Electron Spin Resonance Evidence for the Formation of N_2O^- from Nitrous Oxide by γ-Radiation

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Summary Carbon disulphide solutions of nitrous oxide at 77 K after exposure to ^{60}Co γ-rays showed e.s.r. spectra of a species containing two dissimilar nitrogen atoms thought to be N_2O^-.

NITROUS OXIDE is widely used in aqueous solution as a scavenger for solvated electrons, e^-_{solv}, in radiolytic studies.[1] Generally the interaction is written as reaction (1), although

$$N_2O + e^-_{solv} \rightarrow N_2 + O^- \qquad (1)$$

it probably proceeds *via* the transient formation of N_2O^-, for which there is some slight circumstantial evidence. However, we know of no direct spectroscopic evidence for the formation of N_2O^- despite the efforts of many workers.

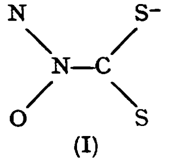
In our own work on frozen aqueous glasses we have been unable to detect N_2O^- by e.s.r. spectroscopy, but our observation that many anions are readily protonated, even at 77 K suggests that reaction (2) might be responsible. We

$$N_2O^- + H_2O \rightarrow N_2 + OH + OH^- \qquad (2)$$

therefore sought a suitable aprotic solvent, and selected carbon disulphide since both molecules are linear and triatomic, and γ-radiolysis of carbon disulphide at 77 K results only in a relatively weak singlet in the free-spin region. Sets of lines were obtained in the wings of the centra solvent line, which have been analysed in terms of two in equivalent nitrogen atoms as indicated in the Table.

The anion N_2O^- is expected to be bent since it is isoelectronic with NO_2, and this is strongly supported by the orbital populations for the central nitrogen atom which have been calculated in the usual manner[2] on the assumption that all hyperfine components are positive. The total spin density on nitrogen is less than that for NO_2 but more than that on the central atom of $N_3{}^{2-}$, again in accordance with expectation for an antibonding M.O.

The results for the ligand nitrogen atom are of the expected magnitude (*cf.* the results for $N_3{}^{2-}$ given in the Table), but are probably not principal values of the hyperfine tensor since the directions for this will differ from those for the central nitrogen atom which, being large, tend to control the form of the envelope spectra.



(I)

E.s.r. data derived from the features assigned to N_2O^- *radicals, together with results for the isoelectronic radicals* NO_2 *and* N_3^{2-}. (*z is the* C_{2v} *axis and* y *passes through the ligand atoms*).

Radical	Hyperfine values (in G)								
	Central ^{14}N			Ligand ^{14}N			*g*-Tensor components		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
N_2O^-	31 ± 3	31 ± 3	47 ± 1	7 ± 3	7 ± 3	15 ± 2	2·008	2·004	2·004 (±0·001)
NO_2[a]	50·6	49·7	70·2	—	—	—	2·0066	1·9920	2·0022
N_3^{2-}[b]	20	16·5	31	7·5	6·2	14·0	2·004	2·000	1·996

[a] Ref.2. [b] See P. L. Marunkas, *J. Chem. Phys.*, 1970, **52**, 5147.

We have considered the possibility that N_2O^- might react with CS_2 to give a species, such as (I), but the high electron affinity of N_2O relative to CS_2 renders this improbable. Also, it is significant that in the e.s.r. spectra reported for irradiated neopentane containing N_2O at 77 K[3] we have been able to detect several features characteristic of N_2O^- in addition to those for $\cdot CH_2CMe_3$ and $\cdot CMe_3$ radicals.

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[1] E. J. Hart and M. Anbar, 'The Hydrated Electron,' Wiley–Interscience, New York, 1970.
[2] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.
[3] J. Lin and F. Williams, *J. Phys. Chem.*, 1968, **72**, 3707.