Interaction of Polynitro-compounds with Aromatic Hydrocarbons and Bases. Part XIII. The Effect of changing the Nitro-compound.*

By B. DALE, R. FOSTER, and D. LL. HAMMICK.

[Reprint Order No. 5588.]

The results are recorded of a study of the interactions in *cyclo*hexane solution of a number of *N*-alkylanilines with a series of nitrobenzenes. Association constants as defined in Part XII * have been taken as a measure of the degree of interaction of the two components and are discussed in the light of charge-transfer (Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801).

THE interactions of a number of nitrobenzenes have been studied with a view to displaying the effect of the number and orientation of the nitro-groups on the association constants. Increase in the number of nitro-groups is expected to augment the Lewis acidity of nitrobenzene. Introduction of methyl groups (*e.g.*, *s*-trinitrotoluene) may be expected (apart from possible steric effects) to diminish the Lewis acidity. The bases used for the interactions with the nitro-compounds were chosen to reveal whether or not the order of apparent Lewis acidities of the nitro-compounds is independent of the base.

EXPERIMENTAL

The association constants for the interactions were determined by the colorimetric method previously described (Foster, Hammick, and Wardley, *J.*, 1953, 3817). Optical densities were measured in 10-mm. cells. A Beckman Quartz Spectrophotometer (model DU) was used.

All the determinations were made in *cyclo*hexane. The results quoted in the Table represent the mean of two or more determinations. The individual results in all cases are within ±0·15 l./mole of the mean values quoted. Owing to absorption by the components, none of the solutions had a spectrum showing a maximum characteristic of the complex. However, it has been shown (Foster and Hammick, *J.*, 1954, 2685) that, for example, in the case of the *NN*-dimethylaniline–*s*-trinitrobenzene interaction, the photometric estimation of the concentration of a complex at wave-lengths other than its characteristic maximum is possible, provided that the wave-length used is away from the absorption bands of either component. For these reasons, most of the estimations were made in the region 450—480 mμ. No attempt has been made to resolve the spectra of the complexes from the spectra of the components at shorter wave-lengths and so to find the wave-length of maximum absorption due to the complex.

Materials.—Aniline, *N*-alkylanilines, and *cyclo*hexane were purified as described by Foster and Hammick (*loc. cit.*). Nitrobenzene (I), prepared by the nitration of pure benzene, had

---

* Part XII, *J.*, 1954, 2685.

b. p. 210°/761 mm. *o*-Dinitrobenzene (II), recrystallised four times from aqueous alcohol, had m. p. 118°.

m-Dinitrobenzene (III), recrystallised three times from aqueous alcohol, had m. p. 88°. *p*-Dinitrobenzene (IV) recrystallised four times from aqueous alcohol, had m. p. 172°.

Association constants of nitrobenzene–alkylaniline complexes * *in* cyclo*hexane at* 18·5—20°.

Aniline derivative	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	pK_a [d]
(Aniline)	— [a]	— [a]	— [a]	0·5	3·1 [b]	2·7	— [c]	— [a]	4·58
N-Methyl-	0·3	0·5	0·4	0·9	7·3 [b]	3·1 [b]	1·7	— [a]	4·85
N-Ethyl-	0·3	0·8	0·7	1·2	8·4 [b]	3·8 [b]	2·0	— [a]	5·11
NN-Dimethyl-	0·4	1·1	1·2	1·8	9·5 [b]	5·8 [b]	— [c]	— [a]	5·06
NN-Diethyl-	0·3	1·1	1·4	1·7	6·5 [b]	2·4 [b]	— [c]	— [a]	6·56

* For numerals in column headings, see nitro-derivatives recorded in the text; (V) is trinitrobenzene.

[a] Too small to measure. [b] Foster and Hammick (*loc. cit.*). [c] Not measurable owing to the low solubility of *s*-trinitro-*m*-xylene in the respective alkylanilines. [d] From Hall and Sprinkle (*J. Amer. Chem. Soc.*, 1932, **54**, 3469).

s-Trinitrotoluene (VI), recrystallised twice from alcohol, had m. p. 81°. *s*-Trinitro-*m*-xylene (VII) prepared by Beilstein and Luhmann's method (*Annalen*, 1867, **144**, 274), had m. p. 182°. Trinitromesitylene (VIII), recrystallised twice from alcohol, had m. p. 232°.

Discussion

It is assumed that these interactions may be described as charge-transfer processes (Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801; Foster and Hammick, *loc. cit.*). The Lewis acids are the nitro-compounds, the Lewis bases are the anilines.

The order of the stabilities of the complexes of *s*-trinitrobenzene with certain alkylanilines has already been shown to be: aniline < *N*-methyl- < *N*-ethyl- < *NN*-dimethyl- > *NN*-diethyl-aniline (Foster and Hammick, *loc. cit.*). This also appears to be the order of stability of the complexes of these alkylanilines with *o*-, *m*-, and *p*-dinitrobenzene. A possible exception is the *m*-dinitrobenzene-*NN*-dimethylaniline complex, which may be less stable than the *NN*-diethylaniline complex; in this case, however, it will be seen that the difference is within the experimental error. In the case of the mononitrobenzene complexes the experimental error is too large to permit the assignment of an order to the complex stabilities, except that *NN*-dimethylaniline has the highest and aniline the lowest association constant.

This order is not the order of the Brønsted basicities of the respective alkylanilines (last column in the Table). The pK_a values are a measure of the relative stability of the anilinium ion in which a proton has been added to the nitrogen atom of the aniline molecule. In the case of the association constants a measure is being made of the Lewis basicities of the π-orbital of the respective anilines. This orbital, though it extends over the nitrogen atom, is not localised on it. Also the Lewis acid which it attracts, namely, the nitrobenzene molecule, is of a shape which will involve stereochemical factors absent in the case of the proton–aniline interaction.

The order of the degrees of interaction of a given aniline with the various nitrobenzenes appears to be: nitrobenzene < *o*-dinitrobenzene = *m*-dinitrobenzene < *p*-dinitrobenzene < *s*-trinitrobenzene > *s*-trinitrotoluene > *s*-trinitro *m*-xylene > trinitromesitylene. In the case of the dinitrobenzenes the results suggest that the *p*-isomer may have the lowest electron density in the π-orbital. The various dinitrobenzene isomers may also differ in their steric interference with the approach of an aniline molecule. *s*-Trinitrobenzene with three nitro-groups symmetrically disposed about the benzene ring behaves as a much stronger Lewis acid.

The introduction of methyl groups successively into the remaining unsubstituted positions in *s*-trinitrobenzene causes a rapid fall in the stability of the complexes. This may be due to a combination of two effects. The methyl groups will by their inductive effect tend to increase the electron density of the π-orbital, thus decreasing the potential Lewis acidity (Hammick and Hellicar, *J.*, 1938, 761). Also the introduction of a methyl group *ortho* to nitro-groups will cause some steric interference. In particular the nitro-groups may no longer be able to lie in the plane of the benzene ring. In the case of *s*-trinitrotoluene, a planar configuration may be obtained with only a small adjustment of the bond angles. However, in *s*-trinitro-*m*-xylene and trinitromesitylene one or more groups are effectively held out of the plane of the ring. The result is a loss of resonance of the nitro-groups with the benzene ring so that the electromeric removal of electrons by the nitro-groups is hindered. Thus again the Lewis acidity is reduced. Other evidence for the steric inhibition of resonance of this type has been given by Brown and Reagan (*J. Amer. Chem. Soc.*, 1947, **69**, 1032) and by Fielding and Le Fèvre (*J.*, 1950, 2812).

THE DYSON PERRINS LABORATORY,
OXFORD UNIVERSITY.

[*Received, July* 26*th*, 1954.]