

## Formation of Meisenheimer–Jackson Complexes in a Non-polar Solvent

By Anthony R. Butler, Department of Chemistry, The University, St. Andrews, Fife

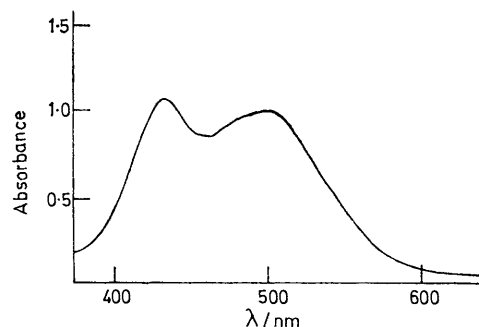
In the presence of dicyclohexyl-18-crown-6 ether in benzene solution, trinitrobenzene forms Meisenheimer–Jackson complexes with a number of anions, some of which do not react in aqueous solution. Such complexes are also formed with dinitrobenzene under these conditions, and there is some evidence that nitrobenzene reacts in a similar way.

ONE of the most important factors facilitating formation of Meisenheimer–Jackson<sup>1</sup> or  $\sigma$ -complexes from anions and polynitro-compounds is delocalisation of the negative charge by the inductive and mesomeric effects of the nitro-groups on the aromatic ring. Simple MO calculations have shown that the electron density on the benzene ring in a  $\sigma$ -complex is actually lower than in benzene itself,<sup>2</sup> although more sophisticated Pariser–Parr–Pople type SCF-CI calculations do not confirm this result.<sup>3</sup> The fact that a 2 : 1 complex is formed between sulphite and picrate, with an overall negative charge of five,<sup>4</sup> is further evidence of the remarkable effect of the nitro-groups. Any slight change in the geometry of the molecule which hinders the process of delocalisation has a dramatic effect on its reactivity. For example, although sulphite  $\sigma$ -complexes are normally formed readily, there is no reaction between sulphite and 3-methyl-2,4,6-trinitrophenol,<sup>5</sup> presumably because the methyl group prevents complete coplanarity. A possible consequence of the ability of the nitro-groups to delocalise negative charge is that solvation plays a smaller role in stabilising  $\sigma$ -complexes than it does with anionic species in which the charge is more concentrated. Therefore,  $\sigma$ -complexes should be relatively more stable in non-polar solvents. It is possible to test this prediction by bringing the cationic counterion into the non-polar solvent by use of a crown ether. Such reagents are known to facilitate nucleophilic aliphatic substitution,<sup>6</sup> and a  $\sigma$ -complex has been suggested, but not substantiated, as an intermediate in the reaction of potassium methoxide with dichlorobenzene in benzene solution.<sup>7</sup>

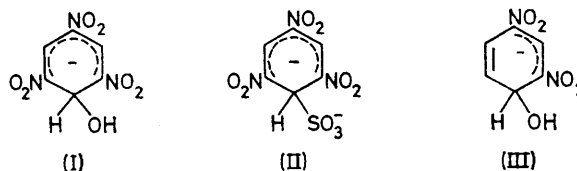
### RESULTS AND DISCUSSION

Addition of solid potassium hydroxide to a solution of 1,3,5-trinitrobenzene (TNB) and dicyclohexyl-18-crown-6 ether in benzene immediately produced an intense red colour, the spectrum of which is shown in the Figure. This spectrum is so similar to that of the complex (I) obtained in aqueous solution by Gold and Rochester<sup>8</sup> (maxima at 430 and 480 nm) that it may be identified as a  $\sigma$ -complex without doubt. If sodium hydroxide replaces the potassium compound there is no immediate reaction, but over several hours the same red colour is

formed. This reflects the greater ease with which the crown ether complexes the potassium ion. If the  $\sigma$ -complex in aqueous solution is prepared from potassium hydroxide it is not extracted at all by benzene unless the organic solvent contains crown ether; extraction is then immediate and complete. There is no immediate extraction from aqueous solution if sodium hydroxide is used.



Spectrum of the solution resulting from the reaction of a saturated solution of potassium hydroxide in benzene containing crown ether (0.0006M) and TNB (0.0002M) (10 mm path length)



Sulphite anion readily forms  $\sigma$ -complexes with TNB.<sup>9</sup> This is surprising as in nucleophilic aliphatic substitution sulphite is not a particularly strong nucleophile,<sup>10</sup> and yet stronger nucleophiles, such as azide, do not form  $\sigma$ -complexes with TNB. Addition of solid potassium sulphite to a solution of TNB and crown ether in benzene again resulted in an intense red colour,<sup>11</sup> whose spectrum is similar to that reported by Norris<sup>11</sup> for the 1 : 1 TNB–sulphite  $\sigma$ -complex (II) in aqueous solution ( $\lambda_{\text{max}}$  460 and 510–540sh nm). The same result was obtained with toluene as solvent, so benzene does not play an intimate and unique role in the reaction. Most  $\sigma$ -complexes in aqueous solution disappear during a few hours,<sup>12</sup> but the

<sup>1</sup> J. Meisenheimer, *Annalen*, 1902, **323**, 205; C. L. Jackson and F. H. Gazzolo, *Amer. Chem. J.*, 1900, **23**, 376.

<sup>2</sup> P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, 1967, **50**, 848.

<sup>3</sup> H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, 1968, **12**, 117.

<sup>4</sup> M. R. Crampton and M. El-Ghariani, *J. Chem. Soc. (B)*, 1969, 330.

<sup>5</sup> A. R. Butler and B. Medcalf, unpublished observation.

<sup>6</sup> C. L. Liotta and H. P. Harris, *J. Amer. Chem. Soc.*, 1974, **96**, 2250.

<sup>7</sup> D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, 1974, **96**, 2252.

<sup>8</sup> V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1710.

<sup>9</sup> F. Čuta and E. Beránek, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1501; C. F. Bernasconi and R. G. Bergstrom, *J. Amer. Chem. Soc.*, 1973, **95**, 3603; M. R. Crampton, *J. Chem. Soc. (B)*, 1967, 1341.

<sup>10</sup> W. P. Jencks and J. Carriuolo, *J. Amer. Chem. Soc.*, 1960, **82**, 1778.

<sup>11</sup> A. R. Norris, *Canad. J. Chem.*, 1967, **45**, 174.

<sup>12</sup> R. A. Henry, *J. Org. Chem.*, 1962, **27**, 2637.

TNB-sulphite complex in benzene appears to be indefinitely stable. If any one of the reactants is omitted no colour develops and there is no obvious reaction between TNB and the crown ether. Thus formation of  $\sigma$ -complexes in benzene occurs readily.

A more surprising observation is that some anions which do not form  $\sigma$ -complexes in aqueous solution react readily with TNB in benzene solution. Intense colours were obtained with the following potassium salts: carbonate, hydrogen carbonate, nitrite, fluoride, and acetate. At the crown ether concentration employed (0.1M), chloride, bromide, nitrate, and perchlorate did not react. There was no obvious reaction with sodium salts. The spectra of all the coloured species obtained were similar to that shown in the Figure and are certainly those of  $\sigma$ -complexes. Absorption maxima are listed in the Table. The observation that a number of anions,

Spectra of  $\sigma$ -complexes of TNB in benzene solution

Anion	$\lambda_{\max.}/\text{nm}$	$\lambda_{\max.}/\text{nm}$
Hydroxide	430	495
Carbonate	426	500
Hydrogen carbonate	432	500
Fluoride	450	
Acetate	452	520infl
Nitrite	435	510
Sulphite	458	500—540sh

\* Extinction coefficients are not given as, from the present study, it is not known whether conversion of TNB into  $\sigma$ -complex is complete or partial.

when not perturbed by solvation, react with TNB to form  $\sigma$ -complexes is further evidence that reactivity in aqueous solution is controlled as much by solvation as by electronic influences.

Two salts gave results of special interest. Reaction with potassium iodide produced an orange solution with a single absorption maximum at 444 nm. The shape of the band was different from those of the  $\sigma$ -complexes obtained previously and a different reaction may occur in this instance. Further study is in progress. The solubility of potassium permanganate in benzene in the presence of crown ether is well known. Addition of TNB resulted in the ubiquitous red colour and it appears that even the permanganate anion can form a  $\sigma$ -complex. The species is not stable and rapidly deposits manganese dioxide. The other products were not determined.

<sup>13</sup> C. J. Pedersen and K. H. Frensdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16.

Previous work, and the present study, show that anions have enhanced nucleophilicity in benzene solution and may, therefore, form  $\sigma$ -complexes with substrates less reactive than TNB. Potassium hydroxide, carbonate, and acetate in benzene all react with 1,3-dinitrobenzene (DNB) to give coloured solutions. The spectra suggest the products are all  $\sigma$ -complexes. There is no reaction with DNB in aqueous solution although DNB does form a coloured species with potassium hydroxide in aqueous dimethyl sulphoxide. The structure of the  $\sigma$ -complexes of DNB is almost certainly (III); attack at the 4-position is more likely because of the electronic influence of a nitro-group in the *para*-position of the resulting adduct. With nitrobenzene the results are less certain. Addition of potassium hydroxide to nitrobenzene and crown ether in benzene gave no obvious colour change. However, a broad, low shoulder (430—650 nm) appears on the intense absorption band of nitrobenzene, which commences at 430 nm. A similar, but smaller effect occurs with potassium carbonate. The evidence is too slight to lead to any firm conclusion.

As  $\sigma$ -complexes of TNB are highly coloured and readily extracted from aqueous solution by crown ethers, they may have some use as indicators of the complexing ability of the array of coronate, catapinate, and cryptate<sup>13</sup> ligands and 'octopus' molecules<sup>14</sup> which have been reported recently.

#### EXPERIMENTAL

All inorganic reagents were AnalaR grade and dried in an oven before use. Potassium sulphite was prepared by digesting barium sulphite with an equimolar amount of potassium sulphate. TNB was recrystallised from methanol. Dicyclohexyl-18-crown-6 ether (Emanuel) was dried in a desiccator before use. Crown ether and TNB were dissolved in reagent grade benzene to give 0.1M- and 0.04M-solutions, respectively.

The spectra were recorded on a Unicam SP 800 spectrophotometer. In some cases considerable dilution with benzene was necessary.

Mr. A. Duffin is thanked for preliminary experiments.

[5/273 Received, 10th February, 1975]

<sup>14</sup> F. Vögtle and E. Weber, *Angew. Chem. Internat. Edn.*, 1974, **13**, 814.