause considerable steric strain. It has been shown[56] previously that adducts formed by addition at C_3 in 1-X-2,4,6-trinitrobenzene ($X = NH_2$, NMe_2, etc.) have greater stability than those from 1,3,5-trinitrobenzene. This has been ascribed partly to a steric effect which makes the conformation of the molecule particularly attractive for addition. It may be that the greatly enhanced reactivity of 1,2,3,5-tetranitrobenzene also derives partly from steric effects.

The rate constant for nucleophilic displacement of nitro-groups by hydroxide ion in 1,2,3,5-tetranitrobenzene (2×10^2 $1.mol^{-1}sec^{-1}$) is surprisingly only slightly greater than with 1,2,4,5-tetranitrobenzene (50 $1.mol^{-1}sec^{-1}$). Murto[129] has shown that for a number of picryl compounds the rate-determining step in the reaction with hydroxide ion is the addition of hydroxide ion and that the rate of this process depends on the electron density at the reaction centre. It seems likely that an intermediate such as IV formed from 1,2,3,5-tetranitrobenzene will lose nitrite ion rather than hydroxide ion so that the measured rate constants for reaction will similarly correspond to the rates of hydroxide addition. However due to the presence of nitro group at C_2 the electron density at this position in 1,2,3,5-tetranitrobenzene would be expected to be smaller than that at C_4. On this basis the adduct with structure IV should be formed more rapidly than that with structure III. The fact that the latter adduct is in fact more quickly produced infers that base addition is faster at C_4 than at C_2 which in turn implies some steric hindrance to addition at C_2. This can perhaps be understood in terms of shielding of the reaction centre from the incoming hydroxide ion by the adjacent nitro-groups. Similar effects have been observed with other crowded nitro-compounds.[21,27] This effect is likely to be less important for 1,2,4,5-tetranitrobenzene, perhaps explaining the similar rate of nucleophilic displacement for the two isomers.

Section III

Interaction of 1,3-Dimethoxy-4,6-Dinitrobenzene with Sodium Methoxide in Dimethyl Sulphoxide-Methanol Mixtures

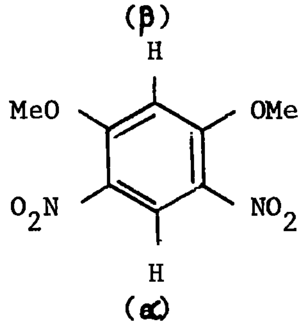
INTRODUCTION

Gitis and Glaz[11,130] have reported recently that transetherification reactions of alkyl and aryl ethers of aromatic nitro-compounds belong to the general class of nucleophilic substitution reactions which occur by a bimolecular S_N2 mechanism. Thus they suggested that transetherification of 1,3-dimethoxy-4,6-dinitrobenzene by a variety of alkoxides proceeds via intermediates of structure type (II). More recently, Pollitt and Saunders,[70] in the course of the study of Janovsky reactions found that the visible spectra of 1,3-disubstituted-4,6-dinitrobenzene (substituents = Cl,Cl; OMe,Me; OMe,OMe; Cl,NMe_2; CO_2Me,CO_2Me; Me,Me; Me,Cl) in acetone in the presence of sodium hydroxide show in general a single band in the visible region. This absorption band was attributed to the complexes formed by addition at the 2-position.

In the present work the interaction of 1,3-dimethoxy-4,6-dinitrobenzene and sodium methoxide in protic-dipolar aprotic solvents was studied by visible and NMR spectroscopy.

i) NMR Spectroscopic Study

The NMR spectrum of 1,3-dimethoxy-4,6-dinitrobenzene in dimethyl sulphoxide given in Figure 1a shows in addition to the solvent bands a set of absorption bands at -8•66, -7•05 and -4•25 ppm relative to TMS, with intensity ratio 1:1:6 respectively. The two sharp singlets at -8•66 and -7•05 ppm are attributed respectively to the protons (a) and (b) in structure (I), while the strong resonance at -4•25 ppm is attributed to the protons of the two equivalent methoxyl groups.



(I)

The addition of methanolic sodium methoxide to solutions of 1,3-dimethoxy-4,6-dinitrobenzene in dimethylsulphoxide caused the formation of red colour. The NMR spectrum now showed the presence of a new set of bands in addition to those from the parent compound. As the ratio of methoxide to 1,3-dimethoxy-4,6-dinitrobenzene was increased the new bands grew in intensity at the expense of those due to the parent compound until by a mole ratio of 1:1 methoxide:1,3-dimethoxy-4,6-dinitrobenzene the conversion to the complex was complete. The spectrum of the complex is shown in Fig.1c-d. The chemical shifts of these new bands were -8•81, -4•15, -3•65 and -2•93 ppm with intensity ratio 1:1:3:6 respectively. The complex spectrum is interpreted as follows: The resonance at -8•81 ppm is attributed to proton (α) in the complex. This band occurs at almost

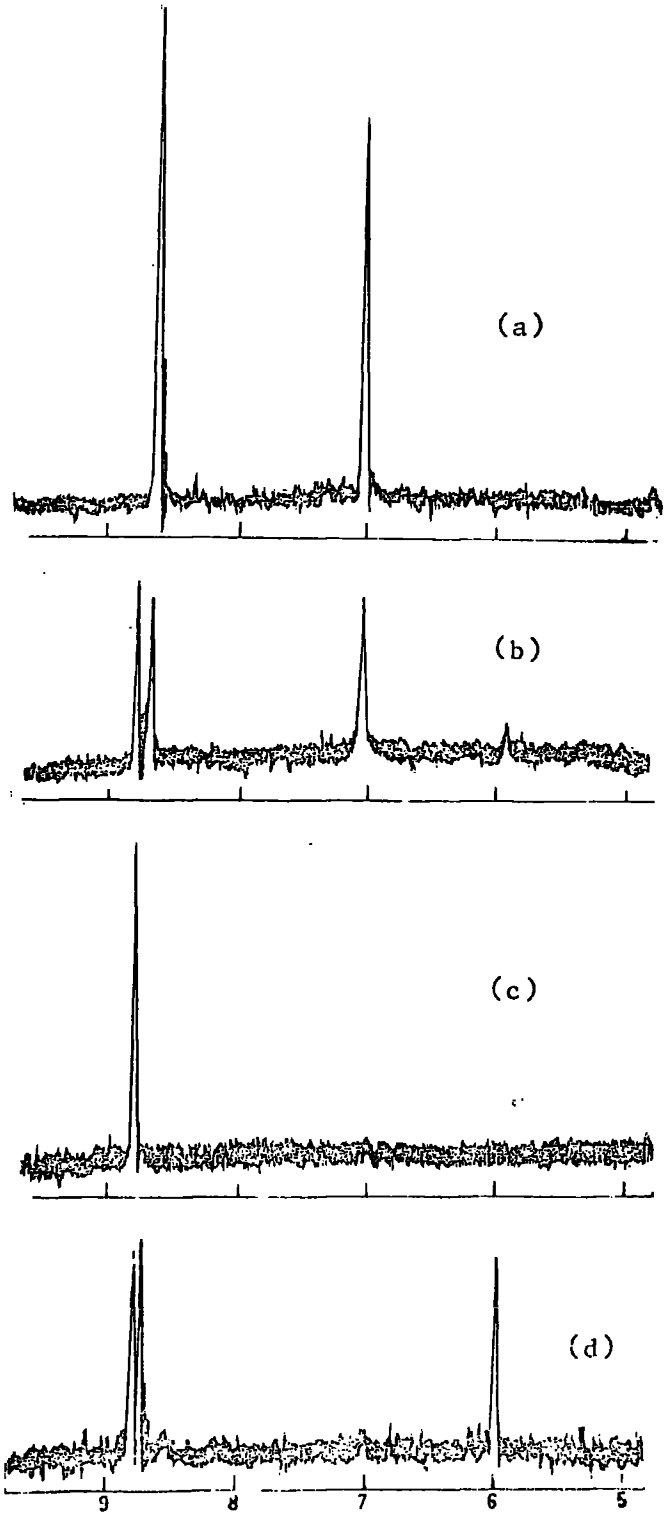
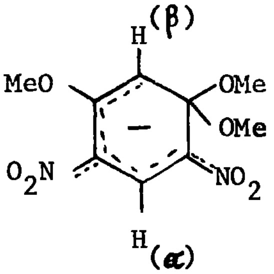


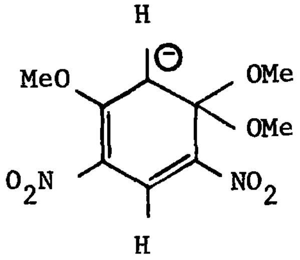
Fig.1. Lowfield NMR spectra of 1,3,-dimethoxy-4,6-dinitrobenzene (0·4M) in DMSO solution containing the following concentrations of NaOMe (a) 0·0; (b) $\frac{1}{2}$ equivalent (c) 1 equivalent (d) spectrum (e) after 1 hour.

the same position as in the parent compound and rules out methoxide addition at this position as this would cause the proton absorption to move considerably upfield as the hybridisation at the carbon atom changes from sp^2 to sp^3. In addition the possibility of methoxide addition at the second unsubstituted position (β) is very unlikely as this position is meta to the two nitro groups. Also the position and intensities of the methoxyl resonances argues against this possibility. The complex spectrum is consistent only with the structure (II) where the methoxide ion is bonded to a ring-carbon carrying a methoxyl group. This structure has two distinct types of methoxyl groups which would give two distinct NMR bands. Thus the chemical shift at -2•93 ppm is attributed to the six



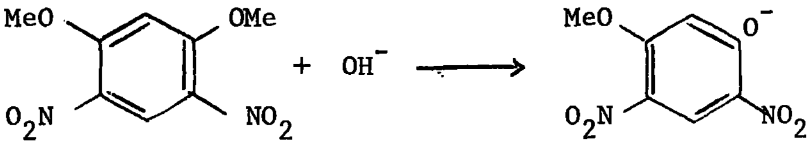
(II)

methoxyl protons at C_1. The position of this absorption is similar to that observed for the methoxyl protons of the 2,4-dinitroanisole-methoxide adduct where addition occurs at C_1.[21] The band at -3•65 ppm is assigned to the methoxyl protons at C_3. The band at -4•25 ppm is attributed to the proton (β). This absorption is shifted upfield by 2•8 ppm compared to the position (-7•05 ppm) in the parent compound. This is almost certainly due to the contribution of the resonance form III which results in a negative charge at this position.



(III)

However the complex spectrum is not stable but changes with time. The change is observed by the build up of new bands which grow at the expense of the complex spectrum. The chemical shifts of these bands are -8•71, -5•90 and -3•76 ppm with an intensity ratio 1:1:3. This change in spectrum with time almost certainly results from the slow production of 3-meth~~yl~~oxy-4,6-dinitrophenole (which will be present as the phenoxide ion).



This may be formed via traces of water in the solvent or by dimethylation of the parent compound by methoxide ions.[88,127] A similar reaction was reported in the case of 2,4-dinitroanisole and sodium methoxide.[21,131]

In a recent structural study of the species formed from a number of aromatic nitro-compounds and bases, Foster et al[131] have obtained an NMR spectrum for the interaction of 1,3-dimethoxy-4,6-dinitrobenzene with sodium methoxide in dimethyl sulphoxide solution. They attributed the observed chemical shifts at -8•70 and -6•00 ppm to the formation of the adduct (II). However, on the basis of the present work, there is no doubt that the spectrum which they observed is due to the formation of 3-methoxy-4,6-dinitrophenol and not to the complex (II).

ii) Visible Spectroscopic Study

The addition of sodium methoxide to solutions of 1,3-dimethoxy-4,6-dinitrobenzene in methanol-dimethyl sulphoxide mixtures caused the appearance of red colour which was shown from NMR spectroscopy to be due to the formation of adduct (II). The spectrum shown in Figure 2 indicates a maximum at 4900Å. Increasing the concentration of methoxide caused an increase in the visible absorption without change in the spectral shape. The equilibrium constants for the formation of the coloured species in various solvent systems were determined by taking measurements of the optical density at 4900Å. Such measurements in 90/10, 80/20 and 70/30 by

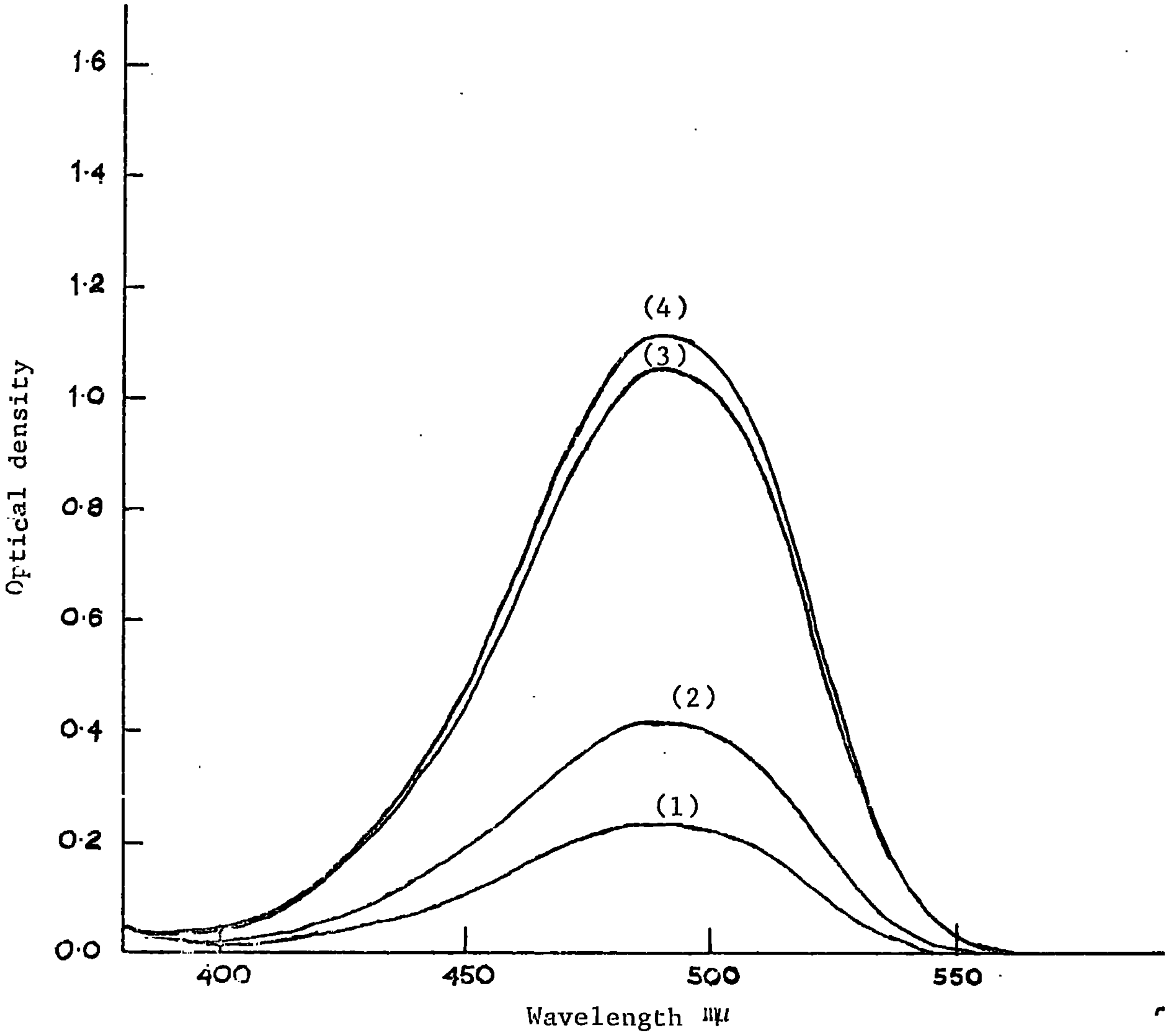


Fig.2. The visible absorption spectra of 1,3-dimethoxy-4,6-dinitrobenzene 5 x 10^{-5}M 90/10 (v/v) DMSO/MeOH containing (1) 0·008M, (2) 0·02M, (3) 0·1M and (4) 0·2M sodium methoxide.

volume dimethylsulphoxide-methanol mixtures and the calculated equilibrium constants are given in Tables 1, 2 and 3. These results indicate that the value of the equilibrium constant increases with increasing sodium methoxide concentration. This is not unexpected since the activity coefficient of the charged species will probably vary with concentration in these solutions. It was found empirically that plots of the logarithm of the calculated equilibrium constants versus the methoxide concentration were linear. Two such plots are given in Figure 4 and 5. Extrapolation of these plots to zero methoxide concentration where all the activity coefficients will tend to unity allowed the equilibrium constant to be found in these solutions. Values were found to be 38•8 $1.mol^{-1}$ in 90 vol % DMSO; 1•66 $1.mol^{-1}$ in 80% DMSO and 0•16 $1.mol^{-1}$ in 70% DMSO.

Table 4 gives the measurements of the optical density due to the formation of complex II at fixed sodium methoxide concentration (0•25M) in solvents of various composition. It has been mentioned previously that the thermodynamic equilibrium constants for the formation of addition complexes from unreactive aromatic nitro-compounds can be determined by the use of acidity functions.[97] In this way it has been possible to compare the reactivity of a variety of aromatic nitro-compounds towards the methoxide ion in methanol. In the present work it is of interest to compare the reactivity of 1,3-dimethoxy-4,6-dinitrobenzene towards the methoxide ion with certain other aromatic nitro-compounds in

TABLE 1

Dependence of optical density on base concentration and calculated equilibrium constants in 90/10 (v/v) DMSO/MeOH

[NaOMe] M	O.D. 4900Å	K $l.mol^{-1}$	$\log_{10} K$
0	0·005	-	-
0·002	0·069	40·45	1·607
0·004	0·129	41·05	1·613
0·006	0·183	41·95	1·623
0·008	0·229	42·65	1·63
0·01	0·268	42·38	1·627
0·02	0·43	45·7	1·67
0·03	0·545	51·16	1·709
0·04	0·64	61·3	1·787
0·05	0·69	65·68	1·817
0·06	0·725	69·02	1·839
0·08	0·77	74·00	1·869
0·10	0·83	118·5	2·07
0·20	0·90	-	-
0·25	0·90	-	-
0·30	0·88	-	-

TABLE 2

Dependence of optical density on base concentration and calculated equilibrium constants in 80/20 (v/v) DMSO/MeOH

[NaOMe] M	O.D. 4900Å	K l.mol^{-1}	$\log_{10}$ K
0	0•005	-	-
0•05	0•092	2•3	0•361
0•1	0•21	3•2	0•505
0•15	0•337	4•29	0•633
0•20	0•462	5•8	0•763
0•25	0•578	8•19	0•913
0•30	0•67	11•75	1•07
0•40	0•78	24•35	1•386
0•50	0•846	120•69	2•08
0•60	0•86	-	-
0•70	0•86	-	-

TABLE 3

Dependence of optical density on base concentration and calculated equilibrium constants in 70/30 (v/v) DMSO/MeOH

[NaOMe] M	O.D. 4900Å	k l.mol^{-1}	log$_{10}$ K
0	0·005	-	-
0·25	0·113	0·64	$\bar{1}$·806
0·30	0·158	0·991	$\bar{1}$·995
0·40	0·262	1·24	0·093
0·50	0·394	1·99	0·30
0·66	0·59	4·47	0·65
0·77	0·70	10·09	1·037
0·88	0·76	22·77	1·538
0·99	0·79	-	-
1·1	0·77	-	-

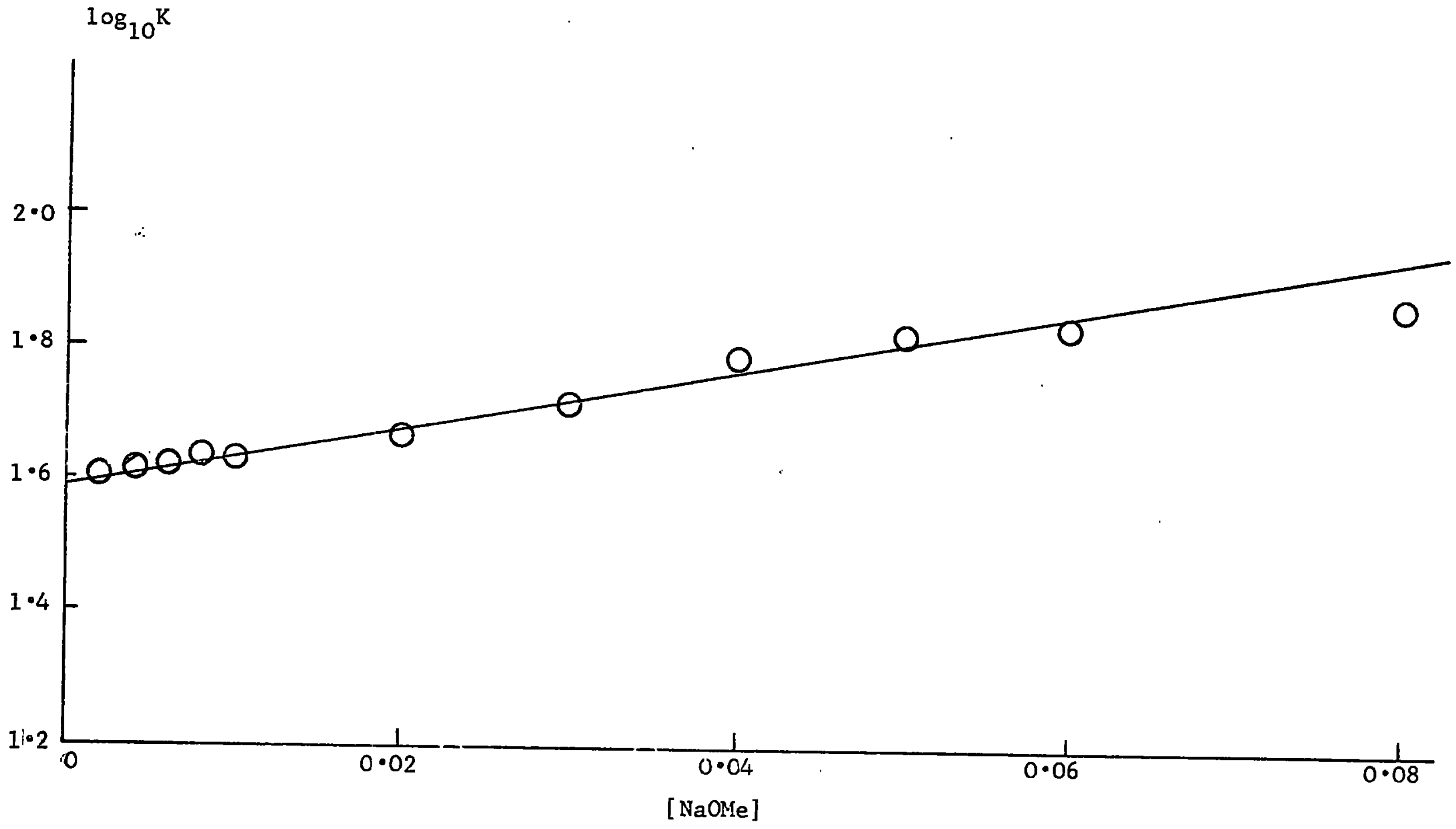
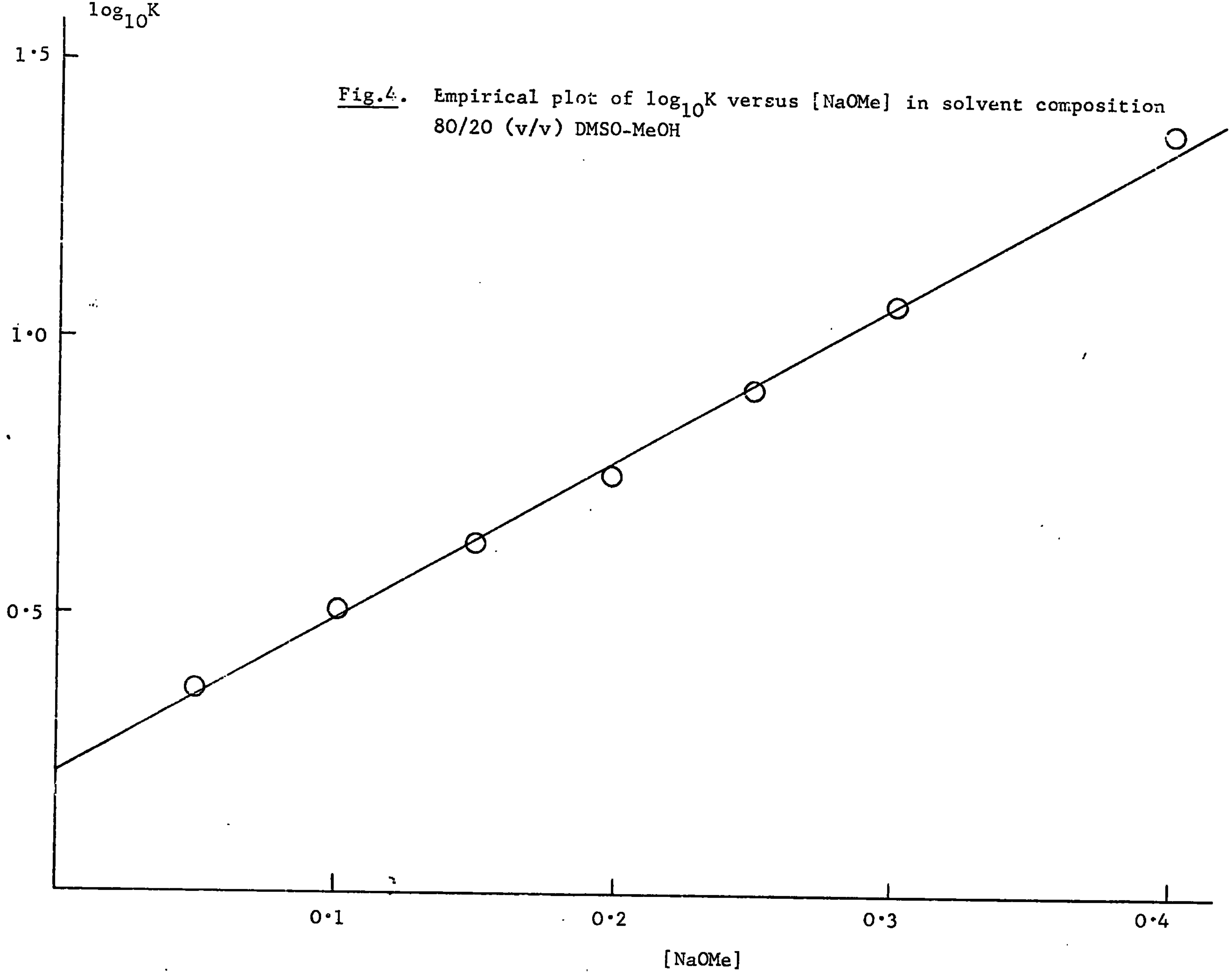


Fig.3. Empirical plot of $\log_{10}K$ versus the [NaOMe] in solvent composition 90/10 (v/v) DMSO-MeOH



<u>Fig.4</u>. Empirical plot of $\log_{10}K$ versus [NaOMe] in solvent composition 80/20 (v/v) DMSO-MeOH

methanol where the data for the latter compounds are available. The equilibrium constant for the formation of (II) from 1,3-dimethoxy-4,6-dinitrobenzene in methanol can not be determined directly. However, the data in Table 4 which involve base addition, would be correlated best with the acidity function J_- where

$$J_- = -\log_{10}K - \log_{10} K_{MeOH} + \log_{10}\frac{[\text{complex}]}{[\text{parent}]}$$

Unfortunately J_- data in this solvent system are not available. However use of the acidity function H_- may yield a satisfactory value for the equilibrium constant. Crampton and Gold[132] have determined the values of H_- in methanol-dimethyl sulphoxide mixtures containing 0·25M sodium methoxide. These were given in Table 4. A plot of $\log_{10}\frac{[\text{complex}]}{[\text{parent}]}$ versus H_- is linear as shown in Figure 6. The slope is very close to unity (0·98) which indicates that the two acidity functions will probably have similar values in this system. The parent compound is half converted to complex when H_- = 21·74 and taking the autoprotolysis constant of methanol as $10^{-16\cdot7}$ this yields a value of K for complex formation in methanol of 1×10^{-5} l.mol^{-1}. This value of K is smaller than that for 2,4-dinitroanisole where literature values vary from 5×10^{-5} l.mol^{-1},[102a] to 10^{-3} l.mol^{-1}.[47]

On purely statistical grounds the dimethoxy compound would be expected to have an equilibrium constant twice that of the methoxy compound since

TABLE 4

Measurements of optical density at 4900A in various solvent mixtures containing 0•25M sodium methoxide and 4×10^{-5} M 1,3-dimethoxy-4,6-dinitrobenzene

DMSO/MeOH v/v	O.D. 4900Å	$\log_{10}\frac{[\text{complex}]}{[\text{parent}]}$	Mole % MeOH	H_-
90/10	0•90	-	16•7	23•65
85/15	0•82	1•01	24	22•75
80/20	0•578	0•14	31	21•95
75/25	0•282	-0•34	37•5	21•3
70/30	0•113	-0•86	43•5	20•87
65/35	0•049	-1•23	49	20•45

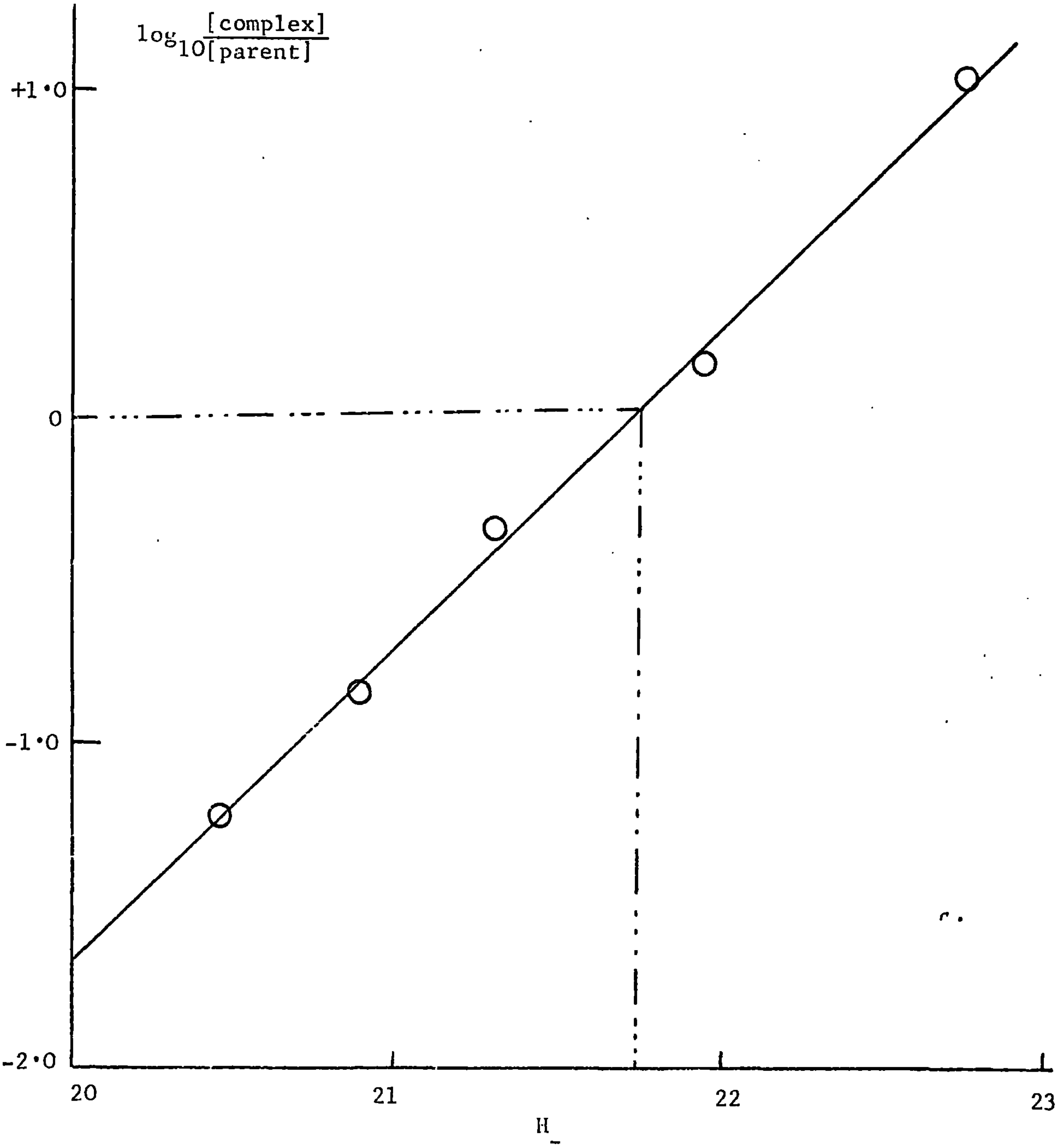
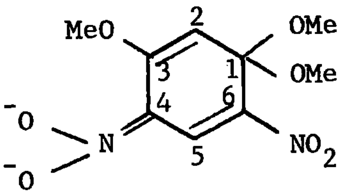
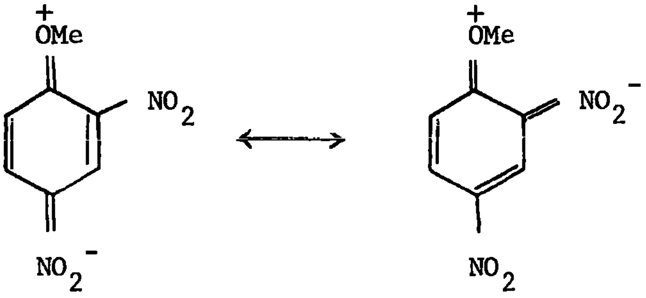


Fig.5. Dependence of the extent of conversion of 1,3,-dimethoxy-4,6-dinitrobenzene to complex on the basicity of the medium in methanol-dimethyl sulphoxide mixtures.

there are two positions where addition can occur. The smaller value for the dimethoxy compound may result in part from steric interaction in the complex between the methoxy group in 3-position and the nitro group in the 4-position. This will cause the nitro group to bend out of the ring plane and so be less effective in accommodating the negative charge. In terms of Bernasconi's latest arguments[102b] the dinitroanisole molecule will lose two resonance forms on complex formation while the dimethoxy compound will lose four such resonance forms. This may also account for the smaller equilibrium constant for formation of the adduct from the dimethoxy compound.





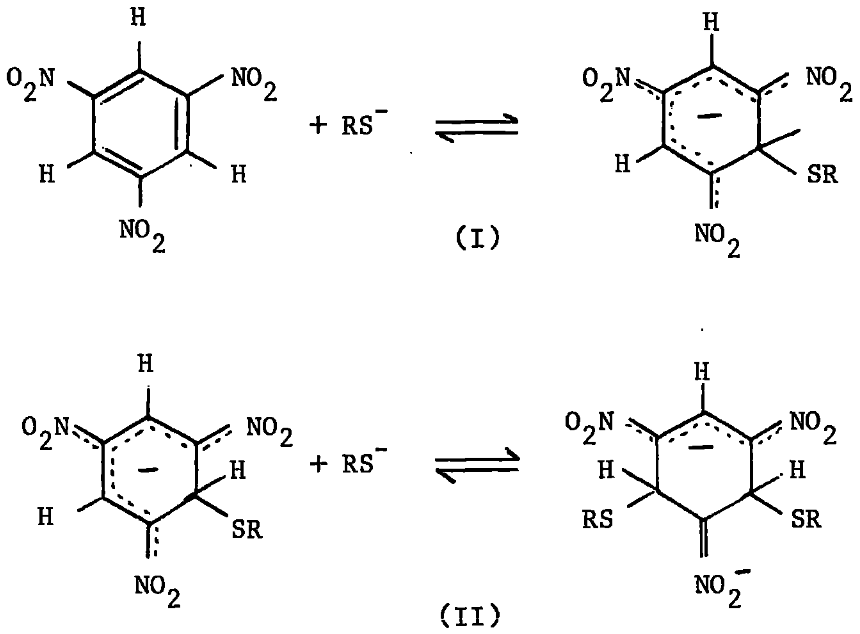
Section IV

Solvent Effects on the Stabilities of Meisenheimer-type Complexes

INTRODUCTION

It was mentioned in the general introduction that changing from protic to dipolar aprotic solvents has a considerable effect on the activity coefficients of ions present in these solutions.[107] It has been shown that 1:1 adducts of Meisenheimer-type have greater stability in dipolar aprotic solvents than in protic solvents. This enhanced stability can be attributed partly to the increased reactivity of the nucleophiles in dipolar aprotic solvents as a result of desolvation, and partly due to the greater ability of these solvents to solvate the anions formed. Furthermore recent studies on Meisenheimer complexes have indicated that 1:2 adducts formed from two molecules of base and one molecule of parent compound have special stability in water relative to alcohols or dipolar aprotic solvents. Thus N,N-dimethyl picramide was found to give only a 1:2 adduct with hydroxide in water. It was also shown previously in this thesis that the major interaction between the picrate ion and the hydroxide ion in water results in the formation of 1:2 adduct.

In view of these reports, it becomes very interesting to study quantitatively the effects of change of solvent on the stabilities of the complexes. Thus in this part of the present work the interactions of 1,3,5-trinitrobenzene with certain sulphur bases have been studied in alcohol-water solvent mixtures. The reason for the choice of the thiolate ions as the reactive base was threefold. Firstly, in the presence of excess thiol the equilibrium concentration of hydroxide and alkoxide ions will be very small so that there are effectively interactions between 1,3,5-trinitrobenzene and a single base (RS^-) rather than with two bases (OH^- and OR^-). Secondly, the thiolate ions have conveniently high reactivity and thirdly the structure of the species formed are already known.[104] The equilibria for the formation of 1:1 adduct (I) and 1:2 adduct (II) from 1,3,5-trinitrobenzene and thiolate ion can be written as follows:



(I)

(II)

In this section it is convenient to present the results followed by the discussion.

RESULTS

i) Interaction of 1,3,5-Trinitrobenzene (135 TNB) and Sodium Thioethoxide in Ethanol-Water Mixture

The addition of sodium thioethoxide to solutions of 135 TNB in ethanol caused the appearance of a red violet species whose visible spectrum, Figure 1a, shows a maximum at 4600Å with pronounced shoulder at longer wavelength. This spectrum is similar to that of the 1:1 adduct formed from 135 TNB and thioethoxide in methanol.[104] Increasing the concentration of thioethoxide up to 0•002M caused an increase in the visible absorption without change in the spectral shape. This was taken to indicate the presence of a single adduct resulting from base addition at a ring carbon carrying hydrogen to give complex A which has structure (I) (R = Et). However, before conversion to complex A was complete a second interaction was indicated by an increase of the visible absorption near 5000Å, Figure 1b, and eventually at high concentration of thioethoxide all the 135 TNB was in the form of the second complex B which involves addition of two molecules of base at two ring carbons carrying hydrogen to give adduct (II) (R = Et).

As the solvent system was made more aqueous, the visible spectra observed were similar in general terms to those observed in ethanol. However, small shifts in the positions of the absorption maxima and small changes in the values of the extinction coefficients were observed. In

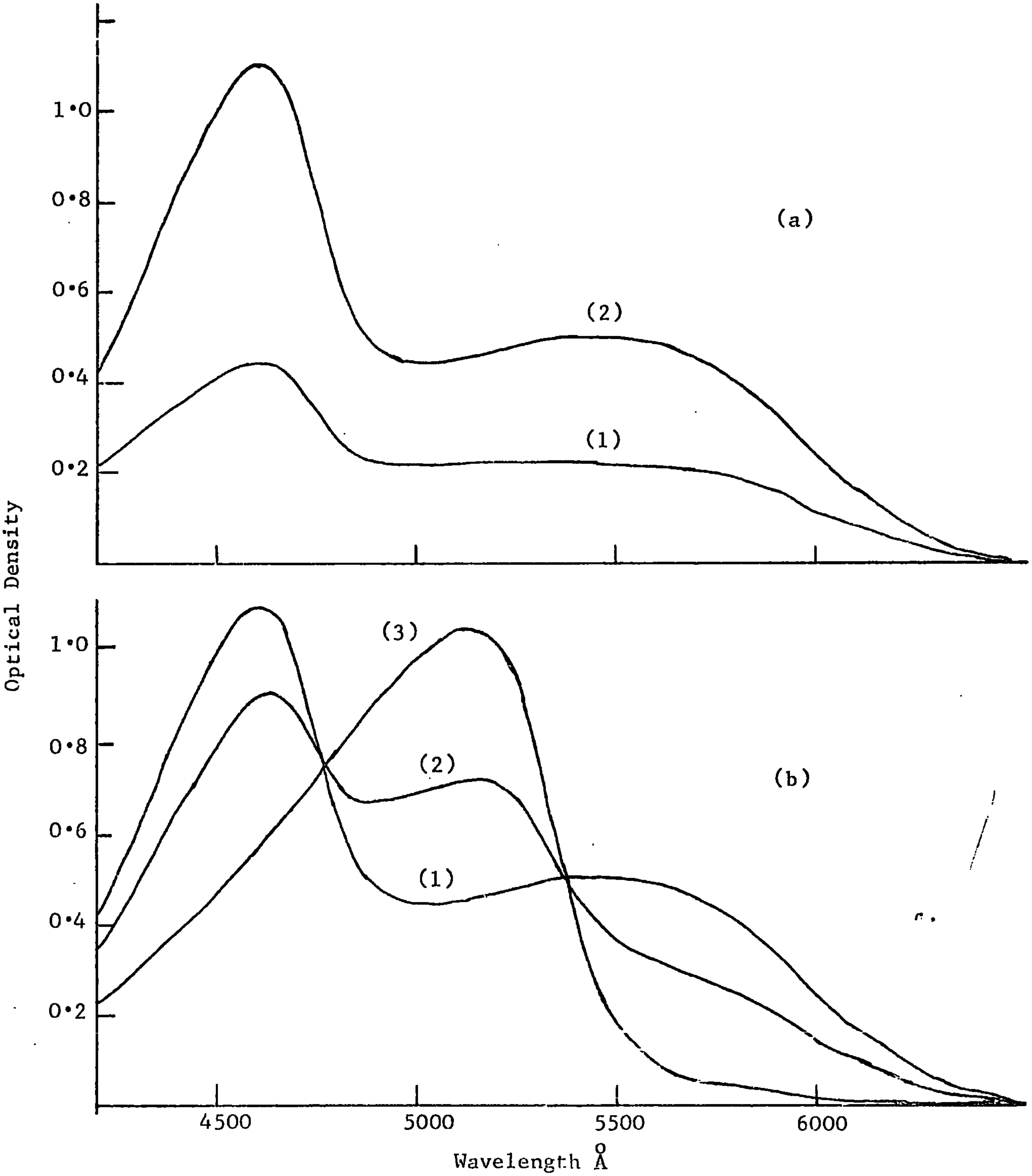


Fig.1. The visible absorption spectra of 1,3,5-trinitrobenzene (4×10^{-5}M) in ethanol containing (a) 1, 12×10^{-5}M; 2, 2×10^{-3}M (b) 1, 2×10^{-3}M; 2, 0·02M; 3, 0·18M sodium thioethoxide.

addition, the formation of 1:2 adduct was found to occur at lower thioethoxide concentrations as the proportion of water was increased. Visible spectra in 30/70 by volume ethanol/water are given in Figure 2. Spectral data for the complexes over the whole range of solvent composition and equilibrium constants are collected in Table 1.

The equilibrium constants for the formation of adducts A and B in various solvent mixtures were determined by measurements of the optical density at suitable wavelengths. Such measurements and the calculated values of the equilibrium constants are given in Tables 2 to 12. It is necessary at this stage to give an account of how the data given in Tables 1 to 12 were obtained.

In pure ethanol or ethanol-rich mixtures with water formation of the lower adduct was favoured at low base concentrations. Increasing the base concentration from 10^{-4} mol.litre^{-1} to 10^{-3}mole litre^{-1} caused an increase in the visible absorption without change in the spectral shape. Since conversion of 135 TNB to 1:1 adduct was at no stage complete, the extinction coefficients were determined from Benesi-Hildebrand[93] plots. The Benesi-Hildebrand plot for optical densities at 5900Å obtained in pure ethanol is shown in Figure 3. The points corresponding to the lowest base concentrations appear to be inaccurate but the linear plot for the other points yields a value for the extinction coefficient at this wavelength. It should be noted that the concentration of free base in these solutions are very small (10^{-4}M) so that it is probable that the non-linearity of

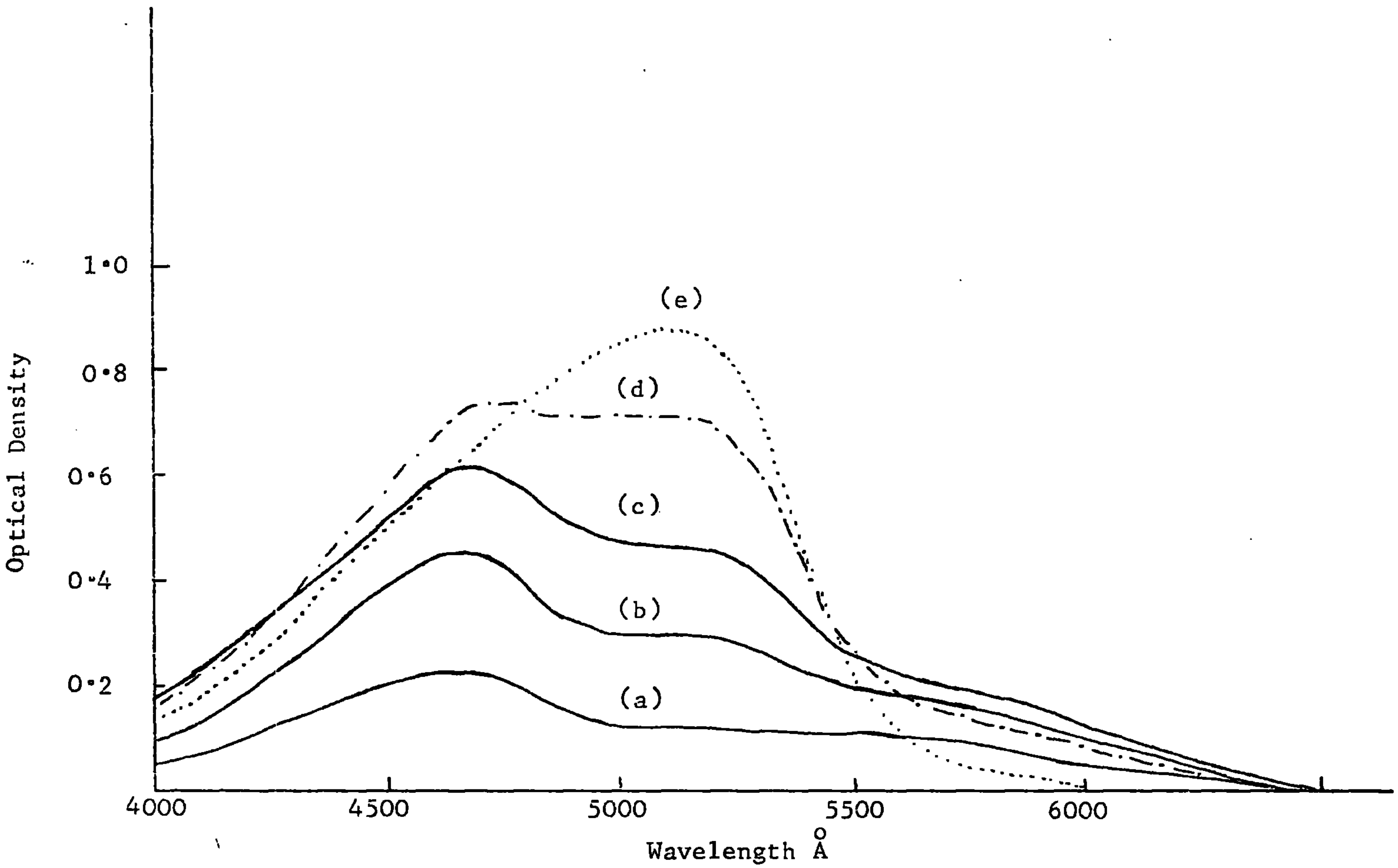


Fig.2. Visible absorption of 1,3,5-trinitrobenzene in 30/70 (v/v) ethanol-water containing the following concentrations of sodium thioethoxide (a) $1{\cdot}6 \times 10^{-4}$M, (b) $3{\cdot}2 \times 10^{-4}$M; (c) $5{\cdot}0 \times 10^{-4}$M; (d) $1{\cdot}0 \times 10^{-3}$M; (e) $8{\cdot}0 \times 10^{-3}$M.

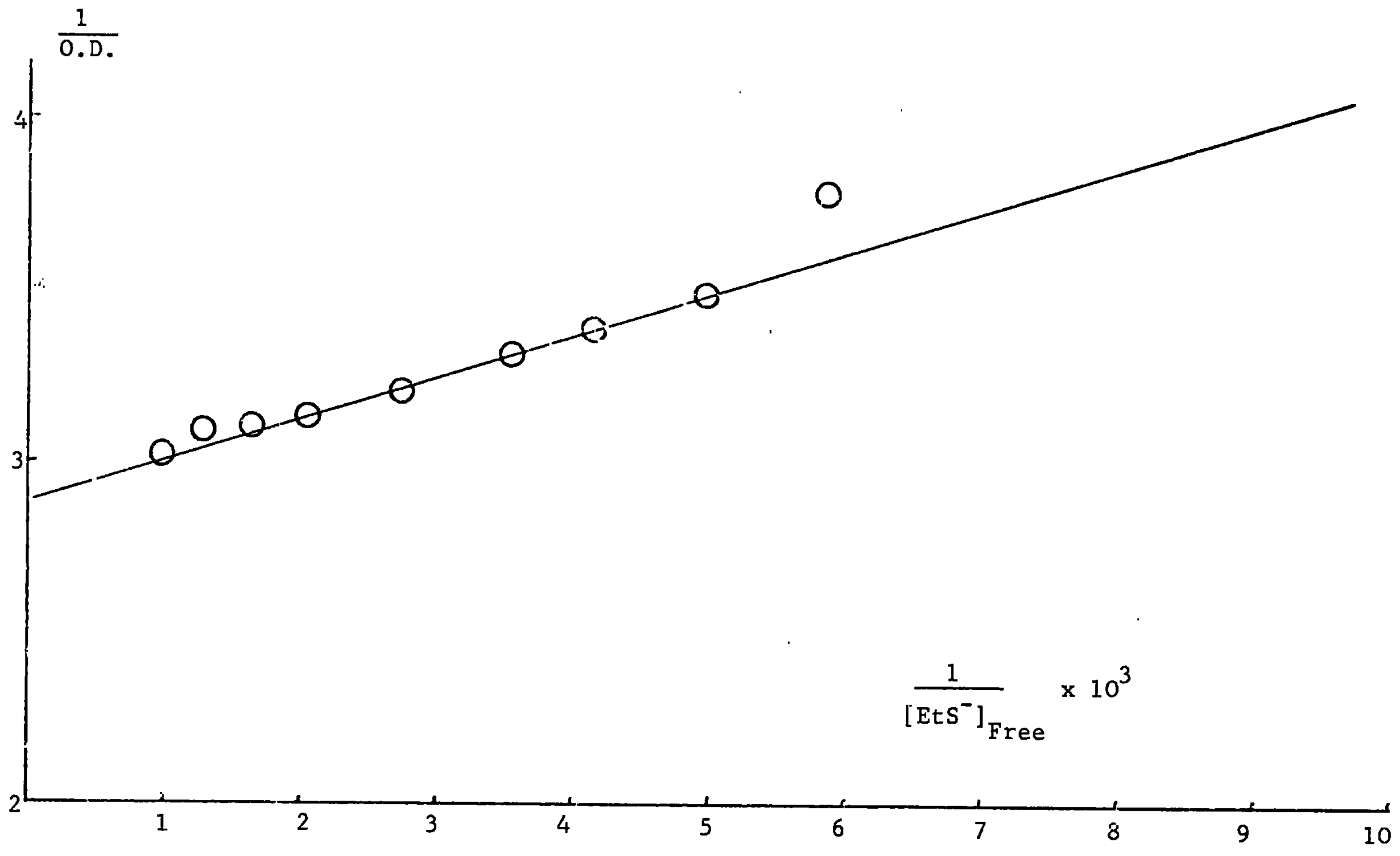


Fig.3. Benesi-Hildebrand plot for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in ethanol, measured at 5900Å.

TABLE 1

Equilibrium constants and spectral data for the adducts from 1,3,5-trinitrobenzene and sodium thioethoxide in ethanol-water mixtures

Solvent % Ethanol by volume	$10^{-2}K_1$ 1 mole^{-1}	K_2 [a] 1 mole^{-1}	1:1 Adduct		1:2 Adduct	
			λ max(nm)	$10^{-3}\epsilon$ (590nm)	λ max(nm)	$10^{-4}\epsilon$ max
100	250 ± 50	7 ± 3	460	8·6	512	2·6
90	360 ± 100	10 ± 3	461	9·0	512	2·55
80	450 ± 100	23 ± 4	461	9·2	512	2·6
70	390 ± 100	38 ± 6	462	9·2	512	2·6
60	300 ± 100	80 ± 10	462	9·4	512	2·6
50	230 ± 70	180 ± 20	463	9·2	512	2·6
40	150 ± 50	500 ± 100	464	9·0 [b]	512	2·4
30	30 ± 10	1500 ± 200	464	9·0 [b]	510	2·3
20	7·5 ± 1	5000 ± 1000	464	9·0 [b]	506	2·2 [b]
10	3·5 ± 0·5	7000 ± 1000	-	8·6 [b]	500	2·1 [b]
0	1·7 ± 0·5	12000 ± 2000	-	8·5 [b]	490	2·0 [b]

(a) extrapolated to zero ionic strength using Debye-Huckel extrapolation.

(b) this value was not determined directly but was used in the calculation of the equilibrium constants.

TABLE 2

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium thioethoxide in ethanol

$[EtS^-]$ stoich.	$[EtS^-]$ Free	Optical Density			Relative Concentration			$10^4 K_1$ M^{-1}	K_2 M^{-1}
		4600Å	5000Å	5900Å	A	B	TNB		
12×10^{-5}	10×10^{-5}	0·518	0·23	0·154	0·45	-	0·55	0·8	-
16×10^{-5}	13×10^{-5}	0·75	0·332	0·23	0·66	-	0·34	1·5	-
20×10^{-5}	17×10^{-5}	0·85	0·365	0·26	0·75	-	0·25	1·75	-
24×10^{-5}	20×10^{-5}	0·91	0·392	0·28	0·81	-	0·19	2·1	-
28×10^{-5}	24×10^{-5}	0·942	0·405	0·29	0·84	-	0·16	2·2	-
32×10^{-5}	28×10^{-5}	0·98	0·418	0·30	0·87	-	0·13	2·4	-
40×10^{-5}	36×10^{-5}	1·02	0·43	0·31	0·90	-	0·10	2·5	-
52×10^{-5}	48×10^{-5}	1·04	0·438	0·317	0·92	-	0·08	2·4	-
64×10^{-5}	60×10^{-5}	1·05	0·441	0·32	0·93	-	0·07	2·2	-
80×10^{-5}	76×10^{-5}	1·06	0·444	0·324	0·94	-	0·06	-	-
0·001	0·001	1·06	0·449	0·328	0·95	-	0·05	-	-
0·0016	0·0016	1·06	0·45	0·328	0·95	-	0·05	-	-
0·002	0·0020	1·06	0·45	0·322	0·96	0·02	0·02	-	-
0·006	0·006	1·03	0·50	0·303	0·88	0·09	-	-	17
0·010	0·010	0·975	0·556	0·27	0·78	0·20	-	-	26
0·14	0·14	0·92	0·614	0·24	0·70	0·30	-	-	30

Table 2 contd.

[EtS$^-$] stoich.	[EtS] Free	Optical Density			Relative Concentration*			$10^4 K_1$ M^{-1}	K2 M^{-1}
		4600Å	5000Å	5900Å	A	B	TNB		
0•018	0•018	0•87	0•675	0•205	0•59	0•42	-	-	40
0•020	0•020	0•825	0•695	0•191	0•54	0•46	-	-	43
0•024	0•024	0•79	0•732	0•165	0•46	0•54	-	-	49
0•028	0•028	0•75	0•76	0•45	0•40	0•60	-	-	54
0•032	0•032	0•72	0•795	0•130	0•35	0•66	-	-	59
0•040	0•040	0•68	0•84	0•103	0•27	0•73	-	-	67•5
0•050	0•050	0•632	0•866	0•08	0•20	0•80	-	-	80
0•080	0•080	0•575	0•926	0•047	0•10	0•92	-	-	115
0•10	0•10	0•555	0•93	0•035	-	-	-	-	-
0•16	0•16	0•51	0•94	0•019	-	-	-	-	-
0•20	0•20	0•497	0•94	0•015	-	-	-	-	-
0•24	0•24	0•497	0•94	0•012	-	-	-	-	-

* See text for method of calculation

TABLE 3

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in 90/10 (v/v) ethanol-water

$[EtS^-]^a$ stoich.	Optical Density			Relative Concentration[b]			$10^{-4}K_1$ M^{-1}	K_2
	4600Å	5000Å	5900Å	A	B	TNB		
12 x 10^{-5}	0·66	0·298	0·215	0·60	-	0·40	1·7	-
16 x 10^{-5}	0·84	0·363	0·273	0·76	-	0·24	2·5	-
20 x 10^{-5}	0·90	0·394	0·295	0·82	-	0·18	2·9	-
24 x 10^{-5}	0·96	0·42	0·315	0·88	-	0·12	3·7	-
28 x 10^{-5}	0·98	0·425	0·32	0·89	-	0·11	3·4	-
32 x 10^{-5}	1·01	0·435	0·327	0·91	-	0·09	3·6	-
40 x 10^{-5}	1·03	0·444	0·333	0·93	-	0·07	3·7	-
52 x 10^{-5}	1·04	0·45	0·34	0·94	-	0·06	3·4	-
64 x 10^{-5}	1·05	0·452	0·34	0·94	-	0·06	-	-
80 x 10^{-5}	1·05	0·458	0·341	0·95	-	0·05	2·6	-
0·014	1·06	0·461	0·341	0·95	-	0·05	-	-
0·002	1·06	0·469	0·34	0·95	0·02	0·03	-	-
0·006	1·02	0·53	0·32	0·89	0·11	0	-	21
0·01	0·94	0·59	0·275	0·77	0·25	-	-	32
0·014	0·884	0·66	0·234	0·65	0·37	-	-	40
0·018	0·83	0·705	0·197	0·54	0·47	-	-	48
0·020	0·81	0·73	0·176	0·48	0·52	-	-	54
0·024	0·764	0·77	0·15	0·41	0·60	-	-	59
0·028	0·72	0·80	0·131	0·36	0·66	-	-	65
0·040	0·651	0·86	0·085	0·23	0·80	-	-	87
0·08	0·551	0·90	0·035	0·10	0·90	-	-	110
0·12	0·500	0·878	0·018	-	-	-	-	-
0·16	0·48	0·82	0·013	-	-	-	-	-
0·20	0·42	0·77	0·003	-	-	-	-	-

a) $[EtS^-]_{Free}$ was used in the calculation of the equilibrium constants

b) based on extinction coefficient given in Table 1.

TABLE 4

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium thioethoxide in 80/20 (v/v) ethanol-water

$[EtS^-]$ stoich.	Optical Density			Relative Concentration			$10^{-4}K_1$ M^{-1}	K_2
	4600Å	5100Å	5900Å	A	B	TNB		
12×10^{-5}	0•715	0•312	0•24	0•65	-	0•35	2•1	-
16×10^{-5}	0•864	0•378	0•292	0•79	-	0•21	2•9	-
20×10^{-5}	0•94	0•403	0•317	0•86	-	0•14	3•8	-
24×10^{-5}	0•98	0•421	0•33	0•89	-	0•11	4•0	-
28×10^{-5}	1•01	0•434	0•339	0•915	-	0•085	4•5	-
32×10^{-5}	1•02	0•441	0•345	0•93	-	0•07	4•4	-
40×10^{-5}	1•046	0•451	0•352	0•95	-	0•05	5•1	-
52×10^{-5}	1•06	0•458	0•355	0•96	-	0•04	4•8	-
64×10^{-5}	1•06	0•465	0•355	0•96	-	0•04	4•0	-
80×10^{-5}	1•07	0•47	0•359	0•97	0•01	0•02	-	-
0•001	1•06	0•474	0•356	0•96	0•02	0•02	-	-
0•00128	1•06	0•481	0•350	0•945	0•032	0•02	-	-
0•002	1•04	0•50	0•341	0•92	0•065	0•01	-	35
0•004	1•00	0•56	0•313	0•84	0•16	0	-	48
0•006	0•958	0•615	0•283	0•76	0•26	-	-	57
0•008	0•92	0•654	0•257	0•69	0•33	-	-	60
0•012	0•836	0•74	0•202	0•535	0•49	-	-	76
0•016	0•78	0•79	0•166	0•43	0•54	-	-	86
0•02	0•73	0•85	0•13	0•33	0•69	-	-	105
0•03	0•67	0•90	0•091	0•215	0•79	-	-	125
0•04	0•625	0•93	0•065	0•145	0•86	-	-	150
0•06	0•58	0•94	0•041	-	-	-	-	-
0•1	0•516	0•89	0•021	-	-	-	-	-
0•16	0•452	0•78	0•012	-	-	-	-	-

TABLE 5

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium thioethoxide in 70/30 (v/v) ethanol-water

$[EtS^-]$ stoich.	Optical Density			Relative Concentration			$10^{-4}K_1$ M^{-1}	K_2 M^{-1}
	4600Å	5100Å	5900Å	A	B	TNB		
12×10^{-5}	0·76	0·283	0·26	0·70	-	0·30	2·5	-
16×10^{-5}	0·85	0·365	0·288	0·78	-	0·22	3·0	-
20×10^{-5}	0·915	0·395	0·305	0·825	-	0·175	2·9	-
24×10^{-5}	0·963	0·415	0·322	0·87	-	0·13	3·3	-
28×10^{-5}	1·00	0·43	0·335	0·905	-	0·095	3·9	-
32×10^{-5}	1·01	0·442	0·34	0·92	-	0·08	3·8	-
52×10^{-5}	1·04	0·47	0·354	0·955	-	0·045	4·2	-
80×10^{-5}	1·058	0·488	0·351	0·95	0·04	-	-	52
0·0014	1·04	0·52	0·342	0·92	0·08	-	-	62
0·002	1·018	0·535	0·326	0·88	0·12	-	-	68
0·003	0·99	0·585	0·30	0·81	0·20	-	-	82
0·004	0·96	0·631	0·278	0·73	0·28	-	-	96
0·005	0·92	0·67	0·254	0·67	0·35	-	-	106
0·007	0·86	0·73	0·212	0·56	0·46	-	-	117
0·010	0·78	0·805	0·165	0·416	0·60	-	-	145
0·015	0·71	0·87	0·121	0·30	0·73	-	-	163
0·02	0·67	0·914	0·091	0·22	0·80	-	-	182
0·03	0·618	0·943	0·061	-	-	-	-	-
0·04	0·545	0·926	0·027	-	-	-	-	-

TABLE 6

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in 60/40 (v/v) ethanol-water

$[EtS^-]$ stoich.	Optical Density			Relative Concentration			$10^{-4}K_1$ M^{-1}	K_2 M^{-1}
	4600Å	5000Å	5900Å	A	B	TNB		
12×10^{-5}	0·642	0·303	0·225	0·60	-	0·40	1·7	-
16×10^{-5}	0·745	0·352	0·262	0·70	-	0·30	1·8	-
20×10^{-5}	0·882	0·411	0·305	0·81	-	0·19	2·6	-
24×10^{-5}	0·92	0·43	0·316	0·84	-	0·16	2·6	-
28×10^{-5}	0·95	0·449	0·328	0·87	-	0·13	2·8	-
32×10^{-5}	0·98	0·481	0·338	0·90	-	0·10	3·1	-
52×10^{-5}	1·02	0·499	0·349	0·93	0·03	0·04	-	-
80×10^{-5}	1·03	0·525	0·345	0·92	0·06	0·02	-	-
0·0014	1·00	0·568	0·325	0·87	0·13	-	-	107
0·002	0·97	0·60	0·30	0·80	0·20	-	-	122
0·003	0·92	0·654	0·262	0·70	0·30	-	-	140
0·004	0·873	0·692	0·228	0·60	0·40	-	-	165
0·005	0·84	0·73	0·20	0·53	0·47	-	-	175
0·006	0·80	0·758	0·18	0·48	0·52	-	-	180
0·008	0·745	0·79	0·144	0·38	0·62	-	-	205
0·010	0·712	0·82	0·121	0·30	0·70	-	-	233
0·015	0·665	0·86	0·087	0·20	0·78	-	-	-
0·020	0·625	0·88	0·084	-	-	-	-	-
0·030	0·595	0·90	0·042	-	-	-	-	-
0·040	0·569	0·89	0·031	-	-	-	-	-

TABLE 7

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in 50/50 (v/v) ethanol-water

$[\mathrm{EtS}^-]$ stoich.	Optical Density			Relative Concentration			$10^{-4}K_1$ M^{-1}	K_2 M^{-1}
	4600Å	5100Å	5900Å	A	B	TNB		
12 x 10^{-5}	0·565	0·26	0·20	0·54	-	0·46	1·5	-
16 x 10^{-5}	0·70	0·321	0·248	0·67	-	0·33	1·7	-
20 x 10^{-5}	0·816	0·37	0·283	0·765	-	0·235	2·0	-
24 x 10^{-5}	0·88	0·403	0·304	0·82	-	0·18	2·2	-
28 x 10^{-5}	0·89	0·416	0·305	0·825	0·02	0·155	2·2	-
32 x 10^{-5}	0·928	0·433	0·315	0·85	0·03	0·12	2·5	-
52 x 10^{-5}	0·967	0·492	0·328	0·89	0·07	0·04	-	157
80 x 10^{-5}	0·956	0·545	0·31	0·84	0·15	0·01	-	230
0·0014	0·90	0·62	0·263	0·70	0·29	0	-	300
0·002	0·859	0·675	0·229	0·61	0·39	-	-	328
0·003	0·79	0·754	0·182	0·48	0·53	-	-	370
0·004	0·74	0·82	0·144	0·36	0·64	-	-	445
0·006	0·685	0·868	0·105	0·26	0·76	-	-	490
0·008	0·652	0·89	0·082	0·19	0·81	-	-	530
0·012	0·615	0·92	0·057	-	-	-	-	-
0·016	0·59	0·926	0·046	-	-	-	-	-
0·020	0·579	0·934	0·037	-	-	-	-	-
0·03	0·55	0·92	0·025	-	-	-	-	-

TABLE 8

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in 40/60 (v/v) ethanol-water

[EtS$^-$]	Optical Density			Relative Concentration			10^{-3} K_1	$10^{-2}K_2$
stoich	4600Å	5000Å	5900Å	A	B	TNB	M^{-1}	M^{-1}
12 x 10^{-5}	0·435	0·22	0·145	0·40	0·02	0·58	7	
16 x 10^{-5}	0·584	0·29	0·192	0·52	0·02	0·46	9	
20 x 10^{-5}	0·65	0·352	0·222	0·60	0·05	0·35	9	
24 x 10^{-5}	0·70	0·39	0·237	0·64	0·07	0·29	10	5·2
32 x 10^{-5}	0·77	0·464	0·26	0·70	0·12	0·18	13	5·7
40 x 10^{-5}	0·79	0·52	0·255	0·69	0·18	0·13	15	7
50 x 10^{-5}	0·813	0·561	0·26	0·70	0·22	0·08	19	6·3
64 x 10^{-5}	0·785	0·615	0·23	0·62	0·32	0·06	17	8
80 x 10^{-5}	0·76	0·652	0·205	0·54	0·41	0·05	14	10
0·001	0·75	0·682	0·19	0·50	0·47	0·03	-	9·4
0·002	0·672	0·782	0·122	0·32	0·68	0	-	10·5
0·003	0·62	0·81	0·076	0·19	0·80	-	-	14
0·005	0·60	0·86	0·051	0·12	0·89	-	-	15
0·010	0·555	0·86	0·035	-	-	-	-	-
0·015	0·545	0·85	0·018	-	-	-	-	-
0·020	0·53	0·834	0·014	-	-	-	-	-

TABLE 9

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in 30/70 (v/v) ethanol-water

$[EtS^-]$ stoich	Optical Density			Relative Concentration			$10^{-3}K_1$ M^{-1}	$10^{-3}K_2$ M^{-1}
	4600Å	5000Å	5900Å	A	B	TNB		
12 x 10^{-5}	0·14	0·080	0·047	0·13	0·02	0·85	1·6	
16 x 10^{-5}	0·218	0·136	0·072	0·20	0·04	0·76	1·8	1·5
24 x 10^{-5}	0·359	0·254	0·115	0·32	0·12	0·56	2·6	1·8
32 x 10^{-5}	0·45	0·35	0·132	0·37	0·20	0·43	3·0	1·9
40 x 10^{-5}	0·51	0·422	0·135	0·37	0·28	0·35	2·9	2·1
50 x 10^{-5}	0·56	0·51	0·135	0·37	0·37	0·26	3·1	2·2
64 x 10^{-5}	0·60	0·605	0·124	0·34	0·49	0·17	3·3	2·4
80 x 10^{-5}	0·61	0·655	0·110	0·30	0·57	0·13	3·0	2·5
0·001	0·62	0·70	0·10	0·27	0·63	0·10	2·8	2·6
0·0015	0·61	0·76	0·072	0·20	0·75	0·05	2·8	3·2
0·002	0·59	0·785	0·052	0·12	0·83	0·05	-	-
0·004	0·56	0·81	0·025	0·07	0·93	-	-	-
0·006	0·55	0·817	0·018	-	-	-	-	-
0·008	0·53	0·80	0·014	-	-	-	-	-
0·01	0·52	0·78	0·010	-	-	-	-	-

TABLE 10

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in 20/80 (v/v) ethanol-water

[EtS$^-$] stoich	Optical Density			Relative Concentration			10^{-3} K_1 M^{-1}	$10^{-3}K_2$ M^{-1}
	4600Å	5000Å	5900Å	A	B	TNB		
20 x 10^{-5}	0·14	0·12	0·035	0·10	0·09	0·81	7·0	5
24 x 10^{-5}	0·176	0·16	0·0405	0·11	0·12	0·77	6·5	5·4
32 x 10^{-5}	0·258	0·256	0·049	0·14	0·24	0·62	7·5	5·7
40 x 10^{-5}	0·318	0·336	0·055	0·15	0·32	0·53	7·5	5·8
50 x 10^{-5}	0·39	0·438	0·056	0·16	0·45	0·39	8	6·1
60 x 10^{-5}	0·438	0·51	0·054	0·14	0·55	0·31	8	7·0
70 x 10^{-5}	0·472	0·559	0·0515	0·13	0·61	0·26	7·5	6·5
80 x 10^{-5}	0·49	0·60	0·0475	0·12	0·68	0·20	8	7·1
0·001	0·52	0·65	0·0425	0·11	0·76	0·13	8·4	-
0·0015	0·54	0·708	0·031	0·06	0·88	0·06	7·0	-
0·002	0·545	0·728	0·022	0·04	0·39	-	-	-
0·003	0·538	0·732	0·016	0·02	-	-	-	-
0·004	0·53	0·73	0·012	0·02	-	-	-	-
0·006	0·51	0·71	0·008	0	-	-	-	-

TABLE 11

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium thioethoxide in 10/90 (v/v) ethanol-water

$[\mathrm{EtS}^-]$ stoich	Optical Density			Relative Concentration			$10^{-2}K_1$ M^{-1}	$10^{-6}\ K_2'$ * M^{-2}
	4600Å	5000Å	5900Å	A	B	TNB		
40×10^{-5}	0·215	0·225	0·029	0·08	0·22	0·70	3·0	2·2
50×10^{-5}	0·282	0·31	0·0325	0·10	0·34	0·56	3·7	2·5
60×10^{-5}	0·34	0·38	0·033	0·10	0·42	0·48	3·6	2·8
70×10^{-5}	0·376	0·43	0·034	0·10	0·48	0·42	3·6	2·5
80×10^{-5}	0·404	0·47	0·031	0·09	0·54	0·37	3·2	2·5
90×10^{-5}	0·44	0·515	0·0305	0·09	0·60	0·31	3·5	2·5
0·001	0·463	0·55	0·030	0·09	0·67	0·24	3·7	2·8
0·0015	0·515	0·625	0·0235	0·07	0·75	0·18	2·6	-
0·002	0·522	0·648	0·018	0·03	0·80	-	-	-
0·003	0·514	0·642	0·014	0·02	0·79	-	-	-
0·004	0·50	0·62	0·011	-	0·75	-	-	-

* determined from

$$K'_2 = \frac{[\mathrm{B}]}{[\mathrm{TNB}][\mathrm{EtS}^-]^2}$$

taking $K_1 = (3\cdot5 \pm 1) \times 10^{-2}\ \mathrm{l.mol}^{-1}$

and $K_2' = K_1 \times K_2 = 2\cdot5 \times 10^6$

$\therefore\ K_2 = 7\cdot2 \times 10^3$

TABLE 12

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium thioethoxide in water

$[EtS^-]$ stoich	Optical Density			Relative Concentration			$10^{-2}K_1$	$10^{-6}K_2$ *
	4600Å	5000Å	5900Å	A	B	TNB	M^{-1}	M^{-2}
20×10^{-5}	0·045	0·04	0·008	0·024	0·04	0·93	1·5	1·4
40×10^{-5}	0·154	0·155	0·016	0·047	0·20	0·57	1·7	1·9
50×10^{-5}	0·206	0·215	0·019	0·056	0·29	0·65	1·8	2·0
60×10^{-5}	0·275	0·29	0·019	0·056	0·39	0·55	1·7	2·2
70×10^{-5}	0·314	0·338	0·019	0·056	0·46	0·48	1·7	2·2
80×10^{-5}	0·355	0·387	0·020	0·056	0·53	0·41	1·8	2·2
0·001	0·422	0·47	0·017	0·05	0·65	0·30	1·7	2·2
0·0015	0·478	0·54	0·014	0·04	0·77	0·19	-	-
0·002	0·49	0·56	0·010	0·02	-	-	-	-
0·0025	0·485	0·554	0·007	-	-	-	-	-
0·003	0·478	0·551	0·007	-	-	-	-	-
0·004	0·455	0·525	0·005	-	-	-	-	-

* See Table 11

the plot results from destruction of some base by traces of acidic impurities. The extinction coefficient of 1:2 adduct in pure ethanol was determined by Beer's law from the absorption at 5100Å where at sufficiently high base concentration all the nitro-compound was present as the higher adduct. Once the extinction coefficients are known, measurements of the optical density at 5000 and 5900Å allow the concentration of the two adducts and unchanged 135 TNB to be determined as follows:

In pure ethanol Benesi-Hildebrand plot at 5900Å gives

$$\epsilon_A(5900\text{Å}) = 8 \cdot 625 \times 10^3$$

Thus the concentration of complex A is given by

$$[A] = \frac{\text{O.D.}(5900\text{Å})}{0 \cdot 345} \times 4 \times 10^{-5}$$

From measurements of O.D. at 5000A and 5900A due to complex A

$$\frac{\text{O.D.}(5000\text{Å})}{\text{O.D.}(5900\text{Å})} = 1 \cdot 37$$

Thus the optical density at 5000Å due to 1:1 adduct is given by

$$\text{O.D.}(5000\text{Å}) = 1 \cdot 37 \times \text{O.D.}(5900\text{Å})$$

The concentration of the 1:2 adduct was determined from measurements at 5000Å after subtraction of the optical absorption due to the 1:1 adduct at this wavelength and is given by:

$$[B] = \frac{O.D.(5000\overset{o}{A}) - 1{\cdot}37 \times O.D.(5900\overset{o}{A})}{0{\cdot}96} \times 4 \times 10^{-5}$$

where 0•96 is the optical density due to complete conversion to 1:2 adduct.

Once the concentration of complex A and complex B were determined, the concentration of the unchanged 135 TNB was determined from the stoichiometric concentration by difference:

$$[TNB] = 4 \times 10^{-5} - [A] - [B]$$

The equilibrium constants K_1 and K_2 are given by

$$K_1 = \frac{[A]}{[TNB][EtS^-]}$$

$$K_2 = \frac{[B]}{[A][EtS^-]}$$

In other ethanol-rich systems the extinction coefficients for the 1:1 adducts were determined by means of Benesi-Hildebrand plots. However it was noticeable that as the concentration of the base was increased the optical densities at the absorption maximum of 1:2 adduct did not approach a constant value but passed through a maximum. This is very likely to be due to the formation of some 1:3 adduct which would be expected to have no visible absorption.[26] To determine the extinction coefficient of the 1:2 adduct the following method was used: when only 1:1 and 1:2 complexes are present then the decrease in absorption at 5900Å will correlate with the increase in absorption at 5000Å (or 5100Å) so that the optical density at 5000Å corresponding to zero absorption at 5900Å could be obtained.

As the medium was made more aqueous spectra indicated the presence of complex B in addition to complex A even at the lowest concentration of base used. Because of this it was not possible to determine directly the extinction coefficients of the lower adduct by use of Benesi-Hildebrand plots.[93] The extinction coefficients of 1:2 adduct could be determined in solution containing up to 70 vol.% water. However in more aqueous solutions it appears that formation of 1:3 adduct becomes more important so that the extinction coefficient of the 1:2 adduct could not be found with any accuracy.

As a result the extinction coefficient of the adducts in the more aqueous solutions were estimated as outlined below. The spectral data given in Table 1 indicate that in ethanol-rich solvents the visible spectrum of the 1:1 adduct varies little with solvent composition. The initial increase in the values of the extinction coefficient at 5900Å almost certainly results from the observed bathochromic shift which moves the shoulder to higher wavelength. In addition, the values of the extinction coefficient for the 1:2 adduct tend to decrease as the solvent is made more aqueous. It was assumed that this trend would continue throughout the solvent composition and that this effect would also be displayed by the 1:1 adduct. On this basis, it was possible to estimate values for the extinction coefficients ϵ_A and ϵ_B in the more aqueous solutions. Though these values are not expected to be very accurate, the error would not be expected to be greater than 20%. Having estimated the extinction coefficients, the relative concentrations of the species and the equilibrium constants were determined in similar way to that in pure ethanol or ethanol-rich solvent mixtures.

The results given in Tables 2 to 12 indicate that in each solvent composition the value of K_1 is independent of the ionic strength of the medium while the values of K_2 increase with increasing ionic strength. This behaviour no doubt reflects changes in the activity coefficients of the charged species in these solutions. Thus the constancy of K_1 indicates that the activity coefficient ratio f_{A^-}/f_{RS^-} must remain close to unity in all solvent compositions and this is not surprising in view of the single negative charge on the 1:1 adduct. Also the base concentrations used are very low. The constancy with increasing ionic strength of the values of K_1 in the more aqueous solutions provides a check on the estimated extinction coefficients. It was found that fairly small changes in the values of ϵ_A used resulted in large variations with ionic strength in the calculated values of K_1. This gives increased confidence to the estimated values of the extinction coefficients. However, the 1:2 adduct carries two negative charges so that the ratio $f_{B^=}/f_{A^-}f_{RS^-}$ would not be expected to remain constant with increasing ionic strength. This behaviour is similar to that observed for the reaction of 135 TNB with two molecules of sodium sulphite in water[56] and tw o molecules of thioethoxide in methanol.[104] The values of K_2 at zero ionic strength were determined for each solvent mixture from Debye-Huckel extrapolation. These values are given in Table 1.

A brief comment on the accuracies of the equilibrium constants in Table 1 is necessary. In highly aqueous media the maximum concentration of 1:1 adduct is only about 10% of the stoichiometric 135 TNB concentration. This together with the uncertainties of the extinction coefficients in these solutions means that the equilibrium constants are accurate probably only to ± 25%. In some ethanol water mixtures the equilibrium constants for formation of 1:1 adduct are large (*ca.* 5×10^4 $1.mol^{-1}$). Because of this it was necessary to use a very low concentration of thioethoxide ion in order to determine the values of K_1 and there is danger that traces of acidic impurities, such as carbon dioxide, will neutralise some of the base. It is possible that the values of K_1 may slightly underestimate the true value of K_1 in the ethanol-rich solvent range.

ii) Interaction of 1,3,5-Trinitrobenzene and Sodium Thiophenoxide in Ethanol-Water Mixtures

As in the case of the thioethoxide, addition of sodium thiophenoxide to solutions of 135 TNB in ethanol caused the appearance of a red-violet colour. The spectrum shown in Figure 4 indicates a maximum at 4640Å with a broad shoulder at 5600Å. This spectrum is similar to that of the 1:1 adduct formed from 135 TNB and thioethoxide in ethanol. Increasing the

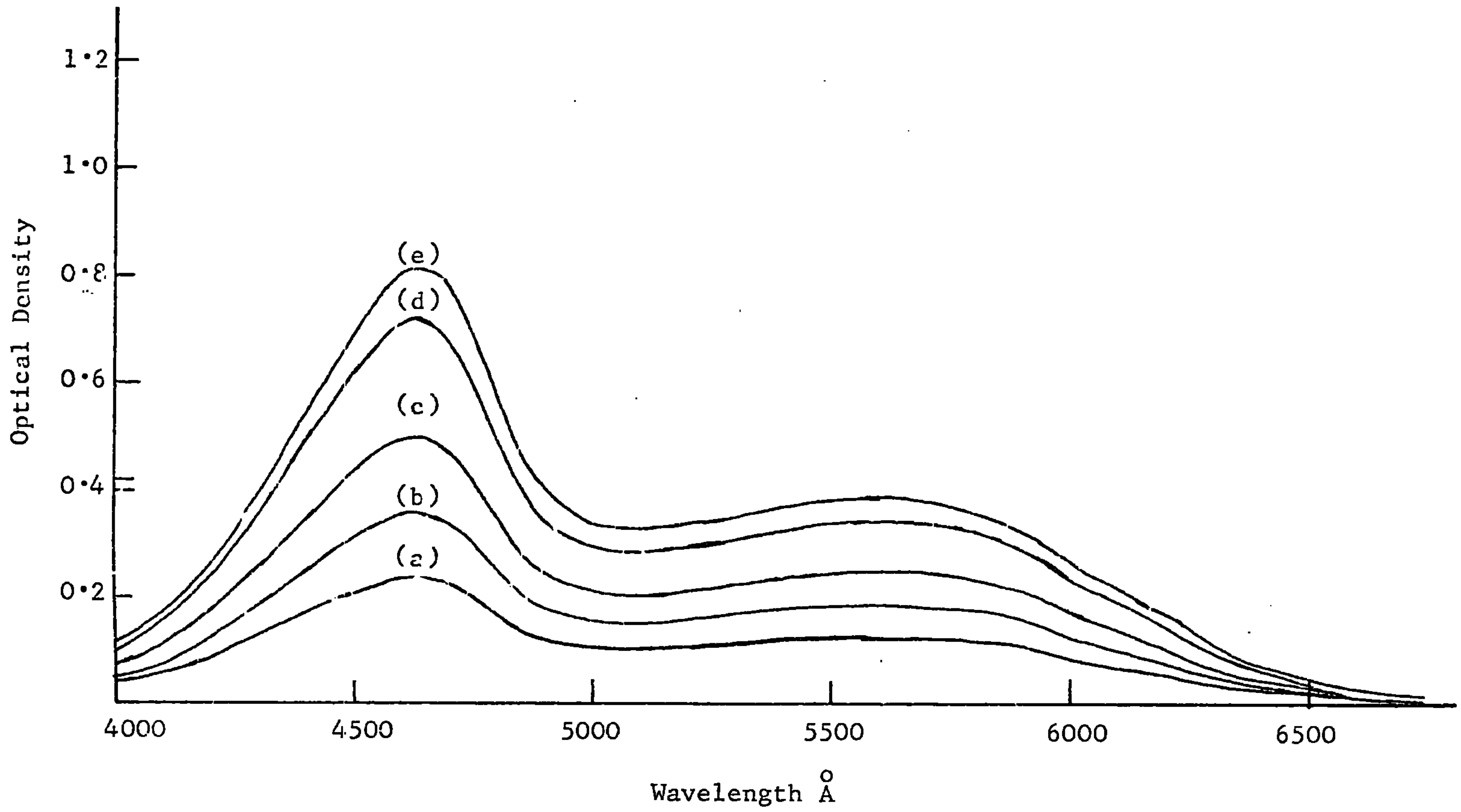


Fig.4. Visible spectra of 1,3,5-trinitrobenzene in ethanol containing (a) 0·01M, (b) 0·02M, (c) 0·04M, (d) 0·15M, (e) 0·5M sodium thiophenoxide.

concentration of thiophenoxide ion up to 0•15M caused an increase in the visible absorption without change in the spectral shape. This was taken as evidence for the presence of a single species which will have structure (I) (R = Ph). At base concentrations above 0•15M some increase in absorption near 5000Å was observed probably due to the formation of higher complex.

As water was progressively added, no change in the general shape due to the 1:1 adduct was observed though a small bathochromic shift towards longer wavelength occurred. Formation of 1:2 adduct became more noticeable as the proportion of water in the solvent system was increased. This trend is similar to that observed for 135 TNB and thioethoxide in ethanol. However, due to the insolubility of thiophenol in water, the study was limited to solutions containing 50% or more ethanol. Thus no quantitative measurements were made in water-rich media..

The equilibrium constants for the formation of the 1:1 adduct in various solvent compositions were determined by measurements of the optical density at 4640Å and 5600Å. Benesi-Hildebrand plots[93] gave the extinction coefficients and two such plots are given in Figure 5. Once the extinction coefficients were determined, the equilibrium constants were calculated in similar manner to that used for 135 TNB and thioethoxide in ethanol. Measurements of the optical density and the calculated equilibrium constants in various solvent mixtures are given in Tables 13 to 18. The values of K_1 obtained by these calculations are in a good

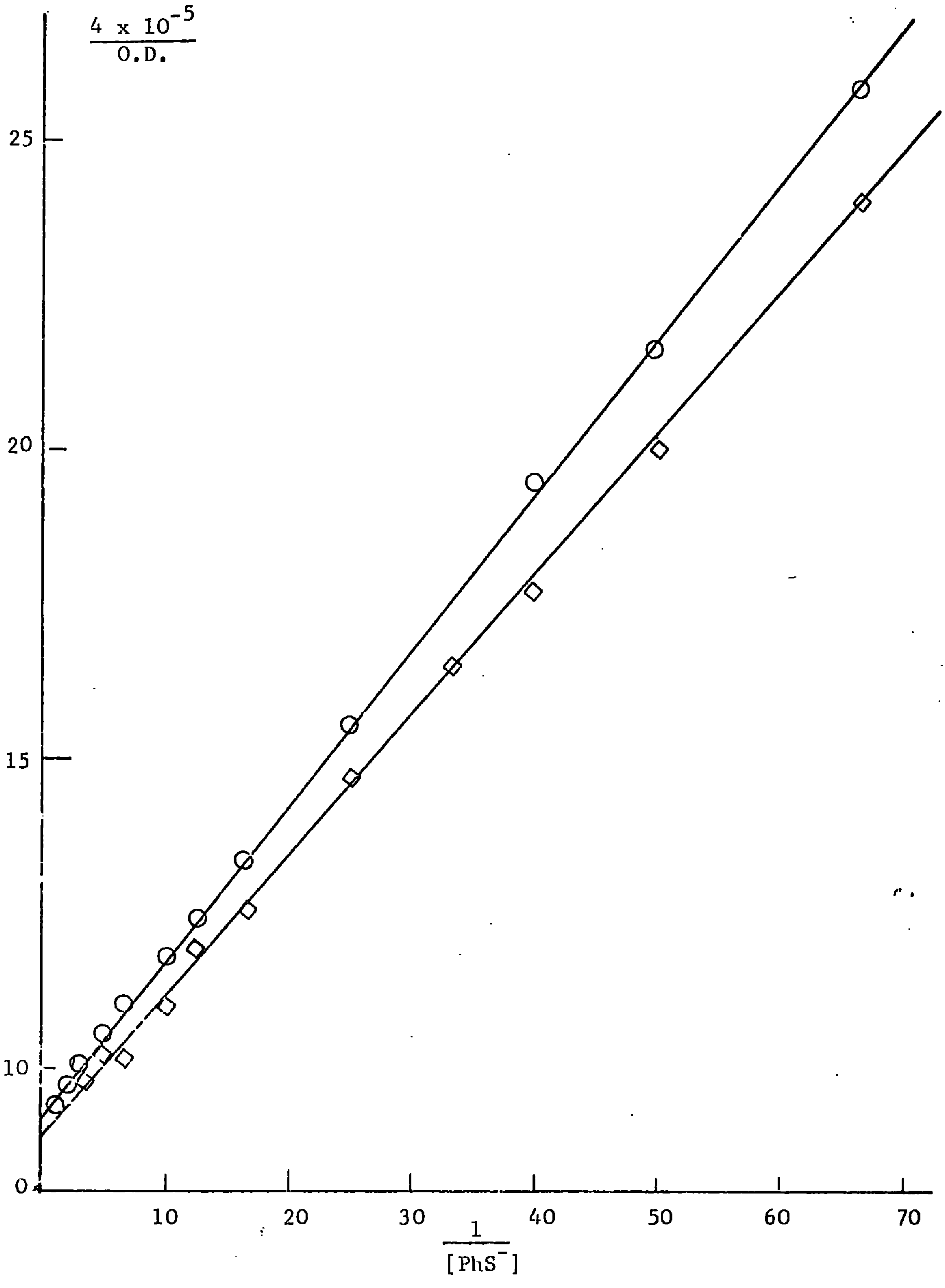


Fig.5. Benesi-Hildebrand plot for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium thiophenoxide in ethanol, measured at 5600Å.

TABLE 13

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thiophenoxide in ethanol

$[PhS^-]$ stoich. M	Optical Density			K $l.mol^{-1}$ 4640Å
	4640Å	5000Å	5600Å	
0•01	0•243	0•10	0•116	35•4
0•015	0•326	0•135	0•115	36•0
0•02	0•385	0•16	0•185	35•3
0•025	0•435	0•18	0•205	35•1
0•04	0•534	0•222	0•257	34•0
0•06	0•638	0•268	0•304	36•0
0•08	0•675	0•286	0•322	33•0
0•10	0•715	0•30	0•338	34•7
0•15	0•78	0•328	0•363	35•4
0•20	0•815	0•344	0•38	41•0
0•3	0•86	0•365	0•40	44•0
0•4	0•88	0•378	0•414	35•0
0•5	0•88	0•379	0•414	-
0•6	0•90	0•395	0•428	50

TABLE 14

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thioethoxide in 90/10 (v/v) ethanol-water

$[PhS^-]$ stoich. M	Optical Density			K l.mol^{-1} 4640Å
	4640Å	5000Å	5600Å	
0·01	0·32	0·136	0·155	55·6
0·015	0·40	0·174	0·195	53·86
0·020	0·46	0·198	0·222	52·87
0·025	0·507	0·217	0·244	52·26
0·03	0·56	0·236	0·266	55·72
0·04	0·615	0·26	0·29	54·9
0·06	0·68	0·292	0·326	52·7
0·08	0·72	0·312	0·345	51·43
0·1	0·753	0·325	0·36	53·03
0·15	0·79	0·34	0·375	50·16
0·2	0·83	0·36	0·391	57
0·3	0·84	0·37	0·398	50·9
0·4	0·86	0·384	0·40	61·4
0·5	0·87	0·392	0·402	-

TABLE 15

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thiophenoxide in 80/20 (v/v) ethanol-water

$[PhS^-]$ stoich. M	Optical Density			K $l.mol^{-1}$ 4640Å
	4640Å	5000Å	5600Å	
0•01	0•338	0•152	0•168	61•2
0•015	0•428	0•189	0•208	61•76
0•020	0•49	0•222	0•242	61•25
0•025	0•538	0•248	0•26	61•13
0•03	0•57	0•25	0•275	59•37
0•04	0•635	0•279	0•304	62•25
0•06	0•70	0•312	0•334	61•40
0•08	0•74	0•33	0•356	61•66
0•1	0•765	0•345	0•37	61•20
0•15	0•802	0•357	0•387	60•76
0•20	0•823	0•368	0•383	61•42
0•3	0•84	0•375	0•383	56•0
0•4	0•85	0•39	0•39	53•0

TABLE 16

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thiophenoxide in 70/30 (v/v) ethanol-water

[PhS$^-$] stoich. M	Optical Density			K $l.mol^{-1}$
	4640Å	5000Å	5600Å	4640Å
0•0055	0•23	0•11	0•115	60•6
0•011	0•35	0•163	0•176	55•82
0•0165	0•44	0•21	0•22	55•55
0•022	0•51	0•24	0•255	56•54
0•0275	0•55	0•26	0•276	54•05
0•033	0•595	0•275	0•295	55•47
0•044	0•65	0•302	0•323	54•71
0•066	0•722	0•34	0•358	55•25
0•088	0•76	0•36	0•38	53•98
0•110	0•79	0•37	0•385	55•24
0•165	0•83	0•385	0•408	55•89
0•22	0•85	0•40	0•418	55•2
0•33	0•87	0•42	0•425	52•73
0•44	0•88	0•426	0•424	50•00
0•77	-	-	-	-

TABLE 17

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thiophenoxide in 60/40 (v/v) ethanol-water

$[PhS^-]$ stoich. M	Optical Density			K $l.mol^{-1}$
	4640Å	5000Å	5600Å	4640Å
0·0055	0·20	0·10	0·103	51·2
0·011	0·32	0·16	0·165	49·3
0·165	0·41	0·205	0·21	49·7
0·022	0·48	0·24	0·245	50·7
0·0275	0·515	0·253	0·26	47·4
0·033	0·565	0·275	0·285	49·6
0·044	0·635	0·32	0·325	52·47
0·066	0·70	0·341	0·35	50·5
0·088	0·74	0·361	0·368	49·43
0·11	0·768	0·373	0·377	49·14
0·165	0·80	0·395	0·395	44·06
0·22	0·83	0·415	0·41	47·1

TABLE 18

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium thiophenoxide in 50/60 (v/v) ethanol-water

$[PhS^-]$ stoich. M	Optical Density			K $l.mol^{-1}$
	4640Å	5000Å	5600Å	4640Å
0•005	0•154	0•081	0•081	42•4
0•01	0•253	0•16	0•16	40•35
0•015	0•332	0•166	0•166	40•4
0•020	0•395	0•202	0•20	40•7
0•025	0•444	0•227	0•225	40•7
0•03	0•485	0•249	0•242	40•9
0•04	0•545	0•278	0•272	40•7
0•06	0•628	0•32	0•314	41•5
0•08	0•68	0•344	0•335	42•5
0•10	0•714	0•365	0•365	43•0
0•15	0•76	0•395	0•39	42•2
0•20	0•778	0•41	0•39	38•14
0•30	0•808	0•44	0•38	37•4

TABLE 19

Equilibrium constants and spectral data for the adduct from 1,3,5-trinitrobenzene and sodium thioethoxide in Ethanol-Water mixtures

Solvent % EtOH by vol.	K^* $l.mol^{-1}$	λ_{max}	$\epsilon(4640\text{Å})$	$\epsilon(5600\text{Å})$
100	36	4620	2•337	1•085
90	57	4640	2•2	1•05
80	61•5	4650	2•3	1•06
70	57•8	4660	2•27	1•12
60	50	4660	2•2	1•15
50	43•6	4660	2•19	1•08

* determined from Benesi-Hildebrand plots for the measured optical density at 5600Å.

agreement with those obtained from Benesi-Hildebrand plots and are independent of the wavelength. Spectral data for complex formation are collected in Table 19. The results in Tables 13 to 18 indicate that the values of K_1 are independent of the base concentration. This can be understood on similar argument for the invariance of K_1 in the case of 135 TNB and thioethoxide in ethanol.

iii) Interaction of 1,3,5-Trinitrobenzene and Sodium p-aminothiophenoxide in Methanol-Water Mixture

The interaction of 135 TNB and sodium p-aminothiophenoxide in methanol or methanol-water mixtures was studied ina similar way to that used for 135 TNB and thioethoxide or thiophenoxide in ethanol. The methanol was used in this case because it was thought that the p-aminothiophenoxide would be very reactive in ethanol and this would cause some uncertainty in the values of K_1 similar to that met in the case of thioethoxide in ethanol. This reaction is also limited to solvent mixtures containing 40% methanol or more due to the insolubility of p-aminothiophenol in more aqueous solvent mixtures.

However, in general the visible spectra of the coloured species formed on addition of sodium p-aminothiophenoxide to solutions of 135 TNB in methanol or methanol-water mixtures are similar to those previously shown for 135 TNB and thiophenoxide in ethanol or ethanol-water mixtures. The maximum was found at 4700Å which is slightly shifted toward longer wavelength. A bathochromic shift in the position of the maximum was observed as the solvent was changed from pure methanol to methanol-water mixtures. Formation of 1:2 adduct at high concentration of base was indicated by the increase in the absorption at 5100Å. This absorption becomes more notable in the more aqueous solutions.

The equilibrium constants for the formation of 1:1 adduct in various solvent compositions were determined in the same way as for 135 TNB and thiophenoxide in ethanol, by measurements of the optical density at 4700 and 5600Å. Such measurements and the calculated values of K_1 are given in Tables 20 to 26. These values of K_1 obtained in this way are consistent with the values obtained from Benesi-Hildebrand plots. Such values and other spectral data are given in Table 27.

iv) Interaction of 1,3,5-Trinitrobenzene and Lithium p-Aminothiophenoxide in Methanol-Water Mixtures

In order to study the possible effects of ion pairs formation which will be discussed later, the reaction of 135 TNB with lithium p-aminothiophenoxide in methanol and in methanol-water mixtures was studied. The general picture of the visible spectra is similar to that for 135 TNB and sodium p-aminothiophenoxide in methanol, though the maximum at 4760Å is shifted at longer wavelength. Here again the study was limited to solvent media containing 40% methanol or more. Measurements of the optical density were made at 4800Å and 5700Å and the values of K_1 calculated in a similar way to that for 135 TNB and thiophenoxide in ethanol. These measurements and the calculated equilibrium constant K_1 are given in Tables 28 to 34. In Table 35 are collected the spectral data for complex formation.

TABLE 20

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium p-aminothiophenoxide in 100% Methanol

[p-NH_2PhS$^-$] stoich M	Optical Density			$10^{-2}K_1$ l.mol^{-1}
	4700Å	5200Å	5600Å	4700Å
0•01	0•453	0•205	0•218	1•15
0•015	0•530	0•238	0•25	1•12
0•02	0•590	0•267	0•278	1•15
0•025	0•62	0•276	0•292	1•10
0•03	0•65	0•288	0•303	1•11
0•04	0•685	0•30	0•315	1•06
0•05	0•72	0•315	0•329	1•14
0•06	0•733	0•32	0•334	1•08
0•08	0•765	0•34	0•352	1•27
0•1	0•79	0•35	0•365	1•41
0•2	0•82	0•37	0•385	1•57

TABLE 21

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium p-aminothiophenoxide in 90/10 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich M	Optical Density			10^{-2} K_1 $l.mol^{-1}$ 4700Å
	4700Å	5200Å	5600Å	
0·005	0·352	0·165	0·173	1·41
0·0075	0·44	0·204	0·213	1·43
0·01	0·498	0·23	0·24	1·41
0·015	0·572	0·265	0·277	1·37
0·02	0·625	0·29	0·302	1·39
0·025	0·658	0·30	0·311	1·37
0·03	0·69	0·322	0·333	1·44
0·04	0·728	0·33	0·347	1·49
0·05	0·745	0·345	0·358	1·42
0·06	0·76	0·353	0·363	1·41
0·08	0·78	0·362	0·37	1·39
0·1	0·795	0·371	0·382	1·44
0·2	0·80	0·387	0·392	-

TABLE 22

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium p-aminothiophenoxide in 80/20 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich M	Optical Density			10^{-2} K_1 l.mol^{-1} 4700Å
	4700Å	5200Å	5600Å	
0·005	0·37	0·18	0·185	1·48
0·0075	0·458	0·22	0·227	1·48
0·01	0·52	0·251	0·258	1·485
0·015	0·60	0·287	0·293	1·48
0·02	0·65	0·312	0·318	1·48
0·025	0·684	0·328	0·333	1·47
0·03	0·712	0·338	0·345	1·50
0·04	0·74	0·355	0·36	1·42
0·05	0·76	0·365	0·368	1·38
0·06	0·78	0·368	0·37	1·44
0·08	0·785	0·386	0·389	1·15
0·1	0·79	0·39	0·39	-
0·2	0·79	0·417	0·398	-

TABLE 23

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium p-aminothiophenoxide in 70/30 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich M	Optical Density			10^2K_1 l.mol^{-1} 4700Å
	4700Å	5200Å	5600Å	
0•005	0•35	0•175	0•177	1•37
0•0075	0•432	0•217	0•218	1•35
0•010	0•494	0•245	0•245	1•35
0•015	0•571	0•286	0•286	1•32
0•020	0•63	0•315	0•315	1•37
0•025	0•665	0•332	0•329	1•36
0•03	0•69	0•345	0•343	1•35
0•04	0•725	0•368	0•363	1•34
0•05	0•74	0•378	0•37	1•23
0•06	0•75	0•39	0•381	1•14
0•08	0•755	0•399	0•39	-
0•1	0•762	0•415	0•399	-
0•2	0•72	0•45	0•41	-

TABLE 24

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium p-aminothiophenoxide in 60/40 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich M	Optical Density			10^{-2} K_1 l.mol^{-1} 4700Å
	4700Å	5200Å	5600Å	
0•005	0•312	0•162	0•16	1•25
0•0075	0•39	0•203	0•20	1•24
0•01	0•448	0•232	0•228	1•24
0•015	0•533	0•28	0•273	1•28
0•020	0•58	0•309	0•301	1•26
0•025	0•61	0•327	0•316	1•22
0•03	0•642	0•349	0•337	1•27
0•04	0•665	0•366	0•35	1•15 x
0•05	0•68	0•382	0•365	1•05 x
0•06	0•69	0•40	0•38	1•0 x
0•08	0•69	0•425	0•392	-
0•1	0•68	0•438	0•404	-

x The drift in these values may be due to the formation of 1:2 adduct.

TABLE 25

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4×10^{-5}M) and sodium p-aminothiophenoxide in 50/50 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich M	Optical Density			K $l.mol^{-1}$ 4700Å
	4700Å	5200Å	5600Å	
0•005	0•232	0•125	0•121	87•6
0•0075	0•305	0•167	0•160	89•0
0•01	0•358	0•20	0•19	88•67
0•015	0•437	0•248	0•235	89•7
0•02	0•491	0•287	0•27	90•68
0•025	0•52	0•31	0•292	86•06
0•03	0•55	0•38	0•317	86•6
0•04	0•579	0•368	0•341	79•25
0•05	0•60	0•40	0•365	74•28
0•06	0•60	0•418	0•38	-

TABLE 26

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and sodium p-aminothiophenoxide in 40/60 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich M	Optical Density			K l.mol^{-1} 4700Å
	4700Å	5200Å	5600Å	
0•005	0•151	0•09	0•084	55•00
0•0075	0•202	0•124	0•114	54•00
0•01	0•253	0•158	0•145	56•59
0•015	0•32	0•21	0•194	56•12
0•02	0•37	0•255	0•232	56•00
0•025	0•408	0•298	0•267	55•87
0•03	0•425	0•327	0•292	51•51
0•04	0•46	0•372	0•335	47•9
0•06	0•48	0•438	0•385	36•36

TABLE 27

Equilibrium constants and spectral data for the adduct from 1,3,5-trinitrobenzene and sodium p-aminothiophenoxide in Methanol-Water mixtures

Solvent % MeOH by vol	K * $l.mol^{-1}$	λ_{max}	$\epsilon(5600\mathring{A})$	$\epsilon(4700\mathring{A})$
100	121	4696	$9{\cdot}7 \times 10^3$	2•11
90	150	4700	1×10^4	2·12
80	156	4720	$1{\cdot}04 \times 10^4$	2•17
70	143	4720	$1{\cdot}05 \times 10^4$	2•15
60	123	4730	$1{\cdot}05 \times 10^4$	2•02
50	81•9	4740	$1{\cdot}04 \times 10^4$	1•9
40	39	4740	$1{\cdot}24 \times 10^4$	1•74

* Determined from Benesi-Hildebrand plots of the measured optical density at 4700Å.

TABLE 28

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and lithium p-aminothiophenoxide in 100% methanol

$[p\text{-}NH_2PhS^-]$ stoich. M	Optical Density		$10^{-2}K$ $l.mol^{-1}$
	4800A	5700A	4800A
0•005	0•30	0•147	1•11
0•0075	0•375	0•186	1•075
0•01	0•43	0•211	1•04
0•015	0•52	0•253	1•08
0•02	0•572	0•28	1•067
0•03	0•645	0•315	1•10
0•05	0•705	0•342	1•04
0•08	0•75	0•365	1•04

TABLE 29

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and lithium p-aminothiophenoxide in 90/10 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich M	Optical Density		$10^{-2}K$ $l.mol^{-1}$ 4800Å
	4800Å	5700Å	
0•005	0•343	0•170	1•30
0•0075	0•422	0•208	1•28
0•01	0•485	0•238	1•29
0•015	0•57	0•28	1•31
0•02	0•62	0•302	1•29
0•03	0•689	0•335	1•34
0•05	0•742	0•36	1•26
0•08	0•78	0•38	1•22

TABLE 30

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and lithium p-aminothiophenoxide in 80/20 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich. M	Optical Density		$10^{-2}K$ $l.mol^{-1}$
	4800Å	5700Å	4800Å
0•005	0•366	0•182	1•39
0•0075	0•45	0•22	1•36
0•01	0•51	0•25	1•34
0•015	0•60	0•293	1•38
0•02	0•655	0•32	1•39
0•03	0•713	0•342	1•34
0•05	0•77	0•375	1•28
0•08	0•80	0•388	1•25

TABLE 31

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and lithium p-aminothiophenoxide in 70/30 (v/v) methanol-water

[p-NH_2PhS$^-$] stoich. M	Optical Density		10^{-2}K l.mol^{-1}
	4800Å	5700Å	4800Å
0•005	0•365	0•18	1•39
0•0075	0•451	0•222	1•37
0•01	0•51	0•25	1•34
0•015	0•60	0•292	1•38
0•02	0•648	0•313	1•34
0•03	0•71	0•347	1•34
0•06	0•77	0•378	1•28

TABLE 32

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and lithium p-aminothiophenoxide in 50/50 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich. M	Optical Density		$10^{-2}K$ $l.mol^{-1}$ 4800Å
	4800Å	5700Å	
0•005	0•318	0•156	1•24
0•0075	0•397	0•195	1•22
0•01	0•463	0•228	1•26
0•015	0•54	0•265	1•24
0•02	0•59	0•28	1•23
0•03	0•668	0•330	1•37
0•06	0•72	0•36	1•09

TABLE 33

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and lithium p-aminothiophenoxide in 50/50 (v/v) methanol-water

$[p\text{-}NH_2PhS^-]$ stoich. M	Optical Density		10^{-2}K $l.mol^{-1}$ 4800Å
	4800Å	5700Å	
0•005	0•24	0•12	94
0•0075	0•31	0•152	94
0•01	0•368	0•182	96
0•015	0•44	0•215	94•6
0•02	0•50	0•25	100
0•03	0•57	0•290	105
0•06	0•63	0•335	87•5

TABLE 34

Measured optical densities and calculated equilibrium constants for 1,3,5-trinitrobenzene (4 x 10^{-5}M) and lithium p-aminothiophenoxide in 40/60 (v/v) methanol-water

[p-NH_2PhS$^-$] stoich. M	Optical Density		K l.mol.$^{-1}$ 4800Å
	4800Å	5700Å	
0•005	0•149	0•074	45•7
0•0075	0•208	0•104	46•8
0•01	0•258	0•128	47•6
0•015	0•33	0•17	46•8
0•02	0•38	0•20	45•2
0•03	0•45	0•245	42•5

TABLE 35

Equilibrium constants and spectral data for the adduct from 1,3,5-trinitrobenzene and lithium p-aminothiophenoxide in Methanol-Water mixtures

solvent % MeOH by vol.	K* l.mol^{-1}	λ_{max}	ϵ(4800Å)	ϵ(5700Å)
100	114	4750	$2\cdot105 \times 10^4$	1×10^4
90	138	4770	$2\cdot15 \times 10^4$	$1\cdot03 \times 10^4$
80	148	4780	$2\cdot22 \times 10^4$	$1\cdot06 \times 10^4$
70	148	4780	$2\cdot22 \times 10^4$	$1\cdot04 \times 10^4$
60	126	4790	$2\cdot08 \times 10^4$	$1\cdot01 \times 10^4$
50	98•4	4800	$1\cdot886 \times 10^4$	$9\cdot09 \times 10^3$
40	40•3	4800	$2\cdot00 \times 10^4$	$1\cdot13 \times 10^4$

* Determined from Benesi-Hildebrand plots of the measured optical density at 5700Å.

DISCUSSION

The results presented in this section give useful information about solvent effects on the stability of Meisenheimer complexes in alcohol-water mixtures. Thus in each case, in both ethanol-water or methanol-water solvent systems, it was found that the value of the equilibrium constant K_1 for the formation of 1:1 adduct passes through maximum at about 80% by volume alcohol and then falls sharply as the solvent is made more aqueous. It is worth mentioning, though in a slightly different context, that for aromatic nucleophilic substitution and for a number of other reactions, England et al[133-135] observed an increase in the reaction rates as the solvent was changed from alcohol to water. They attributed this behaviour to the successive dissociation of ion pairs (M^+, OR^-) as the solvent was made more aqueous and hence more polar. This attribution can be understood if the free ions are more effective than ion pairs in causing the reaction. However, although Terrier[136] has recently found evidence for ion pairs in solutions containing a high concentration of metal alkoxides, he apparently found a little association in solutions containing low (10^{-3}M) concentrations of base.

In the systems studied in the present work, it was found that the thiolate ion concentration required for the formation of the 1:1 adduct is very low; for example the concentration of thioethoxide is less than 10^{-3}M. In addition it is expected that sulphur bases will be less associated than oxygen bases. Therefore the initial increase in the values of K_1 cannot be explained in terms of ion pairs since it is unlikely that a significant quantity of ion pairs will be present in the studied systems. This conclusion is supported by almost identical values for the equilibrium constants obtained for sodium and lithium salts of p-aminothiophenol. If ion pair formation were important smaller values for K_1 would be expected for the lithium salt. It seems more likely that the initial increase in the values of K_1 can be attributed to some change in the solvating ability of the medium as the solvent composition is changed. Murto and Tommila[137] have used a similar argument to account for the rate maximum observed in the nucleophilic displacement reaction of 2,4,-dinitrophenetole with hydroxide ion in ethanol-water mixtures. Furthermore Long et al[138] who measured the ability of mixed aqueous solvents to abstract a proton from t-butylmalonnitrile found that the basicity of the medium went through maximum as the solvent composition was changed. In fact a number of thermodynamic and other properties of mixed water-non-aqueous solvent systems are known[139,140] to go through maxima so that perhaps the maxima observed for the values of K_1 are not surprising.

However, the results indicate that the values of K_1 for the formation of the 1:1 adduct fall sharply in more aqueous media. This trend can be understood in terms of the Hughes-Ingold[141] theory of solvation. The thioethoxide ion which carries a fairly localised negative charge should better solvated by the more polar solvent water than by alcohol. 135 TNB and the 1:1 adduct, where the negative charge is delocalised about the ring and the nitro-groups, are large polarisable species and will be better solvated by alcohols than by through London dispersion forces. The equilibrium constants in water and ethanol can be related via the solvent activity coefficients for transfer of the species involved.

$$K_1 \text{ (water)} = K_1 \text{ (ethanol)} \frac{{}^{W}\gamma^{E}_{TNB.RS^-}}{{}^{W}\gamma^{E}_{TNB} \quad {}^{W}\gamma^{E}_{RS^-}}$$

It is interesting to compare the equilibrium constants for formation of the 1:1 adducts between EtS^- and OH^- in water, EtS^- and OMe^- in methanol and EtS^- and OEt^- in ethanol. These values are in Table 36. The equilibrium constants, K_1, measure the affinity of the bases for an aromatic carbon atom and thus give an indication of the carbon basicities[126] of the bases. However the results in Table 36 are not directly comparable since they refer to three different solvents. If the very large assumption is made that

$$\frac{{}^{W}\gamma^{E}_{TNB.RS^-}}{{}^{W}\gamma^{E}_{TNB.OEt^-}} \times \frac{{}^{W}\gamma^{E}_{OEt^-}}{{}^{W}\gamma^{E}_{RS^-}}$$

has the value of unity then the carbon basicities of all four bases can be

TABLE 36

Equilibrium constants for formation of 1:1 adducts from 1,3,5-trinitrobenzene and bases

	Water	Methanol	Ethanol
K_1 (EtS$^-$) M^{-1}	$1{\cdot}7 \times 10^2$	$3{\cdot}5 \times 10^3$ (a)	$2{\cdot}5 \times 10^4$
K_1 (lyate ion) M^{-1}	$3{\cdot}73$ (OH$^-$)$^{(b)}$	$23{\cdot}1$ (OMe$^-$)$^{(b)}$	$1{\cdot}21 \times 10^3$ (EtO$^-$)$^{(b)}$
$\frac{K_1\text{ (lyate)}}{K_1\text{ (EtS}^-\text{)}}$	0•022	0•0066	0•048

(a) Ref.104　　(b) Ref.102b

compared in a common solvent. This assumption leads to a ratio of carbon basicities.

$$OH^- : OMe^- : OEt^- : EtS^- = 1 : 0{\cdot}3 : 2{\cdot}2 : 45$$

The relative Bronsted basicities have been found to be 1•0 : 0•6 : 1•8 for OH^-, OMe^- and OEt^- in water and 1•0 : 0•3 : 1•3 in isopropanol so that the relative affinities of the oxygen bases for carbon and protons seems to be similar. The enhanced carbon basicities of thiolate ions relative to their Bronsted basicities has been previously noted.[104]

The values of K_1 for the aromatic thiols in ethanol-water mixtures follow a similarpattern to the values with EtS^-, although measurements could be made only in ethanol rich solutions. It seems very likely that the more polarisable PhS^- ion will be destabilised, relative to EtS^-, on transfer from ethanol to water. However the rather similar trend in values of K_1 for the two types of base indicate that the activity coefficient ratios

$$\frac{{}^{W}\gamma^{E}_{TNB.EtS^-}}{{}^{W}\gamma^{E}_{TNB.PhS^-}} \quad \text{and} \quad \frac{{}^{W}\gamma^{E}_{EtS^-}}{{}^{W}\gamma^{E}_{PhS^-}}$$

behave in a similar way with solvent change.

Although the insolubility of the aromatic thiols has prevented a quantitative study of the formation of the 1:2 adduct in these systems, the results obtained with thioethoxide are sufficient to clarify the situation. These results indicate that the value of the equilibrium constant K_2 for formation of the 1:2 adduct increases steadily as the solvent is changed from pure ethanol to pure water. The value of K_2 in water is about 1000 times greater than the value in pure ethanol. In fact the values of K_2 in highly aqueous mixed solvents are so high compared with K_1 that the major interaction in these media is the formation of 1:2 adducts and the maximum concentration of the 1:1 adduct is only about 10% of the stoichiometric 135 TNB concentration. The increased stability of the 1:2 adduct as the solvents become more aqueous can be explained on the basis of Hughes-Ingold[141] theory of solvation. In terms of this theory the ions which carry a more localised negative charge would be solvated better by polar solvents than by less polar solvents. Thus the 1:2 adduct which contains a localised negative charge on the nitro group between the positions of addition and hence will be certainly better solvated by water than by alcohols. These results are consistent with that earlier presented in this thesis for the formation of the 1:2 adduct from picrate ion and hydroxide ion. It has also been mentioned that N,N-dimethyl picramide gives only 1:2 adducts with hydroxide in water.[51] The fact that the localised negative charge of the 1:2 adduct will not be well solvated by solvents such as dimethyl sulphoxide explains the relatively small tendency to form higher adducts in this type of solvent.

On this basis it is possible to account for the decrease in the visible absorption at high concentration of thioethoxide in highly aqueous solution. This decrease was attributed to the colourless 1:3 adduct. This species carries three negative charges localised on the nitro-groups and therefore will be well solvated by water.

It is evident, in view of the present work, that adducts formed by addition of more than one molecule of base to 135 TNB are formed more readily in water than in alcohols. Recently Gaboriaud and Schaal[49] have reported visible spectra obtained by the stopped flow technique of 135 TNB in aqueous sodium hydroxide solutions. The spectra measured soon after mixing of the components showed a maximum at 4300Å. However, with time a species with maximum 4700Å is produced. It seems likely that the initial maximum indicates a fast formation of 1:1 adduct followed by slower production of 1:2 adduct. Thus in this aqueous system there is evidence for the formation of a 1:2 adduct.

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PUBLICATIONS

Some parts of the work described in this thesis have been the subject of the following publications:

1. Interaction of Picric Acid with Aqueous Sodium Sulphite and Sodium Hydroxide, M.R. Crampton and M. El-Ghariani, J. Chem. Soc., B, 330, 1969.

2. Interaction of 1,2,3,5- and 1,2,4,5-Tetranitrobenzenes with Some Nucleophiles in Protic Solvents, M.R. Crampton and M. El-Ghariani, J. Chem. Soc.B, 391, 1970.

3. Solvent Effects on the Relative Stabilities of 1:1 and 1:2 Adducts formed from 1,3,5-Trinitrobenzene and Thiolate Ions. M.R. Crampton and M. El-Ghariani, J. Chem. Soc., in press.