478. *The Interaction of Polynitro-aromatic Hydrocarbons with a Variety of Electron Donors.*

By R. E. Miller and W. F. K. Wynne-Jones.

The interaction of 1,3,5-trinitrobenzene with a wide variety of electron donors has been studied in a range of solvents. The reaction products fall into two distinct classes depending on the donor. Complexes of the first type are formed by typical 'onium or 'onium-anion donors and their properties indicate an ionic structure. Those of the second type are formed by typical π donors and do not show salt-like properties.

Proton transfers do not appear to be involved in the formation of complexes by 1,3,5-trinitrobenzene but electron transfers probably occur.

The difference between the two types of product is best explained by assuming that complexes of the first type involve complete transfer of an electron from donor to acceptor with the formation of an ionic structure. Complexes of the second type are consistent with Mulliken's concept of a hybrid involving a dative and a no-bond structure.

In solutions of complexes of the first type slow irreversible secondary reactions occur. These are probably aromatic nucleophilic substitutions.

Both 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene react with amines but the systems are complicated because proton transfers can occur as well as the electron transfers encountered in similar systems involving 1,3,5-trinitrobenzene.

Although the reaction products of 1,3,5-trinitrobenzene with aromatic amines and hydrocarbons are well known, being usually highly coloured solids with rather low heats of formation, and apparently formed instantaneously in solution, those with aliphatic amines have received little attention. We now describe the reactions of 1,3,5-trinitrobenzene with a wide variety of aromatic and aliphatic electron donors, and draw some broad conclusions.

It has been suggested that 1,3,5-trinitrobenzene may react with an amine in a proton-transfer reaction. Thus Lewis and Seaborg [1] concluded that the small conductivity of its solutions in pyridine [2] must be due to proton transfer. Farr, Bard, and Wheland [3] also claim that proton transfers occur in liquid ammonia solutions of *m*-dinitrobenzene. Kharasch, Brown, and McNab [4] report that 1,3,5-trinitrobenzene undergoes hydrogen exchange in the presence of alcoholic sodium hydroxide, although the experimental conditions were somewhat severe.

On the other hand, Field, Garner, and Smith [5] conclude that proton transfers do not occur in liquid ammonia solutions of *m*-dinitrobenzene and Ketelaar, Bier, and Vlaar [6] report that the reaction between 1,3,5-trinitrobenzene and aqueous sodium hydroxide is not a proton transfer.

This conflicting evidence made reinvestigation desirable, and exchange measurements have been carried out on typical systems with small amounts of heavy water added.

EXPERIMENTAL

Light-absorption was measured with a Unicam quartz photoelectric spectrophotometer S.P. 500 having a thermostatted cell compartment, normally at 25° or 40°. Most measurements employed a pair of matched silica 5 mm. cells having tightly fitting stoppers.

A Tinsley electrolytic conductivity bridge, type 4896, was used for all electrical-conductance measurements. The cells, which were of Monax glass and had a ground glass stopper, carried as electrodes smooth platinum plates which appeared not to catalyse the reaction.

The trinitrobenzene was recrystallised two or three times from ethanol. Aliphatic amines, normally of B.D.H. Laboratory Reagent grade, were dried (NaOH) and distilled, the middle fraction being collected. Aromatic amines were treated similarly and were then distilled from a little zinc dust. "AnalaR" pyridine was dried (BaO) and fractionated. Cyclohexylamine (B.D.H. Laboratory Reagent) for use as a solvent for kinetic measurements was dried ($CaCl_2$), then filtered and dried over freshly cut sodium. After standing overnight the amine was distilled on to freshly cut sodium and fractionated in an atmosphere of dry CO_2-free nitrogen, the fraction of b. p. 129·5—130·5° being collected and stored in a flask fitted with a soda-lime guard tube.

Commercial acetone was dried (K_2CO_3) and distilled, the first and last fractions being discarded. "AnalaR" benzene was refluxed over sodium hydroxide for several hours and then distilled, the first and last fractions being discarded. "Absolute alcohol" was refluxed for 36 hr. over freshly burnt lime and distilled; the first and last fractions were discarded. Other solvents including ether, nitrobenzene, and carbon tetrachloride were of commercial grade and were used without further purification.

RESULTS

Mixtures of 1,3,5-trinitrobenzene with a variety of amines and aromatic hydrocarbons in various solvents produce intensely coloured solutions. The colour is associated with a new absorption band. Sometimes it is developed within the time required to obtain the first reading of optical density (usually 2—3 min.); at others it develops slowly when the amine concentration is less that *ca.* 0·1M. In some systems a slow secondary reaction occurs; this always produces a product with an absorption maximum in the region 505—515 mμ.

In certain systems involving aliphatic amines or similar donors the spectrum changes markedly with the solvent and, in solvents of high dielectric constant, a new band appears with a peak near 570 mμ. In some cases no definite peak is observed, probably owing to overlap of the various bands, but a region of enhanced absorption occurs. In typical non-ionising solvents the absorption in this region is very small.

Data for a variety of systems are recorded in Table 1. $\lambda_{max.}$ refers to the wavelength of

[1] Lewis and Seaborg, *J. Amer. Chem. Soc.*, 1940, **62**, 2122.
[2] Hantzsch and Caldwell, *Z. phys. Chem.*, 1908, **61**, 228.
[3] Farr, Bard, and Wheland, *J. Amer. Chem. Soc.*, 1949, **71**, 2013.
[4] Kharasch, Brown, and McNab, *J. Org. Chem.*, 1937, **2**, 36.
[5] Field, Garner, and Smith, *J.*, 1925, **127**, 1227.
[6] Ketelaar, Bier, and Vlaar, *Rec. Trav. chim.*, 1954, **73**, 37.

maximum absorption for the band associated with the primary equilibrium. D_{570}/D_{470}, which is a measure of the amount of the high-wavelength absorption mentioned above, provides interesting data on the effect of solvent on the spectra of certain systems. The last column provides qualitative information on the rates of both primary and secondary reaction.

A primary equilibrium was set up apparently instantaneously when 1,3,5-trinitrobenzene was added to benzene or ethanol solutions of aniline, *N*-ethylaniline, *NN*-diethylaniline, anthracene, or naphthalene. $\lambda_{\text{max.}}$ varied widely with the donor. Mixtures of 1,3,5-trinitrobenzene with diethylamine, triethylamine, cyclohexylamine, and piperidine reached equilibrium only slowly in ethanol or benzene. Diethylamine–1,3,5-trinitrobenzene mixtures approached equilibrium more slowly in benzene than in ethanol. A slow attainment of equilibrium was also observed with solutions of 1,3,5-trinitrobenzene in pyridine. For these systems $\lambda_{\text{max.}}$ always lay in the region 450—475 mμ and in ionising solvents a new band occurred near 570 mμ; a secondary reaction also occurred in suitable solvents.

The ethoxide ion behaved similarly to the aliphatic amines except that the primary reaction was faster and the secondary reaction rather slower. Ethylenediamine showed a similar primary absorption band near 460 mμ although the new band at 535 mμ did not correspond to any band observed in other systems and no secondary reaction occurred.

TABLE 1. *Spectra of mixtures of donors with* 1,3,5-*trinitrobenzene in a range of solvents.*

Donor	Solvent	$\lambda_{\text{max.}}$ (mμ)	Other maxima * (mμ)	D_{570}/D_{470}	Remarks †
Pyridine	Pyridine	465	514, 570	0·52	1(s), 2(s)
Diethylamine	Acetone	470	515, 570	0·44	1(s), 2(s)
,,	Ethanol	470	515, 550	0·46	1(s), 2(s)
,,	Nitrobenzene	475	515, 570	0·49	1(s), 2(s)
,,	Diethylamine	470	—	0·03	1(f)
,,	Ether	465	—	0·04	1
,,	Benzene	465	—	0·02	1(s)
,,	Carbon tetrachloride	465	—	0·1	1
Triethylamine	Ethanol	470	510	0·4	1(s), 2(s)
,,	Benzene	455	—	0·11	1
Piperidine	Ethanol	475	510, 570	0·33	1(s), 2(s)
,,	Piperidine	450	*A*	—	1(f)
,,	Water	450	—	—	1(f)
Cyclohexylamine	Ethanol	460	510	0·3	1(s), 2(s)
,,	Crude cyclohexylamine	455	505	0·33	1(f), 2(s)
Ethylenediamine	Ethylenediamine	460	535	—	1(f)
Ammonia	Water	490	—	0·01	1(f)
Sodium ethoxide	Ethanol	465	505	—	1(f), 2(s)
Sodium hydroxide	Water	440	—	—	1(f)
Acetone	Acetone	460	570*B*	0·51	Colour only after eight weeks 1(s)
Aniline	Ethanol	395	—	—	1(f)
,,	Benzene	395	—	—	1(f)
N-Ethylaniline	Ethanol	450	—	—	1(f)
NN-Diethylaniline	,,	490	—	—	1(f)
Naphthalene	Benzene	370	—	—	1(f)
Anthracene	,,	450	—	—	1(f)
Water	Water	233	—	—	—
Ethanol	Ethanol	233	—	—	—

* In this column data are only given when definite maxima were observed. In some other cases increased absorption was observed but the maximum could not be determined because of overlap. *A* represents a slight flattening at 510, *B* at 505 mμ.

† 1 denotes the occurrence of a primary reaction and 2 that of a secondary reaction. The symbols (f) and (s) refer to the rates, fast and slow respectively. By a fast reaction we mean one where equilibrium is set up within the time required to obtain the first reading. For example 1(s), 2(s) describes a system where both a primary and a secondary reaction occur slowly enough for the rate to be measured by our methods; 1(f) describes a system where a primary equilibrium is set up within 2—3 min., no further change occurring.

Solutions of 1,3,5-trinitrobenzene in 2- and 4-methylpyridine showed similar spectra to that observed in pyridine. These amines were not carefully purified however and no extensive work was done; the colour developed only on standing for some time. Saturated solutions of 1,3,5-trinitrobenzene in acetone developed a spectrum typical of the aliphatic amine primary complexes only after standing for several weeks and even then no significant amount of secondary product was observed.

Preliminary measurements indicated that the secondary reaction occurred in cyclohexylamine solutions of 1,3,5-trinitrobenzene. The primary absorption band was set up immediately and first-order velocity constants could be obtained from either the fall in optical density at 455 mμ or the increase at 505 mμ. These indicated an activation energy of about 23 kcal./mole. On repeating the measurements with a different batch of amine we found that reproducibility was very bad and on very careful purification of the solvent as outlined in the previous section no secondary reaction occurred.

The effect of solvent on the spectrum of 1,3,5-trinitrobenzene–diethylamine mixtures is shown in Figs. 1 and 2 and the spectra of a number of typical systems in Fig. 3.

Equilibrium measurements have been carried out on mixtures of 1,3,5-trinitrobenzene with various aliphatic amines in ethanol. By using a series of solutions in which the trinitrobenzene concentration was kept constant while the concentration of amine varied we obtained equilibrium constants. In some cases equilibrium was reached only slowly and here the reactions were followed over a period so that both kinetic and equilibrium measurements were obtained. In those cases where secondary reactions occurred the measurement of an equilibrium constant was more difficult. However the secondary reaction was usually much slower than the primary so that the corrections to be applied, because of overlap between the primary and secondary bands, were not very large. By increasing the amine concentration it was found that the equilibrium value of the optical density in the 450 mμ—475 mμ region approached a limiting value. This value corresponds to the condition when the whole of the 1,3,5-trinitrobenzene is converted into primary complex so that it can be used to calculate the molar extinction coefficient for the complex.

FIG. 1.

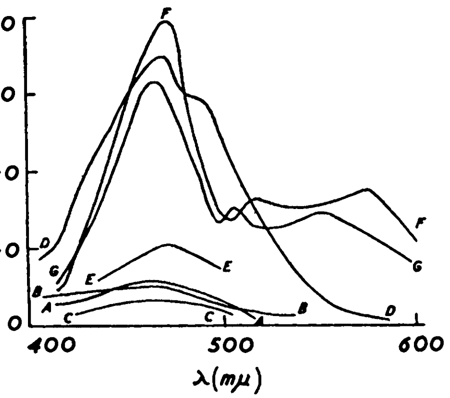

FIG. 2.

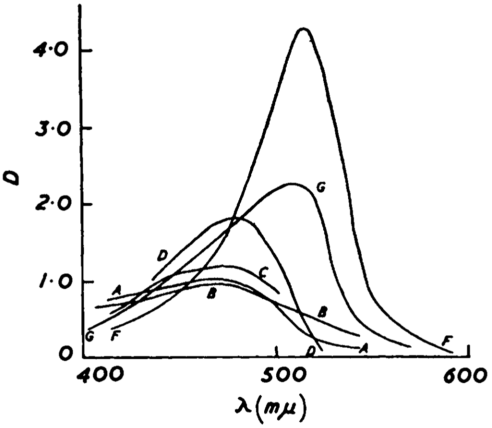

FIG. 1. *Absorption spectra of* 1,3,5-*trinitrobenzene–diethylamine mixtures in various solvents soon after mixing.*

Cell thickness = 1·0 cm.; trinitrobenzene concentration = 1·2 × 10^{-4}M; diethylamine concentration = 0·77M except for solutions *D* and *E*.

Solutions in the following solvents are shown: *A* ether, *B* carbon tetrachloride, *C* benzene, *D* diethylamine, *E* triethylamine, *F* acetone, *G* ethanol.

FIG. 2. *Absorption spectra of* 1,3,5-*trinitrobenzene–diethylamine mixtures in various solvents at a considerable period after mixing.*

Cell thickness, concentrations, and solvents are as in Fig. 1; *t*, the time (hr.) after mixing, is *A* 20, *B* 23, *C* 23, *D* 20, *F* 4, *G* 4.

The equilibrium value of the optical density for the primary complex varied with the amine concentration in such a way as to indicate the formation of a 1 : 1 complex between trinitrobenzene and a variety of amines in ethanol. These amines included diethylamine, triethylamine, piperidine, *N*-ethylaniline and *NN*-diethylaniline.

A more complex variation was found for the equilibrium value of the optical density in pyridine solutions of trinitrobenzene. For dilute solutions the equilibrium concentration of primary product depends largely on the square-root of concentration of trinitrobenzene. The variation can only be explained if the primary complex ionises.

The electrical conductivity of mixtures of 1,3,5-trinitrobenzene with *N*-ethylaniline or *NN*-diethylaniline in ethanol differed little from that of solutions of the amines alone in the same solvent. On the other hand pyridine solutions of 1,3,5-trinitrobenzene showed marked increases in electrical conductivity with time, as did mixtures of 1,3,5-trinitrobenzene with diethylamine in ethanol.

The measurements in pyridine indicate that, at a particular time after mixing, the specific conductivity, κ, depends on the concentration of both primary and secondary products and is given by an equation of the form $\kappa = aD_{570} + bD_{514}$. The equation holds over an interval very much larger than that required for the primary product to reach its maximum concentration. In ethanol the conductivity changes can be explained in a similar way although little detailed work has been done in this solvent.

When the optical densities are those for a 1 cm. cell the average experimental values of a and b are about 8×10^{-7} and 3×10^{-6} respectively. Although the values of the molar extinction coefficient for the primary complex could not be measured directly in pyridine, a value of 10^4 should be of the right order since this is found for the similar systems investigated in ethanol. This suggests a value for Λ, the equivalent conductivity, of about 10 at trinitrobenzene concentrations of 0·01—0·1M. Such a value is by no means unreasonable in view of the uncertainty of ε.

The reversibility of the primary and the secondary reaction has been studied in ethanol. A mixture of diethylamine (0·77M) with 1,3,5-trinitrobenzene ($1{\cdot}1 \times 10^{-4}$M) in this solvent was allowed to stand for 2—3 min. until the primary equilibrium had become established. On acidification (HCl) the spectrum became equivalent to the sum of the spectra of its components thus demonstrating the reversibility of the primary reaction. However, if the mixture was allowed to stand for 4 hr. so that the secondary reaction approached completion, acidification produced an entirely different spectrum and a new band with a maximum near 370 mμ was observed. The results are illustrated in Fig. 4. Attempts to crystallise the complexes of trinitrobenzene with the aliphatic amines or pyridine failed.

Infrared measurements indicate that a band near 3300 cm.$^{-1}$ due to diethylamine disappears on addition of 1,3,5-trinitrobenzene. This band has been identified as an N–H stretching frequency. Pyridine was used as a solvent to obtain this result; although it would compete with diethylamine in a primary association our results indicate that the amount of pyridine complex formed would be extremely small. The result is illustrated in Fig. 5.

Because of the conflicting reports concerning the nature of the reactions of 1,3,5-trinitrobenzene we have carried out exchange measurements on its pyridine solutions containing small amounts of heavy water. For comparison, similar solutions of 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene were also investigated. The solutions were allowed to stand for 2—3 weeks after which the nitro-compounds were precipitated with hydrochloric acid, washed, and dried. After combustion the products were analysed on a mass-spectrometer. The results (Table 2) show clearly that trinitrobenzene does not exchange a proton in pyridine solutions while both the compounds containing a methyl group show considerable exchange.

TABLE 2. *Exchange measurements in pyridine.*

	Mole fraction of nitro-compound	Mole fraction of heavy water	Mole fraction of pyridine	Exchange (atoms %)
1,3,5-Trinitrobenzene	0·0349	0·109	0·856	<0·015
2,4,6-Trinitrotoluene	0·0346	0·109	0·857	23
2,4,6-Trinitro-*m*-xylene	0·00427	0·0398	0·956	40

We have further found that both 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene dissolve in pyridine to form solutions which show electrical conductivity and colour *immediately* after mixing. Further slow increases in optical density and electrical conductivity occur and these have been followed for several weeks without reaching equilibrium. This behaviour is quite different from that of mixtures of pyridine with picric acid. Light-absorption measurements indicated that in such solutions equilibrium was set up instantaneously (or very rapidly) and no further changes were observed.

Typical spectra for solutions of various nitro-compounds in pyridine are given in Fig. 6.

FIG. 3.

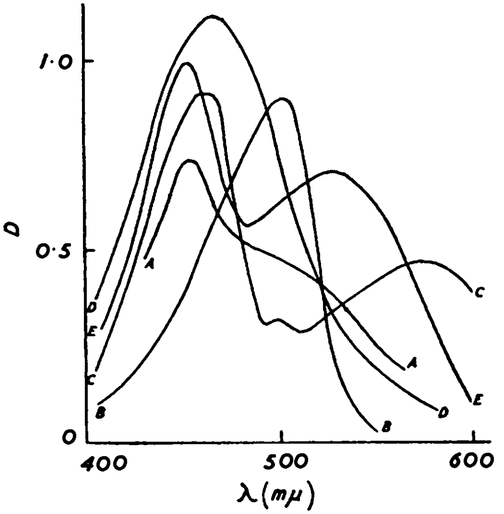

FIG. 4.

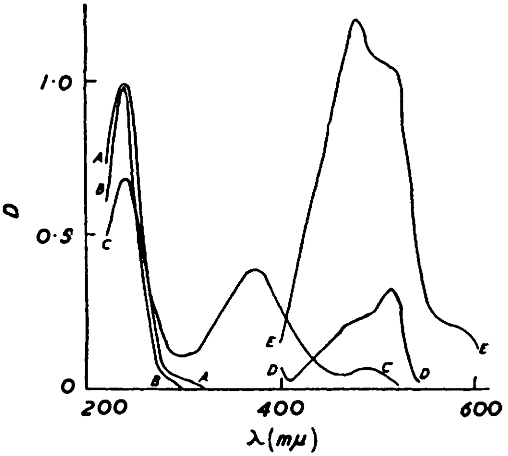

FIG. 3. *Absorption spectra of* 1,3,5-*trinitrobenzene in various solvents.*

Cell thickness = 0·5 cm. in all cases.

A Trinitrobenzene (7·0 × 10^{-5}M) in crude cyclohexylamine immediately after mixing.
B Same solution after 3 hr.
C Saturated solution of trinitrobenzene in acetone after two months.
D Trinitrobenzene (~10^{-4}M) in diethylamine.
E Trinitrobenzene (~10^{-4}M) in ethylenediamine.

FIG. 4. *The reversibility of the* 1,3,5-*trinitrobenzene–diethylamine reaction.*

A Trinitrobenzene with diethylamine quenched after 2 min. with excess of hydrochloric acid.
B The same components as in *A* but with the trinitrobenzene added last.
C As in *A* except that the acid was added after 4 hr.
D As in *C* with excess of amine added after the acid.
E As in *A* with excess of amine added after the acid.

FIG. 5.

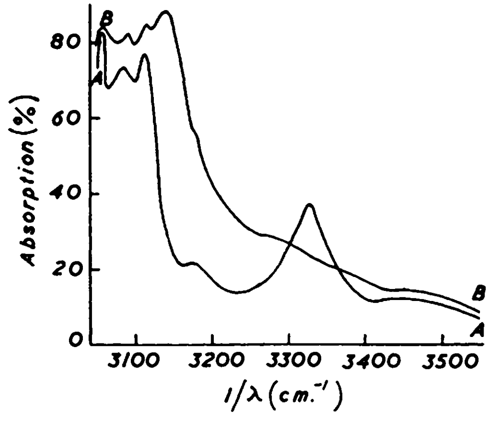

FIG. 6.

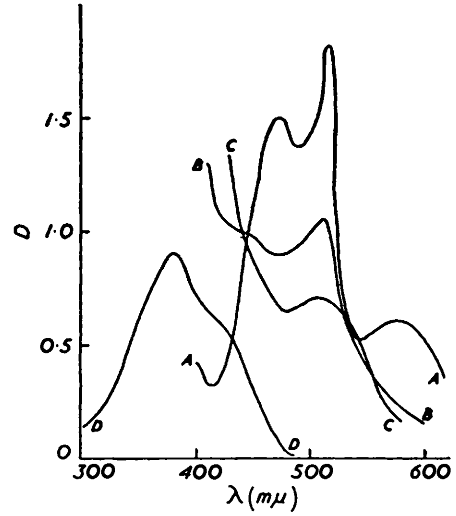

FIG. 5. *The infrared spectrum of a mixture of* 1,3,5-*trinitrobenzene with diethylamine in pyridine.*
A Diethylamine in pyridine, *B* Diethylamine with trinitrobenzene in pyridine within 2 min. of mixing.

FIG. 6. *The spectra of pyridine solutions of various aromatic nitro-compounds.*

A 0·31M-Trinitrobenzene (x = 0·5 cm.; t = 300 min.).
B 0·05M-2,4,6-Trinitrotoluene (x = 0·5 cm.; t = 8800 min.).
C 0·05M-2,4,6-Trinitro-*m*-xylene (x = 5·0 cm.; t = 5500 min.).
D 2·8 × 10^{-4}M-Picric acid (x = 0·2 cm.; t = 0).
x is the cell thickness and t is the time after mixing.

The results in Table 1 show that the complexes of 1,3,5-trinitrobenzene fall into two distinct groups according to the donor. The properties of these complexes are summarised in Table 3, where the heats and entropies of formation for the complexes of 1,3,5-trinitrobenzene with some aromatic amines and hydrocarbons are those reported by Bier [7] while those for the complexes formed by pyridine and the aliphatic amines are our own measurements in pyridine and ethanol.

TABLE 3. *Properties of some* 1,3,5-*trinitrobenzene complexes.*

	Group I (aliphatic type) complexes	Group II (aromatic type) complexes
Donor	Aliphatic amines, pyridine, ethoxide ion (*n* or *n'* donors)	Aromatic amines and hydrocarbons (π donors)
Light absorption for primary complex	Peak always within range 450—475 mμ; new band at 570 mμ in ionising solvents	Varies widely with different donors; no new band in ionising solvents
Molar extinction coefficient at the wavelength of maximum absorption	$\sim 10^4$ l. mole^{-1} cm.$^{-1}$	$\sim 10^3$ l. mole^{-1} cm.$^{-1}$
Rate of primary reaction	Measurable	Apparently instantaneous formation of product
$-\Delta H^\circ$	8—9 kcal./mole	Usually 1—3 kcal./mole
ΔS°	Usually -25 to -31 e.u.	Usually -1 to -3 e.u.
Electrical conductivity	Solutions show marked conductivity	Little or no conductivity
Solubility of primary complex	Has never been isolated as a solid	Easily isolated as a crystalline solid
Secondary reaction	Occurs in ionising solvents	Has never been observed

DISCUSSION

Table 1 shows that while mixtures of 1,3,5-trinitrobenzene with a wide variety of donors produce substantially the same spectra, these spectra change with solvent and the ratio D_{570}/D_{470} may be used to divide solvents clearly into two groups. With aromatic donors however, 1,3,5-trinitrobenzene shows no such regularity in its spectra.

The first group of donors includes the aliphatic amines, pyridine, 2- and 4-methylpyridine, and probably ethylenediamine and the ethoxide ion. These are examples of what Mulliken [8] calls 'onium or 'onium-anion donors. Here we term the complexes formed " Group I " or " aliphatic-type " complexes. The second group are typical π donors and we term the complexes " Group II " or " aromatic type " complexes. This classification is supported by several other properties as shown in Table 3.

The results can be expressed in a general scheme such as:

$$\begin{tikzcd}
A + D \arrow[r, rightleftharpoons] & AD \arrow[r, rightleftharpoons] \arrow[d] & A^- + D^+ \\
B + C \arrow[r, rightleftharpoons] & BC \arrow[r, rightleftharpoons] & B^- + C^+
\end{tikzcd}$$

A represents 1,3,5-trinitrobenzene and D is an electron donor while BC is the secondary product in the state in which it is formed under the experimental conditions. The exchange measurements in pyridine indicate that the primary reaction is not a proton transfer and, since it is freely reversible, an electron transfer seems to be the most probable reaction. However, the exchange results shed no light on the nature of the secondary reaction so that it is quite possible that this is a proton transfer.

With aromatic donors it seems that only the first equilibrium is set up and even with aliphatic donors the other reactions do not occur in non-ionising solvents. With aliphatic amines in ionising solvents however all the equilibria set out above occur.

[7] Bier, *Rec. Trav. chim.*, 1956, **75**, 866.

[8] Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.

The formulation of the primary complex formed by aliphatic amines and pyridine as a charge-transfer complex is supported by Ainscough and Caldin's conclusions [9] on the similar 1,3,5-trinitrobenzene–ethoxide ion complex.

The spectra of the aromatic-type complexes vary with the donor under consideration. Various workers [10] have attempted to derive, for similar complexes, a relationship between the position of the light-absorption band and a suitable property of the donor, especially the ionisation potential. Their results suggest that complexes formed by 1,3,5-trinitrobenzene with pyridine and probably the aliphatic amines should show an absorption band with a peak below 300 mμ. In particular benzene and pyridine have ionisation potentials which are closely similar. In the former solvent, 1,3,5-trinitrobenzene gives a colourless solution, a complex having an absorption peak at 284 mμ being formed. In the latter, a red solution is formed slowly having a peak near 470 mμ.

It has been pointed out [11] that the above correlations have no theoretical significance. Nevertheless they have proved widely applicable and suggest that there is a fundamental difference in the nature of the two types of complex. Such a difference is borne out by all the properties listed in Table 3.

The primary complexes of 1,3,5-trinitrobenzene with a wide variety of 'onium and 'onium-anion donors show substantially the same absorption spectrum, and conductivity measurements indicate that ions are present in these solutions. The heats and entropies of formation measured in pyridine or ethanol solutions are consistent with the formation of a solvated ionic product.

For aliphatic-type complexes we therefore consider that the absorption spectrum is that of an ion in agreement with Weiss's suggestion [12] that molecular complexes were formed by transfer of an electron. Weiss also postulated that such an ion would have an odd number of electrons. In the ion $C_6H_3(NO_2)_3^-$ there would be an electronic level so situated as to produce absorption of light in the visible region.

It seems clear that if the visible spectrum is due to an ion the ion must be formed from the trinitrobenzene molecule rather than from the donor. In support of this Field, Garner, and Smith [5] show that, on electrolysis of a liquid ammonia solution of *m*-dinitrobenzene, the coloured ions migrated to the anode, the cation NH_3^+ (or $N_2H_6^{2+}$) being colourless.

Weiss's idea has been criticised because the observed heats of formation for molecular complexes were too low for the type of structure suggested.[13] This is undoubtedly true for the aromatic-type complexes but Table 3 shows that for the aliphatic type complexes the heats of formation are by no means unreasonable. Thus Maryott found [14] a value of $-11{\cdot}4$ kcal./mole for the heat of formation of tribenzylammonium picrate in benzene. This substance exists as an ion-pair similar to the structure proposed for the aliphatic-type complexes considered here. The very large negative values observed for the entropy of formation are also consistent with the structure suggested by Weiss.

For the aromatic-type complexes the variation of the spectra as the donor is changed is consistent with Mulliken's [15] and Brackmann's [16] view that the light absorption is that of the complex as a whole. The spectra and properties of these complexes are consistent with resonance between a no-bond and a dative structure: conductivity measurements on their solutions do not indicate any appreciable concentration of $C_6H_3(NO_2)_3^-$ ions.

A new band appears in ionising solvents when aliphatic amines act as donor. The ratio D_{570}/D_{470} may be regarded as a measure of its intensity and, for 1,3,5-trinitrobenzene–diethylamine mixtures, this assumes one of two values (either *ca.* 0·5 or less than *ca.* 0·1)

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[9] Ainscough and Caldin, *J.*, 1956, 2540.

[10] McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, **21**, 66; Hastings, Franklin, Schiller, and Matsen, *J. Amer. Chem. Soc.*, 1953, **75**, 2901.

[11] Reid and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 3869.

[12] Weiss, *J.*, 1942, 245.

[13] Dewar, " Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 185.

[14] Maryott, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 7.

[15] Mulliken, *J. Phys. Chem.*, 1952, **56**, 801; *J. Amer. Chem. Soc.*, 1952, **74**, 811.

[16] Brackmann, *Rec. Trav. chim.*, 1949, **68**, 147.

according to the solvent. Thus D_{570}/D_{470} is less than 0·05 in ether, diethylamine, and benzene and in carbon tetrachloride it is 0·1; in ethanol, acetone, and nitrobenzene it lies between 0·44 and 0·49 and for pyridine solutions of 1,3,5-trinitrobenzene it is 0·52.

It seems unlikely that separation of the ions would give rise to an entirely new absorption band if the complex is already an ion-pair. At the same time the appearance of the band appears to depend more on the type of solvent than on the properties of the individual complex. For instance D_{570}/D_{470} is approximately the same for 1,3,5-trinitrobenzene–diethylamine in ethanol as it is for pyridine solutions of 1,3,5-trinitrobenzene. Equilibrium measurements on the former system agree well with those to be expected if a 1 : 1 complex were formed. That the complex formed in the latter system is ionised appreciably is shown both by the dependence of the equilibrium upon reactant concentration and by the value of the equivalent conductivity, which is approximately 10 at trinitrobenzene concentrations of 0·01—0·1M, while Λ_0 for comparable salts in pyridine is approximately 50 to 100. The ionic nature of such complexes is clearly shown by Kraus's observation[17] that the equivalent conductivity of 1,3,5-trinitrobenzene in liquid ammonia was similar to that for a typical salt.

It would be attractive to explain our results by Mulliken's concept of inner and outer complexes.[8,15] The former would be predominantly ionic and, with suitable environmental co-operation, would ionise, thus resembling the group I complexes. Between the two minima in the potential energy curve corresponding to the inner and outer complexes there will be an energy barrier. This is consistent with our observation that small activation energies (probably about 5 kcal./mole) are necessary for formation of a group I complex.

Such a concept makes it possible to fit both the aromatic- and the aliphatic-type complexes into one scheme. Donor and acceptor first form an " outer complex," and under suitable conditions, an " inner complex " is then formed, this being essentially an ion-pair:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \underset{\text{(outer)}}{\mathrm{AB}} \rightleftharpoons \underset{\text{(inner)}}{\overset{-}{\mathrm{A}}\overset{+}{\mathrm{B}}}$$

The latter dissociates in ionising solvents

$$\overset{-}{\mathrm{A}}\overset{+}{\mathrm{B}} \rightleftharpoons \overset{-}{\mathrm{A}}\mathrm{S} + \overset{+}{\mathrm{B}}\mathrm{S}$$

$\overset{-}{\mathrm{A}}$ S and $\overset{+}{\mathrm{B}}$ S being solvated ions.

With aromatic donors it seems that only the outer complex is formed, while with aliphatic donors the inner complex is produced. The above scheme predicts however that in mixtures of 1,3,5-trinitrobenzene with aliphatic donors an outer complex should also be formed, possibly with the production of a new absorption band just below 300 mμ as predicted by the correlations mentioned above. Bier[18] has observed such a band at 300 mμ for mixtures of 1,3,5-trinitrobenzene with diethylamine and some preliminary work in this laboratory by Mr. W. Dodds has indicated that absorption maxima occur at or below 300 mμ for mixtures of 1,3,5-trinitrobenzene with n-hexylamine and pyridine. The existence of two different types of complex in pyridine solutions is also indicated by the abnormally high solubility of 1,3,5-trinitrobenzene in this solvent (112·5 g. per 100 g. of solvent). Our measurements suggest that only very small equilibrium amounts of the ionic complex studied here are formed in such solutions. Pyridine is a special case since it can function either as a π or as an 'onium donor. With n-hexylamine however no such complication occurs.

The slow rate of formation of the aliphatic-type complexes seems to be due mainly to a very large negative value for $\Delta S^{\ddagger}$. The activation energies are not very high (although the results are subject to large errors a value of about 5 kcal./mole does not seem unreasonable). The values of $\Delta S^{\ddagger}$ indicate a highly ordered structure for the transition state complex, with solvent molecules presumably playing a part. It seems reasonable

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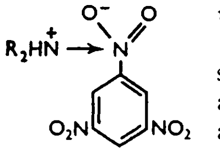
[17] Kraus, *J. Amer. Chem. Soc.*, 1913, **35**, 1315.

[18] Bier, Thesis, Amsterdam, 1943.

to assume that the rate-determining step for aliphatic-type complex formation is the transition from outer complex to inner complex, the first step being extremely rapid as in the case of the aromatic-type complexes.

While Mulliken's ideas are valuable in generalising electron donor–acceptor interactions, they ignore the specific factors which influence these reactions. Complex formation is widespread among nitro-compounds including picric acid, and some aliphatic nitro-compounds, in addition to the polynitro-aromatic hydrocarbons mentioned here.

A suggestion by Lewis and Seaborg[1] that the complexes involve double chelation cannot be true since both pyridine and triethylamine lack hydrogen atoms attached to the basic nitrogen atom. However in 1,3,5-trinitrobenzene resonance gives a partial positive charge to the nitrogen atom of the nitro-group and also to the *ortho-* and *para-*carbon atoms in the ring.



An aliphatic amine might initially attach itself to the acceptor so that the amine-nitrogen atom with its lone pair of electrons was adjacent to the nitrogen atom of the nitro-group. The attack might alternatively be on one of the partially positive carbon atoms in the ring. The former mode of reaction would lead to a product of the type (I) which is rather similar to that proposed by Bennett and Willis[19] except that we do not mean to imply the formation of a covalent bond between the two atoms.

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DEPARTMENT OF PHYSICAL CHEMISTRY,
KING'S COLLEGE, NEWCASTLE UPON TYNE, 1.

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[19] Bennett and Willis, *J.*, 1929, 256.