Reactions of Aromatic Nitro-compounds with Hydroxide and Methoxide: Structural Investigations by Nuclear Magnetic Resonance Spectroscopy

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WE have previously reported the use of nuclear magnetic resonance spectroscopy in the determination of the structures of "Meisenheimer Complexes"[1] and as a method of determining the mode of ionisation of aromatic amines.[2]

We now report the unexpectedly varied structures of a series of complexes formed between aromatic nitro-compounds and sodium methoxide and sodium hydroxide. The results tabulated below give the nature of the major 1:1 and 1:2 interactions in a solvent system of approximately equimolar amounts of dimethyl sulphoxide and methanol or water. Sodium methoxide in methanol or hydroxide in water was added in the form of a concentrated solution to a *ca.* 1M-solution of the nitro-compound in . dimethyl sulphoxide. The change in n.m.r. spectrum of the nitro-compound on the addition of one equivalent of base was found to be characteristic of the nature

of the 1:1 interaction. In some cases further addition of base was accompanied by n.m.r. spectral changes indicative of a 1:2 interaction. Thus N-methylpicramide first loses the amino-proton and this is followed by addition of a basic group to a ring carbon atom.

The effect of dimethyl sulphoxide as solvent is to enhance the basicity of the medium so that for a 1:1 stoicheiometry of components complex formation is in most cases complete.

Only in the case of picramide did the nature of the interaction vary with solvent; in this case experiments with varying proportions of dimethyl sulphoxide and methanol extrapolated to zero concentration of dimethyl sulphoxide indicated 80% addition of methoxide; increasing the proportion of dimethyl sulphoxide caused a slightly greater proportion of picramide to ionize by proton loss. When the system t-butoxide in t-butyl alcohol–dimethyl sulphoxide was used no addition could be detected, the interaction being solely loss of an amino-proton. The changed nature of the reaction is presumably due to steric hindrance. These results largely reinforce arguments derived from visible spectra on the nature of the interactions of picramide,[3] dimethylpicramide,[3] and 2,4-dinitroanisole[4] with base for other solvent systems.

In solutions of s-trinitrobenzene containing less than one equivalent of base, separate signals are obtained for complex and s-trinitrobenzene. With increasing concentration of base there is progressive broadening of the trinitrobenzene resonance without corresponding broadening of
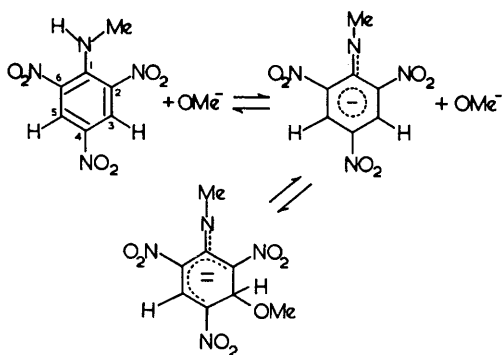
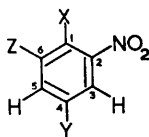[1] M. R. Crampton and V. Gold, *J. Chem. Soc.*, 1964, 4293.
[2] M. R. Crampton and V. Gold, *Proc. Chem. Soc.*, 1964, 298.
[3] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1697.
[4] R. J. Pollitt and B. C. Saunders, *J. Chem. Soc.*, 1964, 1132.

the lines due to complex. This is interpreted as indicating exchange of nuclear protons, presumably *via* a small amount of proton loss from trinitrobenzene to give its conjugate Brönsted base. Indeed, *m*-dinitrobenzene[5] and *s*-trinitrobenzene[6] have been found to exchange nuclear protons with solvent in basic solution by isotopic methods.

X\
Z\\\\\\\\\\\6—1\\\\NO$_2$
5—4—3
H   Y   H

(benzene ring structure with substituents X (position 1), Z (position 6), NO$_2$ (position 2), H (position 3), Y (position 4), H (position 5))

It has been reported[7] that *p*-nitrobenzyl cyanide shows an anomalous ionisation behaviour in basic media. We find that in methanol–dimethyl sulphoxide containing sodium methoxide it ionizes by loss of a methylene proton and the anion so formed is stable to further base. However, in aqueous mixtures the situation is more complex and decomposition rapidly occurs.

Electron spin resonance experiments[9] have shown that many aromatic nitro-compounds form radical anions in dimethyl sulphoxide–t-butyl alcohol containing potassium t-butoxide, and that

Compound	X	Y	Z	Interaction with sodium methoxide		Interaction with sodium hydroxide	
				1 equivalent	2 equivalents	1 equivalent	2 equivalents
s-Trinitrobenzene	H	NO$_2$	NO$_2$	addition at C$_1$	little further interaction[a]	addition at C$_1$[b]	no further interaction
2,4,6-Trinitroanisole	OMe	NO$_2$	NO$_2$	addition at C$_1$	no further interaction	hydrolysis to picric acid	
2,4-Dinitroanisole	OMe	NO$_2$	H	addition at C$_1$	no further interaction	hydrolysis to 2,4-dinitrophenol	
NN-Dimethylpicramide	NMe$_2$	NO$_2$	NO$_2$	addition at C$_3$	addition at C$_5$	addition at C$_3$	addition at C$_5$
N-Methylpicramide	NHMe	NO$_2$	NO$_2$	loss of amino-proton	addition at C$_3$	loss of amino-proton	addition at C$_3$
Picramide	NH$_2$	NO$_2$	NO$_2$	{ loss of amino-proton *or* addition at C$_3$		{ loss of amino-proton *or* addition at C$_3$	
2,4,6-Trinitro-diphenylamine	NHPh	NO$_2$	NO$_2$	loss of amino-proton	addition at C$_3$	—[c]	—
2,4,-Dinitro-diphenylamine	NHPh	NO$_2$	H	loss of amino-proton	no further interaction	—[c]	—
2,4-Dinitroaniline	NH$_2$	NO$_2$	H	loss of amino-proton	no further interaction	—[c]	—
2,6-Dinitroaniline	NH$_2$	H	NO$_2$	loss of amino-proton	no further interaction	—[c]	—
Picric acid	OH	NO$_2$	NO$_2$	loss of acidic proton	no further interaction	loss of acidic proton	no further interaction

[a] Decomposition occurs[8]
[b] Spectrum consistent with exchange of nuclear proton
[c] These systems were not explicitly studied, but are expected to be analogous to corresponding methoxide solutions

It is interesting that no gross change occurs beyond a molar ratio 1 : 1 with trinitroanisole and picric acid with methoxide, but these results do not necessarily imply absence of further reaction at higher base concentrations. Line broadening of the lines due to complex may indicate here that the 1 : 1 complex exchanges ring protons with solvent to a small extent.

there is a relationship between ease of oxidation and formation of the radical.

We rule out the formation of radical anions as a major process in the systems studied by us on two grounds: (i) our systems are stable to atmospheric oxygen and yield the unchanged parent compounds on acidification, and (ii) the n.m.r. spectra obtained are inconsistent with radical anions. These

[5] R. J. Pollitt and B. C. Saunders, *Proc. Chem. Soc.*, 1962, 176.
[6] M. R. Crampton and V. Gold, Unpublished observations.
[7] R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5050.
[8] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1692.
[9] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, 1962, 84, 4153.

findings do not conflict with the evidence or conclusions presented by Russell and Janzen,[9] who noted that, for the two trinitro-compounds studied by them (one of which was 1,3,5-trinitro-benzene) and for *p*-nitrobenzyl cyanide, no radicals (or only traces of radicals) could be detected. None of the compounds reported on in the present communication is included in Russell and Janzen's list of nitro-compounds which form radical anions and are readily oxidisable. It may be significant that we were unable to detect the n.m.r. spectrum of an adduct of *m*-dinitrobenzene in the presence of sodium methoxide under our conditions and that this is a system reported to give radical anions.[10]

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[10] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, 1964, **86**, 1807.