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Photoproducts from the Photolysis of Tris(bipyridine)ruthenium(II) Chloride in Dimethylformamide

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Abstract

Six photoproducts were observed in the photolysis of $[Ru(bpy)_3]^{2+}$ in *N,N*-dimethylformamide (DMF) in the presence of chloride ions. The primary products were *cis*-$[Ru(bpy)_2Cl_2]$ and *cis*-$[Ru(bpy)_2(DMF)Cl]^+$. The remaining ruthenium products, which were thermally unstable to varying degrees, were *cis*-$[Ru(bpy)_2Cl_2]^+$, $[Ru(bpy)_3]^{3+}$, and a binuclear species we have tentatively identified as $[Ru(bpy)_2Cl]_2^{n+}$ ($n = 3$ or 4).

Introduction

In less polar solvents, photolysis of $[Ru(bpy)_3]X_2$ (bpy = 2,2′-bipyridine) leads efficiently to *cis*-$[Ru(bpy)_2X_2]$ [1–4]. In more polar solvents photolysis is characterized by formation of both *cis*-$[Ru(bpy)_2X_2]$ and *cis*-$[Ru(bpy)_2SX]^+$ (S = solvent) by parallel pathways [5, 6]. With Br^- and SCN^- as anions no other products are obtained in significant yield in dimethylformamide (DMF). We report here results with chloride ion, for which we have observed five different ruthenium photoproducts.

Experimental

$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (G.F. Smith) was recrystallized before use, after first passing it through an anion exchange column in Cl^- form. $[Ru(bpy)_2Cl_2]$ [7] and $[Ru(bpy)_2Cl_2]Cl$ [8] were synthesized by literature methods. Photolyses were carried out at two different concentrations of $[Ru(bpy)_3]Cl_2$. 0.02 M solutions, with additional chloride in the form of $(C_2H_5)_4NCl$ present, were used as a prelude to chromatographic separation of products. 5×10^{-5} M solutions were used in order to follow the product development spectrophotometrically. Irradiation was carried out with a 500-W Hg lamp on N_2-purged solutions in DMF. Chromatographic separations were performed on a refrigerated Sephadex LH-20 column, eluting with cold (5 °C) DMF. Absorption spectra were measured on a Hewlett-Packard Model 8451A diode array spectrometer and a Cary 14 spectrophotometer.

Results and Discussion

The colored fractions obtained from LH-20 chromatography of the photolysate from a 30 min irradiation of 0.02 M $[Ru(bpy)_3]Cl_2$ in DMF are listed in Table I in the order of elution. VI is the reactant, $[Ru(bpy)_3]^{2+}$. Photolyses at low Ru concentrations (5×10^{-5} M) and short irradiation times yielded only I and V, which can readily be identified as *cis*-$[Ru(bpy)_2Cl_2]$ and *cis*-$[Ru(bpy)_2(DMF)Cl]^+$, respectively, by analogy with the bromide complexes [6], and by spectral comparison with the directly synthesized dichloro complex [4, 9]. These are the primary photoproducts. Longer irradiation times at low concentration yielded increasing amounts of an additional product, III.

The composition of the low concentration photolysate was monitored by interrupting irradiation periodically and measuring absorption spectra.

TABLE I. Properties of the Components of a $[Ru(bpy)_3]Cl_2$/Et_4NCl Photolysate in DMF

Band[a]	Color	λ_{max} (nm)
I	purple	559, 372
II	red	(560)[b], 386
III	yellow–brown	610sh, 512sh, 465sh, 417[c]
IV	blue	628, 557, 515sh, 382
V	red	515, 345
VI	orange	454
VII	green	630, 450sh

[a] Band I was eluted first, band VII last, from Sephadex LH-20. [b] Due to presence of I. [c] Narrow.

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With the spectra of $[Ru(bpy)_3]Cl_2$ and chromatographically isolated **I**, **V**, and **III** as standards, the spectrum of a photolysis mixture could be resolved into a linear combination of the contributing spectra by a linear least-squares analysis. The coefficients assigned to each standard spectrum are directly proportional to the concentration in the photolysate of the species giving rise to the reference spectrum, and the proportionality constants between the coefficients and the concentrations could be determined from an optimization over all data collected, using the condition of constant total ruthenium. Details of this treatment have been given previously [6].

By referring to the standard spectra, the proportionality constants can be directly converted to extinction coefficients. For $[Ru(bpy)_2Cl_2]$ (**I**), $\epsilon_{560} = 8.2 \times 10^3$ from the optimized proportionality constants, compared to 8.3×10^3 determined directly by dissolving solid $[Ru(bpy)_2Cl_2]$ in DMF. For $[Ru(bpy)_2(DMF)Cl]^+$ (**V**), $\epsilon_{515} = 1.2 \times 10^4$. The proportionality constant for **III**, however, was zero. **III** played no role in the mass balance, and is therefore not a ruthenium species.

The product development during a typical photolysis experiment is illustrated in Fig. 1. **III** is included for comparison, although the absolute concentrations are not known. The buildup of **III** as a secondary photoproduct after the appearance of the bis(bipyridine) species **I** and **V** suggests that it is derived from the bipyridine released in the primary photoprocess.

1,10-phenanthroline undergoes photohydrogenation to 1,10-dihydro-1,10-phenanthroline upon irradiation in a variety of solvents [10]. An equivalent photoprocess has apparently not been observed for 2,2′-bipyridine. Chemical and electrochemical reduction of bipyridine have yielded several isomeric dihydrobipyridines, although none of them have been isolated [11, 12]. It is likely that **III** is a reduced bipyridine species of some kind, its formation probably sensitized by one or more of the ruthenium complexes present. The loss of aromaticity is the most likely explanation for the appearance of the conspicuous, relatively narrow band at 417 nm (Fig. 2). A brown color has been noted for one dihydro-2,2′-bipyridine, although no spectral data were reported [12].

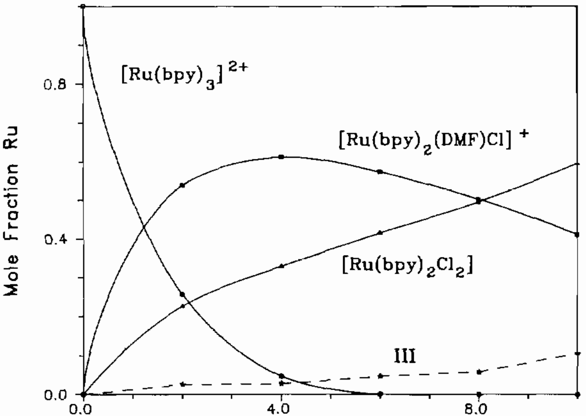

Fig. 1. Time development of the reaction mixture on irradiation a solution containing 5×10^{-5} M $[Ru(bpy)_3]Cl_2$ and 6×10^{-4} M $(C_2H_5)_4NCl$ in DMF. Concentrations of III, the reduced bipyridine species, could not be determined absolutely and are only relative.

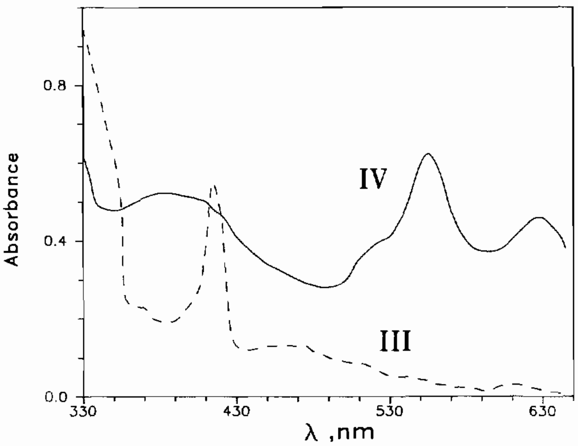

Fig. 2. Visible absorption spectra of III, the reduced bipyridine species, and IV, the chloride-bridged dimer, in DMF.

$[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_2(DMF)Cl]^+$ can be interconverted photochemically and thermally, although the thermal reaction is slow. Complete solvolysis of $[Ru(bpy)_2Cl_2]$ to **V** in DMF requires several days. The photochemical interconversion is observable in Fig. 1. The ratio of **I** to **V** in the photostationary state, which is approached only slowly, depends on the chloride ion concentration, and is different from the ratio in which **I** and **V** are created from $[Ru(bpy)_3]^{2+}$ in parallel primary photoprocesses. The latter is equal to the ratio of the initial slopes in Fig. 1. The quantum yield for the photochemical interconversion of the bis(bipyridine) species is about an order of magnitude higher in these solutions than in solutions of pure **I** or **V**.

When more concentrated solutions were irradiated and the products separated chromatographically, **I**, **V**, **III**, and three additional products were found, as listed in Table I. The three new products were all thermally unstable over a period of hours or days. The green fraction **VIII** was obtained only in very low concentrations. It reacted completely within hours, but the product(s) could not be identified. The spectrum and color match that of $[Ru(bpy)_3]^{3+}$ reasonably well [13]. The red fraction **II** was identified as *cis*-$[Ru(bpy)_2Cl_2]^+$, by comparison with the spectrum in DMF of samples synthesized by literature procedures [8].

When *cis*-$[Ru(bpy)_2Cl_2]^+$ is dissolved in DMF, it is reduced to *cis*-$[Ru(bpy)_2Cl_2]$, both thermally, to some extent, and photochemically. Thermal reduction proceeds quite rapidly to a stationary state that is more favorable to Ru(II) the lower the concentration. More Ru(II) is formed upon irradiation. Although the crystals are red, moderately concentrated (10^{-2} M) solutions are yellow, the color deriving primarily from a band at 386 nm ($\epsilon = 1.1 \times 10^3$). More dilute solutions are red or purple, due to the presence of Ru(II).

The blue fraction **IV** was also unstable. Within 6 h its spectrum was largely replaced by that of $[Ru(bpy)_2Cl_2]^+$ (**II**), with some $[Ru(bpy)_2Cl_2]$. The blue color arises from a peak at 628 nm (Fig. 2). Meyer and coworkers have shown numerous examples of polynuclear ruthenium complexes, many of which have the feature of a band in the red or near-infrared in common [14–16]. The existence of this band does not appear to depend on whether the complexes are mixed-valent or not, but is not characteristic of species with Ru(II) alone [15, 16]. The appearance of this complex only at high ruthenium concentrations is consistent with the assignment of **IV** to a binuclear (or possibly higher order) complex. There are numerous examples of chloride-bridged ruthenium complexes [17–21], including $[Ru(bpy)_2Cl]_2^{n+}$ [15]. The stable (II,II) complex ($n = 2$) has been shown to generate transient (II,III) and (III,III) complexes electrochemically in CH_2Cl_2, although they were so short-lived that no spectral data could be obtained [15].

The thermal dissociation of **IV** initiates a sequence of thermal reactions through identifiable species

$$\mathbf{IV} \xrightarrow{6\ h} \mathbf{II} \xrightarrow{48\ h} \mathbf{I} \xrightarrow{72\ h} \mathbf{V}$$

The complete reduction of $[Ru(bpy)_2Cl_2]^+$ to $[Ru(bpy)_2Cl_2]$ is evidence that there is more to the dissociation of **IV** than this shows, since by itself $[Ru(bpy)_2Cl_2]^+$ is not completely reduced. Meyer and coworkers have shown that the oxidation of the dimer $[Ru^{II}(bpy)_2Cl]_2^{2+}$ is followed by decomposition to $[Ru(bpy)_2Cl_2]^+$ [15]. Presumably the cleavage left a disolvated $[Ru(bpy)_2S_2]^{2+}$ species, though apparently spectral evidence was lacking [15]. It is possible that the second fragment was very reactive.

We therefore suggest that the blue species **IV** is the dichloro-bridged $[Ru(bpy)_2Cl]_2^{n+}$ (n = 3 or 4). Its stability in DMF, though not high, appears to be greater than in less polar solvents. We too cannot trace the fate of the second decomposition fragment. It is possible that it reacts quickly with $[Ru(bpy)_3]^{3+}$ or excited $[Ru(bpy)_3]^{2+}$ to eventually generate another dimer.

The order of elution on Sephadex LH-20 is a potential source of information for characterization purposes. The molecular properties that lead to separation on LH-20 with organic solvents are not entirely known, although a specific preference for molecules with aromatic rings has been noted [22]. In this study, the ionic charge appears to be a major factor. The five mononuclear ruthenium species are eluted in order of increasing charge. The quixotic nature of LH-20 is demonstrated by the elution order of $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(EtOH)Cl]^+$, and $[Ru(bpy)_2Cl_2]$ when the photolysis and chromatography are done in ethanol: it is exactly the reverse of the order in DMF.

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