Low Temperature Ultraviolet Photolysis of Various Glasses of the Pentacyanonitrosylferrate(II) Ion, $[Fe(CN)_5(NO)]^{2-}$†

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Exposure of dilute solutions of $[Fe(CN)_5(NO)]^{2-}$ ions to u.v. light at 77 K gave a range of paramagnetic products detected by e.s.r. spectroscopy. In aprotic solvents the major route involved electron transfer from solvent to give $[Fe(CN)_5(NO)]^{3-}$ (I′) which, on annealing, gave $[Fe(CN)_4(NO)]^{2-}$(I) + CN^-. Such a route cannot be invoked for aqueous systems and an alternative route involving photoionisation followed by electron capture to give $[Fe(CN)_5(\dot{N}O)]^{3-}$ (II) is suggested. Species (I′) and (I) have their unpaired electrons primarily in the $3d_{z^2}$ ion orbital whereas for species (II) it is largely localised on the NO ligand. On annealing, species (II) also gave species (I) plus CN^-.

The photosensitivity of solutions of $Na_2[Fe(CN)_5(NO)]$ has long been recognised.[1,2] Mitra *et al.*[3] studied the photolysis of $[Fe(CN)_5(NO)]^{2-}$ solutions and proposed the following reaction sequence to explain their observations [equations (1)—(4)]. These authors detected one equivalent of nitrite ion

$$[Fe(CN)_5(NO)]^{2-} \xrightarrow{h\nu} [Fe(CN)_5]^{3-} + NO^+ \quad (1)$$

$$NO^+ + H_2O \rightleftharpoons NO_2^- + 2H^+ \quad (2)$$

$$[Fe(CN)_5]^{3-} + H_2O \longrightarrow [Fe(CN)_5(H_2O)]^{3-} \quad (3)$$

$$[Fe(CN)_5]^{3-} + NO_2^- \longrightarrow [Fe(CN)_5(NO_2)]^{4-} \quad (4)$$

and two equivalents of hydrogen ion consistent with equation (2) and an increase in the absorbance at 394 nm which is consistent with both equations (3) and (4).[4] In addition, these investigators[3] found that a photolysed solution, when placed in the dark, very nearly re-attained its original pH. This observation would be consistent with the well established equilibrium[4] shown in equation (5).

$$[Fe(CN)_5(NO_2)]^{4-} + 2H^+ \rightleftharpoons [Fe(CN)_5(NO)]^{2-} + H_2O \quad (5)$$

In contrast, Swinarski and Gogolin[5] more recently have postulated total decomposition of the complex ion with NO, CN^-, and Fe^{3+} as products. The production of the nitrite ion is explained by the hydrolysis of NO and the decrease in pH by hydrolysis of both Fe^{3+} and NO. The increase in the absorbance in the 400 nm region of the spectrum was explained as being due to a secondary reaction of CN^- with $[Fe(CN)_5(NO)]^{2-}$ to produce $[Fe(CN)_6]^{3-}$. Also, these investigators[5] observed, after a rapid decrease in pH, a subsequent gradual increase in pH which they assigned to the hydrolysis of CN^-. This hydrolysis step evidently becomes important after the concentration of $[Fe(CN)_5(NO)]^{2-}$ has been depleted.

Buxton *et al.*[6] also report the initial formation of NO, but by a different primary reaction. These authors propose that upon exposure to u.v. light the following two changes occur [equations (6) and (7)]. It should be noted that the aquated electron formed in equation (7) could then react with a second $[Fe(CN)_5(NO)]^{2-}$ to form either of two possible Fe^I species[7,8] {*i.e.*, $[Fe(CN)_5(NO)]^{3-}$ or $[Fe(CN)_4(NO)]^{2-}$}. Previously, Hockings and Bernal[9] proposed $[Fe(CN)_5(NO)]^{3-}$ {more recent studies[8] indicate that the species is best formulated as $[Fe(CN)_4(NO)]^{2-}$} as the photolysis product of $[Fe(CN)_5(NO)]^{2-}$ in *NN*-dimethylformamide (dmf) solution while $[Fe(CN)_5(H_2O)]^{3-}$ was thought to be formed in aqueous solution.

$$[Fe(CN)_5(NO)]^{2-} \xrightarrow{h\nu} [Fe(CN)_5]^{2-} + NO \quad (6)$$

$$[Fe(CN)_5(NO)]^{2-} \xrightarrow{h\nu} [Fe(CN)_5(NO)]^{-} + e^-(aq) \quad (7)$$

Most recently, the work of Jarzynowski *et al.*[10] has been cited[11] as being the only complete analysis of the mechanism of photolysis of $[Fe(CN)_5(NO)]^{2-}$. They indicate that two pathways are possible because of the overlapping of photochemically active bands.[10] The two steps involve replacement of NO^+ by H_2O to yield $[Fe(CN)_5(H_2O)]^{3-}$ and replacement of NO by H_2O to yield $[Fe(CN)_5(H_2O)]^{2-}$. The former would be in agreement with a combination of equations (1) and (3) while the latter would correspond to process (6) by Buxton *et al.*[6]

Recently, we have been interested in the effect of γ-radiation on both solids[12] and solid solutions[13] involving this anion. Because of this interest, as well as the large variety of mechanisms suggested, we have undertaken a study of the photolysis at 77 K. In this study a wide variety of solvents have been used to make frozen glasses containing sodium pentacyanonitrosylferrate(II), and we have employed e.s.r. spectroscopy to study the primary products. Low temperature glass photolysis may sometimes be extremely helpful in elucidating photomechanisms as shown, for example, in our studies of permanganates,[14] chromates,[15] and periodates.[16] However, it should be noted at the outset, that if cage-back reactions are important, the solid-state mechanism may be different from that in the liquid state.

Experimental

Sodium pentacyanonitrosylferrate(II) dihydrate (AnalaR) was used in all experiments and all solvents employed were of Reagent grade. The dihydrate water molecules were removed by heating the solid in a vacuum oven at 60 °C for several days and their loss was established gravimetrically.

Solutions were prepared in a darkened room, transferred to 3 mm borosilicate glass tubes, and frozen immediately to 77 K in liquid nitrogen. The photolysis was accomplished by placing the frozen tubes in a large liquid nitrogen-filled Dewar set into a Rayonet Reactor. The photolyses were attempted at

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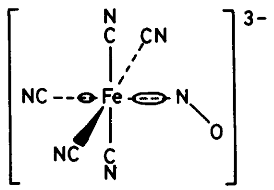
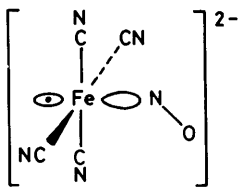
† *Non-S.I. unit employed*: 1 G = 10^{-4} T.

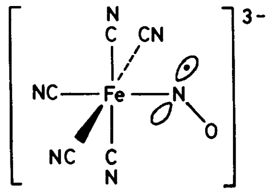
Table. Typical e.s.r. parameters for species (I), (I′), and (II)

Species [a]	^{14}N hyperfine coupling/G $\parallel$	$\perp$	*g* Values $g_{\parallel}$	$g_{\perp}$
(I)	16.9	14.3	2.005	2.032
(I′)	*ca.* 17	13—15 [b]	*ca.* 2.005	*ca.* 2.035 [b]
(II)	9	30 27	1.928	1.996 2.006

[a] See text for structures. [b] The spectra for (I′) were very poorly resolved, but the overall form of the spectra was similar to that for species (I). It is probable that the symmetry is less than axial.


(I′)


(I)


(II)

three different wavelengths (*i.e.*, 3 500, 3 000, and 2 537 Å) with 3 h being the standard exposure time.

Electron spin resonance spectra were recorded on a Varian E3 spectrometer at 77 K. Samples were allowed to warm in the tubes inside a conventional insert Dewar with the liquid nitrogen removed. Changes occurring during this annealing period were monitored by re-cooling to 77 K and recording the spectrum.

Results and Discussion

We have employed the symbolism of (I′), (I), and (II) as in our previous studies [12,13] to identify the products of photolysis; (I′) represents the electron gain species with the unpaired electron primarily localised in the $3d_{z^2}$ orbital on iron, (I) represents the five-co-ordinate $[Fe(CN)_4(NO)]^{2-}$ again with the electron localised mainly on iron, and (II) represents $[Fe(CN)_5(\dot{N}O)]^{3-}$, the electron being largely in a π^* molecular orbital on the NO ligand. E.s.r. data are given in the Table, and on the basis of these identifications, given previously,[12,13] are accepted herein.

Aprotic Solvents.—These are considered first because the results are relatively clear and establish a basis for discussing the remaining systems. We used *NN*-dimethylformamide (dmf) and hexamethylphosphoramide (hmpa) because sodium pentacyanonitrosylferrate(II), commonly called nitroprusside, was sufficiently soluble to give good yields of photoproducts. In both solvents, after exposures of 1—2 h, we detected at 77 K species (I′) and (II) with the intensity of (I′) > (II). We expect that some (I) was also present. On annealing above 77 K well defined features of (I) grew initially, with no change in (II), and on further annealing (II) was converted to (I). Central features from solvent radicals were detected, but did not constitute a major component. These were rapidly lost on annealing with no obvious conversion into any iron species. Figure 1 gives some typical spectra.

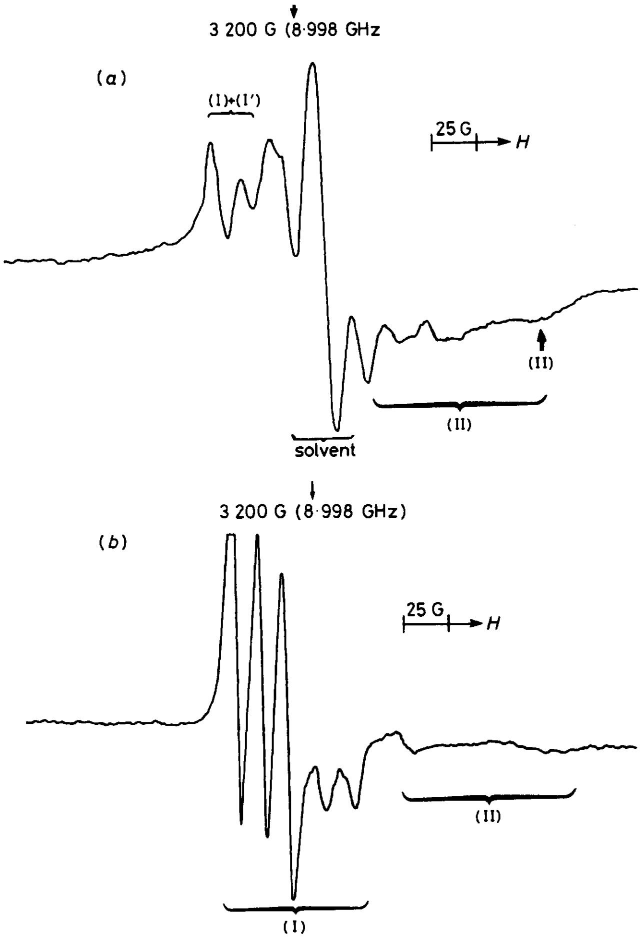


Figure 1. First derivative *X*-band e.s.r. spectrum for $Na_2[Fe(CN)_5(NO)]$ in dmf after exposure to 350 nm light at 77 K: (*a*) at 77 K showing features assigned to species (I), (I′), and (II) and solvent radicals and (*b*) after partial annealing showing growth of species (I), loss of solvent radicals, and partial loss of species (II)

We suggest that there are probably two modes of photolysis leading to paramagnetic products. The first involves initial excitation of the $[Fe(CN)_5(NO)]^{2-}$ ions *via* a ligand to metal charge transfer process (c.t.t.m.). This is followed by a further charge transfer, either from solvent molecules [17] or from neighbouring $[Fe(CN)_5(NO)]^{2-}$ ions present in clusters. Process (*i*) (Scheme) leads to species (I′) rather than (I) or (II), (I′) having e.s.r. parameters similar to (I) (Table). Solvent radicals are also formed, and these must be able to move away from species (I′), presumably by electron transfer prior to becoming trapped, since there is no clear evidence for pair trapping. Electron transfer from $[Fe(CN)_5(NO)]^{2-}$ leads to species (I′), but, additionally, to $[Fe(CN)_5(NO)]^{-}$ ions which are formally iron(III) derivatives. We have obtained no clear evidence for their formation by e.s.r. spectroscopy, and assume that if they are indeed formed, their spectra are too broad to be detected under the conditions of our study.

Process (*ii*) is envisioned as the charge transfer to solvent (c.t.t.s.) process, equation (7). Again, the Fe^{III} product is not

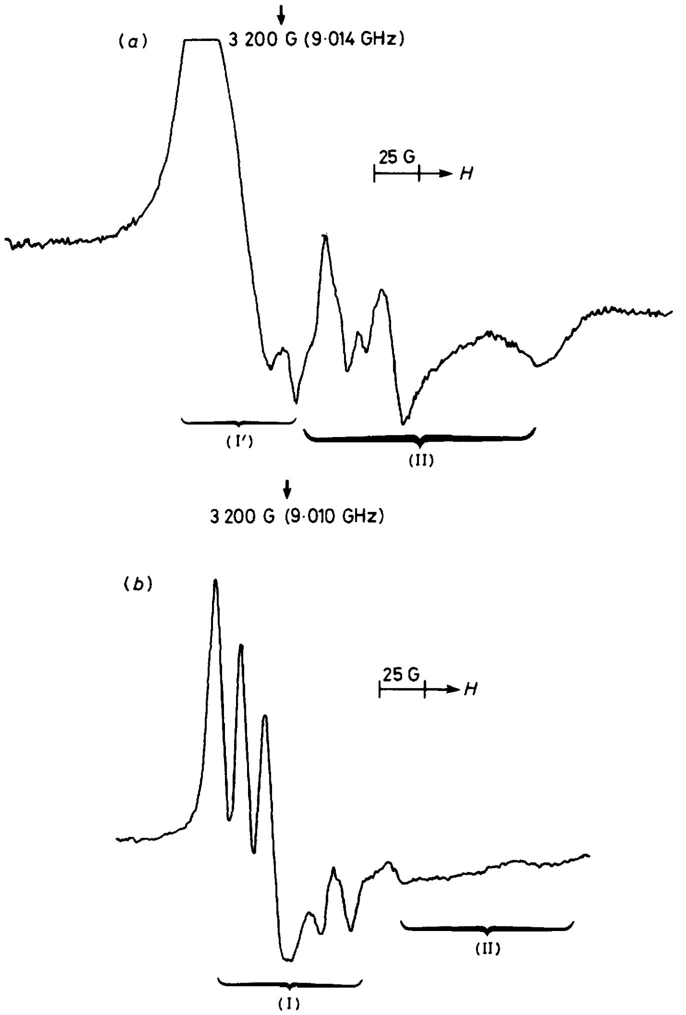


Figure 2. First derivative *X*-band e.s.r. spectrum for $\mathrm{Na_2[Fe(CN)_5(NO)]}$ in aqueous 6 mol dm^{-3} $\mathrm{MgCl_2}$ after exposure to 350 nm light at 77 K: (*a*) at 77 K showing features assigned to species (I′) and (II) and (*b*) after extensive annealing, showing loss of (I′), partial loss of (II), and growth of (I) [The gain in (*b*) is 1.6 times that in (*a*)]

detected, but electron capture by $\mathrm{[Fe(CN)_5(NO)]^{2-}}$ is known to give species (II), which is the main product on exposure to ionizing radiation.[12,13]

We suggest that species (I′) is the precursor to species (I), the excess electron being in the $3d_{z^2}$ orbital on iron, with the *trans* cyanide ligand remaining weakly attached rather than being lost, as is the case for species (I). In these solvents loss of $\mathrm{CN^-}$ occurs readily on annealing. We stress that conversion of (II) to (I) involves electron transfer from the NO ligand to iron, with concurrent loss of the axial cyanide. This process, which requires a higher temperature, is identical to that observed in our γ-radiolysis experiments.[13]

We justify the formation of (I′) [probably with (I)] after the c.t.t.m. process rather than (II) on the following argument. The c.t.t.m. absorption moves an electron onto iron, leaving a hole on the ligand. Electron transfer from neighbouring species replaces this electron so that the excess electron is left on iron rather than being on the NO ligand. At 77 K the axial cyanide is not normally lost, but this could still be a minor process.

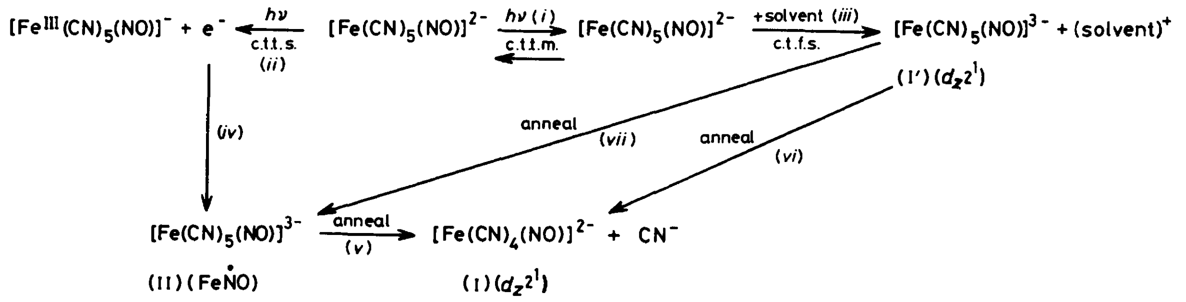
Aqueous Solvents.—As well as studying pure aqueous systems, which probably undergo some phase separation on freezing, we also studied solutions containing $\mathrm{MgCl_2}$ (6 mol dm^{-3}) and $\mathrm{Mg[ClO_4]_2}$ (6 mol dm^{-3}) which form good glasses on freezing. The results were similar except that the formation of species (I) on annealing was facile for the glasses, but only occurred on melting for the pure aqueous solutions. No differences were observed in the iron species formed when $\mathrm{H_2O}$ was replaced by $\mathrm{D_2O}$.

Initially, on photolysis at 77 K, species (I′) and (II) grew in together with approximately equal intensities. No hydroxyl radicals were detected. The pure aqueous systems gave some (I) in addition to (I′) but only (I′) was clearly detected for the glasses (Figure 2). No $\mathrm{Fe^{III}}$ features were detected from solutions containing good grades of the pentacyanonitrosylferrate(II) salt.

On initial annealing, species (I′) was lost and species (II) grew in intensity by a factor of *ca.* 1.7. On further annealing, (II) was converted into normal (I) after some fluidity had occurred. Formation of (II), explained by the c.t.t.s. process, is clearly more important in these systems. We suggest that this is because the c.t.t.m. excited state is unable to extract an electron from the solvent, and the probability of having two $\mathrm{[Fe(CN)_5(NO)]^{2-}}$ ions close enough for charge transfer to occur is small. Thus formation of (I) and (I′) is suppressed, leaving (II) as the major product.

The most important result for these aqueous systems is the clear growth in (II) as the signal for (I′) disappears during the initial anneal. It seems clear that the process (I′)→(II) occurs in favour of (I′)→(I), despite the fact that on further annealing (II)→(I) occurs. We suggest that species (I′), in which the axial $\mathrm{CN^-}$ is retained, is unstable both with respect to (I) (loss of $\mathrm{CN^-}$) and to (II) in which the excess electron is on the NO ligand. In the aprotic media, loss of $\mathrm{CN^-}$ is relatively unrestricted and occurs at low temperatures (this is also apparently true for methanol-rich glasses).

However, in the aqueous systems the anions are surrounded by a rigid, three-dimensional hydrogen-bonded lattice, and movement of the axial cyanide seems to be strongly resisted.



Scheme. c.t.f.s. = Charge transfer from solvent

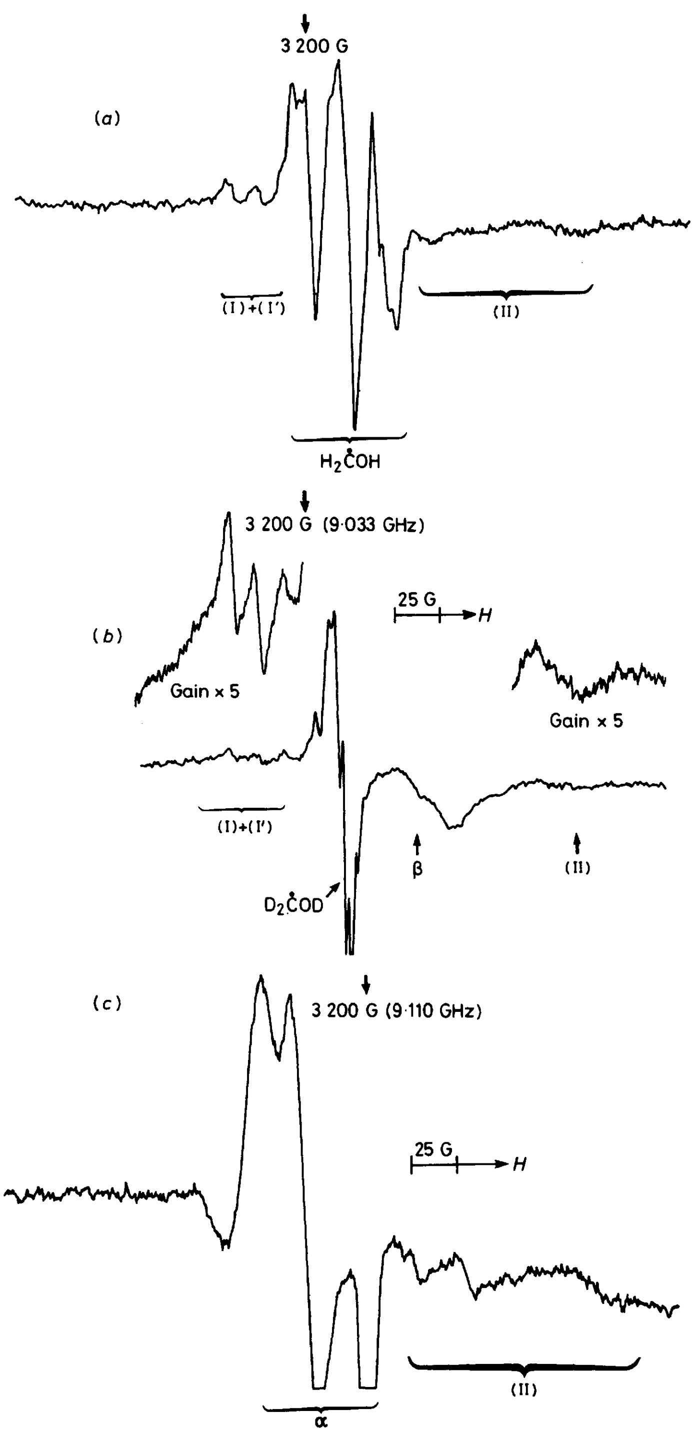


Figure 3. First derivative *X*-band e.s.r. spectrum for $Na_2[Fe(CN)_5(NO)]$ in MeOH (60%) + H_2O (40%) after exposure to 350 nm light at 77 K: (*a*) at 77 K showing features assigned to species (I) + (I′) and $H_2\dot{C}OH$; (*b*) in CD_3OD after slight annealing showing features assigned to species (I) + (I′), (II), $D_2\dot{C}OD$, and species β (?NO); and (*c*) in MeOH (70%) + H_2O (30%) after further annealing, showing features for species α

Therefore, in these systems, electron transfer from the metal to the ligand occurs. This concept is in accord with the fact that the conversion (II)→(I) is quite facile for non-aqueous solvents, and also for the aqueous glasses, but only occurs on melting for the pure water systems.

Methanolic Solvents.—Water rich methanol–water glasses gave results similar to those for the $Mg[ClO_4]_2$ glasses. However, from *ca.* 15% MeOH onwards, intense features for $H_2\dot{C}OH$ radicals (or $D_2\dot{C}OD$) were detected (Figure 3). For methanol rich systems, these features dominated the spectra. In all cases, (I′) together with some (I) was detected, but the relative yield of (II) fell steadily, and (II) was a minor component for the pure methanol systems. Clearly, charge transfer from solvent becomes the dominating process with the formation of (I′) together with some (I).

On annealing, $H_2\dot{C}OH$ ($D_2\dot{C}OD$) radicals were rapidly lost, (I′)→(I), and later, (II)→(I). However, several complicating results confused this simple picture.

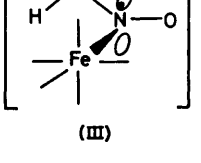
For pure methanolic and methanol-rich systems, there was overall growth in the yield of iron species on annealing, by factors as large as *ca.* 4. This may in part be due to reaction of $H_2\dot{C}OH$ with the parent complex followed by decomposition to give species (I) (see below), but we suggest that it is largely due to a degree of line broadening by spin–spin coupling in pair-trapped systems. For example, in the reaction shown by equation (8) conversion of $CH_3\dot{O}H^+$ into $H_2\dot{C}OH$ may occur

$$[Fe(CN)_5(NO)]^{2-} + CH_3OH \longrightarrow [Fe(CN)_5(NO)]^{3-} + CH_3\dot{O}H \quad (8)$$

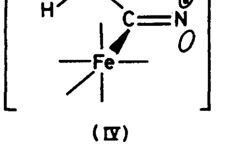
so rapidly that movement of CH_3OH by charge transfer may not compete, so that $H_2\dot{C}OH$ radicals become trapped close to species (I′). This would give rise to marked and probably variable zero-field splitting which would lead to extensive line broadening.

Another complication was the appearance of a broad singlet in the $g = 1.97$ [Figure 3(*b*)] region (species β). This only appeared in certain annealing experiments and the species must be transient since it was rapidly lost on further annealing. One possibility is that NO radicals are responsible. These $(\pi^*)^1$ radicals, in the absence of strong solvation, are not expected to give rise to a detectable resonance, so if NO is responsible it must be undergoing some very specific interaction with solvent.

Another transient signal sometimes formed during the annealing process is shown in Figure 3(*c*) (species α). This signal is either due to an iron complex having $g_1 = 2.004$, $g_2 = 2.025$, and $g_3 = 2.040$, or to a species with $g_\parallel$ and $g_\perp$ values in the 2.025 region, and a 'parallel' coupling to ^{14}N of *ca.* 30 G. If the former analysis is correct, the species would probably be a transient Fe^{III} derivative. The latter possibility suggests the formation of a species with high spin density on nitrogen. If we take $A_\parallel = 30$ G and $A_\perp \approx 0$, then $2B \approx 20$ G and $a_p^2 \approx 0.6$. This species only appears after the loss of the $H_2\dot{C}OH$ signals, so it may be formed by attack of these radicals on $[Fe(CN)_5(NO)]^{2-}$ ions. Two alternatives are structures (III) and (IV). Complex (III) is a nitroxide and could well have properties of the type found.[18,19] However, the *g* shifts and extent of delocalisation onto iron are larger than has previously been found for such complexes. Structure (IV), on the other hand, is also expected to have a ^{14}N contribution of the type



(III)



(IV)

observed, and the *g* values and delocalisation could well be of the magnitude observed. This is because σ–π overlap is very large for such species.[20] We favour structure (IV), and suggest that further annealing leads to the reaction (IV)→(I) + $HOCH_2$-CN which helps to account for the growth in (I) on annealing.

Conclusion

The complex set of results is, in our view, rationalised by the Scheme shown earlier. The first stage of process (*i*) is reversible, and only proceeds if (*iii*) can follow. Process (*ii*) occurs in all systems. It is a relatively minor pathway for most solvents, but dominates for aqueous solutions, for which (*iii*) does not occur. Various relaxation processes occur on annealing above 77 K. Species (I′) usually gives (I) by loss of cyanide, but in some mixed aqueous systems process (*vii*) is preferred. Process (*v*) is the least thermally efficient of these steps, but ultimately, species (I) is the stable product. There was no marked wavelength sensitivity in these studies.

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