Kinetic and equilibrium studies of the reactions of some aromatic nitro compounds with metal alkoxides

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KINETIC AND EQUILIBRIUM STUDIES OF THE REACTIONS OF SOME AROMATIC NITRO COMPOUNDS WITH METAL ALKOXIDES

by

Ahmad D.A. Al-Aruri, B.Sc. (Kuwait)

(Collingwood College)

A thesis submitted for the degree of Ph.D.
in the University of Durham,
September, 1981

To my parents

DECLARATION

The material in this thesis is the result of research carried out in the Department of Chemistry, University of Durham, between October 1978 and July 1981. It has not been submitted for any other degree, and is the author's own work, except where acknowledged by reference.

PUBLICATIONS

Some of the results described in this thesis have been published in the following papers.

The Stabilities of Meisenheimer Complexes. Part 20.
"Kinetic and Equilibrium Data for the Reaction of Some Aromatic Nitro-compounds with Propoxide Ions in propan-1-ol"
by
A.D.A. Al-Aruri and M.R. Crampton*, J. Chem. Res., (S) 140; (M) 2157, (1980).

The Stabilities of Meisenheimer Complexes, Part 26.
"The reactions of some Aromatic Nitro-compounds with Base in t-Butyl Alcohol-Water Mixtures"
by
A.D.A. Al-Aruri and M.R. Crampton*, J.C.S., Perkin II, 807, (1981).

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ABSTRACT

Kinetic and equilibrium measurements have been made for σ-adduct formation from propoxide ions in propan-1-ol with 1,3,5-trinitrobenzene and a series of 1-propoxy-2,4-dinitro-6-x-benzenes (x = NO_2, Cℓ, CO_2Pr, H). The results are compared with those for similar additions of other alkoxide ions. There is evidence for strong association with sodium ions of the 1,1-dipropoxy adducts, but adducts formed by base additions at unsubstituted ring positions are not strongly associated. In the nucleophilic substitution reaction with 1-chloro-2,4-dinitrobenzene free propoxide ions show greater reactivity than sodium propoxide ion pairs.

Rate and equilibrium studies are reported for the reactions of three aromatic nitro-compounds with tetramethylammonium hydroxide in t-butyl alcohol water mixtures. There is evidence that the reactive nucleophile is the hydroxide ion rather than the t-butoxide ion. The reaction of 1,3,5-trinitrobenzene in this system leads to a σ-adduct, while 1-chloro-2,4-dinitrobenzene gives 2,4-dinitrophenol. That the rates of both these reactions falls rapidly with increasing water content is attributed mainly to the good solvation of the hydroxide ion by water. In contrast the rate of formation of picric acid from picryl chloride increases with water content due to initial formation of the 3-hydroxy adduct. Similar studies have been made using sodium and/or potassium butoxide The interpretation here is complicated by association with anions of the alkali metal cations.

In the presence of methoxide ions in methanol 2-methoxy-3,5-dinitrobenzoic acid gives a σ-adduct. Using this reaction, acidity functions for lithium, sodium and potassium methoxide solutions have been defined. The observed basicity order : sodium methoxide > potassium methoxide > lithium methoxide may derive from specific interactions of the alkali

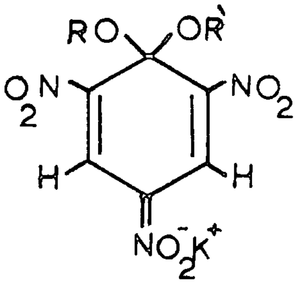
cations with the σ-adduct. Using U.V./visible data the reversible equilibria between 1-x-2,4,6-trinitrobenzenes (x = NMe_2, NHMe, NH_2, OMe or OCH_2CH_2O) and alkali metal methoxides have been investigated. Usually 1:1, 1:2 and 1:3 interactions are observed. One conclusion is that in general 1:2 and 1:3 adducts associate more strongly with sodium ions than with potassium ions or with lithium ions.

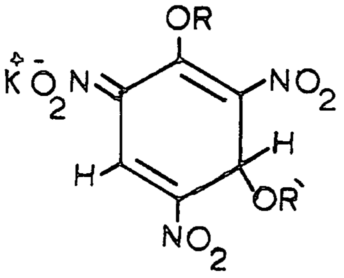
CHAPTER 1

INTRODUCTION

1. History

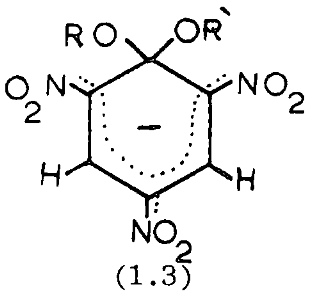
Hepp in (1882)[1] and Lobry de Bruyn in (1890)[2] succeeded in preparing and separating some coloured complexes by the addition of bases to solutions of aromatic trinitro compounds. Lobry de Bruyn and van Leent (1895)[3] prepared other complexes, others followed them[4-9]. Meisenheimer[10] (1902) gave a strong piece of chemical evidence for the structures formed when he obtained the same complexes by addition of potassium methoxide to 2,4,6-trinitrophenetole and potassium ethoxide to 2,4,6-trinitroanisole, acidification gave a mixture of the phenetole and the anisole derivatives. This led him to conclude that these complexes were formed by covalent addition of base at C1 to give (1.1) rather than addition at the unsubstituted 3-position to give (1.2).


(1.1)


(1.2)

Such complexes are commonly termed Meisenheimer or Jackson Meisenheimer complexes.

The present-day representation for Meisenheimer complexes would be (1.3), where the negative charge is delocalised about the ring and the nitro-groups.



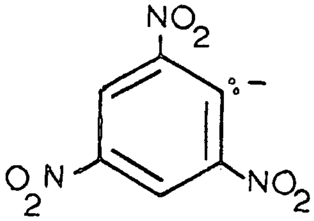
(1.3)

2. Aromatic nitro compounds

Aromatic nitro compounds which are activated by one or more nitro groups may react reversibly with bases by three main routes[11].

(i) Proton abstraction

Activitated aromatic compounds such as 1,3,5-trinitrobenzene and 1,3-dinitrobenzene will exchange ring hydrogens for deuterium or tritium in basic solutions[12-14]. The exchange is likely to involve carbanions such as (1.4). Recent[134,142] kinetic results indicate that the rate of exchange from the 2-position of 1,3-dinitrobenzene (1.5) is considerably more rapid than from the 4-position. Tritium n.m.r. studies indicate that exchange in 1,3-dinitronaphthalene (1.6) occurs at the 4-position.



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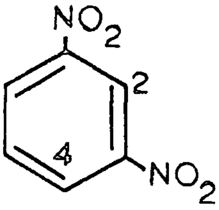

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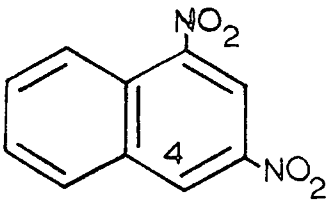
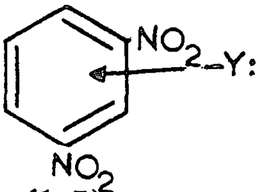


(1.6)

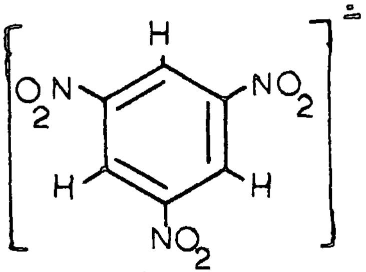
(ii) Electron transfer

A partial transfer, through orbital overlap, of electronic charge from the base (Y : or Y^-) to the aromatic nucleus depleted of π-electron density owing to the electronegative nitro-substituents gives rise to charge-transfer complexes known as donor-acceptor or π-complexes[15].



(1.7)

A further degree of interaction may lead to an electron from Y^- becoming completely transferred to the nitro compound, in which case a radical anion (1.8) is produced[11,15].



(1.8)

Such anions have been detected in basic solutions of nitro-toluenes and 1,3-dinitrobenzene,[16-18] and may be preliminary intermediates in certain nucleophilic aromatic substitution reactions. In contrast to the electron-transfer process is the interaction by which the unshared electron pair of Y^- is used in formation of a covalent bond to an aromatic carbon atom. The resulting species is then a sigma-complex[19].

Both proton abstraction and electron transfer have been found to make a relatively small contribution in aromatic compounds activated by three electron withdrawing groups.

(iii) σ Adduct Formation

This involves covalent bond formation between the attacking nucleophile and a ring carbon atom. The very wide scope of these reactions is described in detail later in the introduction. When the substrate contains a leaving group then nucleophilic substitution may occur.

Aromatic Nucleophilic Substitution

There are several possible mechanisms for nucleophilic substitution reactions.

(i) The S_N1 Mechanism

This mechanism is rare for substitution at aromatic carbon atoms, and kinetically is a first order process[19,20]. The thermal decomposition of aromatic diazonium ions in aqueous solution is kinetically first order, and the rate of reaction (apart from solvent and salt effect) is not altered upon addition of methanol or of chloride ions. (equations 1.1 and 1.2).

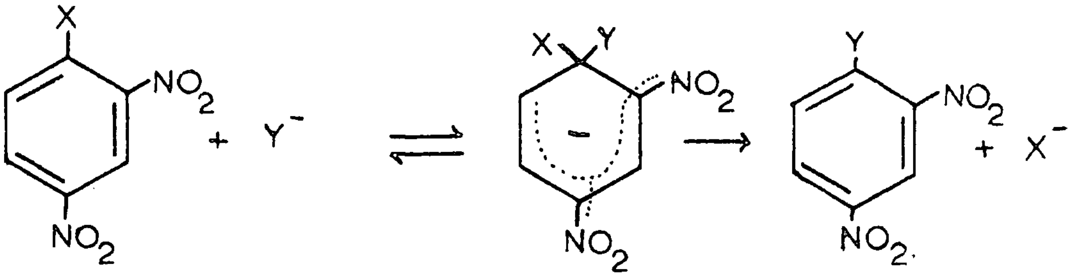
$$ArN_2^+ \xrightarrow{slow} Ar^+ + N_2 \qquad 1.1$$

$$Ar^+ + X^- \xrightarrow{fast} ArX \qquad 1.2$$

(ii) The S_NAR Mechanism

The great majority of aromatic mucleophilic substitutions occur by a bimolecular mechanism. Second-order kinetics, first order in both substrate and reagent are regularly observed[19,21].

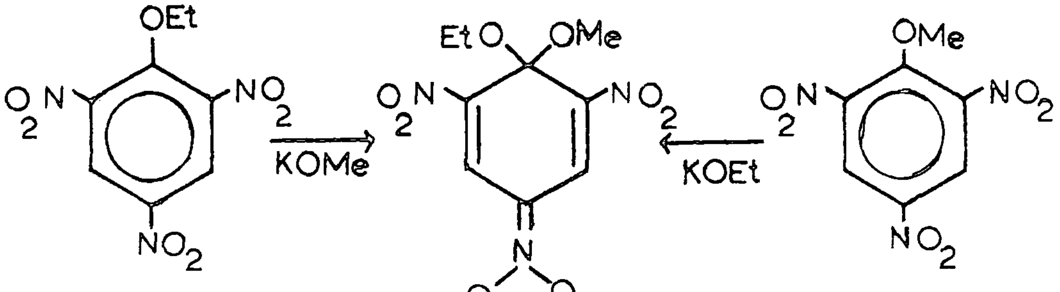
A two-step intermediate complex mechanism theory[22] has taken precedence over the old one-step mechanism of synchronous bond formation and bond breaking[23,24]. (scheme 1.1).



scheme 1.1

The S_NAR mechanism generally consists of formation of an intermediate complex in the first step and the departure of the leaving group in the second step.

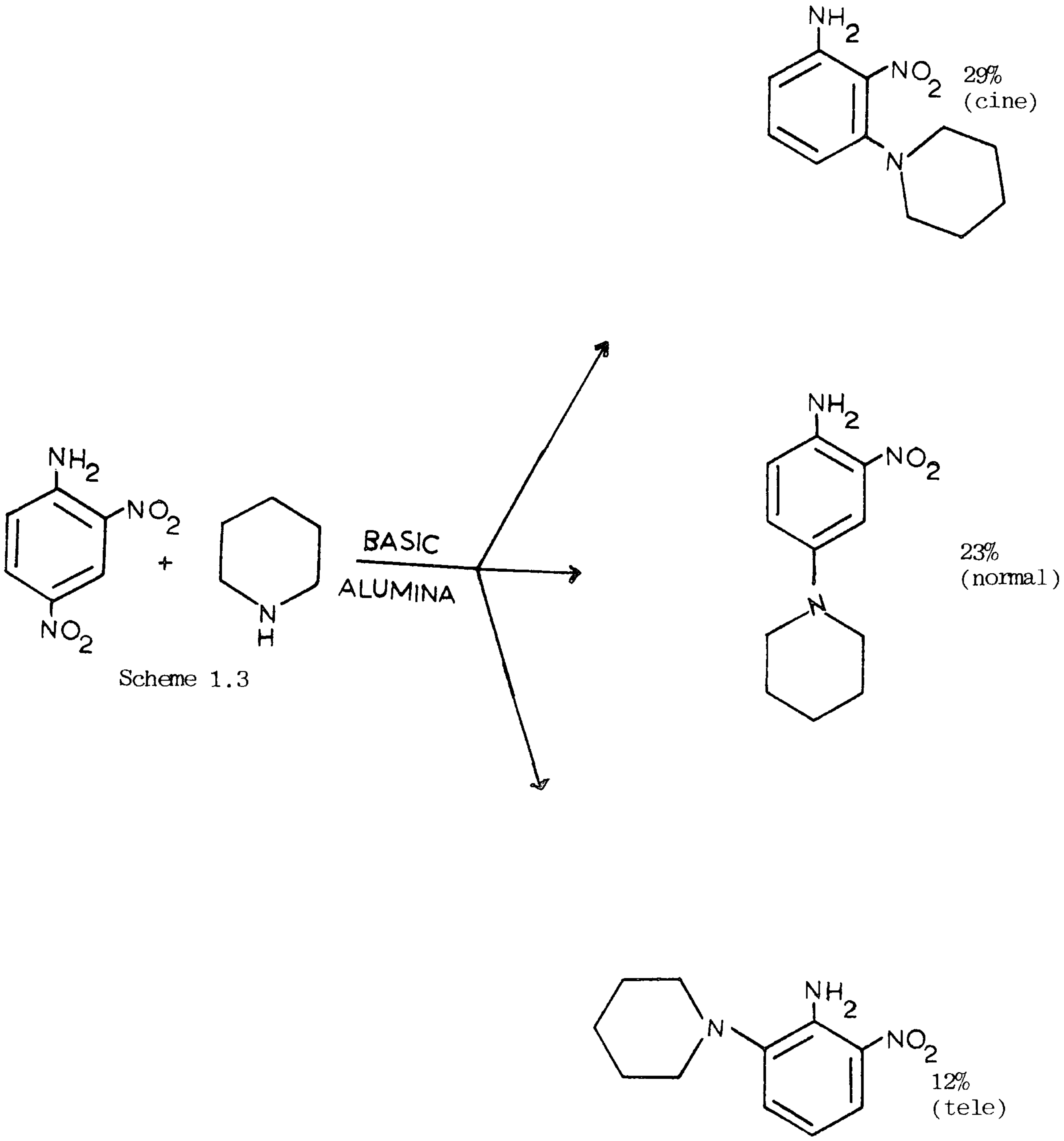
This mechanism was justified by preparing one of these intermediates(A Meisenheimer complex in 1882) as described by the scheme[20]: 1.2



scheme 1.2

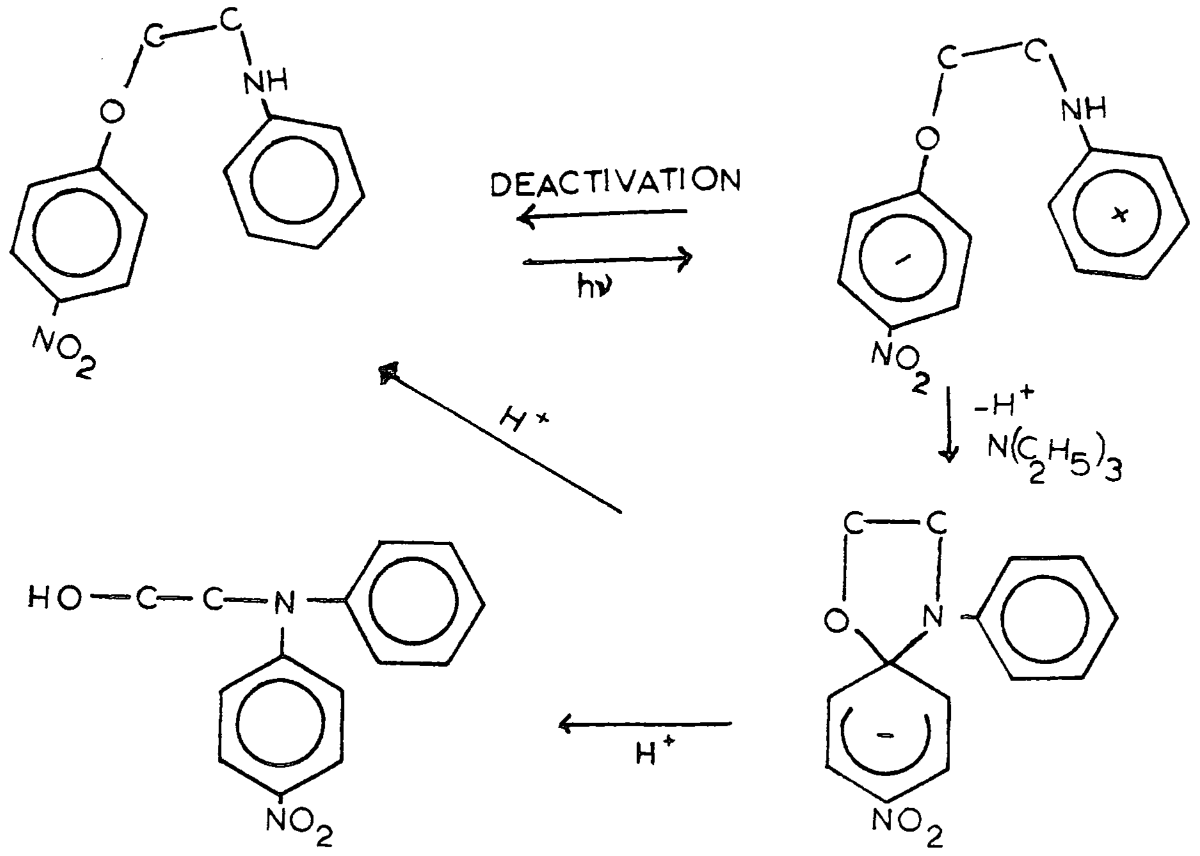
When the nucleophilic attack occurs at an atom other than that carrying the leaving group then cine-substitutions (substitution with rearrangement, where the enetering group comes in ortho to the leaving group) and tele-substitutions (where the entering group takes up a position more than one atom away from the atom to which the leaving group was attached) may occur.

An example of this is the reaction of 2,4-dinitroaniline with piperidine which gives three isomeric nitropiperidinoanilines as follows[26] (scheme 1.3)



Scheme 1.3

Intramolecular substitution of N-[ω-(4-nitrophenoxy)alkyl] aniline has been described by the following mechanism[27] (scheme 1.4).



scheme 1.4

Catalysts play a notable role in nucleophilic substitutions, an example being the use of tetra bis-(triphenyl phosphine) palladium (o) catalyst with alumina[25,28,25] (equations 1.3 and 1.4)

ArX + Pd(o) $\longrightarrow$ ArPdX 1.3

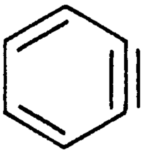
ArPdX + RS^- $\longrightarrow$ ArSR + Pd(o) + X^- 1.4

Nucleophilic substitutions in heterocyclic systems have been reviewed by many researchers[21,25,29].

Many factors affect the aromatic nucleophilic substitutions and such reactions are often favoured in dipolar aprotic solvents. Activation by a nitro group requires conjugation between the substituent and the reaction site. This in turn requires that the $\overset{+}{N}{\begin{smallmatrix}\nearrow\!\!\!\nearrow O\\ \searrow O^-\end{smallmatrix}}$- group is nearly coplanar with the benzene ring, and if this is prevented, by a bulky group, the nucleophilic attack will be reduced,[20] this is an example of the steric factor. The nature of both the substrate and nucleophile[21] are also effective factors in this mechanism.

(iii) The Elimination-addition mechanism

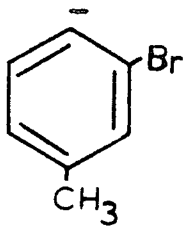
This mechanism proceeds via Aryne species, which are usually generated by the action of a very strong base. Bunnett[30] discussed the identification of such species: (1.9)



(1.9)

Since arynes are usually generated by basic reagents, themselves nucleophiles, the only nucleophiles whose additions to arynes have been observed are those which can compete successfully with the aryne-generating bases. These good competitors are anions with negative charge on carbon, nitrogen, or sulphur. Oxygen anions, such as CH_3O^- are weak competitors.

The reaction of 2-bromo-4-methylbenzophenone with potassium amide in ammonia is a recent example of this mechanism and gives species such as (1.10).



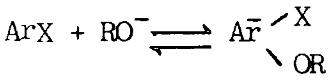
(1.10)

Here addition of a proton to form aryl bromide competes with elimination of halide ion to give the aryne[31].

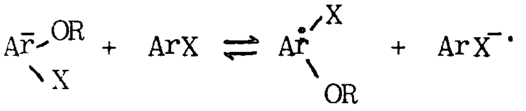
(iv) Free-Radical Mechanism

The $S_{RN}1$ mechanism which involves free radical intermediates provides a means for nucleophilic substitution in substrates which are not activated by strongly electron-withdrawing groups. A mechanism[135] involving radicals may also be involved in the reaction of 1-chloro-2,4-dinitrobenzene with potassium isopropoxide in isopropanol : benzene mixtures. The main product of reaction is 1-isopropoxy-2,4-dinitrobenzene. However in the presence of crown-ethers substantial amounts of 2,4-dinitrophenol are formed and the kinetic order in base is less than unity. The addition of the complexing agent makes it possible for separation of the ion-pairs formed between the σ-adduct and the cation to occur. The unshielded negative charge of the complex makes it more reactive and more prone to lose one electron.

The mechanism can be described by equations : 1.5 and 1.6.



$$\mathrm{ArX} + \mathrm{RO}^- \rightleftharpoons \overset{-}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\diagup \mathrm{X}}{\diagdown \mathrm{OR}} \qquad 1.5$$



$$\overset{-}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\diagup \mathrm{OR}}{\diagdown \mathrm{X}} + \mathrm{ArX} \rightleftharpoons \overset{\bullet}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\diagup \mathrm{X}}{\diagdown \mathrm{OR}} + \mathrm{ArX}^{-\bullet} \qquad 1.6$$

Then the fate of the radical anion of the halogenobenzene, can be described by : (equations 1.7 - 1.9)

$$ArX^{-\cdot} \rightleftharpoons Ar^{\cdot} + X^{-} \qquad 1.7$$

$$Ar^{\cdot} + RO^{-} \rightleftharpoons ArOR^{-\cdot} \qquad 1.8$$

$$ArOR^{-\cdot} \rightleftharpoons ArO^{-} + R^{\cdot} \qquad 1.9$$

This can explain the possibility that a fragment, formed from reaction of aryl ethers with alkali metals, may give phenoxide and an alkyl radical.

Covalent (σ) complexes[11,21,32]

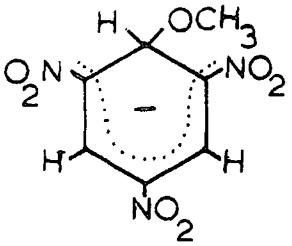
Are formed due to charge transfer between two types of molecules in which one of them acts as an electron acceptor and the other as an electron donor, forming a full bond. Streitweiser concludes from his calculations that σ-complex is a good model for the transition state in an aromatic nucleophilic substitution reaction.

Meisenheimer Complexes

Are simply anionic sigma complexes (or adducts) formed from the addition of nucleophiles to activated aromatic substrates. Given below are some examples of different types of adducts classified according to the nature of the nucleophile. As reviews of σ-adducts are available most emphasis has been put on recent work.

(i) With Alkoxides and Hydroxide Ions

Crampton and Gold identified unambiguously by N.M.R. spectroscopy the structure of the adduct formed 1,3,5-trinitrobenzene with potassium methoxide in DMSO[35] as (1.11)

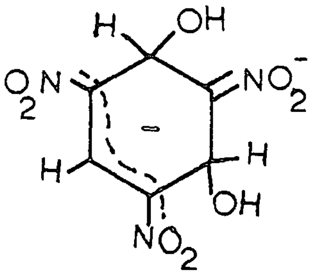


1:1 adduct

(1-11)

The parent shows a single resonance for the three equivalent hydrogens at 9.2 p.p.m. Complex formation results in a covalency change for the hydrogen at C-2 from sp^2 to sp^3 bonding, and the resonance is shifted to high field (6.14 p.p.m), while the other two equivalent hydrogens at C-4 and C-6 show a smaller shift to 8.42 p.p.m. The three methoxyl protons give a band at 3.10 p.p.m. Similar observations have been made in acetonitrile and dimethyl formamide[35], taking the solvent effect in consideration. For the same parent in DMSO, Foster and Fyfe[36] carried out similar measurements for ethoxide and n-butoxide adducts. Another comparative N.M.R. study with thioethoxide and thiophenoxide ions has been reported[37].

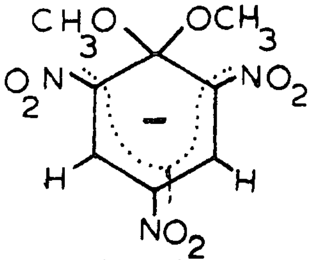
At high nucleophile concentrations 1:2 adducts may be formed. Visible spectra have been used to distinguish between the 1:1 adduct from 1,3,5-trinitrobenzene which has two absorptions and the 1:2 adduct which has a single absorption[11]. Kinetic analysis for the addition of aqueous sodium hydroxide to trinitrobenzene reveals two reversible equilibria. The first involving the 1:1 adduct, the second produces the 1:2 adduct[11] (1.12)



1:2 adduct

(1.12)

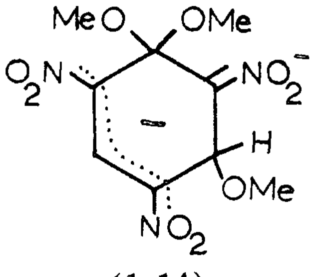
N.M.R. spectra supported the structure (1.13) formed from potassium methoxide and 2,4,6-trinitroanisole in DMSO where a single band is observed for the six methoxyl protons indicaitng their equivalence. This adduct is preceeded by a less stable short-lived isomer where methoxide ions attach C-3. Similar adducts containing various alkoxy groups have been studied.[36,38]



(1.13)

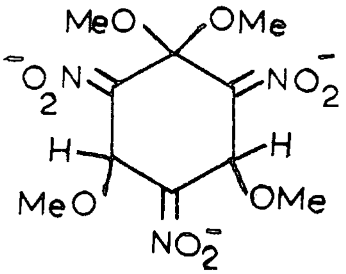
An N.M.R. spectrum has been taken for the C-3 adduct.[39] Methanol and methoxide ions have been found to enhance the rate of isomerisation to the thermodynamically more stable C-1 adduct[14].

A di-adduct (1.14) formed at high alkoxide concentrations has been proposed from an N.M.R. study[36].



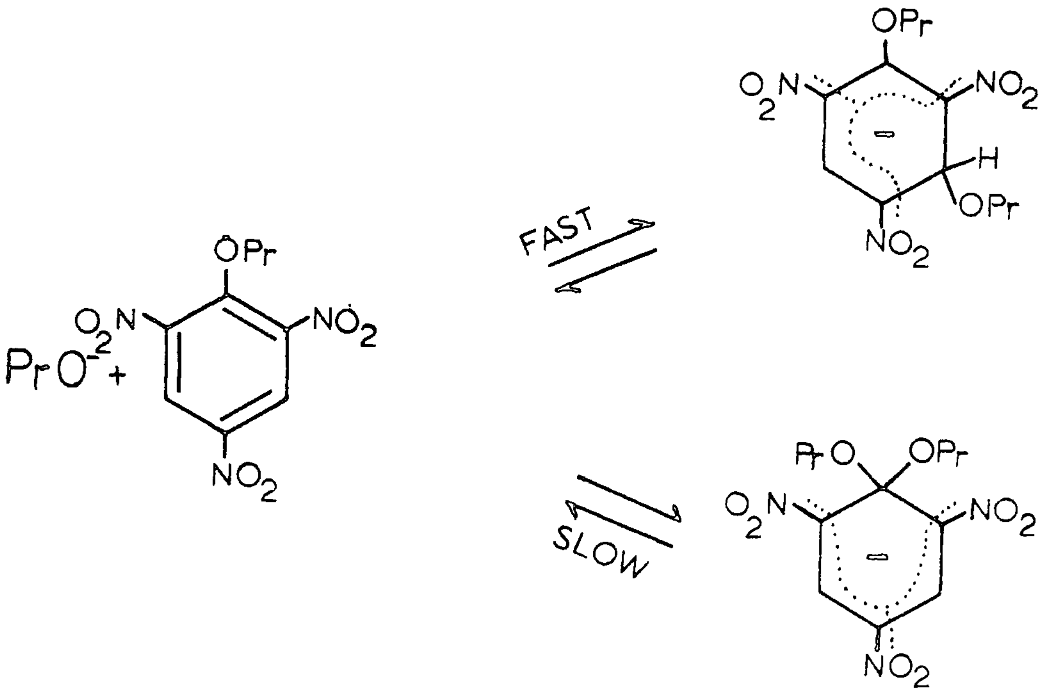
(1.14)

Another colourless species has been attributed to tri-adduct at very high alkoxide concentrations (1.15).



(1.15)

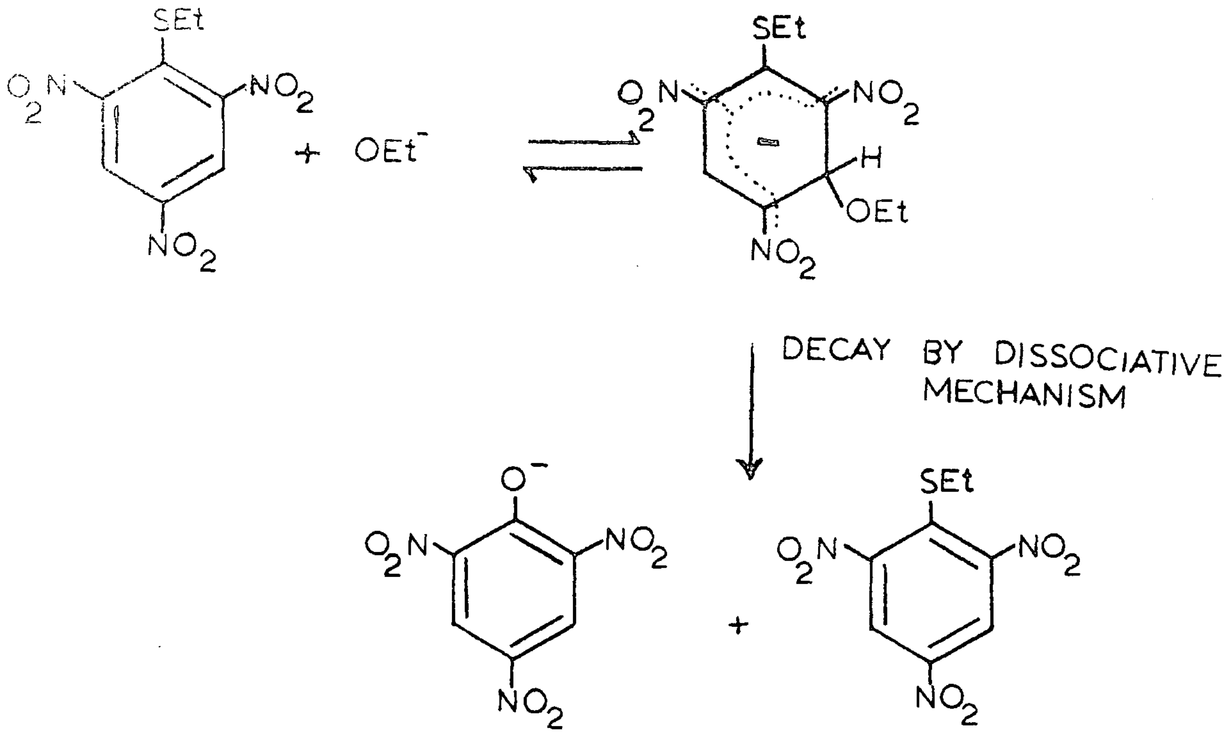
As part of the present work a kinetic study has been made of the reaction of propoxide ions in propanol with 1,3,5-trinitrobenzene and a series of 1-propoxy-2,4-dinitro-6-substituted benzene. With 1-propoxy-2,4,6-trinitrobenzene the scheme below was shown to apply.



scheme 1.5

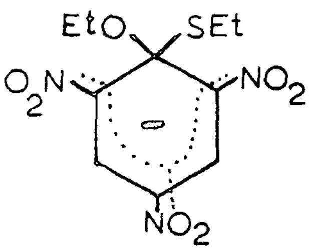
Other kinetic studies for reactions of similar substrates with methoxide in methanol[42], ethoxide in ethanol and tert-butoxide in tert-butanol-water mixtures[43] have been made.

A recent study by N.M.R. of the reaction of ethoxide ions with ethyl thiopicrate in DMSO shows that the initial product is 3-ethoxy ethyl thiopicrate and this is followed by the substitution reactions[34] (scheme 1.6)

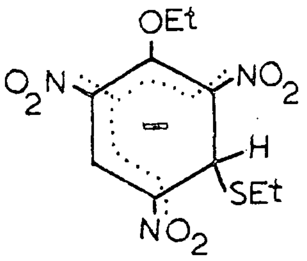


Scheme 1.6

However attack of ethanethiolate ions in ethylpicrate yields the isomeric adducts (at C-3 or C-1) (1.16) and (1.17).

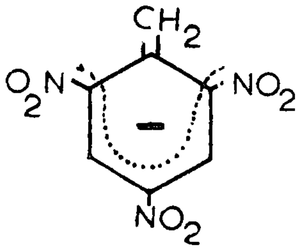


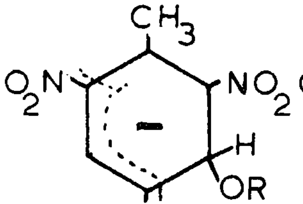
(1.16)



(1.17)

The reaction of alkoxide ions with 2,4,6-trinitrotoluene (TNT) results in proton abstraction, σ-complex formation and radical anion formation[44]. (1.18 - 1.21).


(1.18)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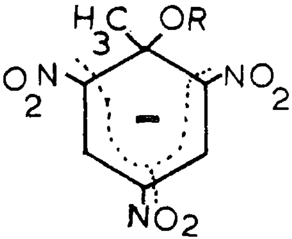
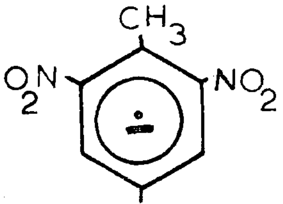
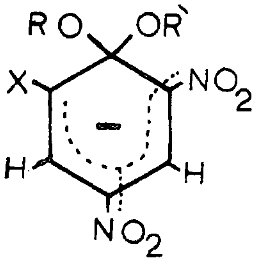

(1.20)

σ-complex


(1.21)

radical anion

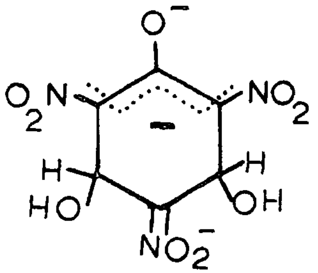
Although, reducing the number of nitrogroups activating the aromatic ring reduces the tendency to form covalent adducts,crystalline adducts such as (1.22) have been isolated from reactions of dinitroanisoles with alkoxides. The structure has been confirmed by N.M.R. spectroscopy 36,45,46.


(1.22)

(R = R' = Alkyl, X = H)

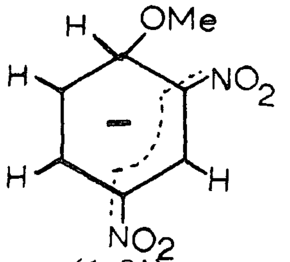
The addition of methanolic sodium methoxide to a DMSO solution of 2,4-dinitroanisole doubles the band due to methoxyl protons and shifts it from 4.10 p.p.m in the parent up to 2.94 p.p.m., which proves the identity of the methoxyl groups in the complex. Small shifts to high field due to ring protons have been observed. Another piece of evidence showing that the addition occurs at C1 comes from the spin-

spin coupling constants which are not affected since no covalency change occurs at a ring carbon carrying hydrogen. Byrne et al[47] observed similar spectra from dissolving a solid dinitroanisole salt in DMSO. The same thing has been proved by N.M.R. by methoxide addition to 2,6-dinitroanisole. The extent of conversion of the picrate ion (picric acid exists as picrate ion in dilute aqueous solution of sodium hydroxide due to its high acidity, λ_{max} = 3600Å)[11] to complex depends on a high power of base concentration[48]. N.M.R. measurements proved that such reaction involves more than one hydroxide ion,[49,50] giving the structure (1.23)



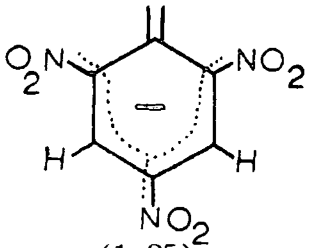
(1.23)

There is a strong upfield shift of the ring proton band from 8.8 p.p.m in the picrate ion to 6.1 p.p.m in concentrated sodium hydroxide solution. With sodium methoxide in methanol, a change in visible spectrum indicates the possibility of the addition of one, and two methoxide ions at ring carbons carrying hydrogen. The addition of methanolic sodium methoxide to 1,3-dinitrobenzene in DMSO produces a red solution (λ_{max} 520 nm) giving the adduct (1.24) whose structure has been confirmed by N.M.R.[12,46].

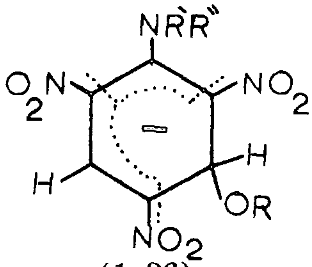


(1.24)

The amino group in 2,4-dinitroaniline loses a proton in[46] methanolic DMSO. N.M.R. showed no change in the pattern of ring protons in the presence of base, except a shift to high field which is consistent with fast exchange between the parent and Bronsted base (proton acceptor), and there is no evidence for methoxide addition. Gold and Rochester[52] suggested from a study using visible spectroscopy that picramide and its N-substituted derivatives produce two species, one due to proton loss from the amino-group (R = H, alkyl, phenyl) (1.25) and the other due to attack of alkoxide at C-3. (1.26).

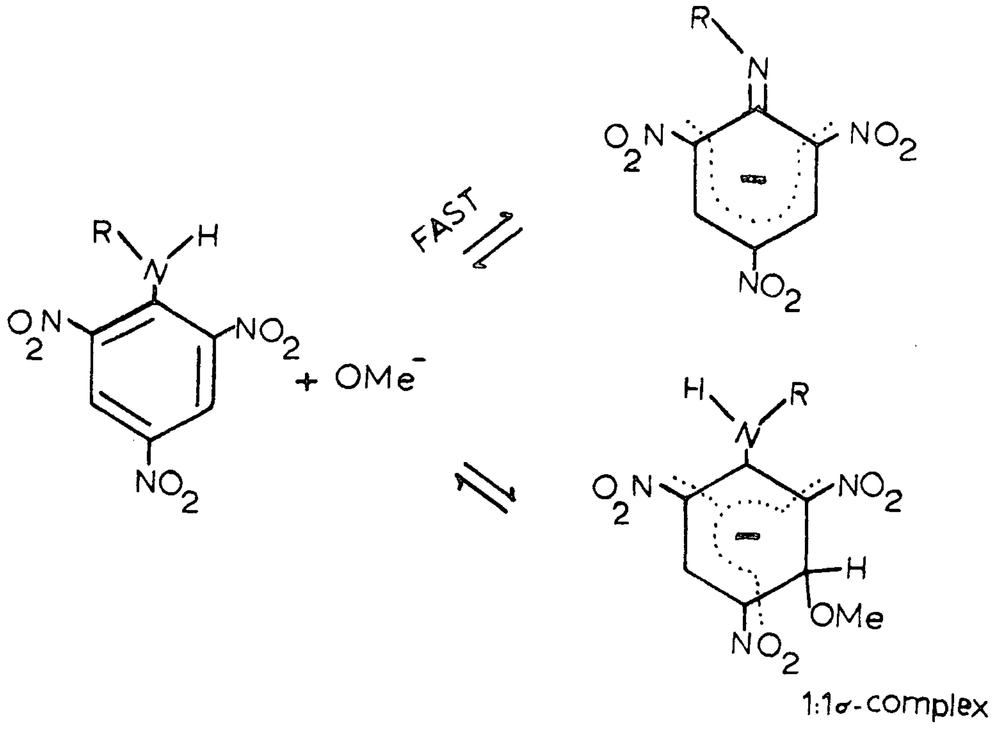


(1.25)



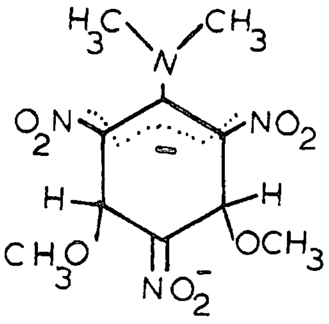
(1.26)

Kinetic study[55] of the reaction in methanol with methoxide ions indicates a very rapid process (measurable by T-jump) which is attributed to proton transfer to give the conjugate base, and to a slower process (measurable by stopped-flow) attributed to methoxide addition at the unsubstituted 3-position (scheme 1.7).



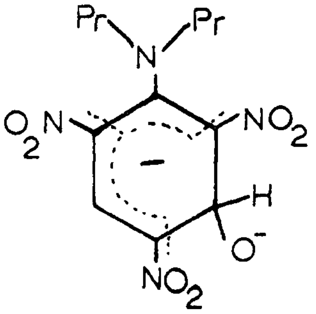
scheme 1.7

These interactions have been confirmed by N.M.R. in DMSO-methanol solvent[53]. At high base concentration the 1:2 adduct of N,N-dimethylpicramide is formed and visible spectra have been taken for the 1:1 and 1:2 adducts[54]. (1.27)



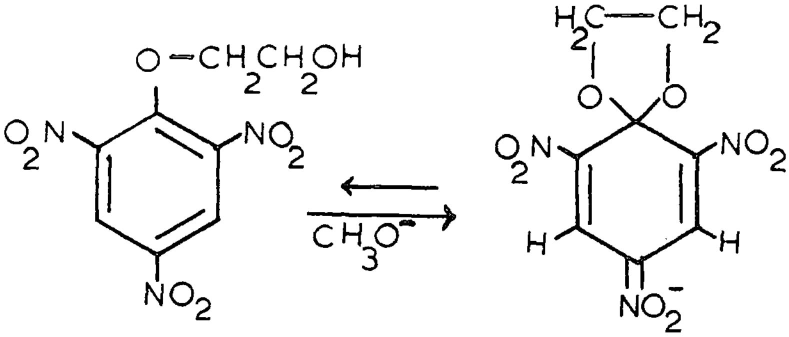
(1.27)

The conclusions are that the reactions of picramide and N-alkyl picramides with methoxide ions involve very rapid proton transfer to give the conjugate base and a slower process for addition at C-3. At high base concentrations 1:2 and 1:3 complexes are observed[54,55]. Gold and Rochester noted the unusual stability of the 1:2 adduct formed from N,N-dimethyl picramide with sodium hydroxide in water[56]. The reaction of N,N-dipropyl-2,6-dinitro-4-(trifluoromethyl) aniline with hydroxide ions in water DMSO mixtures results in the formation of the 3-hydroxy adduct. There is evidence that, as with related compounds ionization of the added hydroxyl group occurs to give the dianion[57] (1.28)



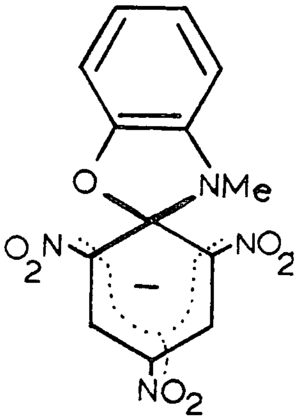
(1.28)

Intramolecular attack may occur to yield the spiro σ-complex when methoxide is added to 1-(2-hydroxyethoxy)-2,4,6-trinitrobenzene according to the scheme 1.8[11,32,38,58]



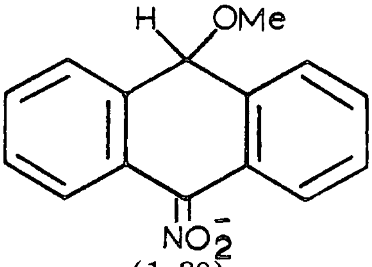
scheme 1.8

Two bands are observed in the N.M.R. spectrum for the complex at 8.7 p.p.m due to the sp^2 ring proton and at 4.3 p.p.m due to the equivalent methylene protons. Drozd[59] and co-workers have identified a number of spiro-complexes including (1.29) formed from an o-hydroxylphenyl picramide derivative.



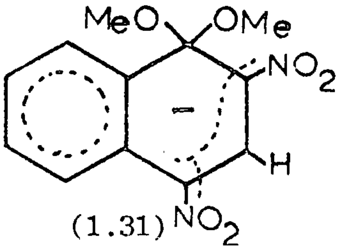
(1.29)

Meisenheimer[10] prepared and separated a solid crytalline salt from 9-nitroanthracene and potassium methoxide. He proposed the structure (1.30) for the adduct depending on elemental analysis results. This structure has been confirmed by N.M.R. study[60] The change in hybridization of the C-10 atom from sp^2 to sp^3, results in a resonance shift from 8.93 p.p.m in nitroanthracene to 4.93 p.p.m. in the complex.



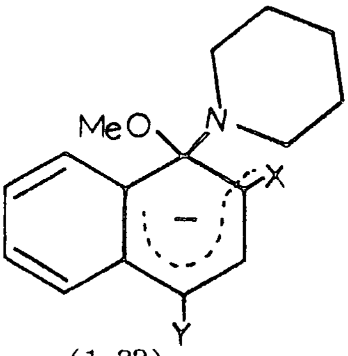
(1.30)

Alkoxide addition at C-1 in 2,4-dinitro-1-methoxynaphthalene has been confirmed by N.M.R.[60,61] and yields the structure (1.31).



(1.31)

A study[138] using visible and infra-red spectroscopy has been reported for methoxide addition to 1-piperidino-2,4-disubstituted naphthalenes (1.32).

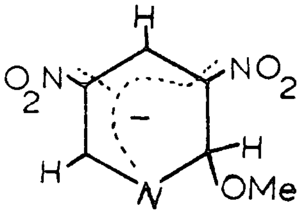


(1.32)

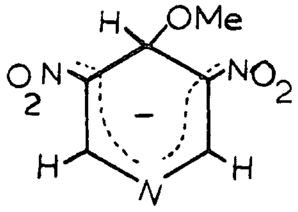
X = NO_2,CN

Y = NO_2,CN

The aza group,-N=, in a heterocychic system behaves similarly to a nitro group in an aromatic ring, in that both activate the ring to nucleophilic substitution[62]. However, the steric requirements of the ring nitrogen are considerably reduced relative to a nitro group. 3,5-dinitropyridine with sodium methoxide in DMSO gives the following Meisenheimer adducts (1.33) and (1.34) whose structures have been confirmed by N.M.R.[63,64]

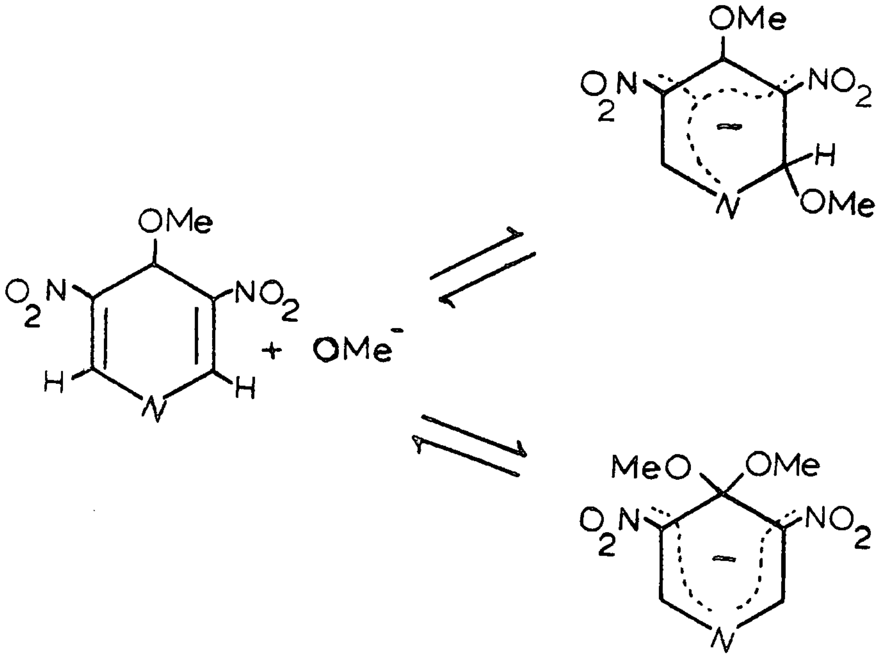


(1.33)



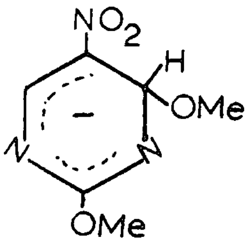
(1.34)

Also the following reaction (scheme 1.9) has been confirmed by N.M.R[63,64].



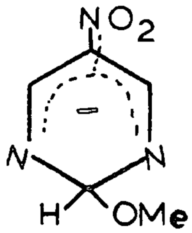
Scheme 1.9

Addition of methoxide ions to 2-methoxy- 5-nitropyrimidine gave (1.35)



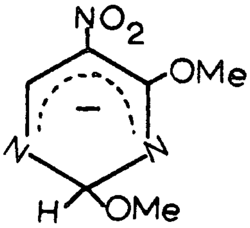
(1.35)

and with 5-nitropyrimidine (1.36) adduct was formed



(1.36)

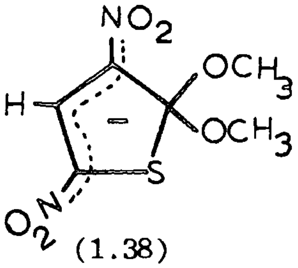
while with 4-methoxy- 5-nitropyrimidine, the following species was formed (1.37).



(1.37)

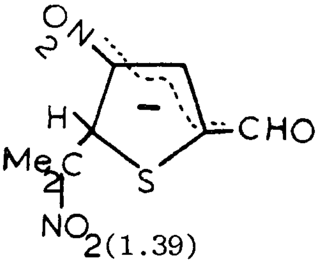
Steric effects are also much less important in five membered heterocyclic rings relative to benzene derivations[66].

The formation of the thiophen σ-adduct (1.38) in DMSO has been reported[67].



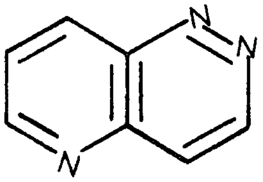
(1.38)

Recently evidence for the formation of the thiophen product (1.39) during reaction of 4-nitro-2-thenylidene diacetate with 2-nitropropan-2-ide ions has been reported[68].



(1.39)

5-azacinnoline (1.40) has been found to react with hard bases (having a low ionization potential) to give the anion radical and with soft bases (having a high ionization potential) to give the σ-complex[69].



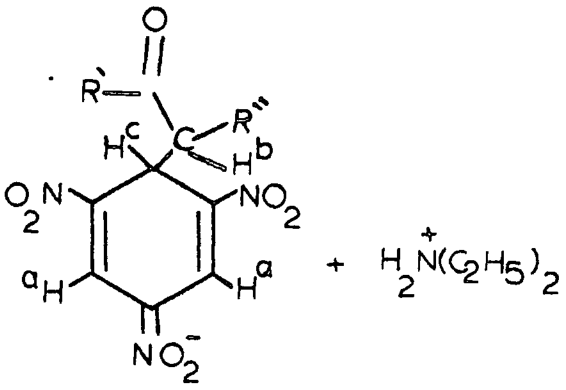
(1.40)

(ii) With Carbon Bases[70]

Carbon bases are organic compounds which, when treated with a base, undergo ionisation by cleavage of a carbon-hydrogen bond to give carbanions. Generally solutions of 1,3,5-trinitrobenzene and triethylamine in ketonic solvents give complexes where the ketonate ion is slowly generated by proton transfer to the amine (equation 1.10).

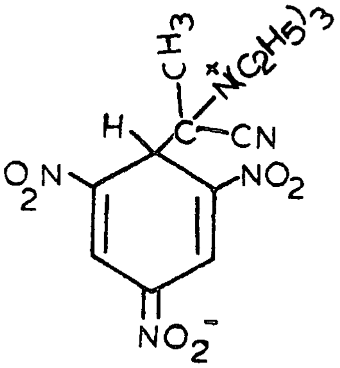
$$NR_3 + CHRCOR \rightleftharpoons {}^{-}CRCOR + NHR_3^{+} \qquad 1.10$$

The N.M.R.[32,71] spectrum is in accord with this structure (1.41) showing the absence of a bond from C-1 to oxygen and of a coupling constant (J = 3-6 cps) between H^c and H^b.



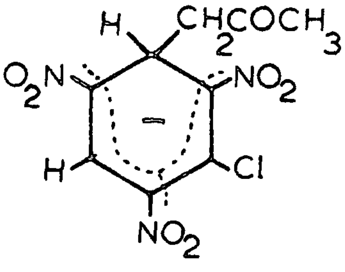
(1.41)

A zwitterionic complex (1.42) has been characterized by N.M.R., which forms when triethylamine is added to solution of 1,3,5-trinitrobenzene in acrylonitrile[72]. (Zwitterion is a dipolar ion, it is a product of reaction between an acidic group and a basic group that form part of the same molecule).



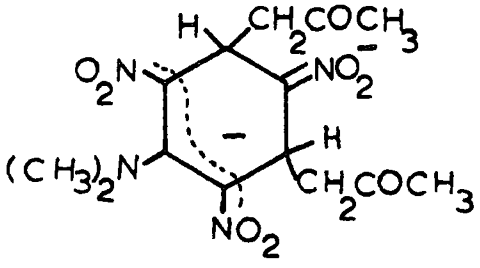
(1.42)

N.M.R. indicates the presence of the complex (1.43) in an acetone solution of picryl chloride containing triethylamine[60]. The sp^2 proton give a triplet centered at 5.2 p.p.m. (J = 6 cps).



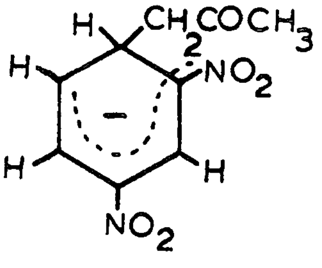
(1.43)

In acetone solutions of N,N-dimethyl picramide containing a large excess of triethylamine there is NMR evidence for the σ-complex[60] (1.44).



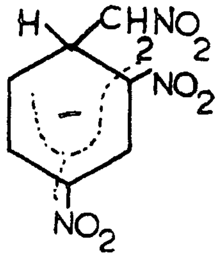
(1.44)

The interaction of aromatic nitrocompounds with ketones in ketone-water or similar solvent mixtures results in the Janovsky reaction[73]. (This is a colour forming reaction between carbonyl compounds, especially aliphatic aldehydes and ketones, and poly-nitrobenzene compounds). One of these reactions is that of 1,3-dinitrobenzene with alkaline acetone. Suggestions[73-75] followed by chemical and spectroscopic evidence[76] supported the structure (1.45).



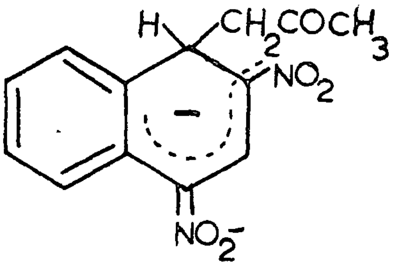
(1.45)

N.M.R. measurements[77] indicate the formation of the adduct (1.46) when sodium methoxide is added to 1,3-dinitrobenzene in a solvent of DMSO/nitromethane (60/40)(v/v).

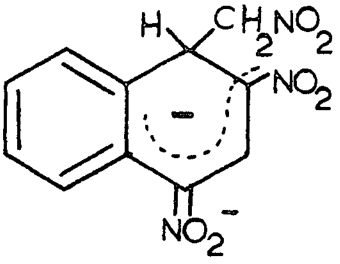


(1.46)

Similarly, there is N.M.R. evidence from the formation from 2,4-dinitronaphthalene of (1.47) in acetone containing triethylamine and (1.48) in nitromethane containing triethylamine[78].

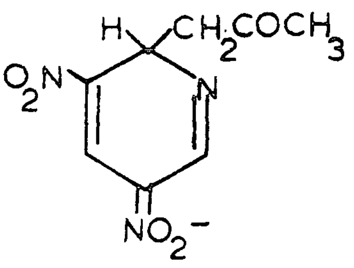


(1.47)

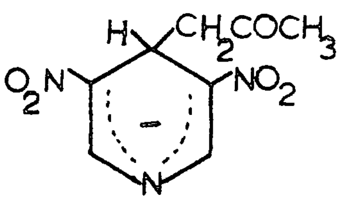


(1.48)

N.M.R. studies show that 3-5-dinitropyridine reacts with base in acetone to give a mixture of the following structures[63].



(1.49)

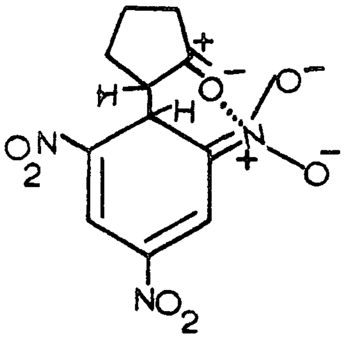


PREDOMINATING SPECIES

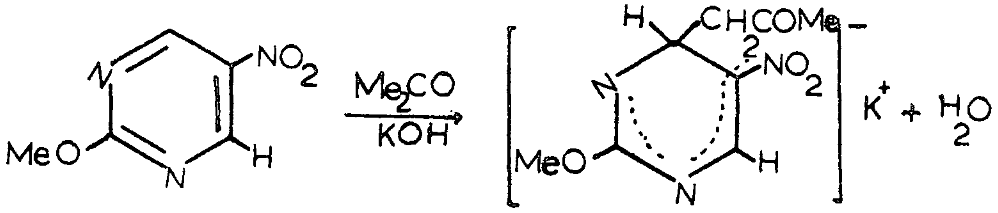
(1.50)

^{13}CNMR has been used to give some information about the structure of the very stable complex formed from 1,3,5-trinitrobenzene and cyclopentanone. The unusually low field position of the carbonyl carbon in the complex, relative to other complexes, indicates a highly polarized C=O function[79] as shown in structure (1.51).

(1.51)



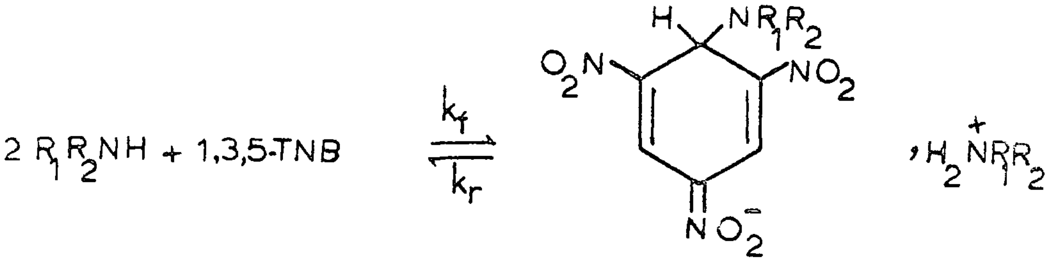
N.M.R., I.R. and U.V. spectroscopy[139] confirmed structures of the sigma complexes of 5-nitropyrimidine and its methoxy derivatives with acetonate anion. One of these separated salts is formed by the reaction in scheme 1.10.



Scheme 1.10

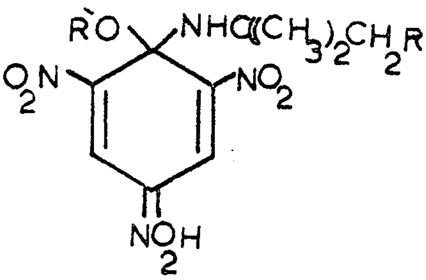
(iii) <u>With Amines</u>

The addition of ammonia, methyl amine, dimethyl amine, diethylamine and piperidine to DMSO solutions[80,81] of 1,3,5-trinitrobenzene can be explained by the equation 1.11.



.... 1.11

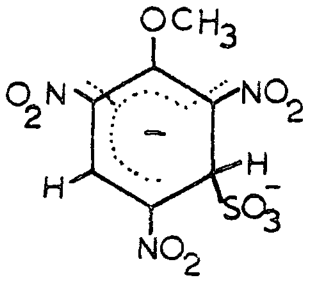
N.M.R. studies show a large shift to high field for the sp^3 hybridised carbon atom as in case of alkoxide adducts, but the absence of coupling (i.e. $J_{sp^2\ sp^3} = 0$) is in contrast with alkoxide adducts ($J \sim 1$ cps)[32]. This has been attributed to the short lifetime for amine complexes[81]. 1,3,5-Trinitrobenzene gives more intense colour with ammonia, primary amines and secondary amine than with tertiary amines, since with tertiary amines only zwitterion formation is likely[82]. Amines may add to C-1 in picryl ethers, an example[83] is the neutral complex (1.52) formed at low temperature, and when the para nitro group is protonated. The anionic σ-complex salt is formed at high amine concentration. At room temperature the alkoxide group is lost to give a picramide derivative.



(1.52)

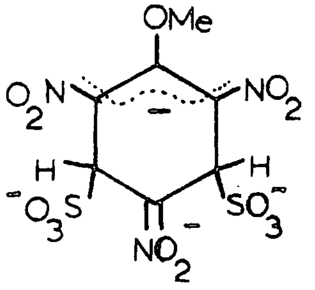
(iv) With Other Nucleophiles

The sulphite ion adds to C-3 of 2,4,6,-trinitroanisole in aqueous DMSO giving the (1.53) adduct[84,85] which has two resonances due to ring protons at 8.4 p.p.m. and 6.1 p.p.m.

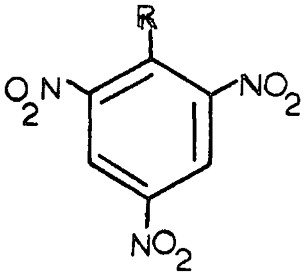


(1.53)

While in water a di-adduct (1.54) is formed whose N.M.R. spectrum shows a single band due to ring protons at 6.0 p.p.m.



(1.54)



(1.55)

(1.55) (R = MeO, $P(O)(OMe)_2$) have been found to form anionic - complexes with trialkylphosphites and with dialkyl phosphites in the presence of Et_3N. N.M.R. and U.V. spectral data confirm the addition of the phosphite group meta to R[141].

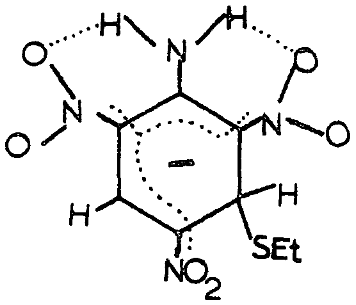
3. Methods of Structure Determination for Meisenheimer Complexes

(i) Nuclear Magnetic Resonance (N.M.R.) spectroscopy

This technique often gives very clear evidence for the structure of Meisenheimer complexes. Chemical shifts and spin-coupling resonance constants give a large amount of information about complex structure, and nature of substituents on the benzene ring. N.M.R. has been used successfully[86] to distinguish between isomers and their stability. Thus the addition of methoxide to 2,4,6-trinitroanisole in DMSO gives the C-3 adduct, followed by the more thermodynamically stable C-1 isomer (1.13) and (1.14). Similarly the observation of di- and tri-adducts at high alkoxide concentrations was possible by N.M.R.[36] (1.15). Generally nucleophilic addition to nitroaromatic substrates leads to change in hybridization from sp^2 (in substrate) to sp^3 (in adduct). Simply this gives rise to a change in the chemical shift.

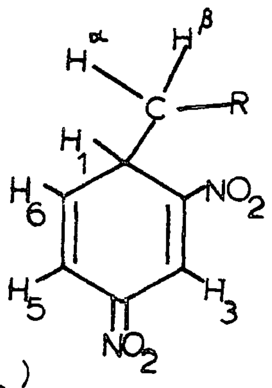
The change in shift of other ring protons has been attributed to the increased negative change in the ring of the complex[11]. A diminished diamagnetic anisotropy resulting from ring current may also be important[32].

Detection of hydrogen-bonding is also possible by this technique. The adduct formed from sodium thioethoxide and picramide (1.56) has two bands[37] for the non-equivalent amino protons, indicating hydrogen bonding.



(1.56)

The values of spin-coupling may reveal[32,87] information about relative bond angles and stereochemistry of many Meisenheimer complexes. An example (1.57)



($R = NO_2$ or $COCH_3$)

(1.57)

$J_{3,5}$ = 1.9 - 2 cps

$J_{5,6}$ = 10.2 cps

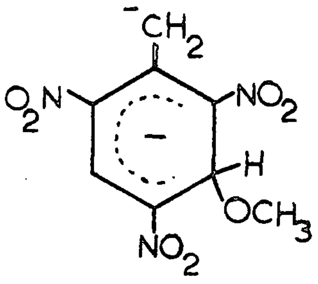
$J_{1,6}$ = 4.4 - 5.0 cps

J_{H-1,H^α} = 5.0 cps

J_{H-1,H^β} = 10.0 cps

Although N.M.R. is a strong identifying tool for Meisenheimer complexes, it has some limitations, where it cannot be used effectively. The presence of free radicals broadens the bands and complicates the spectra. The nature of the solvent used in N.M.R, often DMSO, won't allow, for example, the formation of 1:2 and 1:3 adducts. The use of isotopes, especially hydrogen isotopes, was and is still of great help to N.M.R. studies.

Flow N.M.R. spectroscopy[137] enables measurements to be made in the range of 50 ms - 5 min and thus covers a range of reaction times previously inaccessible to N.M.R. investigation. This technique provides an excellent diagnostic tool for the identification of transient intermediate species. The reactant solutions flow continuously through a mixing chamber and through the transmitter-receiver coils of the probe where the spectrum of the flowing, chemically reacting system is measured. At a constant flow rate the solution will have constant composition and no change in the spectrum is observed. Kinetic measurements can be repeated by varying the flow rate. An application of this technique was the identification of the products of 2,4,6-trinitrotoluene with methoxide ion in (87.5% DMSO - 12.5% methanol) (v/v) solvent mixture. The reaction of equimolar quantities yields first the complex (1.19), (R = Me) in a very fast reaction ($t_{\frac{1}{2}} \sim 25$ s) and the anion (1.18) in a second slower reaction. On doubling the base concentration in the same solvent mixture, the only species observed is the dianion (1.58) which is relatively stable.



(1.58)

(ii) U.V. and Visible Spectroscopy (Electronic spectroscopy)

The strength of U.V/visible spectroscopy lies in its ability to measure the extent of multiple bond or aromatic conjugation within molecules. This has been attributed to transitions from highest occupied M.O. to lowest unoccupied M.O. Specifically, transitions in the visible region are due to charge transfer between the ring and nitrogroups[90]. Since extinction coefficients are high, small concentrations are needed for this technique relative to those needed in N.M.R. The position of absorption maxima and the molar extinction coefficient depend somewhat on the solvent employed (besides, of course the nature of the substrate)[11,15,32]. The 1:1 adducts of picryl ethers with alkoxides show generally two absorptions in the visible region[52,91]. The 1:2 adduct has a single absorption band, where as the 1:3 adduct is a colourless species[92]. Adducts of 2,4-dinitro-6-X-anisoles and 2,6-dinitro-4-X-anisoles with alkoxides give two bands in the visible region[93], the wave lengths varying with the substrate. U.V/visible spectroscopy is less diagnostic in giving structural information about Meisenheimer complexes than is N.M.R. spectroscopy. On the other hand it is very useful in determining equilibrium and rate constant associated with complex formation.

The Benesi-Hildebrand equation is one example of its applications.

Derivation of Benesi-Hildebrand equation[94]

$\mathrm{Nu} + \mathrm{P} \rightleftharpoons \mathrm{C}$

where Nu = nucleophile, P = Parent and C = complex.

The equilibrium constant

$$K = \frac{[C]}{([Nu]_{st} - [C])([P]_{st} - [C])} \qquad 1.12$$

where st = stoichometric concentration and where the two terms in the denominator represent the molar concentrations of free nucleophile and free parent, respectively, and $[C]$ = molar concentration of the complex.

If $[Nu] \gg [C] \rightarrow [Nu] - [C] \simeq [Nu]$

$$\varepsilon_c = \frac{\log(Io/I)}{[C]\ell} \qquad 1.13$$

(A form of the Beer-Lambert law)

where ε_c is the molar extinction coefficient for the complex C at the wavelength of absorption. From 1.12

$$K = \frac{[C]}{[Nu]_{st}([P]_{st} - [C])} \qquad 1.14$$

rearranging

$$[C] = K([P]_{st} - [C])[Nu]_{st} \qquad 1.15$$

$$\therefore [C] = K([P]_{st} - \frac{\log(Io/I)}{\epsilon_c \ell})[Nu]_{st} \qquad 1.16$$

$$\because [C] = \frac{\log(Io/I)}{\epsilon_c \ell} \quad \text{(from equation 1.13)} \qquad 1.17$$

Equating 1.16 by 1.17, rearranging and dividing both sides by ε_c

$$\therefore \frac{1}{K[Nu]_{st}\epsilon_c} + \frac{1}{\epsilon_c} = \frac{[P]_{st}\ell}{\log(Io/I)} \qquad 1.18$$

putting $\log \frac{Io}{I} = O.D$ and $\ell = 1$

Substituting these values in equation 1.18

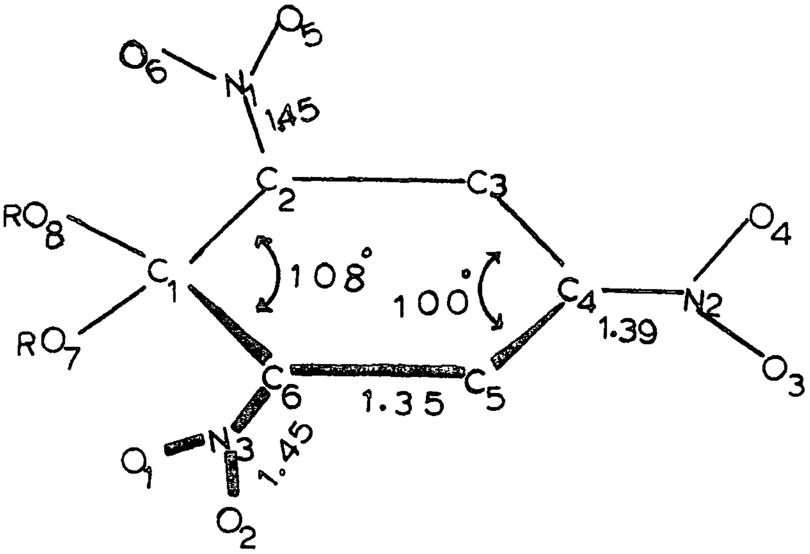
$$\frac{1}{K\epsilon_c}\frac{1}{[Nu]_{st}} + \frac{1}{\epsilon_c} = \frac{[P]_{st}}{O.D} \qquad 1.19$$

where $[P]_{st}$ is the stoichometric concentration of parent.

So the slope (from equation 1.19) of $\frac{[P]_{st}}{O.D}$ versus $\frac{1}{[Nu]_{st}}$ plot gives the thermodynamic equilibrium constant. Usually this equation is applied when the extinction coefficient is not known. Linearity of Benesi-Hildebrand plots doesn't necessarily mean that only one coloured species is present[140].

(iii) Crystallography

Crystallographic studies have confirmed the Meisenheimer complexes structures obtained using N.M.R. and infra-red spectroscopy.



1.59

Crystallographic investigation has been carried for some picryl ether adducts[95,96]. The main features from X-ray crystallographic, can be summarised in the following points (1.59).

* C4 - N2 bond is shorter than C2 - N1 and C6 - N3 bonds which supports the fact that a large proportion of negative charge is localized on oxygen atoms of the NO_2 group para to C1.

* The plane containing the two alkoxy groups in perpendicular to the aromatic plane.

- The length (1.42Å) of the C1-O8 and C1-O7 bonds in the alkoxide groups is close to that observed in aliphatic ethers and is much greater than that in 2,4,6-trinitrophenetole where delocalization of an oxygen ion pair into the aromatic ring occurs.

* The C6 - C1 - C2 bond angle is 109°, very close to the tetrahedral angle required for an sp^3 hybridization.

(iv) Infra-red Spectroscopy

The infra-red spectra of σ-complexes have been studied. Spectra for picryl ethers show bands typical of ketals supporting the Meisenheimer complex structure. The nitro group has characteristic strong absorption frequencies, and can be distinguished in the substrate or complex where they carry more negative charge[131-133]. Analysis of i.r spectra is not an easy matter. The difficulties are[103] : overlapping of other bands, overtones (harmonics) may shift the frequency of the original band and a shift with incorrect identification of the band may result from hydrogen-bonding, conjugation and other structural features.

Relative Stabilities of Meisenheimer Complexes

(A) Variation of nature of parent molecule

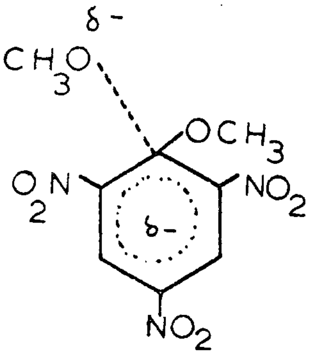
It is usually found that alkoxide addition at un-substituted positions of nitro-activated aryl ethers is kinetically favoured but that alkoxide addition to the ring carbons carrying the alkoxy group leads to a thermodynamically more stable adduct. One explanation for this effect is in terms of steric factors[95,97]. In alkyl picrate parent molecules, the alkoxy groups are in the ring plane, and rotations up to 61.3° have been observed for an ortho nitro group. The two alkoxy groups in 2,4,6-trinitro-1,1-dialkoxy benzene adduct are out of the ring plane, thus relieving the steric strain implemented by the flanking ortho nitro group[95]. The nitro groups are planar with ring in the di-alkoxy picrate adduct.

TABLE 1.1

Stability of complexs with methoxide ions in methanol at 25°C.

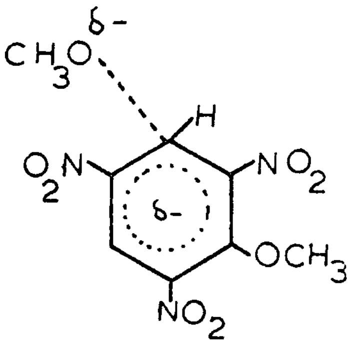
(Parent)	$k_{forward}$ (l $mol^{-1}s^{-1}$) [1:1]	Keq (l mol^{-1})	[1:2] Keq (l mol^{-1})	[1:3] Keq (l mol^{-1})	Ref
1,3,5-Trinitrobenzene	-	15.4			98
2,4-Dinitroanisole	2.1×10^{-3}	5×10^{-5}			99
2,4,6-Trinitroanisole	17.3	17,000	1.3×19^{-4}	10^{-5}	100
2,4-Dinitrobenzene	-	5×10^{-7}			14
2,4-Dicyano-6-nitro anisole	2.0	10			101
2,6-Dicyano-4-nitro anisole	34	12			101
N,N-dimethyl picramide	-	7			52
Picramide	-	38			52

Steric factors will be less important for alkoxide additions to 1,3,5-trinitrobenzene and 1,3-dinitrobenzene. Addition of an alkoxide ion at C-3 in activated anisoles is kinetically preferred relative to addition at C-1 despite the fact that C-1 complex is less strained than the parent compound. The transition state leading to C-3 (1.61) complex is less strained than transition state leading to C-1[46] (1.60).



(1.60)

Transition State leading to C-1 adduct formation.



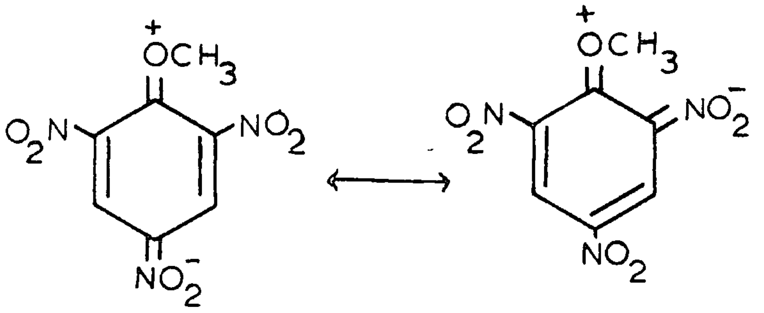
(1·61)

Transition State leading to C-3 adduct formation.

The higher stability of the 1:1 trinitroanisole complexes is due to release of steric strain in the parent and to the inductive effect of the methoxy group.

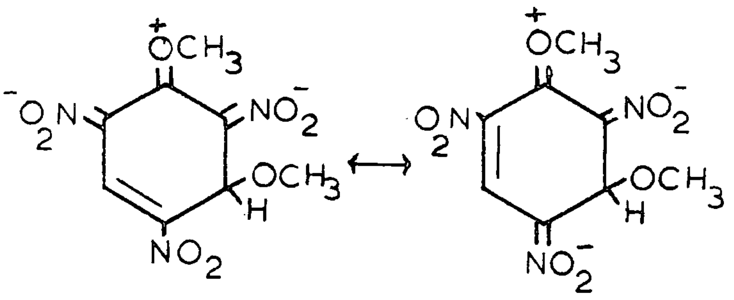
The stabilisation of sp^3 hybridised carbon atoms by multiple alkoxy substitution may also be an important factor.

The ground-state resonance stabilisation for the parent 2,4,6-trinitroanisole can be represented by: (equation 1.20).



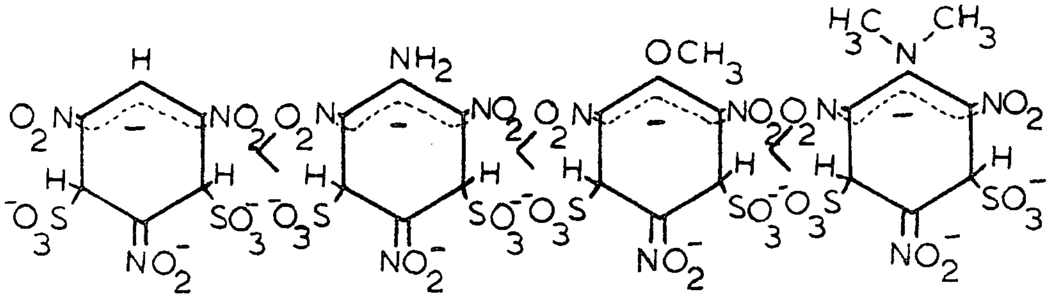
....1.20

The 1,3-complex can also benefit from resonance stabilisation involving the methoxy groups as shown in equation 1.21.



....1.21

However addition at C-1 results in the loss of such resonance stabilisation. This will tend to reduce the rate of 1,1-complex formation compared to the rate of 1,3-complex formation from trinitroanisole and also relative to alkoxide addition to trinitrobenzene[102]. The data in the Table 1.1 demonstrates the importance of the presence of a strong electron withdrawing group para to the position of addition also in stabilising Meisenheimer complexes. The more the ring current is delocalized the more stable is the complex[32]. Measuring the stabilities of di-adducts (propenide complexes) is not an easy task due to the high concentrations of nucleophile usually required. Such equilibrium constants are strongly dependent on ionic strength, so extrapolation to infinite dilution is necessary in this case. The stability of di-adducts formed from 1-substituted 2,4,6-trinitrobenzenes increases with increasing size of the 1-substituent (1.62 - 1.65). This may be attributed to the increasing release of steric compression between the 1-substituent and the two ortho nitro groups[32].



(1.62) (1.63) (1.64) (1.65)

⟶

Increase of stability

(B) Variation with attacking nucleophile

Definitions of some terms relating to this subject are given below.

(i) Carbon basicity[35,112]

Is a measure of the thermodynamic affinity of nucleophiles for an aromatic carbon atom in the parent molecule.

(ii) Bronsted basicity

Is a measure of the thermodynamic affinity of nucleophiles for protons.

Accordingly, the values of the equilibrium constants in the table 1.2 give a measure of the carbon basicities of the nucleophiles.

TABLE 1.2

Equilibrium constants for formation of adducts from 1,3,5-Trinitrobenzene with various nucleophiles.

Nucleophile	Solvent	K, ($l\ mol^{-1}$)	Ref.
OMe^-	Methanol	1.54×10^1	98
SEt^-	Methanol	3.50×10^3	37
SPh^-	Methanol	1.95	37
OPh^-	Methanol	$< 2 \times 10^{-3}$	37
OMe	D.M.S.O.	$\sim 10^9$	37
SPh^-	D.M.S.O.	8×10^4	37

The order of carbon basicity in methanol is:

$EtS^- > OMe^- > PhS^- > PhO^-$

While the order of Bronsted basicity is

$OMe^- > EtS^- > PhO^- > PhS^-$

These quantities depend on the nature of the solvent. The mode of interaction may depend on the nature of the nucleophile. Thermodynamically, stable adducts of 2,4,6-trinitroanisole are formed with OMe^-, N_3^- or NEt_2^- by addition at C-1. While, with the same substrate, addition at the unsubstituted carbon C-3 is observed with nucleophiles such as SO_3^{--} or $CH_3.CO.CH_2^-$. This may be attributed to steric strain associated with having two bulky groups attached to the same carbon atom[11]. Another example is the ionization of the activated N-substituted picramides. Sulphur bases like SEt^- or SPh^- form addition complexes at unsubstituted ring carbon[37].

While alkoxides (OMe^-) abstract an amino proton or add to unsubstituted ring carbon[55].

(C) Solvent Effect:

Defining[103] some terms in connection with this subject.

Dipolar Aprotic Solvents:

Polar solvents of moderately high di-electric constants, which don't contain acidic hydrogen, such as D.M.S.O. and sulfolane. These solvents are able to dissolve ionic compounds, by solvating cations most strongly, and leaving anions relatively un-encumbered and highly reactive.

Protic Solvents:

Are acidic due to the hydrogen attached to oxygen or nitrogen, such as water and alcohols. Through hydrogen-bonding such solvents tend to solvate anions particularly strongly, thus reducing their nucleophilic power.

Accordingly, solvents may have large effects on the stability of Meisenheimer complexes. Generally cations, polar molecules, and large polarisable anions such as σ-adducts, are better solvated by dipolar aprotic solvents than by protic solvents. In protic solvents only small anions (strong hydrogen-bond acceptors) are well solvated. Hence equilibrium constants for σ-adduct formatin are generally enhanced on transfer from protic to dipolar aprotic solvents.

TABLE 1.3[101]

Interaction of 2,6-Dicyano-4-nitroanisole with Sodium methoxide in D.M.S.O-methanol solvent.

DMSO, M	K, l mole^{-1}
0	33.5
1.41	77.0
2.82	221
4.23	695

It is found that on increasing the amount of DMSO in the solvent there is an increase in value for the rate constant (k_1)[101] for the formation of the complex: sodium-1,1-dimethoxy-2,4-dicyano-6-nitro cyclohexadienate, and a decrease in complex decomposition rate constant (k_{-1}). Desolvation of the methoxide ion as D.M.S.O. concentration is increased leads to an increase in k_1. The formed Meisenheimer complex (highly polarisable) is well solvated by D.M.S.O., leading to a decrease in k_{-1} value. It has been noticed[46] that the formation of 1,1-adduct (from sodium methoxide and 2,4,6-trinitroanisole) is catalysed by increasing the concentration of methanol and methoxide. Meanwhile increasing D.M.S.O. concentration stabilises the initial C-3 adduct. In early seventies[105-107] the change in enthalpy was measured for the reaction of 2,4,6-trinitroanisole with sodium methoxide. The heat of formation of the 1,1 adduct, formed from 1,3,5-trinitrobenzene and sodium thiophenoxide ($C_6H_5S^-Na^+$) has also been measured in solvent mixtures of D.M.S.O. and methanol. The enthalpy of transfer for sodium methoxide from pure methanol to 95% DMSO - 5% methanol (v/v) solvent mixture is equal to ΔH 10 kcal/mole, while for sodium thiophenoxide in the same system, the enthalpy change is equal to ΔH 0.94 kcal/mole. The values of ΔH for transfer of the adducts formed are similar and have values of ca - 7 kcal/mole^{-1}.

From previous studies[106,107], it has been argued that the stabilisation of the methoxide ion due to hydrogen-bonding decreases as the amount of D.M.S.O. increases. However the Meisenheimer complex is stabilised much more in D.M.S.O. than is the parent, and the heat of transfer of the adduct from methanol to D.M.S.O. becomes more exothermic as D.M.S.O. concentration increases. The observed negative entropy arises from the increased solvation of the complex corresponding to the starting materials. (An entropy loss will arise because of a decrease in the number of species from two reactants to one adduct and/or from increased solvation of the adduct). From this study in which ion-pairing is of low importance, enthalpies and entropies for complex formation become more negative as the alcohol becomes less polar.

A study[108] for the reaction of 1,3,5-trinitrobenzene with cyanide ion in different alcoholic solvents revealed smaller value for K in methanol (40 l/mole) compared with that in t-butanol (5×10^5 l/mole). Enthalpy changes vary from zero in methanol to -15.5 k cal/mole^{-1} in t-butanol, while entropy changes decreases from +7 in methanol to -26 cal deg^{-1} mole^{-1} in t-butanol. This has been attributed to the desolvation of cyanide ion, as t-butanol solvates the cyanide ion to a limited extent. In contrast methanol is a good solvating solvent for the small cyanide ions. In alcohol-water mixtures[109] a rapid equilibrium between hydroxide and alkoxide ions is reached according to the chemical equation 1.22.

$$OH^- + ROH \rightleftharpoons RO^- + H_2O \qquad 1.22$$

Generally, such equilibrium studies have been neglected, one of the main reasons was that the reactivity of hydroxide ion with many substrates are low compared with some alkoxide ions. Although, according to the present work the presence of traces of water in some alcohols has a large effect on the kinetics of some σ-complex forming reactions.

Danil de Namur[110] found that the free energy of simple cations and anions increases along the series of the following alcohols:

$$\text{MeOH} < \text{EtOH} < \text{1-PrOH}$$

(D) Acidity Functions

The breakdown of the pH scale as a useful measure of acidity for solutions whose ionic strength is greater than 0.1 m leads to the necessity for some other quantitative scale which expresses the acidity of more concentrated solutions. Taking this into consideration, Hammett and Deyrup[113] suggested in 1932 a scale using spectrophotometric techniques, to measure the ability of the acid solution to protonate a neutral solute species (or indicator). The equilibrium is of type equation 1.23.

$$B + H^{+} \rightleftharpoons BH^{+} \qquad 1.23$$

The acidity function was defined by equation 1.24

$$Ho = pK_{BH^{+}} - \log_{10} \frac{[BH^{+}]}{[B]} \qquad 1.24$$

where $pK_{BH^{+}}$ is the acid dissociation constant for BH^{+} (conjugate acid of B) and $\frac{[BH^{+}]}{[B]}$ is the concentration ratio for the indicator after and before the protonation. Spectrophotometry provides a dependable means for the determination of the indicator ionisation ratios and the conjugate base dissociation constant. The evaluation of $pK_{BH^{+}}$ follows directly from knowledge of $(\frac{BH^{+}}{B})$ as a function of acid concentration as described in the equation 1.25

$$pK_{BH^{+}} = -\log_{10}\left(\frac{[B]\ f_{B}}{[BH^{+}]\ f_{BH^{+}}} \cdot a_{H^{+}} \right) \qquad 1.25$$

At infinite dilution, all activity coefficients tend to unity giving equation 1.26

$$pK_{BH^{+}} = \log_{10} \left(\frac{[BH^{+}]}{[B]}\right) - \log_{10} [H^{+}] \qquad 1.26$$

The knowledge of $pK_{BH^{+}}$ provides the correct thermodynamic dissociation constant $K_{BH^{+}}$ referred to pure solvent as standard state.

The H_{-} acidity function measures the ability of the strongly basic solution to abstract a proton from the weakly acidic neutral solute SH, and is defined by[114,115] equation 1.27 and 1.28

$$SH + OH^- \rightleftharpoons S^- + H_2O \qquad 1.27$$

$$H_- = pK_{SH} + \log_{10}\frac{[S^-]}{[SH]} \qquad 1.28$$

The measurement of an H_- scale involves the determination of pK_{SH} and the variation of log $\frac{[S^-]}{[SH]}$ with increasing hydroxide ion concentration for a weakly acidic neutral indicator SH. The ratio ($[S^-]/[SH]$) is measured by electronic absorption spectrophotometry, a method which is used under two conditions. The neutral acid SH and its conjugate base S^- must have measurably different absorption spectra, and the extinction coefficient of either SH or S^- at the selected wavelength of study must be such that the concentration of indicator necessary for measurable absorption changes has negligible effect on the overall acidity of the medium. One of two methods to determine pK_{sh} are followed; the first is an extrapolation of, $\log_{10}\frac{[S^-]}{[SH]} - \log_{10}[MOH]$ versus MOH , to zero concentration of MOH, giving a value for the intercept of $pK_w - pK_{SH}$[114]. The ionization ratio $\frac{[S^-]}{[SH]}$ can be found by the relation equation 1.29

$$\frac{[S^-]}{[SH]} = \frac{D - D_{SH}}{D_{S^-} - D} \qquad 1.29$$

From a series of base concentrations for a fixed SH, D_{SH} is the optical density in dilute base solution, D_{S^-} is the optical density at very concentrated base solution and D refers to some intermediate acidity. Here the presence of isobestic points is a good test for the reliability for the direct calculation of the ratio $\frac{[S^-]}{[SH]}$.

It has been found[116] that more acidic indicators give linear plots of $\log_{10}\frac{[S^-]}{[SH]} - \log_{10}[MOH]$ versus $[MOH]$, where less acidic indicators give curved plots, because of shifts in wave lengths due to medium effects. In the latter case, the second method of stepwise comparison, should be used. This method[117,118] is simply the mean of ionization ratios at n studied wavelengths and is given by the equation 1.30

$$\frac{[S^-]}{[SH]} = \frac{1}{n} \sum_{j=1\rightarrow n} \left(\frac{D - D_{SH}}{D_S - D} \right)_{\lambda j} \qquad 1.30$$

The H_M acidity function for methanol is defined by the equation 1.31

$$H_M = pK^{M}_{SH} + \log_{10} \frac{[S^-]}{[SH]} \qquad 1.31$$

where pK^{M}_{SH} is the dissociation constant of indicator SH in methanol. Because[70] of the low dielectric constants of the alcohols ion-association is important even at low concentrations of base. Not surprisingly therefore the trend in basicity as a function of the metal cation is more pronounced than in water-hydroxide media although the order is:

$$H_M(KOMe) > H_M(NaOMe) > H_M(LiOMe)$$

The J_- acidity function is defined by the equation 1.32 and 1.33

$$R + OH^- \rightleftharpoons ROH^- \qquad 1.32$$

$$J_- = pKK_w + \log_{10}\left\{ \frac{[ROH^-]}{[R]} \right\} \qquad 1.33$$

in which K is the equilibrium constant for the addition of OH^- ions to an electrically neutral indicator molecule R[117,119].

Rochester[120] defined a J_M acidity function for methanolic sodium methoxide referring to pure methanol as standard state as equations 1.34 and 1.35.

$$R + OMe^- \rightleftharpoons ROMe^- \qquad 1.34$$

$$J_M = p(KK_{MeOH}) + \log_{10} \frac{[ROMe^-]}{[R]} \qquad 1.35$$

where pK_{MeOH} is the autoprotolysis constant for methanol and K is the thermodynamic equilibrium constant for methoxide addition to the neutral indicator species R. Similar treatment for J_M as in case of H_- are usually followed.

Crampton[121] et al. measured J_M acidity function for methanol - D.M.S.O. mixtures using nitro-activated anisoles as indicators. They used the concept of J_M acidity function to calculate the thermodynamic equilibrium constant (K_1) for sodium methoxide addition in methanol to some X-substituted dinitroanisoles to form Meisenheimer complexes as given in the equation 1.36

$$J_M = pK_1K_{MeOH} + \log_{10}\frac{[\text{complex}]}{[\text{parent}]} \qquad 1.36$$

(where $pK_{MeOH} = 16.92$)[116]

ION-ASSOCIATION

1. Introduction[122,123]

Twenty years ago ion pairs were not thought to be an important factor in reaction kinetics, now no detailed mechanism is drawn up without recognising ion association. The Bronsted-Bjerrum equation:

$$\log_{10}k = \log k_o + 2Z_AZ_BA\sqrt{\mu} \qquad 1.37$$

[where k_o is the rate at infinite dilution ($k = k_o\frac{f_Af_B}{fc}$). Z_A and Z_B are the charges of reacting species A and B. For water as solvent $A = 0.509\ \text{mol}^{-\frac{1}{2}}\ \text{dm}^{-\frac{3}{2}}$ at 25°c, and μ is the ionic strength of the medium] is not always successful due to ion-association.

For instance a centrally charged sphere will be an unsatisfactory model for a large organic ion with more than one polar group. Ion-association can affect reaction kinetics in a variety of ways, it will lead to a reduction of the ionic strength, if reactants are involved, drastic influences on the rate will be observed, further the associated ion may influence the reactivity of the reacting species. Ion-pairing will be mostly important when the dielectric constant of the medium is low, when ions have high charge, and if ions are present at high concentration. Because of the low dielectric constants of alcohols relative to water, ion association would be expected to play a more important part in reaction kinetics investigation in these media. Acidity function measurements[120,124] of concentrated alkoxide solutions show that for a given concentration:

$$H_M(\text{KOMe}) > H_M(\text{NaOMe}) > H_M(\text{LiOMe})$$

this order being the same as for the corresponding hydroxide and attributable to ion association.

2. Ion-pairing relation with rate constants

Crampton and Khan[125] have suggested that the variation of equilibrium constant with alkoxide concentration, for σ-complex formation, is partly due to ion-association, and that this is more marked between the cation and the anion "Meisenheimer adduct" than between the cation and alkoxide ion. Crampton [126] proposed a model (Scheme 1.11) accounting the effect of ion-pairing in formation of Meisenheimer adducts equation 1.38.

$$\begin{tikzcd}
P + OR^- + M^+ \arrow[r, shift left, "k"] \arrow[d, shift left] & P.OR^- + M^+ \arrow[l, shift left, "k_-"] \arrow[d, shift left] \\
P + M^+, OR^- \arrow[u, shift left, "K_{M+,OR^-}"] \arrow[r, shift left, "k_{ip}"] & P.OR^-, M^+ \arrow[l, shift left, "k_{ip}"] \arrow[u, shift left, "K_{M+,P.OR^-}"']
\end{tikzcd}$$

M^+ = metal cation (univalent).

P = Parent molecule.

OR^- = Alkoxide anion.

Scheme 1.11

$$K_c = \frac{[P.OR^-] + [P.OR^-,M^+]}{[P]\,([OR^-] + [M^+,OR^-])} \qquad 1.38$$

The activity coefficients have been implemented in this model in the following way: assuming $[OR^-] > [P.OR^-]_{total}$. The degree of dis-association of metal alkoxide ion pairs is evaluated by equation 1.39.

$$K_{M+,OR^-} = \frac{(1 - \alpha)}{\alpha^2 y^2 [OR^-]_{stoich}} \qquad 1.39$$

where y is the mean activity coefficient for free ions and is related to the overall concentration of alkoxide by a modified Debye-Huckel equation, equation 1.40

$$-\log y = \frac{A(\alpha[OR^-]_{stoich})^{\frac{1}{2}}}{1 + Bq(\alpha[OR^-]_{stoich})^{\frac{1}{2}}} \qquad 1.40$$

where $q = \frac{e^2}{2DkT}$ (Bjerrum critical distance).

(A and B are Debye-Huckel parameters).

($A \approx 2.319$, $B = 5.907\ mol^{-1}dm^3nm^{-1}$ and $q = 1.153$ nm for ethanol system).[127] The two unknowns α and y were evaluated from equations 1.39 and 1.40, by iteration. Inserting the activity coefficients in equation 1.38 we obtain equation 1.41

$$K_c = \frac{K(1 + [M^+]y^2K_{M^+,P.OR^-})}{1 + [M^+]y^2 K_{M^+,OR^-}} \qquad 1.41$$

where $K = \frac{k}{k_-}$ (scheme 1.11).

The variations with metal ion concentration with the forward, k_f, and reverse, k_r, rate coefficients are given by equations 1.42 and 1.43

$$k_f = k\alpha + k_{ip}(1-\alpha) \qquad 1.42$$

$$k_r = \frac{k_- + [M^+]y^2k_{-ip}K_{M^+,POR^-}}{1 + [M^+]y^2K_{M^+,POR^-}} \qquad 1.43$$

where $k_{obs} = k_f[MOR]_{stoich} + k_r$ 1.44

3. Importance of ion association

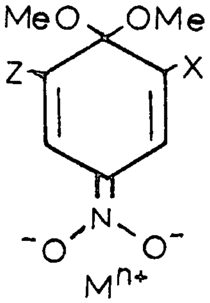
Crampton and Khan[126] found that addition of sodium salts caused an increase in value of the equilibrium constant, K_c, indicating that

$K_{M^+,P.OR^-} > K_{M^+,OR^-}$ (see scheme 1.11)

They found that association constants of Meisenheimer complexes (formed from 2,4,6-trisubstituted anisoles with some metal methoxies, barium and calcium[126] salts) with cations decrease in the order:

$$Ba^{2+} > Ca^{2+} \gg Na^{+} \sim K^{+} > Li^{+}$$

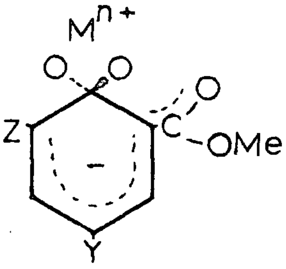
Lithium ions have little tendency to associate with the studied Meisenheimer complexes due to their strong solvation. Speculating about the structure of the ion associates produced we have the following possibilities:



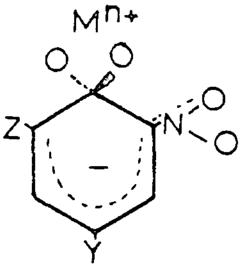
(1.66)

where metal ion associates strongly with the nitro group (1.66). Similar association occurs when other electronegative substituent such as CO_2Me, at the positions para-ortho to addition.

The small tendency[126] of 1,3,5-trinitrobenzene adduct to associate relative to the anisole adduct has been explained by the cage effect, where the cation is being held by the oxygen atoms around the position of addition. The ortho - CO_2Me group provides better stabilisation than ortho - NO_2 group (1.67) and (1.68).



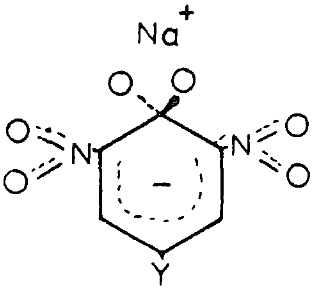
(1.67)



(1.68)

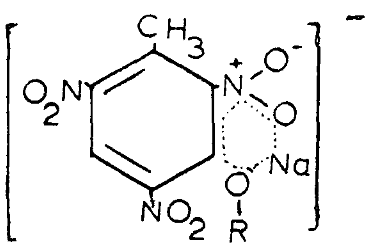
It has been found[125,128] that the methoxide adduct of 1,3,5-trinitrobenzene and also spiro-Meisenheimer complexes show no evidence for association with cations in methanol. The interaction thus appears to be specific to 1,1-dimethoxy-complexes[129].

As shown in (1.69) four oxygen atoms are available for complexing



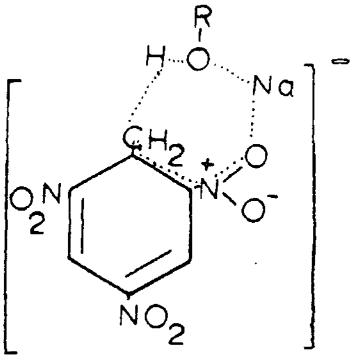
(1.69)

Buncel and co-workers [44] have compared the efficiencies of free anions and of ion-pairs in σ-complex forming reactions and in proton-transfer reactions (e.g. 2,4,6-trinitrotoluene). The ion-pair may be more effective in σ-complex formation than in proton transfer. For instance in the case of T.N.T. which is described by (1.70) and (1.71).



6-membered structure

(1.70)



8-membered structure

(1.71)

Here, a six-membered cyclic transition state should be much more favourable than the eight-membered structure. The dependence of the equilibrium constant for formation of a Meisenheimer adduct on base concentration has been interpreted in terms of ion-pairing effects. In the previous[126,127] and present work, the 1:2 complexes appears to undergo specific ion pairing effects with cations, What made ion-association an important effect is the nature of the solvent especially when they have low dielectric constants.

Recent kinetic study[130] of the reaction of 4-nitrobenzenefuroxan with isopropoxide ion in isopropanol showed that plots of k_{obs}, for σ-complex formation, versus (i_PrO^-) are linear indicating surprisingly that ion-pairing effects are not a problem at the concentrations of base employed in these studies.

CHAPTER 2

EXPERIMENTAL

I Solvents :

water:	Distilled water was boiled to remove carbon dioxide and subsequently protected from the atmosphere with soda lime guard tube.
n-propanol:	A.R propanol (n-propyl alcohol) was used without purification.
t-butanol:	A.R methyl isopropyl alcohol was used either as supplied or was dried over[143,144] potassium or molecular sieve and fractionated, or was dried by fractional recrystallisation[145]. The dried alcohol was stored in a desicator containing silica gel.
methanol:	A.R methanol was used without purification.
Dimethyl-sulphoxide:	A purified solvent was available, thanks to Dr. B. Gibson. The commercial solvent was dried with calcium hydride and fractionated under reduced pressure. The middle fraction was collected and stored in a desicator containing silica gel.

II Solution of bases :

sodium hydroxide:	Standard solutions of Analar sodium hydroxide were used after checking the concentration by titration with standard hydrochloric acid.
Potassium hydroxide:	Standard solution of Potassium hydroxide were used after titration with standard hydrochloric acid.

Tetra methyl ammonium n-propoxide:	Was prepared by diultion of concentrated tetramethylammonium hydroxide in water with n-propanol. The solution was then titrated with standard hydrochloric acid. This prepared solution contained small concentrations of water. In very dilute solutions no unwanted effects were observed from this source although in solutions containing 0.02 mol 1^{-1} base where 0.8% water is present a slow side reaction giving the corresponding phenol was observed, notably in the reaction of 1-propoxy-2, 4-dinitro-6-propoxy carbonyl benzene.
Tetramethyl ammonium t-butoxide:	Was prepared by diluting the concentrated tetramethylammonium hydroxide in water with t-butanol. The tetramethyl ammonium hydroxide is less soluble in t-butanol than in n-propanol. The diluted solution was titrated with standard hydrochlocic acid.
Tetra ethyl ammonium t-butoxide:	Was prepared by diluting concentrated tetra ethyl ammonium hydroxide in water with t-butanol. The prepared solution was titrated with standard hydrochloric acid.
sodium propoxide:	Was prepared by dissolving clean sodium in Analar n-propanol under nitrogen and was titrated with standard hydrochloric acid.
sodium t-butoxide:	Clean sodium was dissolved in warm Analar t-butanol. The base was then titrated with standard hydrochloric acid and stored in a warm place.
potassium t-butoxide:	Clean potassium was dissolved in warm Analar t-butanol, then titrated with standard acid and stored in a warm place.

sodium methoxide: Was prepared by dissolving clean sodium metal in Analar methanol in a nitrogen atmosphere. The cloudy solution was centrifuged until a clear solution was obtained. The base was titrated with standard sulphuric acid.

Potassium methoxide: The freshly cut pieces of potassium metal were dissolved in Analar methanol under nitrogen. The cloudy, solutions were centrifuged and titrated with standard sulphuric acid.

Lithium methoxide: The freshly cut pieces of lithium metal washed then dissolved in a warm Analar methanol. The cloudy solutions were centrifuged and titrated with standard sulphuric acid.

III Salts : used to maintain constant ionic strength.

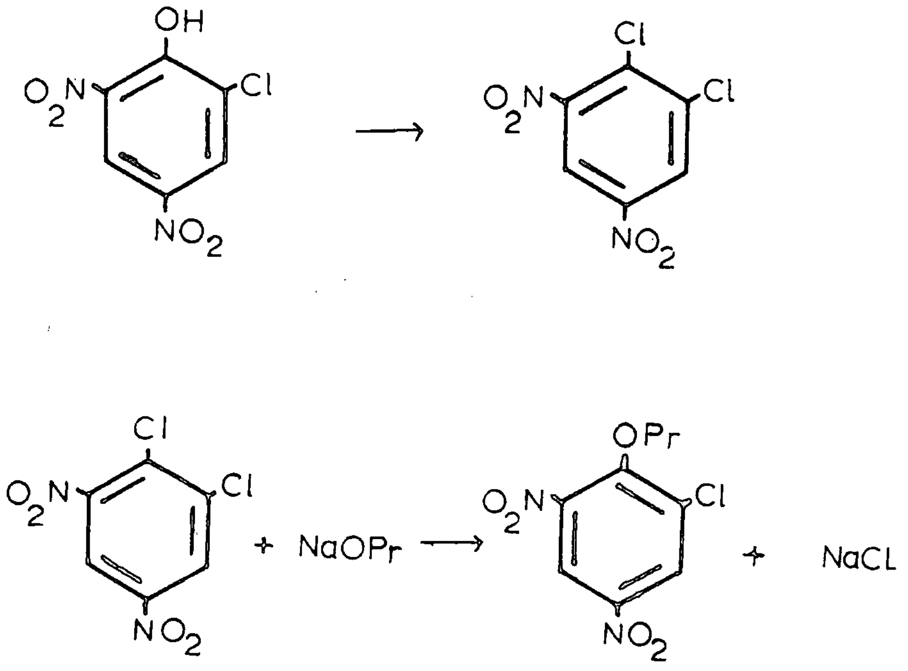
sodium tetraphenyl boron: A dried A.R grade reagent from BDH.

Sodium perchlorate: A.R grade reagent which was dried under vacuum before use.

IV Nitro compounds :

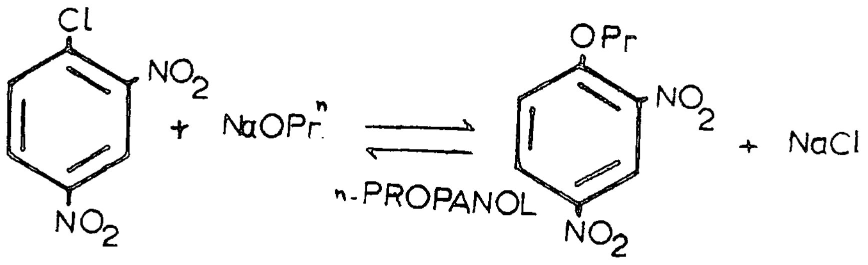
1,3,5-Trinitrobenzene: A recrystallised commercial 1,3,5-Trinitrobenzene was available and was used without further purification (m.p 122°C, lit[150] m.p 122.5°C).

1-propoxy-2,4-dinitro 6-chlorobenzene: The preparation was started with 1,2-dichloro-4,6-dinitrobenzene (m.p 56°C) which was prepared by Dr. H. Khan[146] following the method of Ullman and Sane[147], by chlorinating 2-chloro-4,6-dinitrophenol 3.5 grams of 1,2-dichloro-4,6-dinitrobenzene was dissolved in a hot n-propanol and one equivalent of soidum propoxide was added with stirring. The reaction mixture was heated on a water bath for two hours, allowed to cool then acidified with dilute hydrochloric acid, when the required ether separated as a pale "brown" oil. This was separated and solidified by addition of solid CO_2 (dry ice), then re-crystallised from n-propanol to give yellow crystals (mp. 40°C). ^{1}H.n.m.r confirmed the product's structure. Equations describe this reaction as follows:

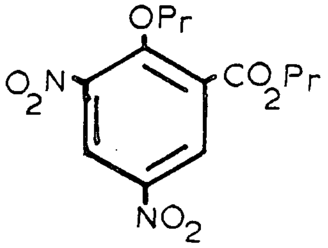


<u>1-propoxy-2,4-dinitro benzene:</u>

10.1 grams of 1-chloro-2,4-dinitrobenzene (m.p 53°C, lit[148] m.p 53°C) were dissolved in the least amount of n-propanol with heating (∿ 50°C). After the halobenzene had dissolved, one equivalent of sodium propoxide was slowly added. A deep brown colour was formed. After this addition the mixture was heated for about 30 minutes (during which the solution became transparent). The flask was allowed to cool. An excess amount of distilled water was added, followed by acidification with a small amount of HCl. The required product appeared as oily drops, which were separated. Crystallisation from n-propanol gave a product with (m.p 31°C, lit:[149] m.p 30.7 - 31.2°C). ^{1}H.n.m.r showed band consistent with the required compound and indicated the absence of impurities. This preparation is described by the equation:



1-propoxy-2,4-
dinitro-6-propoxy
carbonyl benzene:



Was prepared from 2-chlorobenzoic acid in three stages:

(a) 41 grams of 2-chlorobenzoic acid and 198 mls of conc. sulphuric acid (d = 1.84) were placed in a two litre round bottomed flask and warmed on a heating mantle with mechanical stirring, until the benzoic acid dissolved. 66 mls of fuming nitric acid was added with stirring and the mixture was allowed to stand for an hour. (The sulphuric acid and fuming nitric acid were both added slowly). A solid mass accumulated on the surface. The mixture was heated at 90° - 100°C for three hours, allowed to cool down and 50 mls of more fuming nitric acid (sp. gr 1.54) was added with stirring and the reaction mixture was then heated at 100 - 110°C for a further three hours. (It is important to keep the temperature in the range mentioned above, taking into account that this reaction process is an exothermic one). The mixture was allowed to stand overnight and was then poured onto crushed ice. The resulting solid was filtered off and pumped, washed with distilled water and dried (m.p 199°C, lit[150] m.p 199°) giving white crystals.

(b) 42 grams from the resulting 3,5-Dinitro-2-chlorobenzoic acid was dissolved in 325 mls of warm n-propanol and 23 mls of conc. sulphuric acid "d = 1.84" was added.

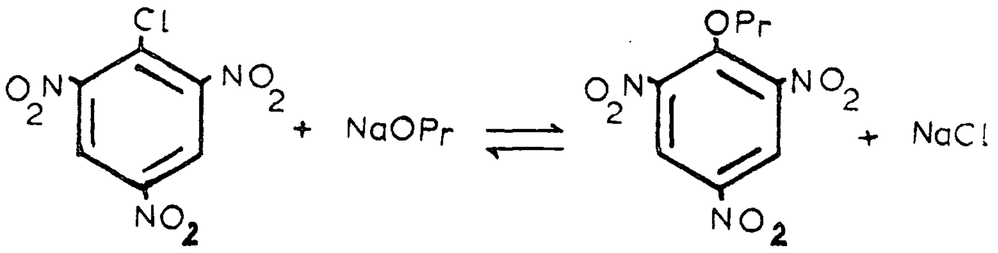
The mixture was then heated on a water bath for an hour and then allowed to cool, when the propyl ester of the acid separated as a crystalline solid. This was filtered and washed with aqueous sodium bicarbonate then water, and recrystallised from n-propanol (m.p : 45 - 46°C).

(c) The propyl ester of 2-chloro-3,5-dinitrobenzoic acid obtained above was subjected to nucleophilic replacement of chlorine by reaction with one equivalent of sodium propoxide, and the resulting compound was crystallised from n-propanol (m.p 38°C).

The ^{1}H.n.m.r sepectra showed bands consistent with the required compounds indicating the absence of impurities.

It is of interest to mention that a literature search indicated that the final product had not been previously prepared.

<u>1-propoxy-2,4,6-trinitrobenzene:</u> Was prepared by reaction of picryl chloride with sodium propoxide.



13.1 grams of picryl chloride was dissolved in the least amount of n-propanol with heating (50°C). After all the picryl chloride had dissolved, 66 mls of (0.805 M) sodium propoxide was slowly added. A dark colour formed. The mixture was heated for half an hour then cooled down. A 20 cm^3 portion of this solution was added to 100 cm^3 of distilled water, and a white precipetate quickly formed. An excess of distilled water was added to the main bulk of the solution followed by acidification with small amount of HCl. The product separated as an oil which was crystallised from n-propanol. The final product had (m.p 41°C, lit:[4]43°C).

Picrylchloride:	Recrystallised commercial specimen (m.p 82°C, lit[148]: m.p 83°C).
Picric acid:	Recrystallised commercial specimen (m.p 122°C, lit[148]: m.p 122 - 123°C).
2,4-dinitrophenol:	Recrystallised commercial specimen (m.p 113°C, lit[148]: m.p 115 - 116°C).
1,3-dinitrobenzene:	Recrystallised commercial specimen (m.p 90°C, lit :[148]m.p 90.02).

1-chloro-2,4-dinitrobenzene:	Recrystallised commercial specimen (m.p 50°C, Lit :[148] m.p 53°C).
6-methoxy-2,5-dinitro benzoic acid:	Recrystallised sample prepared in previous work[146]. (m.p 110°C, lit :[150] m.p 112°C).
2,4,6-Trinitroanisole:	Recrystallised sample prepared by Dr. M.A. El-Ghariani (m.p 77°C, lit : m.p 68°C)[150]
2,4,6-Trinitroaniline: (picramide)	Recrystallised sample prepared in previous work[152]. (m.p 195°C, lit:[150] m.p 192 - 195°C).
N,N-dimethyl picramide:	Recrystallised sample prepared in previous work[152]. (m.p 139°C, lit :[150] m.p 138°C).
1-(2-Hydroxy ethoxy)-2,4,6-trinitrobenzene:	Pale yellow crystalls prepared by Dr. M.J. Wilson[153]. (m.p 62°C, lit :[154] 61°C).
N-methyl picramide:	Recrystallised sample prepared in previous work[152]. (m.p 116°C, lit :[150] 115°C).

V Spectroscopic measurements :

Visible spectra

Optical density measurements, for use in the measurements of rates of slow reactions or for determination of equilibrium constants, were measured on an SP500 spectrophotometer using matched silica cells of 10 mm path length. The temperature in the cells was maintained constant at 25°C by circulating water from a constant temperature bath through a specially designed cell holder in the spectrophotometer. The recording instruments, Unicam SP8000, Beckman S25 and Pye-Unicam SP8-100 were used at 30 ± 1°C. The technique usually used was to allow the solvent containing base to come to thermal equilibrium in the cell compartment before adding the parent solution.

The stock solutions were made up immediately before taking measurements. In some cases complete conversion of the parent substrate to complex could be achieved in the basic media used. In these cases the extinction coefficient ε_M of the complex could be found directly by using Beer's Law:

$$\text{Optical density} = \log_{10} \frac{I_o}{I} = \varepsilon_M.C_M.1$$

where C_M is the complex concentration, which could be determined in less basic solutions. Otherwise the Benesi-Hildbrand expression was used as discussed in the previous chapter. Kinetic measurements for fast rates at 25 ± 0.1°C (30 ± 0.5°C for t-butanol solutions) were made with a Canterbury stopped-flow spectrophotometer. The rate constants of first order reactions, where $[\text{base}] > [\text{Substrate}]$, were calculated by standard methods and were reproducible within 5%.

Proton magnetic resonance spectroscopy :

^{1}H.n.m.r spectra were measured with a Bruker 90 MHz (HX 90E) instrument. Measurements were usually made at ambient probe temperature (25 ± 1°C). Tetramethylsilane (TMS) was used as an internal reference. DMSO or DMSO-d_6 were used as solvents with the alcoholic alkali solutions in the n.m.r. tube.

Stopped-flow spectroscopy :

The "Canterbury" instrument was developed by Caldin and co-workers[155].

Monochromatic light from a high intensity grating monochromator was directed into silica measuring cell (2 mm. path length) by means of a flexible silica light guide and from there to a photomultiplier. The signal from the photomultiplier was fed to a Tektronix 5103ND11 single-beam storage oscilloscope.

The two reactant solutions are taken from reservoirs into 2 ml. driving syringes which are connected to a thermostated coils and mixing chamber. Activating the syringes (pneumatically or manually) causes mixing of reactants in the chamber and their passage into the light path, after this the flow is abruptly stopped by a stopping syringe. At the same time the reaction is followed spectrophotometrically by triggering the oscilloscope time-base switch. For a kinetic run a suitable time-base was chosen so that ∿ 97% of the reaction could be followed on the first trace. The oscilloscope was then triggered by depressing the "automatic trigger" button to obtain an "infinity" scale reading. Where a reliable "infinity" reading could not be obtained owing to secondary reactions, rate constants were calculated by Guggenheim's method[156].

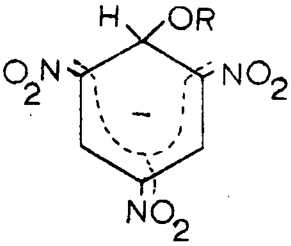
CHAPTER 3

KINETIC AND EQUILIBRIUM DATA FOR THE REACTIONS OF SOME AROMATIC COMPOUNDS WITH PROPOXIDE IONS IN PROPAN-1-ol

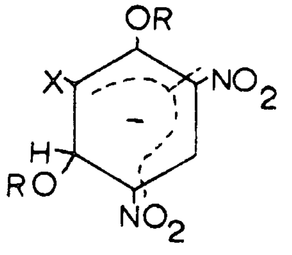
I Introduction :

In this chapter, rate and quilibrium data are given for the formation of σ-adducts by the reaction of propoxide ions in propan-1-ol with 1,3,5-trinitrobenzene and a series of 1-propoxy-2,4-dinitro-6-x-benzenes (x = NO_2, Cl, CO_2Pr, H).

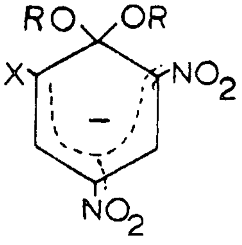
In previous work, kinetic and equilibrium data have been presented for the formation of σ-complexes[11,32] from various aromatic nitro-compounds with methoxide ions in methanol or ethoxide ions in ethanol[136] or isopropoxide ions[152] in propan-2-ol. Alkoxide (OR^-) addition may occur at un-substituted ring positions to give complexes such as (3.1) or (3.2) or at an alkoxy-substituted position to give (3.3).



(3.1)



(3.2)



(3.3)

An important conclusion from previous work is that the 1,1-dialkoxy complexes (3.3) associate strongly with cations such as Na^+, K^+, Ba^{2+} and Ca^{2+}. Evidence for the association with cations of the complex (3.3, x = H, R = Et) formed from 2,4-dinitrophenetole and ethoxide has also been presented independently by Gold and Toullec[127].

We have also shown that in general free alkoxide ions and metal-alkoxide pairs have different reactivities in these systems.

Previously Gan and Norris[33] have measured the rate of reaction of sodium propoxide with 1,3,5-trinitrobenzene and found no evidence of ion-association. The aims of the present work were to compare rate and equilibrium data for prop-1-oxide additions with those for other alkoxides and to examine the effects of ion-association in these reactions. We have also compared the reactivities of free propoxide ions and sodium propoxide ion pairs in the nucleophilic substitution reaction of 2,4-dinitrochlorobenzene.

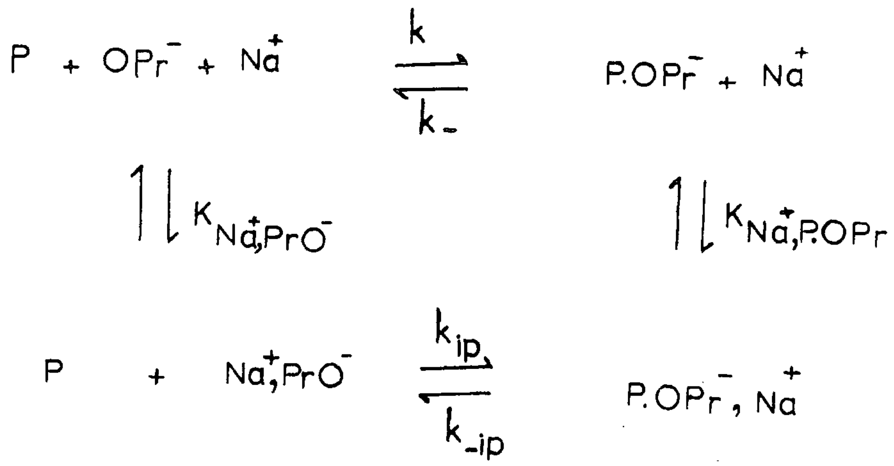
II Experimental :

Sodium perchlorate salt ($NaClO_4$) is less soluble in propanol (2.97×10^{-1} mol dm^{-3}) compared with sodium tetraphenyl boron ($NaBPh_4$) (8.42×10^{-1} mol dm^{-3}) at 25°C. The ion-pair association constant, K_A, for $NaClO_4$ is 240 compared with 1 for $NaBPh_4$, so that sodium tetraphenylboron has been used rather than sodium perchlorate[110].

It was not possible to carry out measurements, on the U.V. spectrophotometer, with the base, tetraalkyl ammonium propoxide, in the presence of the salt, sodium tetraphenylboron, due to the formation of a white precipitate.

III Results and Discussion :

All measurements were made with stoichiometric base concentration in large excess of the substrate concentration. Data are interpreted[152,44] in term of scheme 3.1 which takes account of the association of sodium ions with propoxide ions and with Meisenheimer complexes.



SCHEME 3.1

The value of the ion-pair association constant K_{Na^+,Pro^-}, of sodium ions and propoxide ions has been determined[40] conductometrically as 672 $l\ mol^{-1}$. Previous work from this laboratory has used ion concentrations rather than activities. However as indicated by Gold and Toullec[127] we can include activity coefficients as described in chapter 1, (where R = OPr and M = Na). For propanol solvent the Debye-Huckel parameters are: A = 3.9, B = 6.5 $mol^{-1} l\ nm^{-1}$ and q (Bjerrum distance) = 1.4 nm, and as mentioned in chapter 1, the two unknowns α and y were evaluated by iteration. For example with a stoichiometric base concentration of 10^{-3} $mol\ l^{-1}$, α has the value 0.75 and y the value 0.82.

Rate coefficients were always determined under first-order conditions with base as the excess component and equations 1.42, 1.43 and 1.44 will apply.

Data for σ-complex formation were obtained with the five substrates detailed below; and the rates of nucleophilic substitution of 1-chloro-2,4-dinitrobenzene were also measured.

Measurements were made with varying concentrations of sodium propoxide in propanol where the degree of dissociation (α) of ion pairs will decrease with increasing base concentration. The extent of association of propoxide ions was in some cases increased by the addition of sodium ions in the form of sodium tetraphenylboron. The association of propoxide ions with tetraalkylammonium ions is likely to be small in dilute solution, so that the reactivities of free propoxide ions were determined using tetramethyl-ammonium propoxide.

(a) <u>1-Propoxy-2,4-dinitro-6-propoxy carbonylbenzene</u>

In the presence of dilute (< 0.05 mol l^{-1}) base a single colour forming reaction is observed giving the 1,1-complex (3.3, R = Pr, X = CO_2Pr) with λ_{max}385 and 475 (Figure 3.1 and 3.2). Rates of colour formation, which were sufficiently slow to be measured with an SP500 spectrophotometer, and values of optical density at the completion of the colour forming reaction are in table 3.1.

The data obtained in the presence of sodium propoxide alone show that values of K_c, k_f and k_r increase significantly with increasing base concentration. This indicates, in terms of scheme 3.1, that the value of $K_{Na^+,P.OPr^-}$, the association constant of sodium ions with σ-adduct, is larger than the value of $K_{Na^+,\ PrO^-}$. In the presence of 0.01 mol l^{-1} sodium tetraphenylboron, where ion-pairing will be extensive, values of equilibrium and rate coefficients are increased. Values obtained using tetramethylammonium propoxide are much lower and represent reaction via free ions. Analysis of the data using equations 1.41 - 1.44 (chapter 1) gives a value for $K_{Na^+,\ P.OPr^-}$ of 10,000 l mol^{-1}.

U.V/visible spectra showing the colour forming reaction are shown in figure 3.1 (sodium propoxide) and figure 3.2 (tetramethylammonium propoxide). A slow fading reaction is evident (figure 3.3) at high

Table 3.1

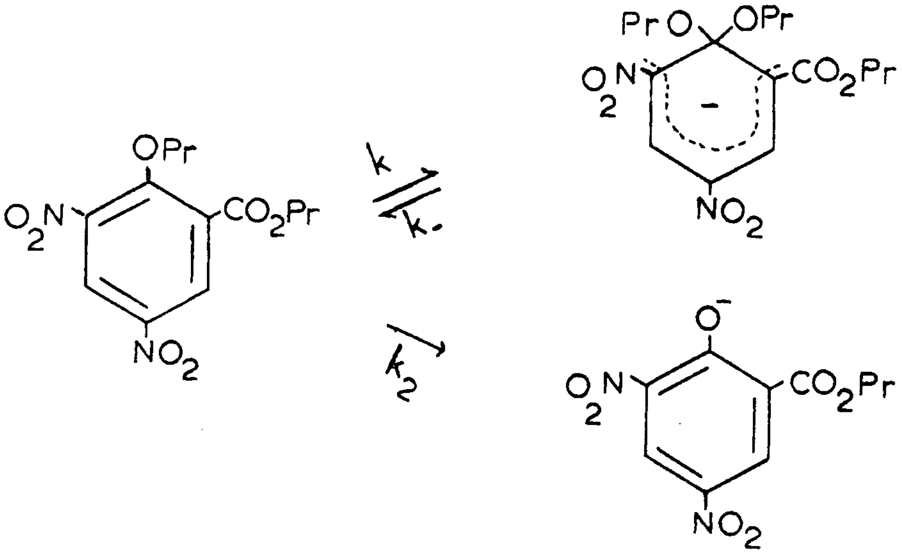
Rate and Equilibrium Data for 1,1-Complex Formation from 1-propoxy-2,4-dinitro-6-propoxycarbonylbenzene (3×10^{-5} M) in propan-1-ol at 25^{o}.

10^{3}[NaOPr]/ mol ℓ^{-1}	[$NaBPh_4$]/ mol ℓ^{-1}	O.D. (475 nm)	K_c/ ℓ mol^{-1}	$10^{3}k_{obs}$/ s^{-1}	k_f/ ℓ mol^{-1}s^{-1}	$10^{3}k_r$/ s^{-1}
0.32	-	0.243	1840	0.87	1.0	0.54
0.39	-	0.285	1950	1.00	1.1	0.56
0.47	-	0.316	1960	0.95	1.0	0.50
0.63	-	0.363	1950	1.38	1.2	0.62
0.93	-	0.48	2880	2.20	1.7	0.60
1.24	-	0.54	3630	3.15	2.1	0.57
1.53	-	0.56	3660	3.50	2.0	0.54
2.90	-	0.61	4200	8.30	2.6	0.63
9.40	-	0,63				
29.0	-	0.65				
43.0	-	0.66[a]				
0.32	0.01	0.464	5800	1.62	3.3	0.57
0.47	0.01	0.52	5500	2.40	3.7	0.67
0.63	0.01	0.58	6300	3.06	3.9	0.62
0.94	0.01	0.626	6500	4.20	3.8	0.59
1.24	0.01	0.646	6300	5.95	4.2	0.67
1.54	0.01	0.66	6200	7.30	4.3	0.69
2.97	0.01	0.70				
43	0.01	0.73[a]				
[$10^{3}NMe_4OPr$]/ mol ℓ^{-1}						
0.56	-	0.139	570	0.47	0.20	0.36
0.99	-	0.205	560	0.61	0.22	0.39
1.99	-	0.298	540	0.69	0.28	0.34
3.94	-	0.395	550	1.20	0.21	0.38
5.93	-	0.438	530	1.60	0.20	0.39
10.2	-	0.502[b]	610	2.50	0.21	0.35

a. This value taken to be that for complete conversion to complex.

b. Benesi-Hildebrand plot gives a value of 0.58 for complete conversion.

tetramethylammonium propoxide concentrations (> 0.015 M with 3 x 10^{-5} M of the parent). This may be attributed to the formation of the phenol, because increasing the amount of base increases the amount of water (a source of OH^- ions) in the media, as explained by scheme 3.2.



SCHEME 3.2

(b) <u>1-Propoxy-2,4-dinitro-6-chlorobenzene</u>

In the presence of dilute base the orange-coloured 1,1-complex is formed with λ_{max} 350, 364 (sh) and 495nm. (Figure 3.4 and 3.5). Rate and equilibrium data were measured at 495nm and are in table 3.2.

As the concentration of sodium propoxide is increased there is only a small variation in value of rate and equilibrium constants. In terms of scheme 3.1 this indicates that the values of the association constants of sodium ions with propoxide ions and with σ-adducts are quite close. However, values obtained in the presence of added sodium ions are distinctly higher than those obtained with tetraalkylammonium propoxide. The data are compatible with a value of 1100 ± 100 ℓ mol^{-1} for $K_{Na^+,P.OPr^-}$.

Illustrative Example

Using SP500 spectrophotometer at 25^{o}C (for technique see chapter 2), the following readings (table 3.3) were obtained at $[\mathrm{NaOPr}] = 12.7 \times 10^{-3}$M and $[\mathrm{Parent}] = 3.96 \times 10^{-5}$M (see table 3.2).

Plotting Log ($\mathrm{O.D}_{\infty} - \mathrm{O.D}_{t}$) versus time gives a value for $k_{obs} = 7.5 \times 10^{-3} s^{-1}$ (figure 3.6).

We have

$$k_{obs} = k_{f}[\mathrm{NaOPr}] + k_{r} \qquad - 3.1$$

and

$$K_{c} = k_{f}/k_{r} \qquad - 3.2$$

To obtain K_c, we plot $\frac{1}{\mathrm{O.D}_{495}}$ versus $\frac{1}{[\mathrm{NaOPr}]}$ (Benesi-Hildebrand), where $\mathrm{O.D}_{495}$ is the optical density reading at infinity time (figure 3.7). From the intercept of the straight line, the optical density for complete conversion is 0.82.

$$\text{Then, } K_{c} = \frac{\mathrm{O.D}_{495}}{\mathrm{O.D}_{\infty} - \mathrm{O.D}_{495}} \; \frac{1}{[\mathrm{NaOPr}]}$$

$K_{c} = 280\ \ell\ \mathrm{mol}^{-1}$ at $[\mathrm{NaOPr}] = 12.7 \times 10^{-3}$M and $\mathrm{O.D}_{495} = 0.64$.

Substituting this value in equation 3.2 we have $280\ k_{r} = k_{f}$

$k_{obs} = 280\ k_{r}[\mathrm{NaOPr}] + k_{r}$, this gives

$k_{r} = 1.7 \times 10^{-3} s^{-1}$ and from equation 3.2,

$k_{f} = 0.46\ \ell\ \mathrm{mol}^{-1} s^{-1}$.

(c) 1-Propoxy-2,4-dinitrobenzene

There is a fast reaction producing the 1,1-complex (3.3, X = H, R = Pr) with λ_{max} 495nm. A much slower reaction yields 2,4-dinitrophenol. Because of the rather low stability of the complex it was necessary to use fairly high concentrations of the parent to obtain measurable optical densities. The data in table 3.4 show that values of K_c are independent of the substrate concentration but increase with increasing sodium ion concentration. This indicates that σ-adduct is more stabilised by

Table 3.2

Rate and Equilibrium Data for 1,1-Complex Formation from 1-Propoxy-2,4-dinitro-6-chlorobenzene (4×10^{-5}M) in propan-1-ol at 25°.

10^3[NaOPr] / mol ℓ^{-1}	[$NaBPh_4$] / mol ℓ^{-1}	O.D. (495 nm)	K_c/ ℓ mol^{-1}	10^3k_{obs}/ s^{-1}	k_f/ ℓ mol^{-1}s^{-1}	10^3k_r/ s^{-1}
1.01	-	0.191	300	1.5	0.35	1.2
2.00	-	0.305	300	2.4	0.45	1.5
3.9	-	0.464	330	3.3	0.48	1.4
6.7	-	0.56	320	5.3	0.54	1.7
12.7	-	0,64	280	7.5	0.46	1.7
25.3	-	0.74	370	14	0.50	1.4
64	-	0.79	-			
128	-	0.81[a]	-			
1.01	0.02	0.292	460	1.9	0.60	1.3
2.00	0.02	0.426	430	3.3	0.76	1.8
3.9	0.02	0,59	450	4.3	0.70	1.6
6.7	0.02	0.66	380	7.8	0.82	2.1
25.3		0.82	-	-	-	-
128		0.91[b]	-	-	-	-
10^3[NMe_4OPr] / mol ℓ^{-1}						
0.98	-	0.161	266	1.05	0.22	0.85
1.95	-	0.257	250	1.1	0.19	0.75
3.86	-	0,43	300	1.5	0.21	0.70
6.72	-	0.52	290	2.1	0.21	0.75
9.4	-	0.58	290	2.7	0.21	0.75
18.1	-	0.65	260	5.2	0.23	0.90
98	-	0.75[c]				

a. Value of 0.82 taken for complete conversion to complex.

b. Value of 0.92 taken for complete conversion to complex.

c. Value of 0.79 taken for complete conversion to complex (Benesi-Hildebrand).

Table 3.3

Specimen data for reaction of 1-propoxy-2,4-dinitro-6-chlorobenzene (4.0×10^{-5}M) with sodium propoxide (1.27×10^{-2}M) in propan-1-ol at 25^{o}C.

Time (sec)	O.D$_{495}$	O.D$_{\infty}$ - O.D$_{495}$	Log (O.D$_{\infty}$ - O.D$_{t}$)
15	0.11	0.53	-0.275
30	0.17	0.47	-0.327
45	0.22	0.42	-0.376
60	0.27	0.37	-0.431
75	0.31	0.33	-0.381
90	0.34	0.30	-0.522
120	0.49	0.24	-0.619
150	0.46	0.18	-0.744
180	0.50	0.14	-0.853
240	0.55	0.09	-1.045
300	0.585	0.055	-1.259
360	0.61	0.030	-1.522
420	0.625	0.015	-1.823
540	0.630	0.01	-2.0

sodium ions than is the propoxide ion. The data fit equation 1.41 (chapter 1) with K, 5×10^{-3} ℓ mol^{-1} and $K_{Na^+,P.OPr^-}$, 1500 ± 200 ℓ mol^{-1}.

Because of the low stability of the σ-adduct the rate process involving its formation is dominated by the k_r term (equation 1.44 in chapter 1). Thus measurements by stopped-flow yielded values of k_r. The value in the presence of sodium ions, where ion-pairing will be largely complete, is smaller than that for reaction of free ions and this decrease largely accounts for the increase in value of K_C in the presence of sodium ions.

To illustrate how k_{obs} is obtained by the stopped-flow technique, the two sets of data are displayed, table 3.5 for sodium propoxide (50×10^{-3}M), where the optical density at infinity is 0.0223 = log (5.1/4.845) and table 3.6 for tetramethylammonium propoxide

Table 3.4

Equilibrium and Rate Data for 1,1-complex Formation from 1-propoxy-2,4-dinitrobenzene in propan-1-ol at 25°.

$10^3[NMe_4OPr]$ / mol ℓ^{-1}	[Parent]/ mol ℓ^{-1}	O.D.[a] (495 nm)	10^3K_c[b]/ ℓ mol^{-1}	k_{obs}[c]/ s^{-1}
2.9	0.144	0.045	5.0	
5.9	0.143	0.090	4.8	
9.7	0.142	0.150	5.0	
19.6	0.138	0.265	4.5	
19.6	0.034	0.065	4.4	
27.3	0.034	0.100	4.9	
50	0.012	-	-	3.14
$10^3[NaOPr]$ / mol ℓ^{-1}				
2.64	0.144	0.065	7.8	
4.76	0.140	0.120	8.2	
8.7	0.142	0.24	8.9	
10.2	0.05	0.11	9.8	
10.2	0.14	0.29	9.1	
49	0.019	0.19	9.5	
50	0.012			1.27

a. Corrected for absorption by parent and base.

b. Assuming an extinction coefficient of 22,000 (Ref. 99).

c. This corresponds to k_r.

Table 3.5

Specimen data for reaciton of 1-propoxy-2,4-dinitrobenzene with sodium propoxide measured by stopped-flow spectrophotometer at 25^{o}.

Time (sec)	V (volts)	$(V-V_\infty)$	Log $(V-V_\infty)$
0.1	7.5	4.4	0.643
0.2	7.1	4.0	0.602
0.3	6.6	3.5	0.544
0.4	6.2	3.0	0.477
0.5	5.8	2.7	0.431
0.6	5.5	2.4	0.380
0.7	5.2	2.1	0.322
0.8	5.0	1.9	0.278
0.9	4.7	1.6	0.204
1.0	4.5	1.4	0.146
∞	3.1	-	-

Table 3.6

Specimen data for reaction of 1-propoxy-2,4-dinitrobenzene with tetramethylammonium propoxide measured by stopped-flow spectrophotometer at 25^{o}.

Time (ms)	V (volts)	$(V-V_\infty)$	Log $(V-V_\infty)$
50	6.0	4.2	0.623
100	5.4	3.6	0.556
150	4.9	3.1	0.491
200	4.4	2.6	0.414
250	4.0	2.2	0.342
300	3.7	1.9	0.278
350	3.5	1.7	0.230
400	3.2	1.4	0.146
450	3.0	1.2	0.078
500	2.8	1.0	0.0
∞	1.8	-	-

$$\left.\begin{array}{l}[\text{Base}] = 50 \times 10^{-3}\text{M} \\ [\text{Parent}] = 1 \times 10^{-5}\text{M}\end{array}\right) \text{ for both above tables.}$$

(50×10^{-3}M), where the optical density at infinity is equal to 0.0096 = Log (5.0/4.89). Two straight lines for both sets of data (table 3.5 and 3.6) are shown in figure 3.8.

We can show numerically, the low contribution of k_f relative to k_r. From table 3.4, the average value for $K_c \simeq 0.005$ ℓ mol^{-1} (for NMe_4OPr), where $K_c = k_f/k_r$, and $k_f = 0.005\ k_r$, substituting this value at the following equation : $k_{obs} = k_f[OPr^-] + k_r = 3.14\ s^{-1}$, where $[OPr^-] = 50 \times 10^{-3}$M (of NMe_4OPr). This gives $k_f = 0.0157$ ℓ $mol^{-1}s^{-1}$ (if $k_r \simeq k_{obs}$), so that $k_f[OPr^-]$ is much less than k_{obs}. Similar treatment can be carried out for sodium propoxide (50×10^{-3}M), assuming $k_f = 0.0085\ k_r$ at $k_{obs} = 1.26\ s^{-1}$, which gives $k_f = 0.0108$ ℓ $mol^{-1}s^{-1}$.

(d) 1,3,5-Trinitrobenzene

In the case of the three previous substrates σ-complex formation results in the formation of 1,1-dipropoxy complexes, (3.3) and the data indicate their strong interaction with sodium ions. The σ-complex formed from 1,3,5-trinitrobenzene has structure (3.1, R = Pr) in which addition occurs at an un-substituted ring-position and the results here indicate a much weaker interaction with sodium ions. Rates of complex formation measured by stopped-flow spectrophotometry are given in figure 3.9. We take the data obtained using tetramethyl ammonium propoxide to represent reaction of free ions and the slope and intercept of the linear plot yield values of k $(8.6 \pm 0.6) \times 10^4$ ℓ $mol^{-1}s^{-1}$ and k_- $10 \pm 1\ s^{-1}$. Combination of these values gives $K(= k/k_-)$, $(8.6 \pm 1.5) \times 10^3$ ℓ mol^{-1}. Measurements were also made with sodium propoxide in media containing 0.03 mol $ℓ^{-1}$ sodium tetraphenylboron; ion association will be extensive here and the linear plot yields values of k_f, 4×10^4 ℓ $mol^{-1}s^{-1}$ and k_r, $10 \pm 1\ s^{-1}$ giving K_c, 4×10^3 ℓ mol^{-1}. This result indicates that the reactivity of sodium propoxide ion-pairs is smaller than that of free propoxide ions.

The data obtained with sodium propoxide alone is quite similar to that with tetraalkylammonium-propoxide. This is to be expected since we calculate (equations 1.39 and 1.40 in chapter 1) that in the most concentrated base solution used >80% of the sodium propoxide will be dissociated. Some downward curvature of the plot at high base concentration is expected but is not apparent in the concentration range we have used.

These results are in reasonable accord with those of Gan and Norris[33] who, using sodium propoxiee, obtained values of k_f 92,600 ℓ $mol^{-1}s^{-1}$ and k_r 11.9 s^{-1}.

Specimen data, using the stopped-flow technique at 480 nm are shown in tables 3.7, 3.8 and 3.9 and in figure 3.10.

In terms of equation 1.41 the decrease in value of K_c in the presence of added sodium ions indicates that the value of $K_{Na^+,P.OPr^-}$ is lower than that of K_{Na^+,OPr^-}. Assuming that the sodium tetraphenylboron is completely dissociated and that activity coefficients may be calculated using equation 1.40 we obtain a value for $K_{Na^+,\ P.OPr^-}$ of 250 ± 50 ℓ mol^{-1}.

(e) <u>1-Propoxy-2,4,6-trinitrobenzene</u>

Examination by stopped-flow spectrophotometry shows the presence of two colour forming reactions which are well-separated in time. The ^{1}H.n.m.r spectra indicate that these give the 1,3-adduct (3.2, R = Pr, X = NO_2) and the 1,1-adduct (3.3, X = NO_2, R = Pr) and that the latter is the thermodynamically more stable (figure 3.11). The results are described by scheme 1.5 (page 13). Since the time-scale of the two processes was well separated equations 3.3 and 3.4 will apply where the subscript denotes the position of addition.

$$k_{fast} = k_{-3} + k_3[PrO^-] \qquad 3.3$$

Table 3.7

Specimen kinetic data for reaction of 1,3,5-Trinitrobenzene (10^{-5}M) with tetramethylammonium propoxide (5.5 x 10^{-4}M) at 25°.

Time (ms)	V_{480nm}	$(V_{480}-V_{\infty})$	Log $(V_{480}-V_{\infty})$
5	7.4	7.0	0.845
10	5.7	5.3	0.724
15	4.4	4.0	0.602
20	3.4	3.0	0.477
25	2.7	2.3	0.361
30	2.1	1.7	0.230
35	1.8	1.4	0.146
∞	0.4	-	-

Table 3.8

Specimen kinetic data for reaction of 1,3,5-Trinitrobenzene (10^{-5}M) with sodium propoxide (5.5 x 10^{-4}M) at ionic strength of 0.03 M ($NaBPh_4$) and at 25°.

Time (ms)	V_{480nm}	$(V_{480}-V_{\infty})$	Log $(V_{480}-V_{\infty})$
20	5.6	4.8	0.68
40	3.5	2.7	0.431
60	2.3	1.9	0.176
80	1.8	1.0	0.0
100	1.3	0.5	-0.301
120	1.1	0.3	-0.522
∞	0.8	-	-

Table 3.9

Specimen kinetic data for reaction of 1,3,5-Trinitrobenzene (10^{-5}M) with sodium propoxide (5.5 x 10^{-4}M) at 25°.

Time (ms)	V_{480nm}	$(V_{480}-V_{\infty})$	Log $(V_{480}-V_{\infty})$
3	4.0	3.6	0.556
5	3.5	3.1	0.491
10	2.8	2.4	0.380
15	2.2	1.8	0.255
20	1.8	1.4	0.146
25	1.4	1.0	0.0
30	1.2	0.8	-0.097
35	1.0	0.6	-0.222
40	0.9	0.5	-0.301
45	0.8	0.4	-0.398
∞	0.4	-	

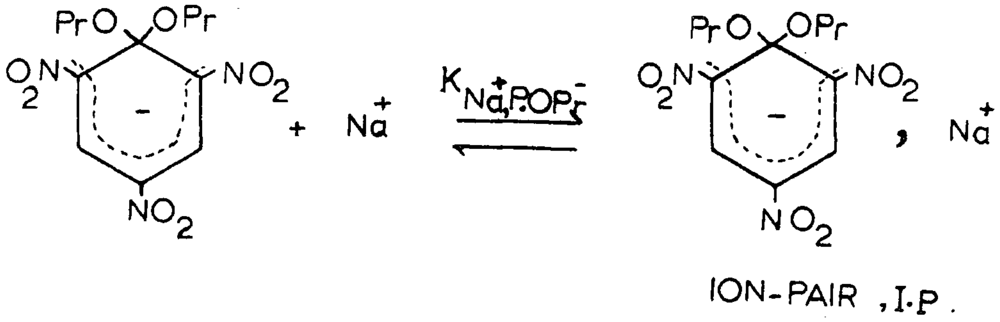
$$k_{slow} = k_{-1} + \frac{k_1[\mathrm{PrO}^-]}{1 + K_3[\mathrm{PrO}^-]} \qquad - 3.4$$

In the presence of sodium ions, ion-pairing will modify the constants to $k_{3,ip}$, $k_{-3,ip}$, $k_{1,ip}$ and $k_{-1,ip}$.

Rate and equilibrium data are in table 3.10. The results obtained with tetramethylammoniumpropoxide will represent reaction of free ions. A linear plot according to equation 3.3 yielded value of k_3, 4500 ℓ mol^{-1}s^{-1} and k_{-3}, 16 s^{-1} giving $K_3(= k_3/k_{-3})$, 280 ℓ mol^{-1}. This value is in good agreement with that obtained independently from the optical density measurements. The corresponding data obtained with sodium propoxide containing added sodium tetraphenylboron gave values of $k_{3,ip}$, 2400 ℓ mol^{-1}s^{-1}, $k_{-3,ip}$, 19 s^{-1} and $K_{3,ip}$, 125 ℓ mol^{-1}. The lower values of the equilibrium constant and rate of base addition obtained in the presence of sodium ions are consistent with a rather weak interaction of the 1,3-complex with sodium ions. This behaviour is in line with that of 1,3,5-trinitrobenzene where base addition also occurs at an unsubstituted ring-position.

The thermodynamic stability of the 1,1-complex is very high and conversion is > 95% in solutions containing 1 x 10^{-4} mol ℓ^{-1} base. A consequence of this high value is that in equation 3.4 the forward rate will be dominant. The value of k_1, 28 ℓ mol^{-1}s^{-1} is significantly lower than that of $k_{1,ip}$, 50 ℓ mo,$^{-1}$s^{-1} consistent with stabilisation of the 1,1-complex (and the transition state leading to it) by sodium ions.

Independent evidence for the association of the 1,1-complex with sodium ions comes from visible spectral changes brought about by the addition of sodium tetraphenylboron to solutions of the complex in propan-1-ol (figure 3.12). The spectrum of the complex in very dilute sodium propoxide solutions shows maxima at 412 and 485 nm with a minimum at 445 nm (figure 3.12). The main effect of increasing the sodium ion concentration is to decrease the optical density at the minimum. However, the optical density at 412 nm is un-affected by change in sodium ion concentration. Using the ratios of O.D (412 nm)/O.D (445 nm) given in table 3.11. It is possible to calculate a value for the equilibrium constant for the reaction:



$$K_{Na^+,P.OPr} = [I.P]/[C][Na^+]$$

If we represent the ratio O.D (412 nm)/O.D (445 nm) by the function x, then

$$[I.P]/[C] = (x - 1.67)/(2.20 - x)$$

The values give $K_{Na^+,P.OPr^-}$, 1000 ± 500 ℓ mol^{-1} (see table 3.11).

Table 3.11

Variation of spectral shape with ion-association.

$[Na^+]_{Total}$	$[Na^+]_{Free}$	O.D (412 nm)/O.D (445 nm)
0^a	0	1.67
8.5×10^{-4b}	6.5×10^{-4}	1.83
1.15×10^{-3b}	9.0×10^{-4}	1.89
1.4×10^{-3b}	1.1×10^{-3}	1.93
1.75×10^{-3b}	1.35×10^{-3}	1.96
2.75×10^{-3b}	2.4×10^{-3}	2.05
4.75×10^{-3b}	4.2×10^{-3}	2.20

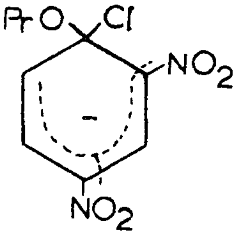
a. Measured using tetramethylammonium propoxide

b. Solutions contain 7.5×10^{-4}M sodium propoxide.

(f) 1-Chloro-2,4-Dinitrobenzene

The rate coefficients for the nucleophilic substitution reaction yielding 1-propoxy-2,4-dinitrobenzene were measured in propan-1-ol at 25°C. Scorrano and co-workers[135] have shown that the reaction of potassium isopropoxide with 1-halo-2,4-dinitrobenzenes in isopropanol-benzene may occur via a radical mechanism giving 2,4-dinitrophenol (see chapter 1). The latter compound was not a major product of our reaction and we conclude that reaction occurs by the usual S_NAr mechanism[21].

Measurements, (table 3.12), were made using tetramethylammonium propoxide where reaction is likely to occur via free propoxide ions and in sodium propoxide solutions containing added sodium tetraphenylboron where the base will be largely ion-paired. That the second-order rate constant is smaller in the latter case shows that the reactivity of sodium propoxide ion-pairs is reduced relative to free propoxide ions with the implication that the intermediate complex 3.4 and the transition state leading to it



(3.4)

do not associate strongly with sodium ions. This can be compared with the observation[51] that in methanol-benzene mixtures the reaction of potassium methoxide with 1-chloro-2,4-dinitrobenzene is accelerated by the addition of crown-ether which will dissociate the base.

IV Ion Association

Rate and equilibrium data for reaction via free ions or ion-paired species are summarised in table 3.13. The final column of this table gives values

Table 3.12

Rate Coefficients for Nucleophilic substitution of 1-chloro-2,4-dinitrobenzene with propoxide in propan-1-ol at 25°.

$10^3[NMe_4OPr]$ / mol ℓ^{-1}	$10^3 k^{a}_{obs}$ / s^{-1}	$k_{obs}/[NMe_4OPr]$ (ℓ $mol^{-1}s^{-1}$)
4.7	0.85	0.18
9.3	1.84	0.20
17.8	3.0	0.17
26.7	5.1	0.19

$10^3[NaOPr]$ / mol ℓ^{-1}	$[NaBPh_4]$ / mol ℓ^{-1}	$10^3 k^{a}_{obs}$ / s^{-1}	$k_{obs}/[NaOPr]$ (ℓ $mol^{-1}s^{-1}$)
4.7	0.05	0.39	0.085
9.5	0.04	0.84	0.090
19	0.03	1.55	0.080
28.5	0.02	2.70	0.095

a. The reaction was followed by the increase in absorption at 300 nm due to the product 1-propoxy-2,4-dinitrobenzene.

for the association constants with sodium ions of the σ-complexes. It is noteworthy that the 1,1-dipropoxy complexes associate much more strongly than do the complexes where base addition occurs at an unsubstituted ring-position. Hence we prefer a structure 3.5 for the ion-associate in which the cation interacts with the oxygen atoms of the propoxy groups and the ortho-substituents. The high value for $K_{Na^+,P.Opr^-}$ when a carbonyl containing substituent is present at the 6-position adds to the strength of this argument. Weak association of complexes of types 3.1 and 3.2 with cations may involve structures analogous to (3.5) where the cation is near the added propoxy-group or alternatively (3.6) where the cation interacts with the negative charge on a nitro-group.

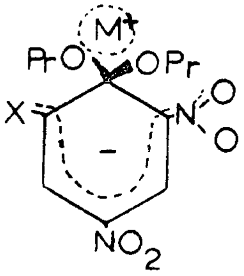
The effects of ion-association on the rate coefficients for forward and reverse reactions will depend on the strength of the interaction of

Table 3.13

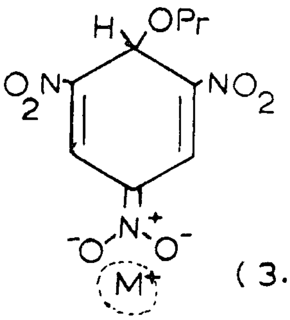
Effects of Ion-Association on σ-Complex Formation in Propan1-ol at 25°.

Structure[a]	$K/$ $\ell\ mol^{-1}$	$k/$ $\ell\ mol^{-1}s^{-1}$	$k_-/$ s^{-1}	$K_{IP}/$ $\ell\ mol^{-1}$	$k_{ip}/$ $\ell\ mol^{-1}s^{-1}$	$k_{-ip}/$ s^{-1}	$K_{Na+,P.OPr^-}$ $\ell\ mol^{-1}$
(3.3), X = CO_2Pr	560	0.21	3.8×10^{-4}	8400	6	7×10^{-4}	10,500
(3.3), X = Cl	280	0.21	7.5×10^{-4}	450	0.75	1.7×10^{-4}	1,100
(3.3), X = H	5×10^{-3}	0.016	3.1	0.011	0.014	1.3	1,500
(3.3), X = NO_2	$>2 \times 10^{5}$	28	-	$>2 \times 10^{5}$	50	-	1,000
(3.1)	8.6×10^{3}	8.6×10^{4}	10	4×10^{3}	4×10^{4}	10	250
(3.2), X = NO_2	280	4.5×10^{3}	16	125	2.4×10^{3}	19	300

a. In all cases R = Pr



(3.5)



(3.6)

sodium ions with the reactants,transition states and products. In the case of the 1,1-dipropoxy complexes the rate coefficients for the forward reaction are in general increased in the presence of sodium ions while the rate coefficients for the reverse reactions are decreased. However for (3.3, X = CO_2Pr, R = Pr) both forward and reverse rate coefficients are increased by sodium ions indicating very strong interaction of the transition state with cations. The rate coefficients for formation of (3.1, R = Pr) and (3.2, X = NO_2, R = Pr) are decreased in the presence of sodium ions in agreement with their weak association with cations.

The rate coefficient for the nucleophilic substitution reaction of 1-chloro-2,4-dinitrobenzene with tetramethyl ammonium propoxide was found to be 0.18 $\ell\ mol^{-1}s^{-1}$ while the value for sodium propoxide containing added sodium tetraphenylboron was 0.085 $\ell\ mol^{-1}s^{-1}$. That the second order rate coefficient is smaller in the latter case shows that the reactivity of sodium propoxide ion-pairs is reduced relative to free propoxide ions with the implication that the intermediate complex does not associate strongly with sodium ions.

V <u>Comparison of Propoxide Adducts with those from other Alkoxides</u>

The data obtained in very dilute solutions of tetramethyl - ammoniumpropoxide are likely to be free from the effects of ion association. Data are summarised in table 3.14 where they are compared with similar data for addition of other alkoxides in the corresponding alcohols.

As has been found in other systems[11,32] the 1,1-dialkoxy complex (3.3, X = NO_2, R = Pr) has considerably greater thermodynamic stability but is formed less rapidly than its 1,3-isomer (3.2, X = NO_2, R = Pr) or the adduct (3.1, R = Pr) formed from 1,3,5-trinitrobenzene. This enhanced stability of 1,1-adducts has been attributed to release of steric strain on addition at the 1-position[52] or to the stabilising influence of multiple alkoxy substitution[102]. Recent evidence from heterocyclic systems indicates that both factors may be important.

Comparison (table 3.14 column 7) of the data for propoxide and isopropoxide additions shows that as expected from solvent basicities[104] the isopropoxide adducts have the greater thermodynamic stabilities. Addition at unsubstituted positions, where steric effects will be small, gives values of $K(PrO^-)/K(isoPrO^-)$ less than 0.03. Values of this ratio for addition at alkoxy substituted positions range from 0.063 to 0.37. It might be argued that since the isopropoxy group is sterically more demanding than the propoxy group there should be greater steric relief on addition of isopropoxide to the 1-position of 1-isopropoxy-2.4-dinitro-6-X-benzenes than on propoxide addition to the corresponding 1-propoxy compounds. However 1,1-diisopropoxy complexes containing bulky substituents at the 2- and 6- positions will themselves be subject to unfavourable steric interactions so that the expected increase in stability is not realised.

The value of the ratio $K(PrO^-)/K(EtO^-)$ is largely independent of the substrate indicating that in these systems the steric requirement of the propoxy-group is not markedly greater than that of the ethoxy group.

Table 3.14

Comparison of Equilibrium and Rate Data for Alkoxide Additions

Structure 3.3		K/ ℓ mol^{-1}	k/ ℓ mol^{-1}s^{-1}	k_-/ s^{-1}	$\frac{K(Pro^-)}{K(Eto^-)}$	$\frac{K(Pro^-)}{K(isoPro^-)}$
R	X					
Pr	NO_2	>2 x 10^5	28	<1.4 x 10^{-4}	5.6	0.37
Pr	CO_2Pr	560	0.21	3.8 x 10^{-4}	5.3	0.25
Pr	Cl	280	0.21	7.5 x 10^{-4}	3.3	0.063
Pr	H	5 x 10^{-3}	0.016	3.1		
Et	NO_2	3 x 10^5	17	6 x 10^{-5}		
Et	CO_2Et	100	0.13	1.3 x 10^{-3}		
Et	Cl	53	0.14	2.6 x 10^{-3}		
Et	H	1.5 x 10^{-3}	0.01	7		
isoPr	CO_2Pr^i	1500	0.11	7 x 10^{-5}		
isoPr	Cl	1100	0.10	1 x 10^{-4}		
isoPr	H	0.08	0.01	0.12		
Structure 3.1						
Pr		8.6 x 10^3	8.6 x 10^4	10	4.3	<0.03
Et		2 x 10^3	4 x 10^4	20		
isoPr		>3 x 10^5	1.6 x 10^5	< 1		
Structure 3.2						
Pr	NO_2	280	4.5 x 10^3	16	4.0	<0.003
Et	NO_2	70	2.1 x 10^3	30		
isoPr	NO_2	>1 x 10^5	8 x 10^3	<0.1		

It is of interest that for addition at unsubstituted ring positions, where we expect steric effects to be small, the rate constants for alkoxide addition are in the order iso PrO$^-$ > PrO$^-$ > EtO$^-$ paralleling the stabilities of the complexes. However, for formation of the 1,1-dialkoxy complexes the order, with respect to similarly activated substrates, is PrO$^-$ > EtO$^-$ > iso PrO$^-$. This inversion probably reflects the greater steric hindrance on approach of the reagent associated with 1,1-complex formation[88,111].

VI Structural Study Using N.M.R. technique

^{1}H.n.m.r. spectra were measured (see chapter 2) and the spectral data for the parent compounds in $^2H_6$ DMSO are in table 3.15.

The addition of 1 mol.equiv. of sodium propoxide in propan-1-ol to solutions in $^2H_6$ DMSO of 1-propoxy-2,4-dinitro-6-X-benzenes gave rise to spectra consistent with the formation of 1,1-complexes. Details

Table 3.15

^{1}H N.m.r. parameters for parent[a] molecules in $^2H_6$ DMSO

	Ring	Propyl[b]		
1 Propoxy-2,4,6-trinitrobenzene	9.08	4.16(t)	1.69(st)	0.91(t)
1-Propoxy-2,4-dinitro-6-propoxycarbonylbenzene	8.97(d) 8.70(d)	4.32(t) 4.11(t)	1.74(m) 1.74(m)	0.98(t) 0.92(t)
1-propoxy-2,4-dinitro-6-chlorobenzene	8.74(m)	4.18(t)	1.79(st)	0.98(t)
1-Propoxy-2,4-dinitrobenzene	8.71(d) 8.48(d,d) 7.57(d)	4.26(t)	1.77(st)	0.97(t)

a. d = doublet, t = triplet, st = sextet, m = multiplet

b. Coupling is observed J ∿ 6.5 Hz.

are in table 3.16. The solvent composition was usually 50/50 (V/V) although to obtain appreciable conversion of 1-propoxy-2,4-dinitrobenzene to complex 70% DMSO was required. In the case of 1-propoxy-2,4,6-trinitrobenzene transitory bands at δ 6.23 and 8.53 (J, 2Hz) were observed due to the 1,3-complex (3.2, X = NO_2, R = Pr).

Table 3.16

Chemical shift Data for 1,1-adducts

Structure 3.3		Ring	OCH_2[a]
X	R		
NO_2	Pr	8.63	3.08(t)
CO_2Pr	Pr	8.78(d) 8.39(d)	3.00(t) 4.10(t)
Cl	Pr	8.68(d) 7.40(d)	3.06(t)
H	Pr	8.67(d) 7.15(d,d) 5.0(d)	2.95(t)

a. The bands due to other protons in the alkyl chain are hidden by solvent.

FIG. 3.1

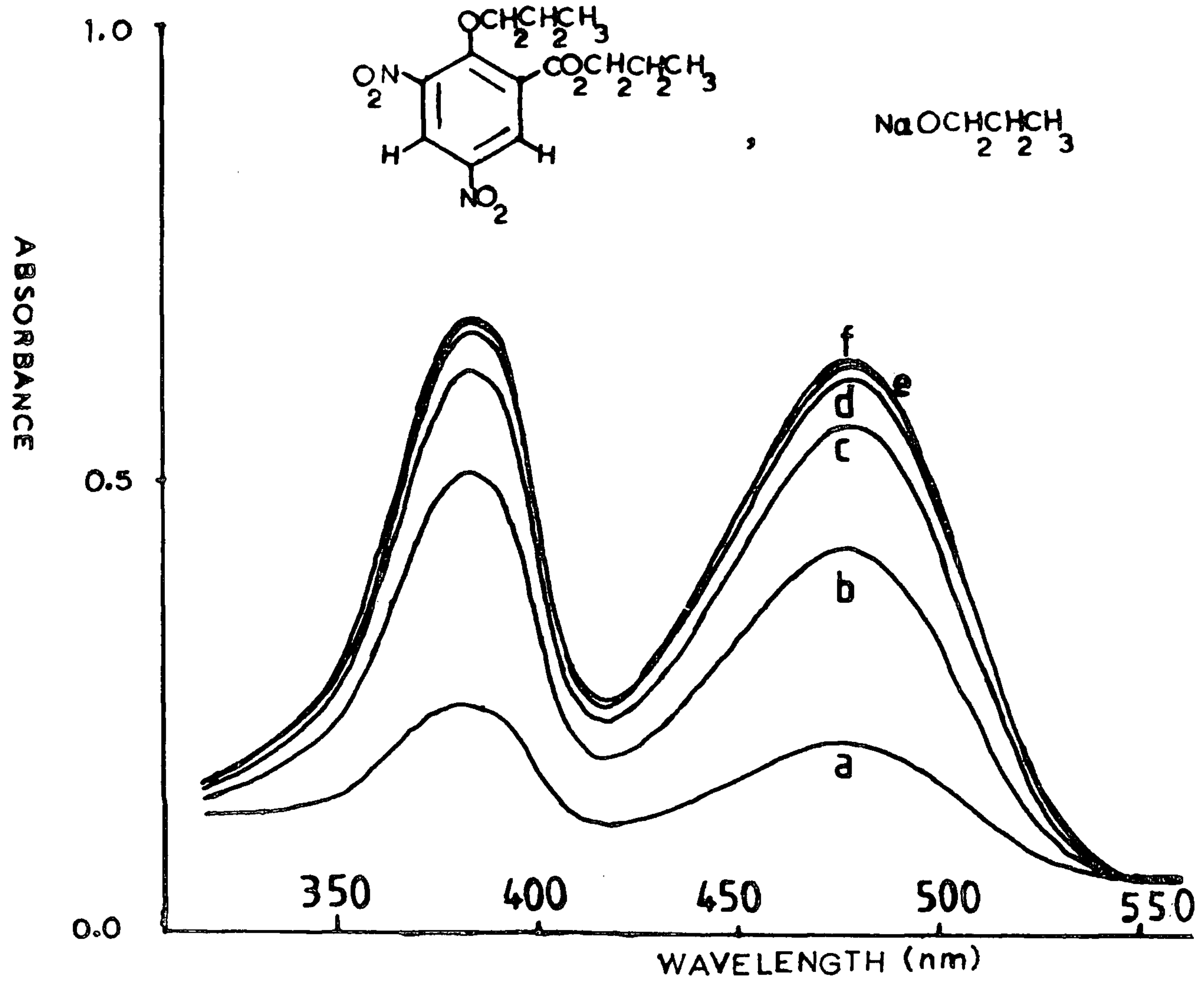


FIGURE 3.1 Visible absorption spectra of 1-propoxy-2,4-dinitro-6-propoxy carbonyl benzene(3.6×10^{-5} M) in propanol containing 1×10^{-3} M NaOPr at 25°. The change with time is a ⟶ f .

FIG. 3.2

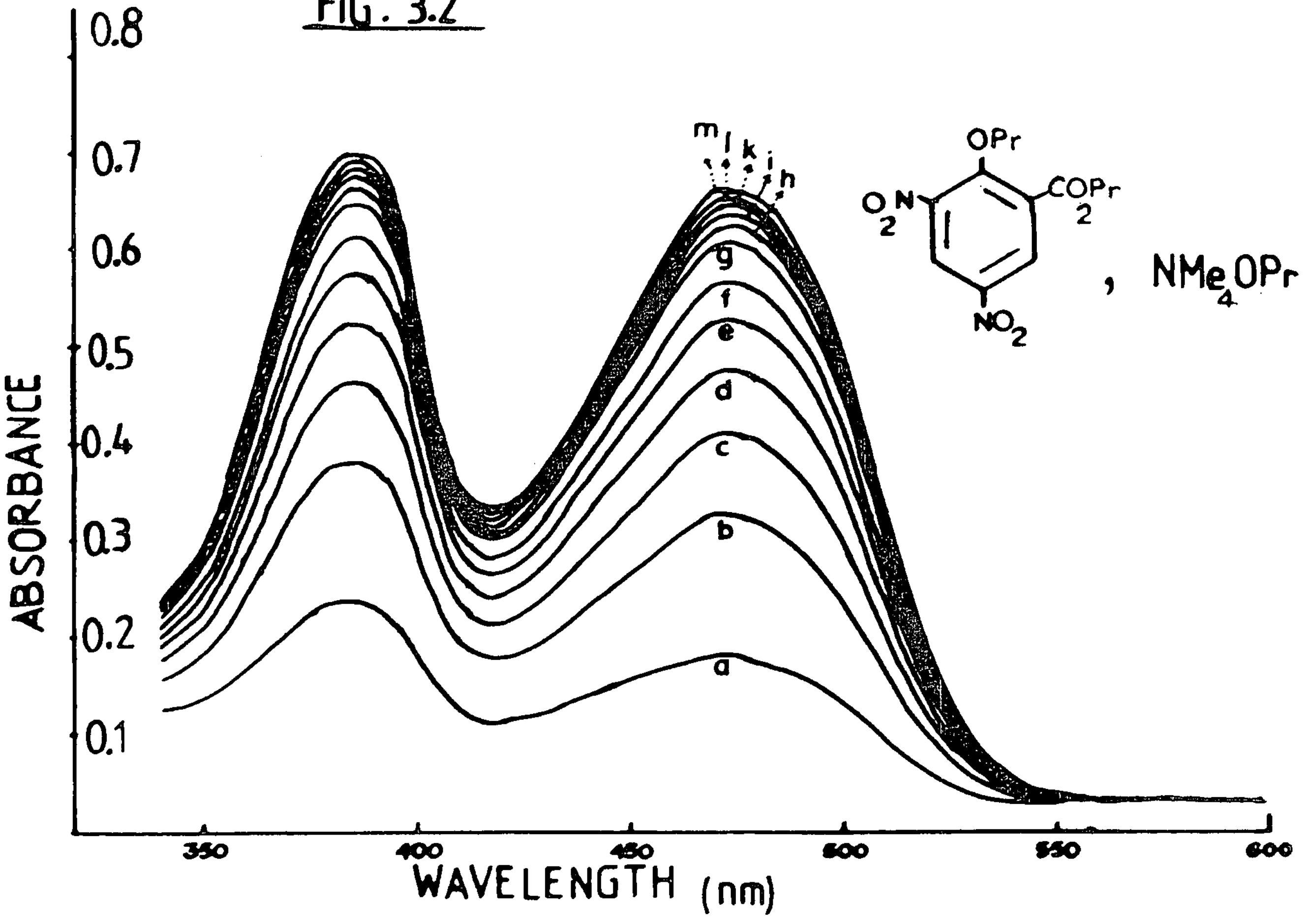


FIGURE 3.2 Visible absorption spectra of 1-propoxy-2,4-dinitro-6-propoxy carbonyl benzene (3.5 X 10^{-5} M) in propan-1-ol containing 1 X10^{-2} M, tetramethylammonium propoxide at 25°. The change with time is a → m .

FIG. 3.3

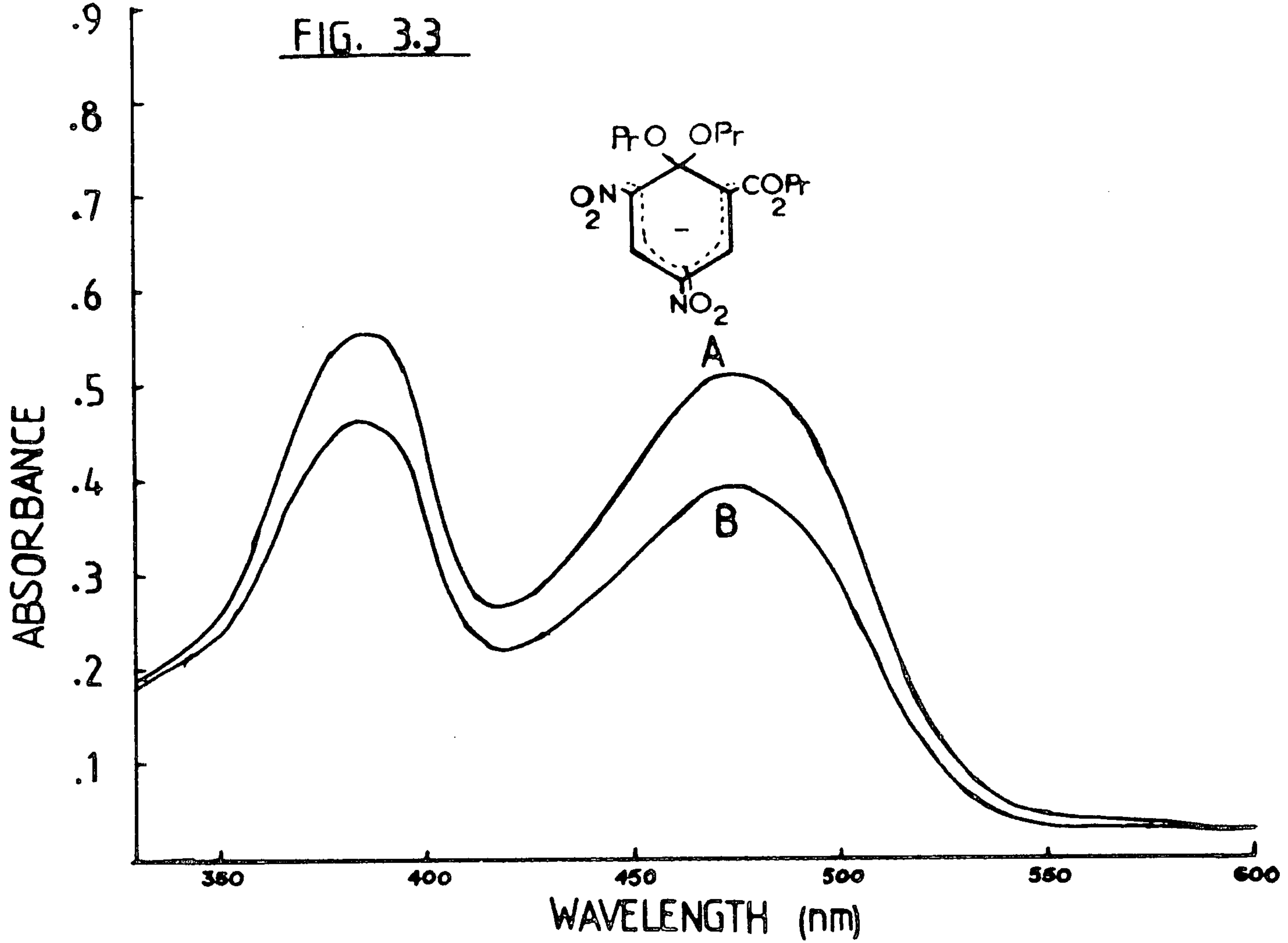


FIGURE 3.3 Visible absorption spectra of 1-propoxy-2,4-dinitro-6-propoxy carbonyl benzene (3.3×10^{-5} M) with 2.9×10^{-2} M, tetramethylammonium propoxide in propan-1-ol at 25°. A change with time from A to B after 11 minutes .

FIG. 3.4

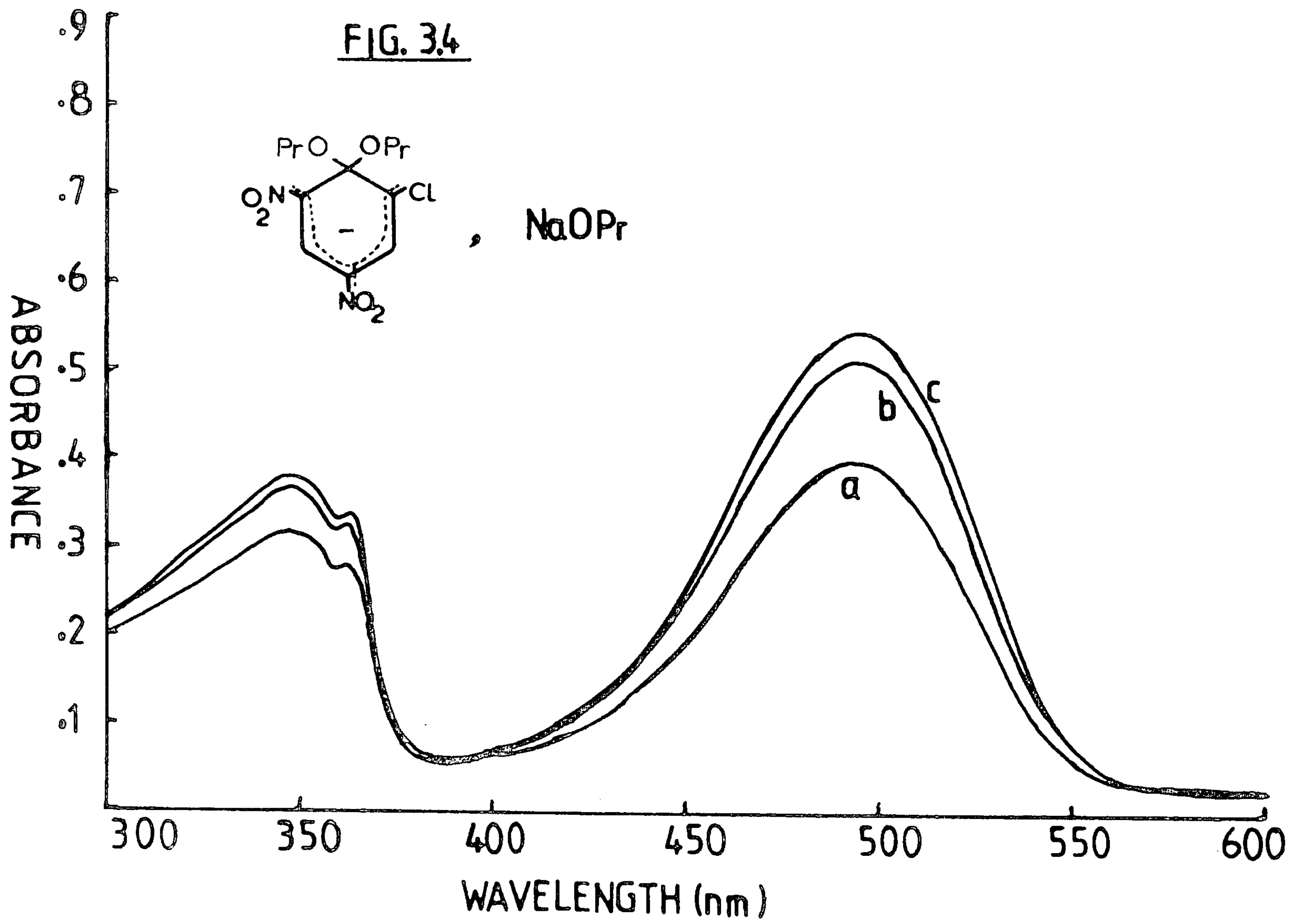


FIGURE 3.4 U.V/Visible spectra of 1-propoxy-2,4-dinitro-6-chlorobenzene (4×10^{-5} M) with NaOPr(1×10^{-2} M) in propan-1-ol at 25°. The change with time is a ⟶ c .

FIG. 3.5

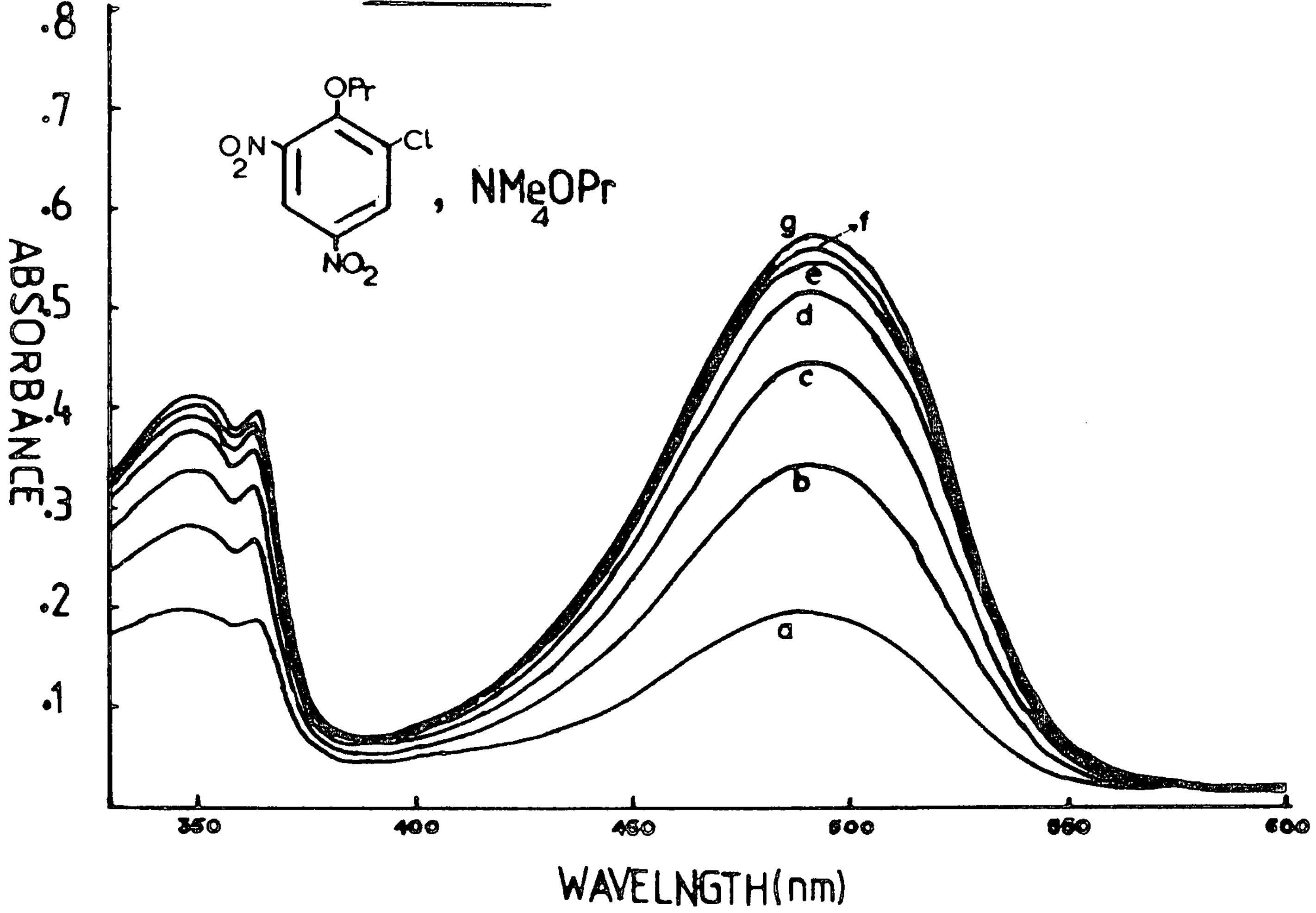


FIGURE 3.5 Visible spectra of 1-propoxy-2,4-dinitro-6-chlorobenzene(4×10^{-5}M) with tetramethylammonium propoxide in propan-1-ol at 25°. The change with time is a ⟶ g. [BASE]=1×10^{-2} M.

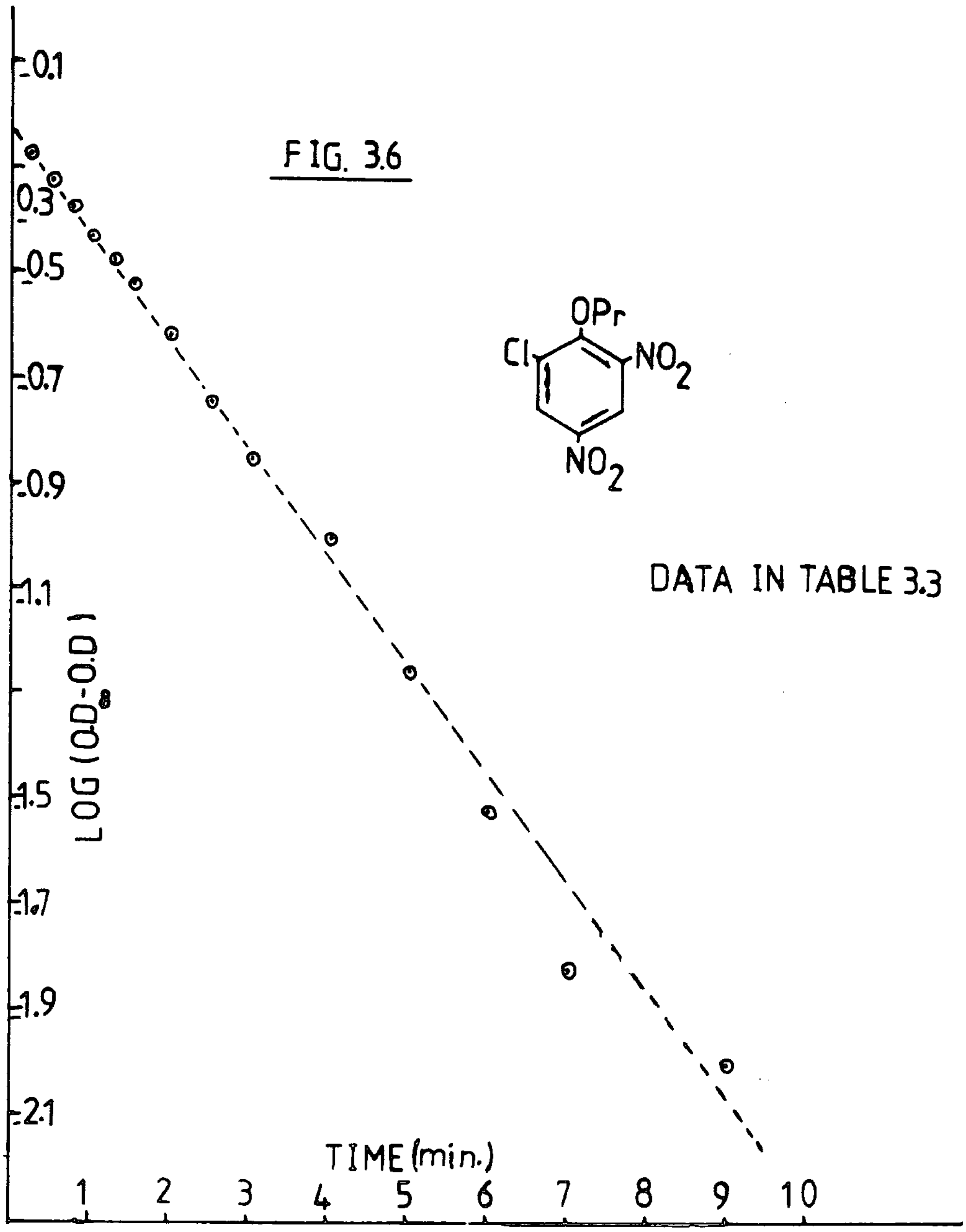


FIGURE 3.6

A plot of Log ($O.D_{\infty}$ - O.D) versus time for the reaction of 1-propoxy -2,4-dinitro-6-chlorobenzene with sodium propoxide Data are in table 3.3 .

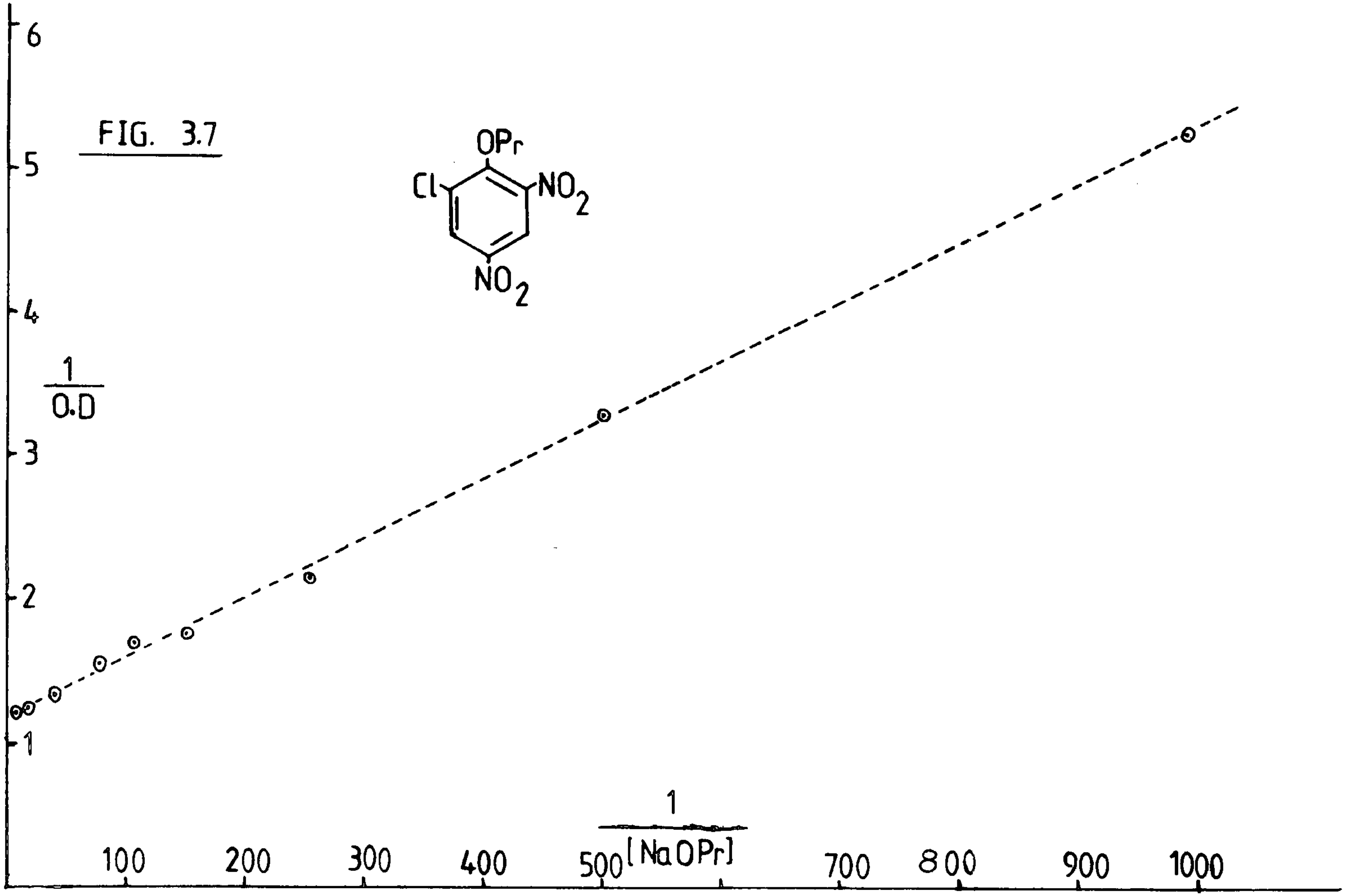


FIG. 3.7

FIGURE 3.7 Benesi-Hildebrand plot for reaction of 1-propoxy -2,4-dinitro -6-chlorobenzene with sodium propoxide in propan-1-ol at 25° .

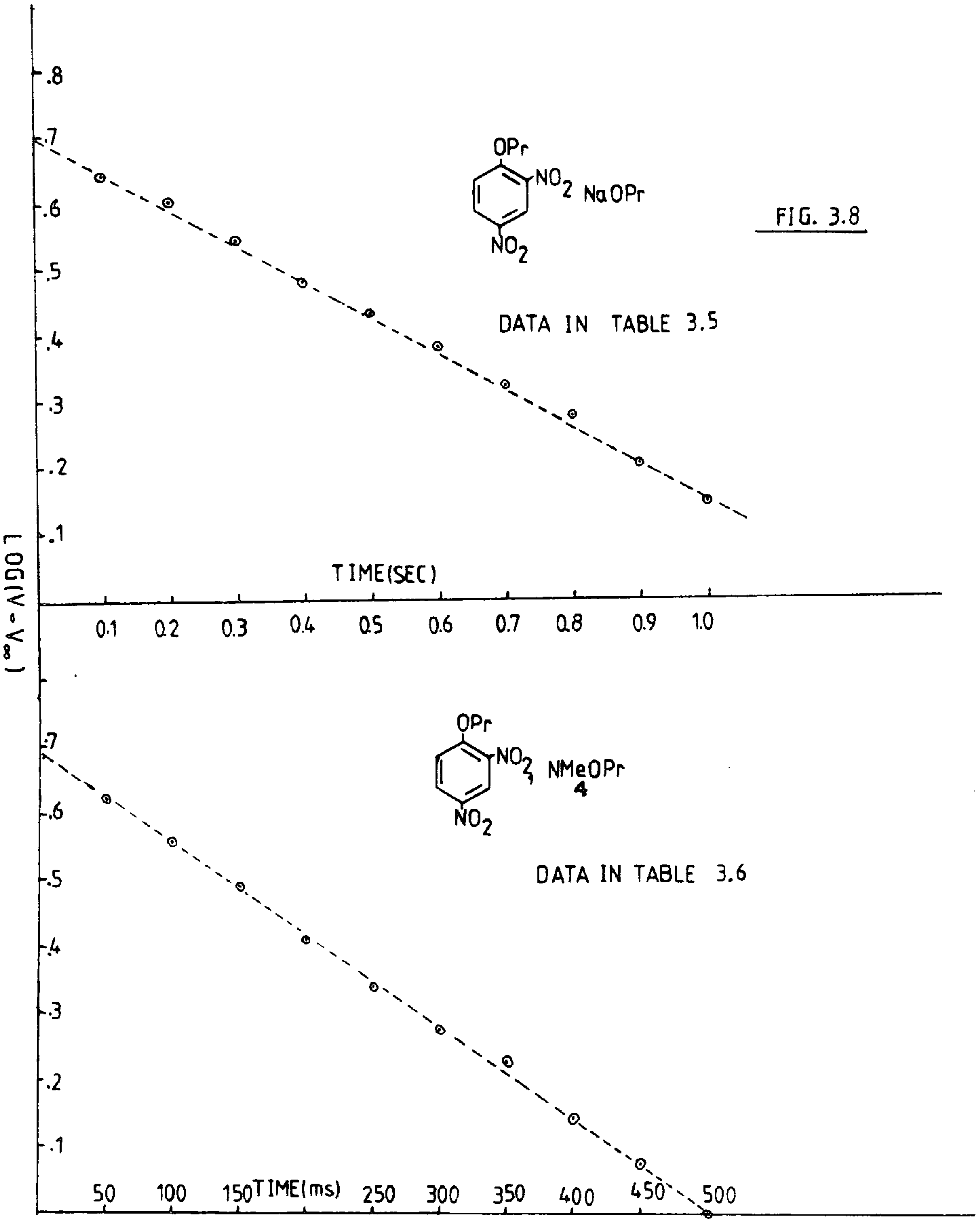


FIGURE 3.8

Specimen data for reaction of 1-propoxy-2,4-dinitrobenzene with sodium propoxide (above) and tetramethylammonium propoxide(below) measured by stopped- flow spectrophotometry .

FIG. 3.9

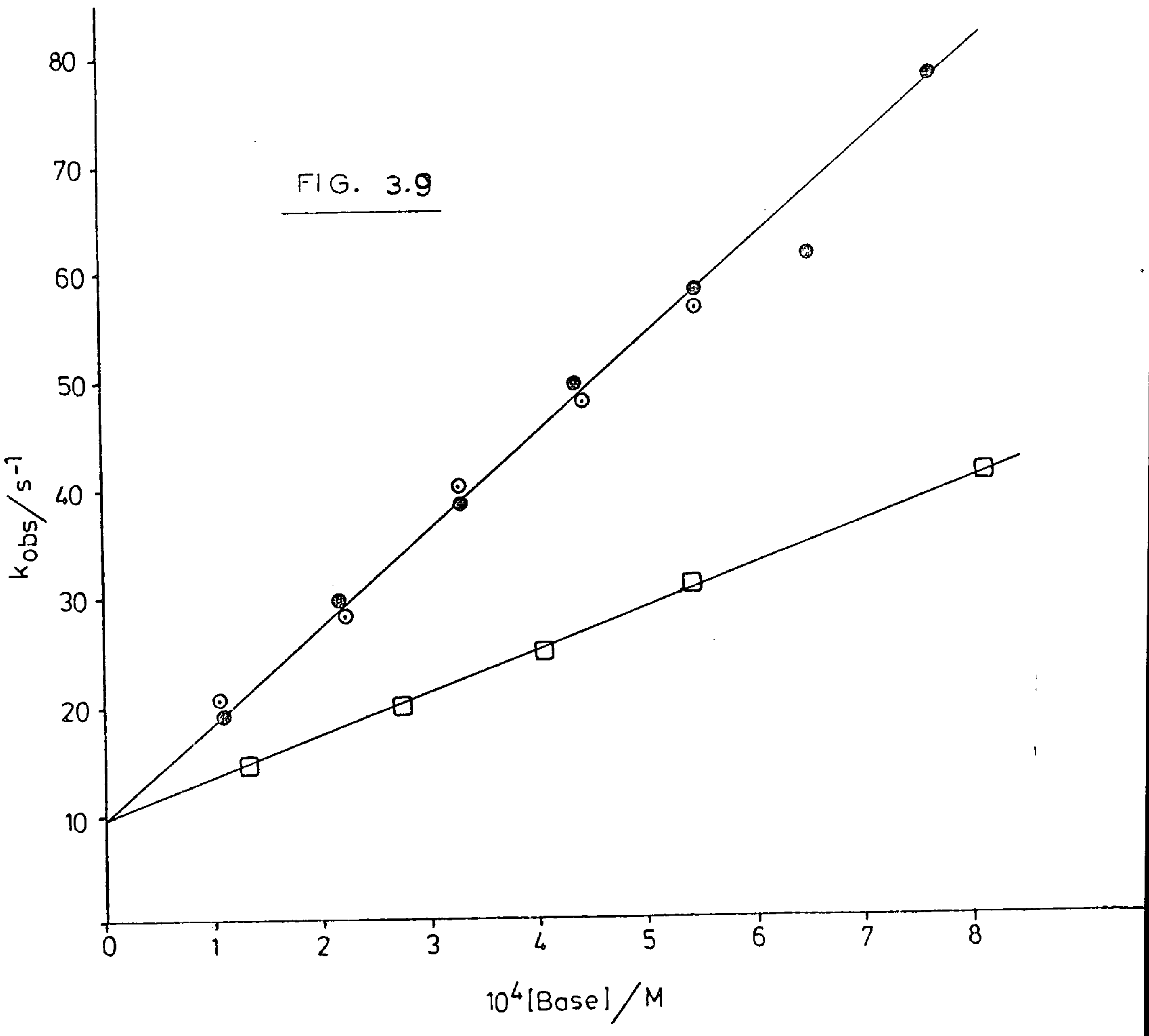


FIGURE 3.9

Rate coefficients for the reaction in propan-1-ol of 1,3,5 - trinitrobenzene with ⊙ tetramethylammonium propoxide, ○ sodium propoxide and ▣ sodium propoxide with 0.03 mol l sodium tetraphenyl boron at 25° .

FIG 3.10

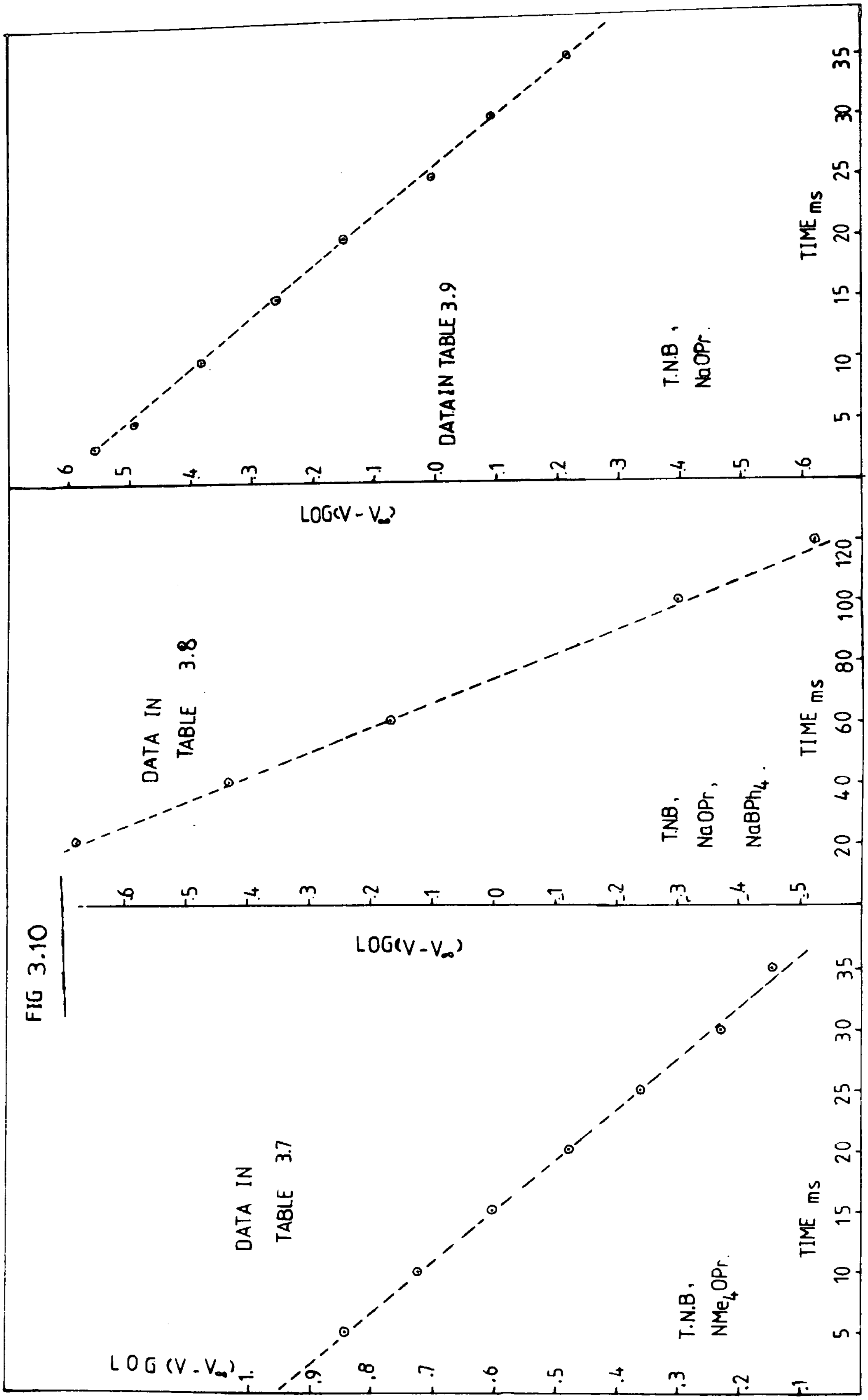


FIGURE 3.10 Specimen data measured by stopped-flow for the reaction of 1,3,5-trinitrobenzene (10^{-5} M) with tetramethylammonium propoxide (5.25×10^{-4} M)(above) and with sodium propoxide(5.45×10^{-4} M) at the presence of sodium tetraphenylboron (0.03M)(middle) and with sodium propoxide alone(5.45×10^{-4} M)(below) at 25°.

FIG. 3.11

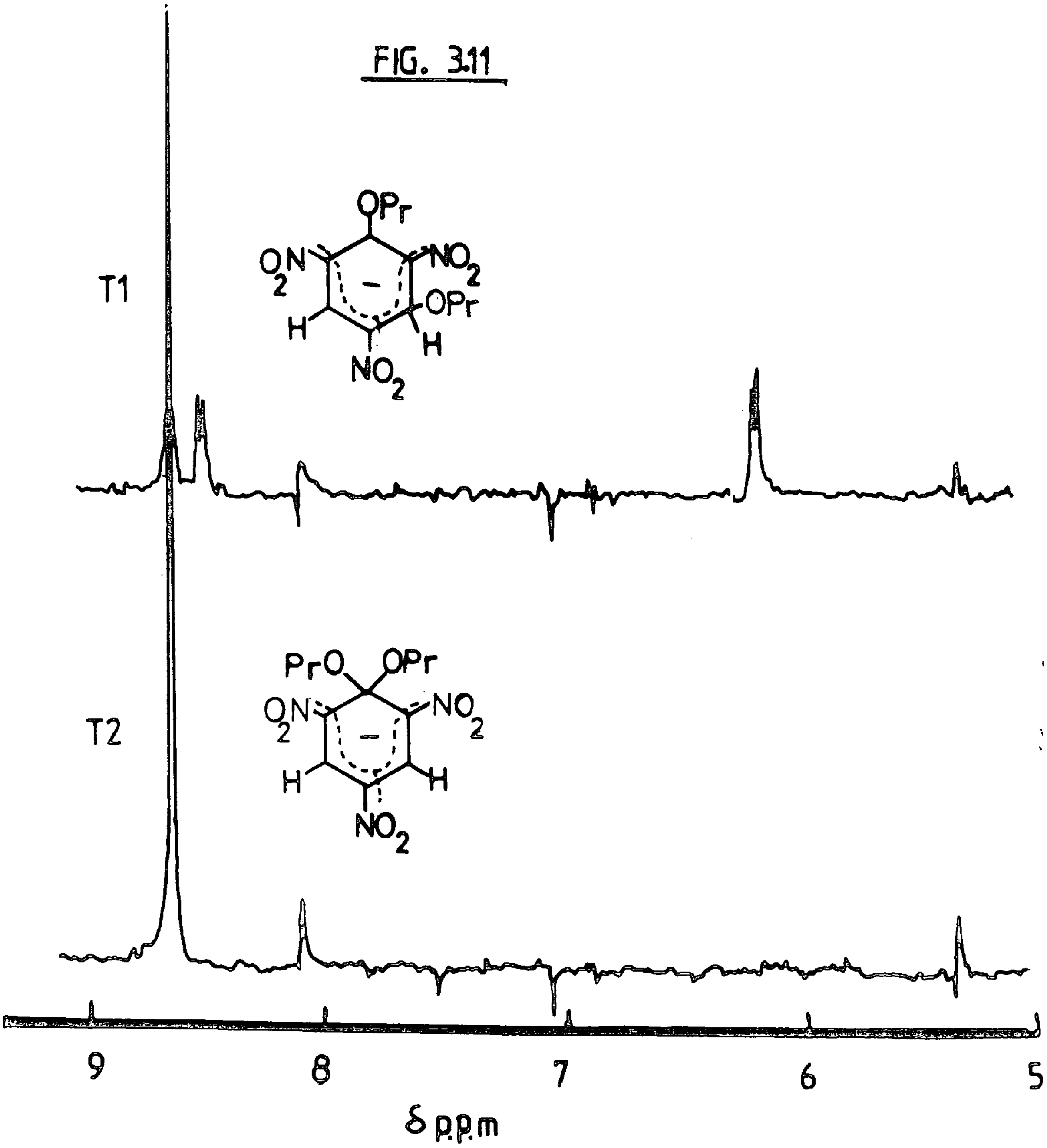


FIGURE 3.11

^{1}H.n.m.r spectra of 1-propoxy-2,4,6-trinitrobenzene and sodium propoxide in propanolic dimethyl sulphoxide .Initial spectra at T1 ,which changes to T2 after 3 minutes (at 25°) .

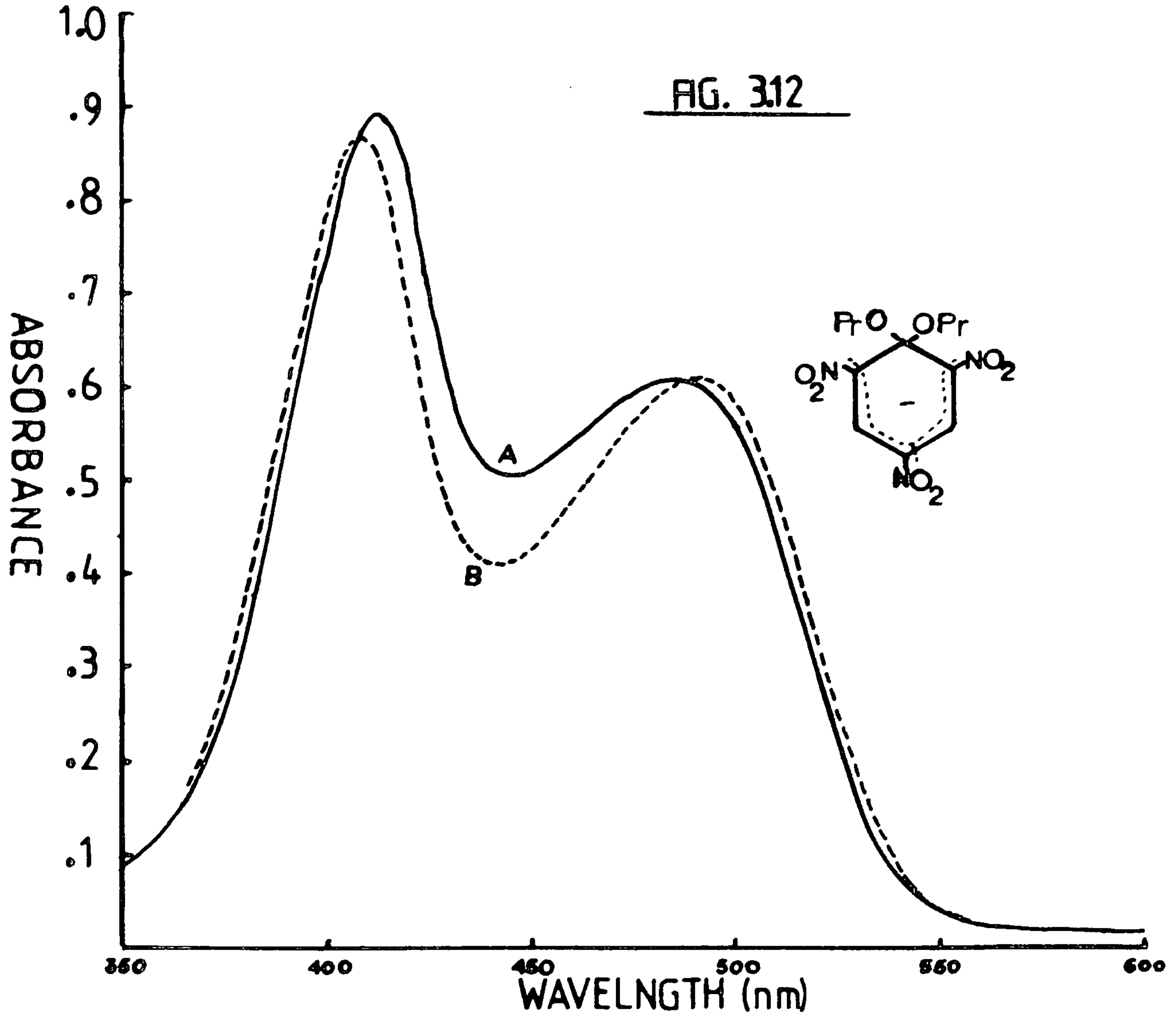


FIGURE 3.12 Visible spectra of 1-propoxy-2,4,6-trinitrobenzene (3×10^{-5} M) and sodium propoxide (7.5×10^{-4} M). At A, no salt present, B, 3.9×10^{-3} M of sodium tetraphenylboron at 25°.

FIG. 3.13

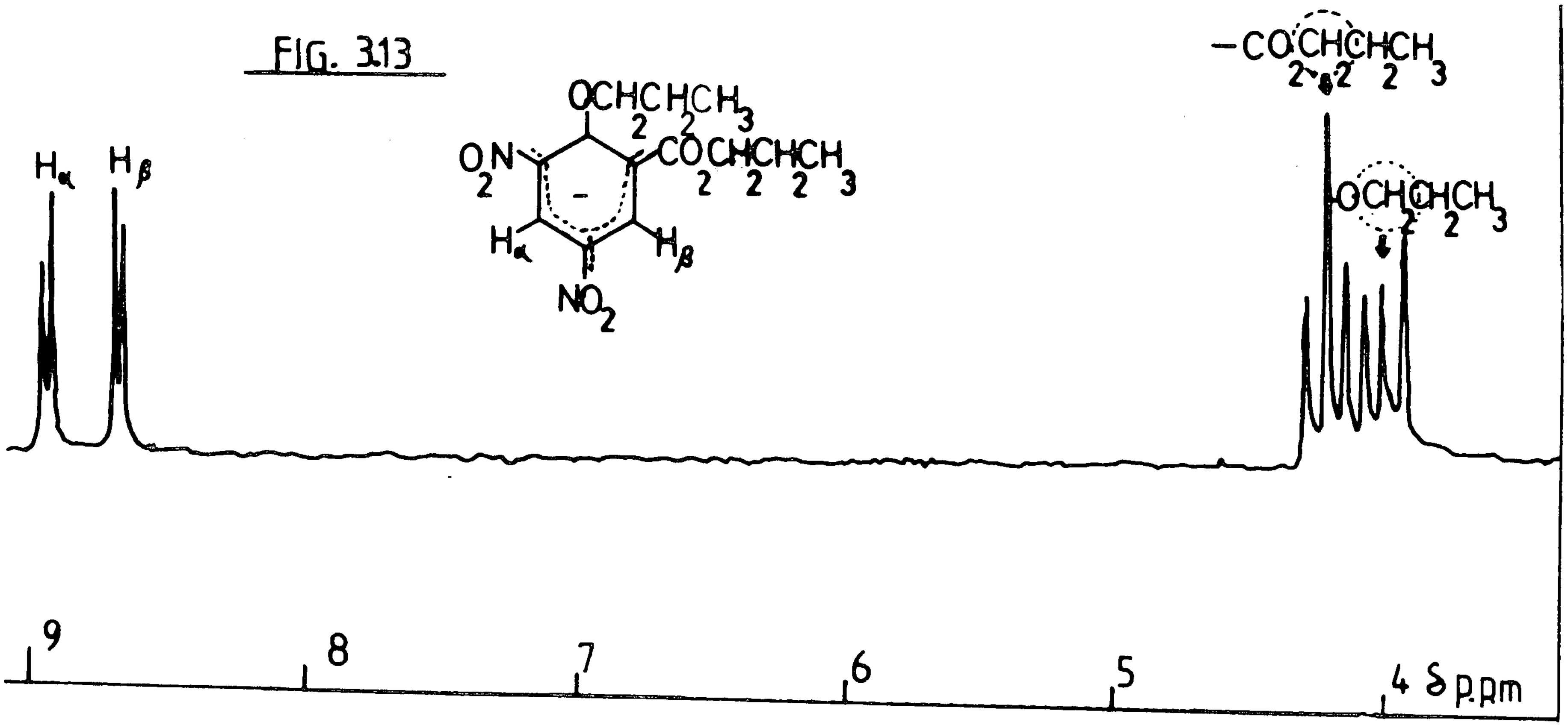


FIGURE 3.13 ¹H.n.m.r spectrum of 1-propoxy-2,4-dinitro-6-propoxy carbonyl benzene in $^2H_6$ DMSO ,at 25°.

FIG. 3.14

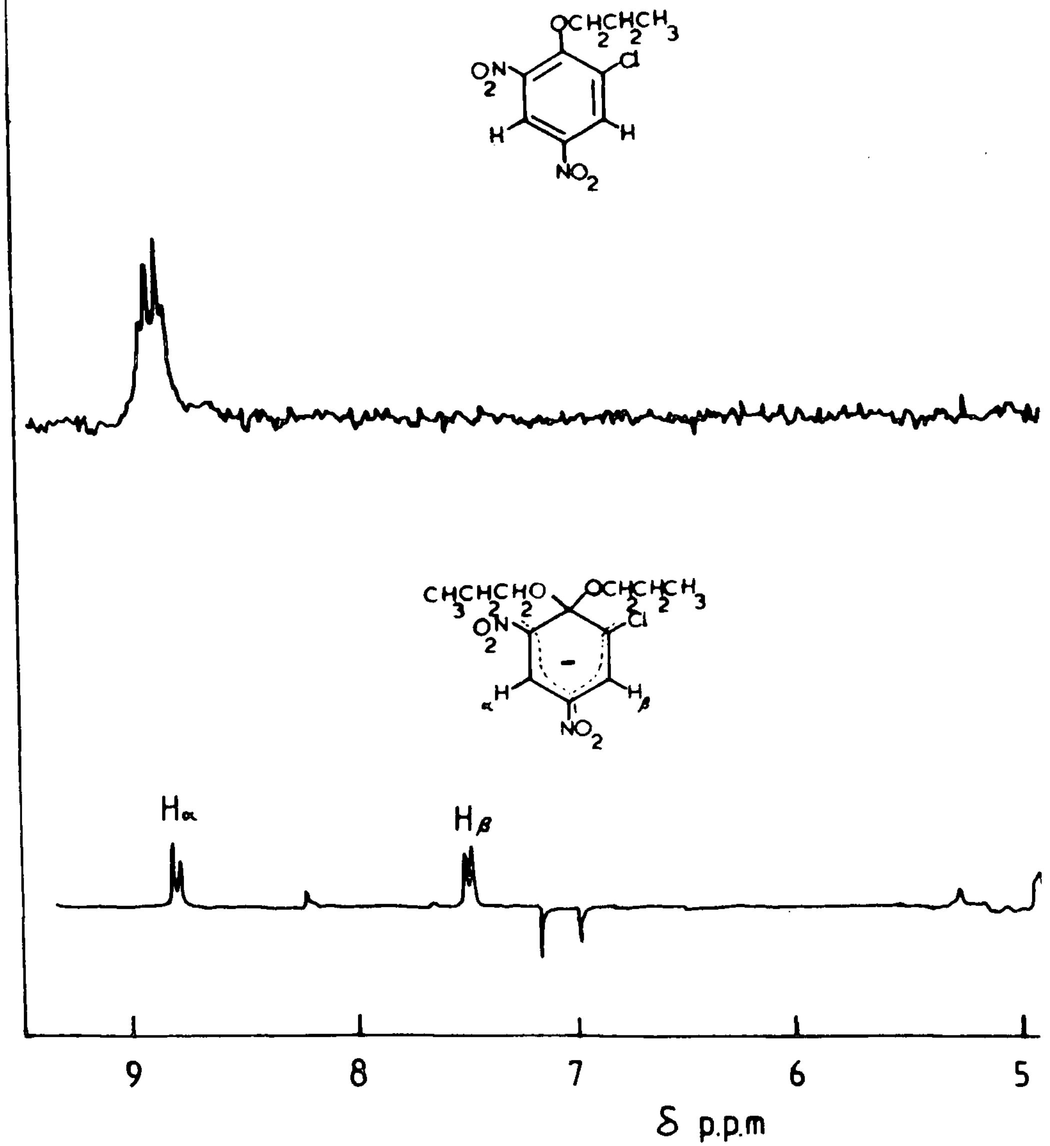


FIGURE 3. 14 ^{1}H.n.m.r spectra for 1-propoxy-2-chloro-4,6-dinitrobenzene in propanol(above) and with sodium propoxide(below) in propanolic DMSO- d_6 at 25°.

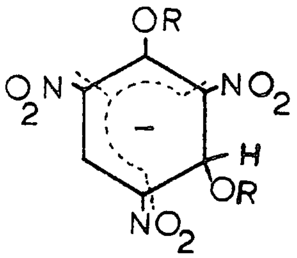
CHAPTER 4

THE REACTIONS OF THREE NITRO-AROMATIC COMPOUNDS WITH TETRAMETHYLAMMONIUM HYDROXIDE AND METAL BUTOXIDES IN t-BUTANOL CONTAINING WATER

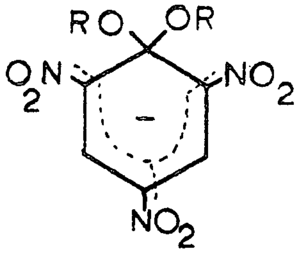
Introduction

In this part, kinetic and equilibrium data are reported for the reaction of three nitro-compounds with tetramethylammonium hydroxide and potassium and sodium butoxides in t-butanol containing water. In all solvent systems studied the reactive nucleophile is thought to be the hydroxide ion rather than the t-butoxide ion.

The initial reaction of 1,3,5-trinitrobenzene with alkoxide ions is to give the σ-adducts (3.1, R = alkyl) while alkyl ethers of 2,4,6-trinitrophenol generally yield the 3-alkoxy adducts (4.1) which isomerize to the thermodynamically more stable 1,1-dialkoxy adducts (4.2). The results have shown the importance in these reactions of ion-association with alkali-metal cations of the alkoxide ions and the negatively charged σ-adducts (the 1,1-dialkoxy complexes associate particularly strongly with cations).



(4.1)



(4.2)

There have been relatively few reports of σ-complex formation involving t-butoxide ions. Gan and Norris[33] reported kinetic data for formation of an adduct from 1,3,5-trinitrobenzene and sodium t-butoxide in t-butanol. The linearity of plots of k_{obs} versus base concentration was taken to indicate the absence of ion-pairing effects. However a more recent study[131] from the same laboratory of the reaction of 2,4,6-trinitrotoluene-d_3 with sodium and potassium t-butoxides, in which σ-complex formation is thought to compete with deuteron transfer, recognises the importance of ion-association.

In order to minimise the effect of ion-pairing we have used tetraalkylammonium as the counter-ion, since we have shown[42] that in dilute solutions it associates with alkoxide ions and σ-adducts much less strongly than do alkali-metal cations.

A further complication is the possibility that in the presence of traces of water, t-butoxide ions will be converted to hydroxide ions (equation 4.1). Murto has defined[109] an equilibrium constant (equation 4.2) in terms of mole-fractions of water, X_{H_2O}, and alcohol X_{BuOH} for which he quotes a value of $\leqslant 5 \times 10^{-4}$.

$$\text{t-BuO}^- + H_2O \rightleftharpoons \text{t-BuOH} + OH^- \qquad 4.1$$

$$K'_{ha} = \frac{X_{H_2O}}{X_{BuOH}} \cdot \frac{[BuO^-]}{[OH^-]} \qquad 4.2$$

Experimental

Two methods which have been previously mentioned to dry t-butanol (see chapter 2) are distillation from potassium, by which Bethel[144] obtained a product containing 0.05% (w/w) of water, or refluxing with molecular sieve followed by distillation.[131] We obtained similar results using AnalaR t-butanol treated by either of these methods. 'H.n.m.r spectra of the dried product showed a small band due to residual water whose intensity indicated a water content of 0.07% (v/v). Solutions of base were obtained by diluting with t-butanol a concentrated (ca. 2M) aqueous solution of tetramethylammonium hydroxide. This necessarily increases the water content of the solvent. However, in dilute base solutions the water added in this way is small compared with the residual water in the solvent. Thus a base concentration of 2 x 10^{-4}M will increase the water content by 0.01% (v/v). Because of the high freezing point of t-butanol (25°) measurements were made at $30^{\circ} \pm 0.5$.

A solubility test was carried for some mineral salts in purified t-butanol and it was found that sodium and potassium chloride are insoluble, while sodium perchlorate has a very low solubility. Sodium tetraphenylboron is soluble to some extent in this alcohol but forms a white precipitate in the presence of tetraalkylammonium bases, which makes it difficult to deal with in U.V /visible studies.

PART I[43]: REACTIONS WITH TETRAMETHYLAMMONIUM HYDROXIDE

Results and Discussion

(a) 1,3,5-Trinitrobenzene

In the presence of dilute solutions of base, prepared as above 1,3,5-trinitrobenzene gives an orange species whose visible spectrum obtained by stopped-flow or conventional spectrophotometry shows maxima at 430 nm, ε, 2.2 x 10^4 ℓ $mol^{-1}cm^{-1}$ and 500 nm, ε, 1.5 x 10^4 ℓ $mol^{-1}cm^{-1}$. This spectrum is typical of that of 1:1 σ-adducts formed by attack on TNB of oxygen bases[11] so that we formulate the reaction as shown in equation 4.3. With base in excess of the nitro-compound equation 1.44 will hold.

$$\mathrm{TNB} + \mathrm{OR}^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (3.1) \qquad 4.3$$

$$k_{obs} = k_f[\mathrm{OR}^-] + k_r \qquad 1.44$$

Table 4.1

Kinetic Data for the Reaction of 1,3,5-Trinitrobenzene[a] with Base in t-Butanol-Water at 30°.

10^4 [Base] / M	% Water by Volume	k_{obs}/s^{-1}	k_{obs}/[Base] ℓ $mol^{-1}s^{-1}$	OD (480 nm)[b]
0.57	0.07	135 ± 10	2.4×10^6	0.030
0.85	0.07	240	2.8×10^6	0.030
1.15	0.07	320	2.8×10^6	0.030
1.0	0.32	150	1.5×10^6	0.030
1.0	0.57	95	9.5×10^5	0.030
1.0	1.07	55	5.5×10^5	0.028
2.0	1.08	110	5.5×10^5	0.032
2.0	2.08	48	2.4×10^5	0.028
2.0	4.08	17	8.5×10^4	0.028
1.0	7.07	2.4	2.4×10^4	0.030
1.0	10.1	1.9	1.9×10^4	0.030
100	50	6.5	6.5×10^2	0.020
100	65	5.0	5.0×10^2	0.015
100	80	6.5 ± 1	-	0.009
200	80	8	-	0.013
400	80	10.5	-	0.017
100	90	15 ± 1	-	0.0025
200	90	13	-	0.0046
400	90	14	-	0.0095
600	90	14	-	0.0125

a. [TNB] is 1×10^5 M throughout.

b. Measured by stopped-flow spectrophotometry with 2 mm cell.

Kinetic measurements were made by stopped-flow spectroscopy in dried t-butanol and in its mixtures with water. Only a single colour forming reaction was observed on the stopped-flow time-scale under all conditions. Data are in table 4.1. In media containing 10% water or less conversion of 1,3,5-trinitrobenzene to adduct is essentially completed at equilibrium in solutions containing very low base concentrations. This indicates very high values for K, the equilibrium constant for adduct formation, so that $k_f[OR^-] >> k_r$. Hence the values in column 4 of table 4.1 give values of k_f the rate coefficient for base attack on TNB.

In media rich in water conversion to adduct is incomplete at equilibrium. If we assume that the extinction coefficient at 480 nm is unaffected by change in solvent we may use the equilibrium optical densities to calculate values of the equilibrium constant. Values so calculated are 35 ± 10 ℓ mol^{-1} in 80% water and 10 ± 2 in 90% water. The rate measurements in 80% water yield values of k_f 140 ℓ $mol^{-1}s^{-1}$ and k_r 5 s^{-1}. In 90% water the rate expression (equation 1.44 in chapter 1) is dominated by the k_r term which has a value of 14 s^{-1}.

One interpretation of the data is that attack by the t-butoxide ion on 1,3,5-trinitrobenzene yields the adduct (3.1, R = t - Bu). The decrease in the value of k_f with increase in water in the solvent could then be attributed to a depletion in the t-butoxide concentration via the equilibrium shown in equation 4.1 and also to a solvent effect which reduces the nucleophilicity of the t-butoxide.

A second interpretation, and one which I favour, is that the reactive species is the hydroxide ion and that the decrease in its nucleophilicity with increasing water content is due to a solvent effect. Using a value[109] for K_{ha} of 5×10^{-4} we calculate equation 4.2 that even in our dried solvent the concentration of hydroxide will be ca. seven times higher than that of butoxide. It might be argued that the t-butoxide ion should have considerably higher reactivity than the hydroxide ion. However, the t-butoxide adduct of 1,3,5-trinitrobenzene would be subject to considerable steric strain which will lower its stability. Thus recent crystallographic evidence[132] indicates that even the methoxide adduct of TNB is subject to steric strain. Further the values of rate and equilibrium constants we calculate in water rich media, are similar to those reported by Bernasconi and Bergstrom[133] for reaction of TNB with hydroxide ions in 81 : 19 water/ethanol. (Their values are k_f 70 ℓ $mol^{-1}s^{-1}$, k_r 7 s^{-1}, K 10 ℓ mol^{-1}).

The regular increase in reactivity of the hydroxide ions as the proportion of t-butanol in the solvent is increased can be attributed to its progressive desolvation. This in agreement with the observation by Bethel[144] that the addition of small quantities of water to t-butanol containing benzyl trimethylammonium hydroxide drastically reduces the ability of the medium to abstract a proton from the indicator 4-nitroaniline.

Further evidence that the reactive species is the hydroxide ion comes from a study of the reaction of 1-chloro-2,4-dinitrobenzene with base in t-butanol-water mixtures.

(b) 1-Chloro-2,4-dinitrobenzene

In the presence of tetramethylammonium hydroxide in t-butanol, 1-chloro-2,4-dinitrobenzene is converted into a yellow species whose visible spectrum is identical with that of 2,4-dinitrophenol in the same medium (λ_{max} 367nm, ε, 17,500 ℓ $mol^{-1}cm^{-1}$, and 410 nm, ε, 17,000 ℓ $mol^{-1}cm^{-1}$) (figure 4.1). In media containing 1% or more of water conversion is essentially quantitative. In media containing less water 2,4-dinitrophenol is the major product as judged by U.V/visible spectroscopy but conversion is not complete. Here the visible spectra show more absorption in the 300-350 nm region than does 2,4-dinitrophenol indicating the formation of another product, possibly the t-butyl ether of 2,4-dinitrophenol. The increase with time of the absorption at all wavelengths above 300 nm (figure 4.1) proceeds at the same rate indicating that formation of 2,4-dinitrophenol and the side-product is concurrent rather than consecutive.

There are several possible mechanisms available for the formation of 2,4-dinitrophenol. The most straight forward is the direct S_NAR replacement of halide by hydroxide ion. However, the formation of radical anions upon interaction of halogenonitrobenzene with alkoxides is well documented[16]. That these radicals may contribute to the overall substitution process has been shown by Scorrano and co-workers[135] in the reactions of 4-chloronitrobenzene with alkoxides[138]. Characteristic features of reactions involving radicals[135,138] are a less than first order dependence on base concentration and a susceptibility to the presence of oxygen. The data in table 4.2 show neither of these characteristics. Thus the results in rows 13 to 15 indicate a strictly first order dependence on base concentration while those in rows 9 to 11 indicate that the presence or absence of oxygen has little effect on reaction rate. While we cannot rule out the possibility that a small amount of reaction proceeds by radical intermediates, particularly in those media containing the least water, the data are in accord with the formation of 2,4-dinitrophenol by direct attack of hydroxide ions on 1-chloro-2,4-dinitrobenzene. The decrease in reaction rate with increasing proportion of water in the solvent is shown in figure 4.2. The variation is similar to that of the TNB-hydroxide reaction, indicating that it is very likely that the same nucleophile, OH^-, is the reactive species in each case.

Table 4.2

Kinetic Data for Reaction of 1-Chloro-2,4-dinitrobenzene[a] with Base in *t*-Butanol-Water at 30^{o}.

10^3 [Base] / *M*	% Water by Volume	10^3 k_{obs}/ s^{-1}	k_{obs}/[Base] ℓ $mol^{-1}s^{-1}$	OD (410 nm)
0.2	0.08	2.2	11	0.45
0,4	0.09	4.0	10	0.32
0.6	0.10	4.3	7	0.40
1.0	0,12	7.4	7	0.42
2.0	0.16	12.3	6	0.44
1.0	0.35	2.2	2.2	0.52
1.0	0.59	1.5	1.5	0.60
1.0	1.06	0.84	0.84	0.62
1.0	2.06	0.40	0.40	0.64
0.43[b]	2.10	0.18	0.42	0.63
0.43[c]	2.10	0.15	0.35	0.63
1.0	3.95	0.14	0.14	0.60
10	5.6	0.83	0.083	0.05
7.7	5.5	0.59	0.078	0.63
5.1	5.3	0.41	0.080	0.64
57	13	0.54	0.01	0.67
54	18	0.35	0.007	0.67
51	23	0.19	0.004	0.67
45	32	0.09	0.002	0.67

a. 1-chloro-2,4-dinitrobenzene is 4×10^{-5} *M*.

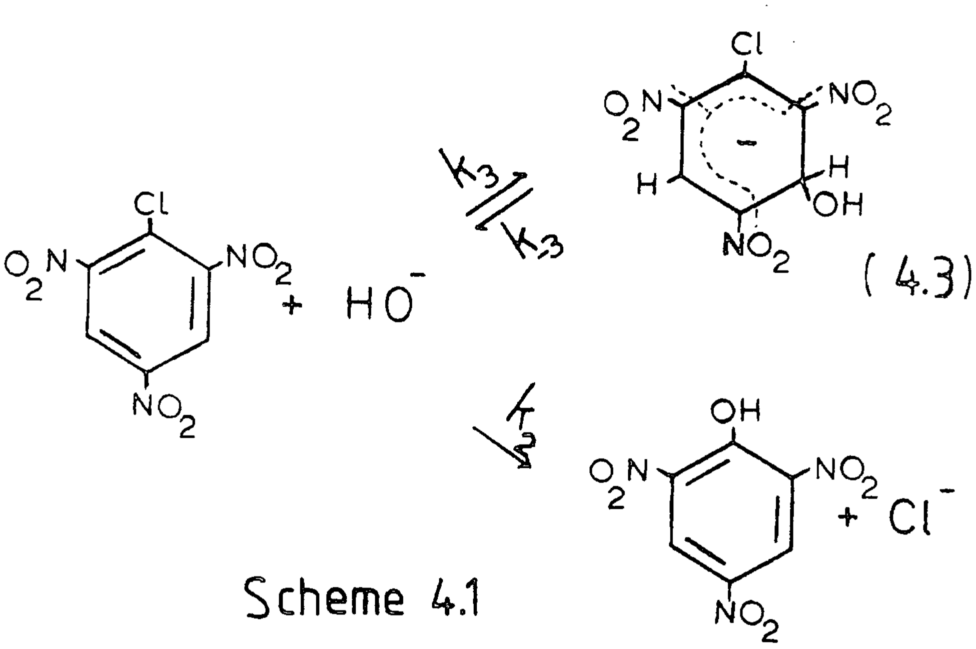
b. Solutions flushed with nitrogen.

c. Solutions flushed with oxygen.

(c) 1-Chloro-2,4,6-trinitrobenzene

The reaction of picryl chloride with dilute solutions of tetramethylammonium hydroxide in t-butanol proceeds in two stages. There is a rapid reaction giving an orange species whose visible spectrum, with maxima at 425 and 480 nm (figure 4.3), is typical of a σ-adduct. This is followed by a slower reaction giving a yellow species whose visible spectrum, λ_{max} 365 nm, is identical with that of picric acid in the same medium. Specimen data for the calculation of the rate coefficient of the slow process by Guggenheim's method is in table 4.4.

We interpret the data according to reactions shown in the scheme 4.1. The initially formed adduct (4.3) might result from attach of either t-butoxide or hydroxide ions. The data relating to this reaction, table 4.3 are in accord with attack by hydroxide. Thus the decrease in the value of k_3 ($\equiv k_{obs}/[\text{Base}]$) with increasing water in the solvent parallels the decrease in rate coefficients for hydroxide attack on 1,3,5-trinitrobenzene and 1-chloro-2,4-dinitrobenzene. In media



Scheme 4.1

containing 5% or 10% water only partial conversion to σ-adduct is achieved with 1 x 10^{-4}M base. The optical densities at completion of this reaction, but before appreciable conversion to picric acid has occurred, allow the calculation of values of K_3. These values together with the values of k_{obs} give values in 5% water of k_3 1.2 x 10^4 ℓ $mol^{-1}s^{-1}$, k_{-3}0.6 s^{-1} and in 10% water of k_3 2.2 x 10^3 ℓ $mol^{-1}s^{-1}$ and k_{-3}1.1 s^{-1}.

Comparison of tables 4.1 and 4.3 shows that at a given solvent composition values of rate constants and equilibrium constants for hydroxide attack at the 3-position of picryl chloride are lower than those for attack at un-substituted position of 1,3,5-trinitrobenzene. A similar reactivity order has been found previously in studies of methoxide[157] or ethoxide[158] attack on these substrates. The lower reactivity of picryl chloride may be due to steric interference between the chlorine atom and the nitro-groups which disrupts the planarity of the molecule and reduces the electron withdrawing ability of the nitro-groups.

In previous work[159] it has been shown that in water containing sodium hydroxide the hydroxy-group in adducts such as (4.3) will ionise to give a dianionic species. However, little ionisation occurs in solutions containing < 10^{-2} M base. At the very low base concentrations used in the present work we would not expect appreciable ionisation of (4.3) to occur.

With time picryl chloride is converted to picric acid. In all media examined converison is > 80%. We have no evidence that reaction occurs other than by direct displacement of chlorine by hydroxide ion. Thus visible spectra show an isobestic point at 400 nm indicating the absence of any reaction intermediate such as the t-butyl ether of picric acid. The kinetic expression corresponding to the reaction sequence shown in the scheme is given in equation 4.5. At the base

Table 4.3

Kinetic and Equilibrium Data for the Rapid Reaction of Picryl Chloride (10^{-5} M) with Base in t-Butanol-Water at 30°.

10^4 [Base] / M	% Water by volume	k_{obs}/ s^{-1}	k_{obs}/[Base] $\ell\ mol^{-1}s^{-1}$	OD (480 nm)[a]	K_3[b]/ $\ell\ mol^{-1}$
0.5	0.07	60±10	1.2×10^6	0.030	-
1.0	0.07	130	1.3×10^6	0.030	-
1.5	0.07	250	1.7×10^6	0.030	-
1.1	0.30	50	4.5×10^5	0.030	-
1.0	0.6	24	2.4×10^5	0.030	-
1.0	1.1	14	1.4×10^5	0.028	-
1.0	5.0	1.8	-	0.020	2×10^4
1.0	10.0	1.3	-	0.006	2×10^3

a. At the completion of the rapid reaction.

b. Defined as OD (480)/(0.030-OD (480)) [Base].

Table 4.4

Specimen Data for Slow Process at 470 nm (from figure 4.3), Where Guggenheim's Method is Applied.

t(s)	$O.D_\lambda(t)$	$O.D_\lambda(t + T)$	$O.D_\lambda(t) - O.D_\lambda(t+T)$	$\text{Log}\{O.D_\lambda(t) - O.D_\lambda(t+T)\}$
0	0.737	0.298	0.439	-0.357
110	0.670	0.281	0.389	-0.410
220	0.623	0.269	0.354	-0.451
330	0.575	0.253	0.322	-0.492
440	0.529	0.243	0.386	-0.543
550	0.482	0.233	0.249	-0.604
660	0.446	0.224	0.222	-0.653
770	0.310	0.210	0.200	-0.699
880	0.382	0.198	0.184	-0.735
990	0.358	0.195	0.163	-0.788
1100	0.330	0.190	0.140	-0.853

λ = 470 nm , T = 1320 sec.

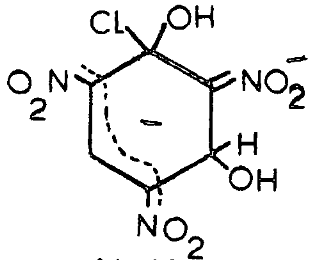
---

concentrations used to measure the slow reaction $K_3[OH^-] > 1$, so that equation 4.5 reduces to 4.6

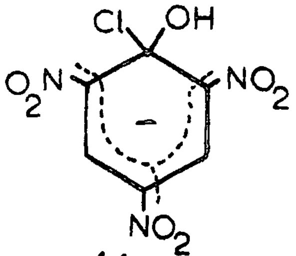
$$k_{obs} = k_2[OH^-]/(1 + K_3[OH^-]) \qquad 4.5$$

$$k_{obs} = k_2/K_3 \qquad 4.6$$

Measurements obtained at 480 nm are in table 4.5. They show that, as required by equation 4.6, values of k'_{obs} are independent of base concentration in media containing > 2% water. In media containing less water there appears to be a component of the rate which increases with base concentration. Thus the first three results in table 4.5, referring to solutions where the water content changes little, show a marked dependence on base concentration. It is possible that in these solutions where the hydroxide ions will be least solvated and thus most reactive, attack of hydroxide occurs on the σ-adduct (4.3) to give nucleophilic substitution via the di-adduct (4.4). Such an adduct would be unstable with respect to loss of chloride ion and would not be an observable intermediate. That such a pathway exists in water containing high concentrations of sodium hydroxide has been shown previously[159].



(4.4)



(4.5)

It is worth noting that our kinetic data allow us to discount the possibility that the σ-adduct we have observed is (4.5) rather than (4.3). The argument is as follows. If we were to assume that the observed adduct is (4.5) then the rate constants in table 4.5 would refer to loss of chloride ion from this adduct and would give a value in 5% water of 1 x 10^{-2} s^{-1}. An example is shown in figure 4.3 and table 4.4 demonstrating the use of Guggenheim's method. However the measurements of the more rapid reaction give a value in the same solvent system for expulsion of hydroxide ion of 0.6 s^{-1}. Since chloride is known to be a considerably better leaving group than hydroxide this hypothesis is untenable.

From the known values of k'_{obs} and K_3 we calculate, using equation 4.6, a value for k_2 of 200 ℓ $mol^{-1}s^{-1}$ in a medium containing 5% water. Since base addition will be the rate-limiting step in the substitution reaction, this value refers to the rate of hydroxide attack at the 1-position of picryl chloride. The corresponding value for hydroxide attack at the 3-position is 1.2 x 10^4 ℓ $mol^{-1}s^{-1}$ in the same medium. That attack at the unsubstituted position is faster than at the chloro-substituted position is in agreement with results obtained in water[159].

The results, table 4.5, indicate that the rate of conversion of picryl chloride to picric acid increases with water content of the solvent. This in marked contrast with the large decrease in rate of conversion of 1-chloro-2,4-dinitrobenzene to 2,4-dinitrophenol with increasing water. The difference in behaviour is understandable when it is remembered that the equation relevant to picryl chloride is equation 4.6. As outlined below it is expected that the values of both k_2 and K_3 will decrease with increasing proportion of water in the

Table 4.5

Rate Data for the 'Slow' Reaction of Picryl Chloride (4 x 10^{-5} M) with Base in t-Butanol-Water at 30°.

10^4 [Base] / M	Volume % Water	10^4 k'_{obs}/ s^{-1}
2.0	0.08	3.6 ± 0.3
4.0	0.09	5.2
8.4	0.11	10
30	0.22	30
50	0.32	23
4.8	1.1	33
25	1.2	42
4.8	2.1	44
25	2.2	62
4.8	3.1	67
25	3.2	84
4.8	4.1	89
25	4.2	97
5	5.0	108
10	5.0	105
20	5.0	96
50	5.0	87
100	5.0	200
10	10.0	210
20	10.0	200
50	10.0	180
100	10.0	

solvent. However, if the decrease in K_3 is larger than the decrease in k_2 then the value of k'_{obs} will increase. The change in value of K_3 with solvent composition will depend on the change in energy of the adduct (4.3) relative to the reactants. A major factor contributing to the expected decrease in value is likely to be the better solvation and corresponding lowering in energy of the hydroxide ion as the proportion of water is increased. Similarly the value of k_2 will be expected to decrease as the water concentration is increased. However here the relevant energy change is between the transition state for formation of (4.5) and the reactants. Since in the transition state desolvation of the hydroxide ion will be incomplete the smaller decrease in value of k_2 can be understood.

PART II : REACTIONS WITH METAL BUTOXIDES

Results and Discussion

a) 1,3,5-Trinitrobenzene

The visible spectra for 1,3,5-trinitrobenzene with sodium or potassium t-butoxides are similar to that obtained with tetraalkyl t-butoxide (part I). A spectrum obtained by stopped-flow is shown in figure 4.4 and table 4.6 and is typical of 1:1 σ-adducts (equation 4.3 and 1.44).

Kinetic measurements were made by stopped-flow spectrophotometry in dried t -butanol and in its mixtures with water. Only a single colour forming reaction was observed on the stopped-flow time scale under all conditions. Data are in table 4.7 for sodium t-butoxide and in table 4.8 for reaction with potassium t-butoxide. Conversion of 1,3,5-trinitrobenzene to adduct is essentially complete at equilibrium in solutions containing 10% water or less at the base concentrations used. According to this we expect high values for K (the equilibrium constant for adduct formation) so that $k_f [OR^-] >> k_r$. Hence column 5 of table 4.7 and column 4 of table 4.8 give values of k_f (the rate coefficient for base attack on TNB which is described in equation 1.44). The value of k_f for reaction with sodium alkoxide in the "anhydrous solvent" is 4×10^4 ℓ $mol^{-1}s^{-1}$ which is close to the value obtained by Gan and Norris[33] (38,000 ± 2,000). The value is affected very little by the presence of sodium ions in the form of $NaBPh_4$ so that it can be concluded that reaction occurs via Na^+OR^- ion pairs. The value with the potassium base 3.7×10^4 ℓ $mol^{-1}s^{-1}$ is similar. Both these values are very much smaller than the value for reaction with tetraalkylammonium base (3×10^6 ℓ $mol^{-1}s^{-1}$) which will be largely dissociated. These results do not of themselves indicate whether the reaction being studied involves t-butoxide attack or hydroxide attack. However the fact that the addition of water to the medium does not give rise to a second rate process might be taken as evidence that reaction involves Na^+OH^- and K^+OH^- ion pairs rather than the t-butoxide species.

The observed rate coefficients decrease much less rapidly on addition of water than do those obtained with tetraalkylammonium hydroxide. This may be attributed to the counterbalancing of two factors, (i) an increase in the extent of dissociation of ion pairs with increasing water content, (ii) a decrease in reactivity of free ions with increasing water content due to better solvation. In media containing 10% or more of water the rate coefficient is virtually independent of the cation.

^{1}H.n.m.r spectra were taken of TNB (0.2 M) and potassium t-butoxide (0.2 M) in a 50/50 (V/V) mixture of Anala R t-butanol/DMSO-d_6. Bands were observed at δ 8.43, 6.30 and 6.40, due to 1:1 adducts (the intensity ratio of the 6.30 and 6.40 bands being 2:1). It seems possible that in this medium both OH^- and OBu^- addition is occurring and gives rise to the bands at 6.30 and 6.40. In media containing 1.5% and 5% added water bands were only observed due to the hydroxy adduct at δ8.43 and 6.30. The observation of a band due to a butoxy adduct may result from the relatively high concentration of TNB and base used so that no free water remains in solution.

b) 1-Chloro-2,4 Dinitrobenzene

In the presence of potassium t-butoxide in t-butanol the visible spectra, figure 4.5, indicate the formation of 2,4-dinitrophenol. It is of interest that the visible spectrum of 2,4-dinitrophenol shows a distinct difference in the presence of tetraalkylammonium alkoxide and sodium/potassium butoxide. This difference can be attributed to the different extent of ion-pairing of the 2,4-dinitrophenoxide ion with $^{+}NR_4$ and $\overset{+}{Na}$. The spectra in figure 4.6(a) show the gradual change in spectrum as sodium ions, in the form of $NaC\ell O_4$, are added to a solution of 2,4-dinitrophenol and tetraethylammonium hydroxide in t-butanol.

Similarly the visible spectra of the picrate ion (figure 4.6(b)) are affected by ion association.

In media containing 1% or more of water conversion of 1-chloro-2,4-dinitrobenzene to 2,4-dinitrophenol is virtually complete as judged by infinity O.D values.

In "anhydrous" t-butanol there is evidence for the formation of another product with absorption in the region 300 - 350 nm (figure 4.5) which may be the t-butyl ether. This side product is formed concurrently with the 2,4-dinitrophenol.

Again we attribute reaction to give 2,4-dinitrophenol to the direct attach of hydroxide, or potassium hydroxide ion pairs, on the substrate. The rate coefficients in the "anhydrous solvent" are more than an order of magnitude lower than those obtained with the dissociated tetraalkylammonium hydroxide. In a given solvent (i.e. containing a fixed proportion of water) the value of the second order rate coefficient

Table 4.6

Specimen Data Obtained by Stopped-flow Spectrophotometer, for the Initial Spectrum, for KOBu (10^{-3}M) with TNB (10^{-5}M) in Dried t-Butanol at 30°C (see figure 4.4).

λ(nm)	V_o^a(volt)	V^b(volt)	O.D
520	5.0	4.725	0.0245
510	5.0	4.695	0.0273
500	5.0	4.700	0.0268
490	5.0	4.702	0.0266
480	5.0	4.725	0.0245
470	5.0	4.715	0.0255
460	5.0	4.705	0.0264
450	5.0	4.640	0.0324
440	5.0	4.610	0.0352
430	5.0	4.560	0.040
420	4.8	4.420	0.0358
410	4.0	3.760	0.0268
400	3.0	2.890	0.0162
390	2.1	2.050	0.0104
380	1.4	1.379	0.0065

a. corresponds to incident light intensity.

b. corresponds to intensity after passage through the sample.

$$\text{O.D} = \text{LOG}[V_o / V]$$

Table 4.7

Kinetic Data for

the reaction of 1,3,5-Trinitrobenzene (10^{-5}M) with Sodium Butoxide in t-Butanol-Water at 30°C.

10^4[Base]^a /M	[NaBPh$_4$] /M	% Water by volume	k_{obs}/ s^{-1}	$10^{-4}k_{obs}$/[Base] ℓ mol^{-1} s^{-1}	$O.D^c_{480}$
5.0	0	0.57	22 ±2	4.4	0.028
6.0	0.003	0.67	25 ±3	4.2	0.024
3.0	0.003	0.37	8.5±0.3	3.0	0.023
9.0	0.003	0.97	28 ±3	3.1	0.0255
3.0	0	0.37	10 ±1	3.3	0.0268
2.9	0	1.615	9 ±1	3.1	0.0259
6.0	0	1.665	20 ±1	3.3	0.0282
13	0	1.37	39 ±1	3.0	0.0277
10^4[Base]^b /M					
2.36	0	0.07	10 ±1	4.0	0.0193
4.70	0	0.07	22 ±1	4.7	0.0203
7.1	0	0.07	26.8±0.5	4.0	0.0251
10	0	0.07	32 ±2	3.2	0.0255
15	0	0.07	56 ±2	4	0.0273
19.9	0	0.07	72 ±1	4	0.0279
25.0	0	0.07	103 ±1	4	0.0289

a. Base was prepared by diluting aqueous sodium hydroxide with t-butanol.

b. Base was prepared by dissolving sodium metal in t-butanol.

c. Measured by stopped-flow spectrophotometry with 2mm cell.

Table 4.8

Rate Data for 1,3,5-Trinitrobenzene (10^{-5}M) with Potassium t-Butoxide in t-Butanol-Water at 30^{o}C.

10^4[Base]^a /M	% Water by volume	k_{obs}^{b} s^{-1}	$10^{-4}k_{obs}/$[Base] ℓ mol^{-1} s^{-1}	$O.D_{450}$
19	1.07	65±5	3.4	0.0353
19	2.0	63	3.3	0.0346
19	5.07	41 ($t_{\frac{1}{2}}$∿18s)	2.2	0.0348
19	10	16±0.5	0.8	0.0338
19	20	7	0.4	0.0276
9.5	0.07	32±2	3.4	0.0361
20	0.07	79±1	3.9	0.0356
24.7	0.07	85 ($t_{\frac{1}{2}}$∿9s)	3.4	0.0477
30.4	0.07	115±10	3.8	0.0444

a. Base was prepared by dissolving potassium metal in dried t-butanol.

b. In some cases a very much slower reaction was observed, $t_{\frac{1}{2}}$, noted.

decreases with increasing base concentration. This can be attributed to an increase in the fraction of base which is ion-paired as the base concentration increases.

As the fraction of water in the solvent increases, the second order rate coefficient decreases, but much less rapidly than with $^{+}NR_4OH^{-}$. Two factors are involved (i) better dissociation of the $K^{+}OH^{-}$ ion pairs with increasing water content and (ii) reduction in reactivities of hydroxide ions through better solvation.

An example, table 4.11 and figure 4.8, illustrating the linearity of one of the rates on table 4.9,(row 7) is included.

c) <u>1-Chloro-2,4,6-Trinitrobenzene</u>

The reaction of picryl chloride with potassium t-butoxide or sodium t-butoxide in t-butanol proceeds in two stages. There is a rapid reaction giving an orange species (typical of a σ-adduct) at 420 and 480 nm, figure 4.7. This is followed by a slower reaction, giving yellow species, whose spectrum is identical with that of picric acid. However λ_{max} shifts from 350 nm to 400 nm as the concentration of potassium t-butoxide is increased from 3×10^{-4}M to 0.05M, corresponding to ion-association of the picrate ion with potassium ions.

Scheme 4.1 will apply to this reaction, where the rapid process gives adduct 4.3 . The third column in table 4.12 is equal to k_3, scheme 4.1, and decreases with increasing water content in the solvent. This behaviour parallels that of 1,3,5-trinitrobenzene and 1-chloro-2,4-dinitrobenzene.

Comparison of tables 4.8 and 4.12 shows that at a given solvent composition (for potassium t-butoxide), values of rate constants and equilibrium constants for hydroxide attack at the 3-position of picryl chloride are lower than those for attack at

Table 4.9

Kinetic Data for Reaction of 1-Chloro-2,4-Dinitrobenzene (4×10^{-5}M) with Potassium t-Butoxide at 410 nm in t-Butanol-Water at 30°C.

10^3[KOBu] /M	10^3k_{obs} (s^{-1})	% Water by volume	k_{obs}/[Base] ℓ mol^{-1} s^{-1}
$.98^{7}$	.32	.07	.32
1.98	.56	.07	$.28^{3}$
5.12	1.05	.07	.205
10.0	1.77	.07	.177
19.5	2.52	.07	.13
39.0	4.98	.07	.105
58.5	5.09	.07	.087
78.0	6.9	.07	.088
2.45	.14	2.5	.06
4.9	.082	5.0	.017
7.3	.075	7.4	.010
9.8	.075	10.0	$.007^{7}$
12.25	.11	12.4	$.008^{9}$
9.8	.46	2.0	.047
19.3	1.32	1.0	.068

Table 4.10

Kinetic Data for 1-Chloro-2,4-Dinitrobenzene (4×10^{-5}M) with Postassium t-Butoxide in t-Butanol-Water at 30°C.

$10^3[\text{Base}]^a$ /M	% Water by volume	$10^3 k_{obs}$ (s^{-1})	O.D$^{b}_{400}$	$k_{obs}/[\text{Base}]$ $\ell\ mol^{-1}s^{-1}$
1.98	2	0.073	0.525	$.036^{8}$
1.98	4	0.056	0.520	$.028^{3}$
1.98	6	0.033	0.515	.017
1.98	8	0.035	0.515	.0176
1.98	10	0.027	0.525	.0136
3.96	10	0.044	0.520	$.011^{1}$
5.94	10	0.052	0.520	$.008^{7}$
7.92	10	0.063	0.525	$.007^{9}$
9.90	10	0.062^{5}	0.530	$.006^{3}$

a. Base was made by dissolving aqueous potassium hydroxide in purified t-butanol.

b. Optical densities at completion.

Table 4.11

Specimen Data for Reaction of 1-Chloro-2,4-Dinitrobenzene (4×10^{-5}M) with Potassium t-Butoxide (58.5×10^{-3}M) at 410 nm in t-Butanol-Water at 30°C (table 4.9 row 7 and figure 4.8).

Time(s)	O.D$_{410}$	O.D$_{\infty}$-O.D$_{410}$	Log(O.D$_{\infty}$-O.D$_{410}$)
30	0.270	0.280	-0.553
60	0.312	0.238	-0.623
120	0.380	0.170	-0.769
180	0.425	0.125	-0.903
240	0.456	0.094	-1.027
300	0.478	0.072	-1.143
∞	0.55	-	-

Table 4.12

Kinetic Data for the Reaction of Picryl Chloride (10^{-5}M) with Potassium t-Butoxide in t-Butanol-Water at 30°C.

10^3[KOBu] /M	$k_{obs}(s^{-1})$ (fast process)	k_{obs}/[Base] ℓ mol^{-1}s^{-1}	O.D$_{480}$	$10^3k_{obs}(s^{-1})$ (slow process)	K_3[a] ℓ mol^{-1}	% Water by volume
1.0	11.6 ± 0.3	11600	$.024^6$	4.6	-	.07
2.0	27 ± 1	13500	$.025^6$	6.04	-	.07
3.0	38 ± 3	13700	$.022^3$	-	-	.07
4.0	62 ± 2	15500	$.021^8$	-	-	.07
5.0	83 ± 3	16600	.022	-	-	.07
2.0	22 ± 2	11000	$.021^4$	24.4	-	1.07
2.0	17 ± 6	8800	-	58.8	-	2.07
2.0	9.5 ± 0.3	4750	.021	48.4	-	5
2.0	5.2 ± 0.2	2600	.018	26.0	1800	10
2.0	3.3 ± 0.3	1650	.010	23.7	360	20

a. Defined as O.D(480)/(0.023-O.D(480))[Base] .

Table 4.13

Rate Data for the Slow Colour Fading Process at 480 nm of Picryl Chloride with Potassium t-Butoxide in t-Butanol-Water at $30^{\circ}C$.

10^3[KOBu]/M	$10^3 k_{obs}$ s^{-1}	% Water by volume	[Picryl Chloride] /M
0.997	5.10	0.07	3×10^{-5}
2.02	4.76	0.07	
4.04	4.11	0.07	
6.06	4.08	0.07	
10.10	4.27	0.07	
1.98	26.	2.0	
4.06	49.	2.0	
2.02	20.	5.0	
3.94	32	5.0	
10.1	37	5.0	
2.02	25.	10.0	
4.04	28.	10.0	
10.10	27.	10.0	
5.18	4.76	0 .07	4.8×10^{-5}
5.13	107.4	1.0	
5.08	86.5	2.0	
5.18	33.7	5.0	
5.18	30.8	10.0	
1.9	5.76	0 .07	
1.9	42.3	1.0	
1.9	28.3	2.0	
1.9	25.9	10.0	

the unsubstituted position of 1,3,5-trinitrobenzene. This low reactivity of picryl chloride is due to steric interference (part I, between the chlorine atom and the nitro groups. The same argument favouring the formation of (4.3) rather than (4.5) can be applied here as in part 1.

As predicted from equation 4.6 rate coefficients of the slow process are largely independent of base concentration at a given solvent composition. They go through a maximum value as the water concentration is increased. This must result from a combination of factors, including ion-pairing and solvation, affecting the relative reactivities of the hydroxide ion for σ-adduct formation and nucleophilic substitution.

Conclusion

With metal butoxides another factor is introduced here, beside the effect of water. This is ion-association. In these media the reactive species are still hydroxide ions, but metal ions associate with hydroxide ions lowering their reactivities (table 4.14).

Table 4.14

Comparison* of Reactivities of Free ions or Ion-Pairs

Substrate	Base	$k_f/\ell\ mol^{-1}\ s^{-1}$
TNB	NMe_4OBu	$\sim 3 \times 10^6$
	NaOBu or KOBu	$\sim 4 \times 10^4$
1-Chloro-2,4-Dinitrobenzene	NMe_4OBu	~ 10
	KOBu	~ 0.2
Picryl Chloride	NMe_4OBu	$\sim 1.3 \times 10^6$
	KOBu	$\sim 1.3 \times 10^4$

* In t-butanol containing 0.07% water by volume at 30°C.

FIG. 4.1

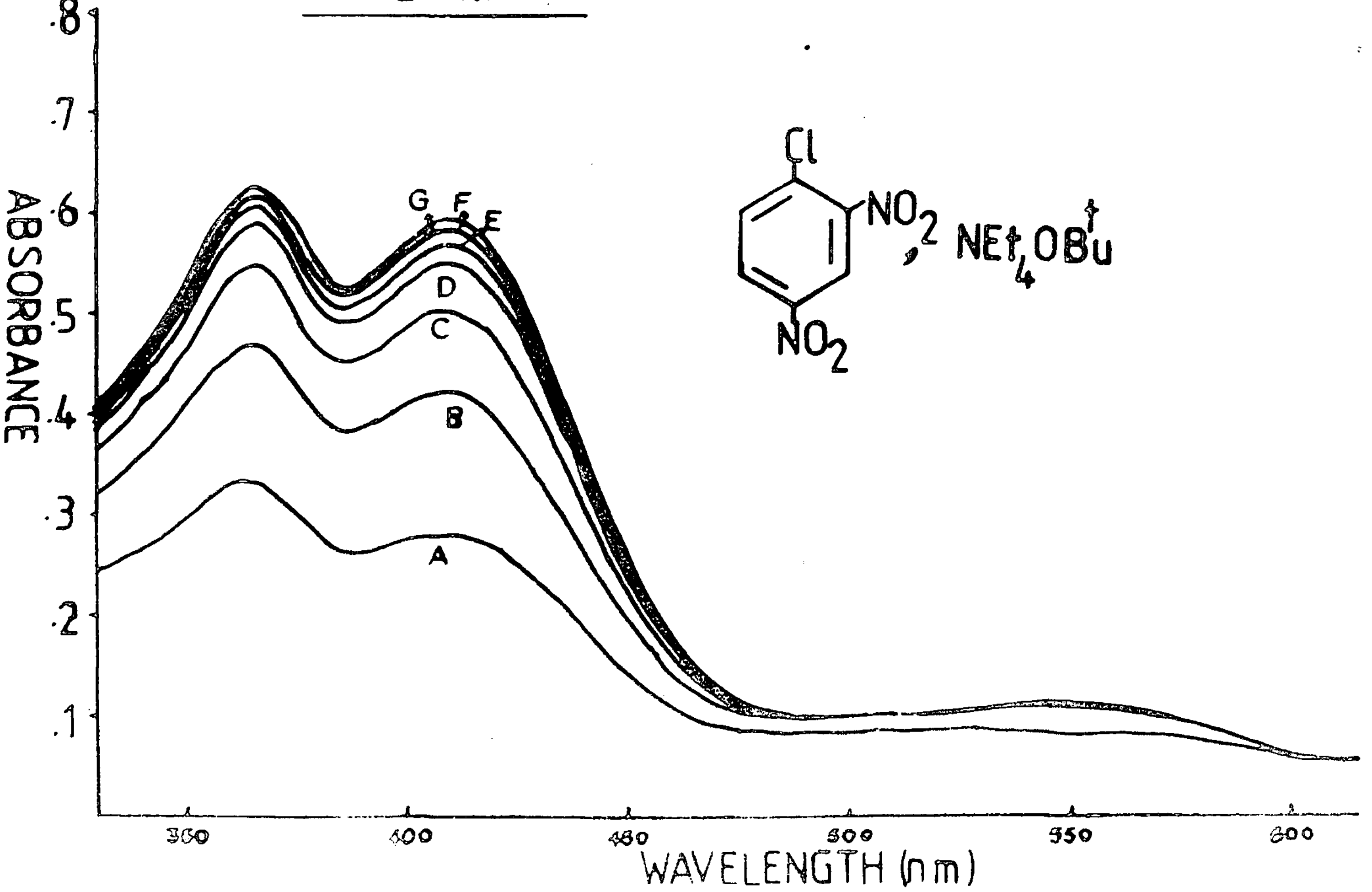


FIGURE 4.1 Visible spectra of 1-chloro-2,4-dinitrobenzene (4 X 10^{-5} M)and tetramethylammoniumhydroxide(3.8 X 10^{-4} M)in purified t-butanol at 30°. A ⟶ G with increasing time .

FIG. 4.2

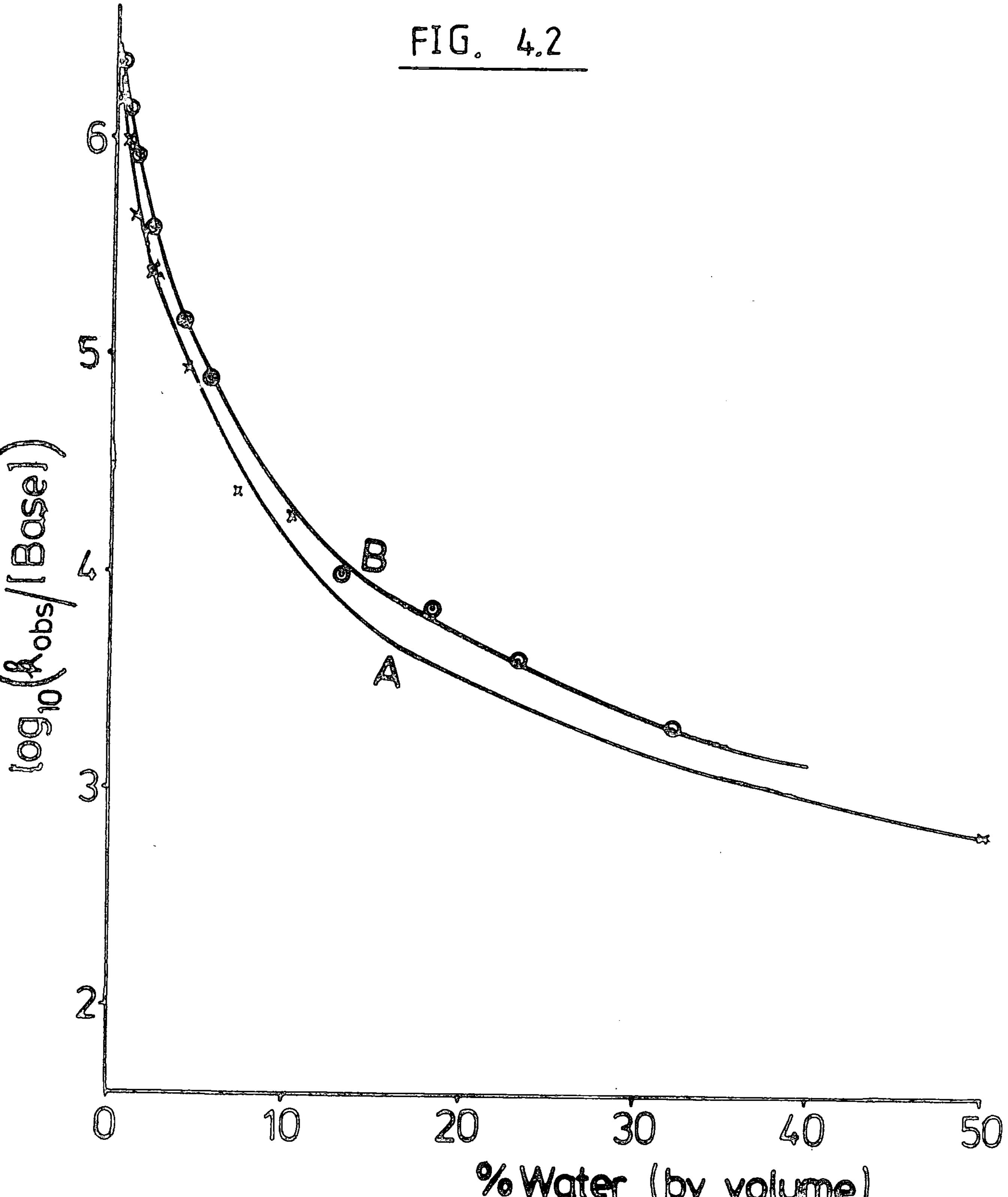


FIGURE 4.2

Variation with solvent composition of the rate coefficients for base attack on A, 1,3,5-trinitrobenzene and B, 1-chloro-2,4-dinitrobenzene For the latter compound the scale is 6+ Log (k_{obs}/ Base) .

FIG. 4.3

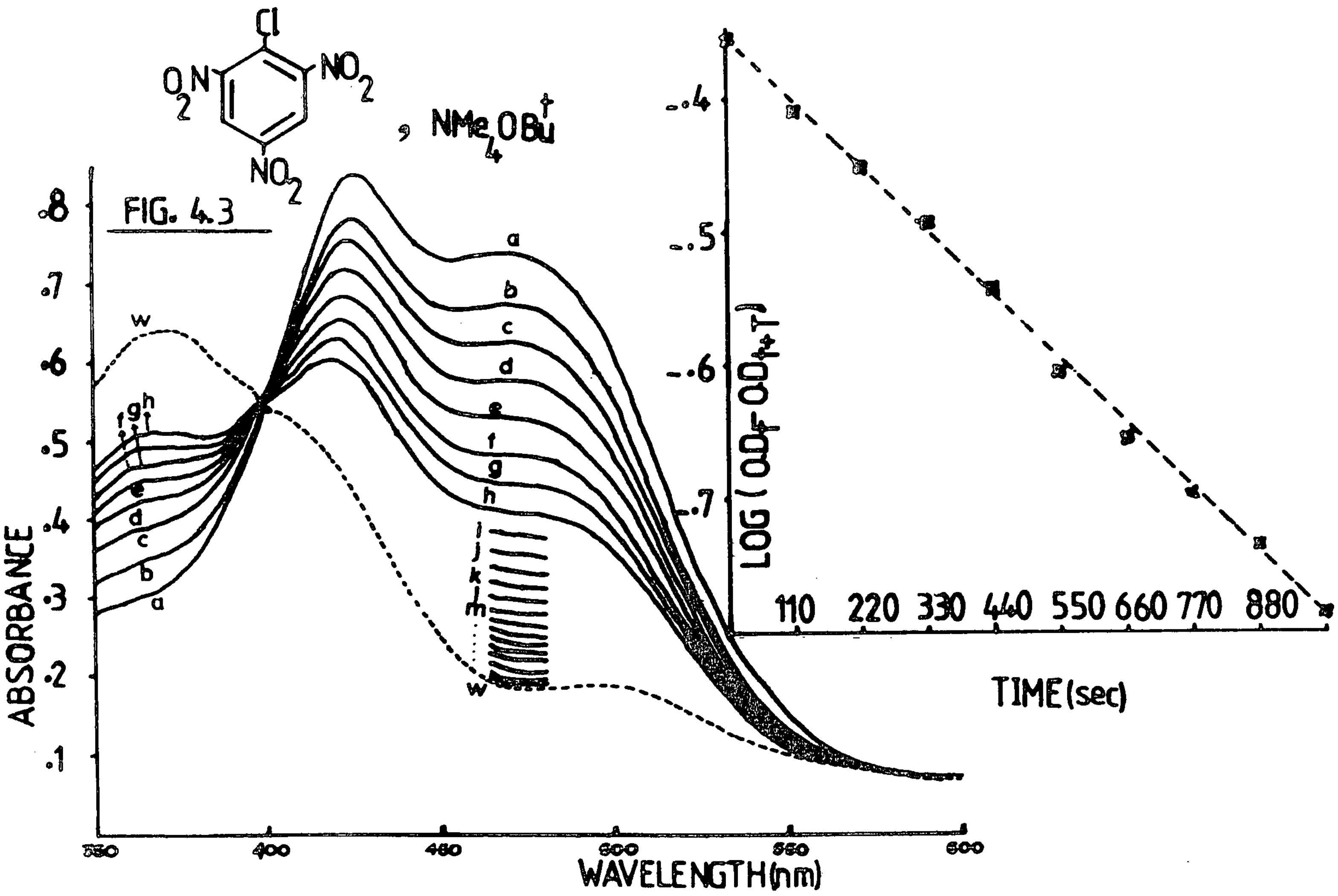


FIGURE 4.3 Visible spectra of picryl chloride (4×10^{-5} M) and tetramethyl - ammonium butoxide (8.4×10^{-4} M)in purified t-butanol at 30° . The change with time is : a ⟶ w ,(table 4.4). A plot of $\mathrm{Log}(O.D_t - O.D_{t+T})$ against time is shown .

FIG. 4.4

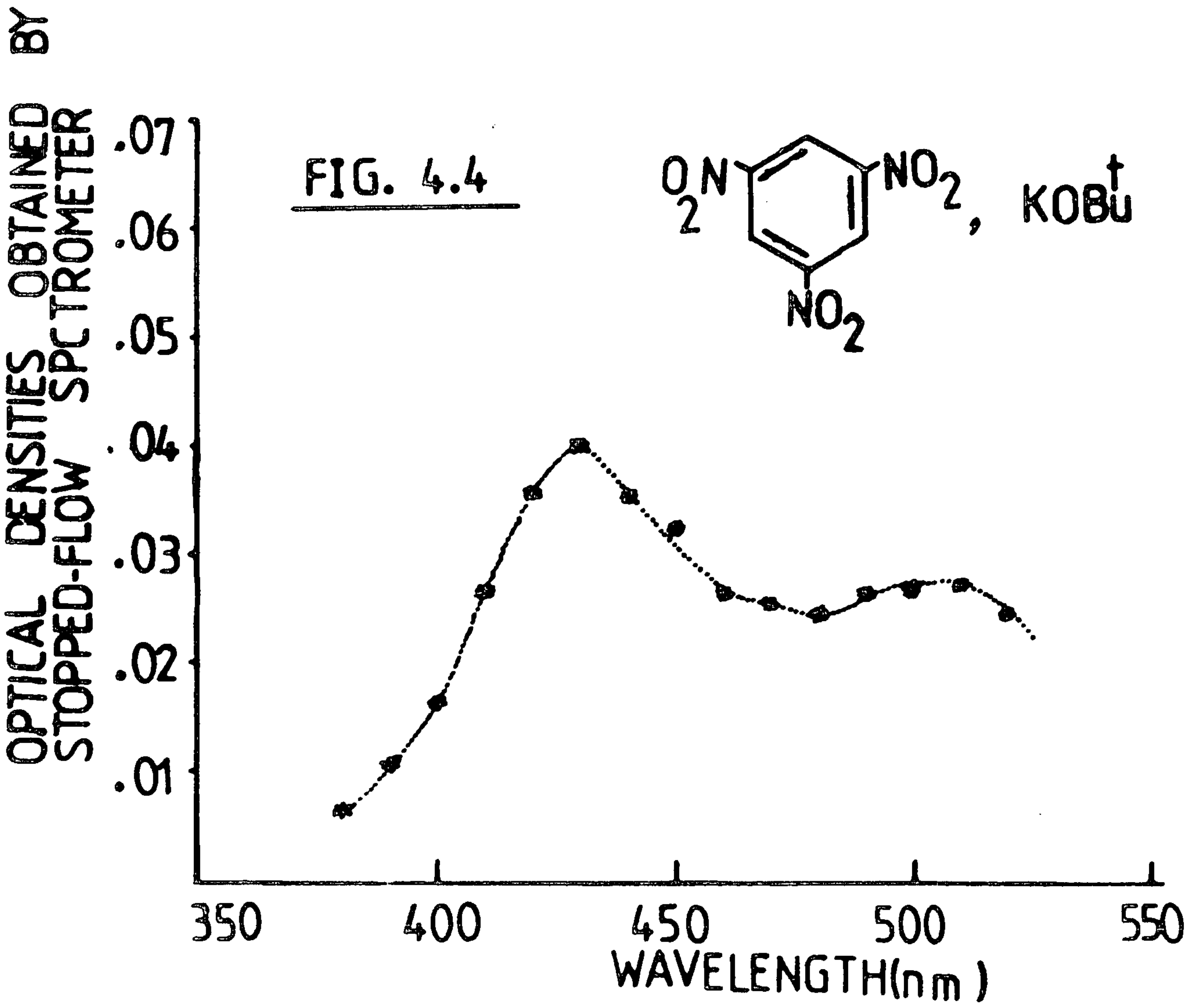


FIGURE 4.4 Initial spectrum determined from stopped-flow spectrophotometer, for 1,3,5-trinitrobenzene (1×10^{-5}M) and potassium t-butoxide (1×10^{-3}M) in purified t-butanol at 30°.

FIG. 4.5

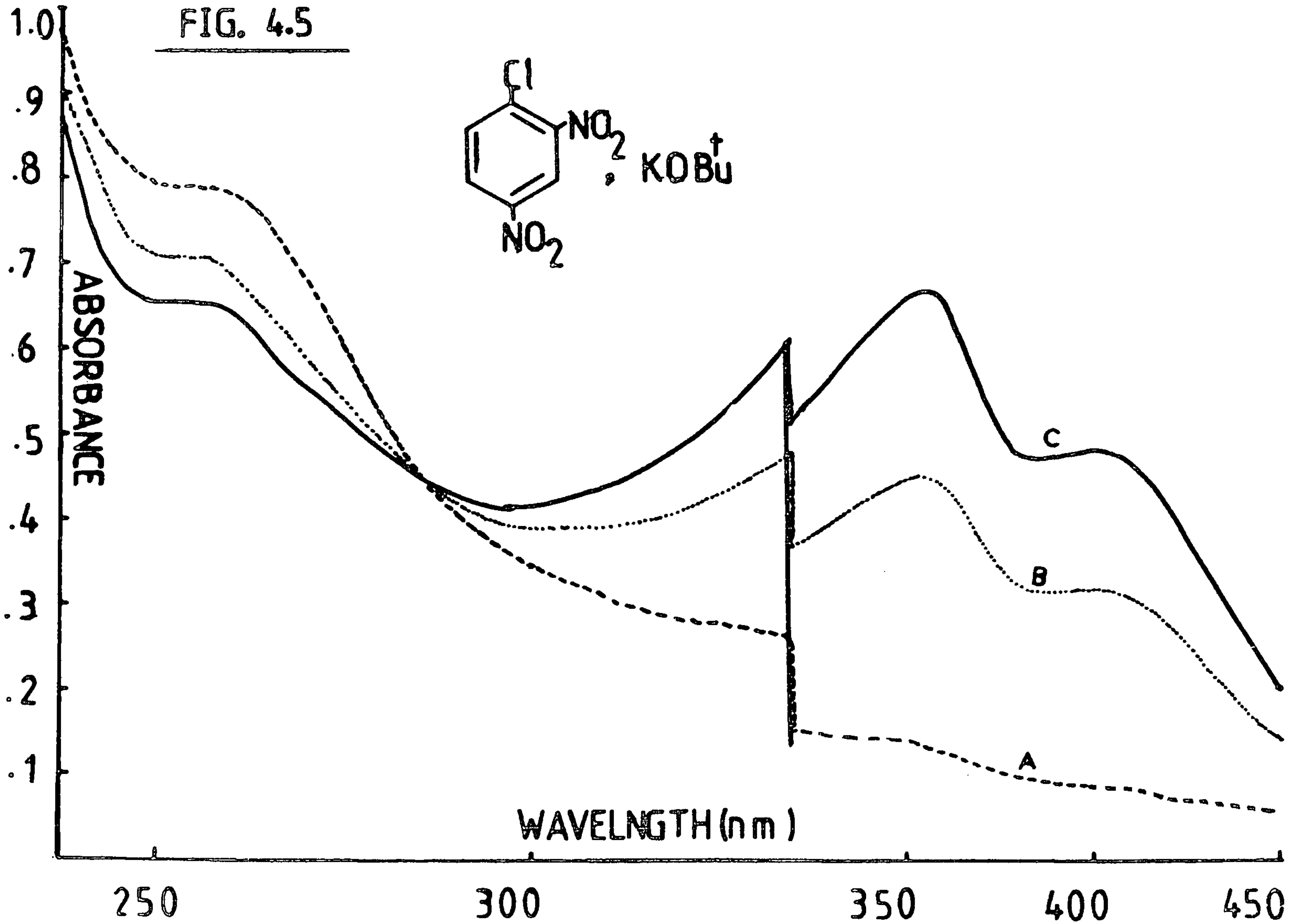


FIGURE 4.5 U.V spectra for 1-chloro-2,4-dinitrobenzene (4×10^{-5} M) with potassium t-butoxide (9.8×10^{-3} M) in purified t-butanol at 30°. The change with time is: A $\xrightarrow{20\ \text{min}}$ B $\xrightarrow{90\ \text{min}}$ C .

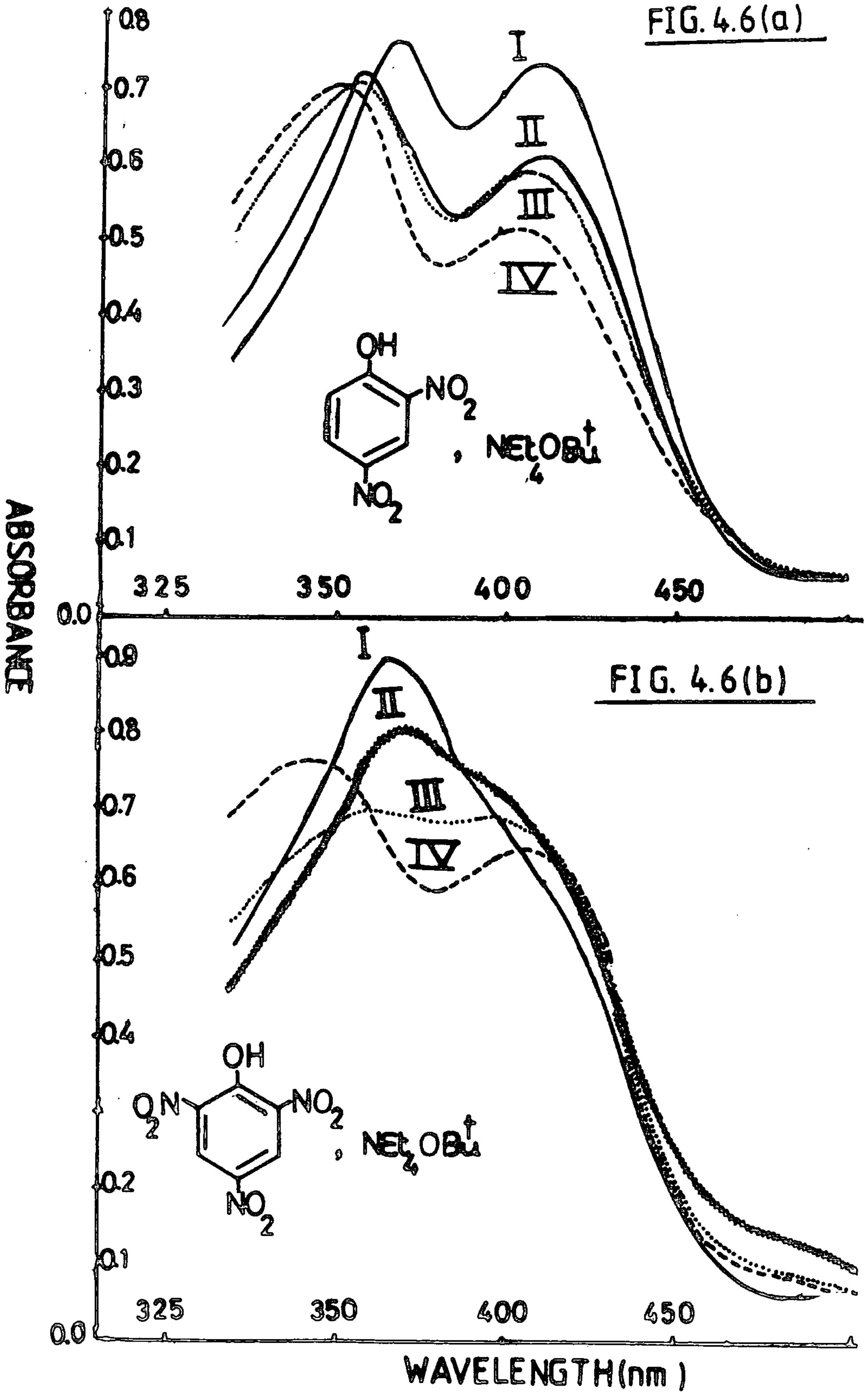


FIGURE 4.6

U.V spectra for parent (4 X 10^{-5} M) and tetraethylammonium - hydroxide (1 X 10^{-3} M) in purified t-butanol at 30°, at varied salt concentrations:I, 1 X10^{-4} M , II , 5 X 10^{-4} M . III , 1 X 10^{-3} M IV,3.5 X 10^{-3} M. ((salt used is NaClO$_4$))

FIG. 4.7

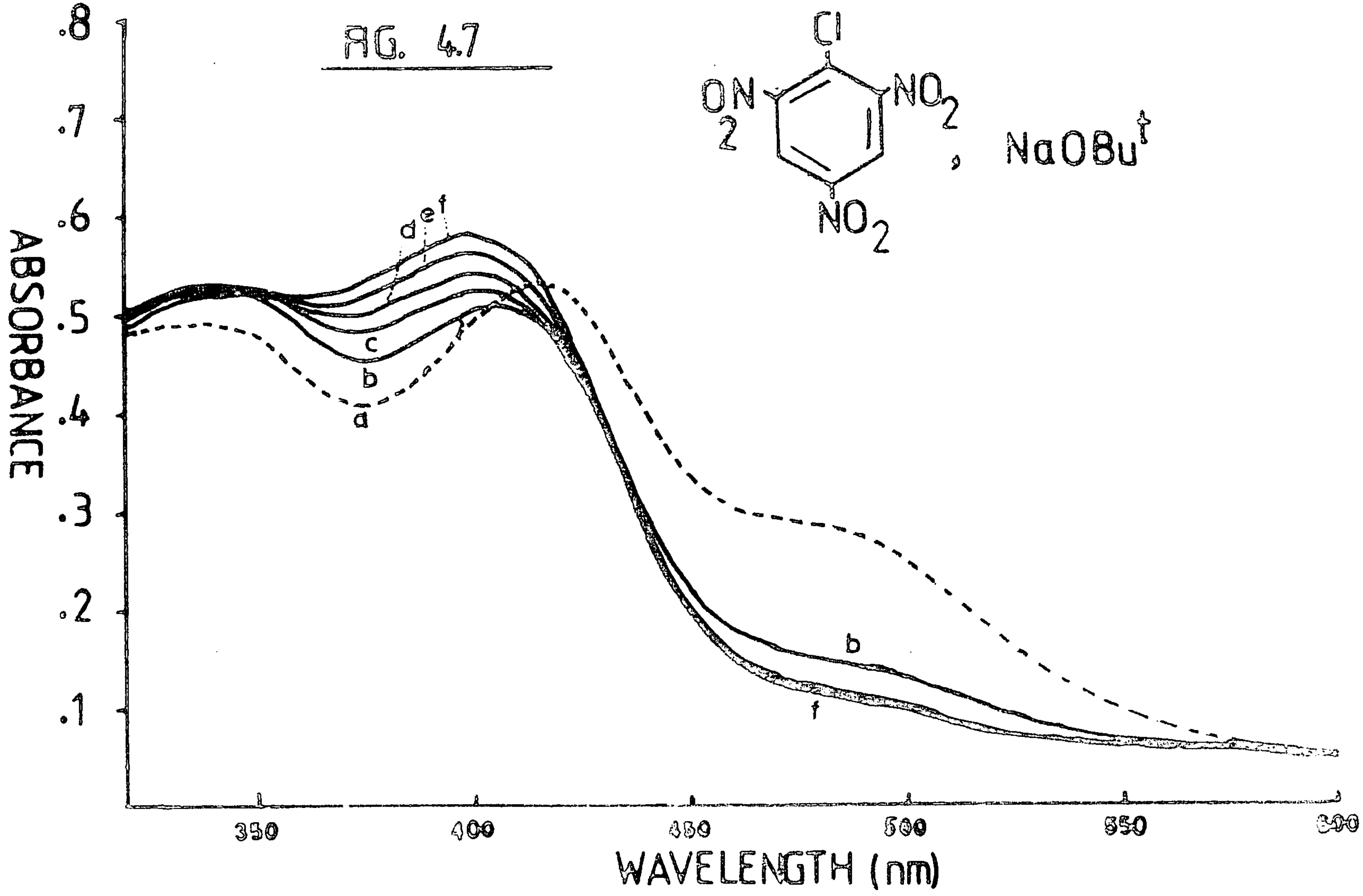


FIGURE 4.7 U.V/ Visible spectra for picryl chloride (4 X 10^{-5} M) with sodium
t-butoxide (1.05 X 10^{-3} M) in purified t-butanol at 30° . The change with time is a ⟶ f (a ,is the initial spectrum) .

FIG. 4.8

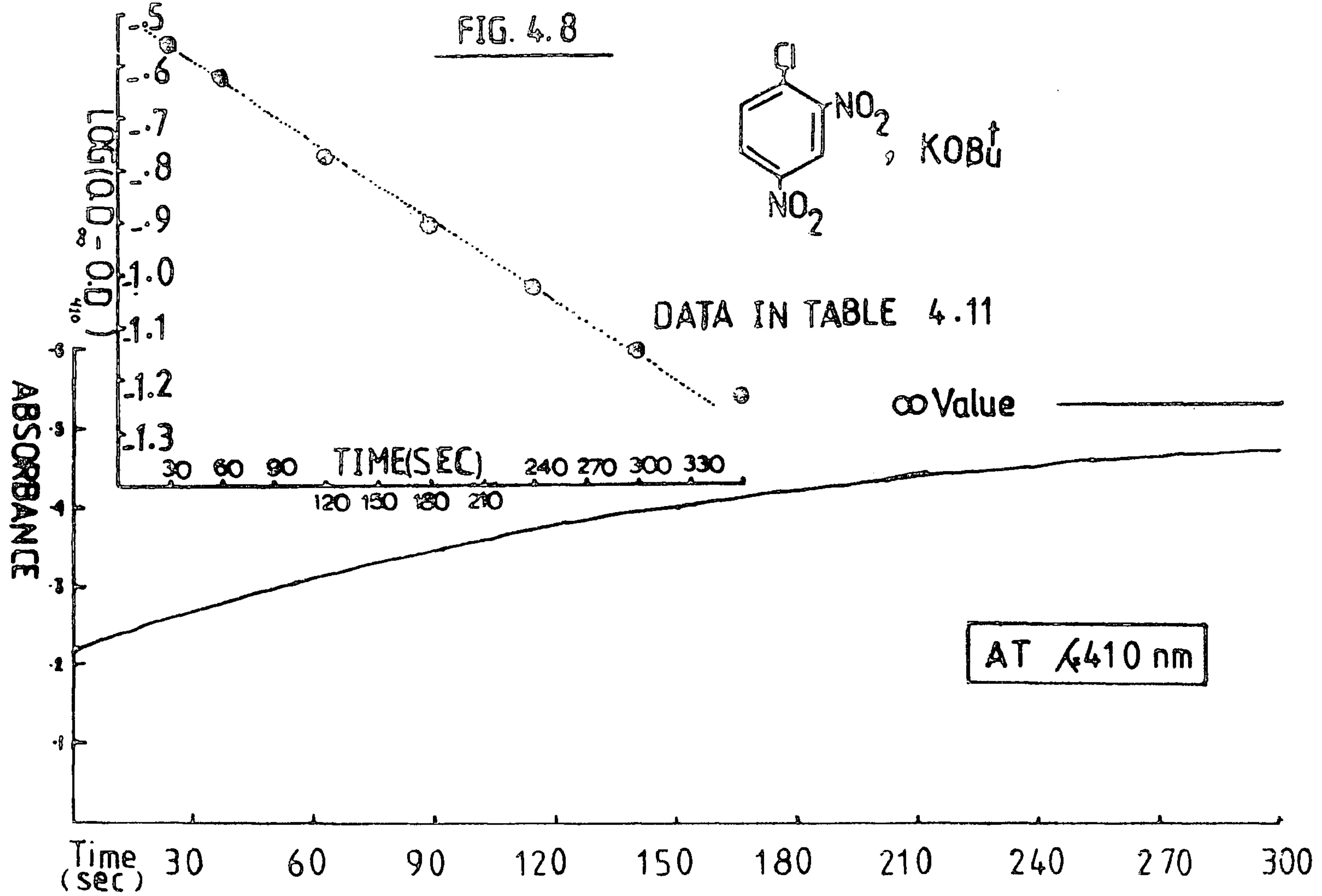


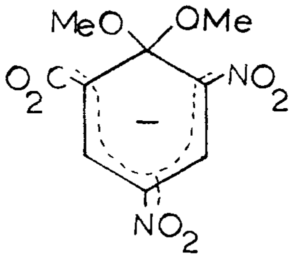
FIGURE 4.8 The change of optical density with time at 410 nm for 1-chloro-2,4-dinitrobenzene (4×10^{-5} M) with potassium t-butoxide(58.5×10^{-3} M) in purified t-butanol at 30°. A plot of this change (Log $O.D_{\infty}$ - $O.D_{410}$)against time is shown .

CHAPTER 5

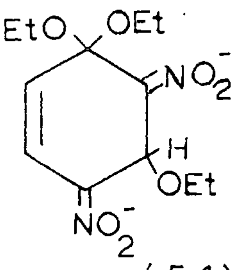
CATION-COMPLEXING OF σ-ADDUCTS IN CONCENTRATED METAL METHOXIDE SOLUTIONS

Introduction

There is much evidence that 1,1-dialkoxy adducts such as (1.22,R=R=Alkyl) associate strongly with alkali metal cations in alcohols. In chapter 3 it was shown that 1,1-dipropoxy complexes undergo such association, and there is a considerable amount of evidence in the literature.[42,126,129,136]



(5.0)



(5.1)

It has been shown that adducts carrying a methoxycarbonyl substituent at the 6-position (1.22, X = CO_2Me) associate particularly strongly. One point in the present study was to examine the association with cations of the methoxy-adduct (5.0) of 2-methoxy-3,5-dinitrobenzoic acid. In basic media the acidic function will be ionised so that the adduct will carry two negative charges. There is the possibility that this will give rise to a very large effect involving strong cation complexing. A further point which it was wished to explore was the association of 1:2 and 1:3 methoxy adducts with cations. Gold and Toullec[127] have shown that the 1:2 ethoxy adduct (5.1) of 2,4-dinitrophenetole forms at a much lower concentration of sodium ethoxide than of potassium ethoxide and have attributed this to a specific assocation of the 1:2 adduct with sodium ions. In the present work the formation of 1:2 and/or 1:3 adducts.

from 2,4,6-trinitroanisole, N,N-dimethyl picramide, N-methylpicramide, picramide and 1-(2`-hydroxy ethoxy) 2,4,6-trinitrobenzene have been examined.

Experimental

Concentrated solutions of base were found to absorb in the ultraviolet region. All measurements of optical densities were corrected for absorption by the base. In some cases, notably with N,N-dimethylpicramide and N-methylpicramide, decomposition of the substrate slowly occurred so that optical densities shown in the tables were those extrapolated back to time of mixing.

Attempts were made to examine the interaction of the adduct (5.0) with silver ions. However silver salts such as silver nitrate have very low solubilities in methanol, and in the presence of methoxide ions gave a brown precipitate. These factors made it difficult to pursue this line of investigation.

All measurements were made in A.R methanol at 25°C. As a rule the concentrated metal alkoxide test solutions were made up by weight. A known weight of base was titrated with standard acid for calibration purposes, and test solutions were made up containing known weights of stock base solution.

Results and Discussion

(a) 2-Methoxy-3,5-Dinitrobenzoic Acid

The parent in methanol shows no absorption above 350 nm. As the base concentration is increased an orange species is produced with maxima at 364 nm and 488 nm (figure 5.2). No change in spectral shape was noted up to 2.3 M potassium methoxide, 2.5 M sodium methoxide or 2.5 M lithium methoxide, although the optical densities increased with increasing base concentration. Hence only the 1:1 adduct (5.0) is formed at these base concentrations and there is no evidence for 1:2 or 1:3 adduct formation

The data with potassium methoxide in table 5.1 show that the optical density at 490 nm reaches a limiting value of 0.61 at high base concentrations and this value is taken to indicate complete conversion to 1:1 adduct.

Equilibrium constants were calculated using equations 5.1 or 5.2. The latter equation being used for the first seven rows where the indicator concentration was increased.

The data with sodium methoxide were treated in a similar manner, and are in table 5.2.

It was not possible to achieve complete conversion using lithium methoxide and in this case a value corresponding to total complex formation with sodium methoxide was used to calculate values of the equilibrium constant (table 5.3).

$$K_c = \frac{O.D_{490}}{0.61 - O.D_{490}} \quad \frac{1}{[\mathrm{Base}]} \qquad 5.1$$

$$K_c = \frac{O.D_{490}}{6.1 - O.D_{490}} \quad \frac{1}{[\mathrm{Base}]} \qquad 5.2$$

The values with lithium methoxide indicate a value for K_c at low base concentrations of $0.02 \pm .005$ ℓ mol^{-1}, The values increase with increasing base concentration. The order at any particular base concentration being:

NaOMe > KOMe > LiOMe. This contrasts with the order of the H_M acidity function in these basic media which decrease in the order: KOMe > NaOMe > LiOMe.^{116}

Two factors which are likely to be important in increasing equilibrium constants for formation of adduct (5.0) with base concentration are (i) a general increase in basicity of the medium and (ii) specific association of the adduct with cations. It is difficult to separate

Table 5.1

Measurements of Equilibrium Constants and J_M Acidity Functions with Varying Potassium Methoxide Concentration (Parent is 2-Methoxy-3,5-Dinitrobenzoic Acid) in Methanol at 25°C.

[KOMe]/M	[Parent] 10^5 /M	$O.D_{490}$	Keq/ $\ell\ mol^{-1}$	J_M
0	33.35	0.0	-	
.0528	33.35	.01	.031	15.84
.074	33.35	.015	.0322	16.01
.1057	33.35	.022	.034	16.18
.211	33.35	.07	.055	16.68
.317	33.35	.175	.093	17.09
.423	33.35	.30	.122	17.33
.52	3.32	.065	.23	17.69
.693	3.32	.133	.40	18.06
.924	3.32	.175	.435	18.22
1.097	3.32	.310	.941	18.63
1.271	3.32	.385	1.344	18.85
1.444	3.32	.490	2.825	19.23
1.617	3.32	.575	10.15	19.84
1.791	3.32	.61	-	
2.253	3.32	.61	-	

$J_M = 18.62 + \log (O.D/6.1 - O.D)$ ..... rows 2-7

$J_M = 18.62 + \log (O.D/0.61 - O.D)$

Table 5.2

Measurements of Equilibrium Constants and J_M Acidity Function with Varying Sodium Methoxide Concentration (Parent is 2-Methoxy-3,5-Dinitrobenzoic Acid) in Methanol at 25°C.

[NaoMe] /M	10^5 [Parent] /M	$O.D_{490}$	Keq/ℓ mol^{-1}	J_M
0	32.27	0	-	
.0497	32.72	0.023	.0761	16.20
.0661	32.72	0.028	.0697	16.28
.0994	32.72	0.048	.0797	16.52
.1988	32.72	.140	.118	16.99
.2982	32.72	.291	.168	17.32
.3976	32.72	.531	.239	17.60
.3976	33.03	.055	.249	17.62
.5964	3.303	.115	.389	17.98
.7952	3.303	.233	.776	18.41
.9691	3.303	.351	1.398	18.75
1.188	3.303	.449	2.345	19.07
1.401	3.303	.525	4.403	19.41
1.583^8	3.303	.580	12.2	19.91
1.797	3.303	.600	33.4	20.4
1.979	3.303	.602	38.0	
2.497	3.303	.515		
2.741	3.303	,605		
2.970	3.303	.580		

J_M = 18.62 + log (O.D/6.1 - O.D) ..... rows 2-8

J_M = 18.62 + log (O.D/0.61 - O.D)

Table 5.3

Measurements of Equilibrium Constants and J_M Acidity Function with varying Lithium Methoxide Concentration (Parent is 2-Methoxy-3,5-Dinitrobenzoic Acid) in Methanol at 25°C.

[LiOMe] /M	10^5[Parent] /M	O.D$_{480}$	O.D$_{490}$	Keq/ℓ mol^{-1}	J_M
0	32.12	0	-	-	
.1068	31.80	.020	-	.0293	16.14
.1918	32.12	.030	-	.0245	16.31
.311	32.12	.040	-	.0202	16.44
.407	32.12	.055	-	.0213	16.58
.815	32.12	.153	-	.0299	17.03
.887	32.12	.168	-	.0304	17.07
.904	30.28	.171	-	.0318	17.08
1.218	3.228	.040	-	.0566	17.47
1.421	3.228	.055	-	.0683	17.62
1.624	3.228	.085	-	.0976	17.83
1.827	3.228	.110	-	.118	17.96
2.030	3.228	.146	-	.1508	18.12
2.284	3.228	.223	-	.245	18.38
2.439	3.102	.256	-	.288	18.48
1.931[a]	3.102	.590	.608	-	20.01
2.33[a]	3.102	.62	.625	-	
2.728[a]	3.164	.623	.650	-	

a. Using sodium Methoxide

J_M = 18.62 + log (O.D/6.1 - O.D) ..... rows 2-8

J_M = 18.62 + log (O.D/0.61 - O.D)

these effects precisely. However it is shown in figure 5.1 that with sodium methoxide the J_M function defined by equation 5.3 increases much more rapidly than does the H_M function. With potassium methoxide there is a smaller difference between the J_M and H_M values while with lithium methoxide the J_M values are lower than are the H_M values.

This may be taken to show the much stronger association of (5.0) with sodium ions than with potassium ions than with lithium ions.

$$J_M = p(KK_{MeOH}) + \log_{10}([Adduct] / [Parent]) \qquad 5.3$$

(b) 2,4,6-Trinitroanisole

The behaviour of 2,4,6-trinitroanisole in concentrated sodium methoxide solutions has previously been examined by Rochester.[92] In agreement with his work it was found that the 1,1-dimethoxy adduct had maxima at 412 nm (ε 25,700 ℓ mol^{-1}cm^{-1}) and 488 nm (ε 17,670 ℓ mol^{-1}cm^{-1}) (figure 5.3). With increasing base concentration the intensity of the band at lower wavelength decreased while that of the band at longer wavelength intensified. These changes corresponding to formation of a 1:2 adduct. In these solutions an isobestic point was observed at 440 nm.

The 1:3 adduct is not expected to absorb in the visible region since all negative charges are localised on to nitro-groups.

Optical density measurements are in table 5.4.

For the first three rows only 1:1 adduct is present allowing the extinction coefficients for this species to be found. Up to 3.4 M base an isobestic point is observed at 440 nm indicating no formation of 1:3 adduct. It was possible to calculate a value for optical density at 488 nm of 0.88 corresponding to complete conversion to the 1:2 adduct. Thus

$$O.D_{488} = [1:1]\ 0.40 + [1:2]\ 0.88 \qquad 5.4$$

and if $[1:1] + [1:2] = m$ 5.5

Then $[1:2] = (O.D_{488} - 0.4\ m)/0.48$ 5.6

But since the 1:1 and 1:2 adducts show an isobestic point at 440 nm

$\therefore\ [1:3] = (0.31 - O.D_{440})/0.31$ 5.7

Also since the concentration of free parent is negligibly small

$[1:1] = 1 - ([1:2] + [1:3])$ 5.8

Hence the relative concentrations of [1:1], [1:2] and [1:3] adducts were calculated, table 5.4.

Visible spectra with Lithium methoxide showed no change in spectral shape, from that expected for the 1:1 adduct, up to the highest base concentration attainable (2.6 M).

(c) N,N-Dimethylpicramide

Here there is evidence only for formation of 1:1 and 1:2 adducts by base addition at unsubstituted ring positions. Since the value of the equilibrium constant $K_{1:1}$ for formation of the 1:1 adduct is not particularly high, unchanged parent is present in these solutions.

Note In tables 5.4 to 5.16 the equilibrium constants for formation of adducts with 1:1, 1:2 and 1:3 stoichiometries are defined as below in terms of the stoichiometric metal alkoxide concentrations

$K_{1:1} = [1:1]/([\text{Parent}][\text{MOMe}])$

$K_{1:2} = [1:2]/([1:1][\text{MOMe}])$

$K_{1:3} = [1:3]/([1:2][\text{MOMe}])$

A study by visible spectroscopy of the reaction in DMSO containing sodium methoxide was reported[54] while this work was in progress. This shows how in media rich in DMSO it is possible to obtain spectra of 1:1 and 1:2 adducts separately. Spectra obtained with N,N-dimethylpicramide are in fig. 5.4. However the equilibrium measurements with which the present work is concerned refer to methanol as solvent. In methanol the formation of 1:1 and 1:2 adducts is not well separated so that visible spectra of these species are not directly obtainable. Because of solvent effects it is to be expected that some changes in spectral shape and extinction coefficients will occur on transfer from methanol to DMSO/methanol mixtures.

In methanol solutions containing only parent and 1:1 adduct show an isobestic point at 360nm. From the data in tables 5.5, 5.6 and 5.7 the amounts of 1:2 species present are obtained by equations 5.9 and 5.10.

$$[1:1] = (0.33 - \mathrm{O.D}_{360})/(0.33 - 0.18) \qquad 5.9$$

for KOMe and NaOMe while for LiOMe equation 5.10 applies

$$[1:2] = (0.365 - \mathrm{O.D}_{360})/(0.365 - 0.185) \qquad 5.10$$

There is evidence from Gold and Rochester's published data[52] and from the spectral[54] in DMSO/MeOH that $\varepsilon(1:1)$ at 480nm has the value 10,000 ℓ $\mathrm{mol}^{-1}\mathrm{cm}^{-1}$ which gives an optical density for complete conversion of 0.3 units at the parent concentration used. Also the parent absorbs 0.013 at 480nm, table 5.6, while at

Table 5.4

Optical densities, Equilibrium constants, and Adduct Ratios for the Reaction of Potassium methoxide with 2,4,6-Trinitroanisole in Methanol at 25^{o}C.

[KOMe] /M	O.D$_{412}$	O.D$_{430}$	O.D$_{440}$	O.D$_{488}$	[1:1]	[1:2]	[1:3]	$K_{1:2}$ /ℓ mol^{-1}	$K_{1:3}$ /ℓ mol^{-1}	log $K_{1:2}$	log $K_{1:3}$
.470	.59	.36	.31	.39	1.0	0	0				
.940	.61	.37	.31	.40	1.0	0	0				
1.18	.62	.37	.31	.40	1.0	0	0				
1.60	.62	.37	.31	.41	.98	.02	0	.013		-1.89	
1.93	.60	.37	.31	.42	.96	.04	0	.022		-1.66	
2.35	.54	.35	.31	.44	.92	.08	0	.037		-1.43	
2.56	.53	.35	.31	.48	.83	.17	0	.080		-1.1	
2.77	.50	.34	.31	.49	.81	.19	0	.085		-1.07	
2.94	.47	.34	.31	.52	.75	.25	0	.113		- .95	
3.19	.40	.32	.31	.58	.62	.38	0	.192		- .72	
3.36	.37	.30	.31	.61	.56	.44	0	.234	-	- .63	
3.53	.30	.30	.29	.64	.40	.54	.06	.38	.031	- .42	-1.50
3.78	.24	.26	,29	.67	.33	.61	.06	.49	.026	- .31	-1.585
4.20	.13	.19	.25	.70	.03	.78	.19	-	.058	-	-1.24

2,4,6-Trinitroanisole = 2.37 x 10^{-5} M

Optical densities were corrected for base absorption and normalised at 440 nm.

480 nm, the 1:2 species, at high base concentrations, absorbs 0.033 in potassium methoxide case, 0.026 in sodium methoxide case and 0.035 in case of lithium methoxide. Accordingly, the following equations hold:

$$[1{:}1] = \{O.D_{480} - 0.03[1{:}2] - 0.013[\text{Parent}]\}/0.3 \qquad 5.11$$

"for KOMe, table 5.5"

$$[1{:}1] = \{O.D_{480} - 0.026[1{:}2] - 0.013[\text{Parent}]\}/0.3 \qquad 5.12$$

"for NaOMe, table 5.6"

$$[1{:}1] = \{O.D_{480} - 0.035[1{:}2] - 0.013[\text{Parent}]\}/0.3 \qquad 5.13$$

"for LiOMe, table 5.7"

For example, in potassium methoxide case, finding $[1{:}2]$ from equation 5.9, substituting this value in equation 5.11, assuming $[\text{Parent}] = 0$, this gives an approximate value for $[1{:}1]$. From the above obtained values of $[1{:}1]$ and $[1{:}2]$, the amount of parent is obtained by this equation:

$$[\text{Parent}] = 1-([1{:}1] + [1{:}2]) \qquad 5.14$$

Substituting this obtained value of Parent in equation 5.11 allows re-calculation of 1:1 . This is done iteratively for every concentration. The same procedure is carried through for sodium and lithium methoxides.

(d) 1-(2'-Hydroxy ethoxy)-2,4,6-trinitrobenzene

Even at dilute base concentrations cyclisation to the spiro-adduct will be complete[58] (K=1.8 x 10^7 ℓ mol^{-1}) in water, and the value in methanol will be around this figure . When spiro and 1:2 adducts are present there is an isobestic point at 440 nm, as seen from spectral shapes (figure 5.5) and from tables 5.8 and 5.9. The values of optical density at the isobestic point are 0.48 (in case of potassium methoxide), and at 0.49 (in case of sodium methoxide), hence the following equations apply

Table 5.5

Optical densities, Equilibrium constants, and Adduct Ratios
Measurements for N,N-Dimethylpicramide with Potassium Methoxide in Methanol at 25^{o}C.

[KOMe] /M	O.D$_{360}$	O.D$_{412}$	O.D$_{480}$	[1:1]	[1:2]	[Parent]	K$_{1:1}$ /ℓ mol^{-1}	log K$_{1:2}$ /ℓ mol^{-1}	log K$_{1:1}$	log K$_{1:2}$
.0123	.333	.185	.029	.057	0	.94	4.93	-	.69	-
.033	.331	.25	.060	.164	.013	.82	6.06	2.4	.78	.38
.049	.323	.27	.074	.210	.065	.73	5.9	6.3	.77	.80
.069	.317	.43	.094	.276	.104	.62	6.45	5.5	.81	.74
.090	.314	.368	.109	.327	.124	.55	6.6	4.2	.82	.625
.131	.295	.463	.128	.386	.248	.366	8.05	4.9	.905	.69
.164	.273	.517	.132	.391	.392	.22	10.8	6.1	1.04	.79
.205	.255	.592	.135	.395	.509	.096	20.1	6.3	1.30	.80
.246	.245	.616	.130	.357	.575	.068	21.3	6.5	1.33	.82
.295	.220	,665	.095	.242	.738	.02	41.0	10.3	1.61	1.01
.393	.209	.708	.089	.21	.81	-	-	9.8	-	.99
.483	.20	.718	.045	.063	.87	0	-	28.6		1.46
.582	.19	.721	.045	.056	.93	0	-	28.5		1.46
.680	.177	.725	.040	0	1.0	0	-	-		-
.819	.179	.738	.033							
.983	.175	.740	.033							

[Indicator] = 3.03 x 10^{-5}M

Table 5.6

Optical densities, Equilibrium constants, and Adduct Ratios Measurements for N,N-Dimethylpicramide with Sodium Methoxide in Methanol at 25^{o}C.

[NaOMe] /M	$O.D_{360}$	$O.D_{412}$	$O.D_{480}$	[1:1]	[1:2]	[Parent]	$K_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	log $K_{1:1}$	log $K_{1:2}$
.0123	.333	.183	.025	.043	0	.96	3.64		.56	-
.0307	.336	.227	.040	.096	0	.904	3.46		.54	-
.0492	.330	.251	.061	.170	0	.83	4.16		.62	-
.0738	.323	.302	.090	.260	.05	.685	5.14	2.6	.711	.415
.0984	.319	.342	.103	.310	.073	.62	1.08	2.4	.706	.376
.135	.308	.399	.120	.37	.15	.48	5.71	3.0	.75	.477
.166	.293	.462	.135	.414	.25	.34	7.33	3.6	.865	.56
.197	.290	.519	.135	.410	.27	.32	6.50	3.3	.81	.52
.246	.264	.579	.137	.412	.44	.148	11.32	4.3	1.05	.64
.295	.243	.614	.114	.325	.58	.095	11.60	6.05	1.06	.78
.394	.238	.70	.113	.32	.61	.069	11.77	4.8		.685
.486	.216	.715	.073	.174	.76	.066		8.9		.95
.578	.205	.740	.059	.123	.83	.047		11.7		1.07
.677	.197	.735	.049	.085	.88	.034		15.3		1.18
.80	.188	.743	.030	.0162	.95	.033		73		1.865
.985	.184	.740	.029	.012	.97	.018		82		
1.17	.179	.733	.026	0	1.0	0				
0	.335	.164	.013							

[Indicator] = 3.03×10^{-5}M

Table 5.7

Optical densities, Equilibrium constants, and Adduct Ratios Measurements for N,N-Dimethylpicramide with Lithium Methoxide in Methanol at 25^{o}C.

[LiOMe] /M	O.D$_{360}$	O.D$_{412}$	O.D$_{480}$	[1:1]	[1:2]	[Parent]	$K_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	log $K_{1:1}$	log $K_{1:2}$
.012	.360	.195	.025	.044	0	.96	3.82		.582	
.033	.362	.234	.045	.133	0	.89	4.53		.656	
.050^{2}	.366	.258	.059	.16	0	.84	3.8		.578	
.068^{7}	.360	.288	.084	.249	0	.75	4.83		.684	
.089^{9}	.368	.307	.089	.265	0	.73	4.04		.606	
.132	.360	.376	.128	.399	.027	.57	5.30	0.51	.724	
.164	.352	.419	.138	.43	.072	.49	5.35	1.02	.728	
.206	.329	.433	.147	.45	.20	.35	6.24	2.16	.795	.333
.248^{5}	.331	.492	.157	.486	.19	.32	6.11	1.57	.786	.197
.296	.322	.525	.161	.499	.24	.26	6.48	1.63	.811	.211
.391	.270	.533	.155	.452	.53	.018		3.0		.476
.481	.280	.645	.161	.48	.47	.05		2.04	-	.31
.581^{7}	.270	.701	.137	.38	.53	.09		2.4	-	.38
.687^{5}	.253	.763	.123	.334	.62	.046		2.7		.32
.846	.24	.783	.114	.298	.69	.012		2.74		.33
1.0	,22	.763	.091	.21	.805	0		3.83		.34
1.16^{3}	.20	.798	.069	.123	.92	0		6.43		.81
1.32^{2}	.20	.795	.077	.149	.92	0		5.70		.67
1.40^{1}	.19^{7}	.793	.056	.078	.93	0		8.51		.93
1.480^{7}	.18^{6}	.781	.0448	0	1.0	0				-
1.692	.184	.799	.035							
1.90^{4}	.188		.034							

[Indicator] = 3.03 x 10^{-5}M

$$[1:3] = (0.48 - O.D_{440})/0.48 \qquad 5.15$$

"for potassium methoxide"

$$[1:3] = (0.49 - O.D_{440})/0.49 \qquad 5.16$$

"for sodium methoxide"

The optical densities for complete conversion to spiro adduct are 0.71 and 0.52 at 414 and 480 nm, respectively, for potassium methoxide. The values are 0.68 at 414 nm and 0.49 at 480 nm, for sodium methoxide. Measurements with base concentration above 4M, where there is little spiro adduct present, allow the spectral shape of the 1:2 species to be found with both potassium **and** sodium methoxide. The ratio of extinction coefficients for 1:2 adduct at 480 and 414 nm is equal to 5.0 (i.e. $y/x = \varepsilon 1{:}2$ at 480 nm$/\varepsilon 1{:}2$ at 414 nm = 5.0).

For potassium methoxide, the amount of 1:1 adduct present in solution can be calculated from the following equations (where y/x = 5.0).

$$O.D_{414} = [1:1](0.71) + [1:2]x \qquad 5.17$$

$$O.D_{480} = [1:1](0.52) + [1:2]y \qquad 5.18$$

Solving the equations leads to

$$[1:1] = (5\,O.D_{414} - O.D_{480})/3.02 \qquad 5.19$$

For sodium methoxide, the following equations (where y/x = 5.0) enables calculation of the amount of 1:1 (equations 5.20 and 5.21).

$$O.D_{414} = [1:1](0.68) + [1:2]x \qquad 5.20$$

$$O.D_{480} = [1:1](0.49) + [1:2]y \qquad 5.21$$

Solving equations 5.20 and 5.21 leads to equation 5.22

$$[1:1] = (5\ O.D_{414} - O.D_{480})/2.9 \qquad 5.22$$

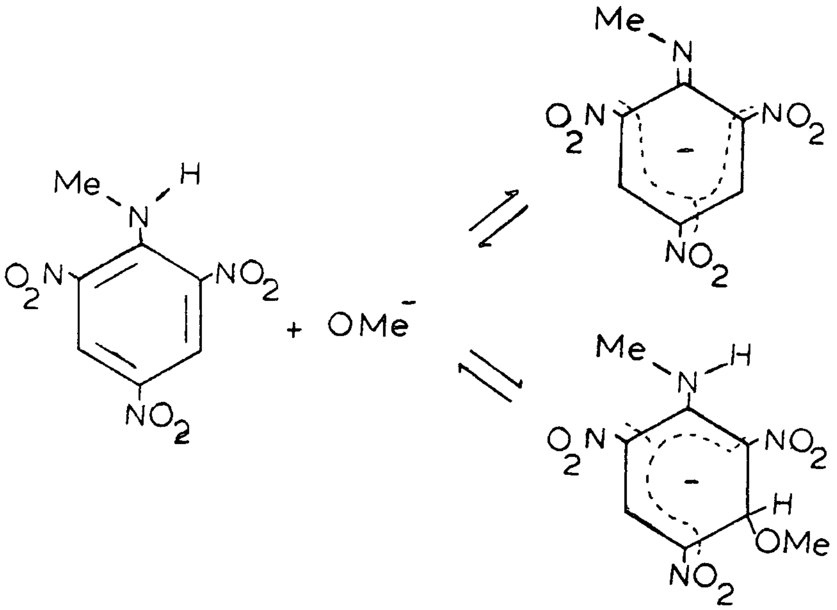
The amount of [1:2] adduct is obtained by subtracting the sum of [1:1] and [1:3] from 1.0 as described by equation 5.23

$$[1:2] = 1 - ([1:1] + [1:3]) \qquad 5.23$$

With lithium methoxide, the spectrum of the spiro-adduct remained unchanged up to the highest base concentrations obtainable (2.6M).

(e) N-Methylpicramide

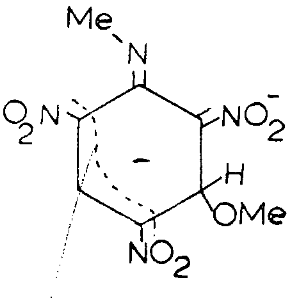
With this substrate two possible modes of 1:1 interactions are proton loss or base attack at the three position (scheme 5.1).



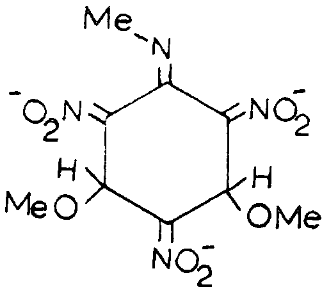
SCHEME 5.1

An assumption that it is necessary to make, is that the fractions ionising by these modes do not vary greatly with base concentration. Hence the spectral shape of the product of 1:1 interaction is assumed to be independent of base concentration.

The products of 1:2 and 1:3 interaction are likely to be (5.2) and (5.3) respectively.



(5.2)



(5.3)

Table 5.8

Optical densities, equilibrium constants, and Adduct Ratios Measurements for 1-(2-Hydroxyethoxy)-2,4,6-Trinitrobenzene with Potassium Methoxide in Methanol at 25^{o}C.

[KOMe] /M	O.D$_{414}$	O.D$_{440}$	O.D$_{480}$	[1:1]	[1:2]	[1:3]	K$_{1:2}$ /ℓ mol^{-1}	K$_{1:3}$ /ℓ mol^{-1}	log K$_{1:2}$	log K$_{1:3}$
.0923	.714	.485	.485	1.0	0	0				
.023	.716	.483	.493	1.0	0	0				
1.846	.707	.486	.511	1.0	0	0				
2.030	.699	.478	.503	.99	0	0				
2.215	.696	.481	.506	.984	-	-				
2.40	.692	.484	.509	.977	-	-				
2.584	.681	.477	.541	.948	.046	.006	.019	.05	-1.73	-1.29
2.768	.668	.472	.536	.928	.055	.017	.021	.112	-1.67	-0.95
2.953	.676	.471	.526	.945	.036	.019	.013	.18	-1.89	-0.75
3.138	.593	.465	.584	.788	.181	.031	.073	.046	-1.14	-1.26
3.322	.530	.4365	.627	.669	.239	.092	.11	.12	-0.97	-0.94
3.507	.460	.419	.639	.639	.234	.127	.104	.155	-0.98	-0.81
3.692	.371	.372	.652	.398	.377	.225	.26	.162	-0.59	-0.79
3.876	.289	.334	.669	.257	.439	.304	.44	.18	-0.36	-0,75
4.06	.214	.277	.632	.145	.432	.423	.73	.24	-0.134	-0,62
4.245	.150	.251	.576	.057	.535	.477	2.21	.21	.345	-0.68
4.430	.109	.197	.537	.003	.407	.59	-	.33		-0.485
4.615	.076	.139	.399	0	.29	.71	-	.53	-	-0.275

[Indicator] = 2.5 x 10^{-5}M

Table 5.9

Optical densities, equilibrium constants, and Adduct Ratios Measurements for 1-(2-Hydroxy ethoxy)-2,4,6-Trinitrobenzene with Sodium Methoxide in Methanol at 25°C.

[NaOMe]	$O.D_{414}$	$O.D_{440}$	$O.D_{480}$	[1:1]	[1:2]	[1:3]	$K_{1:2}$ $/\ell\ mol^{-1}$	$K_{1:3}$ $/\ell\ mol^{-1}$	log $K_{1:2}$	log $K_{1:3}$
.1255	.664	.459	.454	1.0	0	0				
1.022	.689	.472	.479	1.0	0	0				
2.008	.694	.495	.504	1.0	0	0				
2.216	.667	.478	.497	.978	.022	0	.01			
2.37	.675	.497	.522	.98	.02	0	.009		-2.0	
2.59	.663	.485	.545	.955	.035	.010	.014	.110	-2.05	-.96
2.785	.571	.464	.534	.80	.147	.053	.066	.13	-1.85	-.88
2.955	.538	.457	.553	.737	.196	.067	.090	.116	-1.18	-.94
3.172	.457	.436	.577	.59	.30	.11	.160	.116	-1.05	-.94
3.197	.452	.436	.572	.58	.31	.11	.167	.11	- .79	-.96
3.524	.293	.347	.525	.32	.388	.292	.344	.21	- .78	-.68
3.840	.190	.241	.398	.19	.302	.508	.414	.44	- .46	-.36
4.015	.133	.189	.317	.12	.27	.61	.560	.56	- .38	-.25
4.163	.097	.158	.256	.078	.244	.677	.742	.67	- .25	-.17
4.345	.073	.124	.20	.057	.196	.747	.791	.88	- .13	-.06
4.492	.039	.058	.0875	.037	.083	.88		2.36		+.37
4.740	.026	.044	.073	.0196	.07	.91		2.74		+.44
5.130	.008	.0282	.042	0	.06	.94	-	3.05		+.48
0	.54	.366	.472	-	-	-	-	-		

[Indicator] = 2.5×10^{-5} M

From tables 5.11 and 5.12 and from spectral shapes, (see figure 5.6), the following assumptions are justified.

(i) $[\text{Parent}] + [1:1] + [1:2] + [1:3] = 1$ 5.24

(ii) For KOMe and NaOMe, $[1:1]$ and $[1:2]$ adducts show an isobestic point at 460 nm.

(iii) Little parent is present when $[\text{Base}] > 1\text{M}$.

(iv) Little $[1:3]$ adduct is present when $[\text{Base}] < 1\text{M}$.

1. <u>With KOMe</u>

Below 0.2 M of base, the following equation may hold (rows 1-8 in table 5.11).

$$[1:1] = (\text{O.D}_{460} - 0.02)/0.42 \tag{5.25}$$

At this range of base concentration;

$$[\text{Parent}] = 1 - [1:1] \tag{5.26}$$

Since the parent absorbs 0.21 units at 410 nm (for $[\text{Base}] < 0.2\text{M}$), the following equations may hold.

$$\text{O.D}_{410} = [\text{Parent}]\,(0.21) + [1:1]x \tag{5.27}$$

and $$\text{O.D}_{490} = [1:1]\,y \tag{5.28}$$

x and y represent the extinction coefficients for 1:1 adduct at 410 and 490 nm, respectively. Substituting the values of $[1:1]$ obtained from equation 5.25 and values of $[\text{Parent}]$ obtained from equation 5.26 in equations 5.27 and 5.28 gives values of x and y listed in table 5.10. From table 5.10, average, $x = 0.710$ and average $y = 0.280$, and $K_{1:1} \sim 40\ \ell\ \text{mol}^{-1}$. Above 1M base, assuming $[\text{Parent}] = 0$, the amount of 1:3 species can be evaluated by equation 5.29

$$[1:3] = (0.44 - \text{O.D}_{460})/0.44 \tag{5.29}$$

From table 5.11, the following equations are applicable.

$$\text{O.D}_{410} = [1:1]\,x + [1:2]\,z + [1:3]\,0.02 \tag{5.30}$$

$$\text{O.D}_{490} = [1:1]\,y + [1:2]\,w \tag{5.31}$$

where z and w are the extinction coefficients for 1:2 species at 410 and 490 nm, respectively. Assuming w/z = 3.0 and since x and y are known we can re-write equations 5.30 and 5.31 as:

$$O.D_{410} = [1:1](0.71) + [1:2]z + [1:3]0.02 \tag{5.32}$$

$$O.D_{490} = [1:1]\ (0.28) + 3[1:2]\,z \tag{5.33}$$

Solving equations 5.32 and 5.33, and rearranging gives the following equation, which was used to find the amount of 1:1 adduct for rows 14-24 in table 5.11 (equation 5.34).

$$[1:1] = (3\ O.D_{410} - O.D_{490} - 0.06\ [1:3])/1.85 \tag{5.34}$$

At this range of base concentration ([Base] > 1M), assuming [Parent] = 0 the amount of 1:2 adduct is obtained by equation 5.23.

For rows 9-13 (in table 5.11) from the definition of $K_{1:1}$, the following equation can be written

$$[\text{Parent}] = [1:1]\ /K_{1:1}[\text{Base}] \tag{5.35}$$

[1:1] in equation 5.35 is obtained from equation 5.34, putting the term [1:3] = 0, and since $K_{1:1} \sim 40\ \ell\ \text{mol}^{-1}$, it is possible to find the amount of [Parent] , from equation 5.35, and [1:2] from equation 5.36

$$[1:2] = 1 - ([1:1] + [\text{Parent}])\ (\text{where } [1:3] = 0) \tag{5.36}$$

Data and values are shown in table 5.11.

2. <u>With NaOMe</u>

The same procedure as for potassium methoxide is carried out for sodium methoxide. The amount of 1:1 species is obtained (for rows 1-8 in table 5.12) by equations 5.37 and 5.26, which holds in this range, where 1:3 = 0.

$$1:1 = (O.D_{460} - 0.02)/0.44 \tag{5.37}$$

From equations 5.27 and 5.28, x and y values are shown in table 5.10, where, average x = 0.725 (absorption value for 1:1 adduct at 410 nm) and average y = 0.295 (absorption value for 1:1 adduct at 490 nm).

Table 5.10

Absorbance values for 1:1 adducts (Indicator N - Methyl picramide with metal methoxides) in methanol at 25°C.

[KOMe] /M	x_{410}	y_{490}	[NaOMe] /M	x_{410}	y_{490}	[LiOMe] /M	x_{410}	y_{470}
.010	.777	.336	.0103	.721	.302	.011	.644	.415
.020	.715	.276	.0205	.714	.278	.022	.695	.367
.0334	.79	.273	.0308	.735	.286	.275	.715	.37
.0446	.702	.280	.0411	.731	.293	.0385	.718	.393
.0669	.71	.286	.0616	.693	.296	.055	.70	.37
.0892	.73	.275	.0822	.751	.308	.077	.709	.361
.111	.71	.274	.103	.757	.285	.099	.697	.367
.223	.70	.299	.205	.72	.289	.192	.686	.36

[Indicator] = 3×10^{-5}M

Above 1M base (rows 12-22 in table 5.12), 1:3 adduct is found by equation 5.38.

$$[1:3] = (0.46 - O.D_{460})/0.46 \qquad 5.38$$

Substituting the values of x and y, and assuming w/z = 1.45 in equations 5.30 and 5.31 gives:

$$[1:1] = (1.45\ O.D_{410} - O.D_{490} - 0.029[1:3])/0.756 \qquad 5.39$$

In this range, where [Parent] = 0, amount of 1:2 adduct ([Base] > 1M) is calculated by equation 5.23. For rows 9-11 in table 5.12, [1:1] in equation 5.35 is obtained from equation 5.39, where [1:3]= 0 since $K_{1:1} \sim 30\ \ell\ mol^{-1}$ (table 3.12). Accordingly [Parent] is obtained from equation 5.35, using these values to obtain [1:2] from equation 5.36.

3. <u>With LiOMe</u>

For runs 1-8 in table 5.13, the following equations may hold ([Base] < 0.2 M), where [1:3] = [1:2] = 0

$$O.D_{410} = [Parent]\ (0.21) + [1:1]x \qquad 5.40$$

$$O.D_{470} = [1:1]\ y \qquad 5.41$$

Solving both above equations for x and y gives x = 0.71 and y = 0.37 (x and y were defined above and values are shown in table 5.10). An isobestic point at 450 nm which has an absorption of 0.48 is observed between 0.5 and 1.5 M base. Hence

$$O.D_{450} = [Parent]\ (0.045) + ([1:1] + [1:2])(0.48) \qquad 5.42$$

since $[Parent] + [1:1] + [1:2] = 1.0 \qquad 5.24$

Substituting equation 5.24 in 5.42 and rearranging, gives

$$[Parent] = (0.48 - O.D_{450})/0.435 \qquad 5.43$$

(which applied for rows 1-8 in table 5.13).

Above 1M base concentration, equations 5.30 and 5.44 hold

$$O.D_{470} = [1:1]\ y + [1:2]\ w \qquad 5.44$$

assuming w/z = 3.0, and solving equations 5.30 and 5.44 gives (for [Base] > 1M)

$[1{:}1] = (3\ \mathrm{O.D}_{410} - \mathrm{O.D}_{470} - [1{:}3]0.06)/1.76$ 5.45

Above 1M base, [1:3] is determined by equation 5.46

$[1{:}3] = (0.48 - \mathrm{O.D}_{450})/0.48$ 5.46

For rows 9-12 in table 5.13, $K_{1:1} \sim 33\ \ell\ \mathrm{mol}^{-1}$, using this value with [1:1] obtained from equation 5.45, when [1:3] = 0, in equation 5.35 to get the parent's amount. [1:2] is found by equation 5.36.

(f) 2,4,6-Trinitroaniline (Picramide).

In the presence of sodium methoxide an absorption has been observed around 398 nm ($\varepsilon = 28{,}000\ \ell\ \mathrm{mol}^{-1}\mathrm{cm}^{-1}$). This absorption increases with increasing base concentration until [Base] > 1.6M, when another absorption at 470 nm starts to develop and the absorption at 398 starts to decrease. At high base concentrations (> 3M), there was not any absorption in the visible region.

Again as with N-methyl picramide, there are two possibilities for 1:1 interaction: base addition or proton abstraction. We assume that the efficiency of these processes does not vary greatly with base concentration.

1. With KOMe

Below 1M base, the amount of parent can be found by one of the following equations (from table 5.14).

$[\mathrm{Parent}] = (0.93 - \mathrm{O.D}_{400})/0.69$ 5.47

or $[\mathrm{Parent}] = (0.53 - \mathrm{O.D}_{440})/0.455$ 5.48

in this range of base concentrations, only the parent and 1:1 adduct are present, hence the amount of 1:1 adduct is obtained by

$[1{:}1] = 1 - [\mathrm{Parent}]$ 5.49

Above 1M base, there is little parent present. From table 5.14, the optical densities for 1:1 adduct are 0.93 at 400 nm and 0.22 at 480 nm and it is known from visible spectra and from table 5.14 that the 1:2 adduct absorbs at 400 nm and at 480 nm. Estimating an absorption

ABLE 5.11 Optical densities, Equilibrium constants, and Adduct Ratios for the Reaction of N-Methyl picramide with Potassium Methoxide in methanol at 25^{o}C

[KOMe] /M	O.D$_{410}$	O.D$_{460}$	O.D$_{490}$	[Parent]	[1:1]	[1:2]	[1:3]	$K_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	$K_{1:3}$ /ℓ mol^{-1}	log $K_{1:1}$	log $K_{1:2}$	log $K_{1:3}$
.010	.345	.120	.080	.762	.238	0	0	31.2			1.49		
.020	.42	.195	.115	.583	.417	0	0	35.8			1.55		
.0334	.48	.25	.15	.452	.548	0	0	36.3			1.56		
.0446	.52	.285	.177	.369	.631	0	0	38.3			1.58		
.0669	.594	.343	.22	.231	.769	0	0	49.8			1.69		
.0892	.619	.349	.215	.217	.783	0	0	40.5			1.61		
.111	.629	.374	.231	.157	.843	0	0	48.4			1.68		
.223	.668	.417	.283	.055	.945	0	0	-					
.39	.647	.443	.352	.044	.859	.097	0	-	.29			-.54	
.557	.560	.427	.368	.0254	.709	.226	0	-	.57			-.24	
.780	.519	.435	.494	.9147	.575	.410	0	-	.91			-.04	
1.003	.462	.439	.534	.009	.460	.531	0	-	1.15			+.06	
1.170	.456	.438	.561	.007	.436	.557	0	-	1.1			.04	
1.338	.429	.432	.580	0	.3815	.60	.018	-	1.18	.022		.072	-1.66
1.560	.38	.430	.623	0	.278	.699	.0227	-	1.61	.021		.21	-1.68
1.895	.328	.408	.625	0	.1916	.735	.073	-	2.02	.052		.30	-1.28
2.118	.288	.377	.594	0	.141	.716	.143	-	2.4	.094		.38	-1.03
2.341	.265	.361	.572	0	.053	.707	.179	-	2.65	.30		.42	- .52
2.619	.199	.304	.48	0	.021	.638	.309	-	4.6	.19		.66	- .72
2.898	.149	.236	.38	0	0	.518	.461	-	8.5	.31		.93	- .51
3.233	.085	.130	.225	0	0	.318	.682	-		.66			- .18
3.567	.047	.093	.155	0	0	.212	.788	-		1.04			+ .017
3.901	.0294	.045	.076	0	0	.103	.897	-		2.23			.35
4.459	.02	.027	.021	0	-	.062	.938	-		3.4			.53
0	.21	.020	0	0		-	-	-					

[Indicator] = 3 x 10^{-5}M

TABLE 5.12

Optical densities, Equilibrium constants, and Adduct Ratios Ratio Data for the reaction of N,Methyl picramide with Sodium Methoxide in Methanol at 25°C.

[NaOMe] /M	$O.D_{410}$	$O.D_{460}$	$O.D_{490}$	[Parent]	[1:1]	[1:2]	[1:3]	$K_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	$K_{1:3}$ /ℓ mol^{-1}	log $K_{1:1}$	log $K_{1:2}$	log $K_{1:3}$
.0103	.32	.115	.065	.785	.215	0	0	26.6			1.42		
.0205	.40	.177	.105	.623	.377	0	0	29.5			1.47		
.308	.46	.220	.136	.525	.475	0	0	29.4			1.47		
.0411	.50	.265	.163	.443	.557	0	0	30.6			1.49		
.0616	.519	.302	.190	.359	.641	0	0	28.9			1.46		
.0822	.579	.32	.210	.319	.682	0	0	26.1			1.42		
.103	.614	.345	.210	.262	.728	0	0	27.3			1.44		
.205	,669	.415	.260	.102	.898	0	0	42.9	.		1.63		
.376	.658	.439	.33	.088	.790	.122	0		.41			-.39	
.592	.602	.449	.378	.056	.632	.312	0		.83			-.081	
.690	.596	.454	.430	.048	.555	.397	0		1.04			+.017	
1.025	.505	,468	.524		.275	.725	0		2.6			.42	
1.010	.495	.458	.524		.256	.744	0		2.9			.46	
1.170^{8}	.422	.430	.50		.145	.790	.065		4.7	.070		.67	-1.15
1.310^{5}	.389	.420	.508		.070	.843	.087		9.2	.787		.96	- .19
1.481^{6}	.366	.400	.49		.0488	.821	.13		11.4	.107		1.06	- .97
1.887^{8}	.245	.300	.35		-	-	.348		-	-			
2.070	.220	.230	.29		.020	.480	.50		11.6	.50			- .30
2.303^{6}	.145	.140	.182		.010	.294	.696		11.8	1.03			- .30
2.597^{3}	.079	.072	.087		.006	.151	.843		9.7	2.15			.013
2.758	.053	.044	.053		0	.096	.904			3.4			.33
3.013^{5}	.030	.018	.031		0	.040	.96			7.96			.53
													.90

[Indicator] = 3 x 10^{-5}M

Table 5.13

Optical densities, Equilibrium constants, and Adduct Ratios for the Reaction of N-Methyl picramide with Lithium Methoxide in Methanol at 25°C.

[LiOMe] / M	O.D$_{410}$	O.D$_{450}$	O.D$_{470}$	[Parent]	[1:1]	[1:2]	[1:3]	$K_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	$K_{1:3}$ /ℓ mol^{-1}	log $K_{1:1}$	log $K_{1:2}$	log $K_{1:3}$
.011	.320	.155	.105	.747	.253	0	0	30.8			1.48		
.022	.419	.232	.158	.570	.430	0	0	34.3			1.53		
.0275	.449	.25	.175	.528	.472	0	0	32.5			1.51		
.0385	.479	.275	.205	.471	.529	0	0	29.2			1.46		
.055	.533	.332	.244	,340	.660	0	0	35.3			1.55		
.0769	.568	.357	.259	.283	.717	0	0	32.9			1.52		
.0989	.572	.368	.273	.257	.743	0	0	29.2			1.46		
.192	.634	.432	.319	.110	.89	0	0	42.1			1.62		
.385	.638	.463	.369	.069	.877	.054	0		.16			- .79	
.549	.598	.465	.387	.044	.799	.157	0		.36			- .44	
.769	.566	.476	.428	.028	.722	.250	0		.45			- .35	
.989	.529	.477	.450	.0198	.646	.334	0		.52			- .27	
1.154	.484	.479	.478	0	.553	.447	0		.70			- .16	
1.374	.467	.50	.514	0	.504	.496	0		.72			- .14	
1.539	.397	.473	.497	0	.394	.591	.0146		.98	.016		~ 0	-1.79
1.924	.322	.458	.516	0	.254	.70	.046		1.43	.034		+.155	-1.48
2.198	.268	.441	.487	0	.177	.742	.081		1.91	.05		.28	-1.3
2.473	.225	.386	.438	0	.128	.676	.196		2.14	.12		.33	- .92
2.748	.174	.301	.349	0	.0855	.541	.373		2.30	.25		.361	- .60

[Indicator] = 3×10^{-5}M

for 1:3 at 480 nm of 0.03, the following equations apply:

$$O.D_{400} = [1:1]\ 0.93 + [1:2]z + [1:3]\ 0.03 \qquad 5.50$$

$$O.D_{480} = [1:1]\ 0.33 + [1:2]w \qquad 5.51$$

Solving equations 5.50 and 5.51, assuming w = z gives $[1:1] = (O.D_{400} - O.D_{480} - [1:3]\ 0.03)/0.71$ 5.52

while the amount of 1:3 adduct can be estimated by equation 5.53 at 480 nm

$$[1:3] = (0.19 - O.D_{480})/0.19 \qquad 5.53$$

The amount of 1:2 species is found by equation 5.23.

2. With NaOMe

As mentioned before in case of potassium methoxide in media containing 1M base or less, there is an equilibrium between parent and 1:1 complex, the amount of parent can be found by one of the below equations

$$[\text{Parent}] = (0.52 - O.D_{440})/(0.52 - 0.064) \qquad 5.54$$

or $[\text{Parent}] = (0.87 - O.D_{400})/0.62$ 5.55

Equation 5.49 is applied in this range of concentrations to calculate the amount of 1:1 species, where $[1:2] = [1:3] = 0$.

Above 1M base, both 1:2 and 1:3 adducts are present, 1:3 in methanol as solvent.

Solving the equations 5.56 and 5.51, where w = z

$$O.D_{400} = [1:1]\ 0.88 + [1:2]z + [1:3]\ 0.03 \qquad 5.56$$

gives $[1:1] = (O.D_{400} - O.D_{480} - [1:3]0.03)/0.66$ 5.57

The amount of 1:3 intermediate is obtained by equation 5.53, while $[1:2]$ is obtained by equation 5.23. Data and results are shown in table 5.15.

3. With LiOMe

The amount of parent is determined similarly by one of the following equations below. Below 1M base, the amount of 1:1 species is found by equation 5.49

$$[\text{Parent}] = (0.82 - \text{O.D}_{400})/0.58 \tag{5.58}$$

or

$$[\text{Parent}] = (0.48 - \text{O.D}_{440})/0.40 \tag{5.59}$$

Above 1M, the assumption is made that there is little 1:3 complex (i.e. $[1{:}3] = 0$) so that the only species are 1:1 and 1:2 which absorb at 400 nm and 480 nm. Solving equations 5.60 and 5.61 (assuming $w = z$, z and w are the absorbances for 1:2 species at 400 and 480 nm, respectively).

$$\text{O.D}_{400} = [1{:}1]\ 0.82 + |1{:}2|\,z \tag{5.60}$$

$$\text{O.D}_{480} = [1{:}1]\ 0.21 + [1{:}2]\,w \tag{5.61}$$

gives

$$[1{:}1] = (\text{O.D}_{400} - \text{O.D}_{480})/0.01 \tag{5.62}$$

while $[1{:}2]$ can be found by subtracting $[1{:}1]$ from 1 (i.e. $[1{:}2] = 1 - [1{:}1]$).

Table 5.14

Optical densities, Equilibrium constants, and Adduct Ratios Data for the Reaction of picramide with Potassium Methoxide in Methanol at 25^{o}C.

[KOMe] /M	O.D$_{330nm}$	O.D$_{400nm}$	O.D$_{440nm}$	O.D$_{480nm}$	at 400 [Parent]	[1:1]	[1:2]	[1:3]	$K^{400}_{1:1}$ /ℓ mol^{-1}	$K^{440}_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	$K_{1:3}$ /ℓ mol^{-1}	log $K^{400}_{1:1}$	log $K_{1:2}$	log $K_{1:3}$
0	.35	.242	.075	0	1.0	0	0	0	-	-			1.69		
.0108	.325	.48	.245	.10	.652	.348	0	0	49.4	55.3			1.68		
.0216	.309	.59	.33	.125	.493	.507	0	0	47.6	59.2			1.64		
.0433	.281	.69	.382	.155	.348	.652	0	0	43.3	47.9			1.64		
.065	.273	.749	.441	.171	.262	.728	0	0	43.4	61.5			1.78		
.0867	.288	.799	.462	.187	.199	.80	0	0	60.4	65.8			1.53		
.108	.297	.838	.497	.214	.133	.867	0	0	33.8	118.4			1.62		
.217	.284	.847	.507	.213	.12	.88	0	0	42.1	86.7			1.66		
.433	.279	.894	.515	.225	.052	.948	0	0	45.7	67.7					
.758	.28	.91	.536	.221	.028	.97	0	0							
1.083	.271	.926	.507	.208	0	.99	0	0							
1.626	.254	.939	.456	.211	0	1.0	0	0							
2.168	.229	.882	.448	.185	0	.97	0	.026							
2.385	.216	.869	.314	.182	0	.96	0	.04							
2.601	.220	.846	.287	.180	0	.935	0	.052							
2.818	.224	.764	.217	.177	0	.824	.09	.068			.038	.268		-1.42	- .57
3.035	.268	.70	.203	.175	0	.736	.185	.078			.083	.139		-1.08	- .86
3.252	.277	.573	.144	.173	0	.559	.352	.089			.19	.077		- .72	-1.11
3,468	.316	.485	.119	.165	0	.445	.423	.132			.27	.089		- .57	-1.05
3.685	.380	.322	.074	.114	0	.276	.324	.40			.32	.335		- .49	- .47
3.902	.405	.236	.059	.096	0	.176	.329	.495			.48	.385		- .32	- .41
4.120	.411	.186	.042	.084	0	.120	.323	.557			.65	.418		- .19	- .38
4.336	.433	.115	.016	.0412	0	.0708	.146	.783			.475	1.24		- .32	+.093
4.553	.437	.089	.007	.029	0	.0487	.153	.847			.69	1.22		- .16	+.086

[Indicator] = 3.04 x 10^{-5}M

Table 5.15

Optical densities, Equilibrium constants, and Adduct Ratios for the Reaction of picramide with Sodium Methoxide in Methanol at 25°C

[NaOMe] /M	O.D$_{330nm}$	O.D$_{400nm}$	O.D$_{440nm}$	O.D$_{480nm}$	at 400 [Parent]	[1:1]	[1:2]	[1:3]	$K^{400}_{1:1}$ /ℓ mol^{-1}	$K^{440}_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	$K_{1:3}$ /ℓ mol^{-1}	log $K^{400}_{1:1}$	log $K_{1:2}$	log $K_{1:3}$
.0123	.309	.45	.23	.085	.636	.364	0	0	38.7	46.5			1.58		
.0213	.294	.535	.295	.115	.493	.507	0	0	39.9	48.2			1.60		
.0425	.279	.635	.37	.16	.329	.671	0	0	38.6	48			1.58		
.055	.274	.67	.399	.17	.265	.735	0	0	38.2	50.3			1.58		
.0796	.283	.73	.43	.181	.197	.803	0	0	43.2	51.1			1.63		
.103	.270	.754	.439	.197	.177	.823	0	0	42.4	45			1.63		
.191	.266	.788	.479	.199	.089	.911	0	0	34.5	53			1.53		
.365	.268	.837	.498	.211	.048	.952	0	0	48.8	54.05			-		
.653	.272	.865	.507	.217	.0285	.972	0	0	-	52.18			-		
.948	.266	.873	.510	.208	.022	.98	0	0	-	-			-		
1.538	.249	.844	.423	.19	0	.99	0	0	-	-			-		
2.060	.25	.755	.30	.186	0	.86	.14	0	-	-	.079	-	-	-1.1	
2.224	.285	.674	.251	.187	0	.74	.26	.0158	-	-	.158	.027	-	- .80	-1.56
2.241	.310	.568	.179	.180	0	.59	.36	.05	-	-	.27	.062	-	- .57	-1.2
2.592	.373	.40	.118	.144	0	.37	.39	.24	-	-	.407	.24	-	- .39	- .625
2.768	.404	.310	.10	.108	0	.28	.29	.43	-	-	.37	.54	-	- .43	- .272
2.996	.465	.184	.068	.087	0	.12	.34	.54	-	-	.95	.53	-	- .022	- .275
3.181	.496	.107	.025	.045	0	.06	.19	.76	-	-	.995	1.26	-	∼ 0	+ .099
3.35	.503	.091	.0161	.022	0	.06	.06	.88	-	-	-	4.4	-	-	+ .64
3.594	.663	.0695	.015	.028	0	.02	-	-	-	-	-	-	-	-	-
3.784	.564	.038	.007	.009	0	-	-	-	-	-	-	-	-	-	-

[Indicator] = 3.04×10^{-5}M

Table 5.16

Optical densities, Equilibrium constants, and Adduct Ratios for the Reaction of picramide with Lithium Methoxide in Methanol at 25^{o}C.

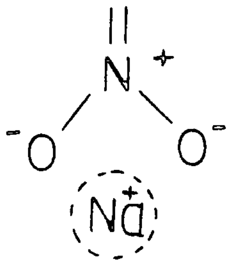
[LiOMe] /M	$O.D_{330nm}$	$O.D_{400nm}$	$O.D_{440nm}$	$O.D_{480nm}$	400 [Parent]	[1:1]	[1:2]	$K^{400}_{1:1}$ /ℓ mol^{-1}	$K_{1:1}$ /ℓ mol^{-1}	$K_{1:2}$ /ℓ mol^{-1}	log $K^{400}_{1:1}$	log $K_{1:2}$
.011	.309	.439	.222	.075	.657	.343	0	47.5	48.3		1.67	
.0193	.308	.519	.287	.110	.519	.481	0	51.8	51.6		1.71	
.0386	.304	.613	.347	.134	.357	.643	0	46.7	50.0		1.67	
.055	.295	.638	.364	.142	.314	.686	0	40	43.0		1.60	
.077	.286	.682	.410	.168	.238	.762	0	41.6	56.5		1.62	
.099	.284	.711	.423	.173	.188	.812	0	43.6	57.4		1.64	
.193	.262	.747	.440	.187	.126	.874	0	36	45.3		1.56	
.386	.256	.785	.468	.214	.06	.94	0	41			1.61	
.689	.254	.813	.473	.214	.01	.99	0					
.933	.249	.821	.479	.227	0	1.0	0					
1.489	.212	.741	.441	.224	0	.847	.153			.121		-.92
1.986	.202	.702	.421	,219	0	.79	.210			.134		-.87
2.207	.244	.701	.435	.257	0	.728	.272			.169		-.77
2.345	.278	.677	.447	.295	0	.626	.374			.254		-.595
2.483	.278	.657	.443	.30	0	.585	.415			.286		-.543
2.758	.307	.556	.452	.358	0	.325	.675			.75		-.123

[Indicator] = 3.04 x 10^{-5}M

Conclusions

The published H_M acidity scales for alkali metal methoxide solutions in methanol[116] show that at a given base concentration the basicity decreases in the order KOMe > NaOMe > LiOMe. This order has been attributed to[70] the greater dissociation of potassium methoxide ion pairs compared with sodium methoxide or lithium methoxide ion pairs. This relies on the assumption that the indicators used, substituted anilines and diphenylamines , do not associate strongly in their anionic forms with cations.

The present data show that for N,N-dimethyl picramide where measurements were made at only moderately concentrated base concentrations the values of equilibrium constants decrease in the ratio KOMe > NaOMe > LiOMe. However, for most substrates the graphs shown in figures 5.8 - 5.15 show that values of equilibrium constants for formation of 1:2 and 1:3 adducts are in the order NaOMe > KOMe > LiOMe. This may be taken as evidence that 1:2 and 1:3 adducts associate more strongly with sodium ions than they do with potassium ions. A possible rationalisation for this may be that in 1:2 and 1:3 adducts negative charge tends to be localised on nitrogroups rather than delocalised about the nitro groups and ring. There is the possiblity that sodium ions may associate particularly well with localised negative charges.



(5.4)

It is possible to attempt a semi-quantitative treatment in terms of ion-pair association constants as follows.

This treats formation of 1:2 adducts from 1:1 adducts and metal alkoxide.

$$\begin{tikzcd}
1:1 \arrow[d, shift left, harpoon, "K_{1:1,M^+}"] & + M^+ + & M^+ + OMe^- \arrow[d, shift left, harpoon, "K_{M^+OMe^-}"] \arrow[r, shift left, harpoon] & 1:2 + 2M^+ \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon, "K_{1:2,M^+}"] \\
1:1,\ M^+ \arrow[u, shift left, harpoon] & & M^+,\ OMe^- \arrow[u, shift left, harpoon] & 1:2,\ M^+ + M^+ \arrow[u, shift left, harpoon] \arrow[d, shift left, harpoon, "K_{1:2,(M^+)_2}"] \\
 & & & 1:2\ (M^+)_2 \arrow[u, shift left, harpoon]
\end{tikzcd}$$

Scheme 5.2

The visible spectra of free and ion-paired species are unlikely to be very different. So that the measured equilibrium constant K_c can be written in the form (equations 5.63 and 5.64)

$$K_c = \frac{[1:2] + [1:2,\ M^+] + [1:2,\ (M^+)_2]}{([1:1] + [1:1],\ M^+)[Base]} \qquad 5.63$$

$$K_c = \frac{[1:2](1 + K_{1:2,M^+}[M^+] + K_{1:2,M^+}\,K_{1:2,\ (M^+)_2}[M^+]^2)}{[1:1](1 + K_{1:1,M^+}[M^+])[Base]} \qquad 5.64$$

where $[Base]$ is a measure of the basicity of the medium including free and ion-paired base.

If K is the equilibrium constant in the absence of association of adducts with cations, equation 5.65 will apply.

$$K = [1:2]/[1:1][Base] \qquad 5.65$$

Then

$$K_c = \frac{K(1 + K_{1:2,M^+}[M^+] + K_{1:2,M^+}.K_{1:2\ (M^+)_2}[M^+]^2)}{1 + K_{1:1}[M^+]} \qquad 5.66$$

Increases with increasing base concentration in the values of K_c indicate that

$$\frac{1 + K_{1:2,\,M^+}\left[M^+\right] + K_{1:2,M^+}\,K_{1:2,(M^+)_2}\left[M^+\right]^2}{1 + K_{1:1}\left[M^+\right]} > 1 \qquad 5.67$$

implying stronger association of 1:2 adducts than 1:1 adducts with cations.

There is evidence that the association constants of 1,1-dialkoxy adducts with sodium and potassium ions have rather similar values[42,125]. Hence the greater values observed for K_c with sodium methoxide than with potassium methoxide when considering 1:2 adduct formation implies that 1:2 adducts associate more strongly with sodium ions than with potassium ions.

A similar argument regarding 1:3 adduct also indicates that they associate more strongly with sodium than with potassium ions.

FIG. 5.1

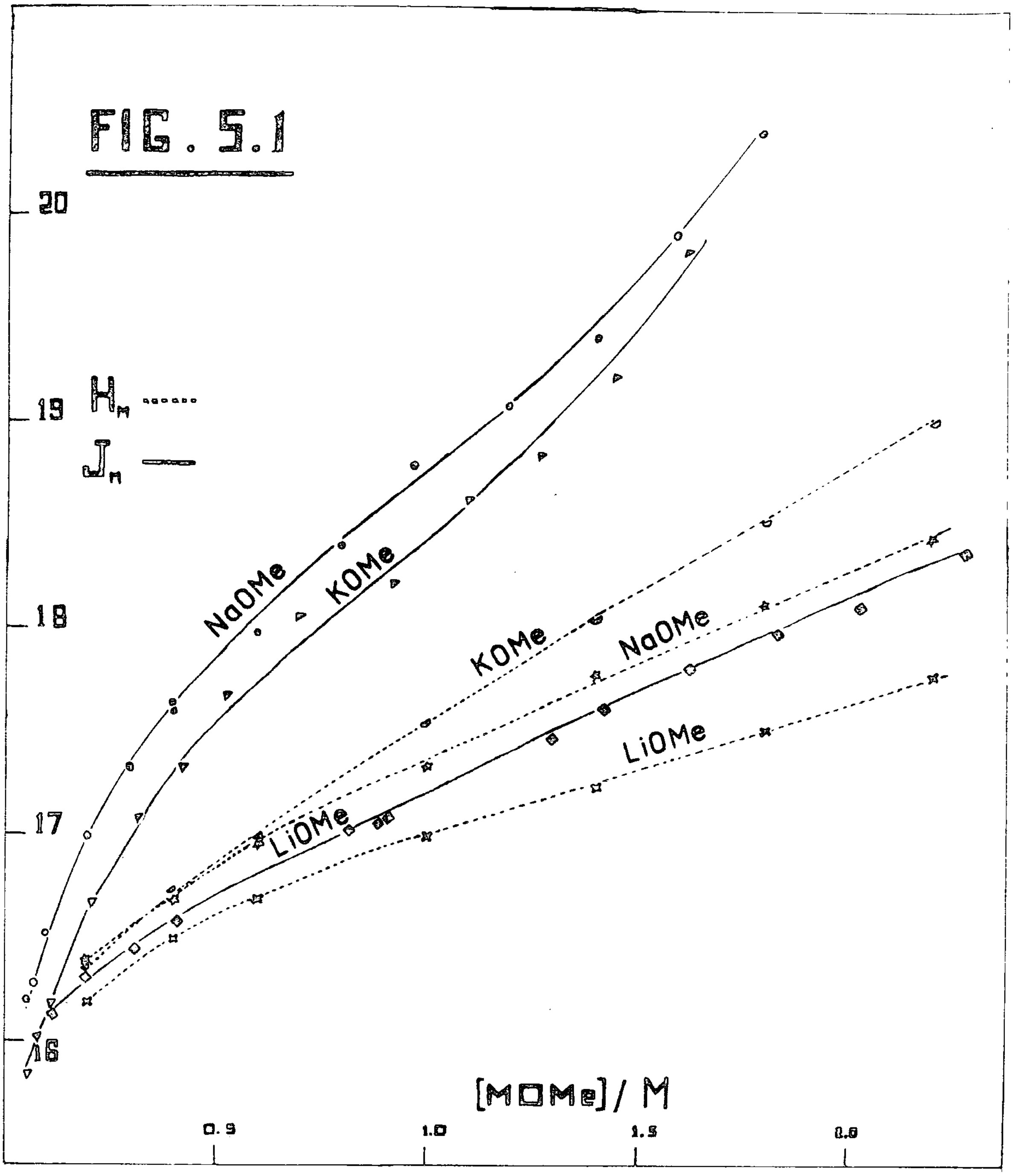


FIGURE 5.1

H_M (from ref.116) and J_M (tables 5.1,5.2 and 5.3)acidity function scales for alkali - metal methoxides in methanol ,the indicator used to determine J_M is 2-methoxy -3,5-dinitrobenzoic acid in methanol at 25° .

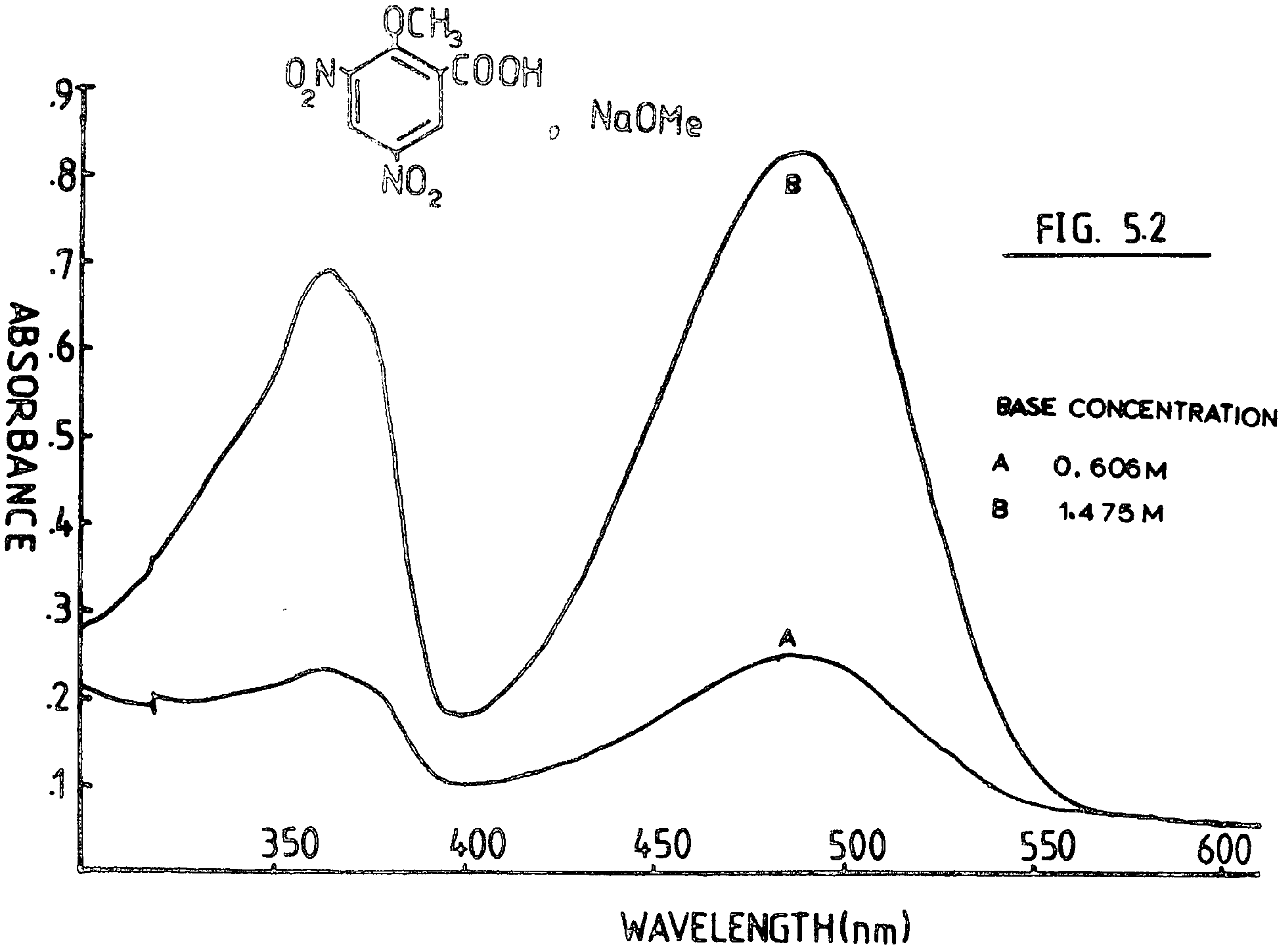


FIG. 5.2

FIGURE 5.2 Visible spectra for 2-methoxy-3,5-dinitrobenzoic acid (4.1×10^{-5} M) with sodium methoxide A, 0.605 M and ,B ,1.475 M in methanol at 25°.

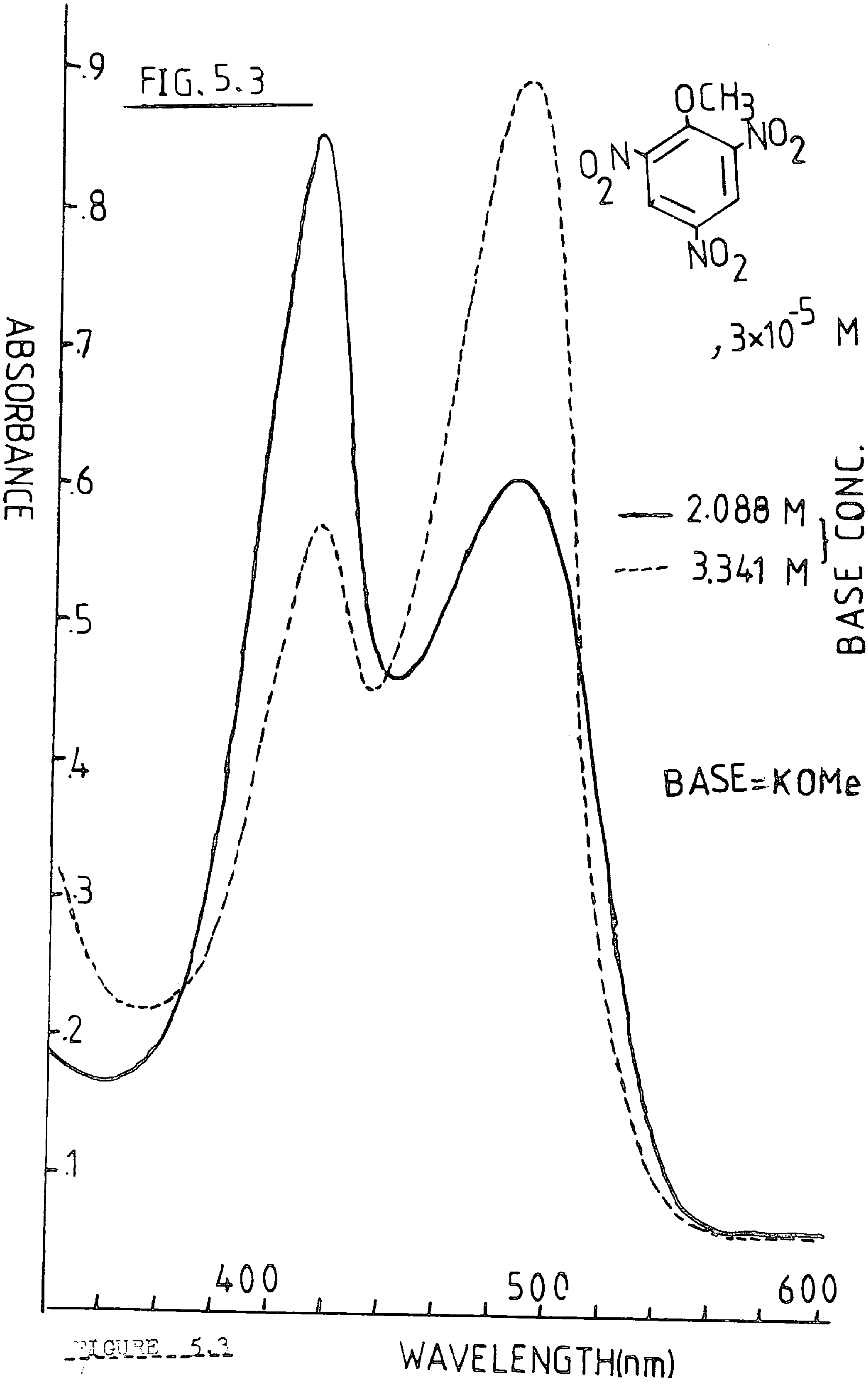


FIGURE 5.3

U.V /Visible spectra for 1,3,5-trinitoanisole(3.2×10^{-5} M) with potassium methoxide , —— 2.088 M . ----- 3.341 M in methanol at 25°.

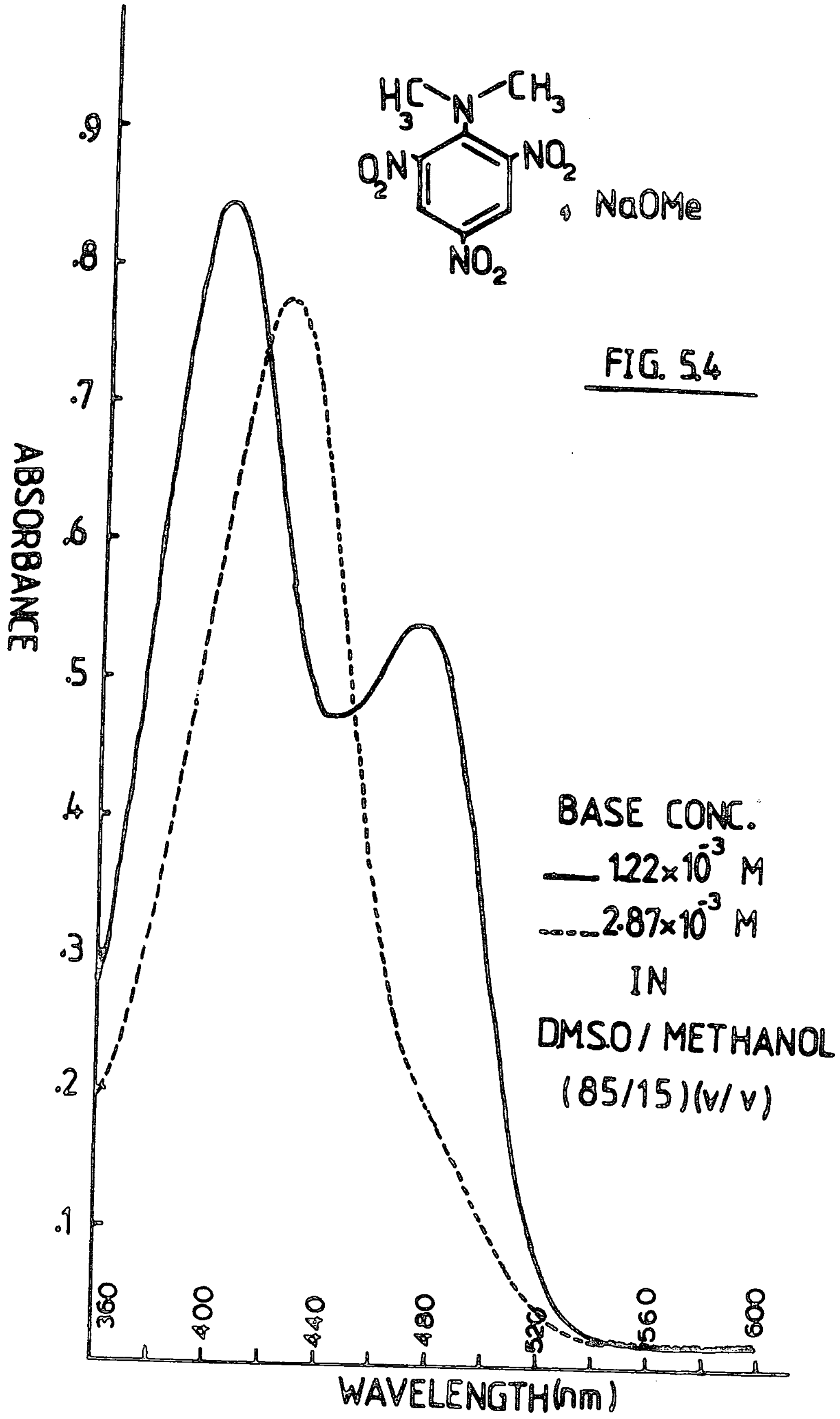


FIGURE 5.4

U.V / Visible spectra for N,N-dimethyl picramide (3×10^{-5} M) with sodium methoxide, 1.22×10^{-3} M (——) and 2.87×10^{-3} M(------), in DMSO/methanol mixture (85/15)(v/v) at 25°.

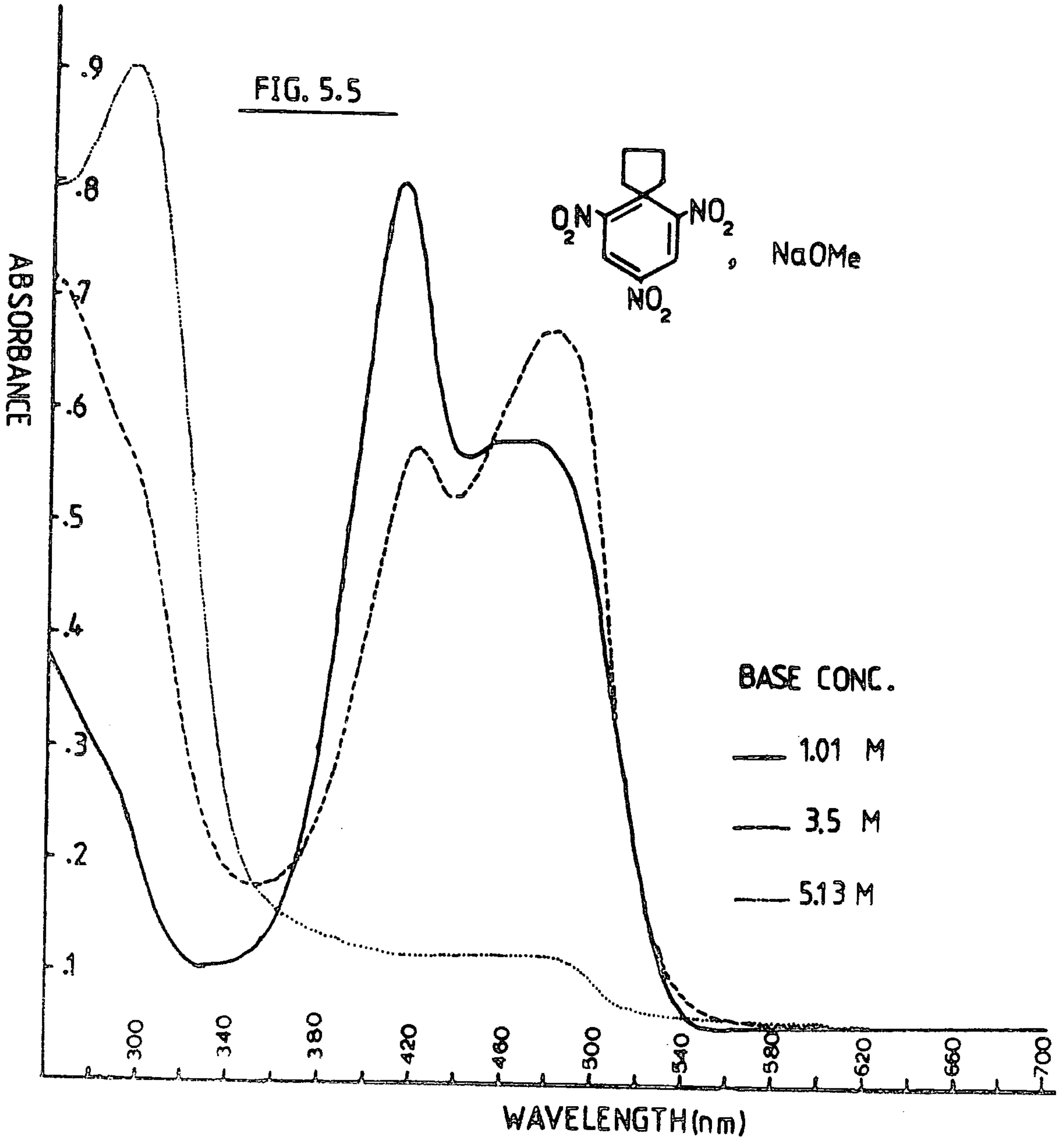


FIGURE 5.5

U.V /Visible spectra for 1-(2-Hydroxy ethoxy)-2,4,6-trinitrobenzen (2.8 X 10^{-5} M) and sodium methoxide at 1.01M(——) . 3.5 M(------) ,5.13 M (········) in methanol at 25°.

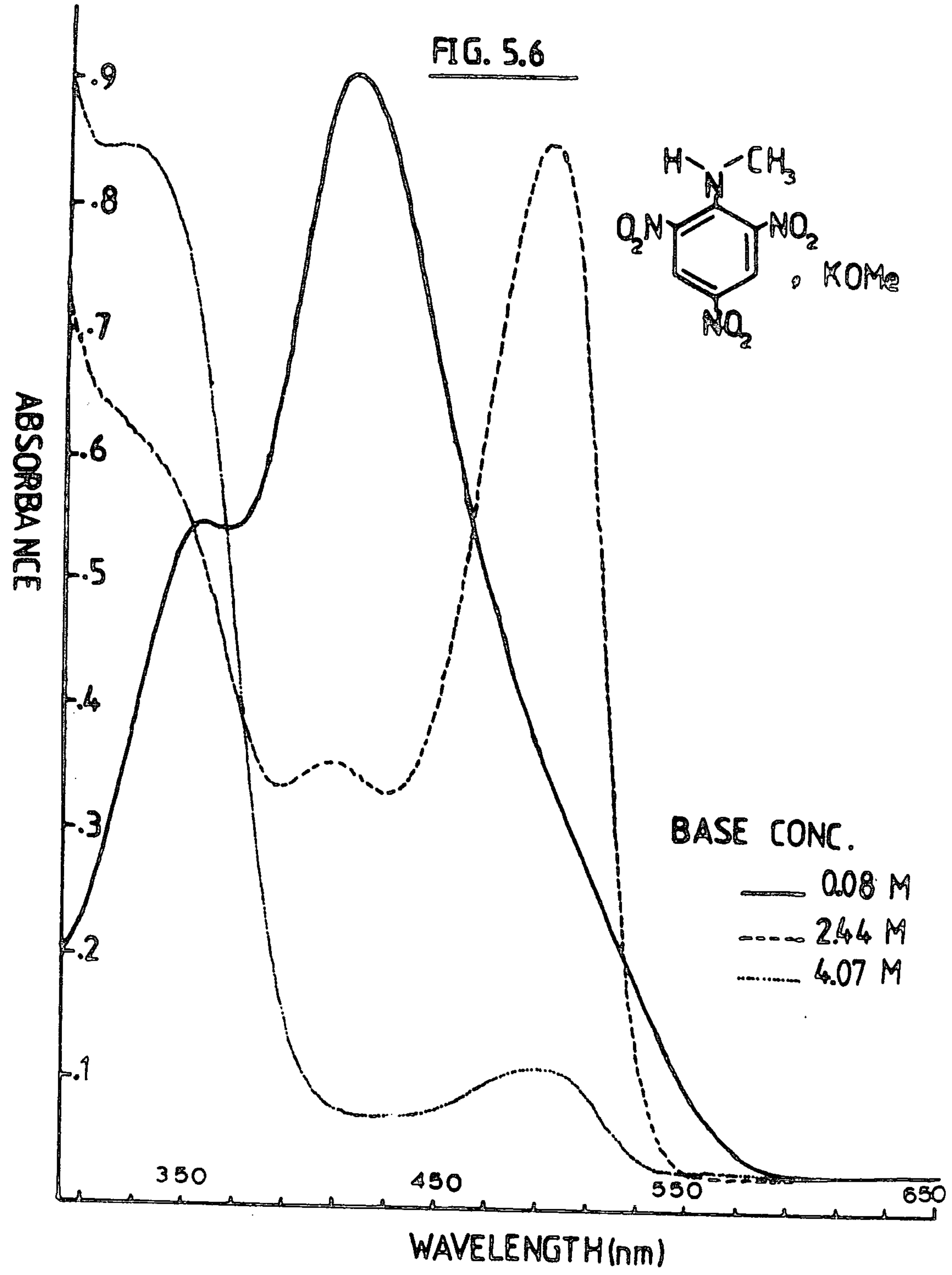


FIGURE 5.6

U.V / Visible spectra for N-methyl picramide (4.8 X 10^{-5} M) with potassium methoxide at 0.08 M (———) , 2.44 M (------) , 4.07 M (··········) in methanol at 25° .

FIG. 5.7

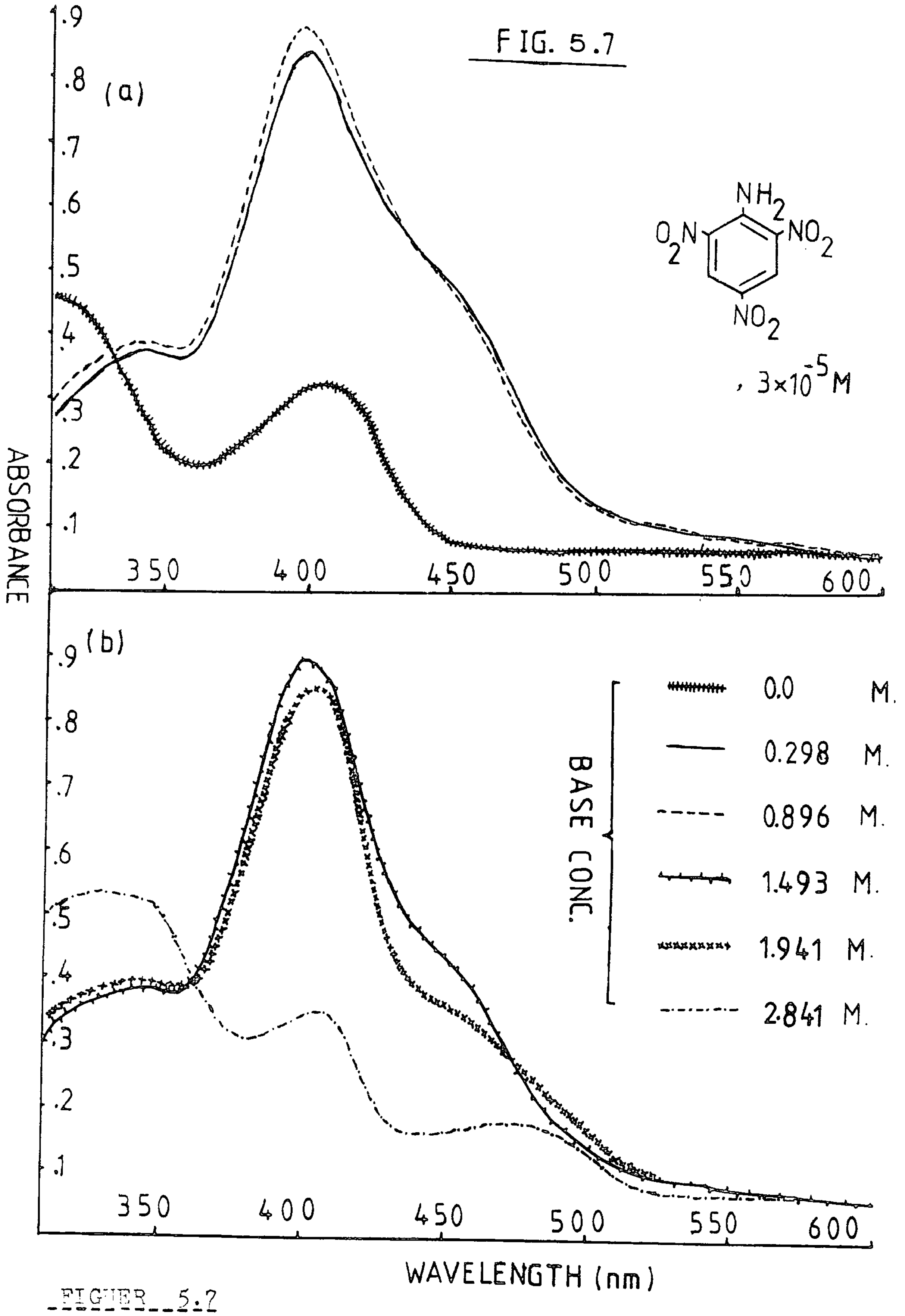


FIGURE 5.7

U.V/Visible spectra for picramide (3 X 10^{-5} M) with sodium methoxide : a) 0.0 M ,0.298 M ,0.896M. b) 1.493 M ,1.941 M,2.841 M in methanol at 25° .

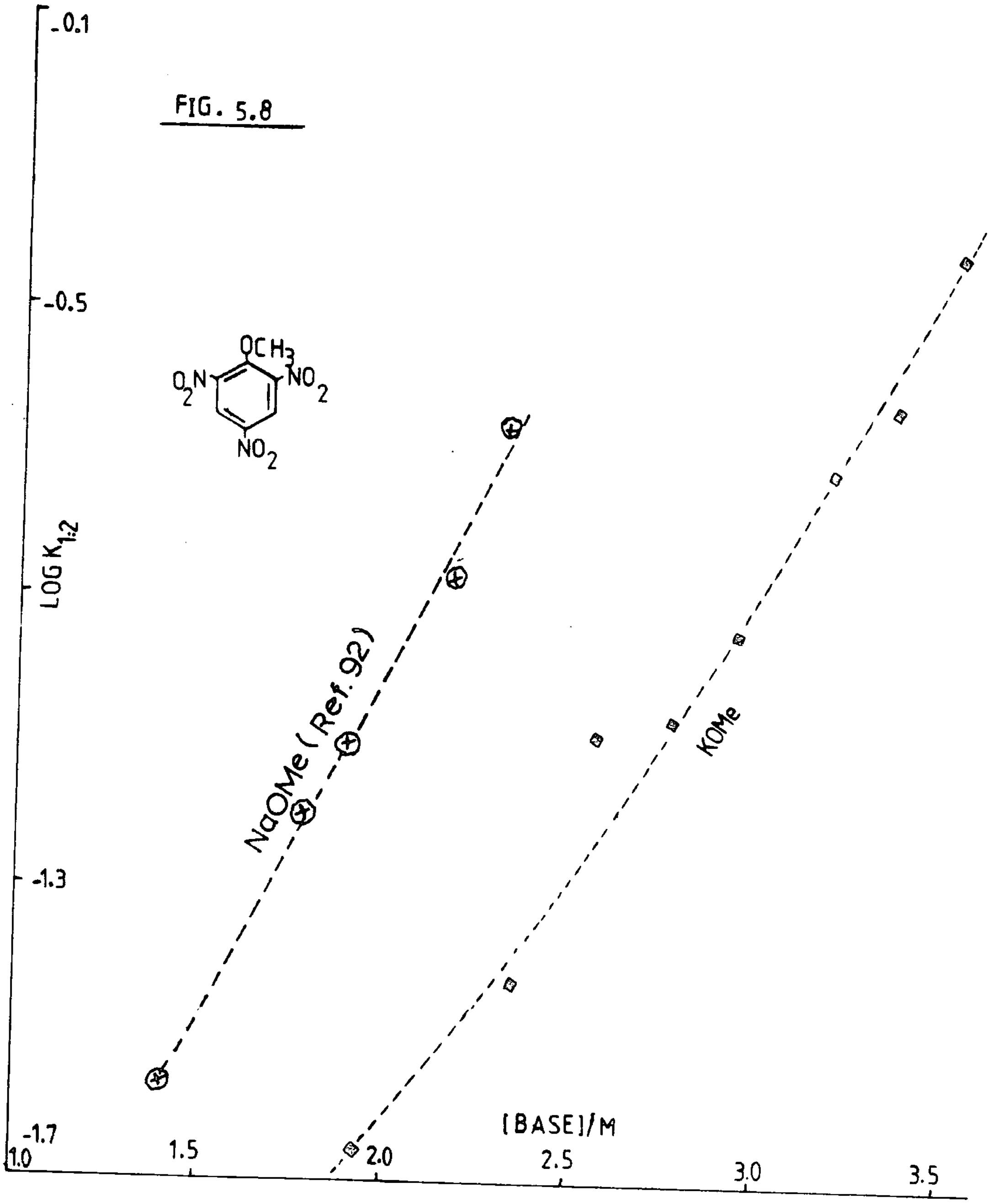


FIGURE 5.8

A plot of Log $K_{1:2}$ versus base concentration .Data are in table 5.4 .

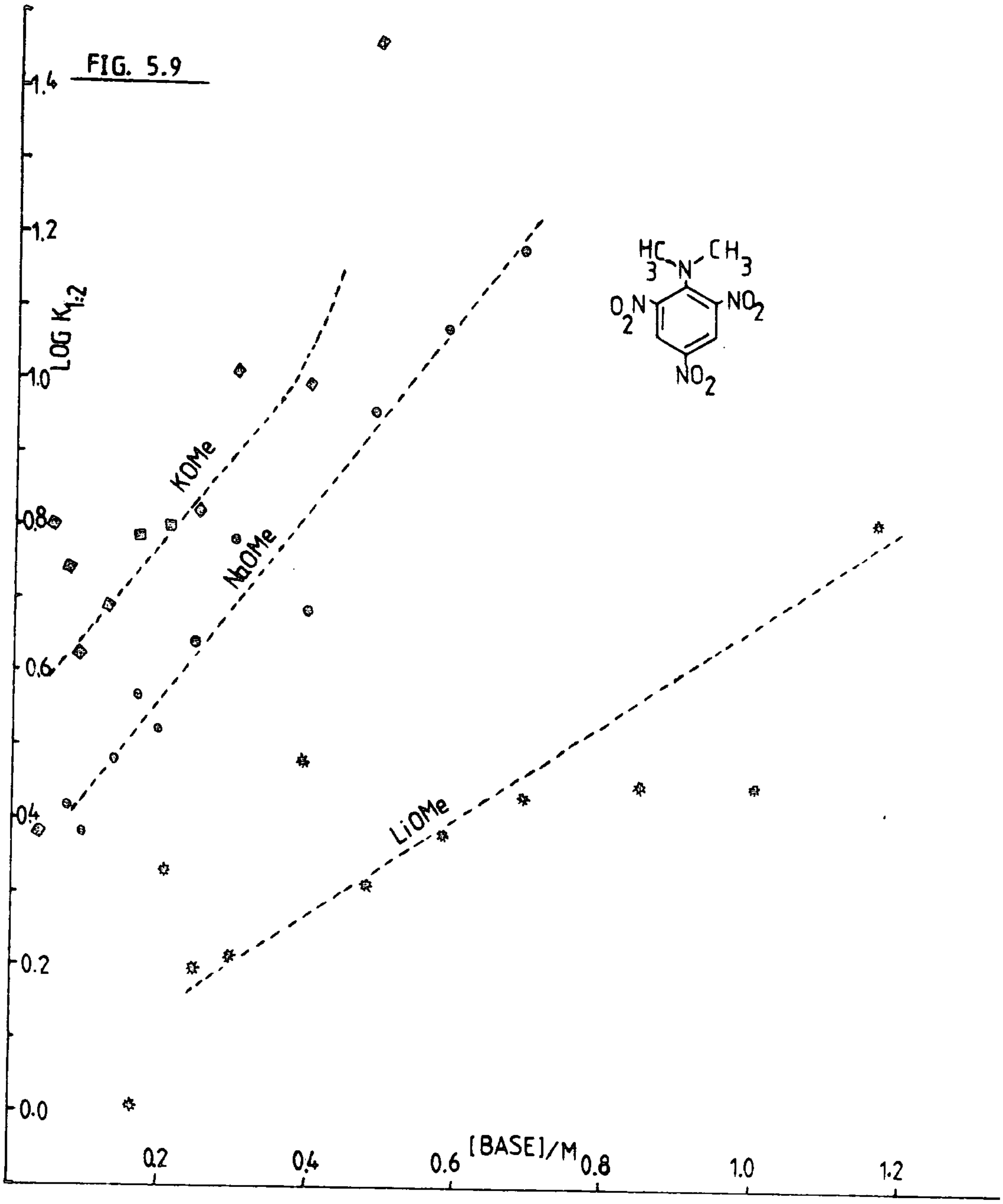


FIGURE 5.9

A plot of Log $K_{1:2}$ versus base concentration . Data are in tables 5.5 ,5.6 and 5.7 .

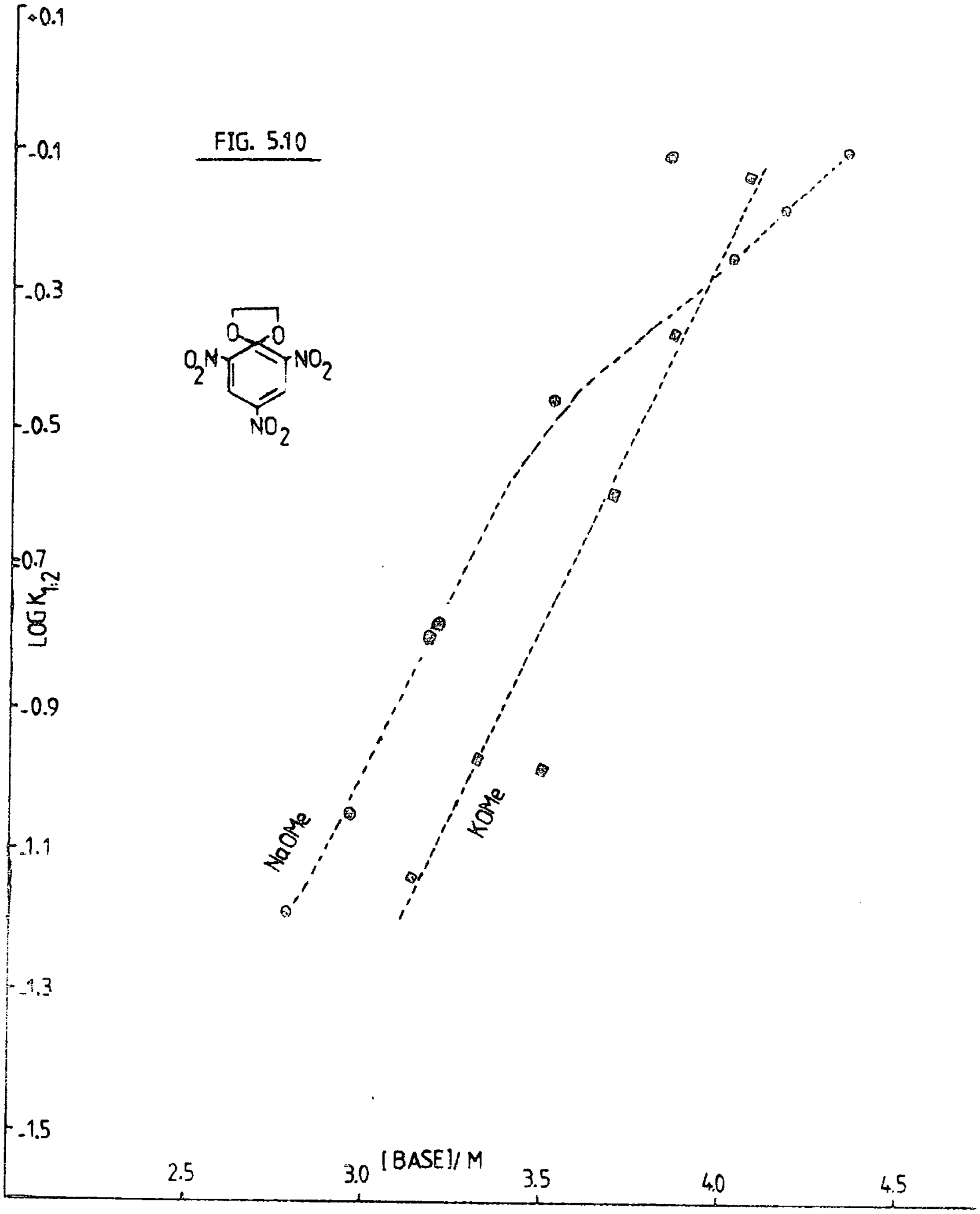


FIGURE 5.10

A plot of Log $K_{1:2}$ versus base concentration . Data are in tables 5.8 and 5.9 .

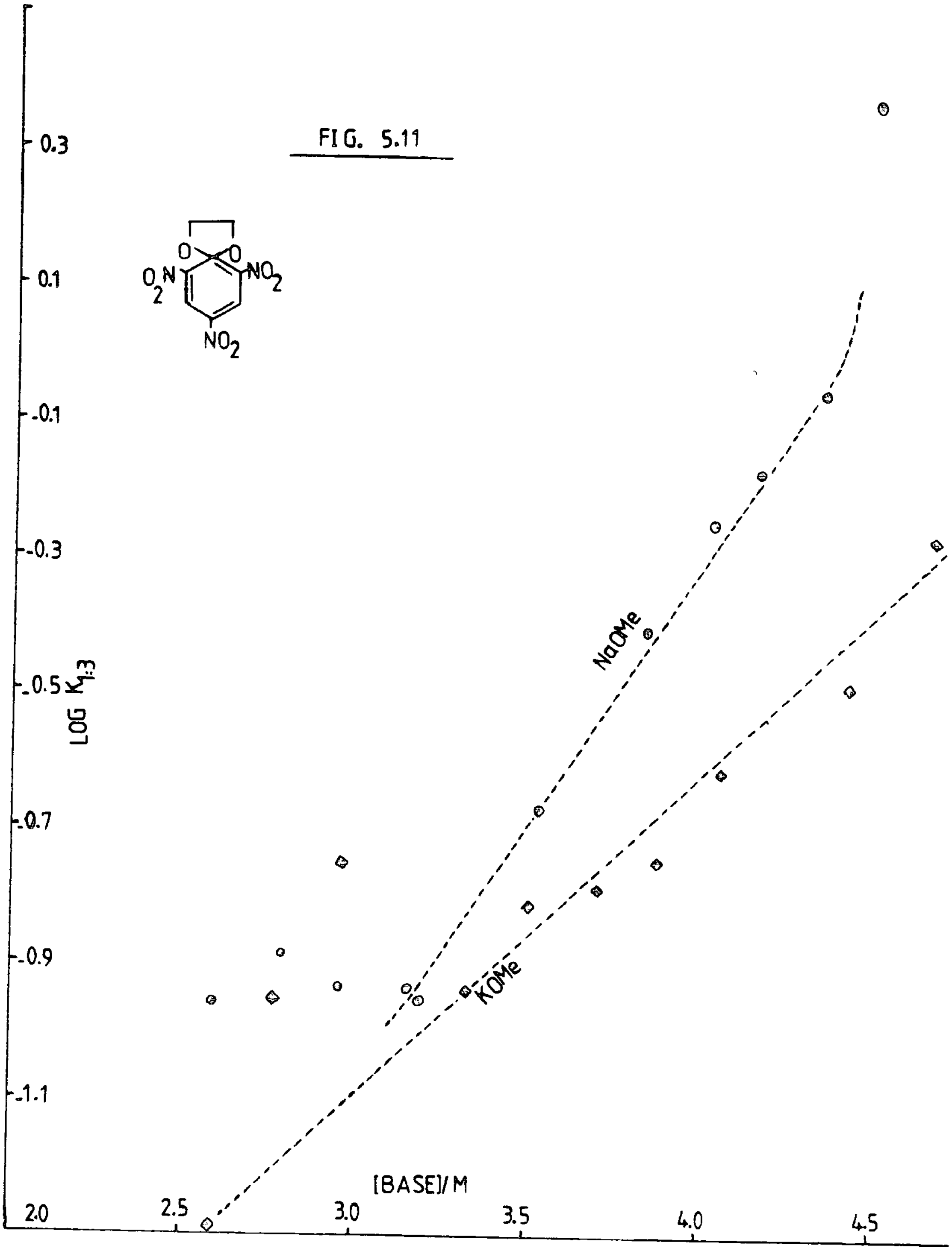


FIGURE 5.11

A plot of Log $K_{1:3}$ versus base concentration .Data are in tables 5.8 and 5.9 .

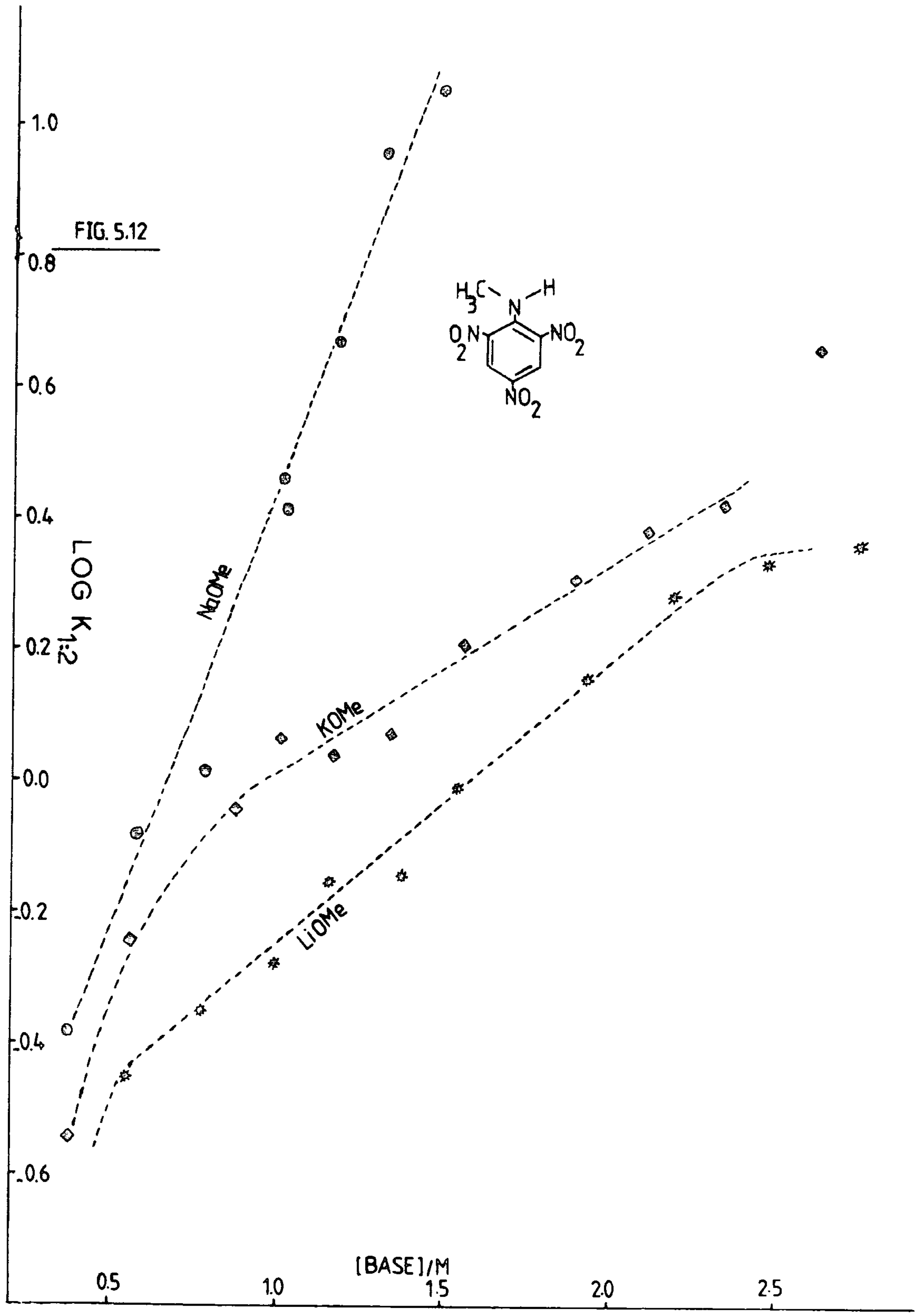


FIGURE 5.12

A plot of Log $K_{1:2}$ versus base concentration .Data are in tables 5.11 , 5.12 and 5.13 .

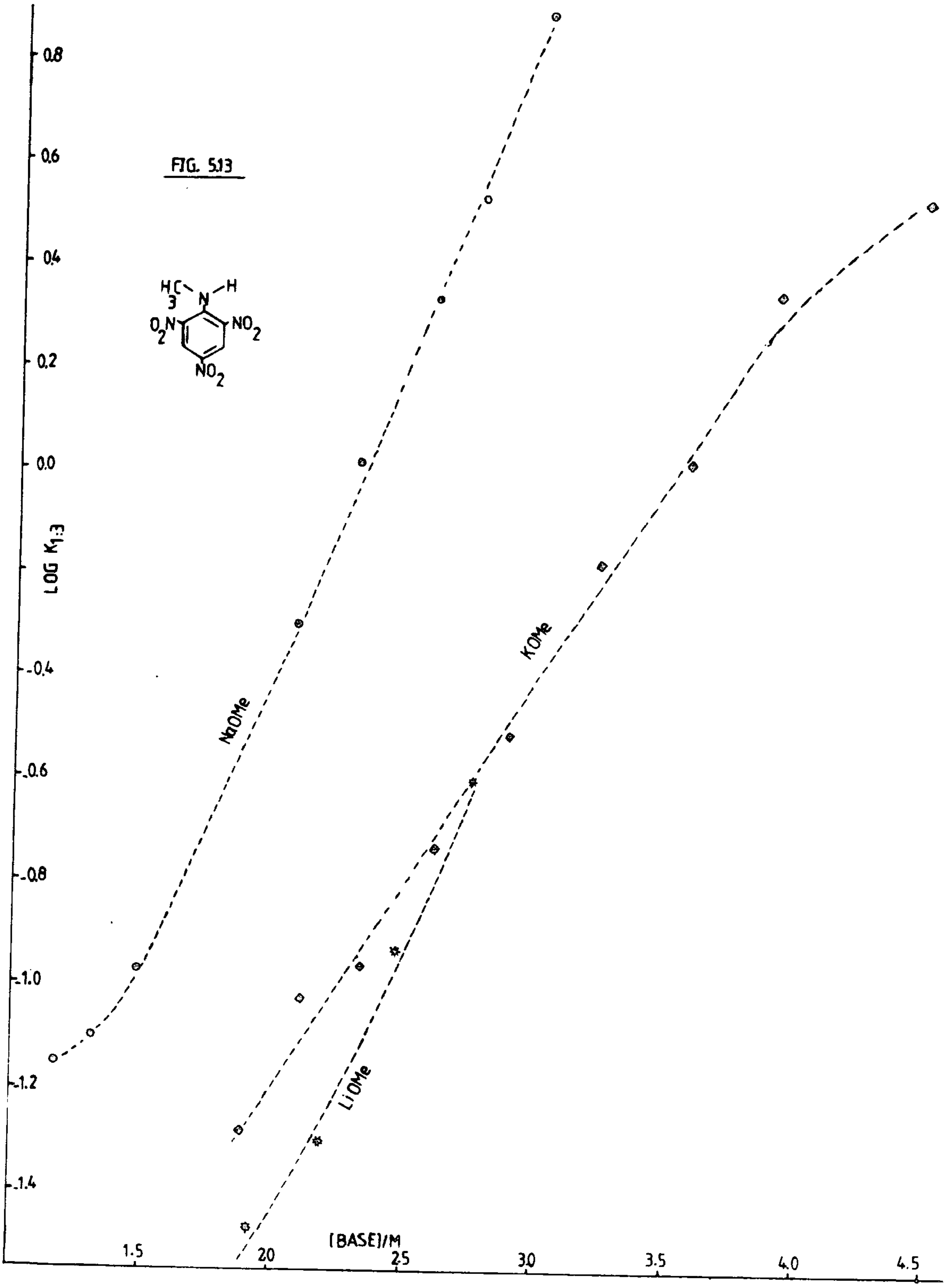


FIGURE 5.13

A plot of Log $K_{1:3}$ versus base concentration . Data are in tables 5.11 , 5.12 and 5.13 .

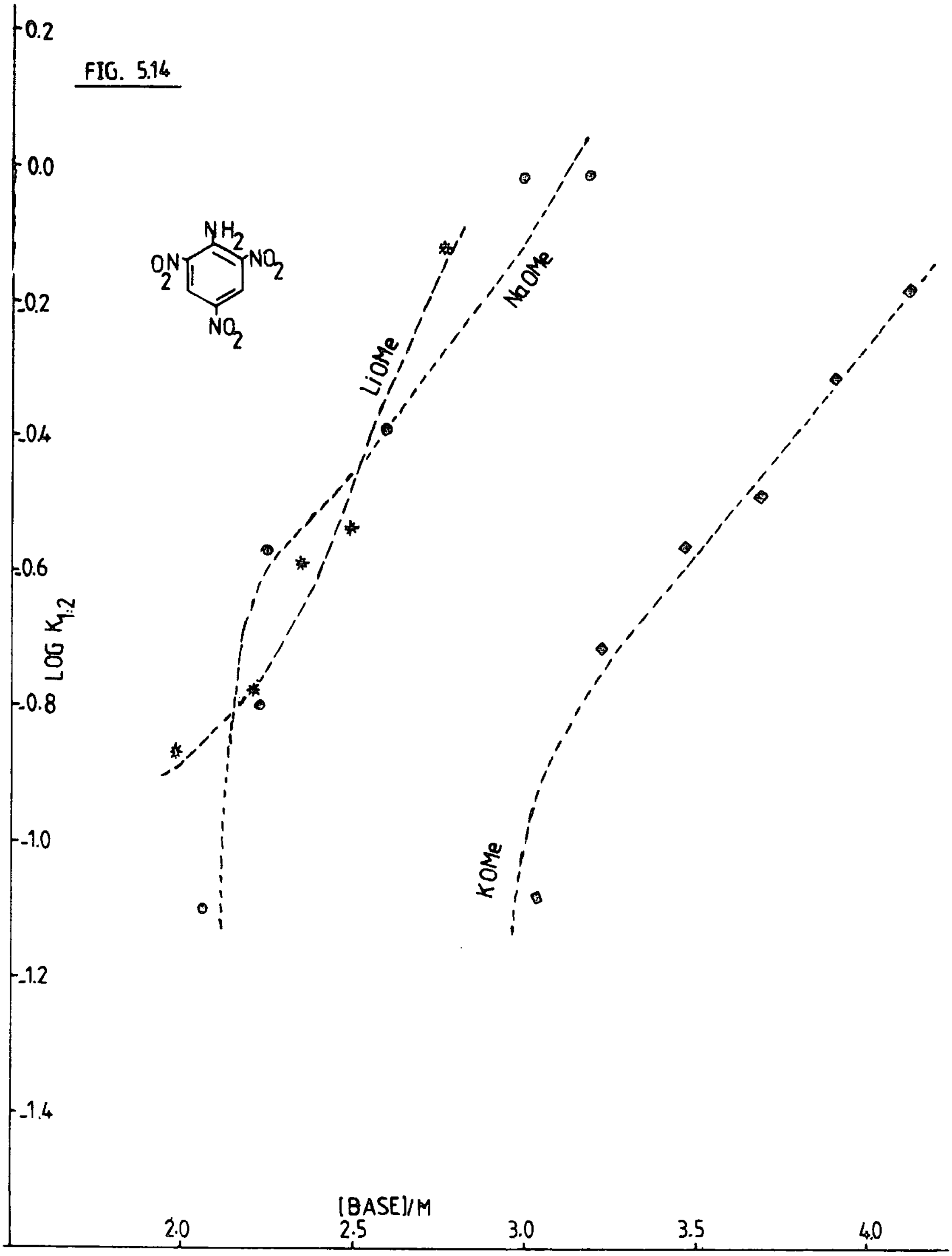


FIGURE 5.14

A plot of Log $K_{1:2}$ versus base concentration . Data are in tables 5.14 .5.15 and 5.16 .

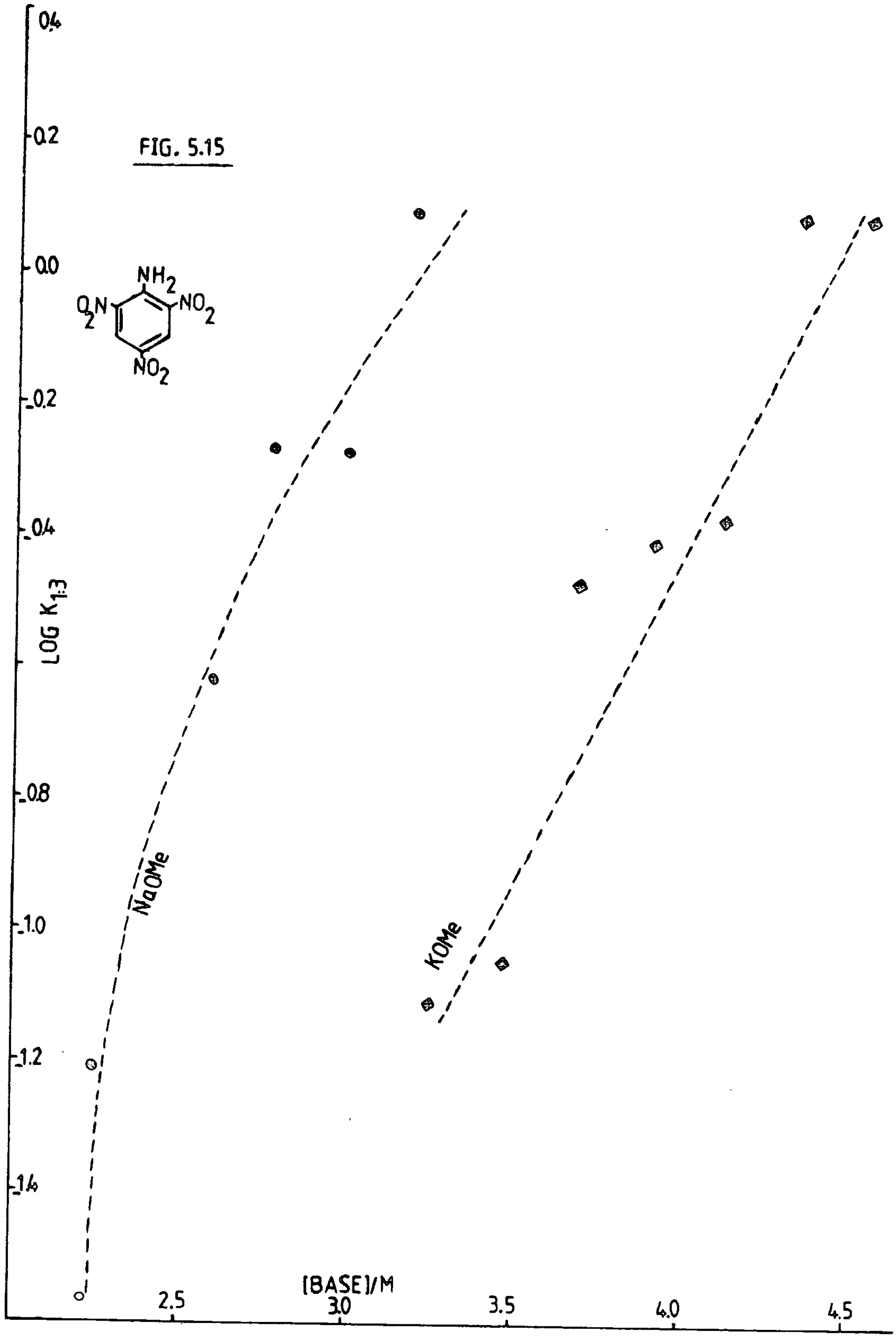


FIGURE 5.15

A plot of Log $K_{1:3}$ versus base concentration. Data are in 5.14 , 5.15 and 5.16 .

APPENDIX

a. Lectures and Seminars organised by the Department of Chemistry during the period 1978-1981.

(* denotes those attended).

15th September 1978

Professor W. Siebert (University of Marburg, West Germany),

"Boron Heterocycles as Ligands in Transition Metal Chemistry".

22nd September 1978

Professor T. Fehlner (University of Notre Dame, USA),

"Ferraboranes : Syntheses and Photochemistry".

* 12th December 1978

Professor C.J.M. Stirling (University of Bangor)

"'Parting is such sweet sorrow' - the Leaving Group in Organic Reactions".

* 14th February 1979

Professor B. Dunnell (University of British Columbia),

"The Application of NMR to the study of Motions in Molecules".

16th February 1979

Dr. J. Tomkinson (Institute of Laue-Langevin, Grenoble),

"Properties of Adsorbed Species".

14th March 1979

Dr. J.C. Walton (University of St. Andrews),

"Pentadienyl Radicals".

20th March 1979

Dr. A. Reiser (Kodak Ltd.),

'Polymer Photography and Mechanism of Cross-link Formation in Solid Polymer Matrices".

25th March 1979

Dr. S. Larsson (University of Uppsala),

"Some Aspects of Photoionisation Phenomena in Inorganic Systems".

* 25th April 1979

Dr. C.R. Patrick (University of Birmingham),

"Chlorofluorocarbons and Stratospheric Ozone : An Appraisal of the Environmental Problem".

* 1st May 1979

Dr. G. Wyman (European Research Office, U.S. Army),

"Excited State Chemistry in Indigoid Dyes".

2nd May 1979

Dr. J.D. Hobson (University of Birmingham),

"Nitrogen-centred Reactive Intermediates".

8th May 1979

Professor A. Schmidpeter (Institute of Inorganic Chemistry, University of Munich).

"Five-membered phosphorus Heterocycles Containing Dicoordinate Phosphorus".

9th May 1979

Dr. A.J. Kirby (University fo Cambridge),

"Structure and Reactivity in Intramolecular and Enzymic Catalysis".

9th May 1979

Professor G. Maier (Lahn-Giessen),

"Tetra-tert-butyltetrahedrane".

10th May 1979

Professor G. Allen, F.R.S. (Science Research Council),

'Neutron Scattering Studies of Polymers".

16th May 1979

Dr. J.F. Nixon (University of Sussex),

"Spectroscopic Studies on Phosphines and their Coordination Complexes".

23rd May 1979

Dr. B. Wakefield (University of Salford)

"Electron Transfer in Reactions of Metals and Organometallic Compounds

23rd May 1979

Dr. B. Wakefield (University of Salford)

"Electron Transfer in Reactions of Metals and Organometallic Compounds with Polychloropyridine Derivatives".

* 13th June 1979

Dr. G. Heath (University of Edinburgh),

"Putting Electrochemistry into Mothballs - (Redox Processes of Metal Porphyrins and Phthalocyanines)".

* 14th June 1979

Professor I. Ugi (University of Munich),

"Synthetic Uses of Super Nucleophiles".

* 20th June 1979

Professor J.D. Corbett (Iowa State University, Ames, Iowa, USA),

"Zintle Ions : Synthesis and Structure of Homo-polyatomic Anions of the Post-Transition Elements".

27th June 1979

Dr. H. Fuess (University of Frankfurt),

"Study of Electron Distribution in Crystalline Solids by X-ray and Neutron Diffraction".

* 21st November 1979

Dr. J. Muller (University of Bergen),

"Photochemical Reactions of Ammonia".

28th November 1979

Dr. B. Cox (University of Stirling)

"Macrobicyclic Cryptate Complexes, Dynamics and Selectivity".

5th December 1979

Dr. G.C. Eastmond (University of Liveprool),

"Synthesis and Properties of Some Multicomponent Polymers".

12th December 1979

Dr. C.I. Ratcliffe (University of London),

"Rotor Motions in Solids".

* 19th December 1979

Dr. K.E. Newman (University of Lausanne),

"High Pressure Multinuclear NMR in the Elucidation of the Mechanisms of Fast, Simple Reactions".

30th January 1980

Dr. M.J. Barrow (University of Edinburgh),

"The Structures of Some Simple Inorganic Compounds of Silicon and Germanium - Pointers to Structural Trends in Group IV".

6th February 1980

Dr. J.M.E. Quirke (University of Durham),

"Degradation of Chlorophyll-a in Sediments".

23rd April 1980

B. Grievson B.Sc., (University of Durham)

"Halogen Radiopharmaceuticals".

14th May 1980

Dr. R. Hutton (Waters Associates, USA),

"Recent Developments in Multi-milligram and Multi-gram Scale Preparative High Performance Liquid Chromatography".

* 21st May 1980

Dr. T.W. Bentley (University of Swansea),

"Medium and Structural Effects in Solvolytic Reactions".

10th July 1980

Professor P. des Marteau (University of Heidelburg),

"New Developments in Organonitrogen Fluorine Chemistry".

7th October 1980

Professor T. Felhner (Notre-Dame University, USA),

"Metalloboranes - Cages or Coordination Compounds?".

* 15th October 1980

Dr. R. Adler (University of Bristol),

"Doing Chemistry Inside Cages - Medium Ring Bicyclic Molecules".

12th November 1980

Dr. M. Gerloch (University of Cambridge),

"Magnetochemistry is about Chemistry".

* 19th November 1980

Dr. T. Gilchrist (University fo Liverpool),

"Nitroso Olefins as Synthetic Intermediates".

3rd December 1980

Dr. J.A. Connor (University of Manchester),

"Thermochemistry of Transition Metal Complexes".

* 18th December 1980

Dr. R. Evans (University of Brisbane, Australia),

"Some Recent Communications to the Editor of the Australian Journal of Failed Chemistry".

18th February 1981

Professor S.F.A. Kettle (University of East Anglia),

"Variations in the Molecular Dance at the Crystal Ball".

* 25th February 1981

Dr. K. Bowden (University of Sussex),

"The Transmission of Polar Effects of Substituents".

4th March 1981

Dr. S. Craddock (University of Edinburgh),

"Pseudo-Linear Pseudohalides".

11th March 1981

Dr. J.F. Stoddard (I.C.I. Ltd./University of Sheffield),
"Stereochemical Principles in the Design and Function of Synthetic Molecular Receptors".

17th March 1981

Professor W. Jencks (Brandsis University, Massechusetts),
"When is an Intermediate not an Intermediate?".

18th March 1981

Dr. P.J. Smith (International Tin Research Institute),
"Organotin Compounds - A Versatile Class of Organometallic Compounds".

9th April 1981

Dr. W.H. Meyer (RCA Zurich),
"Properties of Aligned Polyacetylene".

* 6th May 1981

Professor M. Szware, F.R.S.,
"Ions and Ion Pairs"

10th June 1981

Dr. J. Rose (I.C.I. Plastics Division),
'New Engineering Plastics".

17th June 1981

Dr. P. Moreau (Unviersity of Montpellier),
"Recent Results in Perfluoroorganometallic Chemistry".

b. Conferences attended during the period 1978 - 1981

i. Annual Congress of the Chemical Society and the Royal Institute of Chemistry, Durham University, April 1980.

c. First year induction course (October-November 1978)

A series of one hour presentations on the services available in the Department.

i. Departmental organisation.
ii. Safety matters.
iii. Electrical appliances.
iv. Chromatography and microanalysis.
v. Library facilities.
vi Atomic absorption and inorganic analysis.
vii. Mass spectrometry.
viii. Nuclear magnetic resonance spectroscopy.
ix. Glassblowing technique.

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