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PHOTOCHEMICAL AND THERMAL BEHAVIOUR OF ISOCYANIDE COMPLEXES

V*. PHOTOLYSIS OF $Fe(CNCH_3)_4(CN)_2$ IN ACETONITRILE

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Summary

Direct irradiation of acetonitrile solutions of $Fe(CNCH_3)_4(CN)_2$ in both CT and LF bands leads to gradual ligand–solvent substitution and the solvated intermediates $Fe(CNCH_3)_3(NCCH_3)(CN)_2$ and $Fe(CNCH_3)_2(NCCH_3)_2(CN)_2$ are formed in two subsequent steps. The quantum yield of the first step of photosolvation ($\varphi = 0.5$) is independent of the wavelength of irradiation. Benzophenone is a high energy triplet donor for this compound, and sensitizes the photosolvation with a limit quantum yield of 0.56. The results point to the same reactive triplet state for the direct and the sensitized reaction.

Introduction

Investigations of the isocyanide complexes of Fe^{II} [1–8] have established that in these compounds the primary photochemical reaction is independent of the kind of compound considered and of the nature of the excited state produced by the irradiation. Thus both in compounds with IL and CT bands and in those with only LF bands a heterolytic fission of the Fe–C bond occurs, followed by probable formation of a pentacoordinate intermediate and by fast solvent attack. However, the overall process, resulting from concomitant thermal and photochemical reactions, appears to be a function of the compound considered and of the experimental conditions. To throw further light on this matter we have examined the direct and sensitized photolysis in acetonitrile, of $Fe(CNCH_3)_4(CN)_2$, a compound which exhibits both CT and LF bands.

Experimental

The *trans*-$Fe(CNCH_3)_4(CN)_2$ was prepared from $Fe(CNCH_3)_6Cl_2$ by a procedure reported previously [4]. The monosolvated intermediate $Fe(CNCH_3)_3$-

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* For parts I–IV see refs. 5–8.

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$(NCCH_3)(CN)_2$ was prepared by irradiation of the starting compound in acetonitrile at 300 nm and subsequently precipitated with ether (λ_{max} 363 nm; ϵ 470).

The apparatus for the irradiation, the measurement of the incident light, and the determination of the spectra were as described previously [6].

Direct irradiation was carried out with solutions of $0.5–2.0 \times 10^{-3}$ *M* concentration; more concentrated solutions were slightly turbid.

The sensitization experiments were carried out under the following conditions: [benzophenone] 1.3×10^{-2} *M*; [substrate] in the range $1.7–0.5 \times 10^{-3}$ *M*; λ_{exc} 350 nm. Under these conditions most of the irradiation was absorbed by the sensitizer. However, the photolysis was followed until 10% of the reaction had occurred and the data were corrected for the contribution of the direct absorption. The experiments on quenching of the direct and sensitized photoreaction involved the presence of ferrocene at concentrations up to 10^{-2} *M* and light of 350 nm.

The phosphorescence quenching of the benzophenone was carried out with $0.52–3.9 \times 10^{-4}$ *M* $Fe(CNCH_3)_4(CN)_2$ with exciting light of 365 nm, and was monitored at 455 nm.

Results and discussion

Direct irradiation of $Fe(CNCH_3)_4(CN)_2$ in acetonitrile. The absorption spectra of the *trans*-$Fe(CNCH_3)_4(CN)_2$ showed an LF band at 315 nm (ϵ 355) and a high intensity CT band at 218 nm (ϵ 21500). The shift to higher wavelengths of the CT band relative to that for $Fe(CNCH_3)_6(BF_4)_2$ and the overlapping of the second LF band were expected as a consequence of the replacement of two neutral ligands by

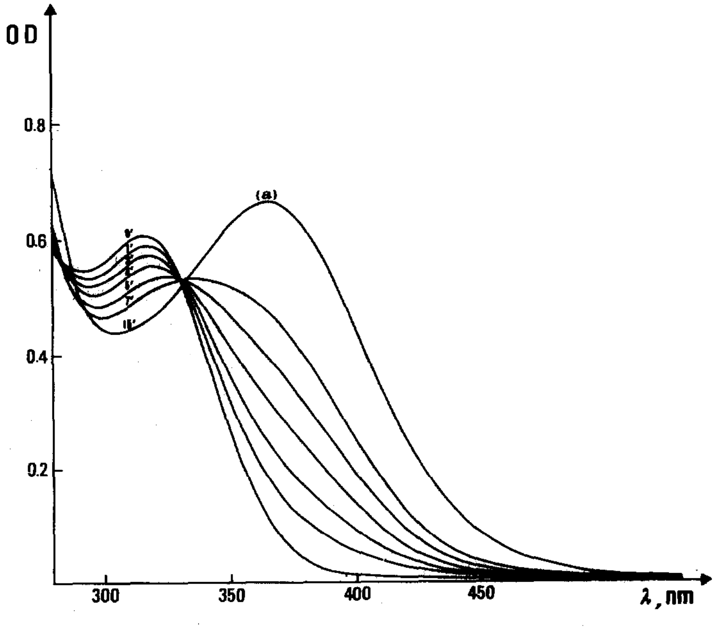

Fig. 1. Results of irradiation of $Fe(CNCH_3)_4(CN)_2$ in acetonitrile at 300 nm for various times: formation of a solution enriched with monosolvated intermediate (a).

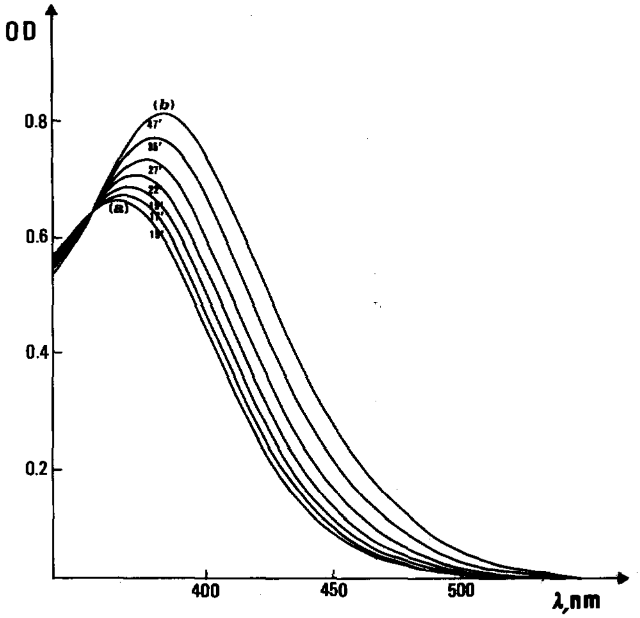

Fig. 2. Irradiation at 350 nm of the solution enriched with monosolvated intermediate (a), and formation of a mixture enriched with bisolvated intermediate (b).

two charged ligands. The compound was stable in the dark, but the irradiation at all the wavelengths used (254, 300 and 350 nm) promoted loss of isocyanide ligands. When the spectral changes were monitored the absorption spectrum was seen initially to shift towards the visible with formation of a maximum at 365 nm; two isosbestic points at 330 and at 286.5 nm were observed at short times of irradiation. When the irradiation was continued, the isosbestic points disappeared and a new maximum, shifted towards 390 nm, appeared. At suitable irradiation wavelengths a new isosbestic point, at 355 nm appeared, but could be observed only for a short time because upon more prolonged irradiation a slight opalescence was produced.

These features of the spectral changes, which are emphasized by subsequently irradiating at two suitable wavelengths, 300 and 350 nm, (Fig. 1 and 2) show that photolysis occurs through two distinct photochemical steps. At first, only a monosolvated intermediate is formed, but when its absorption has attained a value which allows it to compete with the starting compound for the light, it undergoes further photolysis, with formation of a mixture enriched with bisolvated intermediate; a new isosbestic point between the mono- and bi-solvated intermediates is observed when the absorption of the starting compound is negligible. The overall process can be accounted for in terms of the following reaction scheme involving release of two isocyanides one at a time:

$$\mathrm{Fe(CNCH_3)_4(CN)_2} \xrightarrow{h\nu,\ \mathrm{NCCH_3}} \mathrm{Fe(CNCH_3)_3(NCCH_3)(CN)_2 + CNCH_3}$$

$$\mathrm{Fe(CNCH_3)_3(NCCH_3)(CN)_2} \xrightarrow{h\nu,\ \mathrm{NCCH_3}} \mathrm{Fe(CNCH_3)_2(NCCH_3)_2(CN)_2 + CNCH_3}$$

When the irradiation is continued, the bisolvated intermediate probably in its turn undergoes photolysis, and less soluble decomposition products are formed.

We were able to isolate only the first intermediate, all attempts to isolate the second one being unfruitful.

The nature of the isolated intermediate was confirmed by elemental analysis and by its ^{1}H NMR spectrum. In the ^{1}H NMR spectrum of the starting compound the only peak, at 3.43 ppm, is due to the methyl protons of the four equivalent isocyanides. In the ^{1}H NMR spectra of the monosolvated intermediate there are two new peaks, at 3.52 and at 3.33 ppm, with the integration for the first double that of the second, as expected for $Fe(CNCH_3)_3(NCCH_3)(CN)_2$. The peak at 3.52 ppm is attributable to two equivalent isocyanides, and that at 3.33 ppm to the third isocyanide.

Knowledge of the absorption spectrum of the monosolvated intermediate allowed us to calculate the quantum yield for the first step of the photochemical reaction. The quantum yield was found to be the same at 350, 300 and 254 nm, and to have a value of 0.52 ± 0.01.

These findings differ from those for photolysis of the same compound in water, which leads to a diaquo complex and has a low quantum yield ($\varphi = 0.1$). They also differ from those for the photolysis in acetonitrile of the other isocyanide complexes of Fe^{II}, for which the quantum yields are low and are a function of the irradiation wavelengths. For the latter compounds it was suggested [6–8] that the vibrationally excited states are involved in the photochemical process. For $Fe(CNCH_3)_4(CN)_2$, the lowest state of the ligand field, attained directly or by fast radiationless decays from higher states, may well be responsible for the photolysis. The high quantum yield may be related to the effect of the two apical CN ligands, which weaken the bonds of the equatorial isocyanides.

Sensitized photolysis

Benzophenone, benzil and $Ru(bipy)_3Cl_2$ (E_T 288.4, 225.7, and 212.8 kJ, respectively) were examined as possible triplet energy donors for the $Fe(CNCH_3)_4(CN)_2$. Preliminary phosphorescence quenching experiments were performed; in each case the data were corrected for the fraction of light absorbed by the substrate. The benzophenone phosphorescence was quenched by $Fe(CNCH_3)_4(CN)_2$ with a constant of bimolecular quenching rate K_q 1.5×10^9 M^{-1} s^{-1}, whereas the benzil and $Ru(bipy)_3Cl_2$ phosphorescence were not quenched for concentrations of acceptor up to 10^{-3} M; thus only benzophenone is a suitable triplet energy donor.

The benzophenone sensitized the photosolvation of $Fe(CNCH_3)_4(CN)_2$, and the first step of the reaction was studied kinetically and the limit quantum yield was calculated; the value, corrected for the direct reaction, is 0.56 (K_q 8×10^8 M^{-1} s^{-1}). It is evident that the triplet state, populated by energy transfer, leads to the same process as is observed under direct excitation. The almost equal values of quantum yields suggest that there is only one reactive triplet state, populated by energy transfer in sensitization experiments and in the direct irradiation by intersystem crossing with almost unitary efficiency (0.52/0.56). With the aim of confirming this possibility we carried out experiments on direct and sensitized photolysis in the presence of a spectrochemically suitable quencher, ferrocene. Unfortunately, in our conditions, the optimal experimental ones, this quencher does not influence either the direct photoreaction or the sensitized one, and so these experiments were unsuccessful and only indicate a value of $K_{SV} \simeq 0$ (i.e. the lifetime of the triplet is too small or the transfer process inefficient).

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