253. *Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons and Bases. Part VI. The Interaction between* s-*Trinitrobenzene and some Aromatic Bases.*

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The relative stabilities of the coloured complexes formed in carbon tetrachloride solution between *s*-trinitrobenzene and a series of aromatic bases have been determined by a colorimetric method previously described. It is found that in general the stronger the base the more stable the complex.

The influence of the structure of the constituent base on the maximum of absorption of the coloured complexes is illustrated.

In Parts III and V (J., 1936, 1463; this vol., p. 764) it has been shown that the stabilities of the coloured products of the interaction of tetranitromethane with aromatic hydrocarbons can be compared by finding the variation of colour density as increasing quantities of hydrocarbon are added to a fixed amount of nitro-compound, the volume of the mixture (in carbon tetrachloride) being kept constant. We have now applied an exactly similar technique in an investigation of the interaction with the production of colour that takes place when *s*-trinitrobenzene is mixed with aromatic bases in carbon tetrachloride solution.*

If to a fixed weight (*a* g.) of *s*-trinitrobenzene, progressively increasing quantities

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* It is generally agreed that there is no essential difference in the nature of the interaction, whatever it may be, that occurs between nitro-compounds and aromatic hydrocarbons on the one hand and organic bases on the other. We have therefore brought the present paper into line with the previous articles by adding " and bases " to the general title of the series.

(b g.) of base are added in carbon tetrachloride to a constant volume $V = 4$ c.c., then the variation of D, the colour density of the mixture, with b is related to the equilibrium constant

$$K = [\text{coloured complex}]/[\text{trinitrobenzene}]\ .\ [\text{base}]$$

by the equation $(\partial D/\partial b)_{a,V} = \varepsilon daK/V^2$, when K is small, so that

$$\left(\partial\frac{D}{a/V}\bigg/\partial\frac{b}{V}\right)_{a,V} = \varepsilon dK,$$

where ε is the extinction coefficient for a given wave-length, and $d = 2$ cm. is the thickness of the absorbing solution (*loc. cit.*).

In the table below are collected values of εdK found from the linear plots of $D/(a/V)$ against b/V for admixtures of various bases with *s*-trinitrobenzene in carbon tetrachloride at two temperatures, 25° and 60°. To save space, individual values of D and b are not given (smoothed values of D for given values of b can be found, if required, from the quoted values of the slopes and of a and b); the groupings of values of $D/(a/V)$ for values of b/V about a mean straight line were in all cases as close as those quoted in previous papers (*locc. cit.*).

The two values of b/V are the extreme concentrations in g.-mol./l. of the added base in the constant volume $V = 0{\cdot}004$ l. of carbon tetrachloride, in which the concentration of *s*-trinitrobenzene was in all cases 0·0125 g.-mol./l. Under $(\varepsilon dK)_{t^\circ}$ are the values of the slopes

$$\left(\partial\frac{D}{a/V}\ \ \partial\frac{b}{V}\right)_{a,V}$$

at 25° and 60°; λ is the wave-length at which D was determined; K_b is the basic constant calculated from the acid dissociation constant for the corresponding anilinium ions (Brönsted and Duss, *Z. physikal. Chem.*, 1925, *B*, **117**, 299); $-\Delta H$ is the heat of interaction calculated by means of the van't Hoff isochore, $\Delta H = [\partial(\log_e \varepsilon dK)/\partial T]\boldsymbol{R}T^2$; and the other symbols are as already defined.

Base.	b/V.	$[\epsilon dK]_{20^\circ}$.	$[\epsilon dK]_{60^\circ}$.	$K_b \times 10^{10}$.	λ, A.	$-\Delta H$, kg.-cals.
o-Toluidine	0·0198—0·1586	813	571	3·4	4900	2·0
m- ,,	0·0750—0·2499	514	359	6·7	4900	2·0
p- ,,	0·0502—0·2006	562	414	14·0	4900	1·7
Aniline	0·1074—0·3759	314	223	5·0	4900	1·9
o-Bromoaniline	0·0463—0·2777	195	126	—	4900	2·5
m- ,,	0·0456—0·2733	130	91	—	4900	2·0
p- ,,	0·0437—0·2619	298	204	—	4900	2·1
o-Chloroaniline	0·1025—0·7175	160	110	0·05	4900	2·1
m- ,,	0·1010—0·6060	114	80	0·33	4900	2·0
p- ,,	0·0943—0·5186	239	170	1·1	4900	1·9
Methylaniline	0·0497—0·3476	458	305	—	5500	2·3
Dimethylaniline	0·0256—0·1533	1089	675	—	5700	2·7
Diphenylamine	0·0710—0·3078	386	279	—	5500	1·8
Triphenylamine	0·1224—0·3673	203	168	—	5700	1·1
a-Naphthylamine	0·0035—0·0212	3132	1598	—	5400	3·8

With a knowledge of ε, the extinction coefficient, we could obviously find K in each case and so compare the stabilities of the coloured products of the base–nitro-compound interactions. As, however, ε cannot be determined, we have to proceed on the assumption that, for a given wave-length, ε for the coloured complex does not vary much with variation of the constituent base. The validity of this assumption has been confirmed (J., 1936, 1463) in cases where the orders of stability of nitro-compound–hydrocarbon complexes, derived from colour measurements (εdK, as above), have been found to agree with orders based on absolute values of K (*loc. cit.*). Bearing this in mind, we notice that the order of stability (εdK) of the coloured products of interaction diminishes from the toluidines through aniline and the bromoanilines to the chloroanilines, this being the order in which the basicity of the bases might be expected to diminish under the influence of the inductive effects of the substituents in the aniline molecule. Comparison with the values K_b of the experimentally derived basicity constants shows that basic strength and stability of complex run roughly parallel. It must, however, also be noticed that the sequence of εdK values places aniline as a weaker reagent towards trinitrobenzene than the toluidines, whereas as a base it comes between *o*- and *m*-toluidine. Moreover, the *o*-, *m*-, *p*-sequences on the colour basis are not those of the true basicities. The basic strengths of the isomerides are, where known accurately, in the order *o*-$<$*m*-$<$*p*-; on the colour basis for the toluidines ($+ I$), the *o*- forms a more stable complex than the *p*-isomer, the opposite of what is found for the halogen derivatives in which the inductive effect is $- I$.

Direct comparisons of the εdK values for the *N*-substituted anilines and α-naphthylamine with those of the other anilines are not possible because, owing to the differences in tint, colour densities could not in the former cases be measured at the same wave-length as in the latter. Nevertheless, having found with the nuclear-substituted anilines that, on the whole, the stronger the base the more stable are the nitro-compound complexes, we should expect to find that the latter would increase in stability in the order aniline, methylaniline, dimethylaniline. The values of εdK are, in fact, in this order, even though the colour densities upon which they depend were measured at slightly different wave-lengths. Similarly, the diminishing basicity in the sequence aniline, diphenylamine, triphenylamine is followed by the order of complex stability as indicated by the sequence of the values of εdK

Some relation between the electron-donating power (which is measured by its basicity) of a base and the stability of the complex it forms with a nitro-compound is to be expected if the views developed by Bennett and co-workers as to the mechanism of the interaction and the structure of the products are correct (J., 1928, 2305; 1929, 256; 1936, 1108). Evidence is, however, accumulating that these and analogous interactions may be due to mutual polarisation and attraction of benzene nuclei face to face at distances apart that preclude the existence of any kind of chemical bond between them (Briegleb, "Ahrens Sammlung," Part 37, New Series, 1937; Anderson, *Nature*, 1937, **140**, 583; H. W. Powell, private communication). Should it ultimately turn out that this view is correct, it will be impossible to associate the production of colour that almost always accompanies these interactions with the setting up of specific structures in the ordinary chemical sense. It is, moreover, the fact that polynitro-compounds absorb strongly in the near ultra-violet, and it is not *a priori* impossible that alteration in the intramolecular fields resulting from intermolecular polarisations may result in a shift in absorption towards the region of longer wave-length (Briegleb, *op. cit.*).

In the course of the present work we have measured the variation in colour density with wave-length for the coloured solutions in carbon tetrachloride of the various base–trinitrobenzene complexes. For aniline and its nuclear-substituted derivatives the shapes of the absorption curves in the violet show that the maxima of absorption lie just outside the visible in the ultra-violet; all the *N*-substituted aniline complexes studied have, however, maxima in the visible violet. The wave-lengths, λ, at maximum absorption are as follows:

	Aniline.	Methyl-aniline.	Dimethyl-aniline.	Diphenyl-amine.	Triphenyl-amine.	α-Naphthyl-amine.
λ, A.	4200	4200	4900	4600	4900	4700

It will be noticed that the heats of interaction, $-\Delta H$, of *s*-trinitrobenzene with the various bases are of the same order (*ca.* 2 kg.-cals.) as the heats of interaction of polynitro-compounds in general with aromatic hydrocarbons (Briegleb, *op. cit.*; Parts III and V of this series; *locc. cit.*). Briegleb has pointed out that the induction energy between a dipole $\mu \approx 4$D. (nitro-group) and a non-polar but polarisable hydrocarbon molecule at a distance of 3 A. is about 2 kg.-cals.

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