706. *The Reaction of* 1,3,5-*Trinitrobenzene with Aliphatic Amines.*

By R. Foster.

Spectrophotometric study of the interaction of 1,3,5-trinitrobenzene with a series of aliphatic amines in chloroform and dioxan discloses, in most cases, a fast reaction (which may be a charge-transfer complex interaction) and a slow reaction. Job continuous-variation plots indicate that for methyl-, ethyl-, dimethyl-, and diethyl-amine the molar ratio amine : trinitrobenzene is 3 : 1, for both reactions, whereas for more bulky amines the stoicheiometry is 1 : 1.

1,3,5-Trinitrobenzene behaves as a Lewis acid in interactions with aromatic hydrocarbons and aromatic amines. Mulliken [1] has described the results of these reactions, both in solution and in the solid state, as charge-transfer complexes. The forces involved include local dipole and dispersion forces together with a contribution from a covalent structure in which an electron has been donated from the π-molecular orbital of the hydrocarbon or amine molecule to an anti-bonding π-orbital of the trinitrobenzene molecule. These complexes have characteristic absorption bands. Most observations of these complexes in solution are in accordance with the assumption that only 1 : 1 complexes are formed, although in at least one case it has been suggested [2] that there are contributions from complexes with aromatic amine : trinitrobenzene ratios also of 2 : 1 and 1 : 2. Orgel and Mulliken [3] recently suggested that there may be absorption from donor–acceptor pairs in ephemeral contact as well as from those which are held together for a finite time as discrete complexes.

The absorption bands characteristic of the complex do not alter with time, and complex formation of the above type must therefore be very fast.

By contrast, colour develops slowly when trinitrobenzene is mixed with aliphatic amines. Such solutions in chloroform or dioxan develop absorption bands in the region 420—600 mμ. The actual maxima are difficult to determine owing to the broadness of the bands and their dependence on time. There is often more than one maximum. There is no simple relation between the frequency of the absorption maxima of these complexes and the ionisation potentials of the component aliphatic amines (Table 1), whereas a linear relation normally exists between the frequency of the charge-transfer bands of complexes of a given acceptor and the ionisation potentials of the component aromatic amine or aromatic hydrocarbon molecules.[4]

Table 1. *Frequencies* (ν) *of the absorption band of the adduct of various amines with trinitrobenzene in chloroform measured several hours after mixing, and the ionisation potentials* (*Ip*).

Base	ν (cm.$^{-1}$)	*Ip* (ev) [a]	Base	ν (cm.$^{-1}$)	*Ip* (ev) [a]
NH_3	21,000	10·15	NMe_3	24,000	7·82
NH_2Me	23,000, 20,000	8·97	$CH_2Ph{\cdot}NH_2$	21,000	7·56
$NHMe_2$	21,000	8·24			

[a] Watanabe and Mottl, *J. Chem. Phys.*, 1957, **26**, 1773.

The rate of development depends on the amines, the order being ammonia $\ll$ methylamine $>$ dimethylamine $\gg$ trimethylamine. Ultimately, a relatively stable colour is obtained. After several hours trinitrobenzene can be recovered quantitatively by acidification or precipitation, although after several days an irreversible reaction occurs. In most cases plots of optical absorption with time against the time of mixing indicate that a substantial colour often develops immediately and is followed by further slow development (see Figures 1 and 2).

[1] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 605; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.
[2] Ross and Labes, *J. Amer. Chem. Soc.*, 1957, **79**, 76.
[3] Orgel and Mulliken, *ibid.*, p. 4839.
[4] McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, **21**, 66; Briegleb and Czekalla, *Z. Electrochem.*, 1955, **59**, 184; Bier, *Rec. Trav. chim.*, 1956, **75**, 866.

Previous work [5] on the intensity of the band at 475 mμ of mixtures of varying composition appeared to show that the interaction of dimethylamine with trinitrobenzene involves a 4 : 1 ratio of the two components, but this has been re-interpreted by Ross and Labes [6] as a 3 : 1 association. We have confirmed the 3 : 1 ratio for this system and have determined the ratio for other aliphatic amine–trinitrobenzene systems in chloroform and in dioxan solutions, using Job's method of continuous variations.[7] Optical-density values for these plots have been obtained, first by extrapolating the optical density–time plots

FIG. 1.

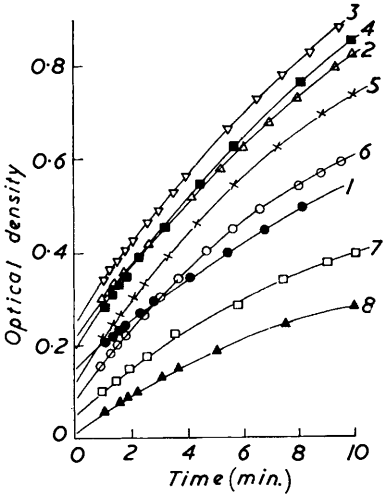


FIG. 2.

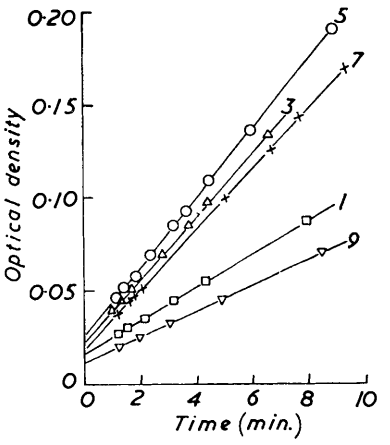


FIG. 1. *Development of absorption at* 480 mμ *for solutions of trinitrobenzene* (TNB)*–diethylamine in chloroform.*

Curve	1	2	3	4	5	6	7	8
[TNB] (M)	0·022	0·044	0·066	0·088	0·110	0·132	0·154	0·176
[Amine] (M)	0·198	0·176	0·154	0·132	0·110	0·088	0·066	0·044

FIG. 2. *Development of absorption at* 480 mμ *for solutions of trinitrobenzene* (TNB)*–di-s-butylamine in chloroform (for clarity only half the continuous-variation solutions are shown).*

Curve	1	3	5	7	9
[TNB] (M)	0·023	0·069	0·115	0·161	0·207
[Amine] (M)	0·207	0·161	0·115	0·069	0·023

to zero time to give the molar ratio of the instantaneous interaction product and, secondly from optical densities of the solutions at a time when further colour development is very slow relatively to the initial rate. The results are summarised in Table 2.

TABLE 2. *Molar ratios of amine : trinitrobenzene obtained from Job plots* (i) *at time of mixing,* (ii) *at "equilibrium."*

Amine	Solvent	(i)	(ii)	Amine	Solvent	(i)	(ii)
NH_3	$CHCl_3$	*a*	*a*	$NHEt_2$	$CHCl_3$	3 : 1	3 : 1
NH_2Me	,,	3 : 1	3 : 1	,,	Dioxan	3 : 1	3 : 1
,,	Dioxan	3 : 1	3 : 1	$NHBu^s_2$	$CHCl_3$	*a*	1 : 1
NH_2Et	$CHCl_3$	3 : 1	3 : 1	NMe_3	,,	*a*	1 : 1
$NHMe_2$	,,	3 : 1	3 : 1	NH_2Me [b]	,,	*a*	1 : 1
,,	Dioxan	3 : 1	3 : 1				

[a] No measurable additional absorption above 440 mμ in solutions of total concentration [amine] + [TNB] ~0·25M. [b] *m*-Dinitrobenzene in place of trinitrobenzene.

Ainscough and Caldin [8] have shown that there are two colour-producing reactions when sodium ethoxide is added to 2,4,6-trinitroanisole: a "fast" reaction, the product of which

[5] Foster, Hammick, and Wardley, *J.*, 1953, 3817.
[6] Ross and Labes, *J. Org. Chem.*, 1956, **21**, 1049.
[7] Job, *Compt. rend.*, 1925, **180**, 928; *Ann. Chim.*, 1928, **9**, 113; 1936, **6**, 97.
[8] Ainscough and Caldin, *J.*, 1956, 2528.

is probably a charge-transfer complex, and a " slow " reaction probably involving an addition compound as described by Meisenheimer.[9] There is evidence that a product of this latter type is also formed on addition of sodium ethoxide to trinitrobenzene.[10] It is possible that these two processes occur in the systems we are studying. The optical density at zero time would then be accounted for by the fast formation of the charge-transfer complex, which is followed by the slow interaction.

Further evidence for initial complex formation is the intensification of colour shown by chloroform solutions when cooled in ethanol–solid carbon dioxide. This is to be expected because of the increased degree of association at lower temperatures. Ham,[11] for example, calculates the association constant of pyridine–iodine to be $3{\cdot}1 \times 10^{19}$ at 77° K compared with 1250 at 298° K. The effect is large for complexes of trinitrobenzene with the sterically " small " amines: methylamine, ethylamine, dimethylamine, and diethylamine. With these amines, estimations by eye of colour intensity of the appropriate cooled solutions confirm a 3 : 1 stoicheiometry of the initial complexes. This temperature effect is only slight in the systems with the " bulky " amines di-s-butylamine and trimethylamine, and also in the system *m*-dinitrobenzene–methylamine. With ammonia no colour appear until the solution has solidified, whereafter an intense red is observed. In the last systems, initial complex formation appears to be very slight or absent.

FIG. 3.

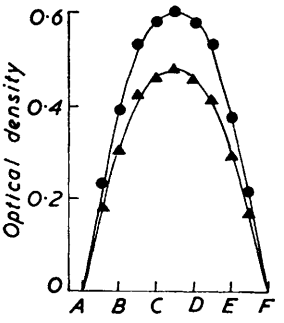


FIG. 4.

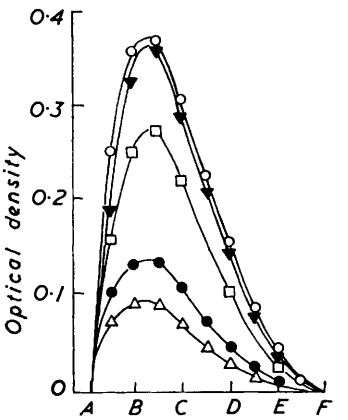


FIG. 3. *Continuous variation plot*: m-*dinitrobenzene* (DNB)–*methylamine in chloroform two days after mixing*: ● 450 mμ, ▲ 460 mμ.

	A	*B*	*C*	*D*	*E*	*F*
[DNB] (M)	0·000	0·030	0·059	0·089	0·119	0·148
[Amine] (M)	0·148	0·119	0·089	0·059	0·030	0·000

FIG. 4. *Continuous variation plot*: *trinitrobenzene* (TNB)–*methylamine in chloroform* 20 *min. after mixing*: ○ 450 mμ, ▼ 490 mμ, □ 520 mμ, ● 540 mμ, △ 570 mμ.

	A	*B*	*C*	*D*	*E*	*F*
[TNB] (M)	0·000	0·044	0·088	0·132	0·175	0·219
[Amine] (M)	0·219	0·175	0·132	0·088	0·044	0·000

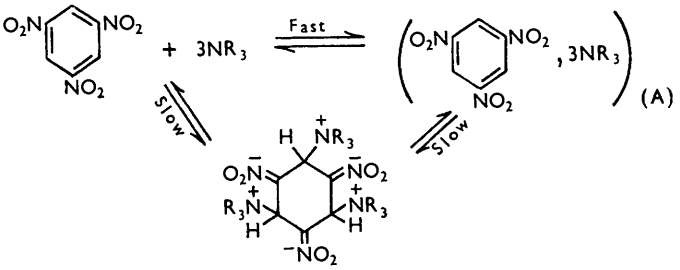
The second process, because of its slowness, may involve covalent-bond formation. Lewis and Seaborg [12] had previously assumed that there is attachment of only one amine molecule to the trinitrobenzene molecule and considered three possible mechanisms of interaction: (1) direct loss of hydrogen from trinitrobenzene, (2) direct addition of the base to one of the ring-carbon atoms that is not attached to a nitro-group, and (3) attachment of the base to one of the nitrogen atoms. The first is unlikely from general principles and

[9] Meisenheimer, *Annalen*, 1902, **323**, 205.
[10] Foster, *Nature*, 1959, **183**, 1042.
[11] Ham, *J. Amer. Chem. Soc.*, 1954, **76**, 3875.
[12] Lewis and Seaborg, *ibid.*, 1940, **62**, 3529.

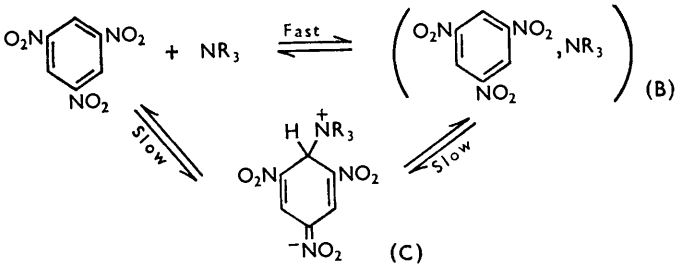
from the work of Ketelaar, Bier, and Vlaar [13] who showed that there is no exchange between trinitrobenzene and heavy water in the presence of sodium hydroxide. If (3) were the mechanism, then by analogy with the formation of a 3 : 1 methylamine–trinitrobenzene compound we might expect each of the three dinitrobenzenes to give 2 : 1 adducts. In fact there is no observable interaction between *o*- or *p*-dinitrobenzene and aliphatic amines at room temperature. With *m*-dinitrobenzene a colour develops very slowly. From measurements of optical density made two days after mixing, a continuous-variation plot indicates a 1 : 1 interaction (Fig. 3). If, after this time, the amine and solvent are removed *in vacuo*, *m*-dinitrobenzene is recovered quantitatively. The most likely of Lewis and Seabourg's suggestions seems therefore to be (2) which corresponds to the Meisenheimer type of addition, except that in cases where it is sterically possible we suggest that three molecules of amine add to the trinitrobenzene. This is feasible as here the nucleophile is uncharged species; in contradistinction the attack on trinitrobenzene by the methoxide ion results in an anion which repels the attack of a second and a third methoxide ion.

It is therefore suggested that there may be immediate formation of a charge-transfer complex and a concurrent or consecutive addition reaction:

(a) for " small " amines, $NR_3 = NH_2Me$, NH_2Et, $NHMe_2$, $NltEt_2$



(b) for " bulky " amines, $NR_3 = NMe_3$, $NH_2Bu^s_2$:



A: Charge-transfer complex.
B: Charge-transfer complex weak (if present at all).
C: Or other canonical structures.

The supposition that the amine nucleophile will only attack a carbon atom activated by two nitro-groups *ortho* to that position would also account for the reaction of methylamine with *m*-dinitrobenzene to yield a 1 : 1 adduct and the absence of reaction with *o*- and *p*-dinitrobenzene.

Absence of free ions in these solutions is indicated by their low electrical conductivity; for example, a chloroform solution 0·2M with respect to both methylamine and trinitrobenzene has a conductivity of $\sim 10^{-6}$ ohm^{-1} cm.$^{-1}$.

Experimental

Materials.—1,3,5-Trinitrobenzene, recrystallised four times from ethanol, then twice from carbon tetrachloride, had m. p. 123°. *m*-Dinitrobenzene, similarly purified, had m. p. 90°.

[13] Ketelaar, Bier, and Vlaar, *Rec. Trav. chim.*, 1954, **73**, 37.

Methyl-, ethyl-, dimethyl-, and diethyl-amine hydrochloride were recrystallised twice from absolute ethanol, concentrated aqueous solutions of these salts were dropped on solid sodium hydroxide, and the gaseous free bases, dried through 2′ columns of soda-lime, were absorbed in the appropriate solvent. Trimethylamine solutions were similarly obtained from the hydriodide twice recrystallised from methanol. Other amines were fractionally distilled from solid potassium hydroxide. " AnalaR " chloroform was washed eight times with equal volumes of water to remove ethanol, stored over calcium chloride, then refluxed for 2 hr. over phosphoric oxide and distilled. Dioxan was purified by Vogel's method.[14]

Analyses.—Job's continuous-variation method [7] has been used to determine the molar ratios. The formation of the product of an interaction between trinitrobenzene (A) and an amine (B) may be represented: $A + nB \rightleftharpoons AB_n$. To determine n, solutions of A and B of the same molar concentration are mixed in varying proportions by the additions of x ml. of a solution of B to $(10 - x)$ ml. of a solution of A, and a suitable property of the resulting solutions is measured. The difference between the value found and the corresponding value of the property calculated for no reaction is plotted against composition. The resulting curve will show a maximum (or minimum) at the value of x such that $n = x/(1 - x)$.

Such plots (Figs. 3 and 4) have been constructed by measuring the optical density at given wavelengths; first, from values extrapolated against time (Figs. 1 and 2) to give the molar ratio for the instantaneous interaction product and, secondly, from optical densities of solutions which have come to equilibrium or in which the rate of colour development is relatively very slow. The only purpose of the plots of optical density against time has been to determine the values at the time of mixing. No attempt has been made to interpret the kinetic data.

Solutions of nitro-compounds were made up gravimetrically; the amine solutions were standardised by acidimetry. From primary solutions sets of solutions for the continuous-variation plots were made up volumetrically. The optical densities were measured in 1 cm. stoppered fused silica cells at 20° with an Optica grating spectrophotometer.

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Queen's College (University of St. Andrews), Dundee. [*Received, May 22nd,* 1959.]

[14] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 175.