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Auto-sensitized oxidation of Ru(II) complexes

I. Studies on the stability of two Ru(II) complexes ($[Ru(NH_3)_5NCPy{-}R]^{3+}$, $R \equiv CH_3$ and $C_6H_5CH_2$) in a medium containing singlet oxygen

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Abstract

The generation of singlet oxygen by a photochemical pathway, involving the excited state of a pentaammine Ru(II) complex containing an *N*-substituted 4-cyanopyridine ligand and molecular oxygen in aqueous solution, is reported in this work. A two-step degradation process occurs by virtue of the action of singlet oxygen. This species promotes the oxidation of Ru(II) to Ru(III) in the ground state of the complex. The cyanopyridine ligand then suffers hydrolysis, resulting in an Ru(III) complex containing a carboxyamidopyridine ligand. The influence of the substituent on the stability of the complex in the presence of singlet oxygen is studied, showing that a methyl substituent leads to a more stable complex than a benzyl substituent. A kinetic treatment of this process shows that the quenching of singlet oxygen by the complex has diffusional character, and is predominantly physical. Chemical quenching is related to the electron transfer process between Ru(II) and singlet oxygen.

Keywords: Singlet oxygen; Sensitization; Oxidation; Ru(II) complexes

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1. Introduction

The photochemical generation of singlet oxygen, induced by inorganic complexes [1–9] via energy transfer from the excited state of the complex to oxygen, is well known [2,6]

$$M^* + {}^3O_2 \longrightarrow M + {}^1O_2$$

In particular, certain Ru(II) complexes exhibit this tendency. $Ru(bpy)_3{}^{2+}$ (bpy, bipyridine) complexes have been demonstrated to be efficient in the sensitization of singlet oxygen. Chattopadhyay et al. [10] have estimated a value of 0.86 for the quantum yield of this process.

It has been reported that, for some complexes, after the promotion of singlet oxygen sensitization, the ground state of the complex is attacked by this species and is oxidized. Shukla et al. [9] have reported this behaviour for Pt(II) complexes.

Owing to its importance in biological systems [11,12] and many chemical processes [13,14], singlet oxygen has received considerable interest. Singlet oxygen is one of the most reactive oxygen species [15]. In solution, despite its short lifetime which is strongly influenced by solvent interactions, the reactions induced by singlet oxygen (${}^1\Delta_g$) are extremely important [13–16].

Coordinated nitriles generally tend to suffer hydrolysis, resulting in amides as products [17–22]. The rates of hydrolysis in the complexes $Ru(III)NCCH_3$ and $Ru(III)NCC_6H_5$ are higher than that observed for the free ligands. This tendency is better observed in alkaline medium. The lower hydrolysis rate constant of Ru(II) relative to Ru(III) shows the influence of the charge decrease and the back-donation of Ru(II). The $d\pi^*$ electron donation from Ru(II) to the antibonding orbitals of the nitrile ligand increases the electron density of the carbon in the nitrile, making nucleophilic attack difficult. Diamond et al. [23], in a study of the reactivity of nitriles coordinated to Ru(II), observed that, during oxidation of these complexes, the stabilization by back-

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donation is lost, resulting in a strong Lewis acid, i.e. Ru(III) coordinated to the nitrile nitrogen. After oxidation, the complex suffers rapid hydrolysis with the conversion of the nitrile into amide. This behaviour was also observed by Naal and coworkers [18,24,25] in studies on the electrochemical behaviour of these complexes.

In this work, we report the occurrence of the autosensitized oxidation of two pentaammine Ru(II) complexes containing an *N*-substituted cyanopyridine ligand, induced by singlet oxygen. The stability of these complexes in the presence of singlet oxygen is evaluated. Kinetic parameters, related to $^1O_2$ generation and reactivity and the role of the substituent and the solvent polarity on the stability of the complexes, are estimated. A mechanistic scheme is proposed.

2. Experimental details

The complexes were synthesized according to Rocha [26]. Aqueous solutions of the complexes at pH 5 were photolysed with visible radiation at 450 nm, furnished by an incandescent 125 W lamp at a distance of 4 cm from the reactor. The reactions were performed using a continuous flux of oxygen over the reaction medium. The incident radiation causes excitation of the metal-to-ligand charge transfer (MLCT) band. All the experiments were performed at 298 ± 1 K.

Different concentrations of the complexes were studied in order to evaluate the relationship between the oxidation rate and the concentration of the complex. This was performed by monitoring the changes in absorbance of the MLCT band: 552 nm for the benzyl complex and 540 nm for the methyl complex. The measurements were made using a Hitachi U-2000 spectrophotometer. In order to avoid the interference of parallel reactions on the kinetic measurements, the disappearance of the MLCT band was monitored until a reduction of 20% in the original absorbance was achieved. The decrease in intensity of the MLCT band gives the pseudo-first-order rate constant of oxidation of the complexes.

In order to confirm the presence and active participation of singlet oxygen, β-carotene and dehydrodivanillin were used as quenchers. These compounds act as physical and chemical quenchers of singlet oxygen, reducing the rate of degradation observed for the complex. Dehydrodivanillin [27] was dissolved in a small quantity of methanol, giving a 5% methanolic solution containing the complex. For the experiments using β-carotene, 9% methanolic solutions were employed. A Stern–Volmer correlation was performed to describe the singlet oxygen participation by plotting the ratio between the rate constants for the reactions with and without quencher vs. the concentration of the quencher. The effect of the solvent polarity on these reactions was studied to confirm the occurrence of an electron transfer process between singlet oxygen and Ru(II). For this, aqueous solutions of the methyl-substituted complex containing different concentrations of methanol were used, resulting in solutions with different polarities.

Various amounts of the complexes, varying between 20 and 40 mg, were photolysed in aqueous solution, and the products were isolated. The unique product observed in both cases was characterized by cyclic voltammetry (potentiostat/galvanostat PARC 273), IR spectrophotometry (FT-IR Shimadzu model 8000), using a mixture of the product and KBr in pressed discs, and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (Brucker 80 MHz). The cyclic voltammograms were obtained in 0.1 M tetrafluoroacetic acid/acetate buffer (0.1 M, pH 3), using a millimolar concentration of the complex. The solutions were deaerated with treated argon before measurement. Three electrodes were used: a glassy carbon electrode, an Ag/AgCl reference electrode immersed in a 3 M NaCl solution saturated with AgCl and a platinum wire as auxiliary electrode immersed in the solution under study.

3. Results and discussion

The UV–visible spectra of one of the complexes studied in aqueous solution, before and after photolysis in the presence of oxygen, are shown in Fig. 1. During photolysis in the presence of oxygen, there is a gradual disappearance of the MLCT band, and the appearance of a less intense band at 355 nm (3050 M^{-1} cm^{-1}) for the methyl-substituted complex and at 347 nm (2400 M^{-1} cm^{-1}) for the benzyl-substituted complex. These new bands correspond to the MLCT involving Ru(III) and the carboxyamidopyridine ligand in both cases. A band of this type occurs in several $(NH_3)_5$Ru(III)–amide complexes [18,28]. During photolysis in oxygen, a unique product is obtained, identified as an Ru(III) complex with a carboxyamidopyridine ligand. Naal and coworkers [18,24,25,28] have isolated a similar product obtained electrochemically. The final product of the reaction involving the benzyl-substituted complex has an amber colour in aqueous solution, with characteristic bands at 265 and 355 nm, and is similar to that obtained by electrochemical oxidation [18,24,25] or by hydrolysis in alkaline media.

3.1. Electrochemical behaviour

Cyclic voltammetry of the photolysis product of the benzyl- substituted complex (positive scan started at 0.0 V) shows that the initial species is not present ($E_{1/2}$ = 400 mV vs. a saturated calomel electrode (SCE) in tetrafluoroacetic acid/acetate buffer [18]). Scanning in the inverse way yields two cathodic peaks,

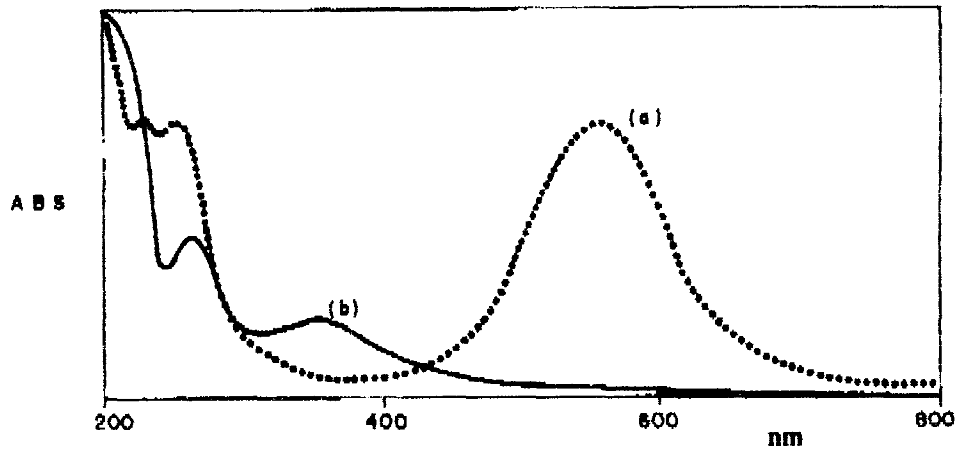


Fig. 1. UV–visible spectra of an aqueous solution of the pentaammine Ru(II) complex (*N*-benzyl-4-cyanopyridine): (a) before photolysis; (b) after photolysis.

$E_{CP1} = -260$ mV and $E_{CP2} = -820$ mV, and an anodic peak, $E_{AP} = -50$ mV, vs. Ag/AgCl for 100 mV s^{-1} scans.

This result illustrates that the species Ru(II)L′ (L′ ≡ *N*-benzyl-carboxyamidopyridine) is not stable, resulting in $[(NH_3)_5Ru(OH_2)]^{3+}$, with the Ru(II)/Ru(III) oxidation occurring at −50 mV and the reduction L′/L′$^-$ at −820 mV; this is in agreement with Naal [18] for an electrolysed Ru(II) complex, who concluded that the product was a pentaammine Ru(III) complex with a carboxyamidopyridine ligand.

Comparing the product of photolysis with that obtained by electrolysis [18], we can conclude that the product of photolysis is an $(NH_3)_5$Ru(III)–amide complex. The E_{CP} peak is related to the carboxyamidopyridine ligand reduction: this peak corresponds to the electrode process in the free amide. A comparison of E_{CP} with the potential of *N*-benzyl-4-carboxyamidopyridine, obtained chemically [18], shows that they are identical.

In order to obtain the peak associated with the Ru(II)/Ru(III)–amide process, the scans were varied up to 40 V s^{-1}. However, it was not possible to obtain the E_{AP} value corresponding to E_{CP1}.

A similar behaviour was observed in the methyl-substituted complex. With an inverse scan, at 200 V s^{-1}, cathodic peaks, $E_{CP1} = -329.7$ mV and $E_{CP2} = -934.7$ mV, and an anodic peak, $E_{AP} = -40.3$ mV, were observed. The oxidation potential Ru(II)/Ru(III) is −40.3 mV and the reduction potential L′/L′$^-$ is −934.7 mV.

3.2. NMR spectrum

The ^{1}H NMR spectrum obtained in water for the reaction product of the benzyl-substituted Ru(II) complex has the following characteristic signals (ppm): 2.50 (CH_2); 5.90 (NH_3); 7.50 (aromatic ring (5H)); 7.95 (amide); 8.4 and 9.1 (H from pyridine ring).

A similar behaviour was observed for the derivative obtained from the methyl-substituted complex. Signals at 4.80 ppm, corresponding to the methyl group, and 8.45 and 9.05 ppm, corresponding to the protons of the pyridine ring, were detected in the ^{1}H NMR spectrum of an aqueous solution of the oxidation product.

3.3. IR spectrum

An analysis of the IR spectrum of the derivative obtained from the benzyl-substituted complex shows the disappearance of the stretching associated with the C≡N band, observed in the precursor. The signals at 3445, 1667 and 1628 cm^{-1} are related to the carboxyamidopyridine ligand. The bands between 1458 and 1400 cm^{-1} are attributed to the aromatic and pyridine rings. These data are identical with those reported by Naal [18].

Similarly, an analysis of the spectrum of the oxidation product obtained from the *N*-methyl-substituted complex shows the following characteristic peaks: 3459.5, 3420.2, 1620.4 and 1400.5 cm^{-1}, related to the carboxyamidopyridine ligand.

These results show that there is no doubt about the transformation which occurs during the photolysis of an aqueous solution of the complex in an oxygenated medium. The degradation of the complex in an oxygenated medium in the absence of light is extremely slow when compared with the photochemical process. From these results and other evidence pointing to efficient singlet oxygen generation from the excited state of Ru(II) and other transition metal complexes [1–9], in particular Pt(II) complexes [9], we can conclude that the photochemical process involves the generation of singlet oxygen.

In Fig. 2, the typical behaviour of an aqueous solution of the benzyl-substituted complex on photolysis in an oxygen-rich atmosphere is shown.

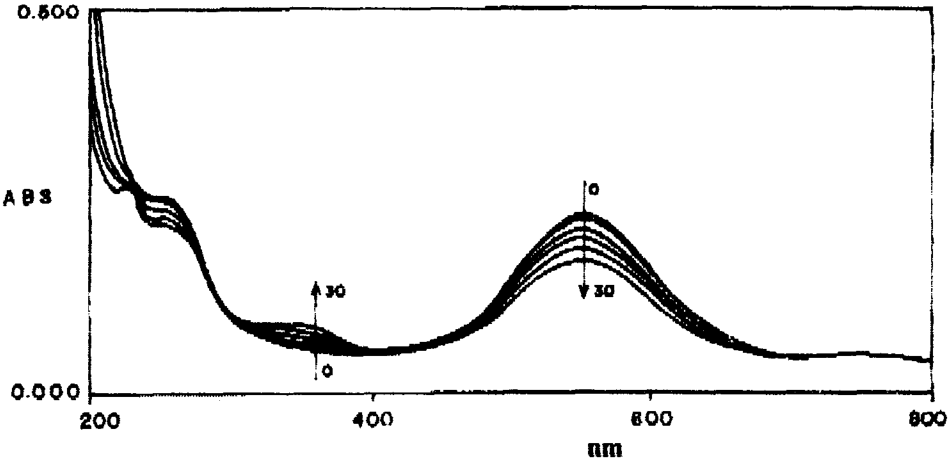


Fig. 2. Spectroscopic change observed during the degradation, induced by oxygen, of an aqueous solution of the pentaammine Ru(II) complex (*N*-benzyl- 4-cyanopyridine).

In oxygen-free solutions, the complexes are sufficiently stable on photolysis, and significant alterations are not observed in the UV–visible spectrum.

From the literature, it is expected that, on photochemical excitation of the MLCT band of the Ru(II) complex, a 1MLCT* state based on Ru(III) will be formed

$$\mathrm{Ru^{II}NC\text{–}R} \xrightarrow{h\nu} {}^1[\mathrm{Ru^{III}NC^-\text{–}R}]^*$$

This ^{1}MLCT* state has a very short lifetime as observed with other Ru(II) complexes [29]. This state decays to a ^{3}MLCT* state from which the observed reaction can occur.

3.4. Stern–Volmer correlation

A Stern–Volmer-like correlation was constructed from the data collected for the degradation of the methyl-substituted complex. A plot of $k(I)_0/k(I)$ vs. [Q] (Fig. 3) gives the relationship between k_Q and k_d, i.e. the quenching constant and deactivation constant of singlet oxygen by the action of the solvent respectively. These results confirm the active participation of singlet oxygen in the process. The addition of singlet oxygen quenchers to the reaction medium results in a reduction in the rate of degradation of the complexes.

Considering $k_d = 4.4 \times 10^5$ s^{-1} [15], as expected k_Q has diffusional character (1.2×10^{10} M^{-1} s^{-1}), and for this value physical quenching is dominant. Considering the typical rate constants for the oxidation of substituted phenols, chemical quenching must contribute with a rate constant between 10^6 and 10^7 M^{-1} s^{-1} to the value of k_Q [15,30]. These results show that competition exists between the quencher and the complex for the deactivation of singlet oxygen.

Fig. 4 shows a Stern–Volmer-like correlation obtained for the action of β-carotene as singlet oxygen quencher. The k_Q value has diffusional character (3.1×10^{10} M^{-1} s^{-1}), considering the value of k_d, and is in agreement with the results of Ref. [15], although the data for comparison are all related to non-aqueous solvents.

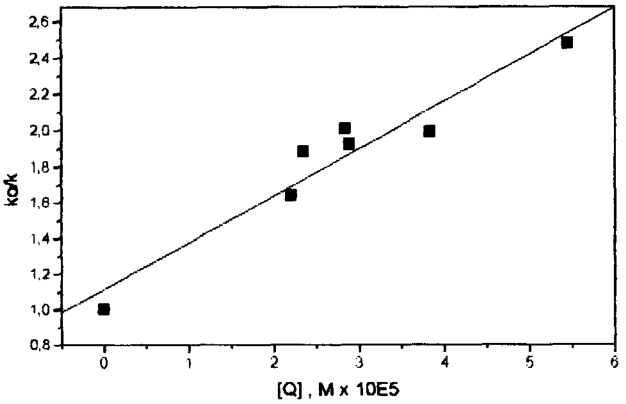


Fig. 3. Stern–Volmer correlation for the oxidation of the methyl-substituted complex in the presence of dehydrodivanillin as quencher. $k_Q/k_d = 26106.47$ M, $r = 0.9638$.

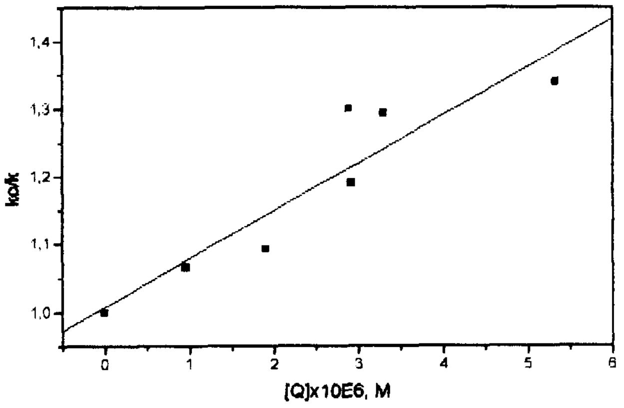


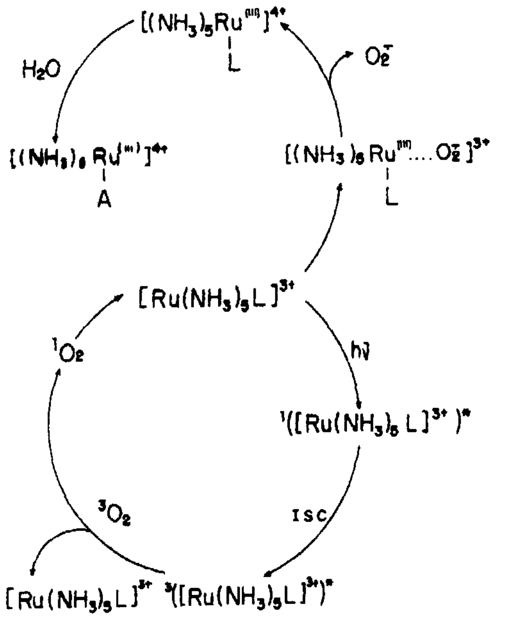
Fig. 4. Stern–Volmer correlation for the oxidation of the methyl-substituted complex in the presence of β-carotene as quencher. $k_Q/k_d = 70950$, $r = 0.9226$.

A mechanism (Scheme 1) can be suggested on the basis of these results. Singlet oxygen induces the oxidation of Ru(II) to Ru(III), which eliminates back-donation. As a result, the cyanopyridine ligand suffers rapid hydrolysis on the nitrile, forming a carboxyamidopyridine ligand associated with Ru(III).

3.5. Electron transfer step

The above mechanism proposes an electron transfer step for the interaction between Ru(II) and singlet oxygen. The electron transfer step can be confirmed by varying the polarity of the aqueous solution of the complex.

With the addition of increasing amounts of methanol, a decrease in the rate of degradation of the complexes is observed (Fig. 5).



Scheme 1.

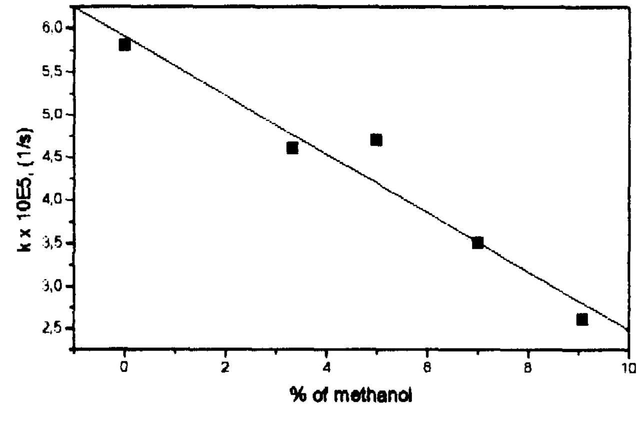


Fig. 5. Correlation between the k^{I} value and the percentage of methanol for the singlet oxygen-induced degradation of the methyl-substituted Ru(II) complex.

The solvent polarity decreases when the percentage of methanol is increased in aqueous solutions. As the interaction between singlet oxygen and Ru(II) can result in a radical ion pair, a decrease in the solvent polarity prejudices the solvation of the separated species. Thus electron transfer can be reversed and as a result singlet oxygen is suppressed.

$$A_5Ru^{II}R + {}^1O_2 \longrightarrow [A_5RRu^{III}:O_2^{\cdot -}]$$

$$\xrightarrow[\text{increasing}]{} \text{Product}$$

$$\xrightarrow[\text{decreasing}]{} A_5RRu^{II} + {}^3O_2$$

The state involving the encounter of singlet oxygen and Ru(II) must have the characteristics of an exciplex. A similar behaviour was observed for the complex with a benzyl substituent.

3.6. Kinetic treatment

On the basis of our results and kinetic studies on similar systems [15], we propose the following mechanism for the generation of $^1O_2$

$$C \xrightarrow{h\nu} {}^1C^* \xrightarrow{\text{ISC}} {}^3C^* \qquad v = I_a \Phi_T$$

$$^3C^* + {}^3O_2 \xrightarrow{k_1} C + {}^1O_2$$

$$C + {}^1O_2 \xrightarrow{k_2} C + {}^3O_2$$

$$C + {}^1O_2 \xrightarrow{k_r} \text{Product}$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2$$

where I_a is the intensity of incident radiation, Φ_T is the quantum yield of the triplet state produced from the complex in the presence of oxygen and v is the rate of formation of the triplet state of the complex.

The efficiency of triplet state formation from the excitation of the MLCT band must be very high, considering the characteristics of the Ru(II) complexes [31], and can therefore be neglected for the kinetic treatment. The measurement of the pseudo-first-order rate constants for different concentrations of the complex enable the rate constant k_{obs} $(k_2 + k_r)$ and the reactivity index β (related to the interaction between singlet oxygen and the Ru(II) complex) to be obtained. The singlet oxygen concentration was considered to be constant, because the $^3O_2$ concentration in these experiments is around 10^{-3} M vs. between 10^{-6} and 10^{-5} M for the complex. Then

$$\frac{d[{}^1O_2]}{dt} = 0$$

The rate law for the consumption of the complex, resulting in the formation of products, is

$$-\frac{d[C]}{dt} = k_r[C][{}^1O_2] = k^{\text{I}}[C] = \nu_{\text{ox}} \tag{1}$$

The quantity k^I was estimated for each concentration of the complex. Applying the steady state hypothesis

$$k_1[^3C^*][^3O_2]-k_2[C][^1O_2]-k_r[C][^1O_2]-k_d[^1O_2]=0$$

and substituting in Eq. (1), we obtain

$$\frac{d[C]}{dt}=k_r[C]\frac{\gamma[^3C^*][^3O_2]}{[C]+\beta}=k^I[C]=v_{ox}$$

with

$$\beta=\frac{k_d}{k_2+k_r}$$

and

$$\gamma=\frac{k_1}{k_2+k_r}$$

with

$$(v_{ox})^{-1}=(k^I[C])^{-1}=\frac{[C]+\beta}{\alpha[C]}=\frac{1}{\alpha}+\frac{\beta}{\alpha[C]}$$

Inverting this expression with

$$\alpha=\gamma k_r[^3O_2][^3C^*]$$

Then, plotting $1/v_{ox}$ vs. $1/[C]$, we can obtain the reactivity index and, indirectly, k_{obs}. The pseudo-first-order constants can be graphically evaluated from the equation

$$\ln A_t-\ln A_0=k^I t$$

where A_t is the absorbance after t min of reaction and A_0 is the absorbance of the sample before photolysis.

Fig. 6 shows a plot of $1/[C]$ vs. $1/v_{ox}$. Based on the value of k_d of $^1O_2$ in water [15], the value calculated for k_{obs} is 8.23×10^9 M^{-1} s^{-1}. This constant has diffusional character, signifying that the quenching of $^1O_2$ by the complex is very efficient. Estimates of k_r have shown that chemical quenching possesses a rate around 10^7 M^{-1} s^{-1}. This information, and the fact that the reaction is influenced by the solvent polarity, indicates that the chemical reaction between the complex and singlet oxygen must involve a charge transfer intermediate between Ru(II) and singlet oxygen with exciplex character. This exciplex intermediate can result in an electron transfer reaction.

3.7. Reactivity of the two complexes

The behaviour observed for the methyl-substituted complex (Fig. 7) is very similar to that observed for the benzyl-substituted complex, except that the oxidation of the benzyl-substituted complex occurs at a higher rate. However, the value of k_{obs} for the methyl-substituted complex is higher than that observed for the benzyl-substituted complex. This indicates that the physical deactivation of singlet oxygen by the methyl-substituted complex is more efficient than that of the benzyl-substituted complex. These differences in behaviour can be associated with the electronic effects of the substituents: the methyl group has a greater donor character than the benzyl group [32]. Electron donor groups reduce the electrophilic character of the pyridine ring, thus reducing the electron withdrawing effect observed over the cyano group and decreasing the rate of hydrolysis of the cyanopyridine ligand. This effect is reflected in the rate of degradation of the complexes (Fig. 8).

A comparison of the k^I values obtained from the linear regression curve gives a value of 2.34 for the relationship between the reactivities of the two complexes. By analysing the values of β, we can see that singlet oxygen is deactivated more efficiently by the methyl-substituted complex. At first sight these two results seem contradictory, but we must consider that β is related to the physical and chemical quenching of the oxygen species. The values of k^I are related to chemical quenching. Thus we can consider that the physical quenching of singlet oxygen by the methyl-

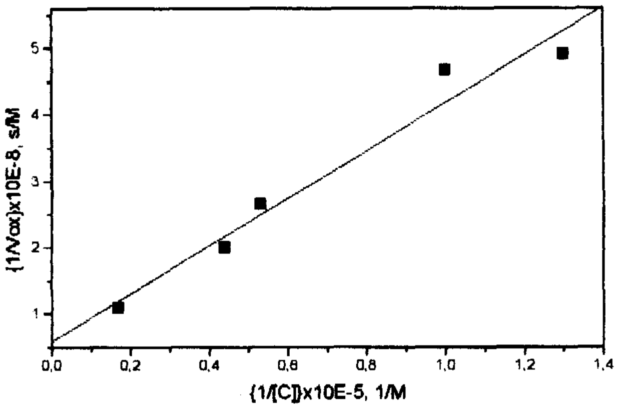


Fig. 6. Plot of $1/[C]$ vs. $1/v_{ox}$ for the interaction between singlet oxygen and the benzyl-substituted Ru(II) complex. $\beta=6.073\times10^{-5}$ M, $r=0.9805$.

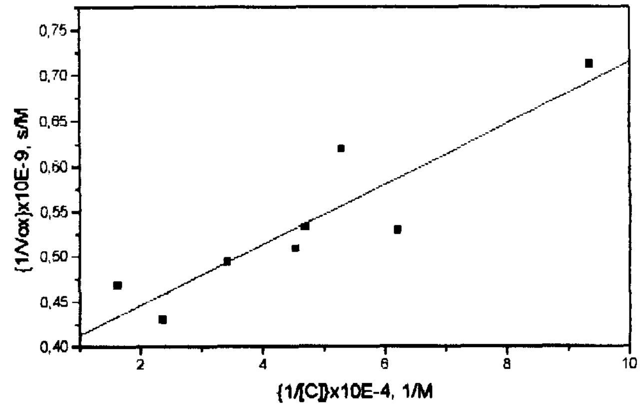


Fig. 7. Plot of $1/[C]$ vs. $1/v_{ox}$ for the interaction between singlet oxygen and the methyl-substituted Ru(II) complex. $\beta=8.848\times10^{-6}$ M, $k_{obs}=5.651\times10^{10}$ M^{-1} s^{-1}, $r=0.9031$.

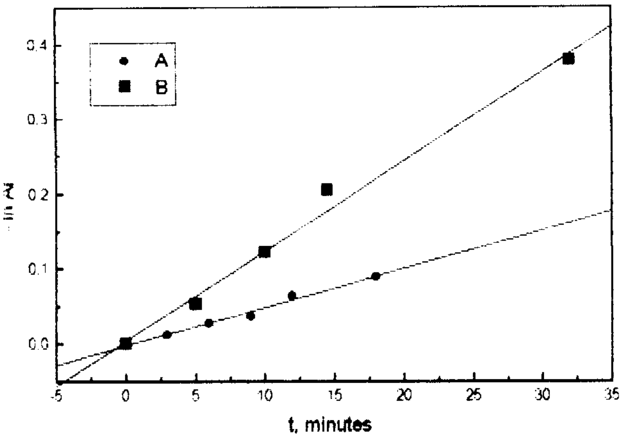


Fig. 8. Pseudo-first-order kinetics: (a) methyl complex; (b) benzyl complex. [C] = 1.89×10^{-5} M, k^1(benzyl)/k^1(methyl) = 2.34.

substituted complex is more efficient. When carrying out the separation of k_r and k_2 this becomes more evident. This effect is associated with the electron donor character of the methyl substituent. The increase in charge density over the cyanopyridine ligand can make electron transfer between Ru(II) and singlet oxygen difficult, resulting in an increase in the physical deactivation process of singlet oxygen. Naal [18], evaluating the effect of the substituent on the hydrolysis of the cyanopyridine ligand, observed the same tendency.

Conclusions

Ru(II) complexes sensitize the production of singlet oxygen, but are not stable in the presence of this species. As a result, Ru(II) is oxidized to Ru(III), and the cyanopyridine ligand suffers hydrolysis, resulting in a carboxyamidopyridine ligand in a new complex with Ru(III). The oxidation to Ru(III) occurs by electron transfer from Ru(II) to singlet oxygen.

The substituent in the N-position in the cyanopyridine ligand exerts considerable influence, increasing the stability of the complex against the action of singlet oxygen if it has electron donor character. This occurs because the donation of electron density reduces the electron deficiency on the pyridine ring, thereby decreasing the electron withdrawing effect on the cyano group coordinated to the metal centre. This prejudices the electron transfer process.

The results reported confirm the generation and active participation of singlet oxygen in these processes.

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