# The Interaction of 1,3,5-Trinitrobenzene and Aliphatic Amines

By M. R. Crampton and V. Gold

(King's College, Strand, London, W.C.2)

We have investigated the interaction of 1,3,5-trinitrobenzene with a series of aliphatic amines in anhydrous dimethyl sulphoxide using three techniques:—(i) proton magnetic resonance spectroscopy, (ii) electrical conductance measurements, (iii) u.v.–visible spectrophotometry.

The results provide the answer for this particular solvent to a long-standing controversy[1] regarding the stoicheiometry and nature of the interaction. They agree with an equilibrium involving two amine and one trinitrobenzene molecules, i.e.:

(I)
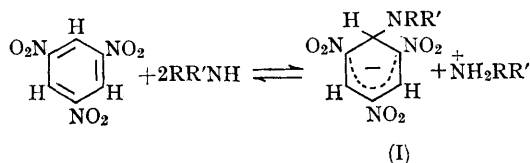
R,R'=H,alkyl

and, for example, are inconsistent with the formation of a zwitterion—(II).
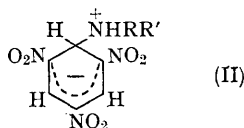
The n.m.r. spectrum of trinitrobenzene in dimethyl sulphoxide in the presence of excess of primary or secondary amine or ammonia consists of two bands of intensity ratio 2:1 with chemical shifts of ca. −8·43 and −5·70 p.p.m. respectively (relative to internal tetramethylsilane). This

spectrum suggests that addition has occurred at a ring position of the trinitrobenzene bearing a proton so that the ring-protons are now non-equivalent. This interpretation is analogous to that given[2] in the case of the methoxide adduct of trinitrobenzene where chemical shifts of −8·42 and −6·14 p.p.m. were observed. In addition, the amino-proton resonance is shifted strongly to low field in solutions containing trinitrobenzene—consistent with the formation of ammonium ions.

The conductivity of 4×10^{-2} M-trinitrobenzene in dimethyl sulphoxide was found to increase linearly with the concentration of added methylamine up to an amine concentration of 8×10^{-2} M. Increasing the amine concentration further caused little increase in conductivity. The conductance in this solution had a value closely similar to that of 4×10^{-2} M-ammonium picrate in the same solvent. This shows that ionic species are produced and suggests a 2:1 stoicheiometry. Similar results were obtained with piperidine.

Visible-spectral measurements on solutions of trinitrobenzene with primary and secondary amines showed double absorption maxima (λ_{max} ca. 450 and 530 mμ), attributed to the negatively-charged trinitrobenzene adduct (I). The variation of both n.m.r. and visible spectra with concentration of the components also indicated 1:2 stoicheiometry and, like the conductance data, showed that the equilibrium constants (for formation of the complexes) are large. Further evidence for the 1:2 stoicheiometry (though in a different solvent) comes from previous kinetic work on complex formation between trinitrobenzene and diethylamine.[3]

The n.m.r. spectra, conductance measurements, and absorption spectra of several primary and secondary amines gave closely similar results

[1] See, e.g. G. N. Lewis and G. T. Seaborg, J. Amer. Chem. Soc., 1940, 62, 2122; J. D. Farr, C. C. Bard, and G. W. Wheland, J. Amer. Chem. Soc., 1949, 71, 2103; V. Baliah and V. Ramakrishnan, Rec. Trav. chim., 1960, 79, 1150; R. E. Miller and W. F. K. Wynne-Jones, Nature, 1960, 186, 149; R. Foster and R. K. Mackie, Tetrahedron, 1962, 18, 161; W. Liptay and N. Tamberg, Z. Elektrochem., 1962, 66, 59.
[2] M. R. Crampton and V. Gold, J. Chem. Soc., 1964, 4293.
[3] C. R. Allen, A. J. Brook, and E. F. Caldin, J. Chem. Soc., 1961, 2171.

(Table). By contrast, the results for tertiary amines indicated a fundamental difference in behaviour. This is to be expected since tertiary amines are unable to give this type of interaction. amines is in fact due to primary and secondary amine impurities in the tertiary amine. Similarly the addition of a trace of water to a mixture containing trinitrobenzene and trimethylamine in

TABLE

Amine	Chemical shift of TNB ring* proton resonances in presence of excess of amine		Conductance (in same cell) of 4×10^{-2} M TNB in excess of amine (ohms^{-1})	Wavelengths of maximum absorption (mμ)
Ammonia	$-5\cdot57(1)$	$-8\cdot29(2)$	not measured	454, 542
Methylamine	$-5\cdot68(1)$	$-8\cdot43(2)$	$7\cdot8 \times 10^{-3}$	452, 538
Dimethylamine	$-5\cdot70(1)$	$-8\cdot43(2)$	not measured	450, 528
Diethylamine	$-5\cdot75(1)$	$-8\cdot40(2)$	$6\cdot8 \times 10^{-3}$	448, 526
Piperidine	$-5\cdot68(1)$	$-8\cdot46(2)$	$6\cdot2 \times 10^{-3}$	448, 525
Trimethylamine		$-9\cdot20(3)$	negligible	**
Triethylamine		$-9\cdot20(3)$	5×10^{-5}	—
NaOMe†	$-6\cdot14(1)$	$-8\cdot42(2)$	not measured	420, 490

* Figures in parentheses indicate relative intensities; chemical shifts quoted relative to internal tetramethylsilane.
** Impure trimethylamine shows maxima at *ca.* 450 and 530 mμ but pure trimethylamine gives negligible absorption above 400 mμ.
† Reference 2.

The addition of the tertiary amines trimethylamine or triethylamine to a solution of trinitrobenzene in dimethyl sulphoxide caused no change in the shift, broadness, or intensity of the trinitrobenzene nuclear magnetic resonance, and no excess of conductance (over that of solutions of the two solutes by themselves in dimethyl sulphoxide) was detected on the addition of triethylamine to trinitrobenzene in dimethyl sulphoxide.

A slight colour was observed in trinitrobenzene slutsions containing tertiary amines but it was found that this colour could be greatly reduced in intensity by purifying the amine. It is suggested that absorption showing the characteristic double absorption maxima in solutions containing tertiary

dimethyl sulphoxide caused a marked increase in colour, presumably because of the production of hydroxide ions which themselves react with trinitrobenzene.

The evidence regarding the structure of the adducts formed from primary and secondary amines was obtained for dimethyl sulphoxide only. However, the observation of absorption spectra, very similar to those in dimethyl sulphoxide, in the solvents ethanol and chloroform[4] makes it seem probable that the same covalency changes occur in some, though probably not all other solvents, but equilibrium constants and states of ionic aggregation are expected to differ.

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4 R. Foster and R. K. Mackie, *Tetrahedron*, 1961, 16, 119.