Unstable Intermediates. Part CXIX.[1] Electron Spin Resonance Studies of Radiation Effects upon Cyanate and Thiocyanate Ions in Alkali-metal Halide Crystals and in Aqueous Glasses

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Irradiated crystalline sodium or potassium cyanate at 77 K had e.s.r. spectra dominated by a quintet assigned to the radical N_2CO^-, and a triplet assigned to NCO^{2-}. The latter had a ^{13}C hyperfine tensor characteristic of a bent radical as expected, since it is isoelectronic with NO_2. In contrast, aqueous glasses containing these salts gave, on irradiation, spectra which have been interpreted in terms of trapped nitrogen atoms and $HCNO^-$ radicals. The latter radicals are characterised by an unusually large proton hyperfine coupling, which is interpreted in terms of protonation on carbon.

Potassium thiocyanate had an e.s.r. spectrum, after irradiation, which has been interpreted in terms of the dimer anion $(NCS)_2^-$, well known in pulse-radiolysis studies, and the anion NCS^{2-}. On being annealed, sharp features, thought to be characteristic of NO_3 molecules, developed. The radical $(NCS)_2^-$ is assigned a σ^*-structure on the basis of its ^{33}S hyperfine tensor components. The radical CNS^{2-}, like CNO^{2-}, is shown to be strongly bent by analysis of its ^{13}C tensor components.

Aqueous glasses gave mainly $HCNS^-$ at 77 K, which is magnetically very similar to $HCNO^-$. Nitrogen atoms were not detected. The radicals CNO and CNS were not positively identified in these studies, although their formation could not be ruled out.

THIS study continues our investigations of irradiated aqueous glasses containing electrolytes in which we are attempting to obtain e.s.r. spectroscopic details of intermediates whose optical spectra are known from pulse-radiolysis or flash-photolysis studies of fluid solutions. In earlier work we observed the formation of MH^+, Hal_2^-, and $HOHal^-$ radicals in aqueous alkali halide glasses,[2] and NH_2 radicals and nitrogen atoms in irradiated aqueous azide glasses.[3]

Irradiated ionic cyanates and thiocyanates have not been widely studied by e.s.r. spectroscopy, so we undertook a thorough study of their sodium and potassium salts in order to supplement and aid our aqueous solution work. Meanwhile a single-crystal study of potassium cyanate irradiated at room temperature appeared.[4] The main species detected in this work was identified as the CN radical:[4] this result is discussed below.

The neutral radical, NCO, has been studied in the gas phase,[5] but the data so obtained unfortunately do not lead to the hyperfine parameters normally obtained by solid-state e.s.r. methods, and cannot be used to derive approximate orbital populations.[6,7]

Pulse-radiolysis studies of aqueous thiocyanate solutions have shown that $(NCS)_2^-$ dimers are formed with high efficiency, and have an intense band centred at 475 nm.[8] This property is now being extensively exploited as a means of scavenging, and hence estimating, hydroxyl radicals in aqueous solutions during pulse-radiolysis studies.

EXPERIMENTAL

Reagent grade salts were recrystallised from water or D_2O before irradiation, and single crystals of potassium cyanate were grown from aqueous solution by slow cooling. Solutions were prepared with water doubly distilled from alkaline permanganate. Rigid glasses were prepared as beads by ejecting droplets directly into liquid nitrogen. That true glasses were formed was checked by use of the Mn^{2+} technique.[9] Salt concentrations ranged from *ca.* 2M to saturation. Sodium cyanate and potassium thiocyanate formed good glasses in this concentration range, but potassium cyanate tended to give phase-separation on freezing. This was overcome by adding potassium hydroxide (*ca.* 9M).

Salts as crystals or fine powders, and aqueous glasses, were γ-irradiated at 77 K with a ^{60}Co Vickrad source (*ca.* 4 Mrad h^{-1}) to total doses of *ca.* 2 Mrad.

E.s.r. spectra were obtained with a Varian E.3 spectrometer and home-made *S*- and *Q*-band instruments.[10,11] Samples were annealed by allowing them to warm for fixed periods and recooling to 77 K.

RESULTS AND DISCUSSION

Results are summarised in Table 1 and typical spectra are given in the Figures. The initial spectra for sodium and potassium cyanate at 77 K were dominated by a set of five shoulders, but the task of unravelling other central lines related to these was rendered difficult by the presence of signals from other species. By a careful comparison of *S*-, *X*- and *Q*-band spectra [Figure 1(a), (b), and (c)] and of *X*-band single crystal spectra [Figure 1(d)], the parameters given in Table 1 were derived. Because of the good agreement obtained, a complete analysis of the single-crystal spectra was not undertaken.

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[1] Part CXVIII, A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1772.

[2] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 185.

[3] I. S. Ginns and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 631.

[4] F. Owens, R. A. Breslow, and O. R. Gillian, *J. Chem. Phys.*, 1971, **54**, 833.

[5] A. Carrington, A. R. Farbis, and N. Lucas, *J. Chem. Phys.*, 1968, **49**, 5545.

[6] H. Bower, M. C. R. Symons, and D. J. A. Tinling, 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Interscience, London, 1968.

[7] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[8] J. H. Baxendale, P. L. T. Bevan, and D. A. Scott, *Trans. Faraday Soc.*, 1968, **64**, 2389.

[9] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 143.

[10] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, and D. O. Williams, *J. Chem. Soc.* (*A*), 1969, 719.

[11] J. A. Brivati, J. M. Gross, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc.*, 1965, 6504.

A relatively weak triplet appeared in the central regions (best resolution was apparent at *Q*-band frequencies), which could possibly arise from nitrogen atoms. However, we were unable to detect the expected outer lines from zero-field splitting.[12]

When the potassium salt was annealed to room temperature, most of these lines were lost, and the spectra were dominated by a central feature, shown by single-crystal studies to comprise a broad singlet and a triplet, as reported by Owens *et al.*[4] Outer features grew in at intermediate temperatures which our aqueous solution studies show to be due to $HCNO^-$ radicals (see below). Also weak outer lines were sometimes obtained which were characteristic of HCN^- and H_2CN radicals. Weak features possibly associated with ^{13}C were sometimes obtained in the same spectral regions as those assigned to HCN^- and H_2CN; similar but better lines were obtained from the sodium salt. Results for sodium cyanate were similar. Again, the central line was not clearly resolved into a triplet, although various inflections suggested that a basic triplet with *g*- and *A*-anisotropy was responsible. At high gain, outer lines in the regions expected for NCO^{2-} containing ^{13}C were detected at the computed intensity level based on the central features. Although these are tentatively assigned to NCO^{2-} radicals in Table 1, we cannot be sure of the assignment because of the proximity of these lines to those from HCN^- and H_2CN radicals[3] which were occasionally detected in both salts. Exposure of both cyanates to γ-rays at room temperature gave results similar to those obtained on annealing samples irradiated at 77 K.

TABLE 1

E.s.r. data for various radicals in γ-irradiated cyanates, thiocyanates, and their aqueous solutions

System	Radical	Hyperfine tensor components/G [a]	*g*-Tensor components [b]
NaNCO	NCO^{2-}	(^{14}N) *ca.* 5, not clear	2·0015; 1·997; 2·002
		(^{13}C) 178; 125; 125	
KNCO	N_2CO^-	(^{14}N) 6·5; 5·5; 24·2	2·009; 2·006; 2·001
NCO^-, aqueous	$HNCO^-$	(^1H) 73·0; (^2H) 11·2	1·999
		(^{14}N) 0 ± 3; 0 ± 3, 25	
	N	(^{14}N) 4·5 ± 0·3 (D = 20·75)	2·001
KNCS	NCS^{2-}	(^{14}N) 0 ± 3; 0 ± 3; 15·0	1·997
		(^{13}C) 80, 80, 120. (5·0 for rotating radical)	
	$(NCS)_2^-$	(^{14}N) 0; 0; 3·25 ± 0·5	2·021; 2·019; 1·997
		(^{33}S) 8·0; 8·0; 56·5	
	NO_3(?)	(^{14}N) 2·0 ± 0·5; 2·5 ± 0·5; 3·0 ± 0·5	2·029; 2·013; 1·995
KNO_3 [c]	NO_3	(^{14}N) 3·46; 3·46; 4·31	2·0232; 2·0232; 2·0031
NCS^-, aqueous	$HNCS^-$	(^1H) 76·2; (^2H) 12·0	2·000; 2·000; 2·002
		(^{14}N) 4·0; 4·0; 35·0	

[a] ±1·0 G or better. [b] ±0·001 or better. [c] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1964, **41**, 4011.

Potassium thiocyanate powder after irradiation at 77 K gave e.s.r. spectra which were again dominated by five-line features (Figure 3) although the derived parameters are quite different from those for the quintet species obtained from the cyanates. At high resolution, extra quintet features were detected having the correct intensities for ^{33}S features, from a radical containing two equivalent sulphur atoms [Figure 3(a)].

At high powers, these features broadened severely thereby revealing a broader central triplet and, at high gain, outer wing lines clearly associated with this triplet and having about the correct intensity for ^{13}C satellites [Figure 3(b)]. This spectrum is assigned below to NCS^{2-} radicals.

On annealing, the five-line features were irreversibly lost, whilst the central anisotropic triplet first broadened and then appeared as an isotropic triplet having a_{iso} = *ca.* 5 G. This change was completely reversible with change in temperature. Together with these changes, sets of narrow triplets grew in irreversibly [Figure 3(c)] which we suggest are caused by NO_3 or some structurally comparable molecule.

Aqueous glasses of these salts had e.s.r. spectra which were initially dominated by features from hydroxyl (or OD) radicals. On slight annealing and recooling to 77 K, doublet features caused by a coupling to a single proton appeared (Figures 2 and 4). This was checked by studying solutions in D_2O and in 1 : 1 H_2O–D_2O solutions: features from radicals containing both ^1H and ^2H were not detected, thus establishing the presence of only one interacting proton.

When the cyanate solutions were further annealed, features characteristic of trapped nitrogen atoms were obtained. These were well resolved for solutions in D_2O [Figure (2c)].

Nitrogen atoms were not detected in irradiated thio-

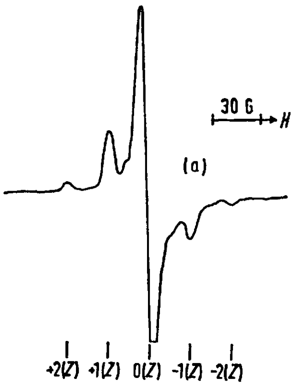

FIGURE 1(a)

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[12] A. Begum and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2062.

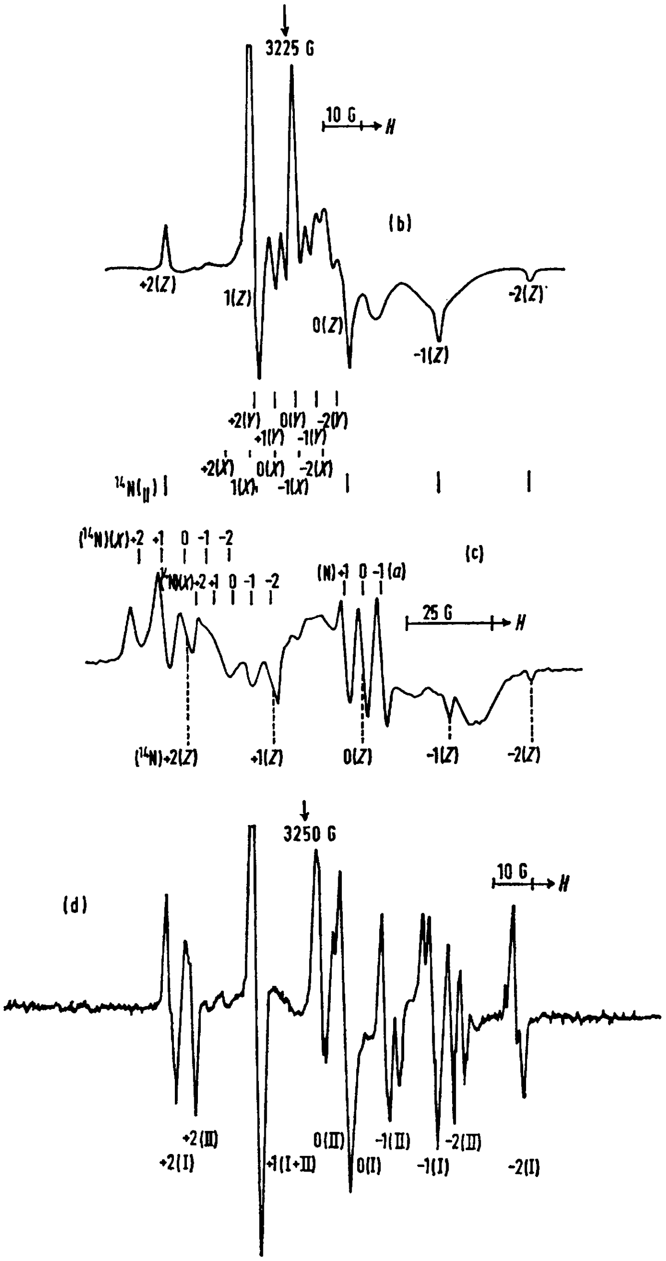

FIGURE 1 Various first derivative e.s.r. spectra for pure potassium cyanate after γ-irradiation at 77 K; (a), (b), and (c) *S*-, *X*-, and *Q*-band powder spectra with marked features assigned to N_2CO^- radicals; (d) typical *X*-band single-crystal spectrum showing N_2CO^- radicals in sites (I) and (II)

cyanate solutions. However, at 77 K central features similar to those assigned to NCS^{2-} radicals were detected. These gave way to the protonated radical after the first annealing.

Identification.—The five-line species obtained from the cyanate salts was at first thought to be the dimer $(NCO)_2^-$. However, the magnetic parameters (*g*- and ^{14}N hyperfine tensor components) differ so greatly from those assigned to $(NCS)_2^-$ radicals that this structure is almost certainly eliminated.

Since nitrogen atoms were obtained from the aqueous glasses, it seemed reasonable to suggest that N_2CO^- radicals were involved, and the derived parameters support this view (see Structure section below). In accord with this assignment, no ^{13}C satellite could be detected, showing that the coupling to ^{13}C is small.

The five-line species obtained from thiocyanate ions is assigned to the dimer $(NCS)_2^-$ for the following reasons. (i) The solids acquire an intense red-orange colour after irradiation at 77 K. This is diagnostic of a narrow absorption band in the 450—500 nm region. The dimer $(NCS)_2^-$ has a band at 475 nm in aqueous solution at room temperature.[8] (ii) Since reaction (1) is very fast

$$N\dot{C}S + NCS^- \longrightarrow (NCS)_2^- \qquad (1)$$

in aqueous solution, it should occur also in the pure solid if NCS is formed and does not decompose unimolecularly. Its initial formation is certainly to be expected, and our results for aqueous solutions suggest that, in contrast with NCO, the radical NCS does not decompose to give nitrogen atoms. (iii) The radical contains two magnetically equivalent nitrogen atoms and, less surely, two equivalent sulphur atoms. (iv) As discussed below, the large magnitude of the hyperfine coupling to ^{33}S is strongly suggestive of a radical of the type $RS{-}SR^-$, having an extra electron in the S–S σ-bond.

The experiments with D_2O solutions establish that the species tentatively described as $HCNO^-$ and $HNCS^-$ contain one strongly interacting proton. They also contain one nitrogen atom which contributes mainly 2*p*-character to the orbital of the unpaired electron. The two most probable reactions leading to protonated radicals are (2) and (3). A consideration of electronic

$$H\cdot + NCS^- \longrightarrow HNCS^- \qquad (2)$$

$$NCS^{2-} + H_2O \longrightarrow HNCS^- + OH^- \qquad (3)$$

structure shows that N- or O-protonation of NCS^{2-} would result in small proton coupling, probably less than *ca.* ±10 G, whilst C-protonation would give a radical which could well have a ^1H coupling in the 70 G region (see below).

The radical described as NCS^{2-} in irradiated potassium thiocyanate contains one weakly interacting nitrogen atom and one strongly interacting carbon. No ^{33}S feature was detected but for NCS^{2-} the coupling is expected to be small, in which case the features would be lost in the broad central lines. Identification of NCO^{2-} is less clear. This radical is expected to have a large hyperfine coupling to ^{13}C, and such features have been detected at high gain. However, the central features were always poorly resolved in the powder spectra, and also, as stressed above, lines from HCN^- and H_2CN radicals span the ^{13}C regions and in several spectra completely obscure the ^{13}C satellites. (We assume that HCN^- and H_2CN are formed from cyanide ion impurity, which seems to be difficult to eliminate. Similar spectra have been obtained from aqueous cyanide ions,[2] and from cyanide in alkali-metal halide matrices.[13])

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[13] K. D. J. Root, M. C. R. Symons, and B. C. Weatherley, *Mol. Phys.*, 1966, **11**, 161; J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc.* (*A*), 1969, 1942.

Single crystals of potassium cyanate do form a triplet species on irradiation at room temperature, having roughly the sort of hyperfine coupling to ^{14}N expected for NCS^{2-}, but unfortunately the signals were far too weak for us to detect ^{13}C wing lines. This species was identified as CN by Owens *et al.*,[4] but we do not find this identification compelling. The CN radical has recently been very well characterised both by its ^{14}N and its ^{13}C hyperfine interaction,[14] and the parameters for the triplet in the irradiated cyanate [4] do not tie in well with these.

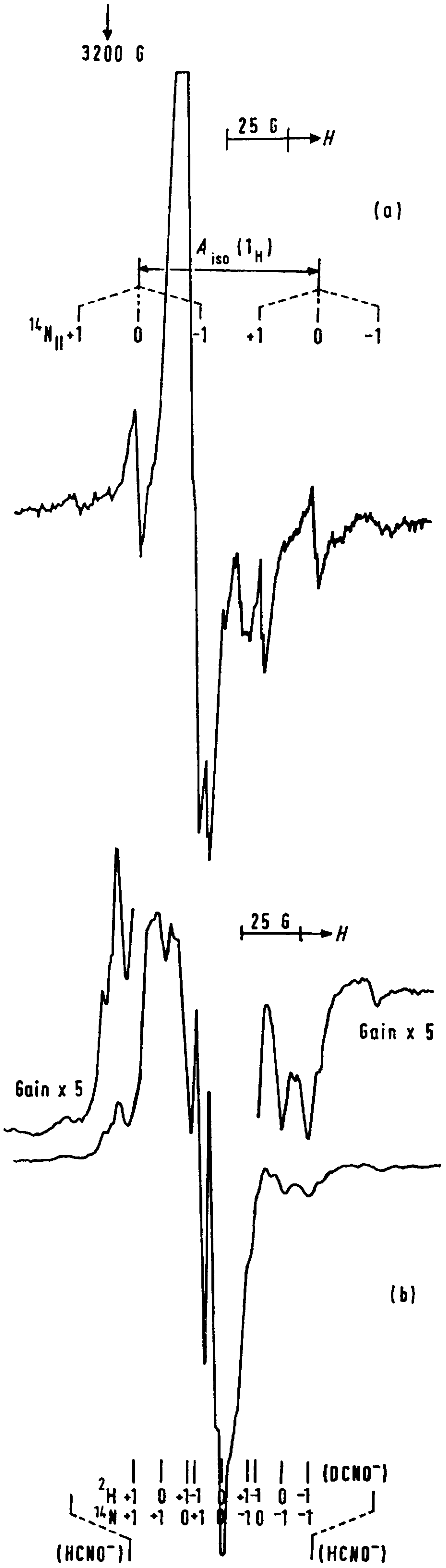

FIGURE 2(a) and (b)

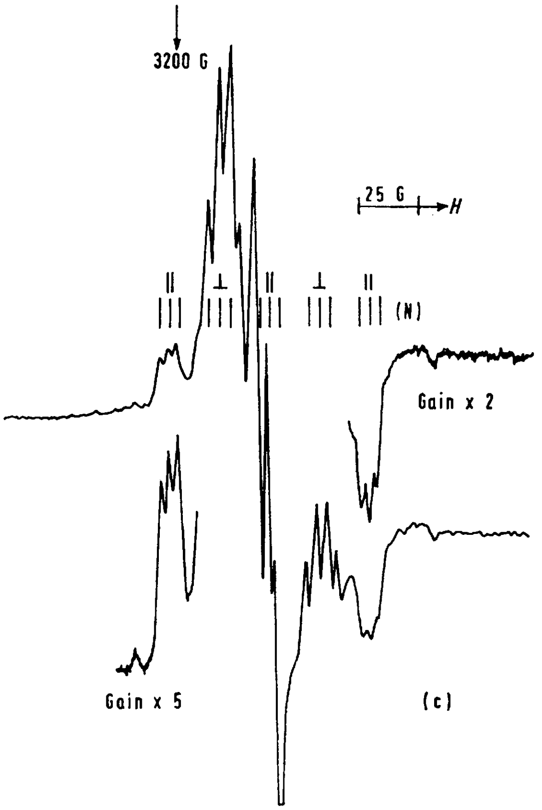

FIGURE 2 Various e.s.r. spectra for aqueous sodium cyanate glasses after γ-irradiation at 77 K and partial annealing; (a) *X*-band spectrum showing features assigned to $HCNO^-$ radicals; (b) as (a) but with D_2O solvent; (c) as (b) but at very low power (0·34 mV) after further annealing, showing features for nitrogen atoms

Surprisingly, no good evidence for the trapping of NCO or NCS radicals has been obtained. Since these radicals are linear and have their unpaired electrons in π-non-bonding orbitals, a relatively strong, asymmetric crystal field is required to give e.s.r. spectra in the free-spin region. Even then, spin–lattice relaxation could well broaden the lines severely. Under good conditions, we would expect spectra to be characterised by a large positive *g*-value for field along the molecular axis which would have a small $(\perp)^{14}N$ coupling, and two features ($\parallel$ and $\perp$) in the free-spin region. The only lines that could have fitted these requirements appeared on annealing potassium thiocyanate crystals above 77 K. Since NCS would hardly be a secondary product, we favour the suggestion that these are due to NO_3 radicals. The data are compared with those for known NO_3 radicals in

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[14] W. C. Easley and W. Weltner, *J. Chem. Phys.*, 1970, **52**, 197.

Table 1. Presumably these arose from nitrate impurities, but recrystallisation did not prevent their formation.

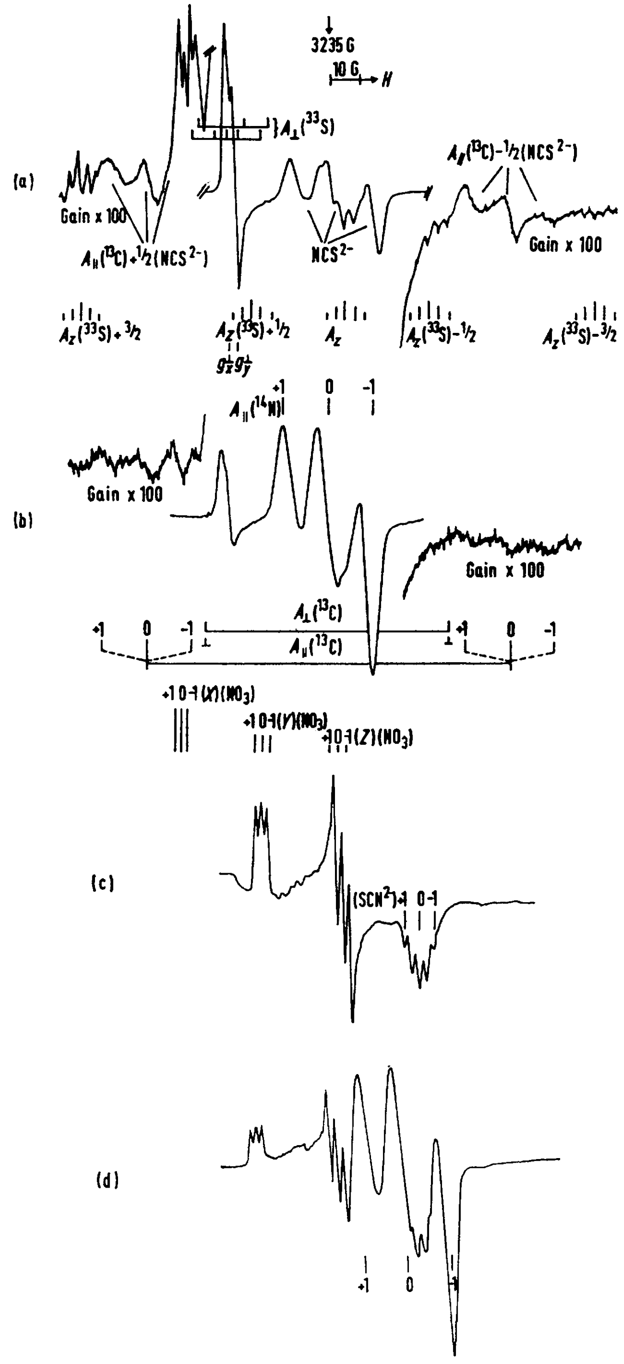

FIGURE 3 Various e.s.r. spectra for pure potassium thiocyanate after γ-irradiation at 77 K; (a) showing features assigned to $(CNS)_2^-$ radicals and including those containing ^{33}S; (b) as (a) but at high microwave power, showing features assigned to NCS^{2-} radicals including those containing ^{13}C; (c) after partial annealing, showing features assigned to NO_3 radicals and rotating NCS^{2-} radicals; (d) as (c) but after recooling to 77 K

Identification of trapped nitrogen atoms in irradiated aqueous cyanate solutions is unambiguous because of the characteristic parallel and perpendicular features, which are quite comparable with those found for nitrogen atoms in powdered sodium azide.[12]

Structural Aspects.—Nitrogen atoms. Although we were able to detect the central narrow triplet for nitrogen atoms formed in aqueous solutions of azide ions,[4] the wing lines were not detected and hence no value could be given for the zero-field parameters. The present results give $D = ca.$ 20·75 G and $E = ca.$ 0. This value of D is between that for the atom in solid nitrogen (11 G)[15] and that for the atom in sodium azide at 273 K (37 G).[10] Thus the interaction is small, and probably arises from a weak hydrogen-bonding with a neighbouring water proton.

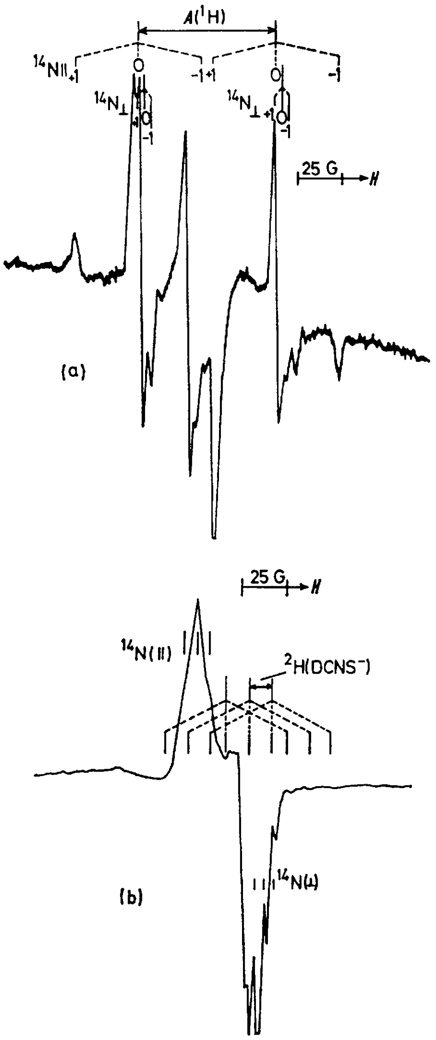

FIGURE 4 Various e.s.r. spectra for aqueous potassium thiocyanate glasses after partial annealing; (a) showing features assigned to $HCNS^-$ radicals; (b) as (a) with D_2O solvent, showing $DCNS^-$ features

The N_2CO^- *radicals.* We know of no e.s.r. study of any radical of this type.[7] The radical is isoelectronic with CO_3^+, which would be expected to have a configuration . . . $(2e')^4(e'')^3$, the e''-level being non-bonding, and

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[15] T. Cole and H. M. McConnell, *J. Chem. Phys.*, 1959, **31**, 451.

composed, primarily, of $p(\pi)$ orbitals on the ligand atoms. Since a hole on nitrogen is more favourable than one on oxygen, the orbital selected will probably be that depicted (I).

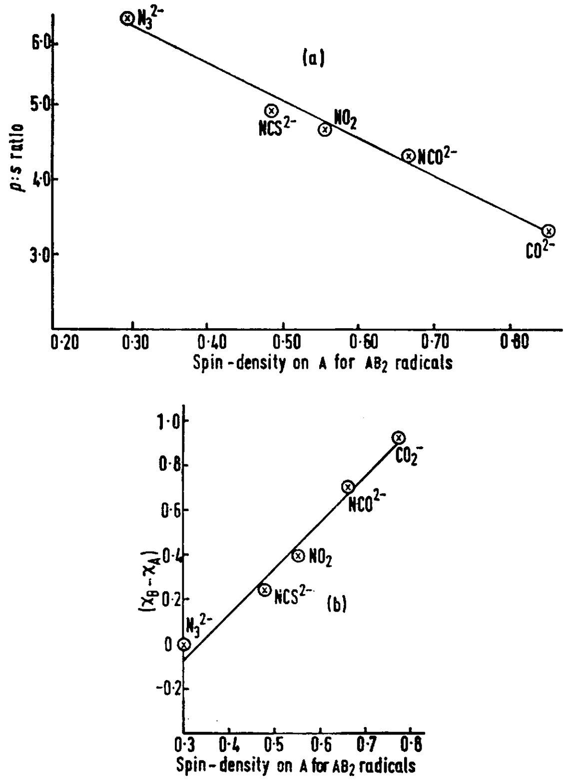
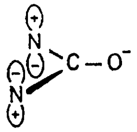
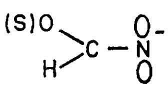


FIGURE 5 Dependence of the spin-density ($a_s^2 + a_p^2$) on A for various AB_2 radicals as a function of (a) the $p:s$ ratio, and (b) the electronegativity difference ($\chi_B - \chi_A$)

(I)



(II)



The estimated orbital populations on nitrogen, derived in the usual manner,[8] are given in Table 2. Two sets of results are included because A_x and A_y could reasonably be either both positive or both negative. In either case the estimated total spin-densities on nitrogen are close enough to unity to confirm the structure of this species. The high values for g_x and g_y are also in good accord with expectation since fields in the radical plane should couple the e'' level with the filled $2e'$ level.

$HCNO^-$ *and* $HCNS^-$. These are assigned the structure (II), with the unpaired electron primarily confined to nitrogen. In some respects they resemble H_2CN radicals, and indeed the proton and nitrogen hyperfine interactions for these radicals are very similar.[16]

NCO^{2-} *and* NCS^{2-}. We accept, for discussion, our tentative assignment for NCO^{2-}. The results for the ^{13}C parameters for these radicals have been used to derive approximate orbital populations (Table 2) and are displayed, together with results for various isoelectronic or isostructural radicals in Figure 5(a). The parameters for both radicals agree well with those for the other, well authenticated, radicals, supporting our identification. Another correlation which we have used extensively shows the trend in spin-density ($a_s^2 + a_p^2$) on the central atom as a function of the electronegativity difference between the mean electronegativity of the ligand atoms and that of the central atom. This is shown in Figure 5(b) and again there is a good correlation.

TABLE 2

Derived orbital populations

Radical	Nucleus	a_p^2 (%)	a_s^2 (%)
NCO^{2-}	^{13}C	53·5	12·6
NCS^{2-}	^{14}N	29·4	0·9
	^{13}C	40·4	8·25
N_2CO^-	^{14}N (i)	35·6	2·2 [a]
	(ii)	59·0	0·7
$(NCS)_2^-$	^{14}N	6·6	0·18
	^{33}S (i)	57·7	2·5 [a]
	(ii)	76·8	1·4
$HNCO^-$	^{1}H		14·5
	^{14}N	*ca.* 50	1·5
$HNCS^-$	^{1}H		15·1
	^{14}N (i)	60·6	2·6
	(ii)	76·5	1·6 [a]

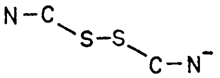
(i) $\perp$ Values being taken as positive. (ii) $\perp$ Values being taken as negative.

[a] These values are preferred.

The $(NCS)_2^-$ *radical.* Although a variety of organic disulphide anions, $RS^-SR'^-$, have been reasonably well established by e.s.r. spectroscopy,[17,18] we know of no study of such radicals containing ^{33}S isotopes. Our derived orbital populations may be compared with those for other σ^* radicals of this type.[2,19,20] The very low 3*s*-character estimated for the σ^*-orbital suggests that these radicals are linear as in (III), rather than staggered as in (IV).[20]

(III) $N-C-S-S-C-N^-$

(IV)



Many alternative structures have been considered for this radical, and M.O. computations are in hand in an attempt to establish more surely the most probable structure for these interesting radicals.[21]

Possible Mechanisms.—In the light of these results, we suggest steps (4)—(11) for the various systems under consideration. We write NCO* as an excited state precursor for trapped nitrogen atoms since it is improbable that the NCO radical would decompose in this way from its ground state at 77 K.

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[16] K. V. S. Rao and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2163.

[17] K. Akasaka, S. I. Ohnishi, T. Snita, and I. Nitta, *J. Chem. Phys.*, 1964, **40**, 3110.

[18] H. C. Box, H. G. Freund, and G. W. Frank, *J. Chem. Phys.*, 1968, **48**, 3825.

[19] I. Marov and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 201.

[20] A. R. Lyons, G. W. Neilson, and M. C. R. Symons, *Chem. Comm.*, 1972, 507.

[21] T. A. Claxton, personal communication.

$$\mathrm{NCO^-(S)} + \gamma \longrightarrow \mathrm{NCO(S)} + \mathrm{e^-} \qquad (4)$$

$$\mathrm{NCO^-(S)} + \mathrm{e^-} \longrightarrow \mathrm{NCO^{2-}(S)} \qquad (5)$$

$$\mathrm{NCO^{2-}(S)} + \mathrm{H_2O} \longrightarrow \mathrm{HCNO^-(S)} + \mathrm{OH^-} \qquad (6)$$

$$\mathrm{NCO^*} \longrightarrow \mathrm{N} + \mathrm{CO} \qquad (7)$$

$$\mathrm{NCO} + \mathrm{NCO^-} \longrightarrow \mathrm{N_2CO^-} + \mathrm{CO} \qquad (8)$$

$$\mathrm{NCS} + \mathrm{NCS^-} \longrightarrow \mathrm{NCS\text{-}SCN^-} \qquad (9)$$

$$\mathrm{H} + \mathrm{NCO^-(S)} \longrightarrow \mathrm{HNCO^-(S)} \qquad (10)$$

$$\mathrm{OH} + \mathrm{NCO^-} \longrightarrow \mathrm{OH^-} + \mathrm{NCO}(\longrightarrow \mathrm{N} + \mathrm{CO}) \qquad (11)$$

These processes may well have some significance for liquid-phase studies. Thus the species N, $HCNO^-$, $HCNS^-$, and N_2CO^-, which have not been postulated as intermediates to our knowledge, clearly require serious consideration.

It has recently been postulated that hydroxyl radicals readily add (12) to thiocyanate ions,[22] the adduct having

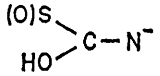
$$\mathrm{OH} + \mathrm{NCS^-} \longrightarrow \mathrm{HONCS^-} \qquad (12)$$

an absorption band in the 390 nm region. This then reversibly forms the NCS radical [reaction (13)]. Whilst

$$\mathrm{HONCS^-} \rightleftharpoons \mathrm{NCS} + \mathrm{OH^-} \qquad (13)$$

this addition is certainly chemically reasonable, we have obtained no evidence for or against its occurrence in rigid solutions. If the oxygen atom adds to carbon to give (V), we would have a radical isostructural with the CO_3^- radical, which has an unpaired electron confined to the ligand atoms in the in-plane $1a_2^1$ orbital.[7] Hence a π-type coupling ($A_{\parallel} \gg A_{\perp}$) to ^{14}N would be expected, with *g*-values somewhat greater than the free-spin value. No clear evidence for this radical was obtained, but it could certainly have been present if the component lines were severely broadened. Similar considerations apply to the radical $HONCO^-$ which could well be formed by attack of hydroxyl on NCO^- ions.

(V)



We thank the S.R.C. for a grant (to I. S. G.).

[2/937 *Received, 2nd April*, 1972]

[22] D. Behar, P. L. T. Bevan, and G. Scholes, *Chem. Comm.*, 1971, 1486.