

MEISENHEIMER COMPLEXES DERIVED FROM HYDROXIDE ION

C.A. Fyfe

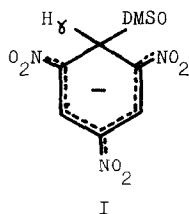
Department of Chemistry, University of British Columbia, Vancouver 8, B.S. Canada

M.I. Foreman and R. Foster

Department of Chemistry, University of Dundee, Dundee, DD1 4HN, Scotland

(Received in UK 12 February 1969; accepted for publication 26 March 1969)

Foster and Fyfe¹ have reported evidence for a species thought to be I, derived from attack by a nucleophilic species from the solvent dimethylsulphoxide (DMSO) on 1,3,5-trinitrobenzene. A similar mechanism was proposed in another context.² In the assignment proposed,²



the n.m.r. absorption of H γ was reported as a singlet peak. This was taken as evidence that bonding in I was through the oxygen or sulphur atom of the DMSO-derived species. Gold and Rochester³ have studied the possible formation of a complex II resulting from hydroxide attack on 1,3,5-trinitrobenzene. Crampton and Gold⁴ have suggested the possibility of II being formed in the systems described

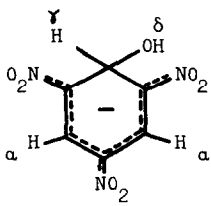
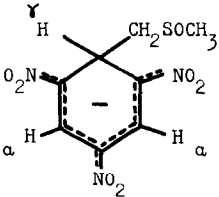
by Foster and Fyfe. In such cases the hydroxide ion would derive from the small water impurity almost invariably remaining in dried DMSO. It is now clear that the view proposed by Gold is in fact correct and the absorptions ascribed to I are due to II.

On adding potassium hydroxide to a solution of 1,3,5-trinitrobenzene in DMSO a deep red colour forms, and new n.m.r. absorptions arise which can be assigned to II (table). The absorption at $\delta = 4.50$ shifts to higher fields and becomes noticeably sharper and more intense on adding successive small quantities of water, suggesting that this absorption is due to the proton of the -OH group in II undergoing rapid chemical exchange with free water. If potassium deuterioxide is used in place of potassium hydroxide the absorption at $\delta = 4.50$ is no longer in evidence, which further confirms this assignment. The complex can be obtained as a red crystalline solid on precipitation with ether. The elemental analysis is in agreement with the proposed structure. Complex II may also be obtained reversibly by hydrolysis of the corresponding methoxy-adduct.

The complex III has also been prepared. Addition of a solution of the ion $\text{CH}_3\text{SOCH}_2^-$ in

dimethylsulphoxide,⁵ to 1,3,5-trinitrobenzene produces a deep red solution with absorptions which can be assigned to III, (table). This complex is very rapidly hydrolysed by traces of water to the complex II and is not isolable by ether precipitation.

TABLE

Complex	Structure	Chemical Shifts ^a		
		H _a	H _γ	H _δ
II		c.20(s)	6.15(s)	4.50(broad s)
III		8.35(s)	6.87(t, J = 1 Hz)	

^a s = singlet, t = triplet

Experimental. Dimethylsulphoxide was dried by refluxing over calcium hydride and stored over 5A molecular sieve. All n.m.r. spectra are at 33.5°C, recorded on a Perkin-Elmer R.10 spectrometer operating at 60.004 MHz. Shifts are measured in p.p.m. downfield from internal tetramethylsilane.

Acknowledgment. This work was carried out during the tenure of an S.R.C. studentship (by M.I.F.) and a Killam Fellowship (by C.A.F.).

References

- ¹ R. Foster and C.A. Fyfe, *Tetrahedron*, **22**, 1831 (1966); *ibid.*, **23**, 528 (1967).
- ² R. Foster and C.A. Fyfe, *Tetrahedron*, **21**, 3363 (1965).
- ³ V. Gold and C.H. Rochester, *J.Chem.Soc.*, 1710 (1964).
- ⁴ M.R. Crampton and V. Gold, *J.Chem.Soc.*, (B), 893 (1966).
- ⁵ E.J. Corey and M. Chaykovski, *J.Am.Chem.Soc.*, **84**, 866 (1962).