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THE INTERACTION OF ELECTRON ACCEPTORS WITH BASES—II[1]

THE SPECTRUM OF S-TRINITROBENZENE IN THE PRESENCE OF AMMONIA AND ALIPHATIC AMINES

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Abstract—The interaction of s-trinitrobenzene with certain aliphatic amines has been studied spectrophotometrically. It is suggested in solutions in ethanol or chloroform, an adduct is initially formed by a dative bond between the nitrogen of the amine molecule and the 2-position in s-trinitrobenzene. The initial reactions are reversed by acid, but in time further irreversible reactions occur.

Aromatic nitro-compounds interact with aromatic amines to form intermolecular charge-transfer complexes.[2] These complexes usually show a single featureless absorption in the near ultra-violet or visible, not present in either component alone. For complexes of a given acceptor with a series of electron donors there is often a linear correlation between the frequency of the maximum of this band and the ionization potential of the electron donor[3,4] although this is theoretically unexpected.[5,6] The stoicheiometry of the components in the complex in solution is nearly always 1 : 1, even where a solid complex of different stoicheiometry may be obtained from the solution.[7,8] The reaction is very fast so that by ordinary techniques it appears to be completed instantaneously.

The behaviour of aliphatic amines with aromatic nitro-compounds appears to be very different.[1,9,10] The absorption which develops on mixing the two components often consists of more than a single band, the shape and intensity vary with time. There appears to be no simple relationship between the frequency of the new absorption band(s) and the ionization potential of the donor. The stoicheiometry of the components in the complex in solution is often other than 1 : 1. Various suggestions have been made as to the mechanism of formation and the structure of the product of these reactions. There is considerable evidence to suggest that several species are involved and that the nature of the products may depend on the time of contact of the two components, temperature, and the particular nitroaromatic—amine pair and the solvent.

RESULTS AND DISCUSSIONS

It is convenient to consider the behaviour of s-trinitrobenzene–aliphatic amine systems in two sections: (I) in ethanolic solution; (II) in chloroform solution.

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[1] *J. Chem. Soc.* 3508 (1959) to be considered as Part I of this series.
[2] R. S. Mulliken, *J. Amer. Chem. Soc.* **72**, 605 (1950); **74**, 811 (1952); *J. Phys. Chem.* **56**, 801 (1952).
[3] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.* **21**, 66 (1953).
[4] R. Foster, *Nature, Lond.* **183**, 1253 (1959); *Tetrahedron* **10**, 96 (1960).
[5] C. Reid and R. S. Mulliken, *J. Amer. Chem. Soc.* **76**, 3869 (1954).
[6] R. S. Mulliken, *Proc. International Conference on Coordination Compounds* p. 371. Amsterdam (1955).
[7] G. Briegleb and J. Kambeitz, *Z. physik. Chem.* **B32**, 305 (1936).
[8] R. Foster, D. Ll. Hammick and A. A. Wardley, *J. Chem. Soc.* 3817 (1953).
[9] R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.* 2375 (1959).
[10] G. N. Lewis and G. T. Seaborg, *J. Amer. Chem. Soc.* **62**, 2122 (1940).

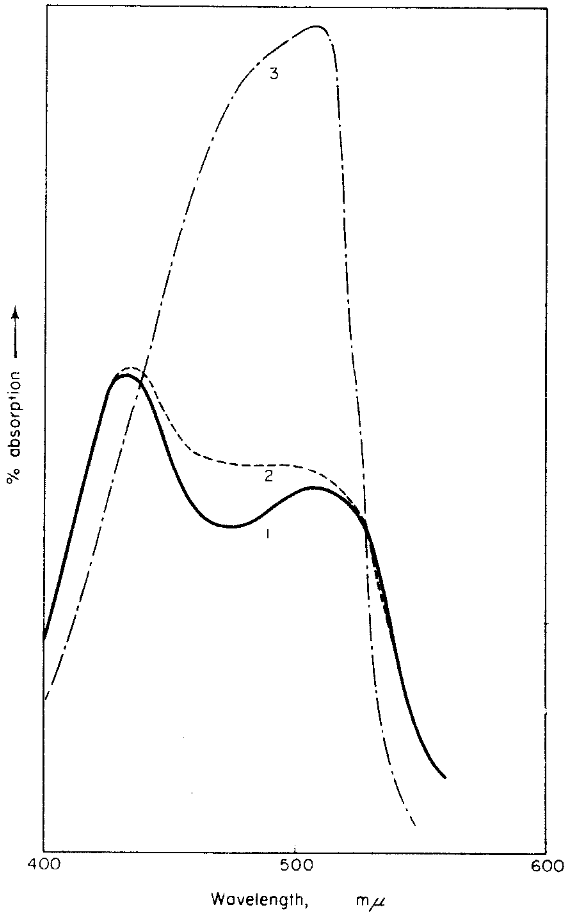


FIG. 1. Absorption spectra of s-trinitrobenzene + ammonia in ethanol at 20°. Times after mixing: (1) 3 min (2) 1 hr (3) 4 days

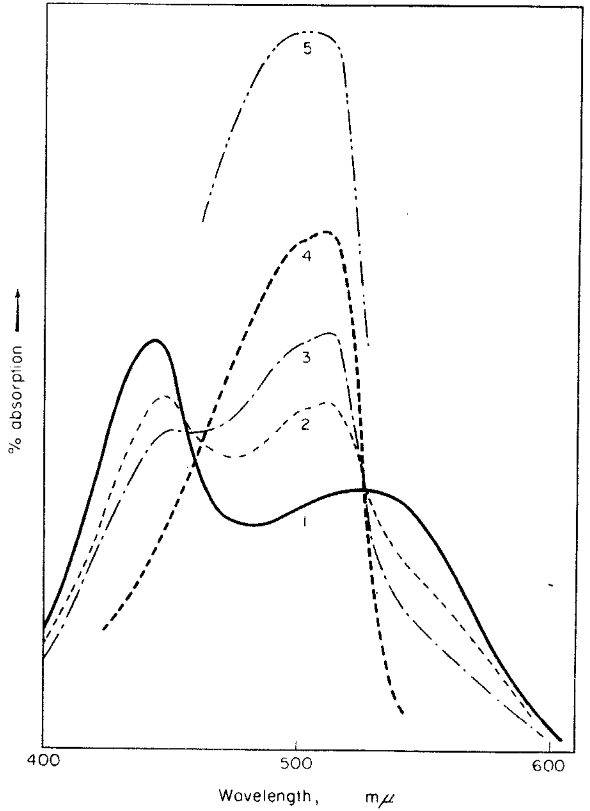


FIG. 2. Absorption spectra of s-trinitrobenzene + methylamine in ethanol at 20°. Times after mixing: (1) 2 min (2) 12 min (3) 1 hr (4) 2 hr (5) 12 hr

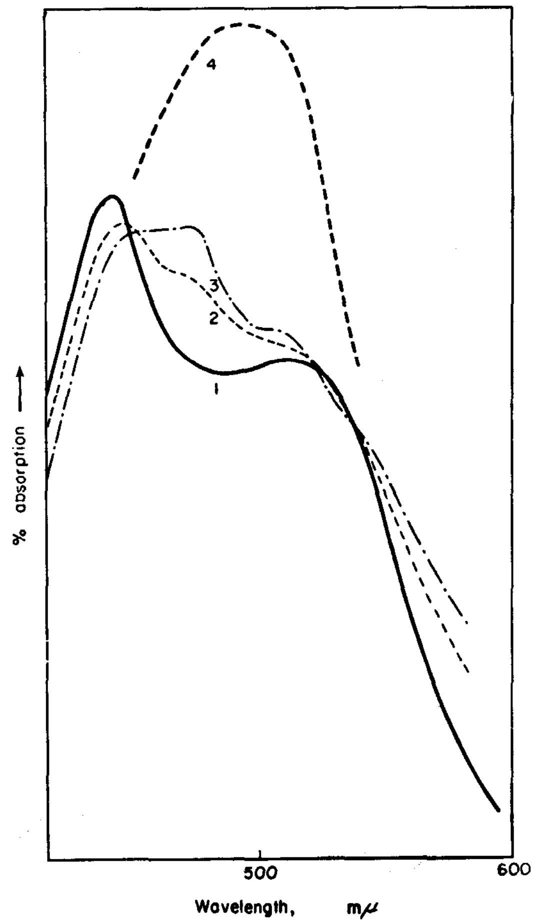


FIG. 3. Absorption spectra of s-trinitrobenzene + dimethylamine in ethanol at 20°. Times after mixing: (1) 2 min (2) 22 min (3) 95 min (4) 4 days

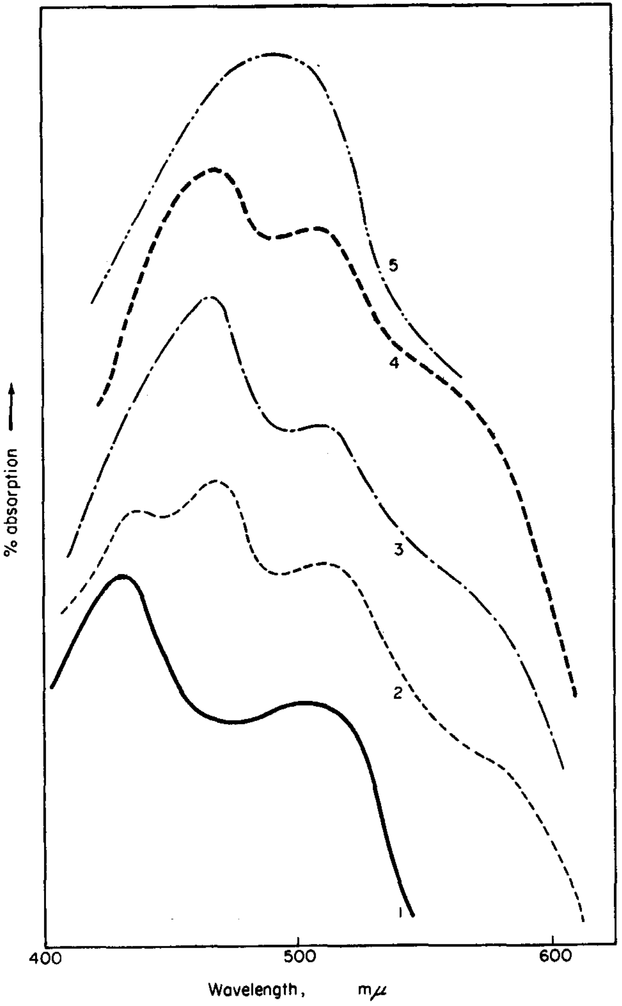


FIG. 4. Absorption spectra of s-trinitrobenzene + trimethylamine in ethanol. Times after mixing: (1) 1 min, −50°; (2) 1 min, 20°; (3) 4 min, 20°; (4) 30 min, 20°; (5) 4 days, 20°.

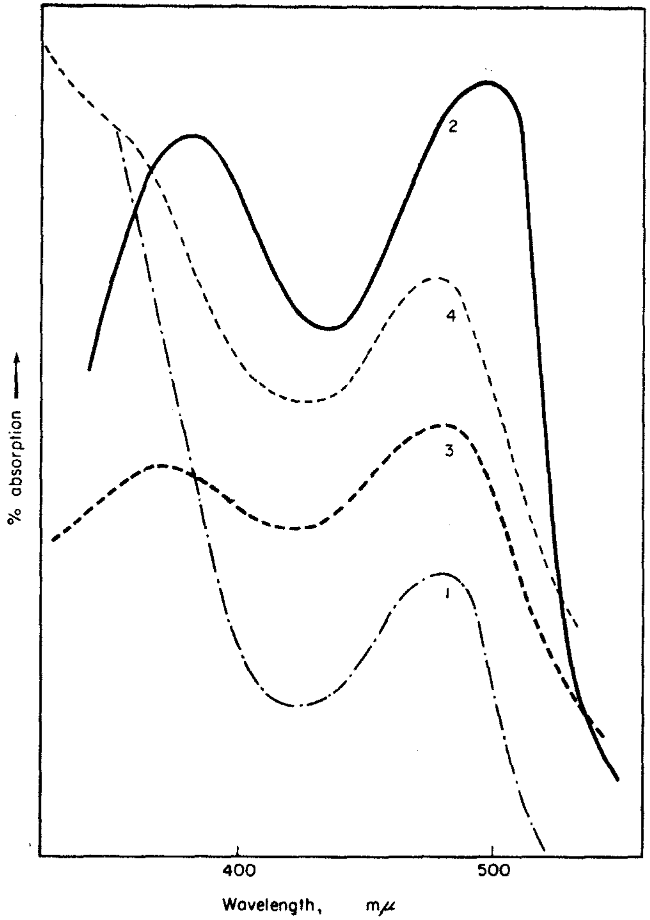


FIG. 5. Absorption spectra of s-trinitrobenzene + amine in ethanol acidified after 4 days; (1) ammonia; (2) methylamine; (3) dimethylamine; (4) trimethylamine.

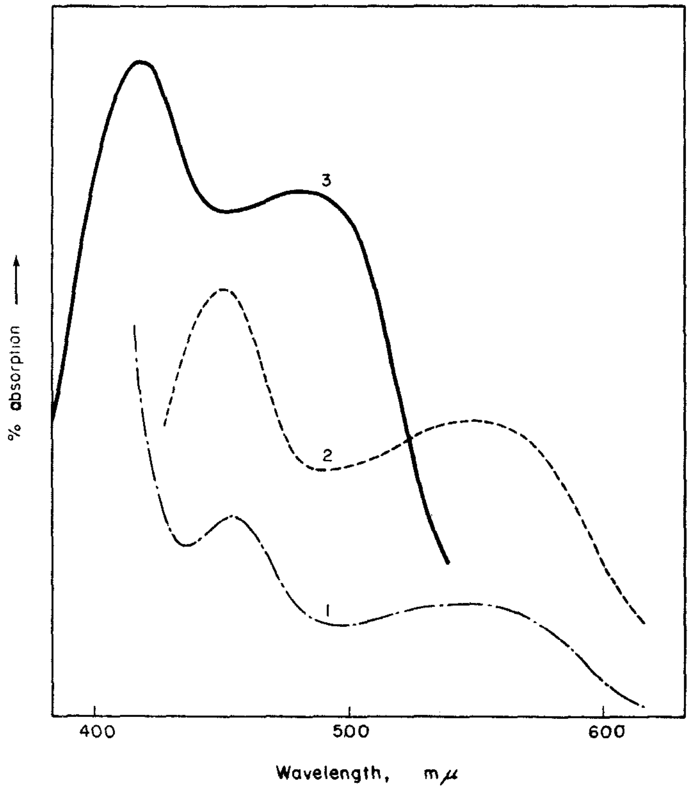
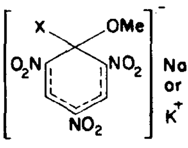


FIG. 6. Absorption spectra: (1) s-trinitrobenzene + ammonia in chloroform on mixing; (2) s-trinitrobenzene + methylamine in chloroform on mixing; (3) potassium methoxyl-ethylpicrate in ethanol, (all at 20°).

I. Alcoholic solutions

The visible absorption spectrum of s-trinitrobenzene with ammonia or an aliphatic amine, when measured within two minutes of mixing, shows either two maxima or one maximum (at about 450 mμ) and one very pronounced plateau at longer wavelengths. With some amines it is necessary to cool the solution to about −50° in order to see this spectrum as it is later masked by absorption which develops in the region 470–520 mμ. The "primary" spectrum reported by Miller and Wynne-Jones[9] appears to be mainly this latter absorption, but depending on the particular amine and on the concentrations of the reactants, it may be the initial spectrum we observe combined with the later development (Figs. 1–4). At first the colour is discharged by dilute hydrochloric acid; after about an hour at room temperature acidification results in a new absorption spectrum with a major absorption in the region 470–500 mμ with, in the case of secondary and tertiary amines a subsidiary absorption at about 550 mμ. After 24 hours, alcoholic solutions of amines with s-trinitrobenzene show a maximum at 350–370 mμ on acidification. This has been previously observed by Miller and Wynne-Jones. However, we find that with most amine s-trinitrobenzene mixtures, the band at 470–500 mμ, referred to above, also persists (Fig. 5).

The initial absorption that we observe is very similar to that of "Meisenheimer" compounds,[11] for example potassium methoxy 1-ethylpicrate[12] (I, X = OEt) (Fig. 6). The possibility was considered that the complexes of aliphatic amines with s-trinitrobenzene in alcoholic solution were obtained similarly by the attack of the substituted amide ion formed by autoprotolysis. The relatively low electrical conductivity could be accounted for by ion-pair formation (Structure II). There are however two pieces of evidence against this mechanism. Firstly, tertiary amines with s-trinitrobenzene in alcoholic solution give spectra similar to the products with primary and secondary amines. If the mechanism is the same with the various aliphatic amines, this eliminates autoprotolysis. Secondly, this mechanism would require the stoicheiometry to be 2 amine molecules to 1 s-trinitrobenzene molecule, whereas Miller and Wynne-Jones[9] have shown that the stoicheiometry is 1:1. We have confirmed this ratio for the initial reaction of ammonia with s-trinitrobenzene in ethanol by a Job plot.[13]



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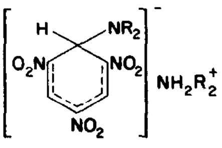
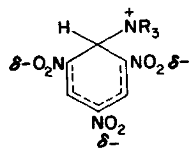


II



III

We suggest that the *initial* absorption spectrum is the result of covalent bond formation between the nitrogen of the amine molecule and the 2-carbon atom in the s-trinitrobenzene molecule (III).

The increase in electrical conductivity with time[9] implies that the subsequent species is ionic. Electrophoretic experiments indicate that the coloured ion is negatively charged. Three explanations of the coloured ion formed in the *secondary* reaction are as follows.

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[11] J. Meisenheimer, *Liebigs Ann.* **323**, 219 (1902).

[12] R. Foster, *Nature, Lond.* **176**, 746 (1955).

[13] P. Job, *C.R. Acad. Sci., Paris.* **180**, 928 (1925); *Ann. Chim.* **9**, 113 (1928); **6**, 97 (1936).

(*a*) A proton is transferred from the s-trinitrobenzene molecule to the amine. This has been disproved in the case of attack by the stronger base OH^- by the lack of deutercum exchange between D_2O and s-trinitrobenzene in the presence of sodium hydroxide.[9,14]

(*b*) The transference of an electron from the amine to the s-trinitrobenzene molecule. This mechanism, suggested by Weiss[15] for hydrocarbon picrates, is favoured by Miller and Wynne-Jones.[9] The resulting s-trinitrobenzene negative ion would be a free radical, and these workers have detected a weak E.S.R. absorption[16] in solutions of s-trinitrobenzene in diethylamine both in the presence and absence of acetone. They report that the free radical concentration slowly increases then decreases with time; the final product is diamagnetic. Dr. D. Bijl has confirmed the presence of a weak E.S.R. absorption for an ethanolic solution $\sim 10^{-2}$M with respect to s-trinitrobenzene and $\sim 10^{-1}$M with respect to diethylamine. The absorption reaches a maximum about one hour after mixing. In neither case was it possible to determine the absolute concentration of the free radical and it may represent only a small fraction of the species present. This explanation in terms of electron transfer implies that the same free radical is formed irrespective of the particular aliphatic amine electron donor. In fact the spectra involving different amines are not identical (Figs. 1–4), although this might be explained by environmental effects including ion pair formation, in addition to any contribution from other reaction products.

(*c*) A third possibility is the formation of the coloured anion by the attack of the amide ion, the conjugate base of the amine formed by autoprotolysis, which was considered above when considering the *initial* reaction. The product would correspond to II but as free ions. The absorption spectrum of this secondary product would be expected to even more closely resemble that of a "Meisenheimer" compound than does the amine adduct (III) proposed for the initial product. This is not the case. Furthermore, whereas s-trinitrobenzene in the presence of methoxide ion initially gives a spectrum characteristic of structure I (X = H), further reaction causes fundamental changes in the spectrum within a few minutes of mixing.[21] If the methoxide adduct of s-trinitrobenzene is so unstable in solution, it is possible that any amide ion adducts are also unstable. The situation may be further complicated by solvolysis:

$$NR_3 + EtOH \rightleftharpoons EtO^- + NR_3H^+ \qquad (R = \text{alkyl or H}) \tag{4}$$

with consequent attack by the ethoxide ion. This is probably of major importance in the secondary reaction of tertiary amines with s-trinitrobenzene in ethanol where amide ions cannot be formed by autoprotolysis. The spectrum of triethylamine and s-trinitrobenzene in ethanol after one hour closely resembles ethoxide and s-trinitrobenzene in ethanol after a comparable time. The attack by ethoxide ion may also be a significant competing reaction with ammonia, or a primary or a secondary amine and s-trinitrobenzene. The nature of this *secondary* product of s-trinitrobenzene and aliphatic amine (or ethoxide) remains unsolved.

II. *Chloroform solutions*

Chloroform was chosen as a relatively inert solvent. Although in this role, chloroform is not as suitable as a paraffin as exemplified by the non-ideality of

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[14] J. A. A. Ketelaar, A. Bier and H. T. Vlaar, *Rec. Trav. Chim.* **73**, 37 (1954).

[15] J. Weiss, *J. Chem. Soc.* 245 (1942).

[16] R. E. Miller and W. K. F. Wynne-Jones, *Nature, Lond.* **186**, 149 (1960).

amine–chloroform solutions; nevertheless, because of the low solubility of s-trinitrobenzene and of the products formed in paraffins, particularly at low temperatures, chloroform was selected.

The absorption spectrum of s-trinitrobenzene in chloroform solution differs considerably according as to whether it is determined in the presence of ammonia, a primary, a secondary, or a tertiary amine. In the presence of ammonia or methylamine the spectrum remains virtually unaltered over a period of thirty minutes and shows maxima at ca. 450 and 545 mμ (Fig. 6). With ethylamine, a similar initial spectrum is observed, but the absorption in the region 520 mμ increases relatively quickly (Fig. 7). In the presence of the secondary amines dimethylamine and diethylamine, chloroform solutions of s-trinitrobenzene show only one maximum at ca. 500 mμ. The intensity of this band increases rapidly with time, with some shift in wavelength (Fig. 8). With trimethylamine in the presence of s-trinitrobenzene no maximum is observed above 380 mμ. On mixing triethylamine with s-trinitrobenzene in chloroform at $-50°$, one transition is observed (469 mμ), but at room temperature, or with the cold solution on standing, a second band (573 mμ) appears (Fig. 9). It is possible that in the case of the secondary amines there may be two maxima, but which are nearly coincident. This would account for the shift in the wavelength of the observed maxima with time if the two bands developed at different rates. With all the amines, the initial spectra with s-trinitrobenzene intensify on cooling.

These spectra could be interpreted as representing the products of two reactions: (a) a fast reaction giving rise to the sharper, usually higher energy band A; (b) a second reaction, also fast when either ammonia or a primary amine is the reactant, but observably slower with secondary or tertiary amines, resulting in the broader, usually lower energy band B.

Kinetic measurements of a fast reaction between diethylamine and s-trinitrobenzene in ether–acetone solution have been made by Allen *et al.*[17] They have shown the reaction to be fast even at $-100°$. We had concluded from previous work[1] that there is an initial fast reaction from the extrapolation of optical density with time to the time of mixing. This always resulted in a significant optical density at wavelengths at which neither component alone absorbed. It was tentatively suggested that this might be the result of intermolecular charge-transfer complex formation. Such a charge-transfer band might correspond to band A. Nevertheless there appears to be no correlation between the ionization potentials of the amine molecules and the frequencies of the A-band, whereas a linear correlation is often observed in the case of charge-transfer complexes. However, as stated above, there is no direct theoretical expectation of such a relationship. Furthermore it would be unwise to predict the position of such a charge-transfer absorption band from the ionization potential of the donor. An example of the breakdown of the relationship is shown in the complex of triethylamine and iodine, which has been assigned to the class of charge transfer complexes by Nagakura.[18] From the charge-transfer spectra of iodine complexes quoted by Hastings *et al.*,[19] one would expect the band of the iodine complex of triethylamine ($Ip = 7{\cdot}50 \pm 0{\cdot}02$ ev)[20] to be about 375 mμ, based on a linear correlation

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[17] C. R. Allen, A. J. W. Brook and E. F. Caldin, *J. Chem. Soc.* 2171 (1961).

[18] S. Nagakura, *J. Amer. Chem. Soc.* **80**, 520 (1958).

[19] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *J. Amer. Chem. Soc.* **75**, 2900 (1953).

[20] K. Watanabe and J. R. Mottl, *J. Chem. Phys.* **26**, 1773 (1957).

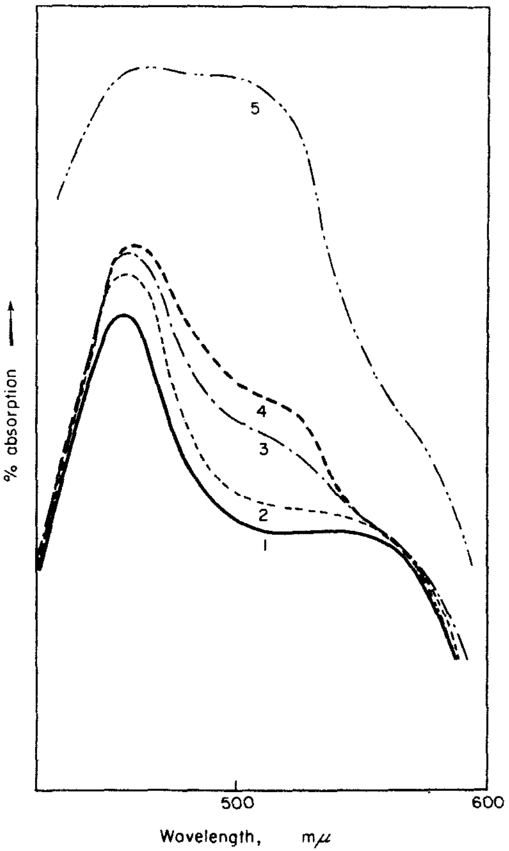

FIG. 7. Absorption spectra of s-trinitrobenzene + ethylamine in chloroform at 20°. Times after mixing; (1) 1 min (2) 3½ min (3) 27 min (4) 40 min (5) 3 hr

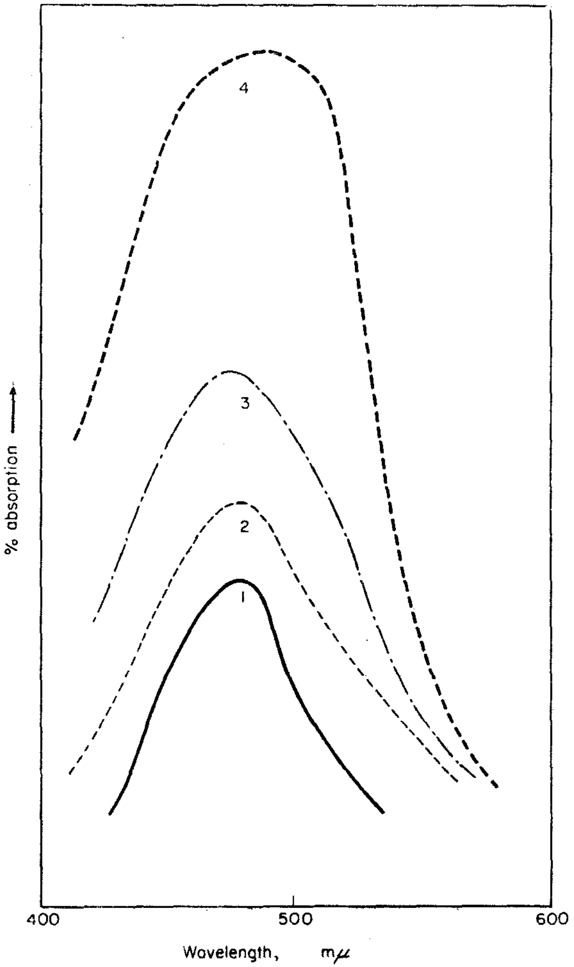

FIG. 8. Absorption spectra of s-trinitrobenzene–diethylamine in chloroform. Times after mixing: (1) 1 min, −50°; (2) 1½ min, 20°; (3) 12 min, 20°; (4) 90 min, 20°.

of ionization potential and frequency of the charge-transfer band, or about 330 mμ on the Hasting *et al.* relationship, whereas the measured band is at 278 mμ.

On the above basis the second band *B* would result from a second product formed more slowly. This type of interaction, involving the immediate formation of a charge-transfer complex which precedes or is concurrent with a second reaction, has also been suggested by Ainscough and Caldin[21] for the reaction of methoxide ion with 2,4,6-trinitroanisole. A similar scheme has been proposed for the interaction of iodine with nitromethane in carbon tetrachloride solution.[22] We think it is unlikely that band *A* can be assigned as a charge-transfer transition. This does not deny the possibility of such a mechanism. Part of the visible absorption may be the result of an extended shoulder of a charge-transfer band which has a maximum in the ultra-violet.

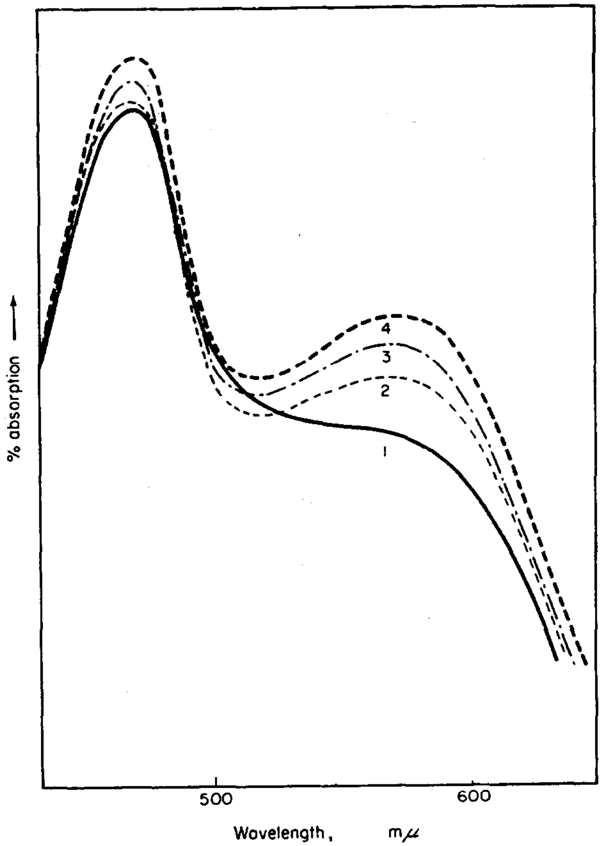

FIG. 9. Absorption spectra of s-trinitrobenzene–triethylamine in chloroform at 20°. Times after mixing: (1) 6 min (2) 16 min (3) 26 min (4) 36 min

Previous work[1] had shown that the stoicheiometry in chloroform solution was three amine molecules to one s-trinitrobenzene, providing the amine molecule is small. Apart from the possibility of charge-transfer complexes, it was suggested that

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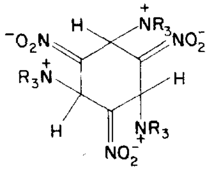
[21] J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.* 2528 (1956).

[22] P. A. D. de Maine and W. C. Ahlers, *J. Chem. Soc.* 211 (1960).

the product had a structure IV (for example, with methylamine), whereas for bulky amines the ratio amine: s-trinitrobenzene is 1:1 corresponding with III.



IV

Cuta and Pisecky[23] have proposed a structure similar to IV for the product formed from s-trinitrobenzene and hydroxide ions in concentrated aqueous sodium hydroxide solution, but have suggested that this should be colourless because of lack of classical canonical structures. It is unlikely that the successive spectra can be explained in terms of successive equilibria in which such complexes as III and IV are formed thus:

$$A + B \rightleftharpoons AB \quad (2); \quad AB + B \rightleftharpoons AB_2 \quad (3); \quad AB_2 + B \rightleftharpoons AB_3 \quad (4)$$

in that development occurs even in cases where the ratio of the components in the complex is 1:1, i.e. where reactions (3) and (4) could not occur.

Although it is possible that species corresponding to III or IV (depending on the particular amine) are formed initially, the close resemblance of the initial spectra of ammonia or primary amines with s-trinitrobenzene in chloroform (i.e. band *A* plus band *B*) compared with the same systems in ethanolic solution suggests that the same species are involved, irrespective of the solvent, namely 1:1 complexes of structure III. If only one amine is covalently bonded to the s-trinitrobenzene molecule, it suggests that in chloroform solutions involving small primary or secondary amines where the overall ratio of amine to s-trinitrobenzene is 3:1 the two extra amine molecules stablize structure III by solvation. This would also explain why successive equilibria, as expressed by equations 2–4, are not observed. The more limited hydrogen bonding of the adduct III in the presence of an excess of a secondary amine, and its absence with tertiary amines may to some extent explain the difference between these spectra and those in which the adduct is solvated by ammonia or a primary amine in chloroform solution, or any of the aliphatic amine–s-trinitrobenzene adducts in ethanol solvated by the solvent.

EXPERIMENTAL

Ethanol. Absolute alcohol, stirred with silica gel for 12 hr, then fractionated.

Chloroform. "AnalaR" chloroform was washed 8 times with equal volumes of water to remove the ethanol, dried over calcium chloride, then refluxed over phosphoric oxide and finally distilled.

s-Trinitrobenzene. Recrystallized 4 times from ethanol then twice from carbon tetrachloride, m.p. 123°.

Methylamine, ethylamine, dimethylamine and *trimethylamine.* These were prepared by dropping concentrated aqueous solutions of the recrystallized hydrochloride salts on to solid sodium hydroxide, and the gaseous free bases, dried through a 4-ft column of sodium hydroxide were absorbed in the appropriate solvent, or liquified in a trap cooled with acetone/solid carbon dioxide. The bases were protected from atmospheric carbon dioxide by soda-lime tubes.

Diethylamine. Purified by fractional distillation.

Triethylamine. Purified by Hinsberg's method,[24] followed by distillation.

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[23] F. Cuta and J. Pisecky, *Coll. Czech. Chem. Comm.* 23, 628 (1958).

[24] A. I. Vogel, *A Textbook of Practical Organic Chemistry* p. 650. Longmans, London (1956).

Analytical. Solutions were $\sim 10^{-4}$ M with respect to s-trinitrobenzene and 0·1–1 M with respect to the amines. Spectra were measured using a CF4R Optica recording spectrophotometer. Measurements at room temp were made on solutions in 10 mm fused silica cuvettes, low temperature measurements were made in all-Pyrex, permanently evacuated version of the vacuum jacketed cell described by Passerini and Ross.[25]

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[25] R. Passerini and I. G. Ross, *J. Sci. Instrum.* **30**, 274 (1953).