Photochemical Behaviour of Ru(BPY)₃Cl₂ Complex in Strong Acidic Media

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Room temperature deaerated solutions containing the Ru(bpy)₃Cl₂ complex are not stable when irradiated for long periods with λ > 400 nm. The decomposition rate increases with decreasing pH of the solution. The pH dependence of the photochemical and photophysical behaviour suggests an association between Ru(bpy)₃Cl₂ and H⁺ both in the ground and in the excited state of the complex.

Introduction

Photochemical studies on Ru(bpy)₃Cl₂* aqueous solutions have been focussed mainly on the energy transfer and electron transfer processes [1, 2]. Little attention, on the other hand, has been paid to the other photochemical reaction of this complex because it is thought to be quite stable both photochemically and thermally [3, 4]. In the course of previous work [5] we reported that (A) in 1 M HCl oxygen free solutions displays spectral modifications upon continuous irradiation with visible light.

Although these results are in contrast with the above mentioned reports [3, 4] they are supported by other Authors [6, 7]. In a preliminary note [8] we reported a study of the pH dependent photodecomposition of (A).

In this paper we report more recent results about the stability of (A) in water solutions. This seems of some interest because Ru(bpy)₃²⁺ is extensively used as energy transfer sensitizer [3] and has been proposed as a possible catalyst for the conversion of solar energy [1, 2].

Experimental Section

Materials

Ru(bpy)₃Cl₂·6H₂O was prepared and purified according to the literature [9].

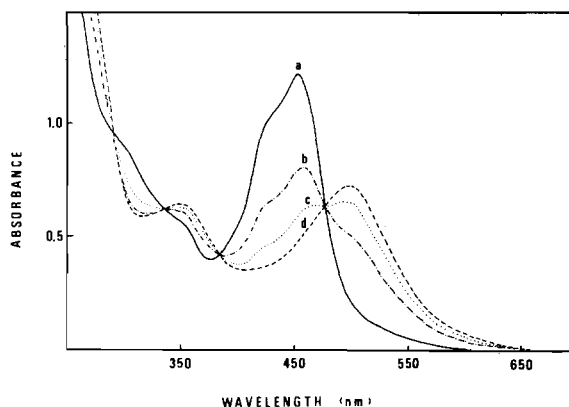---

*Ru(bpy)₃Cl₂ will be indicated as (A).

Fig. 1. Absorption spectrum of (A) as a function of photolysis time; [(A)] = 8 × 10⁻⁵ M in 2 M HCl. Excitation wavelength = 400 nm cut off filter (from Balzers A.G.), two IR filters (from Ealing Corp.); light intensity = 10¹⁷ photons/s; photolysis time: a = 0' b = 10', c = 20' d = 30', cell path = 1 cm.

HCl and H₂SO₄   RPE from Carlo Erba, were used for adjusting the pH of the solutions.

All the solutions used were prepared daily, carefully deaerated and kept in argon atmosphere. All the measurements were performed at room temperature in thermostatted reaction cells (1 cm path length).

Experimental Devices

The experimental devices like light source, photochemical and fluorimetric apparata are described elsewhere [5].

The spectrophotometric measurements were performed by a Perkin Elmer spectrophotometer model 555.

Results

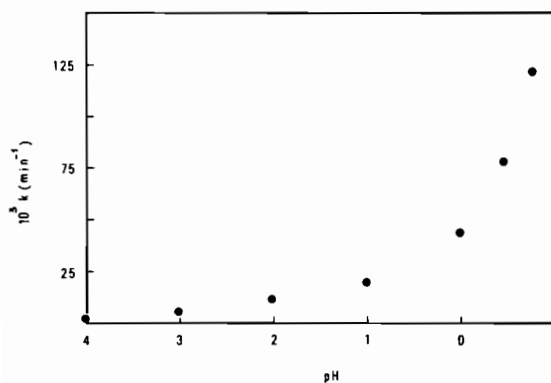The photolability of (A) (tested in the range 2 × 10⁻⁵ M ≤ [(A)] ≤ 2 × 10⁻⁴ M) in oxygen free solu-

Fig. 2. Rates of disappearance, v, of (A) as a function of pH. Initial conditions: $[A] = 1.5 \times 10^{-4}$, $\lambda = 450$ nm interference filter (from Balzers); $I_{ass} = 5 \times 10^{-7}$ Einstein/min. At all the pH the Cl^- concentration was kept constant and $= 3\,M$.

Fig. 3. 450 nm optical density of $[A] = 1.5 \times 10^{-4}\,M$ as a function of pH. $[Cl^-] = 3\,M$ was adjusted with NaCl.

tions is revealed by the changes observed in the absorption spectrum upon irradiation by photons with $\lambda >$ 400 nm. An example of the optical changes as a function of the irradiation time of a solution of the complex $8 \times 10^{-5}\,M$ is reported in Fig. 1. The photoreaction reaches completion in about one hour and during the photochemistry, several isosbestic points are maintained. This implies that possible thermal reactions take place in much longer times.

At the end of the photoreaction, upon basification to pH = 8, in any case, the ligand 2,2'-bipyridine was extracted with n-heptane [10]; the amount of the free ligand extracted corresponds stoichiometrically to the original amount of (A). The irradiated solutions are not stable for long periods, indicating that a very slow secondary thermal reaction takes place.

The rates of disappearance of (A), v, are reported in Fig. 2 as a function of pH and calculated using the straight line portion of the reaction profile $[(A)]_{450} = f\ (t_{irr})$ until a transformation of about 4% of initial complex.

It is to be noted that the decomposition reaction occurs also at neutral pH.

The photochemical quantum yields*, in the same experimental conditions of Fig. 2, is lower than 10^{-4} for pH > 4 and higher than 10^{-3} for pH < 0. The photodecomposition of (A) was confirmed by several experiments using different acids.

To get some information about the primary photoprocess, the absorption spectrum, the phosphorescence spectrum and lifetime of (A) were studied as a function of pH. The shapes of absorption and emis-
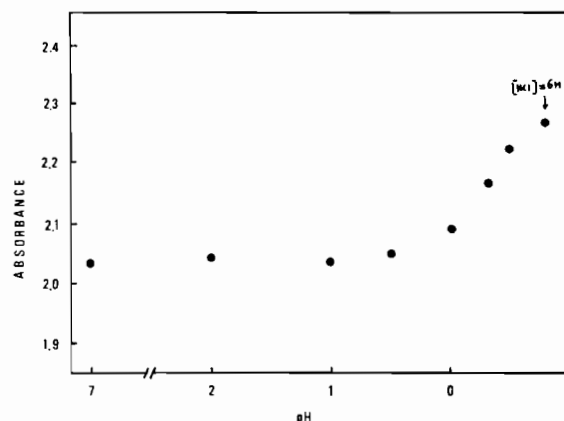
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*The photochemical quantum yields were calculated taking into account the ϵ of initial and final compounds and assuming a total transformation of (A) into the product.
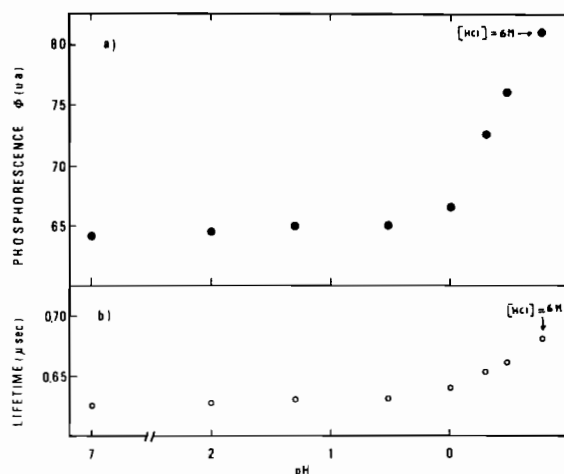

Fig. 4. a) Phosphorescence quantum yield vs. pH. b) Phosphorescence lifetime vs. pH. $[A] = 1 \times 10^{-4}\,M$, $[Cl^-] = 3\,M$; $\lambda_{ex} = 450$ nm, $\lambda_{em} = 610$ nm.

sion spectra are nearly insensitive to changes of the pH of the solution throughout the range of pH investigated. The lifetime shows a slight increase at pH $\cong$ 0. The same trend is shown by the phosphorescence quantum yield and optical density (measured at $\lambda = 452$ nm) of (A) solutions. These results are shown in Figs. 3 and 4. In the same Figs. are also reported the changes of the properties under study for solutions of (A) at [HCl] $= 6\,M$, corrected for the difference in the refractive index.

Discussion

From Figs. 1 and 2 we may see that (A) is not stable in a wide range of pH. The photochemical quantum yields obtained from our measurements are in agreement with those reported by Watts et

Fig. 5. a) Mean activity coefficients in aqueous solutions *vs.* the ion concentration; o = HCl, X = NaCl, □ = CaCl₂; from S. Glasstone, 'Thermodynamics for Chemists', p. 402, Van Nostrand, New York, 1960. b) Refractive index *vs.* the concentration. X = HCl, o = NaCl; 'Handbook of Chemistry and Physics', C.R.C. Press, 54th Edition. c) o = 450 nm optical density of (A) as a function of Ca⁺⁺ concentration; X = 610 nm phosphorescence quantum yield of (A) as a function of Ca⁺⁺ concentration. [A] = 1 × 10^{-4} *M*.

al. for the same complex [6]. As said previously, the shape of both the absorption spectrum (due to the transition $S_0 \rightarrow S_1$ (MLCT)) and the emission spectrum (attributed to the transition T_1 (MLCT) → S_0) are nearly insensitive to pH changes in the range of the investigated H⁺ concentration ($10^{-7} \leqslant$ [H⁺] $\leqslant$ 3 *M*).

However the absorption coefficient, the emission quantum yield and the lifetime show slight but meaningful changes at pH $\cong$ 0. (see Figs. 3 and 4).

These results suggest that the same electronic states are involved in the radiative transitions studied throughout the range of pH used and that these states are little influenced by pH changes.

The log v, calculated from the data reported in Fig. 2, depends linearly on pH and follows the relationship: log v = a − 1/3 pH.

The changes displayed at pH $\cong$ 0 are not due to the variation of refractive index of the solutions employed. In fact as shown in Fig. 5b, the trend of this property *vs.* concentration is similar for aqueous solution of HCl and NaCl. The photochemical and photophysical changes are not due to changes of the ionic strength of the solution. In fact the photophysical and photochemical properties of (A) at

different various concentrations of Ca⁺⁺, do not vary appreciably (Fig. 5c), although the activity coefficients of the ions H⁺ and Ca⁺⁺ plotted *vs.* the ion concentrations show clearly the same trend (Fig. 5a).

Moreover we may exclude that the decomposition of irradiated solutions of (A) is due to an impurity present in the complex and not eliminated with the common methods of purification. In fact the (A) purity was tested by passing the solutions containing the complex onto a 1.8 × 18 cm column of Sephadex C-25 cation exchange resin.

An explanation of the preceding results could be the protonation of the photoreactive state of (A) followed by the loss of the 2,2'-bipyridine ligand and the uptake of solvent molecules (Cl⁻ ion is not excluded owing to the high Cl⁻ concentration).

The main final product(s), therefore, is thought to be of the type Ru(bpy)₂XY with X = H₂O; Y = H₂O, Cl⁻. In fact the spectra of the product(s) reported in Fig. 1 with the maximum at λ = 500 nm, are in agreement with the spectra reported for species of the same type [11, 12].

More recently G. B. Porter and R. Sparks [14] suggest that a common dissociative mechanism involves the photoaquation and the photoracemization of (A) and that the two processes start from a common achiral intermediate which is formed from the ³CT state of Ru(bpy)₃²⁺.

However our results are not sufficient to discriminate with certainty among the possible states responsible for the primary step of the decomposition of Ru(bpy)₃Cl₂ aqueous solutions, firstly owing to the small quantum yield of the process. On the other hand little is known in the literature about this problem [6, 13].

Conclusions

We have observed that Ru(bpy)₃Cl₂, when irradiated with λ = 400 nm for long time at room temperature and in oxygen free solutions, slowly decomposes in a wide range of pH. The photodecomposition involves the loss of one 2,2'-bipyridine ligand. The rate of the photoprocess increases with decreasing pH, and although the quantum yield is low, the decomposition of Ru(bpy)₃Cl₂ should be taken into account if it is used under conditions of prolonged irradiation and particularly, under very strong acidic conditions.

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