

PHOTOCHEMISTRY OF TRANSITION METAL CYANO COMPLEX IONS IN POLY(VINYL ALCOHOL) FILM MATRICES AT 77 - 293 K

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(Received July 3, 1984; in revised form August 16, 1984)

Summary

IR spectroscopy studies have been used for the first time between 77 K and 293 K to investigate reactive ionic species in poly(vinyl alcohol) films; photolysis of $[\text{Cr}(\text{CN})_6]^{3-}$ is proposed to yield the species $[\text{Cr}(\text{CN})_5]^{2-}$ and $[\text{Cr}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ and new species arising from $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ have been detected.

The nature of intermediates in the photochemical reactions of organometallic compounds, especially metal carbonyls, has been established by the IR and UV-visible spectra of such species trapped at 10 - 20 K in frozen gas matrices, e.g. Ar, N₂, CH₄ and CO [1]. In spite of much detailed investigation, the nature of intermediates in the thermal and photochemical reactions of coordination 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. One attempt to overcome this problem entailed the UV-visible irradiation of inorganic complex ions in alkali halide disc matrices at 77 K followed by warming to 293 K [3]. The new unstable species were observed by IR spectroscopy. A possible objection to this procedure was that individual ions could not be truly isolated in alkali halide discs, *cf.* the criteria for matrix isolation studies [1].

As part of a general investigation of the viability of polymer films as alternatives to gas matrices [4], we report here for the first time[†] the use of IR spectroscopy to characterize species formed on irradiation of transition metal cyano complex ions in poly(vinyl alcohol) (pva) film matrices at 77 K.

Irradiation of $\text{K}_3[\text{Cr}(\text{CN})_6]$ in a pva film[‡] at 293 K using light corresponding to the ligand field bands ($\lambda_{\text{max}} = 310 \text{ nm}$ and 375 nm) and charge

[†]The only previous report of the photolysis of an inorganic complex ion in a poly(vinyl alcohol) film matrix employed UV-visible spectroscopy at room temperature and no detailed structural information about reactive intermediates was obtained [5].

[‡]Films (15 - 20 mg complex: 5 g pva (BDH; ~4000 a.m.u.)) were cast from distilled water (200 ml) on glass plates in the dark in a manner similar to that described by Fucaloro and Zanella [5].

transfer band ($\lambda_{\max} = 260$ nm) produced no change in the IR spectrum in contrast with the facile photoaquation at 293 K in solution [6 - 9]. At 77 K with the film clamped between two CaF_2 windows in a glass cryostat evacuated to 10^{-4} Torr, however, irradiation for 60 min using an unfiltered medium pressure 125 W mercury arc lamp produced a decrease in parent molecule bands[†] (ν_{CN} : 2137(w), 2134(s), 2132(m) and 2129(s) cm^{-1})

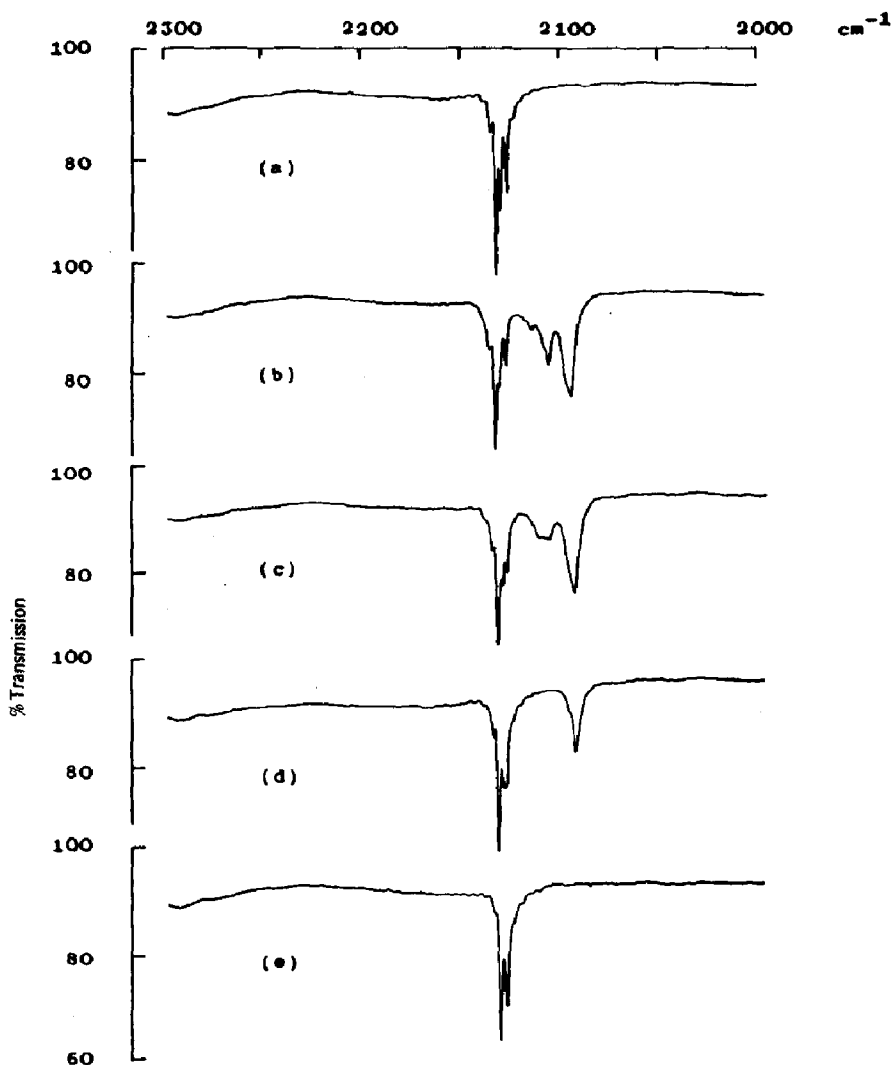


Fig. 1. IR spectra (Nicolet 7199 Fourier Transform IR spectrometer; 1 cm^{-1} resolution) from an experiment with $\text{K}_3[\text{Cr}(\text{CN})_6]$ in a pva film at 77 K: (a) before irradiation, (b) after irradiation with full mercury arc for 60 min, (c) after warming to about 150 K, (d) after warming to about 220 K, and (e) after warming to 293 K.

[†] Splittings of bands in gas matrices are frequently observed and can be ascribed to packing of the host matrix molecules around the substrate [10]. Similar effects will presumably occur for polymer films. Additional splittings were observed when films were subjected to modest stretching ($\sim 5\%$).

together with new IR bands at 2115(w), 2109(w,sh), 2107(m), 2099(m,sh) and 2096(s) cm^{-1} (Fig. 1(b)) and a new UV band at 237 nm (Pye Unicam SP 1800B spectrometer). On allowing the refrigerant (nitrogen) to boil off the film warmed up and it was observed that the new bands disappeared after different times of warm-up (figs. 1(c) and 1(d)), *i.e.* a number of species were present, until complete reversal was noted at 293 K (Fig. 1(e)).

The reversal of the bands on warm-up is reminiscent of gas matrix isolation studies of coordinatively unsaturated metal carbonyl fragments [1], *e.g.* $\text{Cr}(\text{CO})_5$, suggesting that one of the new species is probably $[\text{Cr}(\text{CN})_5]^{2-}$. Such a species would be consistent with a dissociative pathway for the photoaquation of $[\text{Cr}(\text{CN})_6]^{3-}$. Experience with poly(vinyl chloride) (pvc) film matrices shows that fragments not coordinated by the polymer undergo reversal at lower temperatures than those involved in coordination either to the residual casting solvent (approximately 5% by weight of the cast film) or to the polymer [4]. On this basis the bands at 2115, 2109 and 2107 cm^{-1} which reverse below 200 K can probably be assigned to $[\text{Cr}(\text{CN})_5]^{2-}$ while those at 2099 and 2096 cm^{-1} which reverse in the temperature range 220 - 250 K can probably be assigned to $[\text{Cr}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$. It is interesting to note the growth and thermal decay of terminal CN stretching bands in the KBr disc experiments [3] is analogous to that described above for pva films with the exception that the bands in KBr are broader, *e.g.* the doublets at 2099 and 2096 cm^{-1} and 2109 and 2107 cm^{-1} in pva appear as singlets at 2096 and 2104 cm^{-1} in KBr discs. In both pva film matrices and KBr disc matrices no accompanying new band for free CN^- (about 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 [11] and the photoconversion in the primary steps was also modest.

Other cyano complexes also gave new IR and UV-visible bands when irradiated in dilute pva films at 77 K and 298 K, *e.g.* $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ and $\text{K}_3[\text{Co}(\text{CN})_6]$. It seems, therefore, that the pva film technique has considerable potential for elucidating the mechanistic photochemistry of involatile coordination compounds. Future work will aim to characterize definitively the new cyanochromium species[†] and to explore applications of the technique to other ligand dissociation, rearrangement and linkage isomerism processes.

Acknowledgment

We thank the Science and Engineering Research Council for a Studentship (R.H.H.) and for support (A.J.R.).

[†] Attempts to identify the fragments using ^{13}C -labelling and energy-factored force field fitting of the IR spectra in the terminal CN stretching region (*cf.* the identification of metal carbonyl fragments) may not be very successful because the interaction force constants $k_{\text{CN},\text{CN}}$ for metal cyano complexes are very small.

References

- 1 J. K. Burdett, *Coord. Chem. Rev.*, 27 (1978) 1.
R. B. Hitam, K. A. Mahmoud and A. J. Rest, *Coord. Chem. Rev.*, 55 (1984) 1.
- 2 A. W. Adamson, *Pure Appl. Chem.*, 51 (1979) 313.
R. T. Walters, H. Macke and A. W. Adamson, *J. Phys. Chem.*, 83 (1979) 2097.
- 3 G. B. Porter and A. J. Rest, *J. Chem. Soc., Chem. Commun.*, (1980) 869.
- 4 R. H. Hooker and A. J. Rest, *J. Organomet. Chem.*, 249 (1983) 137; *J. Chem. Soc., Dalton Trans.*, (1984) 761.
R. H. Hooker, A. J. Rest and I. Whitwell, *J. Organomet. Chem.*, 266 (1984) C27.
- 5 A. F. Fucaloro and A. W. Zanella, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 515.
- 6 R. Schwarz and K. Tede, *Chem. Ber.*, 60 (1927) 69.
- 7 A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, 76 (1954) 4223.
- 8 L. Moggi, F. Bolletta, V. Bulzani and F. Scandola, *J. Inorg. Nucl. Chem.*, 28 (1966) 2589.
- 9 A. Chiang and A. W. Adamson, *J. Phys. Chem.*, 72 (1968) 3827.
- 10 A. J. Barnes, W. J. Orville-Thomas, in A. Müller and R. Gaufrès (eds.), *Matrix Isolation Spectroscopy*, NATO ASI Series, Reidel, Dordrecht, 1981.
- 11 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn., Wiley, New York, 1978.