Photochemistry of Inorganic Complex Ions in Alkali Halide Matrices

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Summary Infrared spectroscopy of inorganic complex ions in alkali halide discs at 77 K has been used for the first time to investigate reactive species in the photoreactions of Cr^{III}, Fe^{III}, and Co^{III} compounds.

THE nature of intermediates in the photochemical reactions of organometallic compounds, especially metal carbonyls, has been established by the i.r. and u.v.-visible spectra of such species trapped in frozen matrices of the rare gases, N_2, CH_4, and CO at 10—20 K.[1] In spite of much detailed

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investigation, the nature of intermediates in the thermal and photochemical reactions of co-ordination compounds remains a matter of speculation.[2] Intermediates arising from such complexes are not amenable to study in gas matrices because the parent complexes are involatile. We report here for the first time on the wide range of photochemical reactions which can be observed upon u.v. irradiation of inorganic complex ions in alkali halide disc matrices at 77 K.

Irradiation of $K_3Fe(CN)_6 \cdot 3H_2O$ in either KBr or KCl discs (0·2 mg : 250 mg) at 77 K,‡ using a medium-pressure Hg arc, produced four new i.r. bands in the terminal CN stretching region (2079w, 2061w, 2033s, and 2021s cm^{-1}) corresponding to the previously reported[3] bands of $K_4Fe(CN)_6 \cdot 3H_2O$§ in a KBr disc. Unlike the experiments with cobalt and chromium complexes (see below), there was no thermal reversal when the discs were warmed to room temperature. The irradiated disc, on dissolution in water, gave the characteristic blue colour with $FeCl_3$ confirming the presence of $[Fe(CN)_6]^{4-}$.

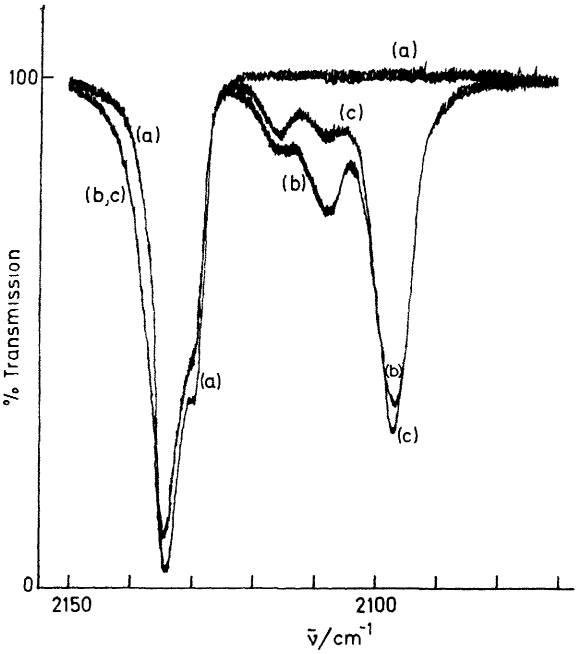

Figure 1. I.r. spectra from an experiment with $K_3[Cr(CN)_6]$ in a KBr disc at 77 K: (a) before irradiation, (b) after irradiation with full Hg arc for 30 min, and (c) after warming to 293 K, recooling to 77 K, and irradiation with $\lambda > 300$ nm for 60 min.

Irradiation of $[Co(NH_3)_5(NO_2)]Cl_2$ in a KBr disc (1 mg : 250 mg) at 77 K gave new i.r. bands in the 1600—800 cm^{-1} region showing quantitative *nitro* → *nitrito-O* linkage isomerisation.[4] Such isomerisation also occurs to a lesser extent on irradiation of KBr disc samples at 293 K and on irradiation of samples of $[Co(NH_3)_5(NO_2)](NO_3)_2$ as Nujol mulls or as finely powdered solids at 293 K.[5] X-Ray crystallographic studies[6] of the *nitro*- and *nitrito-O* isomers of $[Co(NH_3)_5(NO_2)]Cl_2$ have confirmed that thermal *nitrito-O* → *nitro* and photochemical *nitro* → *nitrito-O* isomerisations occur *via* intramolecular processes. After the KBr disc of the *nitrito-O* isomer had been left for a while at 293 K, i.r. bands of the *nitro* isomer reappeared. This is consistent with the greater thermodynamic stability of the *nitro* isomer.[5,6]

A number of new i.r. bands appeared on u.v. irradiation of $K_3[Cr(CN)_6]$ in a KBr disc (1 mg : 250 mg) at 77 K, as indicated in Figure 1. The parent peak, a doublet at 2135 and 2130 cm^{-1}, decreases in intensity as the photolysis proceeds, while product bands appear at 2140w,sh, 2113m, 2109m, and 2096s cm^{-1}. Changing the matrix material to KCl has no apparent effect on the progress or nature of the reaction, nor does mixing and grinding powders of $K_3[Cr(CN)_6]$ and KBr as opposed to freeze drying[7] of a solution of these compounds prior to pressing. These different methods of preparing discs might have been expected to produce macroscopic and microscopic dispersions respectively. However, when $Cs_3[Cr(CN)_6]$ is irradiated in a CsCl disc the product bands are at 2104s and 2097m,sh cm^{-1}. We have determined that the species responsible for the band at 2109 cm^{-1} is either less efficiently formed with $\lambda > 300$ nm (Figure 1) or is preferentially destroyed by long-wavelength light. On warming the irradiated discs to *ca.* 200 K, the new bands disappeared and the spectra reverted to that of the original material [Figure 2(d)]. The different behaviour of the various bands on warm-up (Figure 2) suggests that several different species are involved.

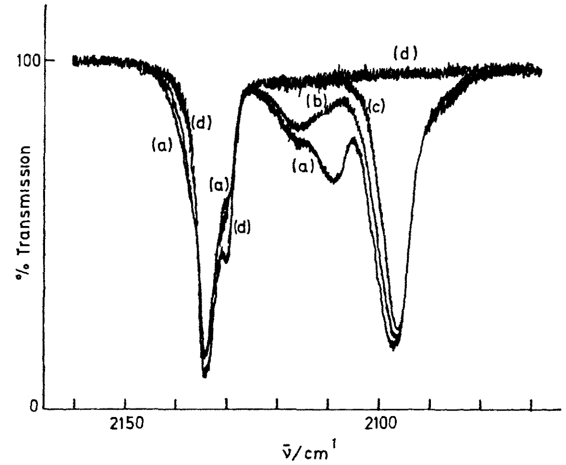

Figure 2. I.r. spectra, all measured at 77 K, from an experiment with $K_3[Cr(CN)_6]$ in a KBr disc (a) after u.v. irradiation and then after warming to (b) *ca.* 170 K, (c) *ca.* 200 K, and (d) 293 K.

Unlike the conversion of $[Fe(CN)_6]^{3-}$ into $[Fe(CN)_6]^{4-}$ described above, the i.r. spectra produced on irradiation of $[Cr(CN)_6]^{3-}$ do not correspond to $[Cr(CN)_6]^{4-}$ which has

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‡ All discs were pressed at 20,000 lb in^{-2} *in vacuo* (10^{-1} Torr), mounted between CsI plates, and cooled by liquid N_2 in a conventional glass cryostat at 10^{-3} Torr. I.r. spectra were recorded using a Perkin-Elmer 225 grating spectrometer.

§ The i.r. spectrum of $K_4Fe(CN)_6 \cdot 3H_2O$ in the crystal is extremely complicated. It has been suggested (V. Lorenzelli and P. Delorme, *Spectrochim. Acta*, 1963, **19**, 2033) that this is because the compound may exist in monoclinic (C_{2h}^6) or quadratic (C_{4h}^6) forms in the crystalline state with extra bands arising from site and factor-group splittings. Similar effects might be found for some ions in alkali halide discs.

been separately characterised by i.r. spectroscopy.[8,9] The warm-up and long-wavelength photolysis reversals are very reminiscent of gas matrix isolation studies of co-ordinatively unsaturated metal carbonyl fragments,[1] *e.g.* $Cr(CO)_5$, suggesting that one of the new species is $[Cr(CN)_5]^{2-}$. Such a species would be consistent with a dissociative pathway for the photoaquation of $[Cr(CN)_6]^{3-}$; *cf.* the dissociative photoaquation of $[Co(CN)_6]^{3-}$.[10] No accompanying new band for free CN^- (2080 cm^{-1}) was observed. However, this band would have been very weak because its extinction coefficient is at least tenfold smaller than that of the parent compound[4] and the photo-conversion in the primary steps was also small.

Future work will aim to elucidate the identity of the new cyanochromium species¶ *via* monosubstituted parent complexes, and to explore applications of the new low temperature alkali halide disc technique to the mechanistic photochemistry of other involatile co-ordination compounds.

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¶ Attempts to identify the fragments using ^{13}CN-labelling and energy factored force field fitting of the i.r. spectra in the terminal CN stretching region failed because the interaction force constants, $k_{\text{CN,CN}}$, in $[Cr(CN)_6]^{3-}$ and the fragments are essentially zero.

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