Journal of Organometallic Chemistry, 289 (1985) 81–90
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOCHEMICAL AND THERMAL BEHAVIOUR OF ISOCYANIDE COMPLEXES

III *. PHOTOCHEMISTRY OF Fe(bipy)$(CNCH_3)_4(BF_4)_2$ AND Fe(bipy)$(CNCH_3)_2(C_4H_{10}N_4)(BF_4)_2$ IN ACETONITRILE

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(Received January 1st, 1985)

Summary

The salt Fe(bipy)$(CNCH_3)_4(BF_4)_2$ reacts with an excess of hydrazine in CH_3CN to give the dicarbene complex *cis*-Fe(bipy)$(CNCH_3)_2(C_4H_{10}N_4)(BF_4)_2$. The reaction is of pseudo first-order, and obeys the rate law $k_{obs} = k[N_2H_4]$. The rate constant k and the activation parameters have been calculated, and a mechanism is proposed. On irradiation in acetonitrile, both Fe(bipy)$(CNCH_3)_4{}^{2+}$ and the dicarbene complex undergo a process of replacement of coordinated CH_3CN by solvating CH_3NC, the reaction involving an initial photochemical step which gives a monosolvated intermediate. In the case of Fe(bipy)$(CNCH_3)_4{}^{2+}$ a subsequent fast thermal step gives a bisolvated intermediate in equilibrium with the monosolvated species, so that a photostationary equilibrium is attained. In the case of the dicarbene complex a second photochemical step leads to a stable bisolvated compound. For both compounds the quantum yields of the photochemical steps, calculated at 254 and 350 nm, increase with the exciting radiation energy, and this is consistent with the hypothesis of a dissociative mechanism for the photosolvation.

Introduction

During our investigations of the photochemical and thermal behaviour of isocyanide complexes, we studied the Fe^{II} isocyanide $Fe(bipy)_2(CNCH_3)_2{}^{2+}$ [1] and its carbene derivative $Fe(bipy)_2(C_4H_{10}N_4)^{2+}$ [2]. In the present paper we consider the

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* For Parts I and II see ref. 2 and 1, respectively.

kinetics of formation of $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$ from $Fe(bpy)(CNCH_3)_4^{2+}$ and N_2H_4 and the photochemistry of both the parent compound and its carbene derivative, with the aim of obtaining a better general understanding of the thermal and photochemical reactivity of isocyanide compounds.

Experimental

Preparation of the compounds

(a) The complex $Fe(bipy)(CNCH_3)_4(BF_4)_2$ (cf. ref 3). A solution of $K_2Fe(bipy)(CN)_4$ (1 g) in $(CH_3)_2SO_4$ (15 ml) was heated under reflux at 50°C for about 5 h, then cooled, filtered, and treated with water. The product was precipitated from the concentrated aqueous solution by addition of saturated aqueous $NaBF_4$ and was recrystallized from acetonitrile/n-propanol. UV spectra (in acetonitrile): λ_{max} 355 nm, ε 2750 (CT band); λ_{max} 312 nm, ε 12800 (mixed CT-IL band); λ_{max}, 302, 278 and 240 nm, ε 10000, 17000 and 21000 respectively (IL bands).

(b) The complex cis-$Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)(BF_4)_2$. A solution of $Fe(bipy)(CNCH_3)_4(BF_4)_2$ (600 mg) and hydrazine hydrate (1 ml) in 20 ml of acetonitrile was refluxed at 50°C for about 2 h, then cooled, acidified with 3.6 ml of 40% HBF_4, and added to 40 ml of ether. Following extraction with 5% aqueous HBF_4 and removal of residual traces of ether by evaporation under vacuum, the product precipitated out as orange crystals and was recrystallized from 10% aqueous $NaBF_4$.

Anal. Found: C, 36.89; H, 3.98; N, 19.0. $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)(BF_4)_2$: C, 37.12; H, 4.12; N, 19.25.

Apparatus

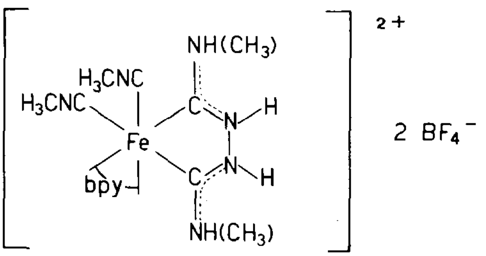
The elemental analyses were carried out with a C. Erba elemental analyzer Mod 1106. The PMR spectra were recorded in CD_3CN at 80 MHz on a Bruker WP-80 spectrometer at room temperature in the FT mode, with TMS as internal standard. All UV and visible spectra were recorded on a Perkin–Elmer 330 spectrophotometer equipped with a 3600 data station. The IR spectra (Nujol and as KBr pellets) were recorded on a Perkin–Elmer Mod. 257 spectrophotometer. The apparatus and procedures used for irradiation and for measuring the incident light were as described previously [1].

Monochromatic radiation of 350 or 254 nm was provided by a Rayonet photochemical reactor equipped with sixteen appropriate 24 W lamps. The intensity of the incident light was 5×10^{-6} einstein min^{-1} for both radiations. Before irradiation all samples were deaerated by prolonged nitrogen bubbling.

Results and discussion

Characterization and formation kinetics of $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$

Reaction of $Fe(bipy)(CNCH_3)_4^{2+}$ with an excess of hydrazine in refluxing acetonitrile yielded a dicarbene complex, which was isolated as the tetrafluoborate salt:



The elemental analysis and the IR and PMR spectra were in accord with the assigned formula. There were IR bands (cm^{-1}) at: 3430 and 3330 (ν(N–H)); 3080 and 2930 (ν(C–H)); 2180 and 2150 (ν(CN)); 1470 and 1445 (ν(N$\cdots$C$\cdots$N) and δ(N–H)). The splitting of the stretching band of CN indicated that the compound had the *cis* configuration. All the stretching frequencies of 2-2′-bipyridine were present.

In the PMR spectrum of $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$ the presence of two singlets (δ 3.23 and 3.47 ppm) attributable to the two coordinated isocyanide molecules, and of two doublets (3.04–3.10 and 2.54–2.60 ppm) due to the methyls bonded to the carbene ring, confirmed the *cis*-symmetry of the complex. The signals from the coordinated bipyridine appear at 7.41–8.45 ppm.

The visible spectrum of the acetonitrile solution of the dicarbene shows a CTML band at 430 nm (ε 2650). The shift of this band to longer wavelength compared with that of the parent compound confirmed the assumption [4] that the dicarbene ligand is a poorer π-acceptor and a stronger σ-donor than the two isocyanides. In the UV region two bands at 292 (ε 23 500) and at 235 nm (ε 19 500) attributable to

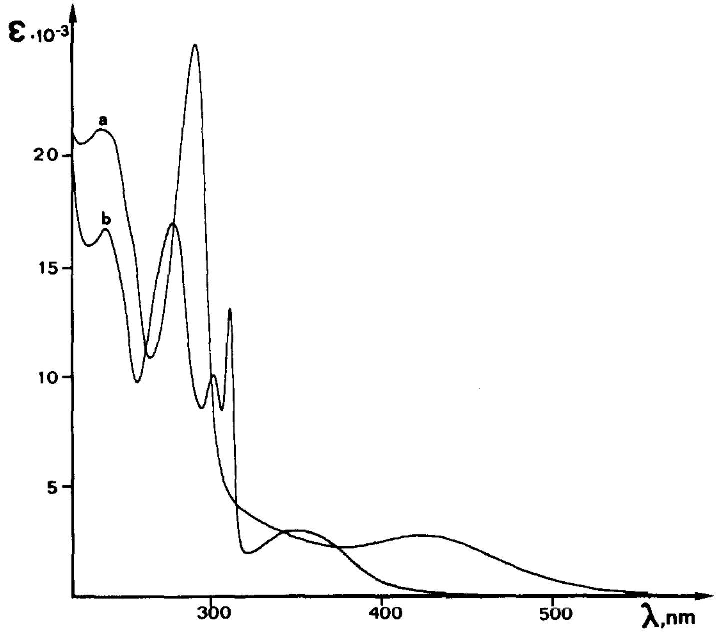


Fig. 1. UV and visible spectrum of $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$ (a) in acetonitrile; for comparison the spectrum of the parent compound $Fe(bipy)(CNCH_3)_4{}^{2+}$ (b) is also shown.

bipyridine are predominant (Fig. 1). Like other dicarbenes [5] this compound exhibits acid-base properties. Thus in the presence of a base such as hydrazine, it undergoes deprotonation to form a monocationic species:

$$\mathrm{Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+} + N_2H_4 \rightleftharpoons Fe(bipy)(CNCH_3)_2(C_4H_9N_4)^{+} + N_2H_5^{+}}$$

As the N_2H_4 concentration was changed, the variation of the ratio of the deprotonated and protonated forms was revealed by the change of the absorption spectrum (Fig. 2). The two isosbestic points (at 407.6 and 457.6 nm) confirmed that only these two species are present. Above a $[N_2H_4]/[\text{dicarbene}]$ ratio of about 800 the spectrum of the solution was practically insensitive to further additions of base, showing the dicarbene compound to be entirely in the deprotonated form. This species has the CT band shifted to 485 nm (ε 2450) in accord with the lower acceptor capacity of the deprotonated dicarbene ligand.

From the spectrophotometric data we derive an equilibrium constant K of 1.75×10^{-2} (error $\simeq$ 5%), which is independent of temperature in the range 25–40°C.

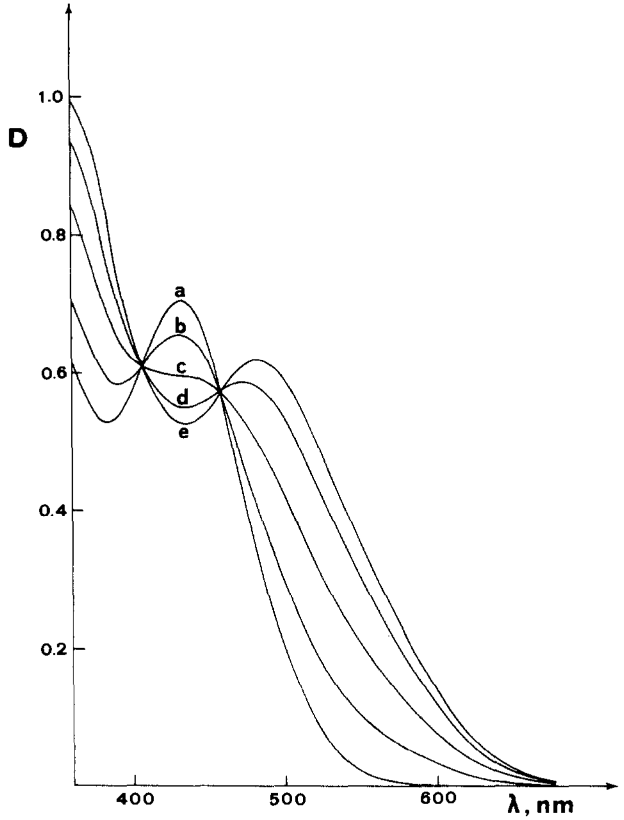
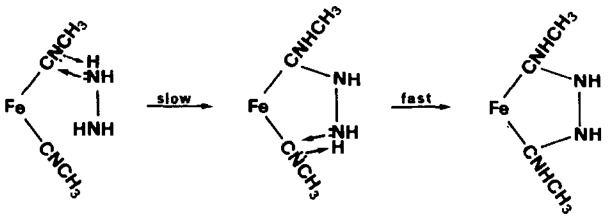


Fig. 2. Changes of the absorption spectra of $\mathrm{Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}}$ (0.3×10^{-3} *M*) at various concentrations of hydrazine, $[N_2H_4] = 0$ (a); 0.12×10^{-2} *M* (b); 1.2×10^{-2} *M* (c); 5.6×10^{-2} *M* (d); 0.2 *M* (e).

By comparing this value with that (8.4×10^{-4}) for the analogous equilibrium involving $Fe(bipy)_2(C_4H_{10}N_4)^{2+}$ [2] we can see that the dicarbene complex is more acidic than the latter complex.

The kinetics of formation of the carbene complex were studied at various temperatures (25–40°C) with concentrations of $Fe(bipy)(CNCH_3)_4{}^{2+}$ in the range 0.8×10^{-3} to 3.5×10^{-3} M and with an excess of hydrazine of 0.06–0.3 M, and were followed spectrophotometrically at the isosbestic points and at the maximum for the monocationic species up to 10% reaction. Under conditions used the reaction was pseudo first-order, and the observed rate constant was a function of the hydrazine concentration, i.e. $k_{obs} = k[N_2H_4]$. The values of k and the activation parameters are summarized in Table 1, in which the data for $Fe(bipy)_2(C_4H_{10}N_4)^{2+}$ [2] are included for comparison. The kinetics were the same as those for $Fe(bipy)_2(C_4H_{10}N_4)^{2+}$ and other carbenes [6], and the same mechanism can be assumed to operate, involving two steps. The first step, which is rate-determining, involves a concerted attack on the C and N atoms of an isocyanide ligand by the N and H of the hydrazine; in the second, fast, step a further interaction between NH and CN leads to ring closure and dicarbene complex formation.



A higher rate constant was expected for $Fe(bipy)(CNCH_3)_4{}^{2+}$ than for $Fe(bipy)_2(CNCH_3)_2{}^{2+}$ since it should be easier to penetrate and modify the coordination sphere in the former because of the lower steric hindrance.

Photochemical behaviour of $Fe(bipy)(CNCH_3)_4{}^{2+}$ *and* $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$

In the dark at room temperature both the compounds were inert even in the presence of free ligands. When the acetonitrile solutions were irradiated there was obvious release of $CNCH_3$, and solvation occurred with a shift in the absorption maximum towards the visible. The photochemical process was monitored by the spectral changes until a photostationary state was attained.

For the compound $Fe(bipy)(CNCH_3)_4{}^{2+}$ (Fig. 3) the maximum for the photostationary state solution varied, in the range 355–385 nm, with the irradiation wave-

TABLE 1

KINETIC DATA FOR FORMATION OF $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$ DATA FOR THE PARENT COMPOUND $Fe(bipy)_2(C_4H_{10}N_4)^{2+\cdot}$ FORMATION ARE SHOWN FOR COMPARISON

	$k(M^{-1}\ s^{-1})$ at 25°C	$\Delta H^\ddagger$ (kJ M^{-1})	$\Delta S^\ddagger$ (J M^{-1} K^{-1})
$Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$	0.15×10^{-2}	59 ± 3	-100 ± 5
$Fe(bipy)_2(C_4H_{10}N_4)^{2+}$	0.55×10^{-4}	57 ± 3	-145 ± 7

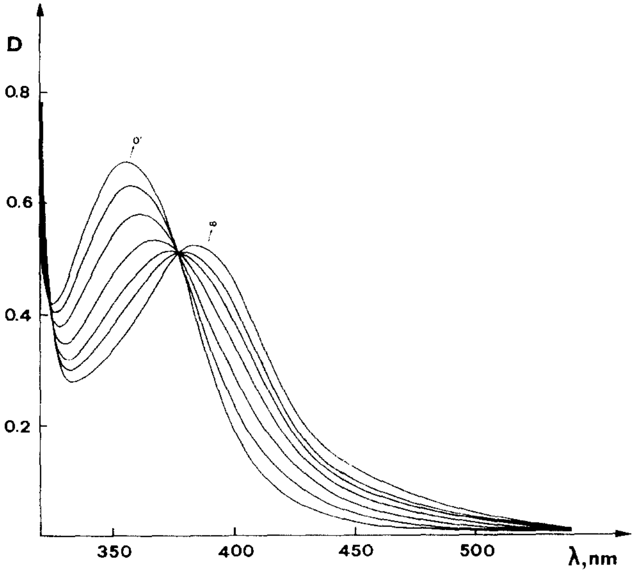


Fig. 3. Spectral changes of Fe(bipy)$(CNCH_3)_4^{2+}$ upon irradiation at 350 nm.

length and with the initial concentration; this indicated that an equilibrium existed. For solutions of concentration in the range 0.5×10^{-3} to 1×10^{-3} *M* and irradiation at 350 nm the maximum appeared at 385 nm. We precipitated the photoequilibrium mixture from the irradiated solutions by addition of a small amount of ether. Because the absorption spectrum of the mixture in acetonitrile and of the reflectance spectrum of the solid were close to that of the irradiated solution at equilibrium, we concluded that no alteration occurred during the isolation process. The elemental analysis of the precipitate was the same as that of the starting compound. The PMR spectra of the precipitate and of the starting compound, both in CD_3CN, are shown in Table 2. They can be accounted for only by assuming that the precipitate was a mixture of monosolvated and bisolvated compounds; thus the peaks at 3.22 and 3.74 ppm can be attributed to methyl groups of a monosolvated intermediate, and those at 3.33 and 3.88 ppm to methyl groups of a bisolvated intermediate in a *cis*

TABLE 2

PMR DATA FOR THE COMPLEXES IN CD_3CN (in ppm)

	$\delta(CNCH_3)$	$\delta(NHCH_3)$	δ(bipy)	$\delta(NCCH_3)$
Fe(bipy)$(CNCH_3)_4^{2+}$	3.26, 3.68		7.60/8.99	–
Fe(bipy)$(CNCH_3)_3(NCCH_3)^{2+}$	3.22, 3.74		7.20/9.00	2.23
Fe(bipy)$(CNCH_3)_2(NCCH_3)_2^{2+}$	3.33, 3.38			
Fe(bipy)$(CNCH_3)_2(C_4H_{10}N_4)^{2+}$	3.23 3.49	2.54, 2.60 3.04, 3.11	7.41/8.45	–
Fe(bipy)$(CNCH_3)(NCCH_3)(C_4H_{10}N_4)^{2+}$	3.32	2.63, 2.70 3.17, 3.23	7.18/8.18	2.23
Fe(bipy)$(NCCH_3)_2(C_4H_{10}N_4)^{2+}$	–	2.57, 2.64 3.25, 3.31	7.65/8.40	2.18

configuration. In addition, a peak from the coordinated acetonitrile, exchanging fairly slowly with the solvent, appears at 2.23 ppm.

The results suggest that the photoequilibrium mixture is formed by firstly a photochemical process followed by a fast thermal step:

$$\mathrm{Fe(bipy)(CNCH_3)_4}^{2+} \underset{\Delta,\text{slow}}{\overset{h\nu,\mathrm{NCCH_3}}{\rightleftharpoons}} \mathrm{Fe(bipy)(CNCH_3)_3(NCCH_3)}^{2+} + \mathrm{CNCH_3} \tag{1}$$

$$\mathrm{Fe(bipy)(CNCH_3)_3(NCCH_3)}^{2+} \underset{\text{fast}}{\overset{\Delta,\mathrm{NCCH_3}}{\rightleftharpoons}} \mathrm{Fe(bipy)(CNCH_3)_2(NCCH_3)_2}^{2+} + \mathrm{CNCH_3} \tag{2}$$

In accordance with this interpretation, when $CNCH_3$ was added to the equilibrium mixture, the equilibria shifted to the left hand side to give the starting compound and when bipyridine was added, the bidentate ligand reacted with the bisolvated compound with a shift of the equilibrium towards the right. The cation $Fe(bipy)_3{}^{2+}$ was predominantly formed ($\simeq 90\%$), and negligible amounts of $Fe(bipy)_2(CNCH_3)_2{}^{2+}$ and $Fe(bipy)(CNCH_3)_4{}^{2+}$ were obtained. The formation of $Fe(bipy)_3{}^{2+}$, which was monitored spectrophotometrically at 520 nm, was of first order; the rate constant, k, calculated for the first 10% of reaction, was 1.9×10^{-4} s^{-1} at 25°C. A lower value of k was found for longer times reflecting the effect of mass retardation due to the increase of the $CNCH_3$ concentration as the reaction proceeded. No photostationary state was attained when the irradiation was carried out with continuous nitrogen bubbling to take off the released ligand.

For the compound $Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}$ (Fig. 4), the absorption maximum of the solution at equilibrium appeared at 505 nm independent of the irradiation wavelength or the initial concentration, and therefore of actual concentration of $CNCH_3$. The photochemical process involves two steps. In the first the dicarbene undergoes solvation to give the intermediate I; the constant isosbestic points at 382 and at 450 nm confirms that only the starting compound and I were present. As the intermediate I accumulates, it competes with the former in the absorption of the light, and in turn reacts to give the final product II. When the concentration of the initial complex was so small that it could not compete with the other compounds for the absorption of the light, two new isosbestic points, at 408 and 485 nm appeared, suggesting that only two species, I and II, were present.

For the isolation of complex II, a concentrated solution of the starting compound was irradiated at 350 nm up to complete conversion to compound II, with nitrogen bubbling to prevent any re-attachment of $CNCH_3$. The solution was evaporated to dryness to remove released $CNCH_3$ completely, and the residue was redissolved in a small volume of acetonitrile and reprecipitated by adding small quantities of ether. The analytical and spectral data suggested that the compound obtained was sufficiently pure; the elemental analysis indicated a composition similar to that of the starting compound. In the IR spectrum, the characteristic bands of the bipyridine and the dicarbene were found at the expected frequencies; the stretching band of the CN group (probably of coordinated solvent molecules) appeared split at about 2170 cm^{-1}. In the PMR spectrum (Tab. 2) there was no peak due to coordinated isocyanide molecules, while the two doublets, at δ 3.25–3.31 and 2.57–2.64 ppm, due to methyl groups bonded to the carbene ring were still present. The peaks due to

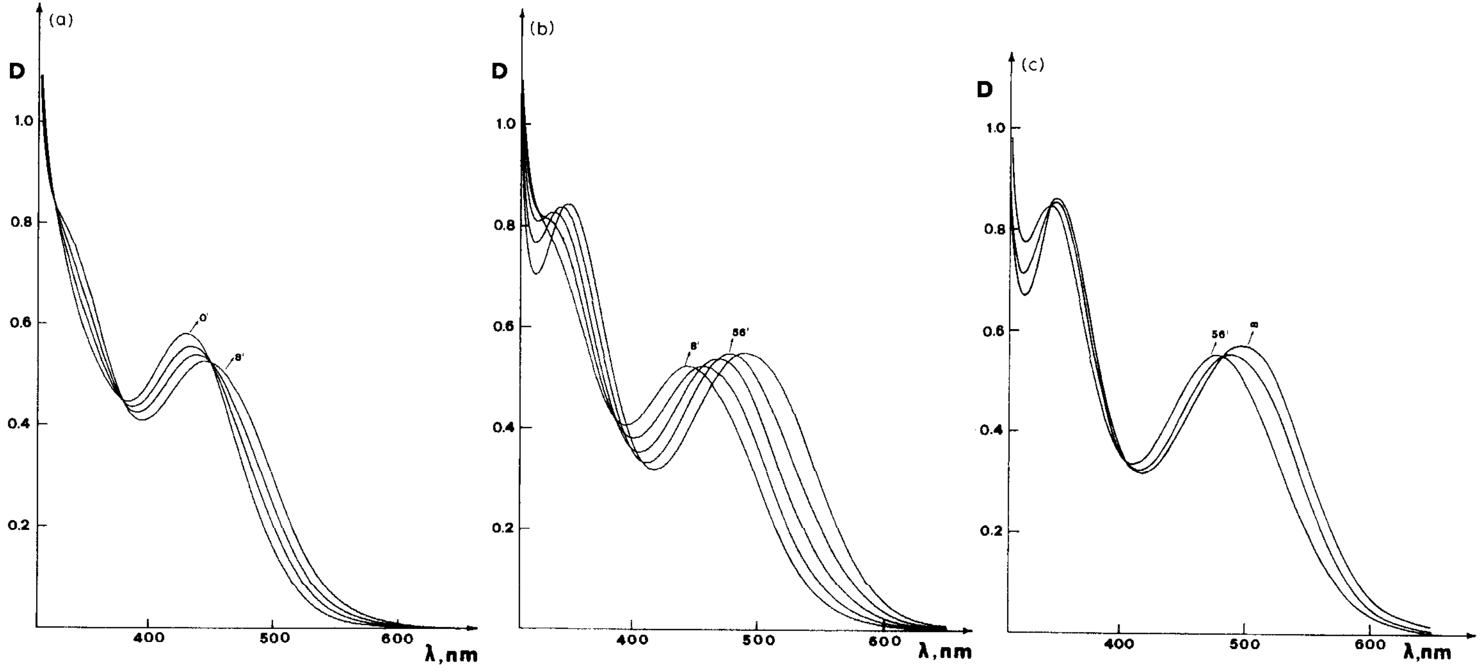


Fig. 4. Spectral changes of Fe(bipy)(CNCH$_3$)$_2$(C$_4$H$_{10}$N$_4$)$^{2+}$ upon irradiation at 350 nm. (The numbers refer to the irradiation times).

coordinated bipyridine were in the range 7.65–8.40 ppm. There was also a broad peak at 2.18 ppm, attributable to acetonitrile but shifted downfield with respect to free acetonitrile (2.11 ppm). This suggested that two acetonitrile molecules of solvation have replaced two isocyanide ligands in the same *cis*-positions, and that the exchange between free and coordinated acetonitrile is fairly slow.

In the visible region the spectrum of II exhibited a band of CT type at 505 nm (ε 2650), and in the UV region the IL bands were slightly shifted compared with those of the initial compound (λ_{max} 298 nm, ε 26 000; λ_{max} 230 nm, ε 29 000). All the data indicate that II is the bisolvated compound $\mathrm{Fe(bipy)(NCCH_3)_2(C_4H_{10}N_4)^{2+}}$.

We were not able to isolate the intermediate I, but it is reasonable to believe that it is the monosolvated species $\mathrm{Fe(bipy)(CNCH_3)(NCCH_3)(C_4H_{10}N_4)^{2+}}$. This assumption was supported by the results obtained on treating compound II with pure $\mathrm{CNCH_3}$ and stopping the re-entry of $\mathrm{CNCH_3}$ after 1 h by removing the free ligand under vacuum, which gave a product with an absorption maximum between 435–505 nm. The PMR spectrum of this product showed the peaks due to $\mathrm{Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}}$, described above and, in addition, there were other new doublets, at δ 3.17–3.23 and 2.63–2.70 ppm (attributable to the methyls of the carbene) and another coordinated isocyanide peak, at δ 3.32 ppm, consistent with the presence of $\mathrm{Fe(bipy)(CNCH_3)(NCCH_3)(C_4H_{10}N_4)^{2+}}$. We derived its absorption spectrum by using the two sets of isosbestic points between this new species and the starting complex and between this new species and II, respectively. It was found that I has the CT band at 470 nm (ε 2500), with the IL band almost unchanged (λ_{max} 295 nm, ε 25 000; λ_{max} 233 nm, ε 25 000). We thus propose the following photosolvation scheme, which is consistent with our results:

$$\mathrm{Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}} \underset{\Delta}{\overset{h\nu,\mathrm{NCCH_3}}{\rightleftharpoons}} \mathrm{Fe(bipy)(CNCH_3)(NCCH_3)(C_4H_{10}N_4)^{2+} + CNCH_3} \tag{3}$$

$$\mathrm{Fe(bipy)(CNCH_3)(NCCH_3)(C_4H_{10}N_4)^{2+}} \underset{\Delta}{\overset{h\nu,\mathrm{NCCH_3}}{\rightleftharpoons}} \mathrm{Fe(bipy)(NCCH_3)_2(C_4H_{10}N_4)^{2+} + CNCH_3} \tag{4}$$

Quantum yields and conclusions

The quantum yields at 350 and 254 nm for the first photochemical step for $\mathrm{Fe(bipy)(CNCH_3)_4^{2+}}$ and of the two consecutive steps for Fe(bipy)

TABLE 3

QUANTUM YIELDS FOR $\mathrm{Fe(bipy)(CNCH_3)_4^{2+}}$ AND $\mathrm{Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}}$ (error < 10%)

λ	$\mathrm{Fe(bipy)(CNCH_3)_4^{2+}}$	$\mathrm{Fe(bipy)(CNCH_3)_2(C_4H_{10}N_4)^{2+}}$	
	φ	φ_1	φ_2
254	1.10×10^{-2}	2.13×10^{-2}	0.46×10^{-2}
350	0.60×10^{-2}	1.23×10^{-2}	0.27×10^{-2}

$(CNCH_3)_2(C_4H_{10}N_4)^{2+}$ were measured (Table 3). For $Fe(bipy)(CNCH_3)_4{}^{2+}$ the extent of photolysis was evaluated at the beginning of the irradiation by adding free bipyridine, which reacts almost quantitatively with the photochemical product to give $Fe(bipy)_3{}^{2+}$. For the dicarbene compound, knowledge of the absorption spectrum of I and II allowed us to calculate the quantum yields of the two consecutive steps of the photochemical process. The value of φ_1 and φ_2 were obtained from the following equations by use of a suitable computer program:

$$-\frac{d[A]}{dt}=\frac{L}{V}\left\{\varphi_1\frac{\varepsilon_A[A](1-10^{-\Sigma\varepsilon c})}{\Sigma\varepsilon c}\right\} \tag{5}$$

$$\frac{d[I]}{dt}=\frac{L}{V}\left\{\frac{(\varphi_1\varepsilon_A[A]-\varphi_2\varepsilon_I[I])(1-10^{-\Sigma\varepsilon c})}{\Sigma\varepsilon c}\right\} \tag{6}$$

$$\frac{d[II]}{dt}=\frac{L}{V}\left\{\frac{\varphi_2\varepsilon_I[I](1-10^{-\Sigma\varepsilon c})}{\Sigma\varepsilon c}\right\} \tag{7}$$

In these equations A is the initial compound, L is the light intensity, and the other symbols have the usual meaning. There was good agreement between the values obtained from eqs. 6 and 7 which strongly supports the validity of the proposed mechanism.

The observed photochemical process, involving displacement of coordinated MeCN by solvent, was expected from our previous studies [1,3,7–9]. The variation of the quantum yield with the nature of the initial complex and with the exciting wavelength can be directly related to the bond energy and the irradiation energy. For the dicarbene compound evidence was obtained for the separate steps of the process, and the photochemical intermediates were isolated and characterized. The partial quantum yields, φ_1 and φ_2, decrease as the wavelength increases, their ratio remaining almost constant at the two wavelengths used. It is thus very probable that both steps involve the same mechanism, viz. heterolytic fission of the Fe–C bond, formation of a photodissociative state involving two fragments (pentacoordinated intermediate and ligand) trapped in the solvent cage, diffusion away of the ligand, and subsequent attack by the solvent or re-entry of the ligand.

Acknowledgements

This work was supported by the Ministero della Pubblica Istruzione, Art. 65, DPR 382/80, Roma.

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