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Photochemical and photophysical processes in fac-Re(CO)$_3$(4-phenylpyridine)$_3$(CF$_3$SO$_3$). Steady state and flash photolysis study

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Abstract

The photophysics and photochemistry of fac-Re(CO)$_3$(4-phenylpyridine)$_3^+$ were investigated by monochromatic steady state and flash photolysis. Two parallel photoprocesses, photogeneration of the emissive metal-to-ligand charge transfer (MLCT) state and photoredox dissociation in [Re(CO)$_3$(4-phenylpyridine)$_2^{2+}$,(4-phenylpyridine$^-$)], were observed. In the former process, the emission originating from the lower MLCT excited state is electron transfer quenched by triethanolamine (TEOA) producing an Re(CO)$_3$(4-phenylpyridine)$_3^{\cdot}$ radical and energy transfer quenched by Cu(TIM)$^{2+}$ (TIM ≡ 2,3,9,10-tetramethyl-[14]-1,4,8,11-tetraene-N$_4$). The primary species Re(CO)$_3$(4-phenylpyridine)$_2^{2+}$ generated in the latter photoprocess undergoes several thermal changes which finally lead to dimeric products. A third photoprocess, namely the photogeneration of the [Re(CO)$_3$(4-phenylpyridine)$_2^{2+}$(4-phenylpyridine$^-$)] species, is involved in the reduction of the copper macrocycle to Cu(TIM)$^+$.

Keywords: Flash photolysis; Re complexes; Steady state photolysis

1. Introduction

Luminescent transition metal complexes have been utilized as photosensitizers in areas such as solar energy conversion [1], electron transfer studies [2], chemiluminescent and electroluminescent systems [3,4], binding dynamics of heterogeneous media [5] and probes of macromolecular structure [6]. In this regard, Re(I) complexes have received much attention in recent years. Many of these compounds exhibit a wide variety of energetically accessible metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT) and intraligand (IL) excited states [7–10]. The photophysical properties of the metal complexes are determined predominantly by the excited states of lowest energy. However, the population of higher excited states leads to photochemical pathways. The rational design of more useful photosensitizers and probes necessitates an intimate understanding of their excited state energetics and dynamics.

Most of the studies on Re(I) complexes have been related to those containing diimine ligands [11]. In this work, we have investigated the photophysics and photochemistry of Re(CO)$_3$(4-phenylpyridine)$_3^+$, an Re carbonyl monoazine complex. Luminescence quenching, continuous photolysis and flash photolysis results are reported.

2. Experimental details

2.1. Materials

The complex fac-Re(CO)$_3$(4-phenylpyridine)$_3$(CF$_3$SO$_3$) was prepared by a procedure involving the substitution of Cl$^-$ by 4-phenylpyridine in the presence of AgCF$_3$SO$_3$, based on a similar method for replacing Cl$^-$ in complexes with bidentate azines [12]. To 250 ml of toluene was added fac-ClRe(CO)$_3$(4-phenylpyridine)$_2$ (3.2 mmol), CF$_3$SO$_3$Ag (3.2 mmol) and 4-phenylpyridine (32 mmol). The solution was magnetically stirred and refluxed for 9 h under an N$_2$ atmosphere. A large excess of ligand was necessary to obtain an acceptable yield (60%). Precipitated AgCl was removed by filtration at a temperature in the range 5–10 °C. The filtrate was roto-evaporated to dryness. The product, redissolved in a minimum volume of CH$_2$Cl$_2$, was applied to a neutral alumina column for chromatography. Elution was initiated with CH$_2$Cl$_2$ until the excess of 4-phenylpyridine had been removed. Elution with CH$_2$Cl$_2$ containing 5% of methanol removed the complex. In order to purify

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the complex, this material was recrystallized from a concentrated solution in CH_2Cl_2 by the addition of *n*-pentane. This procedure was repeated until no changes were observed in the UV–visible and IR spectra. Spectroquality CH_2Cl_2 (Mallinckrodt) and CH_3CN (Mallinckrodt) were dried over molecular sieves. Other solvents (triethanolamine (TEOA) (Carlo Erba) and $AgCF_3SO_3$ (Aldrich)) were used without further purification.

2.2. Equipment and procedures

The conventional flash photolysis set-up has been described previously [13] and only a few important features are given below. Pulses of polychromatic light having a duration of approximately 50 μs were obtained from two FP8-100C xenon flash lamps (Xenon Corp.) fired simultaneously at stored electrical energies of 40–250 J per pulse. The wavelength region was isolated by means of an adequate cut-off filter. Photogenerated transients were detected optically with an analysing light beam directed through the sample cell. The output of the detector phototube, fed into an appropriate sample-hold circuit, was digitized and processed by a personal computer. A fresh solution of photolyte, deaerated with a stream of N_2, was used for each irradiation. The excimer (Lambda Physik) flash photolysis set-up used for excited state lifetime measurements has been described elsewhere [14].

UV–visible spectra were recorded on ZEISS PMQ 3 and CARY 13 spectrophotometers, and quenching experiments were carried out on a CARY 13 total fluorescence accessory. Luminescence spectra were taken with an SLM 8000 (Aminco) spectrofluorometer and infrared spectra on a Shimadzu IR-435 spectrophotometer. Quantum yields of emission were calculated relative to rhodamine B. Excitation spectra were corrected for inner filter effects.

Steady state irradiations (350, 300 and 254 nm) were carried out in an irradiator with appropriate Rayonet lamps for quasi-monochromatic photolysis, i.e. bandwidth of the excitation light of 20 nm. The light intensity was measured with a $Co(NH_3)_5Br^{2+}$ actinometer. The concentration of the photolyte was adjusted to absorb more than 99.99% of the incident light at the corresponding excitation wavelength. These solutions were deaerated with a stream of N_2. The homogeneity of the reaction medium was maintained during irradiation by stirring with magnetic bars.

3. Results

Acetonitrile solutions of fac-$Re(CO)_3$(4-phenylpyridine)$_3^+$, thoroughly deaerated by bubbling with N_2, display a broad luminescence between 420 and 650 nm. The band maximum is observed at $\lambda = 505$ nm. The excitation spectra (Fig. 1) show that the highest emission quantum yield is reached on irradiation at the lowest energy MLCT absorption band. However, at excitation wavelengths corresponding to IL transitions, the quantum yield is still significant.

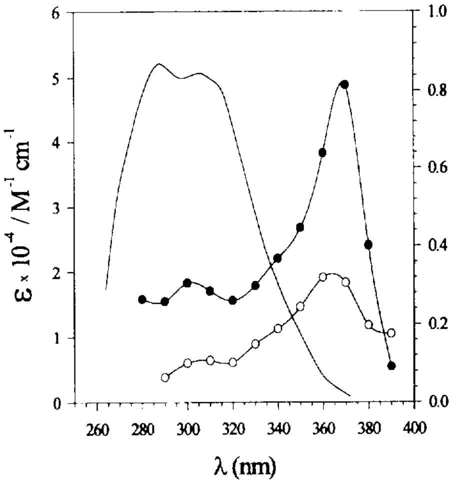

Fig. 1. Excitation spectra based on the emission quantum yields (ϕ) of $Re(CO)_3$(4-phenylpyridine)$_3^+$ fluorescence in CH_2Cl_2 (●) and CH_3CN (○). The absorption spectrum of the Re(I) complex is shown for comparison.

Monochromatic flash irradiation ($\lambda = 308$ nm) of the complex in deaerated CH_3CN solution was used to perform a time-resolved study of the respective luminescence. The corresponding decay of the emission, followed at 520 nm, can be fitted, without appreciable deviation, to a single exponential (Fig. 2, inset). Transient absorption spectra (Fig. 2) were recorded during flash photolysis under similar experimental conditions to those used in the investigation of luminescence. Irradiation at wavelengths corresponding to the

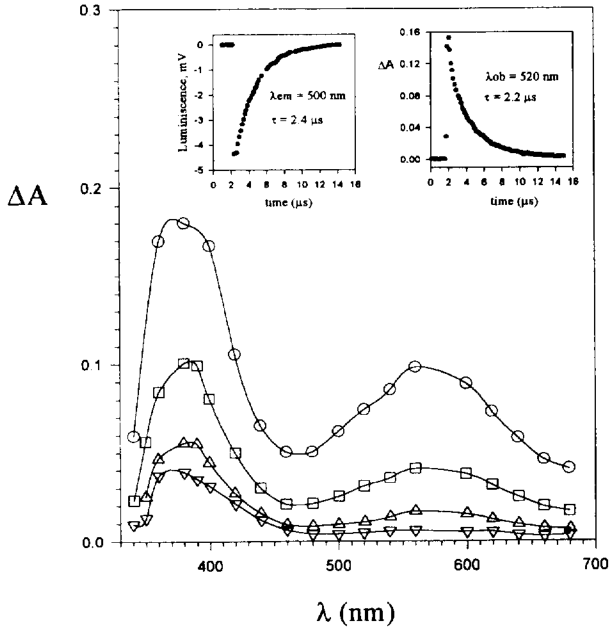

Fig. 2. Transient spectra recorded on 308 nm flash irradiation of 10^{-4} M $Re(CO)_3$(4-phenylpyridine)$_3^+$ in deaerated CH_3CN. The spectra were measured 3.6 μs (○), 5.9 μs (□), 9.1 μs (△) and 15 μs (▽) after the flash; the insets show two typical traces ($\lambda_{em} = 500$ nm and $\lambda_{ob} = 520$ nm) of the luminescence and absorbance decays respectively. The lifetimes τ measured in each case are indicated.

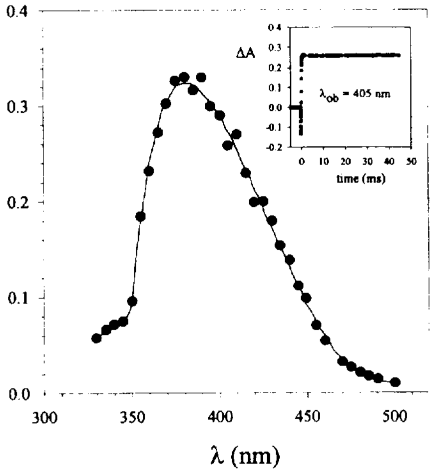

Fig. 3. Primary product spectrum recorded on conventional flash photolysis of 2.5×10^{-5} M Re(CO)$_3$(4-phenylpyridine)$_3^+$ in deaerated CH$_3$CN. Inset shows a typical trace illustrating the invariance of the absorption in the millisecond time domain.

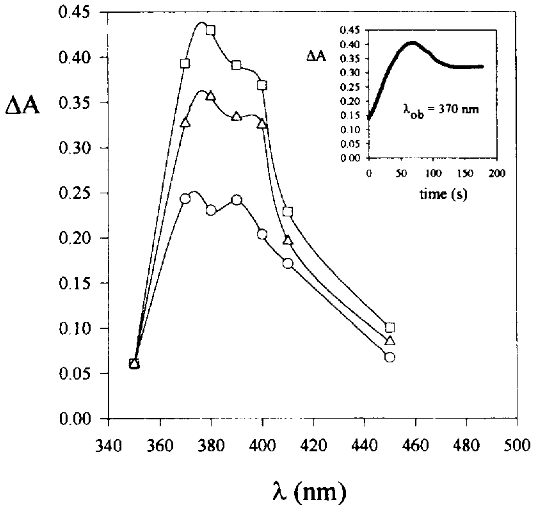

Fig. 4. Time-resolved spectral changes after flash photolysis of Re(CO)$_3$(4-phenylpyridine)$_3^+$ in deaerated CH$_3$CN. Spectra were recorded 20 s (○), 80 s (□) and 120 s (△) after the flash. The inset shows a typical trace for the growth of absorbance in the second time domain.

first absorption band generates a transient spectrum which disappears via first-order kinetics. Since the lifetime of this reaction is the same as that of luminescence, within experimental error, the new absorption is associated with the MLCT excited state which undergoes radiative and radiationless relaxation.

Although the decay of the transient spectrum observed during the laser flash photolysis experiments corresponds to an almost complete recovery of the parent complex, a residual spectrum can be obtained. Thus when deaerated acetonitrile solutions containing Re(CO)$_3$(4-phenylpyridine)$_3^+$ (2.5×10^{-5} M) are photolysed in a conventional flash photolysis set-up, a different long-lived species is observed (Fig. 3) with an absorption maximum at 380 nm. This intermediate is generated within the flash lifetime (approximately 50 μs) and no absorption changes occur up to the millisecond domain (Fig. 3, inset). In this time range, the absorption modifications follow a complicated pattern and the experimental observations cannot be fitted to any simple kinetic scheme (Fig. 4).

By monitoring the quenching with TEOA, typical Stern–Volmer kinetics are obtained (Fig. 5). The slope gives $K_{SV}=(4.7\pm0.2)\times10^3$ M^{-1} and, taking into account the excited state lifetime ($\tau=2.2$ μs), the bimolecular rate constant $k_q=2.1\times10^9$ M^{-1} s^{-1} can be obtained.

Flash photolysis of Re(CO)$_3$(4-phenylpyridine)$_3^+$ in N$_2$-bubbled 10^{-3} M TEOA–CH$_3$CN solution leads to the generation of an intermediate (Fig. 6) whose decay is consistent with a competition between first- and second-order kinetics. From curve fitting analysis of the experimental data, values of $k_1=0.3$ s^{-1} and $k_2/\epsilon_{(560\ \mathrm{nm})}=8.6\times10^2$ cm s^{-1} are obtained.

Flash irradiation of 5×10^{-5} M Re(CO)$_3$(4-phenylpyridine)$_3^+$ in a deaerated acetonitrile solution of Cu^{II}(TIM)$^{2+}$ (TIM≡2,3,9,10-tetramethyl-[14]-1,4,8,11-

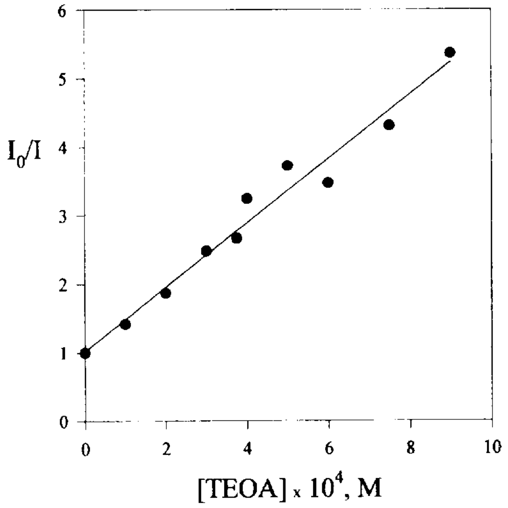

Fig. 5. Stern–Volmer kinetics of luminescence quenching of Re(CO)$_3$(4-phenylpyridine)$_3^+$ with TEOA in N$_2$-deaerated acetonitrile solution.

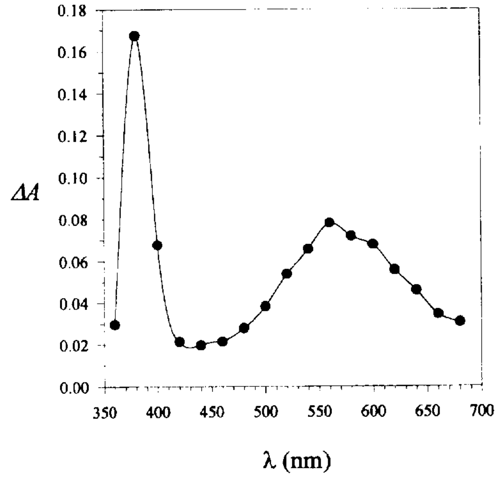

Fig. 6. Transient spectra recorded on conventional flash photolysis of 1×10^{-4} M Re(CO)$_3$(4-phenylpyridine)$_3^+$ in N$_2$-deaerated 1×10^{-3} M TEOA–CH$_3$CN. The values of ΔA were extrapolated to zero time.

tetraene-N_4) results in the reduction of the Cu(II) complex. The amount of $Cu^I(TIM)^+$ formed was measured for several initial concentrations of $Cu^{II}(TIM)^{2+}$ in the range 1×10^{-4} to 9×10^{-4} M. These results were compared with those obtained during the quenching of the luminescence (Fig. 7). While the Cu(I) concentration reaches its limiting value at $[Cu^{II}(TIM)^{2+}] \leq 9\times10^{-4}$ M, only 70% of the emission (follows Stern–Volmer kinetics; $K_{SV}=2.8\times10^3$ M^{-1} s^{-1}) is quenched at this Cu(II) concentration. The two processes are kinetically different, suggesting that two independent and parallel paths, one for the formation and decay of the MLCT excited state and one for the formation of Cu(I), must be operative.

A solution of $Re(CO)_3(4\text{-phenylpyridine})_3^+$ (2.5×10^{-5} M) in N_2-bubbled CH_3CN, contained in a gas-tight cell, was flash irradiated, and the absorption changes were observed with a spectrophotometer at $\lambda_{ob}=380$ nm. From curve fitting analysis of the experimental data points, the following expression was obtained

$$\text{Abs}=0.09172+0.00298\exp(-1.2\times10^{-4}t)$$
$$+0.00799\exp(-4.4\times10^{-6}t)$$

which is consistent with two parallel first-order decays, with $k_1=1.2\times10^{-4}$ s^{-1} and $k_2=4.4\times10^{-6}$ s^{-1}.

Solutions of $Re(CO)_3(4\text{-phenylpyridine})_3^+$ in N_2-saturated CH_3CN undergo significant spectral changes on continuous photolysis. As depicted in Fig. 8, both the absorption band at 277 nm ($\epsilon=5.7\times10^4$ M^{-1} cm^{-1}) and the shoulder located at 300 nm ($\epsilon=5.1\times10^4$ M^{-1} cm^{-1}) experience an apparent blue shift, accompanied by a decrease in intensity. Simultaneously, a new band appears around 380 nm. Two isosbestic points can be observed at 265 and 348 nm. Irradiation at 254, 300 and 350 nm produces similar features.

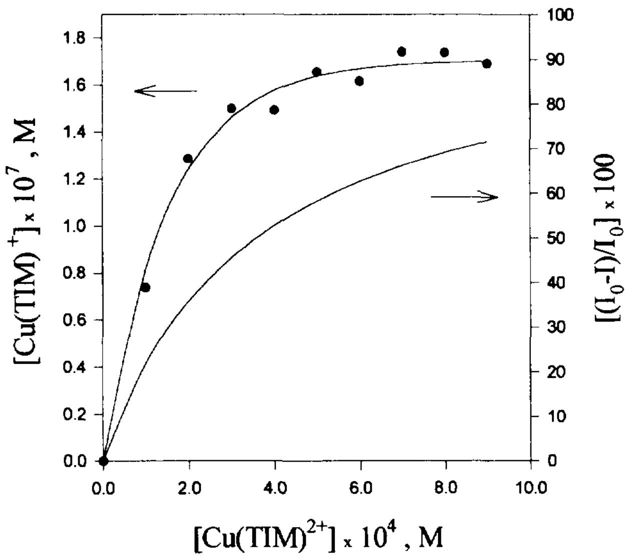

Fig. 7. Experimental observations of the scavenging of a reaction intermediate with $Cu(TIM)^{2+}$ in deaerated CH_3CN. The percentage luminescence of the Re(I) complex quenched by a given concentration of $Cu(TIM)^{2+}$ and the concentration of $Cu(TIM)^+$ generated on conventional flash photolysis of $Re(CO)_3(4\text{-phenylpyridine})_3^+$ in the presence of increasing concentrations of $Cu(TIM)^{2+}$ are shown.

Inset (a) in Fig. 8 shows the difference spectrum obtained by subtracting the initial solution spectrum from that recorded after 3 min of photolysis. The absorption band obtained is similar to that of the primary product (Fig. 3) with $\lambda_{max}=375$ nm. On the other hand, the difference spectrum in the range 230–270 nm (inset (b)) shows the absorption band corresponding to free 4-phenylpyridine released during photolysis. The calculated quantum yields are shown in Table 1.

The nature of the major photolysis product was investigated by scanning the IR spectrum of 1.0×10^{-2} M Re(I) solutions irradiated at $\lambda_{exc}=254$ nm ($I_0=6.9\times10^{-4}$ einstein dm^{-3} min^{-1}). In the region of the CO absorptions (Fig. 9), the spectra show that the intensities of the peaks assigned to $Re(CO)_3(4\text{-phenylpyridine})_3^+$ ($\nu_{max}=2035$ and 1920 cm^{-1}) undergo no significant changes. However, a new band

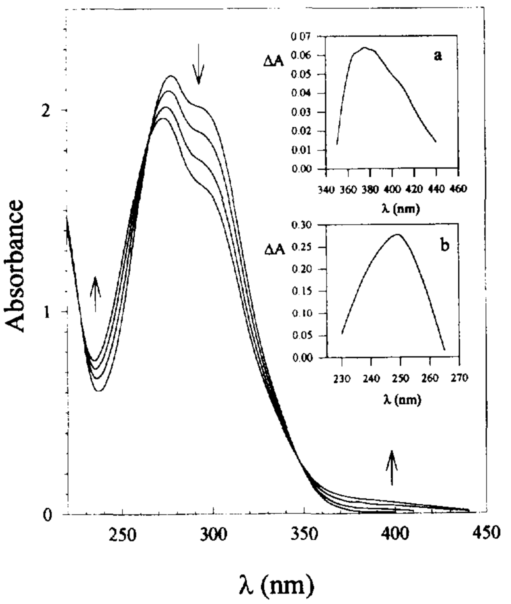

Fig. 8. Spectral changes induced on 300 nm steady state photolysis of $Re(CO)_3(4\text{-phenylpyridine})_3^+$ in deaerated CH_3CN. The UV–visible spectra were recorded using a 2×10^{-4} M solution in a cell with an optical path length of 0.2 cm after successive intervals of irradiation ($I_0=7.1\times10^{-4}$ einstein dm^{-3} min^{-1}). The arrows indicate the progress of the change made every 1 min of photolysis from $t=0$. Insets a and b show the difference spectra obtained by subtracting the initial spectrum from that recorded after 3 min of photolysis.

Table 1

4-Phenylpyridine quantum yields and rate of absorbance growth (dA_{375}/dt is the derivative of the absorbance at $\lambda_{ob}=375$ nm and I_0 is the intensity of light absorbed in einstein dm^{-3} min^{-1}) on 254 nm, 300 nm and 350 nm steady state photolysis of $Re(CO)_3(4\text{-phenylpyridine})_3^+$ in deaerated CH_3CN

λ_{exc} (nm)	$10^4\times I_0$ (einstein dm^{-3} min^{-1})	ϕ	$(dA_{375}/dt)/I_0$ (dm^3 $einstein^{-1}$)
254	6.9	0.027	28.8
300	7.1	0.041	30.6
350	6.5	–	13.4

appears at 1844 cm^{-1} with progressively longer irradiation times. When the solution is kept in the dark for 19 h after irradiation, the intensities of the three bands decrease (Fig. 9).

In an attempt to obtain more information about the nature of the products, 40 ml of Re(CO)$_3$(4-phenylpyridine)$_3^+$ in deaerated CH$_3$CN was irradiated at 300 nm for 10 h. The concentration was sufficiently high to avoid secondary photolysis. A stream of O$_2$-free nitrogen was passed through the liquid during photolysis. The products of the photolysis were separated by column chromatography on neutral alumina previously equilibrated with CH$_2$Cl$_2$. The adsorbed products were eluted in succession with CH$_2$Cl$_2$ and with solutions of CH$_3$OH in CH$_2$Cl$_2$ progressively containing more alcohol. Three principal fractions were collected and roto-evaporated to dryness. The solid materials were recrystallized in CH$_2$Cl$_2$ from saturated solutions by the addition of *n*-pentane. The UV–visible spectra of all the compounds exhibited absorption bands with maxima at 273 nm and 390 nm. Only two showed a shoulder at 309 nm. The Abs(273 nm)/Abs(309 nm) ratio for fraction A (Fig. 10) is the same as that found for ClRe(CO)$_3$(4-phenylpyridine)$_2$. The spectrum of fraction C is very similar to that exhibited by the dimeric product obtained in the photolysis of ClRe(CO)$_3$(4-phenylpyridine)$_2$ [15], which contains only two 4-phenylpyridine moieties per molecule and two bridging CO groups. All the spectra presented an IR absorption band between 1820 and 1840 cm^{-1} (Fig. 11), although only fraction C showed a noticeable decrease in the 2035 cm^{-1} band.

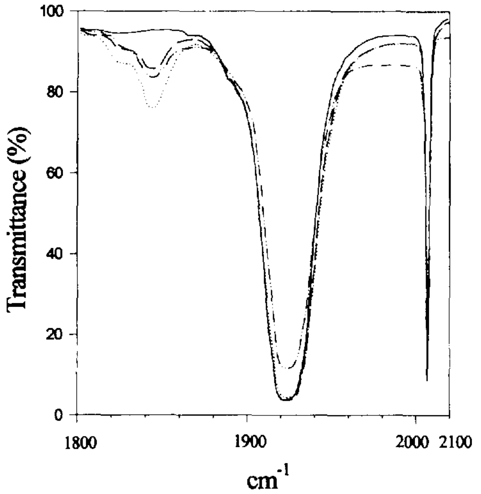

Fig. 9. Spectral changes induced on 254 nm steady state photolysis of Re(CO)$_3$(4-phenylpyridine)$_3^+$ in deaerated CH$_3$CN. The IR spectra were recorded using a 0.01 M solution irradiated for 0 min (———), 45 min (– – –) and 90 min (· · ·). Spectrum recorded 19.3 h after photolysis (– · · –).

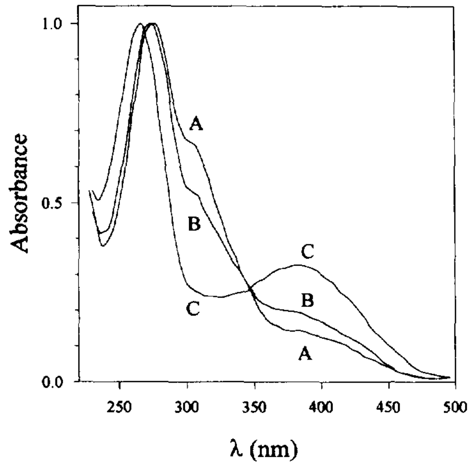

Fig. 10. UV–visible spectra of the three main isolated products on 300 nm steady state photolysis of Re(CO)$_3$(4-phenylpyridine)$_3^+$ in deaerated CH$_3$CN. The spectra of products A, B and C were normalized for comparison.

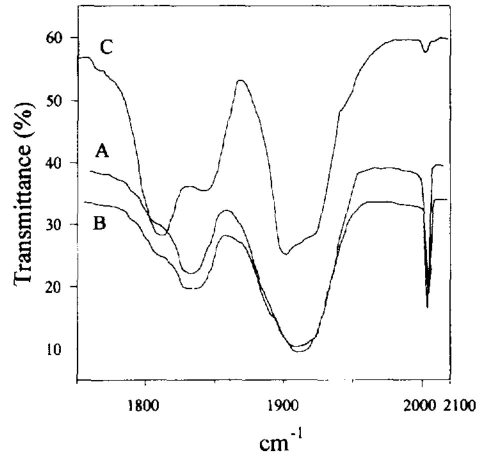

Fig. 11. IR spectra of the three main isolated products on 300 nm steady state photolysis of Re(CO)$_3$(4-phenylpyridine)$_3^+$ in deaerated CH$_3$CN.

4. Discussion

The emission exhibited by Re(CO)$_3$(4-phenylpyridine)$_3^+$ can be attributed to the lowest energy MLCT excited state [15]. However, although monoexponential decay is observed, the excitation spectrum suggests that more than one excited state contributes to the luminescence. This is in agreement with the broadening and shift of the emission band, in addition to the enhancement of the feature near 450 nm, previously observed with decreasing solvent polarity and temperature [16]. It is possible to account for this behaviour by considering two excited states (MLCT and IL) emitting simultaneously, with their interconversion rate being faster than their decay rate.

Like other related Re complexes [17], the luminescence of Re(CO)$_3$(4-phenylpyridine)$_3^+$ is quenched by TEOA, generating a transient which decays by mixed first- and second-order kinetics. In agreement with previous findings [18], it can be assigned as [Re(CO)$_3$(4-phenylpyridine)$_3$]$^{\cdot}$. On the other hand, the experiments in the presence of Cu(TIM)$^{2+}$ suggest that its reduction is not produced by the luminescent excited state, but by another intermediate generated during photolysis as proposed earlier [15,19]. Such an intermediate could be a biradical Re(CO)$_3$(L$_2^+$)(L$^-$) because Re(CO)$_3$(4-phenylpyridine)$_3^+$ should present ligand-to-ligand transitions as does $ClRe(CO)_3$(4-phenylpyridine)$_2$. These experimental observations can be pictured as follows:

$$Re(CO)_3(4-phpy)_3^+ + h\nu_1 \rightarrow [Re(CO)_3(4-phpy)_3^+]^* \quad (1)$$

$$[Re(CO)_3(4-phpy)_3^+]^* + TEOA \rightarrow [Re(CO)_3(4-phpy)_3]^{\cdot} + TEOA^+ \quad (2)$$

$$[Re(CO)_3(4-phpy)_3]^{\cdot} \rightarrow products \quad (3)$$

$$[Re(CO)_3(4-phpy)_3]^{\cdot} + TEOA^+ \rightarrow [Re(CO)_3(4-phpy)_3]^+ + TEOA \quad (4)$$

$$[Re(CO)_3(4-phpy)_3^+]^* + Cu(TIM)^{2+} \rightarrow Re(CO)_3(4-phpy)_3^+ + Cu(TIM)^{2+} \quad (5)$$

$$Re(CO)_3(4-phpy)_3^+ + h\nu_2 \rightarrow [Re(CO)_3(4-phpy)_2^{\cdot 2+}(4-phpy)^{\cdot -}] \quad (6)$$

$$[Re(CO)_3(4-phpy)_2^{\cdot 2+}(4-phpy)^{\cdot -}] + Cu(TIM)^{2+} \rightarrow Re(CO)_3(4-phpy)_3^{2+} + Cu(TIM)^+ \quad (7)$$

The long-lived absorption, detected after the decay of the MLCT state, may be associated with a primary product of the photoreaction proceeding in parallel with the formation and decay of the luminescent excited state [15]

$$Re(CO)_3(4-phpy)_3^+ + h\nu_3 \rightarrow Re(CO)_3(4-phpy)_2^{\cdot 2+} + 4-phpy^{\cdot -} \quad (8)$$

In such a primary product, the central metal should be formally Re(II), showing larger lability than its predecessor Re(I), a d^6 metal ion. On photolysis of $ClRe(CO)_3$(4-phenylpyridine)$_2$, a similar primary product is formed, $ClRe(CO)_3$(4-phenylpyridine)$^+$, with an absorption maximum at 430 nm. The absorption may originate from a charge transfer transition from the metal to the ligand and, in the present case, should be shifted to higher energies ($\lambda_{max} = 380$ nm) because the metal centre bears a greater positive charge.

On the other hand, the final products should be dimeric species because the IR absorption band between 1820 and 1840 cm^{-1} (corresponding to bridging CO) and the features of the UV–visible spectra (absorption band developed at $\lambda_{max} = 380$ nm) are typical of these types of complex [15].

The formation of the final products must involve several steps following the photogeneration of the primary product. In this regard, the absorption changes observed in the second time domain may be associated with the dimerization process, 4-phenylpyridine substitution by the solvent and back electron transfer between some of the Re(II) species and the pyridine anion radical. In addition, the slower spectral transformations can be related to the loss of CO, in accordance with the IR spectral changes observed in the dark after photolysis.

Finally, a few remarks can be made about the effect of the excitation wavelength on the photoprocesses. The excitation spectrum suggests that, on irradiation at 370 nm (corresponding to an energy of 323 kJ mol^{-1}), a ^{1}MLCT state is populated and, via intersystem crossing, the luminescent ^{3}MLCT state is produced. Moreover, when photon energies reach a value of 342 kJ mol^{-1} ($\lambda_{ex} = 350$ nm), the photochemistry becomes evident and the quantum yield of product formation increases with increasing photon energy. However, no loss of CO is observed on photolysis of the complex at photon energies lower than or equal to 471 kJ mol^{-1} ($\lambda_{ex} \geq 254$ nm), showing a different behaviour to that observed when $ClRe(CO)_3$(4-phenylpyridine)$_2$ is the photolyte. Flash photolysis experiments on $ClRe(CO)_3$(4-phenylpyridine)$_2$ demonstrate that biradical generation shows a wavelength dependence. Flash photolysis experiments on $Re(CO)_3$(4-phenylpyridine)$_3^+$ at different excitation energies are required to establish the existence of such a dependence.

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