Photolysis of the $[Fe(CN)_5(NO)]^{2-}$ Ion in Water and Poly(vinyl alcohol) Films: Evidence for Cyano Radical, Cyanide Ion and Nitric Oxide Loss and Redox Pathways

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Ultraviolet–visible and IR spectroscopy and mass spectrometry have been used to investigate photolysis of the $[Fe(CN)_5(NO)]^{2-}$ ion upon irradiation with UV/VIS light in aqueous solutions and in poly(vinyl alcohol) films at 12 and 298 K. Changes in the ν(CN) and ν(NO) bands in the IR and in the d–d and charge-transfer bands in the UV/VIS region were used to monitor the appearance and disappearance of complex ions as a function of photolysis time. Mass spectrometric analysis of the gaseous products released during the irradiation of aqueous solutions revealed NO, HCN and $(CN)_2$. The combined results showed that the $[Fe(CN)_5(NO)]^{2-}$ ion undergoes photoaquation and photoreduction, producing aquacyanoferrate-(III) and -(II) species. The origin of the iron(II) species was shown to be mainly due to the photoreduction of the iron(III) species produced after primary loss of the nitrosyl ligand as molecular NO and not as NO^+. Subsequent thermal reactions between the iron-(II) and -(III) species led to the formation of mixed-valence compounds, *e.g.* Prussian blue. A scheme for the photochemical and thermal reactions with $CN^•$, CN^- and NO loss pathways is proposed. The possible implications of the results for the use of $[Fe(CN)_5(NO)]^{2-}$ as a vasodilator are discussed.

The photosensitivity of transition-metal cyanide complexes has been noted and studied by many authors.[1-5] Among these the photochemistry of sodium pentacyanonitrosylferrate, $Na_2[Fe(CN)_5(NO)]$ (sodium nitroprusside), has received special attention. Part of this interest has been directed towards elucidating the species formed under irradiation.[6-13] A very recent interest in the photosensitivity of this compound, however, has been motivated by its widespread use as a potent vasodilator for the lowering of blood pressure during surgery and in the management of hypertensive crises and cardiac failure.[14,15] In spite of its beneficial action, some authors have reported decomposition reactions on mixing with blood, cyanide being released.[16] Bisset *et al.*[14] have concluded, however, that it is light and not blood which is responsible for the release of the cyanide.

The photosensitivity of $Na_2[Fe(CN)_5(NO)]$ solutions has long been recognized.[17] Mitra *et al.*[6] studied the pH changes during the photolysis of $[Fe(CN)_5(NO)]^{2-}$ solutions with unfiltered light and suggested the primary photochemical process to be as in equation (1) followed by aquation of the cyanoferrate(II) species. A pH decrease was found upon photolysis and this was attributed to hydrolysis of the nitrosyl cation [equation (2)]. It was also observed that there was a larger change in the pH of aerated solutions compared with deaerated solutions.[18] This suggests an alternative photoprocess involving the ejection of NO which can be oxidized to NO_2 and producing NO_2^-, NO_3^- and H_3O^+ ions.

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

$$NO^+ + 3H_2O \rightleftharpoons 2H_3O^+ + NO_2^- \quad (2)$$

Wolfe and Swinehart,[10] however, have ruled out the NO^+ production based on experiments with labelled water and labelled $[Fe(CN)_5(NO)]^{2-}$. They proposed that the change in hydrogen-ion concentration during photolysis could be partly due to NO production followed by hydrolysis of the aquacyanoferrate(III) species according to reactions (3) and (4).

$$[Fe(CN)_5(NO)]^{2-} + H_2O \xrightarrow{h\nu} [Fe^{III}(CN)_5(H_2O)]^{2-} + NO \quad (3)$$

$$[Fe^{III}(CN)_5(H_2O)]^{2-} \rightleftharpoons [Fe(CN)_5(OH)]^{3-} + H_3O^+ \quad (4)$$

Interestingly, Espenson and Wolenuk[19] have shown the species with an absorption maximum at 395 nm to be the aquacyanoferrate(III) ion, $[Fe^{III}(CN)_5(H_2O)]^{2-}$. This lends credence to equation (3) as a primary process.

Schindler and Zink[20] using continuous-wave excited-state Raman spectroscopy and more recently, Stochel *et al.*[21] using UV/VIS spectroscopy, also found evidence for the loss of nitric oxide in a primary photosubstitution process (5) (solv = solvent molecule). The last authors concluded that the formation of NO^+ and $[Fe^{II}(CN)_5(H_2O)]^{3-}$ is only a minor reaction pathway, although such a pathway could become important for highly nucleophilic solvents.

$$[Fe(CN)_5(NO)]^{2-} \xrightarrow{h\nu} [Fe^{III}(CN)_5(solv)]^{2-} + NO \quad (5)$$

Other authors[9,11] have studied the effects of UV light and γ-rays on such solutions and in the solid state at 77 K by electron spin resonance spectroscopy (ESR). It was concluded that in aprotic solvents a major pathway involved electron transfer from solvent to give $[Fe^{I}(CN)_5(NO)]^{3-}$ or $[Fe^{II}(CN)_5(NOH)]^{2-}$ in the protonated form,[22,23] although such a pathway could not be invoked for aqueous systems.

Evidence for the release of NO, HCN and $(CN)_2$ during the photolysis of $[Fe(CN)_5(NO)]^{2-}$ was also obtained by mass spectrometry[8,10] but no mechanisms were proposed to explain the formation of HCN and $(CN)_2$.

In this paper we describe new experiments using IR and UV/VIS spectroscopy and mass spectrometry to identify primary photoproducts, intermediates and volatile gases in the photolysis of $[Fe(CN)_5(NO)]^{2-}$ in water and poly(vinyl alcohol) (pva) films. The use of such films has allowed low-temperature matrix studies of the non-volatile $[Fe(CN)_5(NO)]^{2-}$ ion with the aim of trapping unstable intermediates.

Experimental

Analar grade sodium pentacyanonitrosylferrate(II) dihydrate was used in all experiments. Poly(vinyl alcohol) (*M ca.* 14 000, BDH Lab. Reagents) was used in the preparation of all polymer films. Prussian blue was synthesised according to a literature procedure.[24]

The closed-cycle liquid-helium cryostat, spectrophotometers, photolysis lamp and details of mounting films have been described previously.[25,26] The irradiations with $\lambda > 230$, 415 and 430 nm light were achieved by using wavelength-selective glass filters (Corion Corp.).

To monitor the photolysis of concentrated aqueous solutions, capillary films of the solutions were held between two CaF_2 windows (3 mm thick). In this case, spectra of the same sample were obtained in the IR and UV/VIS regions after each irradiation period. A quartz cuvette (path length 1 cm) with Teflon stopper was used to obtain the UV/VIS spectra of dilute solutions. Films clamped between CaF_2 windows and solutions in the quartz cuvette were placed at 7 cm from the lamp in sample holders for the irradiations.

Neutral solutions of $[Fe(CN)_5(NO)]^{2-}$ were prepared with deionized water in a darkened room, transferred to the cuvette or to the CaF_2 windows and protected against light using aluminium foil until the beginning of the irradiation. They were not degassed, and there was no stirring during irradiation in the cuvettes. Solutions of concentration 3×10^{-2} mol dm^{-3} were used for mass spectrometry, concentrated solutions (*ca.* 0.5 mol dm^{-3}) for IR spectroscopy and dilute solutions ($< 2 \times 10^{-5}$ mol dm^{-3}) for analysis of the changes in the charge-transfer (c.t.) bands near 200 nm.

The pva films containing 1.5% w/w of $Na_2[Fe(CN)_5(NO)]$ and 0.5% w/w of Prussian blue were prepared by casting films from aqueous solutions. In each case, powdered pva (350 mg) was dissolved in hot deionized water in a Petri dish (inside diameter 5.5 cm) on a stirrer-hotplate. After cooling the polymer solution the solid complex was added with stirring in the dark. The water was allowed to evaporate at room temperature in the dark for about 4 d to give solid films of uniform thickness (*ca.* 100 μm). Films were extracted from the Petri dishes, cut to give 20 mm diameter discs using a template and placed between two optical CaF_2 windows for the irradiation and spectroscopic measurements.

Blank pva films containing 5% w/w sodium cyanide were prepared by casting from a basic sodium hydroxide–water solution (pH 10). Neutral saturated aqueous solutions of sodium cyanide, freshly prepared, were used to obtain the IR spectrum of the free CN^- ion in water. Nitric oxide from a commercial cylinder was bubbled through water at 5 °C. A capillary film of this NO-saturated solution between two CaF_2 windows was used to obtain the IR spectrum of free NO in water.

Mass spectra were obtained using a VG Analytical 70-250-SE normal-geometry double-focusing spectrometer. All data were recorded under electron-ionization conditions at 70 eV (*ca.* 1.12×10^{-17} J), with a source temperature of 200 °C, a 6 kV accelerating voltage and a 100 μA trap current. Data were processed and recorded on a PDP 11/73 data system. Samples were introduced into the electron-ionizing ion-source volume using a modified dynamic fast atom bombardment (FAB) probe with a fused-silica capillary (inside diameter 75 μm) *via* a direct-insertion probe lock.[27]

Results

Mass Spectrometry.—Mass spectral measurements using a modified dynamic FAB probe technique were carried out for aqueous solutions of $[Fe(CN)_5(NO)]^{2-}$ at room temperature. Mass-range scans from m/z 500 to 10 showed signals for NO, HCN and $(CN)_2$, in addition to background air and water. The total ion current curves obtained for the monitoring of NO, HCN and $(CN)_2$ using three different filters can be seen in Fig. 1. Irradiation with unfiltered light and with light having $\lambda > 230$ nm led to similar results [Fig. 1(*a*) and 1(*b*)].

The first gases to be detected in the early periods of irradiation are NO and HCN. The signal for HCN increased with time and reached a plateau after *ca.* 1200 s. Nitric oxide was detected with a small delay (after *ca.* 150–220 s) and its signal also increased to a plateau. The amount of HCN released is much smaller than that of NO. The rate of increase of the HCN signal was slightly reduced relative to the NO signal when light with $\lambda > 230$ nm [blocking most of the d–π(CN) absorption] was used. In these two cases a signal for $(CN)_2$ was detected after a longer delay and its growth followed a different pattern, with a smaller rate of increase and with the plateau taking more time to be reached. In addition, the amount of $(CN)_2$ released reached much higher values compared to those of HCN and NO. These differences suggest that NO and HCN are released in primary photochemical process, and that $(CN)_2$ is produced in a secondary photoprocess. However, in this analysis it should be noted that some differences may arise from differences in the solubilities and diffusion coefficients of these gases in water. Interestingly, no NO_2 was detected.

When light with $\lambda > 415$ nm was used the rates of release of NO and HCN were both decreased compared to the irradiation with $\lambda > 230$ nm. The release of $(CN)_2$ in this case was observed with a much longer delay (after *ca.* 1400 s) and its rate of increase followed a different pattern compared to the previous cases, underlining the conclusions that $(CN)_2$ is generated in a secondary photoprocess.

During the irradiation with $\lambda > 430$ nm over 4750 s no HCN or $(CN)_2$ were detected. However, NO was still released although the amount and the rate of increase of the signal were both highly reduced reaching a plateau after *ca.* 2400 s [Fig. 1(*d*)]. These results showed that irradiation with $\lambda > 430$ nm prevents the release of CN^- from the $[Fe(CN)_5(NO)]^{2-}$ ion but NO is still ejected under these conditions.

To check for possible contributions from thermal reactions, mass spectral experiments were performed while heating a concentrated $[Fe(CN)_5(NO)]^{2-}$ solution in the dark for 2400 s. These experiments showed that there was no release of HCN or $(CN)_2$ but that NO started to be released in very small amounts after the temperature of the solution reached *ca.* 60 °C [Fig. 1(*d*)].

Photolysis of the $[Fe(CN)_5(NO)]^{2-}$ *Ion.*—(*a*) *Infrared spectra and band assignments.* The IR spectral data on crystalline $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ and other alkaline-earth metal nitroprussides have been published by many authors.[28–31] A representative spectrum of $[Fe(CN)_5(NO)]^{2-}$ in aqueous solution is shown in Fig. 2(*a*). The main spectral features can be assigned to the terminal CN and NO vibration modes of the anion. Frequencies and assignments of the ν(CN) and ν(NO) vibrations of crystalline $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ in a Nujol mull and of the $[Fe(CN)_5(NO)]^{2-}$ ion in aqueous solutions and pva films are presented in Table 1. In water and pva at 298 K, only the most intense bands corresponding to the antisymmetric CN stretching and NO fundamental stretching vibrations of the $[Fe(CN)_5(NO)]^{2-}$ ion can be observed. The CN band is superimposed on a very broad but weak water band with a maximum near 2125 cm^{-1}. This broad band is the counterpart of the 'association band' in ice which is composed of overtones of intermolecular modes or a combination of the band of 1645 cm^{-1} with an intermolecular mode, or a combination of both.[33] The position of the ν(NO) band shifts from

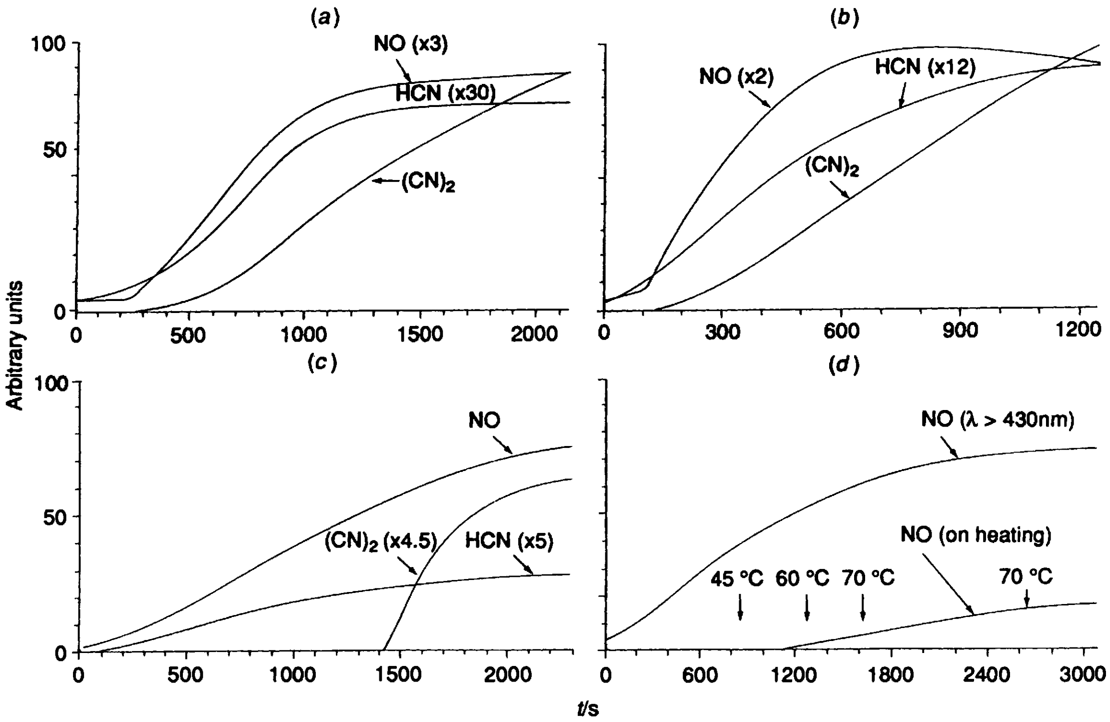

Fig. 1 Reconstructed ion chromatograms representing the amount of NO, HCN and $(CN)_2$ released with time during the photolysis of aqueous solutions of $Na_2[Fe(CN)_5(NO)]$ at 301 K; for details see Experimental section. (*a*) Unfiltered light; (*b*) λ > 230 nm; (*c*) λ > 415 nm; (*d*) comparison of the amount and onset of NO ejected on photolysis with that on heating

Table 1 Terminal CN and NO stretching vibrations of $Na_2[Fe(CN)_5(NO)]{\cdot}2H_2O$ in Nujol mull and of $[Fe(CN)_5(NO)]^{2-}$ in water and pva films

		$\tilde{\nu}/cm^{-1}$				
Vibration*	Species*	Nujol (298 K)	Water (298 K)	pva (298 K)	pva (12 K)	Assignment*
ν_1	A_1	2173				ν(CN)
ν_{16}	E	2161 2157				ν(CN)
ν_2	A_1	2144	2142	2142	2145	ν(CN)
ν_3	A_1	1939	1937	1915	1920	ν(NO)

* Based on ref. 32.

1939 cm^{-1} in the crystal (in Nujol mull) to lower values in pva (1915 cm^{-1}) and water (1937 cm^{-1}). This suggests that ν(NO) in the complex is sensitive to the solvent polarity.

(*b*) *Photolysis in aqueous solution as monitored by IR spectroscopy.* Infrared spectral changes obtained upon irradiation of concentrated solutions of $[Fe(CN)_5(NO)]^{2-}$ are shown in Fig. 2. After brief irradiation periods the principal bands of $[Fe(CN)_5(NO)]^{2-}$ [ν(CN) at 2142 cm^{-1} and ν(NO) at 1937 cm^{-1}] decreased and four new bands appeared at 2115, 2075 (shoulder), 2040 and 1835vw cm^{-1}. The bands at 2115 and 1835 cm^{-1} can be assigned to the aquacyanoferrate(III) ion $[Fe^{III}(CN)_{6-x}(H_2O)_x]^{(3-x)-}$ and to free NO respectively, indicating a photoejection of the NO ligand as NO (*i.e.* nitric oxide) leaving a cyanoferrate(III) species. The assignment of the band at 1835 cm^{-1} is in accordance with the detection of NO by mass spectrometry and was confirmed by comparison with the IR spectrum of NO dissolved in water. [The stretching frequency for free NO is reported at 1840 cm^{-1} while nitrosonium (NO^+) salts absorb at 2200–2300 cm^{-1}.[15,34]] The assignment of the band at 2115 cm^{-1} was confirmed by comparison[35] with irradiated solutions of $[Fe^{III}(CN)_6]^{3-}$. The bands at 2075 and 2040 cm^{-1} both increased with subsequent irradiation times while that at 2115 cm^{-1} started to decrease, indicating secondary processes leading to the consumption of the iron(III) species. Under extended irradiation, the solution became blue indicating the formation of mixed-valence compounds. The band at 2075 cm^{-1} is consistent with the absorption band of Prussian blue.[24,36,37] This assignment has been confirmed by comparison with the IR spectrum of Prussian blue dissolved in water.*

The formation of mixed-valence compounds implies the presence of iron(II) species. This is consistent with the band observed at 2040 cm^{-1} which can be assigned to the ν(CN) vibration of the aquacyanoferrate(II) species $[Fe^{II}(CN)_{6-x}(H_2O)_x]^{(4-x)-}$. This assignment was confirmed by comparison with the spectrum of irradiated solutions of $[Fe^{II}(CN)_6]^{4-}$. The band at 2040 cm^{-1} evolves as the main absorption during the course of photolysis in aqueous solution and becomes the dominant band after extensive irradiation [Fig. 2(*f*)]. The shoulder observed at *ca.* 2080 cm^{-1} can be assigned to the free CN^- ejected and detected as HCN by mass spectrometry. This assignment was confirmed by comparison with the band

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* Prussian blue has been described in two formulations, the 'soluble' form, $KFe^{III}[Fe^{II}(CN)_6]$, and the 'insoluble' form, $Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}6H_2O$, with the common names having historical rather than actual solubility connotations. It has been shown that chemical reduction and oxidation of Prussian blue can lead to Prussian white (Everit's salt), $K_2Fe^{II}[Fe^{II}(CN)_6]$, and Prussian green (Berlin green), $Fe^{III}[Fe^{III}(CN)_6]$, respectively.[38,39]

obtained for free CN^- in aqueous sodium cyanide solution. A shoulder at 2170 cm^{-1} developed after storing the photolysed solution in the dark and can be assigned to the formation of small amounts of iron(III) hexacyanoferrate(III) or Berlin green[38] $Fe^{III}[Fe^{III}(CN)_6]$. A fifth new band appeared at 2270 cm^{-1}. This is in the absorption region of the nitrosyl cation (NO^+). However, it was also observed during the irradiation of aqueous solutions of $[Fe^{III}(CN)_6]^{3-}$ under the same experimental conditions.[35] It cannot therefore be assigned to NO^+.

(*c*) *Low-temperature photolysis in pva films as monitored by IR spectroscopy.* Attempts to form low-temperature media by freezing films of aqueous solutions were unsuccessful because $[Fe(CN)_5(NO)]^{2-}$ precipitated while the dilute solutions were being frozen. Freezing $[Fe(CN)_5(NO)]^{2-}$ dissolved at high dilution in pva films led to reproducible experiments at 12 K and also at 298 K. In order to check for spurious pva photoproducts, films of pva were extensively irradiated at 12 and 298 K. These experiments revealed that under irradiation with unfiltered light for more than 5 h there was no detectable change in the IR spectrum of pva in the range 2400–1800 cm^{-1}.

Infrared spectra of $[Fe(CN)_5(NO)]^{2-}$ in pva film at 12 K in the range 2300–1800 cm^{-1} are shown in Fig. 3. Under irradiation at 12 K the first spectral changes observed were a new broad band with maximum at *ca.* 2084 cm^{-1} and a shoulder at 2050 cm^{-1}. With further periods of irradiation an additional band appeared as a shoulder at *ca.* 2115 cm^{-1}. The absorptions at 2040 and 2115 cm^{-1} can be assigned again to aquacyanoferrate-(II) and -(III) species respectively, while the absorption with maximum at 2084 cm^{-1} can be assigned to the vibration of the ejected free CN^- ligands, trapped in the polymer medium at 12 K. These assignments were confirmed by comparison with the bands of NaCN, $[Fe^{III}(CN)_6]^{3-}$ and

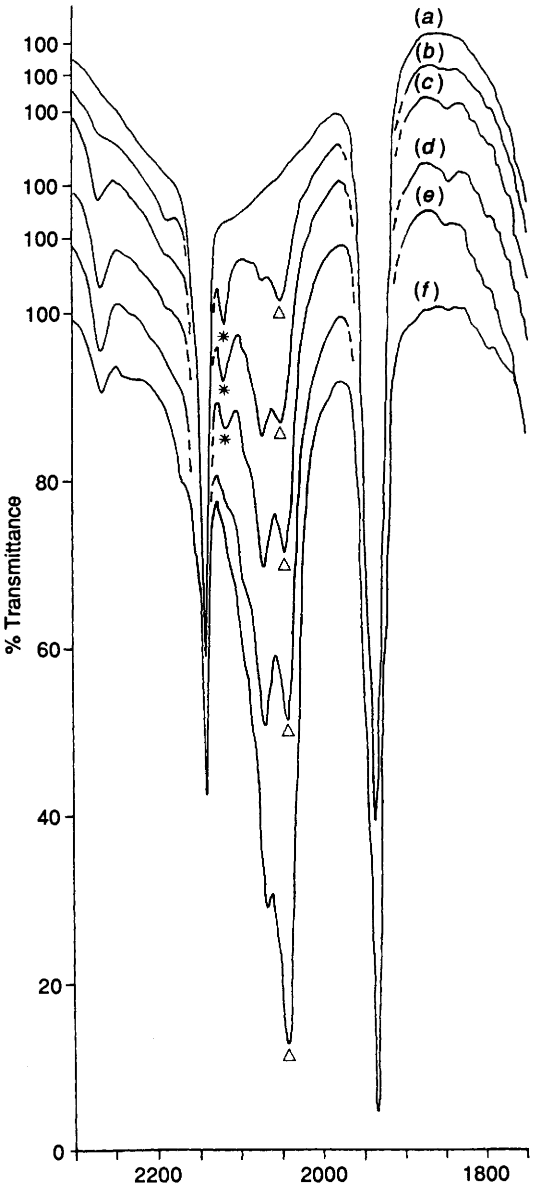


Fig. 2 Infrared spectral changes obtained during the irradiation of a concentrated aqueous solution of $Na_2[Fe(CN)_5(NO)]$ at 298 K with unfiltered light: (*a*) before irradiation and after irradiation for 7 (*b*), 17 (*c*), 32 (*d*), 67 (*e*) and 127 min (*f*). Bands marked * are due to $[Fe^{III}(CN)_{6-x}(H_2O)_x]^{(3-x)-}$ species and those marked Δ are due to $[Fe^{II}(CN)_{6-x}(H_2O)_x]^{(4-x)-}$ species. For clarity, the spectra have been displaced vertically from each other

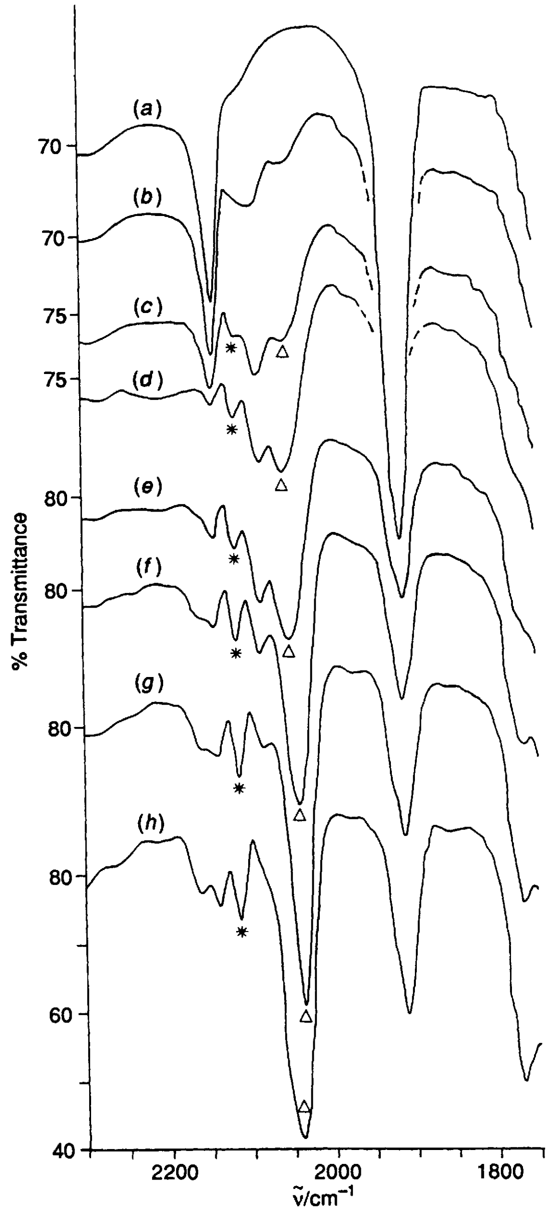


Fig. 3 Infrared spectral changes obtained during the irradiation of $Na_2[Fe(CN)_5(NO)]$ dissolved in pva film (1.5% w/w) at 12 K with unfiltered light: (*a*) before irradiation, after irradiation for 60 (*b*), 470 (*c*) and 570 min (*d*), after warming for 3.5 (*e*) and 5.5 h (*f*) and (*g*) after 1 d in the dark at room temperature. Other details as in Fig. 2

$[Fe^{II}(CN)_6]^{4-}$ dissolved in pva.[35] On warming the sample in the dark, the band at 2084 cm^{-1} shifts to 2080 cm^{-1} and decreases, while the band at 2050 cm^{-1} shifted to 2040 cm^{-1} and increased together with the band at 2115 cm^{-1}. These changes indicate thermal back reactions with diffusion of the free CN^- and H_2O to the iron-(III) and -(II) species. Such back reactions involving water in the pva matrix are to be expected since the polymer contains *ca.* 8% residual water.[40] However, hydrolysis of the free CN^- and release of HCN is expected to occur only to a very small extent in the vitreous polymer media at 298 K. As a consequence, the trapped free CN^- ions can back react in slow diffusion-dependent thermal processes. After storing the sample in the dark for several days the band at 2040 cm^{-1} becomes broader and more intense, overlapping the weak band of the remaining free CN^-, and a shoulder appeared at 2170 cm^{-1}. This shoulder can be assigned to the formation of a small amount of Berlin green.[39] The new band at 2270 cm^{-1} observed in water was not detected in this case.

The transient absorption at 2084–2080 cm^{-1} in Fig. 3 cannot be assigned to Prussian blue because of the lack of the accompanying visible band at 680 nm. In addition, the formation of mixed-valence compounds implies the diffusion of the iron-(III), -(II), CN^- and K^+ species through the medium which is not expected to occur at 12 K on the experimental time-scale.

(*d*) *Electronic spectra and band assignments.* The band maxima and shoulders for the UV/VIS spectrum of aqueous $Na_2[Fe(CN)_5(NO)]$ are listed in Table 2. The band absorption envelopes are made up of several overlapping components (Fig. 4) making it difficult to irradiate into specific isolated electronic transitions. This difficulty was increased by the fact that the bands tail extensively to long wavelengths. The lowest-energy band occurs at *ca.* 500 nm and has been assigned to a metal-to-ligand charge-transfer (m.l.c.t.) [d_{xy} to $\pi^*(NO)$] transition. The second low-energy band occurs at *ca.* 400 nm and has been assigned to a m.l.c.t. [$d_{xy,yz}$ to $\pi^*(NO)$] transition. This transition is from a predominantly metal-localized bonding orbital [61% $d_{xz,yz}$ and 25% $\pi^*(NO)$] to an orbital localized primarily on the NO ligand [23% $d_{xz,yz}$ and 73% $\pi^*(NO)$].[41] The higher-energy band in the region 240–330 nm, which comprises three shoulders, has been assigned to d–d transitions and is overlapped with an intense m.l.c.t. [d_{xy} to $\pi^*(CN)$] band[41] at 200 nm.

(*e*) *Photolysis in aqueous solution monitored in the UV/VIS region.* The UV/VIS spectral changes corresponding to those in the IR region are shown in Fig. 4. Irradiation of dilute solutions of $[Fe(CN)_5(NO)]^{2-}$ with $\lambda < 430$ nm for short periods of time led to an increase in absorption in the 250–450 nm region together with a decrease in the d_{xy}–$\pi^*(CN)$ band at 198 nm [Fig. 4(*a*)]. When concentrated aqueous solutions are irradiated, the increase in the absorption in the 250–450 nm region correlates with the growth of two new bands with maxima at *ca.* 325 and 394 nm [Fig. 4(*b*)]. Comparison of the results for dilute and more concentrated solutions showed that the same photoproducts have been formed, *i.e.* there is no concentration dependence in the range 10^{-1}–10^{-5} mol dm^{-3}.

The new band maxima correspond to the positions for aquacyanoferrate-(II) and -(III) species respectively,[19,35] which suggests that these species are primary photoproducts of $[Fe(CN)_5(NO)]^{2-}$. Upon further irradiation the band at *ca.* 325 nm became the dominant feature in this region, indicating that the production of aquacyanoferrate(II) species is favoured after the initial periods of irradiation. Brief irradiation of more concentrated aqueous solutions and of pva films at 298 K also show a transient increase in the absorption bands at *ca.* 410 and 490 nm [Fig. 4(*c*)] assigned to d–$\pi^*(NO)$ transitions. In subsequent periods of irradiation these absorptions decrease in intensity as expected with ejection of the NO ligand. The initial increase in the intensity of these bands can be assigned to the growth of the band with a maximum at 394 nm [Fig. 4(*b*)], assigned to aquacyanoferrate(III), and raising of the baseline on the high-energy side of this band. After extensive periods of irradiation a new band with maximum at 680 nm appears and the solutions become blue. This band at 680 nm is characteristic of Prussian blue[42,43] and corresponds to the band of Prussian blue prepared in this work. In the last period of irradiation of the concentrated $[Fe(CN)_5(NO)]^{2-}$ solutions the formation of a colloidal red precipitate was observed, which is consistent with iron(III) hydroxide.

The corresponding spectral changes observed in the region 320–680 nm during the photolysis in pva films can be seen in Fig. 4(*c*) and are analogous to those observed in aqueous solution presented above. Again there was no concentration-dependence effect in the range 1–10% w/w. The spectral changes at $\lambda < 320$ nm cannot be studied in pva films because there is a strong absorption band of the polymer in this region.

Discussion

The results of irradiation of the $[Fe(CN)_5(NO)]^{2-}$ ion, which were found to be independent of concentration, are summarized

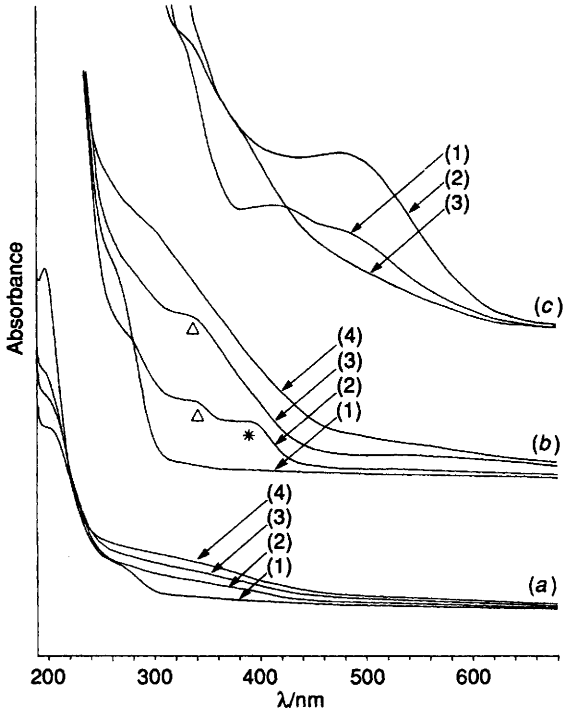


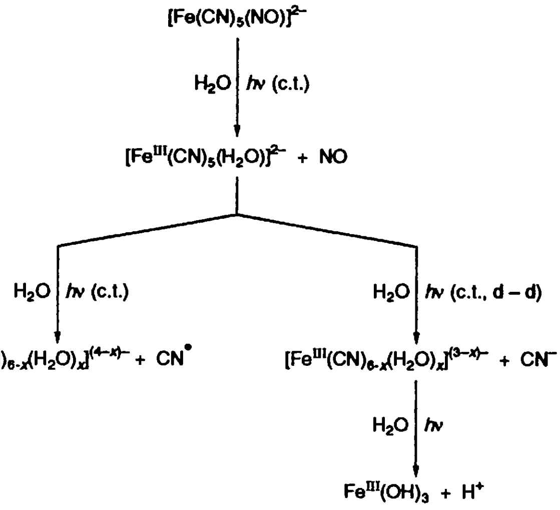
Fig. 4 Spectral changes in the UV/VIS region obtained during the irradiation of $Na_2[Fe(CN)_5(NO)]$ at 298 K with unfiltered light: (*a*) *ca.* 2×10^{-5} mol dm^{-3} solution; (1) before irradiation and after irradiation for 1 (2), 2 (3) and 26 min (4); (*b*) 4.0×10^{-2} mol dm^{-3} solution; (1) before irradiation and after irradiation for 1 (2), 2.5 (3) and 14 min (4); (*c*) in 1.5% w/w pva film; (1) before irradiation and after irradiation for 45 (2) and 290 min (3). Symbols as in Fig. 2

Table 2 Electronic spectral data for $[Fe(CN)_5(NO)]^{2-}$

λ_{max}/nm

Calculated[a]	Literature[b]	This work[c]	Assignment[a]
486	498	490	$d_{xy} \longrightarrow \pi^*(NO)$
398	394	410	$d_{xz,yz} \longrightarrow \pi^*(NO)$
325	330	330 (sh)	$d_{xy} \longrightarrow d_{x^2-y^2}$
265	265	265 (sh)	$d_{xy,yz} \longrightarrow d_{z^2}$
244	238	—	$d_{xz,yz} \longrightarrow d_{x^2-y^2}$
200	200	198	$d_{xy} \longrightarrow \pi^*(CN)$

[a] Adapted from ref. 41. [b] Ref. 10. [c] In aqueous solution.



Scheme 1 Main photochemical pathways in the irradiation of the $[Fe(CN)_5(NO)]^{2-}$ ion in aqueous solution with unfiltered UV/VIS light

in Scheme 1. Mass spectrometry, with the identification of HCN, $(CN)_2$ and NO, has provided a new dimension in determining the photochemical pathways involved in the photodecomposition of $[Fe(CN)_5(NO)]^{2-}$. The mass spectral results and the IR and UV/VIS spectral changes indicate that the primary photoprocess under excitation of the c.t. and d–d bands of the complex is ejection of the NO ligand as NO, leaving a d^5 $[Fe^{III}(CN)_5(H_2O)]^{2-}$ ion with substitution-labile CN ligands.

The solutions in this work were not deaerated because of the intention to compare the model situation with the actual clinical use of $[Fe(CN)_5(NO)]^{2-}$ (see below). Since iron(II) species are photochemically and thermally stable in aerated aqueous solutions, as has been confirmed in parallel work with cyanoferrate(II) ions,[35] the species which is most sensitive to O_2 is NO. This species was clearly detected by mass spectrometry and IR spectroscopy. It would appear, therefore, that aeration/deaeration was not a crucial factor.

The iron(III) complex, $[Fe^{III}(CN)_5(H_2O)]^{2-}$, formed in the primary photoprocess can lose all the remaining CN ligands upon continuous irradiation,[35] explaining the release of HCN and the precipitation of $Fe(OH)_3$. However, prolonged irradiation of $[Fe(CN)_5(NO)]^{2-}$ has been shown to lead to production of the aquacyanoferrate(II) complex as the main photoproduct and finally to the formation of Prussian blue. The formation of iron(II) species and of CN• radicals can result from the photoreduction of the previously formed iron(III) species with ejection of CN• which dimerizes to give $(CN)_2$.

Although the formal and real charge on the Fe atom in $[Fe(CN)_5(NO)]^{2-}$ is a point of debate,[28,32,44] the results obtained in this work indicate that this charge corresponds to Fe^{2+} with a d^6 configuration, in accordance with the observed diamagnetism of $[Fe(CN)_5(NO)]^{2-}$.[22,23] The mass spectral detection of NO upon irradiation of aqueous solutions of $[Fe(CN)_5(NO)]^{2-}$ and the absence of signals in the IR region corresponding to the absorption of the NO^+ cation upon corresponding irradiation in pva provide evidence against the photoejection of NO^+ as a principal photoprocess. However, the ejection of NO^+ cannot be completely ruled out based on the results of this work, but it should be considered as a minor pathway.

In the mechanism discussed above, the ejected CN• and NO ligands are expected to be substituted by water molecules. The mixing of iron(III) species and $[Fe^{II}(CN)_4(H_2O)_2]^{2-}$ in the presence of CN^- can finally lead to the observed formation of Prussian blue and other mixed-valence complexes.

In respect of the use of aqueous solutions of $[Fe(CN)_5(NO)]^{2-}$ as a vasodilator in medical procedures, it is clear that the release of cyanide (and to a lesser extent, cyanogen) in blood can be caused by the action of UV or visible light from room light. This means that such solutions are highly photosensitive and thus extreme care must be taken in manipulating them for infusions.

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