

Photoanation of the Tris(2,2'-bipyridine)ruthenium(II) Cation by Thiocyanate

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Abstract: $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ in dimethylformamide is photolyzed with a quantum yield of 10^{-3} or less depending on thiocyanate concentration. The two main photoproducts, $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, are produced via SCN^- -independent (apparently) and SCN^- -dependent pathways, respectively. A secondary photolysis and an ion-pair/ion-triplet (two primary photolytic steps) model are considered. The latter appears somewhat more reasonable, on the basis of the detailed dependence of the quantum yields on the thiocyanate concentration.

Introduction

In recent years $[\text{Ru}(\text{bpy})_3]^{2+}$ has come to be used increasingly as a triplet sensitizer for transition metal complexes, both for luminescence¹⁻⁶ and for photochemistry.^{2,8-12} Its high extinction coefficient in the blue and ultraviolet spectral region, as well as its efficient energy transfer,³ appear to make it ideal for this purpose. It has also been reported that no permanent photochemical changes are induced by irradiation,^{8-10,13} although a transient species, thought to involve Ru(III), has been observed in flash photolysis experiments.⁹ In addition, in strongly acidic medium $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizes the photoreduction of many transition metal complexes, producing $[\text{Ru}(\text{bpy})_3]^{3+}$,^{2,10} whereby it appears that a direct photoinduced electron transfer is implicated.^{2,14}

As we show in this study, however, the range of conditions under which $[\text{Ru}(\text{bpy})_3]^{2+}$ may be considered photochemically inert is actually rather restricted. In solvents of lesser polarity than water, and in the presence of anions capable of acting as ligands, low quantum yield permanent photoreactions do indeed take place. Since energy transfer experiments using $[\text{Ru}(\text{bpy})_3]^{2+}$ are being carried out increasingly in nonaqueous solvents such as dimethylformamide (DMF),^{3,5,7} a better understanding of the photochemical behavior of this species is essential, especially since $[\text{Ru}(\text{bpy})_3]^{2+}$ is used at very low concentrations, such that even small quantum yields of reaction can seriously deplete the concentration of this sensitizer.

The thiocyanate salt was chosen for detailed study because the presence of isobestic points pointed toward the formation of a single photoproduct under most conditions. Although this conclusion proved illusory, the system was somewhat better behaved than systems with some other anions (Cl^- , Br^- , and CN^- exhibit similar photosubstitution behavior), and the products were both relatively stable thermally.

Experimental Section

Preparation of Complexes. $[\text{Ru}(\text{bpy})_3](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$. $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (G.F. Smith Co.) was dissolved in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1) and passed through a Dowex 1-X8 column in SCN^- form, utilizing <5% of the resin capacity. Upon evaporation of the methanol/water solution, red crystals were formed, which were dried in vacuo. Anal. Calcd for $[\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$: C, 52.0; H, 4.06; N, 15.16. Found: C, 52.0; H, 4.0; N, 14.93.

$[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. $[\text{Ru}(\text{bpy})_3](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ (0.2 g) was dissolved in ethanol (30 mL), placed in a 10-cm spectrophotometer cell, deoxygenated by bubbling nitrogen gas through the cell for 15 min, and irradiated for 48 h with a 100-W Hg lamp. The black crystals which formed were filtered, washed with ethanol, and dried in vacuo. Anal. Calcd for $[\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{NCS})_2] \cdot 0.75\text{H}_2\text{O}$: C, 48.66; H, 3.23; N, 15.48. Found: C, 48.67; H, 3.20; N, 15.13.

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An alternative preparation, following the method of Liu, Liu, and Bailar¹⁵ for $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$, whereby $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ was heated on silica powder under vacuum, was also employed. Extraction with Me_2SO yielded a mixture of complexes, which could be separated on Sephadex LH-20. The spectrum of the product obtained in this fashion (first band on LH-20/ Me_2SO) was identical with that of photolytically produced $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$.

Physical Measurements. Absorption spectra were recorded with a Cary Model 11 spectrophotometer. Infrared spectra were measured on KBr pellets using a Perkin-Elmer Model 225 spectrometer. NMR spectra were recorded with Varian T-60 and HA-100 spectrometers. Conductivity measurements were made with a Radiometer conductivity meter.

Photolyses were carried out with an unfiltered 100-W, medium-pressure PEK mercury vapor lamp. The sample was contained in a round 1.0-cm spectrophotometer cell positioned about 20 cm from the lamp. Unless otherwise mentioned, all samples were deoxygenated by bubbling N_2 through the solution for 15 min.

Ruthenium complex mixtures in DMF were separated chromatographically using DMF-equilibrated Sephadex LH-20 dextran gel with either gravity feed or about $1/3$ atm N_2 overpressure. The 1.5-cm i.d. columns were filled to a depth of ca. 40 cm, and the sample size was generally 2 mL. Elution of the products was usually complete in 3 h using gravity feed.

Quantum yields were determined by ferrioxalate actinometry¹⁶ using the 442-nm line of a helium/cadmium laser for irradiation, delivering a continuous power of about 40 mW.

Results

1. Photolysis of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ without Added Anion.

Several salts of $[\text{Ru}(\text{bpy})_3]^{2+}$, dissolved in DMF at concentrations near 10^{-4} M, decompose upon irradiation with visible or UV light very slowly, with a quantum yield for disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ generally less than 10^{-4} . For the thiocyanate salts isobestic points were observed at 475 and 412 nm which persisted up to 25% decomposition. The quantum yield was decreased as much as a factor of 3 by addition of tetrabutylammonium nitrate as a backing electrolyte.

In order to effect a physical separation of the product and reactant mixture by chromatography, it was necessary to use somewhat higher concentrations than those convenient for spectral analysis. The photolysate from 10^{-3} M solutions of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ in DMF, after the reactant had been depleted by ca. 50%, was resolved into three bands by passage through a DMF-equilibrated Sephadex LH-20 column. The first two bands were red and orange-red in color and represented products I and II, respectively. The last band eluted was the reactant. Electronic spectral data for these compounds are listed in Table I (extinction coefficients for I and II were determined from other experiments). One or more additional minor products were sometimes found as separated bands from the Sephadex column. Neither the yields nor the elution order of the minor products were reproducible, but the longest

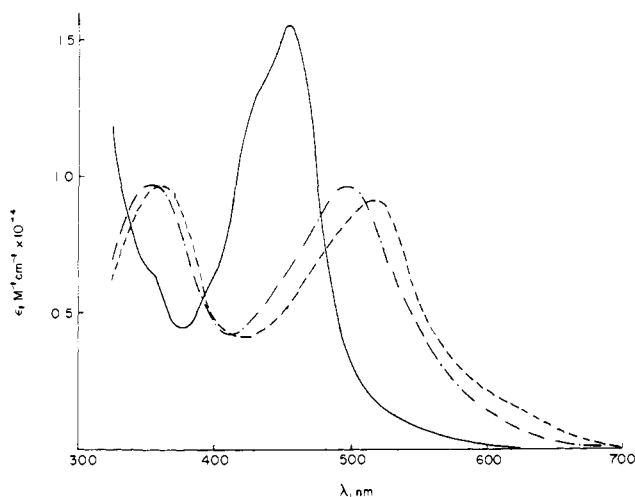


Figure 1. Absorption spectra in dimethylformamide of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ (—), $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ (---), and $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})](\text{SCN})$ (· · ·). The last complex was generated photolytically in solution from $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$.

Table I. Data for Species Found after Irradiation of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$

Order of elution on LH-20/DMF	λ_1^{max} , nm (ϵ)	λ_2^{max} , nm (ϵ)	Molar conductivity, $\Omega^{-1} \text{cm}^2$ (in DMF)
I	515 (0.93×10^4)	360 (0.98×10^4)	3 ± 0.5
II	498 (0.98×10^4)	353 (0.98×10^4)	80 ± 25
III	454 (1.56×10^4)		170 ± 10

wavelength absorption of these materials was generally red shifted relative to the two main photoproducts.

The electronic spectrum of the first band material (I) was identical with that of DMF solutions of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, prepared either photochemically, as outlined above, or thermally.¹⁵ The low conductivity in DMF (Table I) is consistent with the identification of I with $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, with a cis configuration and N-bonded thiocyanate.¹⁷ We were not able to isolate pure solid material from DMF solutions of either I or II.

The electrical conductivity of II suggests a 1:1 electrolyte in DMF. For $[\text{Cr}(\text{en})_2\text{Cl}_2](\text{SCN})$, for example (en = ethylenediamine), a molar conductance of $79 \Omega^{-1} \text{M}^{-1} \text{cm}^{-1}$ at a concentration of $2.7 \times 10^{-4} \text{M}$ ¹⁸ has been reported. The molar conductance reported in Table I is consistent with the formulation of II as $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$. The error limits in the conductivity represent our uncertainty in the extinction coefficient, and therefore in the concentration. The spectrum of II is shown in Figure 1. A solution with a substantially identical spectrum can be generated reversibly by photolysis of I, also consistent with the assignment of II to the monosolvated $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})](\text{SCN})$.

When HgCl_2 (in DMF) was added to a DMF solution of II, an immediate color change occurred, and the band maxima shifted to shorter wavelengths. This is consistent with removal of a remaining thiocyanate from the Ru(II) coordination sphere. The spectrum of $[\text{Ru}(\text{bpy})_2(\text{DMF})_2]^{2+}$ is not known with certainty, but it does appear that substitution of DMF for NCS^- is associated with a blue shift (refer to the spectra of I and II in Figure 1).

In spite of the fact that two main product species were formed at the necessarily higher concentrations used for chromatography, only one of them, $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$, appears to have been present in significant yield in

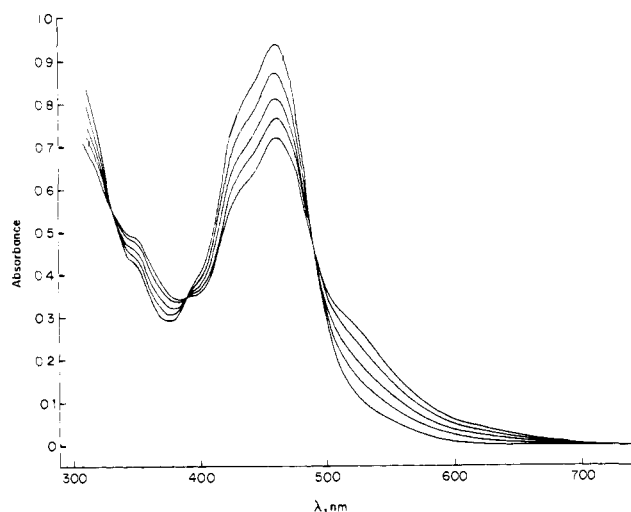


Figure 2. Sequential spectra illustrating irradiation of a N_2 -saturated, $6 \times 10^{-5} \text{M}$ solution of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ in DMF, with 0.096M NaSCN added. Irradiation was with the 442-nm line (ca. 50 mW) of a He-Cd laser. The time intervals are 300 s. Although three isosbestic points are apparent, two products are being formed.

the photolyses run at low concentrations, for which spectrophotometric monitoring was employed. In fact the absorption at the observed isosbestic points is mirrored exactly in the spectrum of the mono-DMF complex at the corresponding wavelengths (this would lead to an estimate of $1.25 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$ for the extinction coefficient of the first band in this complex). Nevertheless, and despite the fact that reasonable isosbestic points were obtained, a detailed reconstruction of the spectrum of a reaction mixture after photolysis was not possible assuming only $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ in the mixture. At least one additional species was present in small amounts which disturbed the fit to the spectrum, especially in the region 360–400 nm. The discrepancy between observed and calculated spectra could not be explained solely by the presence of some $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$.

Since we could not account for all of the products under these conditions, the estimate of the extinction coefficient of $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ from isosbestic points is not reliable, nor can a quantum yield for this process be accurate (ϕ would be about 9×10^{-5} for disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$, if only one product is assumed, and a least-squares fit of the spectrum of the reaction mixture after photolysis is made to the spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$, leaving the extinction coefficient of the latter species to vary for best fit).

2. Photolysis of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ with Added Thiocyanate. Additional NaSCN in DMF solutions of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ increased the rate at which $[\text{Ru}(\text{bpy})_3]^{2+}$ was consumed under irradiation. At Ru(II) concentrations suitable for spectrophotometric monitoring (ca. $5 \times 10^{-5} \text{M}$), three isosbestic points were observed in sequential spectra (Figure 2), but the wavelengths at which the isosbestic points occurred were found to vary with the concentration of thiocyanate, 4 nm being the largest variation observed over the range of thiocyanate used. These isosbestic points (typical values 480, 393, and 338 nm) were shifted markedly from those seen in photolyses with no added thiocyanate (475 and 412 nm).

At the 10- to 30-fold higher concentrations of $[\text{Ru}(\text{bpy})_3]^{2+}$ employed for chromatography only two bands were observed on Sephadex LH-20 when NaSCN (0.02–0.5 M) was added before photolysis. The second band eluted contained the unreacted tris complex, while the spectrum of the first band indicated that it was $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. Separation charac-

Table II. Rates of Disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$, and Formation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ and $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ at Various Thiocyanate Concentrations, $\text{M s}^{-1} \times 10^8$ ^a

$[\text{SCN}^-]$, M	$d[\text{Ru}(\text{bpy})_3]^{2+}/dt$	$d[\text{Ru}(\text{bpy})_2(\text{NCS})_2]/dt$	$d[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+/dt$
0.0089	4.3	1.1	3.4
0.0188	5.5	2.5	3.1
0.0222	6.3	2.7	3.7
0.0279	5.6	3.1	2.6
0.0454	7.9	4.7	3.3
0.0786	8.7	4.2	4.5
0.114	10.0	6.0	4.0
0.169	9.8	7.6	2.3
0.268	12.6	9.2	4.0

^a Straight-line portion of concentration vs. time curve; $[\text{Ru}] \sim 6 \times 10^{-5} \text{ M}$; irradiation with full Hg arc.

teristics on Sephadex LH-20 are impaired by the presence of higher concentrations of electrolyte, so that at the highest thiocyanate concentrations used (0.5 M) no clear separation of the two bands was produced. Nevertheless, monitoring of the leading and trailing edges of both bands did not produce any indication that significant amounts of $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ might have been present at any SCN^- concentration used.

In spite of the maintenance of clear isobestic points up to 40% consumption of the tris complex and in spite of the evidence that only one product is formed at higher ruthenium concentrations, the absorption spectra of irradiated samples could not be even approximately represented as combinations of spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. When $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ was also included as a possible photoproduct, the fit became quite good, deteriorating only after 30–40% consumption of the tris species, and even then only in certain wavelength regions (ca. 400 and >550 nm). The remainder of the analysis of the data from absorption spectra was carried out under the assumption that only these two product species were produced in significant amounts.

Extinction coefficients were readily determined for both $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ and $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, but the monosolvated complex could not be isolated as a solid, nor were the DMF solutions of this complex analyzed for Ru (we were not able to obtain solutions more concentrated than about $1 \times 10^{-4} \text{ M}$ in this complex). Estimates of the extinction coefficient had been obtained by generating $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ from the tris complex with no added SCN^- and from $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. The spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ appeared to be relatively independent of thiocyanate over the range employed in this study (0.009–0.27 M), although a slight decrease in extinction coefficients seemed to occur at the higher thiocyanate concentrations (>0.1 M).

The extinction coefficient of the mono-DMF complex was chosen to give a best fit to the spectral data. The procedure was to resolve each spectrum (for a given $[\text{SCN}^-]$ and irradiation time) as an additive combination of reference spectra chosen for the three Ru(II) component species. This was done by solving for the appropriate coefficients using three points from the spectrum to be analyzed, then resynthesizing the whole spectrum using these coefficients to check the fit. As already mentioned, this procedure generally produced satisfactory fits, especially for shorter irradiation times. The $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ extinction coefficient was then chosen so that the concentrations of the three Ru(II) species added up to the initial $[\text{Ru}(\text{II})]$ as closely as possible for all SCN^- concentrations and irradiation times. Agreement was not always perfect, but in most cases the calculated sum of the Ru(II) concentrations was within 5% of the starting value. The ex-

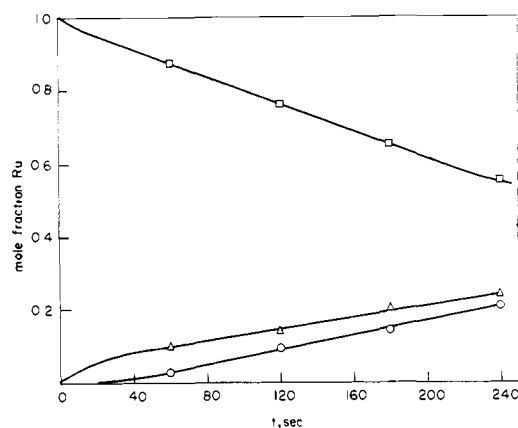


Figure 3. Typical reaction profile for photolysis of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$. Initial conditions are $6 \times 10^{-5} \text{ M}$ $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ and 0.114 M NaSCN. Irradiation source is a mercury lamp. \square , $[\text{Ru}(\text{bpy})_3]^{2+}$; Δ , $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$; \circ , $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$.

inction coefficients in Table I are the ones resulting from this procedure.

In Figure 3 is displayed a typical concentration vs. time profile. Characteristic of such profiles at each thiocyanate concentration are the relatively rapid initial rates for consumption of $[\text{Ru}(\text{bpy})_3]^{2+}$ and for production of $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$, the slow initial rate of formation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, and leveling off to linear rates of formation and disappearance for all three species. The discrepancy between initial rate and the eventual linear rate is much less prominent for the tris complex than for the two photoproducts. The linear rates observed for formation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ vary markedly with the thiocyanate concentration, so that the formation curves for the two products cross under some conditions and diverge under others.

In Table II is a compilation of the rates of formation and disappearance of the three Ru(II) species as a function of SCN^- concentration using the straight line portions of the reaction profiles. It would also be desirable to compare the initial photoreaction rates as a function of thiocyanate, but this would require precise data for short irradiation times beyond the spectrophotometric accuracy available. The sum of the formation rates for the two products in Table II is not always equal to the disappearance rate for $[\text{Ru}(\text{bpy})_3]^{2+}$, which is at least partly a result of the fitting procedure. The relative error in determination of the rate was much smaller for the tris complex than for the bis complexes because of its higher extinction coefficient, and, of course, because it was the main component of the reaction mixture under the conditions investigated.

A determination of the actual quantum yield from these data was not possible, since the entire mercury arc emission was used for irradiation. An estimate was made, however, by photolyzing two solutions of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ (at different SCN^- concentrations) with the 442-nm line of a He-Cd laser, resolving the new absorption spectra to obtain concentrations of the three Ru(II) complexes, as described above, determining the quantum yields by ferrioxalate actinometry,¹⁶ and then interpolating these into the Hg-irradiated data according to the rates expected at the thiocyanate concentrations used. The assumption is that the same photoprocesses (with the same quantum yields) are induced by 442-nm irradiation and by the broad band irradiation provided by the mercury lamp. The reaction profiles under 442-nm irradiation were, in fact, similar to those obtained using broad band excitation. The thiocyanate dependence of the estimated quantum yields is displayed in Figure 4. The large scatter in the data is in part inevitable for

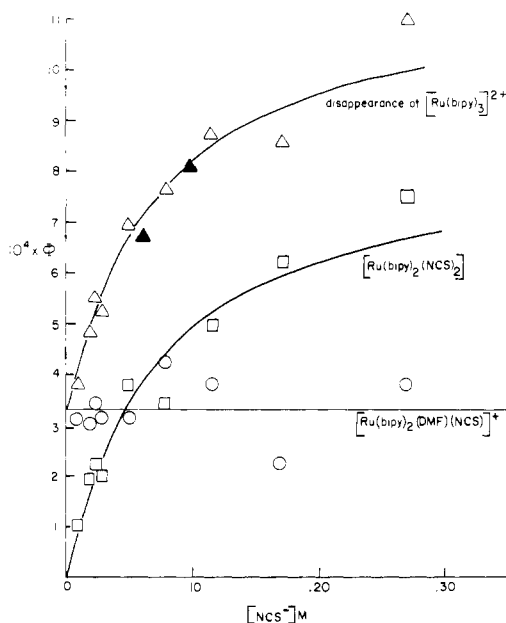


Figure 4. Quantum yields for formation of $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, and disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ as a function of thiocyanate concentration. Open points refer to data from Hg arc irradiation. Solid points refer to He-Cd laser irradiation results, which were used to normalize the Hg arc data. Error bars are not shown, but would be five to ten times as large for the product formation quantum yields as for the disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$. The solid lines are drawn in only as a viewing aid, and are not calculated curves. In particular, the straight line shown for $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ formation would not be supported by any of the models discussed in the text.

a spectral analysis that includes species which have such similar spectra as the two photoproducts (see Figure 1).

3. Photochemical Behavior of Bis(bipyridine) Complexes.

Both $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ and $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ remained unchanged when left standing in DMF for several days at room temperature, as evidenced by their unaltered absorption spectra. After several weeks the spectra would begin to deteriorate somewhat, which may have been caused by absorption of water by the solvent, since both complexes react quickly with water to yield an orange material with a first band maximum near 493 nm. $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ reacted gradually in the presence of high concentrations (ca. 0.2 M) of thiocyanate at room temperature, but in the dark the reaction was very slow; spectral changes were not observed for several hours. The changes in the absorption spectrum were consistent with a $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ product.

Both bis(bipyridine) complexes are themselves photoreactive. When DMF solutions of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ were irradiated with the full Hg arc, the major product formed was $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$. Relatively complete conversion to the solvated complex was possible only at small ($< 1 \times 10^{-4}$ M) ruthenium concentrations, and the photosolvation could be almost completely hindered by 0.5 M NaSCN. At least one other photoproduct was formed in this reaction (with a significantly smaller quantum yield), as evident from the decreased absorption with time in the region > 540 nm and increased extinction around 400 nm, as well as from the absence of isosbestic points. With thiocyanate present this was essentially the only change observed on photolysis.

Irradiation of DMF solutions of $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$, obtained chromatographically from photolysis of $[\text{Ru}(\text{bpy})_3](\text{SCN})_2$ in the presence of thiocyanate, was found to lead to formation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. With no added SCN^- , the only effect observed was the increase in extinction around 400 nm and general decrease elsewhere, noted previously for photolysis of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. At moderate

thiocyanate concentrations, photolysis of either $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ or $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ led to a mixture of the two.

No quantum yields were determined for any of the photo-reactions of the bis(bipyridine) complexes, but if the intensity of absorbed light were the same for $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ as for $[\text{Ru}(\text{bpy})_3]^{2+}$, the quantum yield for photosolvation would be about 7×10^{-4} . The quantum yield for the reverse photoanation would be of the same order of magnitude. In any case, the quantum yields for both processes were enhanced by a factor of about 4 when solutions were saturated with O_2 instead of with N_2 . The presence of oxygen did not lead to a noticeable change in the extent to which the 400-nm region of the spectrum was enhanced by irradiation.

When a commercial (Alfa) sample of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (containing some Ru(IV) as well) was dissolved in DMF, an intense absorption maximum ($\lambda_{\text{max}} 413$ nm, $\epsilon \sim 8 \times 10^3$) was observed. In water no such peak was evident. This is at least consistent with the assumption that, if a single species is responsible for the increased extinction near 400 nm in photolyses of the bis(bipyridine) complexes, it may be a Ru(III) species. Efforts to produce a similar spectral change by treating $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ with several oxidizing agents were unsuccessful.

4. Other Environmental Effects on the $[\text{Ru}(\text{bpy})_3]^{2+}$ Photolysis.

The photoreaction of the tris complex in DMF was quenched by small amounts of water. A 3% water concentration produced a roughly threefold reduction in the quantum yield for disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$. Possible effects on the product distribution were not examined.

Oxygen also acts to quench the photosubstitution of the tris complex. Air-saturated solutions exhibited a quantum yield a factor of 3 smaller than N_2 -saturated solutions (0.08 M NaSCN, straight line portion of concentration vs. time profile), although, curiously, an O_2 -saturated solution showed no further decrease in quantum yield. The initial behavior of the system in the presence of some dissolved oxygen differed from that described above for deoxygenated systems: all three Ru(II) species exhibited slow initial rates of formation or disappearance, accelerating thereafter to linear rates.

The luminescence of $[\text{Ru}(\text{bpy})_3]^{2+}$ was also quenched by O_2 , but not precisely parallel to the quenching of the photochemistry. The emission (monitored at 612 nm, excited at 436 nm) was less intense in air-saturated solutions by a factor of 4.5 compared to N_2 -saturated solutions, while an O_2 -saturated solution showed a decrease in intensity by about a factor of 15.

There is some indication that very low concentrations of O_2 (i.e., incomplete deoxygenation) serve to increase the initial photoreaction rate, oxygen being consumed in the process. When the luminescence intensity was monitored as a function of the irradiation time of a sample, it was normally found to decrease rapidly as $[\text{Ru}(\text{bpy})_3]^{2+}$ was consumed and as the products began to compete for absorbed light. With incompletely deoxygenated solutions, however, the luminescence intensity was found to increase initially, indicating possibly that O_2 was being depleted.¹⁹

5. Other Solvents.

Some preliminary observations were made with regard to the photolytic behavior of $[\text{Ru}(\text{bpy})_3]^{2+}$ in solvents other than DMF. The complex reacted more slowly in ethanol (and the dithiocyanato product was insoluble), and even more slowly in *N*-methylacetamide and in water. In both the latter cases, very high concentrations of a counterion (Cl^- or CN^-) were necessary to see any effect on a time scale of 20–30 min (irradiation with full Hg arc). The reaction was more rapid in CHCl_3 than in DMF, but was not similar to the anation and solvation observed in other solvents.

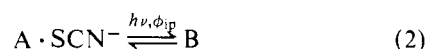
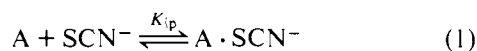
Discussion

1. Ion Pairing.

The dependence on thiocyanate concentration

of the quantum yield for disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ or for formation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, as shown in Figure 4, is suggestive of an ion-pairing mechanism for generation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. The data also show that $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ formation is much less dependent on SCN^- concentration. The quantum yield for disappearance of the tris complex is estimated at 9×10^{-5} (see above) with no added thiocyanate ($[\text{SCN}^-] \sim 1.2 \times 10^{-4} \text{ M}$), so that the quantum yield for $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ formation must decrease from the level indicated in Figure 4 (3.4×10^{-4}) in the limit of low SCN^- .

If an ion pair is the photoreactive species, the thiocyanate dependence of the quantum yield would take the following form, leaving open for the moment the question as to which species is, in fact, subject to the SCN^- dependence of Figure 4.



The observed quantum yield, ϕ , for the formation of B will depend on the fraction of the absorbed light absorbed by the ion pair, f_{ip} . Since the spectra of ion-paired and unpaired complexes are essentially the same,

$$\phi = \phi_{\text{ip}} f_{\text{ip}} \quad (3)$$

K_{ip} is the ion-pair formation constant, and ϕ_{ip} the quantum yield for photoanation of the ion-paired complex. The fraction of light absorbed by the ion pair is

$$f_{\text{ip}} = \frac{[\text{A} \cdot \text{SCN}^-]}{[\text{A}] + [\text{A} \cdot \text{SCN}^-]} = \frac{K_{\text{ip}}[\text{SCN}^-]}{1 + K_{\text{ip}}[\text{SCN}^-]} \quad (4)$$

Therefore

$$\frac{[\text{SCN}^-]}{\phi} = \frac{1}{\phi_{\text{ip}}} \left(\frac{1}{K_{\text{ip}}} + [\text{SCN}^-] \right) \quad (5)$$

and a plot of $[\text{SCN}^-]/\phi$ vs. $[\text{SCN}^-]$ should produce a straight line with slope $1/\phi_{\text{ip}}$ and intercept $1/\phi_{\text{ip}}K_{\text{ip}}$. The corresponding plot is shown in Figure 5, using the quantum yield for $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ formation, yielding values of $K_{\text{ip}} = 14 \pm 4$ and $\phi_{\text{ip}} = 1.0 \times 10^{-3}$ (a corresponding plot of the $[\text{Ru}(\text{bpy})_3]^{2+}$ disappearance data yields values $K_{\text{ip}} = 54$ and $\phi_{\text{ip}} = 1.0 \times 10^{-3}$).

An ion-pair constant of 14 M^{-1} , although subject to considerable error from the data scatter, is almost certainly too small for a (+2, -1) pair in DMF. The ion-pair constant for *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+ \cdot \text{SCN}^-$, for example, calculated from conductimetric measurements using the Fuoss-Onsager-Skinner equation,²⁰ was found to be 124 in DMF.¹⁸ In general (+2, -1) constants appear to be an order of magnitude larger than (+1, -1) pairs in DMF.²¹

2. Mechanism. In postulating a mechanism for $[\text{Ru}(\text{bpy})_3]^{2+}$ photolysis, the following observations must be considered:

- Sequential spectra exhibit isobestic points.
- In the initial stages $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ is virtually the sole photoproduct; $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ is formed only after a short induction period.
- After the induction period all species exhibit near-linear rates of disappearance or formation.
- In the concentration range $0.008 < [\text{SCN}^-] < 0.25$, $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ formation is strongly thiocyanate dependent and $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ formation is much less thiocyanate dependent, perhaps even thiocyanate independent.
- Disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ is thiocyanate dependent.

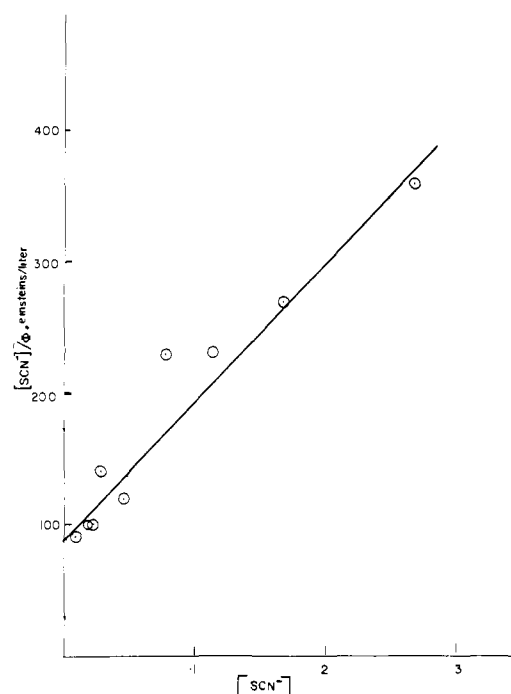
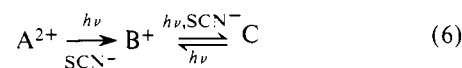


Figure 5. Plot of $[\text{SCN}^-]/\Phi$ vs. $[\text{SCN}^-]$, where Φ is the quantum yield for formation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. A straight line is predicted if the photoactive species is the single ion pair with thiocyanate.

(f) The two bis(bipyridine) complexes are photochemically interconvertible.

It is difficult to account for all these observations in a single mechanism. We will consider two alternative models, one based on secondary photolysis, the other involving photoreactions proceeding through both ion pairs and ion triplets.

The induction period for formation of $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ and the photochemical interconvertibility of this complex with the monosolvated species suggest the secondary photolysis model. The interconvertibility would, in fact, be required if isobestic points are to be accounted for. Representing $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$, and $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ by A^{2+} , B^+ , and C, respectively, we have



Formation of B by an ion-pair mechanism from A is consistent with the near SCN^- independence for this process, since the ion-pair formation constant for $\text{A}^{2+} \cdot \text{SCN}^-$ would be approximately 10^3 and essentially all of the A^{2+} would be ion paired with $[\text{SCN}^-] > 0.01 \text{ M}$. Actually, since the lifetime of the lowest energy charge transfer triplet, the presumed photoactive state, is about $0.8 \mu\text{s}$ in DMF,³ the ion-pair constant would refer to the excited state complex, A^* , which, because of its increased asymmetry, might be expected to be attracted more strongly to an anion than the ground state molecule (large variations (up to a factor of 9) between *cis* and *trans* isomers have been observed for K_{ip} 's in Me_2SO).^{18,22} If the estimated quantum yield for disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the absence of added thiocyanate is used to calculate further the ion-pair formation constant for $[\text{Ru}(\text{bpy})_3]^{2+} \cdot \text{SCN}^-$, a very rough estimate of $K_{\text{ip}}^1 = 3500$ is obtained. This result, and the assignment of the observed $K_{\text{ip}} \sim 14 \text{ M}^{-1}$ to the $\text{B}^+ \cdot \text{SCN}^-$ ion pair, would then be consistent with the data for $[\text{SCN}^-]$ dependence of the quantum yields for product formation.

The processes in eq 6 might be consistent with the observation of isobestic points and linear formation and disappearance rates, if the photoequilibrium between the two bis(bipyridine) complexes were established on a more rapid time

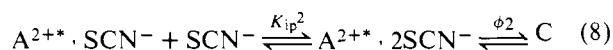
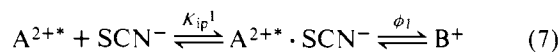
scale than that for photoanation of the tris complex. However, our estimate of the quantum yields for interconversion would not support the establishment of the photoequilibrium at a point in the reaction when only 5–10% of the $[\text{Ru}(\text{bpy})_3]^{2+}$ had been consumed (when the rates become linear). At this stage most of the absorbed light is absorbed by the tris complex.

Energy transfer from the tris to the bis complexes might be invoked at this point. Such a process is possible on an energetic basis, but probably is not feasible kinetically under the conditions used. The bimolecular quenching constant has an upper limit of about $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for energy transfer between a +2 and a +1 species, and about $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for energy transfer between +2 and neutral species.²³ Since the lifetime of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is 0.8 μs in DMF at room temperature,³ the concentration of quencher needed for efficient energy transfer is about 10^{-3} M for $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$, or 10^{-4} M for $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$. The actual concentrations in our experiments were well below 10^{-5} M at the onset of the linear rate region.

A further difficulty concerns the value of the ion-pair constant. It might be argued that 14 M^{-1} is still too low a value for a (+1, -1) ion pair in DMF. For reference, K_{ip} for *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+\text{SCN}^-$ is 124.¹⁸ Taking into consideration that the greater size of the $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ complex should lead to a smaller value for K_{ip} , still the sparse data available²¹ seem to indicate that (+2, -1) ion pairs have larger formation constants than (+1, -1) ion pairs by a factor of 3 (Cl^- ion pairs) to 15 (Br^-). Compared to an estimated 3500 M^{-1} for the $[\text{Ru}(\text{bpy})_3]^{2+}\text{SCN}^-$ formation constant, even though this refers to the excited state, the experimental value seems to us too small to belong to the corresponding (+1, -1) pair, whether or not it too refers to the excited state.

An even more decisive argument against the secondary photolysis model is that disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ should not be dependent on thiocyanate concentration. Since this contradicts the experimental data, this model cannot serve without serious modification.

An alternative mechanism involves formation by excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ of both ion pairs and ion triplets which, in the simplest approximation, react to form $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, respectively.



In this model it is assumed that both ends of a leaving bipyridine ligand dissociate rapidly. The two sites are filled by SCN^- , if two are present in the second coordination sphere; otherwise the second site is filled by solvent.

The ion association constants K_{ip}^1 and K_{ip}^2 are to be identified with the experimental values of ~ 3500 and 14 M^{-1} , respectively. In this model also, the thiocyanate dependence is not convincingly accounted for. The product distribution is dictated by the ratio $\phi_2 C_2 / \phi_1 C_1$, where C_2 is the concentration of ion triplet and C_1 the concentration of ion-paired species. In experiments with added thiocyanate, no significant fraction of $[\text{Ru}(\text{bpy})_3]^{2+}$ would be unassociated, and the ratio C_2 / C_1 would be given by $K_{ip}^2 [\text{SCN}^-]$. In our experiments, $K_{ip}^2 [\text{SCN}^-]$ varied between 0.1 and 3.5 (using $K_{ip}^2 = 14$), which would lead to an expected inverse relation between ϕ_1 and $[\text{SCN}^-]$, unless the model were modified. An inverse thiocyanate dependence can be read into the quantum yield data in Figure 4 for formation of $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$, but a quantitative fit does not seem possible without further assumptions (the secondary photolysis model also predicts an inverse thiocyanate dependence, but it would appear to be a much weaker dependence). Induction periods are also not accounted for in the ion-pair/ion-triplet model.

The calculated ion-pair and ion-triplet constants themselves are reasonable on the basis of the meager data available. The first and second association constants of Cl^- with $[\text{Co}(\text{en})_2(\text{DMF})\text{Cl}]^{2+}$ in DMF were found to be 1.5×10^4 and 80 M^{-1} , respectively, using a spectrophotometric technique.²¹ This is consistent with the two orders of magnitude difference between the two ion association constants involved here.

The ion-pair/ion-triplet model does explain isosbestic point behavior, since the two products will be formed in the ratio $\phi_2 C_2 / \phi_1 C_1$, which would not be altered significantly during the course of one reaction at constant $[\text{SCN}^-]$. The linear rates of formation of both photoproducts with time are also clear. Even after 40% of the tris complex is consumed, it still absorbs itself over 80% of the total absorbed light at 436 nm according to the ϵ values in Figure 1. The model also predicts that disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ should depend on thiocyanate concentration, but should not be as strongly dependent as should $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$ formation. This is one of the strongest features of this model in comparison with the secondary photolysis model, even though the quantitative thiocyanate dependence is not accurately predicted.

We do not feel that the data warrant a complete numerical analysis in terms of either model (suitably modified) or a combination of the two. Nevertheless the ion-pair/ion-triplet model does seem to offer a better overall qualitative explanation of the experimental data.

4. Conclusion. $[\text{Ru}(\text{bpy})_3]^{2+}$ has been found to undergo photosubstitution under conditions such that ion-pair formation is promoted. Neither a secondary photolysis nor an ion-pair/ion-triplet model seems capable of rationalizing all experimental observations, although the latter is qualitatively preferable. Further investigation of the details of the photo-stationary state involving $[\text{Ru}(\text{bpy})_2(\text{DMF})(\text{NCS})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{NCS})_2]$, particularly the thiocyanate dependence, is certainly required at this point. A study of the wavelength dependence of the primary photolysis would also be useful, if only in that monochromatic irradiation would allow calculation of the light intensity absorbed by each species, and such data would be much preferable to full arc data, necessitated by the low quantum yields.

Besides the two main photoproducts discussed here, other minor unidentified products were found in photolyzed solutions on an irregular basis. Further studies might concentrate on evidence for the existence of other species, such as a one-ended bipyridine complex, thiocyanate linkage isomers, etc., and the conditions necessary to generate them.

We emphasize again that it is important to examine possible photochemical consequences when using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a sensitizer in media of low to moderate dielectric constant. This complex is a useful sensitizer partly because of its high extinction coefficient, and is therefore normally used at low concentrations. Although the quantum yield for photosubstitution is small, the $[\text{Ru}(\text{bpy})_3]^{2+}$ often absorbs itself a large fraction of the total absorbed light, and the small concentration may be quickly depleted in a sensitization experiment.

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- (19) An initial photoreaction pathway consuming O₂ may be involved in the initially rapid rate of disappearance of [Ru(bpy)₃]²⁺, and (less probably) in the formation of [Ru(bpy)₂(DMF)(NCS)]⁺. That the rapid initial [Ru(bpy)₃]²⁺ disappearance was generally over after 1% of the complex was consumed (i.e., ca. 5 × 10⁻⁷ M) suggests a residual O₂ effect. In any case, [Ru(bpy)₃]²⁺ does appear to function as a photochemical oxygen scavenger at low O₂ concentrations.
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Photochemical and Photophysical Behavior of *trans*-Diisothiocyanatobis(ethylenediamine)chromium(III)

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Abstract: The photochemistry and luminescence of *trans*-Cr(en)₂(NCS)₂⁺ have been investigated in acidic aqueous solutions under direct irradiation, sensitization, and quenching conditions. Irradiation in the ligand field bands causes two photoreactions, NCS⁻ release and H⁺ consumption, the latter reaction being due to the protonation of a detached ethylenediamine end. Within the experimental errors, Φ_{H⁺} is constant (0.07) for both charge transfer and ligand field excitation, whereas Φ_{NCS⁻} is constant (0.18) in the LF region but decreases (0.13) on CT excitation. CT excitation also causes a redox decomposition of the complex, which has been evidenced by scavenging Cr(II) species with Co(NH₃)₅Cl²⁺. The relative phosphorescence quantum yield is constant from 330 to 540 nm (ligand field region), but it decreases both in the CT region and in the low-energy tail of the lowest quartet LF band. Sensitization by Ru(bpy)₂(CN)₂ causes both photosubstitution reactions with limiting quantum yields which are equal to the quantum yields obtained upon direct irradiation in the LF bands. In contrast, the limiting quantum yield of the sensitized emission is 25% higher than the quantum yield of phosphorescence upon direct LF irradiation. Quenching by Cr(CN)₆³⁻ causes a parallel quenching of the phosphorescence emission and lifetime of *trans*-Cr(en)₂(NCS)₂⁺. Complete phosphorescence quenching leaves 20% of unquenchable part for both NCS⁻ release and en detachment. The results indicate that both photoreactions originate from the same excited state which, in a traditional Jablonsky diagram, is the lowest quartet excited state, ⁴T_{2g}. The results are also discussed on the basis of the spin-orbit coupling framework recently proposed by Kane-Maguire et al.

Introduction

Cr(III) complexes have played a fundamental role in the early development of inorganic photochemistry.¹⁻³ In the last few years, the discovery^{4,5} that several Cr(III) complexes exhibit appreciable phosphorescence under experimental conditions in which photochemistry can also be observed has stimulated the use of quenching⁵⁻¹⁴ and sensitization¹⁵⁻¹⁷ techniques¹⁸ with the aim of elucidating the excited state mechanism of these photoreactions. In addition, the study of mixed-ligand complexes has been extended¹⁹⁻³¹ and important results have been obtained concerning the preferential ligand labilization and the stereochemistry of the photosubstitution reactions. Numerous theoretical papers³²⁻³⁷ have also appeared with the aim of rationalizing and predicting the photochemistry of Cr(III) complexes on the basis of current MO models. Other recent important results on Cr(III) photochemistry are those concerning the redox decomposition of acido pentaammine complexes,³⁸ the bimolecular redox reactions of the lowest excited state of Cr(bpy)₃³⁺,^{39,40} the measurement of the ⁴T₂ → ²E intersystem crossing efficiency,⁴¹ and the finding that its value may depend on the excitation wavelength.^{13,42} The accumulation of these results reveals new subtle aspects of Cr(III) photochemistry and calls for more informative experiments. For example, it would be very interesting to extend the comparison between phosphorescence and photochemistry under quenching or sensitization conditions to complexes which undergo *two* distinct photoreactions. *trans*-Cr(en)₂(NCS)₂⁺ is suitable for such experiments since

it is able to exhibit both a relatively strong phosphorescence in aqueous solution at room temperature⁴ and two distinct, sufficiently efficient photoreactions.²⁵ This complex is also interesting because it shows intense charge transfer bands in the near UV region and is therefore suitable for a comparative study of charge transfer and ligand field photochemistry.

In this paper we report the results of a systematic investigation on the photochemistry and phosphorescence of *trans*-Cr(en)₂(NCS)₂²⁺ in aqueous solution upon direct excitation at several different wavelengths, sensitization by Ru(bpy)₂(CN)₂, and quenching by Cr(CN)₆³⁻.⁴³

Experimental Section

Materials. *trans*-Diisothiocyanatobis(ethylenediamine)chromium(III)thiocyanate, *trans*-[Cr(en)₂(NCS)₂]⁺NCS⁻, was prepared from [Cr(en)₃](NCS)₃ according to the method of Rollinson and Bailar.⁴⁵ The compound so obtained was recrystallized from water, transformed into the perchlorate salt, *trans*-[Cr(en)₂(NCS)₂]⁺ClO₄⁻, and then recrystallized three times from water. The spectral characteristics of the complex were in fair agreement with those given by Bifano and Linck.²⁵ Pure samples of [Ru(bpy)₃]²⁺Cl₂ (bpy = 2,2'-bipyridine),¹⁴ Ru(bpy)₂(CN)₂,¹⁴ K₃[Cr(CN)₆],¹⁶ [Co(NH₃)₅Cl]Cl₂,¹ and [Cr(bpy)₃](ClO₄)₃⁴¹ were available from previous investigations. All the other chemicals were of reagent grade.

Apparatus. For the photochemical experiments, radiations of 313, 365, 437, and 508 nm were obtained as previously described,⁴⁶ whereas 530- and 560-nm radiations were obtained from the Perkin-Elmer MPF 3 spectrofluorimeter with 20-nm band-pass width. The intensity of the incident light, which was measured by means of the ferric oxalate⁴⁷ or reineckate⁴⁸ actinometers, was of the order of 10⁻⁷ Nhν/min