oxidation state 3+, the nitrile group is not readily lost by aquation, and as has been shown in other work, hydrolysis of the nitrile to amide ensues. On reducing ruthenium(III) to ruthenium(II), amide is displaced by water forming aquopentaammineruthenium(II). In principle at least, the conversion of amine to amide under mild conditions can be made catalytic with respect to the metal ion. If in fact the 15% deficit in the intermediate production of nitrile is, as suggested, really caused by N–C hydrolysis at the imine stage, in each cycle ca. 15% of the ruthenium ammine will be lost in being converted to hexaammine.

With methylamine as ligand the primary product of the oxidation of the imine is expected to be the N-bound HCN complex $[(NH_3)_5RuNCH]^{2+}$, and this species was detected by infrared spectroscopy in the solid obtained from a product solution. This species is known to rearrange to $[(NH_3)_5RuCN]^{+}$, more rapidly at a higher pH. The ammonia trans to the cyanide is then labilized whereupon polymer formation ensues.[14]

Little has been done on imines as ligands, and our work shows that the chemistry of the monoimine complexes in water is severely circumscribed by the ease with which hydrolysis to aldehydes or ketones takes place. The work on the benzylamine system shows there to be a stepwise increase in the stability of ruthenium(II) relative to ruthenium(III) as the ligand is taken through the changes amine-imine-nitrile. The stabilization of ruthenium(II) relative to ruthenium(III) is greater for benzylimine than for cyclohexylimine, as might be expected because the interaction of the aromatic ring with the imine group on the former case would render the ligand a better π acceptor.

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Photochemical Reaction Pathways of Ruthenium(II) Complexes.[1,2] Photoredox and Photosubstitution Reactions of the Acetonitrile Complex $Ru(NH_3)_5CH_3CN^{2+}$ and of the Dinitrogen Complex $Ru(NH_3)_5N_2^{2+}$

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Abstract: Quantum yields are reported for the photolysis of the ruthenium(II) complex $Ru(NH_3)_5CH_3CN^{2+}$ in aqueous solution over a wide range of the irradiation wavelength. Ligand field excitation with 366-nm light leads exclusively to substitution reactions with CH_3CN and NH_3 aquation occurring with comparable rates and with an overall quantum yield of approximately 0.26 mol/einstein. Higher energy irradiation results in the formation of both photosubstitution and photoredox products, the latter including Ru(III) complexes and molecular hydrogen. The wavelength dependent quantum yields for Ru(III) formation range from 0.008 with 313-nm irradiation to 0.51 with 213.9-nm light. Quantum yields for H_2 production were markedly enhanced by the presence of isopropyl alcohol in solution implicating the formation of hydrogen atoms as a photochemical consequence. These data are interpreted in terms of at least two competing photochemical mechanisms: ligand substitution occurring via a ligand field excited state of this $4d^6$ complex and oxidation of Ru(II) to Ru(III) resulting from charge transfer to solvent excitation. The photochemical behavior of the dinitrogen complex $Ru(NH_3)_5N_2^{2+}$ under the influence of 254-nm irradiation was also examined. The principal photoreaction was redox in character with a quantum yield for Ru(III) formation equaling 0.17 mol/einstein. H_2 is also a significant photolysis product.

The electronic excited state chemistry of ruthenium(II) complexes is widely varied. For example, irradiation of aqueous $Ru(bipy)_3^{2+}$ leads only to strong phosphorescence in the absence of other substrates[4] but to energy transfer (sensitization) processes[5] and in some cases to electron transfer reactions in their presence.[6] The closely analogous ion, *cis*-$Ru(bipy)_2(4\text{-stilbazole})_2^{2+}$, is only a weak emitter in ambient temperature fluid solution but undergoes relatively efficient reactions of coordinated stilbazole when irradiated at wavelengths corresponding to metal-to-ligand charge transfer (MLCT) or π–π* internal ligand bands.[7] In contrast, the ruthenium(II) ammine complexes of the type

$Ru(NH_3)_5L^{2+}$ display ligand substitution and/or oxidation to ruthenium(III) as the principal photochemical paths when irradiated in aqueous solution.[1,8,9]

In this laboratory we have been studying the reactions resulting from MLCT excitation of complexes such as $Ru(NH_3)_5py^{2+}$ in aqueous solution. Excitation of MLCT bands in the visible region of the spectrum ($\lambda_{irr} \geq 366$ nm) leads almost exclusively to photosubstitution processes.[9] By examining the reactions of various substituted pyridine complexes ($(Ru(NH_3)_5(py\text{-}x)^{2+})$), we have shown that the reactive state in these cases is not MLCT in character but very likely a ligand field excited state.[1] In these cases the presence of such a ligand field state can only be inferred; since the electronic spectra are dominated by broad and intense MLCT and ligand π–π^* absorption bands. For this reason the photochemistry of the acetonitrile complex $Ru(NH_3)_5CH_3CN^{2+}$ is especially interesting. Although the dominant feature of the ion's electronic spectrum is a MLCT absorption,[10] this band occurs at sufficiently high energy (λ_{max} 226 nm) that another, much less intense, ligand field band (λ_{max} 350 nm)[10] is the lowest energy transition in the absorption spectrum. Therefore excitation at the latter wavelength allows examining the chemistry of ligand field excited state(s) populated by direct excitation.

The photochemistry of $Ru(NH_3)_5CH_3CN^{2+}$ is also interesting in the context of redox reactions observed[8] when Ru(II) ammine complexes are irradiated with ultraviolet light. Qualitative studies have demonstrated that both Ru(III) and H_2 are products of uv photolysis.[8] In this article we report a study of the reactions resulting from the photolysis of aqueous $Ru(NH_3)_5CH_3CN^{2+}$ over the wavelength range 366–213.7 nm, including the first quantitative studies of the photoredox reactions of a ruthenium(II) ammine complex.

Earlier qualitative work[11] has demonstrated that white light photolysis of the dinitrogen complex, $Ru(NH_3)_5N_2^{2+}$, resulted in oxidation of Ru(II) to Ru(III). Reported here also is a brief quantitative study of this ion's photoreactions under the influence of 254-nm irradiation.

Experimental Section

Materials. Pentaammineacetonitrileruthenium(II) tetrafluoroborate, $[Ru(NH_3)_5(CH_3CN)][BF_4]_2$ was prepared by the method of Clarke[10] and recrystallized from hot water. The electronic spectrum of carefully recrystallized material differed slightly from that previously reported, the new λ_{max} and extinction coefficients values being 350 (ϵ_{max} 163 M^{-1} cm^{-1}), 290 (poorly defined shoulder, ϵ 747 M^{-1} cm^{-1}), and 226 nm (ϵ 15,400 M^{-1} cm^{-1}). The dinitrogen complex $[Ru(NH_3)_5N_2](BF_4)_2$ was prepared by the method of Allen et al.[12] This material appeared to contain other ruthenium species as impurities and therefore was purified by elution from a Dowex 50W-X4 ion exchange column with pH 2, 1.2 M NaCl solution. The elution aliquots containing $Ru(NH_3)_5N_2^{2+}$ were reduced in volume by rotary evaporation, and the complex was isolated as the chloride salt.

Solutions for photolyses and dark reactions were prepared and deaerated according to the procedure of Chaisson.[9] Redistilled deionized water was used in all solution preparations, reagent sodium chloride and hydrochloric acid were used to maintain ionic strength and solution pH, and solutions were deaerated by entraining with chromous-scrubbed argon. All photolyses reported here were carried out at 25.0 ± 0.5° and with an ionic strength of 0.2 M (HCl-NaCl).

Apparatus. Irradiation sources for 213.9, 228.8, and 254 nm were Phillips 25-W zinc and cadmium spectral resonance lamps and a Phillips 90-W medium-pressure mercury lamp, respectively. These sources were mounted in a cylindrical, convection cooled aluminum housing and powered by an Ealing spectral lamp power supply. Light was collected by a suprasil lens (Oriel) and monochromatization at 254 nm was accomplished variously with a Bausch and Lomb high-intensity ultraviolet monochromator or a 254-nm interference filter (Oriel). Monochromatization at 213.9 and 228.8 nm was accomplished with a chlorine filter which consisted of a 5-cm quartz cell filled with dry Cl_2 gas at 1 atm. This filter absorbs >99.9% of the radiation between 290 and 375 nm and is virtually transparent between 200 and 250 nm, thus providing sufficient monochromatization for the 213.9- and 228.8-nm radiation from the Zn and Cd resonance lamps if neither the complex nor the actinometer absorb light at wavelengths >450 nm. Neither the acetonitrile complex nor the uranyl oxalate actinometer used in these experiments absorbs appreciably in this region. For most photolyses at the lower wavelengths, a rectangular thermostated 1-cm sample cell holder was employed; however, a few photochemical runs with 2-cm cells were performed in a cylindrical thermostated cell holder. Observed quantum yields were independent of cell geometry. Photolyses at 313 and 366 nm were carried out with the apparatus described by Chaisson[9] utilizing a 200-W high-pressure mercury lamp source and a Jarrell-Ash 0.25-m monochromator. Usable intensities generated by these apparatus were 9.2×10^{-7}, 19×10^{-7}, 4.1×10^{-7}, 2.3×10^{-7}, and 1.3×10^{-7} einstein/(l. sec) for wavelengths 366, 313, 254, 228.8, and 213.9 nm, respectively. In the photolysis apparatus, radiation beam intensity stability was monitored with a YSI-Kettering Model 65A radiometer.

Absorbance measurements during photolysis runs were taken on a Cary 14, a Cary 15, or a Beckman DU-2 spectrophotometer. pH measurements were made with a Sargent-Welch Model NX pH meter calibrated with commercial standard buffers. Mass spectra were obtained on a Finnigan Model 1015 mass spectrometer equipped with a Moseley 7101B strip chart recorder.

Actinometry and Quantum Yield Determinations. Ferrioxalate actinometry[9] was used for light intensity determinations at 366, 313, and 254 nm. The uranyl oxalate actinometer[13] was used for measurements at 228.8 and 213.9 nm; however, since the actinometer is not calibrated at these wavelengths, interpolated quantum yields were used. The actinometer quantum yield was assumed linear with irradiation energy between the reported values[13] of 0.51 mol/einstein at 210 nm and 0.65 at 254 nm, thus giving values of 0.57 for 228.8 nm and 0.52 for 213.9 nm. The procedure[14] for spectrophotometric analysis with the uranyl oxalate actinometer was used. Light intensity measurements at 254 nm using both the ferrioxalate and the uranyl oxalate actinometers showed reasonable agreement.

Molecular hydrogen formation quantum yields were examined by using acidic ferrocyanide solution[15] as a reference actinometer. A quantum yield (0.43) for H_2 formation has been measured[15] for 254-nm photolysis of an aqueous solution with the following components at 25°: 1.0×10^{-3} M $K_4[Fe(CN)_6]$, 1.0×10^{-3} M $HClO_4$, and 0.10 M isopropyl alcohol. This quantum yield is relatively insensitive to small changes in acid and isopropyl alcohol concentration. The analysis used was to irradiate the ruthenium(II) solution and the ferrocyanide actinometer consecutively under identical conditions. The two solutions were then subjected to identical procedures involving transfer to an evacuated vessel where the solution was frozen at 77°K. The gas present in this vessel was then sampled by opening the inlet to the mass spectrometer probe. Quantum yields of H_2 formation were evaluated by comparing mass 2 peak intensities of the ruthenium and ferrocyanide systems which had been photolyzed and worked up in identical fashions. Repetitive runs in this manner gave Φ_{H_2} values with a reproducibility of ±30%.

The general procedure used for calculating quantum yields from irradiation induced spectral changes and the extinction coefficient differences of reactants and products have been described previously.[9] Spectral changes were variously examined in two ways: direct recording of the spectra, or recording of a difference spectrum between the photolyzed solution and a solution prepared and treated in an identical manner but not exposed to light. Reported spectroscopic quantum yields are extrapolated to 0% reaction to give best values for the primary photoreaction. Quantum yields for ammonia aquation from $Ru(NH_3)_5CH_3CN^{2+}$ were calculated on the basis of pH change resulting from photolysis of the solution initially pH ~3.3.

Spectra. Quantitative spectra of $[Ru(NH_3)_5(CH_3CN)](BF_4)_2$, $[Ru(NH_3)_5(CH_3CN)](ClO_4)_3$, and $[Ru(NH_3)_5Cl]Cl_2$ were recorded in aqueous pH 3 HCl (μ = 0.2 M NaCl). Solutions of each were prepared several times to minimize random error. The spectrum of $Ru(NH_3)_5CH_3CN^{2+}$ is shown in Figure 1. Spectra of the

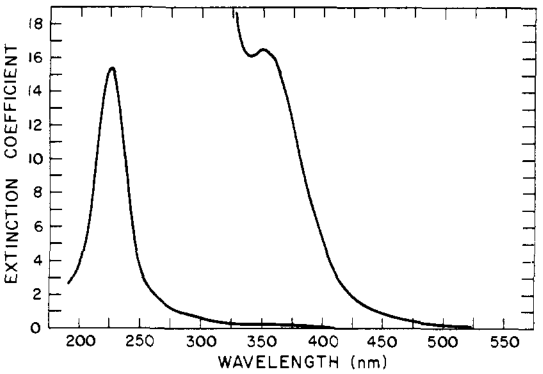


Figure 1. Spectrum of aqueous $Ru(NH_3)_5CH_3CN^{2+}$. Extinction coefficient units for curve on left are $10^3\ M^{-1}\ cm^{-1}$ and for curve on right are $10\ M^{-1}\ cm^{-1}$.

cis and trans bis(acetonitrile) complex ions *cis*-$Ru(NH_3)_4(CH_3CN)_2^{2+}$ and *trans*-$Ru(NH_3)_4(CH_3CN)_2^{2+}$ were obtained by generating the complexes in situ. The appropriate dichloro Ru(III) complex, *cis*- or *trans*-$[Ru(NH_3)_4Cl_2]Cl$, was dissolved in deaerated, acidic, aqueous solution containing a substantial excess of acetonitrile, and the solution was stirred over amalgamated zinc for several hours thus forming the respective bis(acetonitrile) ion.[10] Extinction coefficients were calculated on the basis of known extinction coefficients of the Ru(III) starting material.[9] The spectra showed three maxima for *cis*-$Ru(NH_3)_4(CH_3CN)_2^{2+}$ (λ_{max} 340 (ϵ $2.2 \times 10^2\ M^{-1}\ cm^{-1}$), 223 ($1.77 \times 10^4$), and 204 nm ($1.84 \times 10^4$)) and two bands for *trans*-$Ru(NH_3)_4(CH_3CN)_2^{2+}$ (330(540) and 237 nm (2.37×10^4)). The spectrum of $Ru(NH_3)_5H_2O^{2+}$ was obtained by Zn(Hg) reduction of $Ru(NH_3)_5Cl^{2+}$ in deaerated, pH 3 aqueous HCl ($\mu = 0.2$ NaCl) and displayed λ_{max} at 268 (ϵ 596) and 415 nm (43). Free acetonitrile is virtually transparent at wavelengths >200 nm.

Environmental effects on the absorption spectrum of $Ru(NH_3)_5CH_3CN^{2+}$ were examined in several solvent media. A stock solution of $1.14 \times 10^{-3}\ M$ $[Ru(NH_3)_5CH_3CN][BF_4]_2$ was made up in redistilled water and diluted tenfold with five different solvents: redistilled water, spectrograde acetonitrile, spectrograde methanol, spectrograde ethanol, and saturated aqueous sodium chloride solution (~5.5 *M*). Difference spectra were then recorded using the aqueous solution as the reference.

Results

Photolysis of aqueous $Ru(NH_3)_5CH_3CN^{2+}$ at wavelengths ranging from 366 to 214 nm results in both photoredox and photosubstitution processes. Quantum yields are wavelength dependent with ligand photoaquation the only reaction observed at 366 nm. Photooxidation of Ru(II) to Ru(III) is first observed at 313 nm and increases in importance to become the predominant photoreaction at the lower wavelengths. In the subsequent sections we will summarize the photochemical consequences of irradiating at the various wavelengths. However, before summarizing the quantum yield data, it is necessary to evaluate the analyses used to obtain these.

Three primary photoaquation pathways can be envisioned

$$\begin{array}{lll} Ru(NH_3)_5CH_3CN^{2+} \xrightarrow{h\nu} & Ru(NH_3)_5H_2O^{2+} + CH_3CN & (1) \\ & cis\text{-}Ru(NH_3)_4(H_2O)(CH_3CN)^{2+} + NH_3 & (2) \\ & trans\text{-}Ru(NH_3)_4(H_2O)(CH_3CN)^{2+} + NH_3 & (3) \end{array}$$

Photoreaction 1 leads to very major spectral changes ($\Delta\epsilon_{226nm} \simeq 15{,}000$) while spectral changes resulting from eq 2 or 3 are minor given that the predominant characteristic of both the product and reactant spectra is a metal-to-acetonitrile charge transfer with λ_{max} ~230 nm. Under the reaction conditions (0.2 *M* Cl^-), the formation of photoredox products will be reflected in the observation of chloroammineruthenium(III) species in the photolyzed solution, *if* significant photoaquation accompanies the photoredox reaction.[9] The chloroammine species are easily observed in the electronic spectra owing to their characteristic ligand-to-metal charge transfer (LMCT) bands in the region of 330 nm. The tendency of π-acceptor ligands such as acetonitrile to stabilize Ru(II) vs. Ru(III)[9,16,17] ensures that if the quantum yield for reaction 1 (Φ_{CH_3CN}) exceeds the quantum yield for photooxidation ($\Phi_{Ru(III)}$) then the latter will equal the quantum yield for formation of $Ru(NH_3)_5Cl^{2+}$ (eq 4 and 5). In this case "Ru(III)" represents the probable primary photooxidation product, $Ru(NH_3)_5(CH_3CN)^{3+}$ (vide infra) or other acetonitrile containing Ru(III) species.

$$Ru(III) + Ru(NH_3)_5H_2O^{2+} \rightleftharpoons Ru(II) + Ru(NH_3)_5H_2O^{3+} \quad (4)$$

$$Ru(NH_3)_5H_2O^{3+} + Cl^- \xrightleftharpoons[]{\substack{Ru(NH_3)_5H_2O^{2+} \\ catalysis}} Ru(NH_3)_5Cl^{2+} + H_2O \quad (5)$$

The large extinction coefficient difference between the starting complex and $Ru(NH_3)_5Cl^{2+}$ ($\Delta\epsilon_{328} = 1.74 \times 10^3$) and the low absorptivities of other products at 328 nm makes optical density changes at this wavelength a sensitive indicator of photooxidation processes. The minimum detectable photooxidation quantum yield is estimated to be about 1/150 of the photoaquation quantum yield under these conditions.

366-nm Photolysis. The low extinction coefficient of $Ru(NH_3)_5CH_3CN^{2+}$ at 366 nm ($146\ M^{-1}\ cm^{-1}$) necessitated complex concentrations of $3\text{-}7 \times 10^{-4}\ M$ to allow an appreciable absorption of the incident radiation. At these concentrations, spectral analysis of optical density changes at 226 nm (MLCT λ_{max}) was not practical, so 260 and 253.7 nm were chosen as wavelengths at which to monitor disappearance of the starting material MLCT absorption. The quantum yield calculated from such data is a direct function of the extinction coefficient differences calculated between starting complex and products and is potentially sensitive to the wavelength of observation. To examine this question further, a photolysis was done at a much lower complex concentration ($0.44 \times 10^{-4}\ M$), and the Φ_{CH_3CN} determined on the basis of optical density changes at 226 nm was 0.15 mol/einstein, within the precision of Φ_{CH_3CN} values determined using 260 nm as the observation wavelength (Table I). Similarly for photolyses at 313 and 254 nm reasonable agreement was obtained between values measured at 226, 253.7, or 260 nm. The quantum yield for CH_3CN aquation in pH 3 aqueous solution was measured as 0.16 ± 0.02 (Table I). No increase in absorbance was noted at 328 nm, thus $\Phi_{Ru(III)}$ is estimated to have an upper limit of ~0.001.

The spectroscopic technique does not provide any information regarding NH_3 photoaquation (eq 2 and 3) under these conditions. For this reason, it was necessary to monitor ammonia photoaquation by pH changes in the acidic (pH 3.0 or 3.6) photolysis solution since each equivalent of NH_3 released will neutralize an equivalent of solution acid. Two procedures were employed. In the first, excess acetonitrile (0.2 *M*) was added to the solution ($4\text{-}11 \times 10^{-4}\ M$ in $Ru(NH_3)_5CH_3CN^{2+}$) prior to photolyses in order to remove any aquo complexes formed (eq 6 and 7). The parent complex and the bis(acetonitrile) complexes are stable toward air oxidation thus inhibiting air oxidation of Ru(II) to Ru(III) during the pH measurement at the conclusion of

$$Ru(NH_3)_5H_2O^{2+} + CH_3CN \longrightarrow Ru(NH_3)_5CH_3CN^{2+} + H_2O \quad (6)$$

$$cis\text{- or } trans\text{-}Ru(NH_3)_4(H_2O)(CH_3CN)^{2+} + CH_3CN \longrightarrow cis\text{- or } trans\text{-}Ru(NH_3)_4(CH_3CN)_2^{2+} + H_2O \quad (7)$$

Table I. Quantum Yields[a,b] for the Photolyses of $Ru(NH_3)_5CH_3CN^{2+}$

λ_{irr} (nm)	$10^{-3}\epsilon(M^{-1}\ cm^{-1})$	Φ_{CH_3CN}	Φ_{NH_3}	Φ_{subst}	$\Phi_{Ru(III)}$
366	0.146	0.16 ± 0.01 (5)[c]	0.10 ± 0.02 (7)	0.26 ± 0.03[d]	$<10^{-3}$ (5)[e]
313	0.333	0.13 ± 0.01 (9)[c]	0.10 ± 0.02 (8)	0.23 ± 0.03[d]	0.008 ± 0.001 (9)[e]
		0.13 ± 0.01 (3)[c,f]			0.010 ± 0.002 (3)[e,f]
254	2.92	0.12 ± 0.01 (2)[g]			0.16 ± 0.01 (5)[c]
228.8	15.1	⩽0.03 (5)[e]	<0.03 (2)[h]	0.03 ± 0.03 (5)[e]	0.38 ± 0.09 (5)[c]
213.9	9.89	⩽0.04 (6)[e]	<0.03 (2)[h]	0.04 ± 0.01 (6)[e]	0.51 ± 0.06 (8)[c]

[a] Unless noted, conditions were $T = 25°$, initial pH 3.0, $\mu = 0.20\ M$ (NaCl). [b] Mean value and average deviation reported with number of quantum yield determinations in parentheses. [c] Evaluated from the decrease in MLCT absorption in the region 260–226 nm. [d] Sum of Φ_{NH_3} and Φ_{CH_3CN}. [e] Evaluated from the increase in optical density at 328 nm. [f] pH 0.7. [g] Evaluated from the optical density decrease at 253.7 nm when photolysis is run in 0.1 or 2.0 M isopropyl alcohol (see text). [h] Estimated from failure of photolyzed solution to react with excess CH_3CN.

the photolysis. The value for Φ_{NH_3} obtained was 0.08 ± 0.01 for photolysis carried to about 7% aquation of NH_3. Examination of the MLCT spectral region of these photolysis solutions (in the context of the spectral properties of $Ru(NH_3)_5CH_3CN^{2+}$ and the bis(acetonitrile) complexes) allows evaluation of the stereochemical distribution and formation quantum yields for the bis(acetonitrile) complexes. An overall quantum yield of approximately 0.1 is observed with an estimated stereochemical mix of approximately 10:1 cis to trans. Although evaluation of the isomer ratio is especially susceptible to relatively minor errors in extinction coefficients and perhaps to secondary photolysis of the bis(acetonitrile) complexes once formed, these data do imply that NH_3 photoaquation does not have a strong bias to form trans products.

The second procedure for determining pH changes was to open the cell at the termination of photolysis without added ligand and immediately measure the pH. The Φ_{NH_3} values (0.12 ± 0.01) obtained in this manner were somewhat larger than those obtained in excess acetonitrile; however, both experiments clearly demonstrate that ammonia photoaquation is an important pathway when $Ru(NH_3)_5CH_3CN^{2+}$ is photolyzed with 366-nm light.

Reaction rates of the aquoammineruthenium(II) complexes with ligands such as acetonitrile have been studied,[18] and one might predict that back-reactions such as eq 6 and 7 may have some importance under conditions of the photochemical experiment. (Back-reaction with ammonia is inhibited by NH_3 protonation in the acidic medium.) Consistent with this prediction, solutions containing higher concentrations of $Ru(NH_3)_5(CH_3CN)^{2+}$ were slightly photochromic. For example a deaerated $1.4 \times 10^{-3}\ M$ solution photolyzed to ~60% disappearance of the MLCT absorption recovered ~20% of the lost MLCT optical density when left in the dark overnight. However, the rates are sufficiently slow that such photochromism has little or no influence on the quantum yield measurements.

313-nm Photolysis. Irradiation at 313 nm resulted in small but easily observable production of $Ru(NH_3)_5Cl^{2+}$ in addition to the significantly more prevalent photoaquation pathways. The operation of eq 4 and 5 means that photooxidation regardless of the product initially formed will result in $Ru(NH_3)_5Cl^{2+}$ formation. In addition, since $Ru(NH_3)_5Cl^{2+}$ has a low molar absorptivity in the MLCT region (comparable to that of $Ru(NH_3)_5H_2O^{2+}$), decreases in the MLCT absorbance reflect photoaquation of CH_3CN regardless of the specific mechanism of aquation. Evaluation of spectral changes at 260 and 328 nm gave 0.13 ± 0.01 for Φ_{CH_3CN} and 0.008 ± 0.001 for $\Phi_{Ru(III)}$ in pH 3.0 aqueous solution (Table I). Identical quantum yields for photoaquation were determined in pH 0.7 solution and in pH 3.6 solution, but $\Phi_{Ru(III)}$ increased slightly to 0.010 in the former case. pH measurements as described above showed that NH_3 photoaquation is comparable in magnitude to acetonitrile photoaquation (Table I).

Photolysis at 228.8 and at 213.9 nm. Irradiation of aqueous $Ru(NH_3)_5CH_3CN^{2+}$ ($1–2 \times 10^{-4}\ M$, pH 3.0) results in very efficient disappearance of the charge transfer absorption at 226 nm with quantum yields of 0.38 ± 0.09 and 0.51 ± 0.06 for 228.8- and 213.9-nm irradiation, respectively. At both wavelengths, optical density increases at 328 nm were minor, and if one assumes that $Ru(NH_3)_5Cl^{2+}$ is the product monitored at this wavelength, quantum yields of 0.03 ± 0.02 at 228.8 nm and 0.04 ± 0.01 at 213.9 nm were observed. Product solutions obtained with these high energy irradiations had distinctly different properties than those obtained with photolysis wavelengths 366 and 313 nm. For example, the product solutions were stable when exposed to air, thus indicating the absence of aquoammineruthenium(II) complexes which would oxidize to form the analogous chloroammineruthenium(III) species. Also, addition of excess acetonitrile did not suppress the rate of decrease in the MLCT band, again suggesting that $Ru(NH_3)_5H_2O^{2+}$ is not a major primary photoproduct. Finally, reduction of the photolyte solution over amalgamated zinc reverses the photolysis effect on the spectra and quickly regenerates the starting material. These results indicate that the major photoproduct is $Ru(NH_3)_5CH_3CN^{3+}$ and that the principal primary photoreaction is

$$Ru(NH_3)_5CH_3CN^{2+} + h\nu \longrightarrow Ru(NH_3)_5CH_3CN^{3+} + \text{reduction products} \quad (8)$$

If eq 8 is the predominant photoreaction, then minor competing photoaquation pathways will be reflected in the formation of chloroammine complex owing to the operation of eq 4 and 5 and of eq 9. The equilibrium constant for eq 9

$$Ru(NH_3)_5CH_3CN^{3+} + Ru(NH_3)_4(H_2O)(CH_3CN)^{2+} + Cl^- \rightleftharpoons Ru(NH_3)_4Cl(CH_3CN)^{2+} + Ru(NH_3)_5CH_3CN^{2+} + H_2O \quad (9)$$

has not been determined but, given the affinity of Ru(III) for π-donors such as chloride,[19] it is probable that the equilibrium lies substantially to the right under the reaction conditions. If so, then the $Ru(NH_3)_4Cl(CH_3CN)^{2+}$ isomers may be significant contributors to the absorption noted at 328 nm, given the similarities in λ_{max} and extinction coefficients of $Ru(NH_3)_5Cl^{2+}$ and analogous tetraammine species[9] $Ru(NH_3)_4LCl^{2+}$. If we assume that the $Ru(NH_3)_4Cl(CH_3CN)^{2+}$ isomers have the same molar absorptivities as $Ru(NH_3)_5Cl^{2+}$ at 328 nm, then the quantum yields measured (above) for optical density change at 328 nm corresponds to an approximate value for the sum of the photoaquation pathways (eq 1, 2, and 3) (Table I). In addition, although eq 4 and 9 regenerate parent complex from the Ru(III) analog, taking into account the spectral consequences of eq 1–4 and 9 shows that when eq 8 is the predominant photoreaction, the quantum yield for depletion of the MLCT absorption band is equal to the quantum yield for photooxidation $\Phi_{Ru(III)}$ (Table I).

Photolysis at 254 nm. Irradiation of $Ru(CH_3)_5CH_3CN^{2+}$ in pH 3, aqueous solution leads to roughly equal

Table II. Quantum Yields[a] for 253.7-nm Photolyses of Aqueous $Ru(NH_3)_5CH_3CN^{2+}$

Conditions	$\Phi_{253.7}$[b]	Φ_{328}[c]	Φ_{H_2}[d]
pH 3.0	0.161 ± 0.012 (3)	0.137 ± 0.026 (3)	*e*
pH ~7	0.166 ± 0.010 (2)	0.124 ± 0.024 (2)	*e*
pH 3.0	0.167 ± 0.003 (2)	0.136 ± 0.004 (2)	0.0050 ± 0.0016 (2)
pH 2.0	0.160 (1)	0.102 (1)	0.0057 (1)
pH 3.0, 0.1 *M* isopropyl alcohol	0.117 ± 0.009 (2)	0.045 ± 0.009 (2)	0.08 ± 0.01 (2)
pH 2.0, 2.0 *M* isopropyl alcohol	0.126 ± 0.012 (2)	<0.01 (2)	0.15 ± 0.02 (2)
pH 3.0, 2.0 *M* isopropyl alcohol	0.120 ± 0.004 (2)	<0.01 (2)	0.14 ± 0.02 (2)

[a] $T = 25°$, $\mu = 0.2$ *M* (NaCl), mean value and average deviation are reported with the number of runs in parentheses. [b] Quantum yields for the decrease in MLCT absorption of $Ru^{II}(CH_3CN)$ complexes as monitored at 253.7 nm. [c] Quantum yields for the increase in LMCT absorption of $Ru^{III}Cl$ complexes as monitored at 328 nm. [d] Quantum yield for H_2 formation as monitored by the mass spectral technique. [e] Not determined.

quantum yields for the decrease in the MLCT absorption band monitored at 253.7 nm ($\Phi_{253.7} = 0.16 \pm 0.01$) and for the optical density increase monitored at 328 nm ($\Phi_{328} = 0.14 \pm 0.02$). The similarity of these values makes evaluation of the photosubstitution pathways a complicated problem. Several possibilities exist. One is that $\Phi_{253.7} = \Phi_{Ru(III)}$ and $\Phi_{328} = \Phi_{subst}(\Phi_{CH_3CN} + \Phi_{NH_3})$ according to the analysis presented above for the case where photooxidation (eq 8) is the predominant pathway. Another is that $\Phi_{253.7} = \Phi_{CH_3CN}$ and $\Phi_{328} = \Phi_{Ru(III)}$ according to the analysis when CH_3CN aquation is the predominant photoreaction. The third possibility is that $\Phi_{253.7} = \Phi_{Ru(III)}$ *and* $\Phi_{328} = \Phi_{Ru(III)}$, i.e., that $\Phi_{253.7}$ and Φ_{328} are indistinguishable and $\Phi_{subst} > \Phi_{Ru(III)}$. In this context it should be noted that for individual 254-nm photolysis runs $\Phi_{253.7}$ was systematically 10–20% larger than Φ_{328}; however, the approximations regarding the spectra of tetraammine species make equivalence of Φ_{328} and $\Phi_{253.7}$ reasonable likely.

From the three possibilities described one can conclude that $\Phi_{Ru(III)}$ is either 0.16 or 0.14 (values which are indistinguishable given the precision of the measurements) and that Φ_{subst} has a minimum value of 0.14. Experiments described below involving photolysis in the presence of isopropyl alcohol indicate that $\Phi_{CH_3CN} = 0.12 \pm 0.01$, therefore indicating that CH_3CN aquation is not the predominant reaction. Also, the pattern observed for 313- and 366-nm photolyses was that Φ_{NH_3} is 50–75% of the value of Φ_{CH_3CN} (i.e., 0.06–0.09). If this continues to 254-nm photolyses, Φ_{subst} would fall in the range 0.18–0.21 supporting the argument that $\Phi_{subst} > \Phi_{Ru(III)}$ and that $\Phi_{Ru(III)} \simeq \Phi_{328} \simeq 0.15$.

Irradiation at 254 nm also led to formation of molecular hydrogen as a reaction product. However, the quantum yield Φ_{H_2} was small (0.005 mol/einstein, Table II) under conditions where $\Phi_{Ru(III)}$ is approximately 0.15. Photolysis in the presence of 0.1 *M* isopropyl alcohol led to a 16-fold increase in Φ_{H_2} with corresponding decreases in $\Phi_{253.7}$ and Φ_{328} to 0.12 and 0.05, respectively. Photolysis in 2.0 *M* isopropyl alcohol increased Φ_{H_2} to 0.15 and completely suppressed Φ_{328} but led to no further decrease in $\Phi_{253.7}$ (Table II). Since $\Phi_{253.7}$ represents the decrease in the MLCT absorption of the $Ru^{II}(CH_3CN)$ complexes and since the isopropyl alcohol suppresses Ru(III) formation, the $\Phi_{253.7}$ value in isopropyl alcohol solutions 0.12 mol/einstein) must represent Φ_{CH_3CN} (eq 1) under these conditions.

Medium Effects on the $Ru(NH_3)_5CH_3CN^{2+}$ Spectrum. Spectra of $Ru(NH_3)_5CH_3CN^{2+}$ in mixed solvents (90% ethanol, 90% methanol, and 90% acetonitrile) and in 5 *M* aqueous NaCl solution were run as difference spectra in reference to dilute aqueous $Ru(NH_3)_5CH_3CN^{2+}$ of the same concentration (1.14×10^{-4} *M*). These difference spectra each display maxima in the region of 235 and of 275 nm. The higher energy difference spectrum maxima represent shifts in the principal MLCT band and are expected given the observed solvent shifts of MLCT bands in analogous systems.[20] However, the difference maxima at ~275 nm (representing 40–100% increases in the molar extinction coefficient at that wavelength) indicate the presence of another medium-dependent transition having significant absorption in this region. A Gaussian analysis[21] of the MLCT absorption band of aqueous $Ru(NH_3)_5CH_3CN^{2+}$ also indicates in the substraction spectrum the presence of such an absorption band with a broad maximum at ~260–268 nm ($\epsilon_{264} \simeq 1400$ M^{-1} cm^{-1}).

254-nm Photolysis of the Dinitrogen Complex, $Ru(NH_3)_5N_2^{2+}$. The spectrum of the dinitrogen complex is dominated by an intense MLCT absorption band (λ_{max} 221 nm, ϵ 1.65×10^4 M^{-1} cm^{-1})[22] analogous to that of the acetonitrile complex. Photolysis of pH 2 aqueous $Ru(NH_3)_5N_2^{2+}$ (4×10^{-4} *M*) at 254 nm causes a decrease in this absorption band with a quantum yield of 0.18 ± 0.01 (monitored at 240 nm, Φ_{240}). $Ru(NH_3)_5Cl^{2+}$ is also produced during the photolysis, but initial quantum yields are very low (0.01). However, the rate of $Ru(NH_3)_5Cl^{2+}$ formation increases during the course of the photolysis, thus it appears that the chloro complex results from a secondary reaction subject to autocatalysis by a product (probably $Ru(NH_3)_5H_2O^{2+}$). When $Ru(NH_3)_5CH_3CN^{2+}$ is irradiated under identical conditions, ligand aquation and metal oxidation reactions are competitive primary photoreactions, and formation of $Ru(NH_3)_5Cl^{2+}$ shows no autocatalytic behavior. Thus the reproducibly autocatalytic $Ru(NH_3)_5Cl^{2+}$ formation during photolysis of the dinitrogen complex indicates that significant photooxidation but little photoaquation to $Ru(NH_3)_5H_2O^{2+}$ results from the primary photolysis steps. Nonetheless, production of the Ru(III) analog $Ru(NH_3)_5H_2O^{3+}$ is implied by the eventual formation of the chloro complex. These observations are consistent with a greatly predominant primary photooxidation step (eq 10) followed by rapid aquation of the resulting unstable[22] Ru(III) dinitrogen complex (eq 11). H_2 formation was also

$$Ru(NH_3)_5N_2^{2+} + h\nu \longrightarrow Ru(NH_3)_5N_2^{3+} + \text{reduction products} \quad (10)$$

$$Ru(NH_3)_5N_2^{3+} + H_2O \longrightarrow Ru(NH_3)_5H_2O^{3+} + N_2 \quad (11)$$

observed with quantum yields (Φ_{H_2}) of 0.034 ± 0.002 (after 22% reaction). When photolyses were carried out with 0.5 *M* isopropyl alcohol added, Φ_{H_2} increased to 0.10 ± 0.025. A small increase was also noted for Φ_{240} (0.21 ± 0.01) but virtually no $Ru(NH_3)_5Cl^{2+}$ was produced ($\Phi_{328} < 0.01$) either initially or autocatalytically in the presence of isopropyl alcohol.

The argument that eq 10 and 11 represent the predominant primary pathway of 254-nm photolysis is supported by studies carried out with a sample of $Ru(NH_3)_5N_2^{2+}$ obtained by the synthetic procedure of Allen[12] but not purified by ion exchange chromatography (see Experimental Section). The photolysis solution contained 3×10^{-4} *M* $Ru(NH_3)_5N_2^{2+}$, $\sim 0.5 \times 10^{-4}$ *M* $Ru(NH_3)_5Cl^{2+}$ (according to spectral analysis), and probably smaller concentrations of other Ru(II) and Ru(III) impurities which did not contribute appreciably to the solution spectrum. Photolysis induced disappearance of the dinitrogen complex occurred with a quantum yield ($\Phi_{240} = 0.18 \pm 0.01$) equivalent to that observed with the purified complex. However, this was accompanied by immediate (not autocatalytic) formation of $Ru(NH_3)_5Cl^{2+}$ ($\Phi_{328} = 0.19 \pm 0.01$) suggesting that in this case sufficient $Ru(NH_3)_5H_2O^{2+}$ is present in solution to catalyze the rapid conversion of the $Ru(NH_3)_5H_2O^{3+}$ primary photoproduct to $Ru(NH_3)_5Cl^{2+}$. Hydrogen formation under these conditions was greatly suppressed ($\Phi_{H_2} = 0.006 \pm 0.001$).

Discussion

The results from 366-nm excitation of $Ru(NH_3)_5CH_3CN^{2+}$ clearly demonstrate that the reactivity of the lowest ligand field excited state is substitutional in character. This observation is consistent with the behavior resulting from exciting the lowest ligand field bands of analogous hexacoordinate ammine complexes of the d^6 metal ions cobalt(III)[23] and rhodium(III)[24] including the isoelectronic analog[24b] $Rh(NH_3)_5CH_3CN^{3+}$. In contrast to the latter species where CH_3CN aquation occurs exclusively, the Ru(II) system displays both CH_3CN and NH_3 aquation. This difference can perhaps be rationalized in terms of the affinity of CH_3CN toward the metal center relative to that of NH_3 being greater for the more polarizable Ru(II) than for Rh(III). For ground state complexes, π back-bonding between the metal center and coordinated nitriles is much greater for Ru(II) than for Rh(III).[25]

Another interesting comparison is to the photoreactivity of the pyridine analog $Ru(NH_3)_5py^{2+}$. Photolysis of this complex with visible range light (366–436 nm) involves initial excitation of a strong MLCT absorption band (λ_{max} 407 nm).[9] Nonetheless, only photosubstitution of NH_3 and pyridine are observed in reactions analogous to eq 1, 2, and 3, with overall quantum yields totaling ~0.1 mol/einstein in pH 3 aqueous solution. Substituent effect studies[1] show that the charge transfer states are unreactive toward aquation thus indicating that the MLCT state initially populated decays to another state (presumably ligand field in character) not observable in the absorption spectrum. The behavior of the acetonitrile complex demonstrates that excitation directly into the lowest energy ligand field absorption band of a $Ru(NH_3)_5L^{2+}$ complex does in fact result in photoaquation of both NH_3 and L.

The wavelength dependence of the $Ru(NH_3)_5CH_3CN^{2+}$ quantum yields show the operation of two independent reaction modes, the photosubstitutions occurring at longer wavelengths and the photooxidation which is increasingly important at shorter wavelengths. The redox reactions are first observed at a wavelength (313 nm) where the absorption coefficient (333) is already greater than at the ligand field λ_{max} at 350 nm (163), thus indicating some charge transfer state character at the shorter wavelength. Given the presence of a strong MLCT band at 226 nm, it would be tempting to suggest that both the photoredox reactions and the increased absorptions even at 313 nm are features of this band's tailing to long wavelengths. However, the following points should be noted in this context. (1) Direct photolysis of the lower energy MLCT bands of $Ru(NH_3)_5py^{2+}$ and related species leads to no detectable photooxidation.[1,9] (2) Photooxidation of Ru(II) to Ru(III) has been observed for the qualitative uv photolyses of a number of species[8] including $Ru(NH_3)_5py^{2+}$, where the prominent uv transition is a ligand localized π–π^*. More importantly, photooxidation is also observed for $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$, neither of which shows MLCT bands in their electronic spectra.[8] (3) The spectrum of $Ru(NH_3)_6^{2+}$, while displaying the $^1A_1 \rightarrow {}^1T_1$ (sh, 385 nm) and $^1A_1 \rightarrow {}^1T_2$ (275 nm) transitions expected for an octahedral, low-spin $4d^6$ complex, has an unusually high extinction coefficient for the latter band (670) in comparison to that of the first band (39). (In contrast, the spectrum of the isoelectronic Rh(III) complex $Rh(NH_3)_6^{3+}$ displays two bands of more equal intensity, 305 (143) and 255 nm (101).[24]) The high extinction coefficient of this band suggests charge transfer character, and, since π-acceptor ligands are not involved and the complex undergoes photooxidation when irradiated in this region, charge transfer to solvent (CTTS) character is implied.

Photooxidation of aqueous ferrous ions,[26] ferrocyanide,[15,27] and hexacyanoruthenate(II),[27b,28] $Ru(CN)_6^{2-}$, all occur by photoelectron production, and analyses of medium effects on the spectra have implicated CTTS character for the uv absorptions of the latter two.[21,28] The absorption spectra of $Ru(NH_3)_5CH_3CN^{2+}$ in various mixed solvents showed medium-dependent spectral differences in the region of ~275 nm. The Gaussian curve analysis also suggests the presence of an absorption band near this wavelength, and one might conclude that CTTS absorption occurs in this region. Since the second absorption band of $Ru(NH_3)_6^{2+}$ has a λ_{max} of similar energy, it is conceivable that the band indicated by curve analysis of the $Ru(NH_3)_5(CH_3CN)^{2+}$ spectrum is analogous, formally ligand field in assignment but having significant charge transfer character.

A CTTS reactive excited state is also consistent with the photoreactions resulting from 213.9 and 228.8 nm excitation of $Ru(NH_3)_5CH_3CN^{2+}$. The principal reaction product is $Ru(NH_3)_5CH_3CN^{3+}$ and the CTTS process can be represented as

$$Ru(NH_3)_5CH_3CN^{2+} + h\nu \longrightarrow Ru(NH_3)_5CH_3CN^{3+} + e^-_{aq} \quad (12)$$

The back-reaction, reduction of Ru(III) by e^-_{aq}, would be exceedingly fast ($k = 7.4 \times 10^{10}\ M^{-1}\ sec^{-1}$ for $Ru(NH_3)_6^{3+}$)[29] so observation of net photooxidation requires that some other solution component act as a sink for the reducing equivalents generated under the reaction conditions (pH 3). The reactivity of the hydronium ion ($k = 2.2 \times 10^{10}\ M^{-1}\ sec^{-1}$)[29] makes H^+_{aq} the probable sink for the hydrated electron (eq 13) since for the initial stages of

$$H^+_{aq} + e^-_{aq} \longrightarrow H\cdot_{aq} \quad (13)$$

conversion H^+ is orders of magnitude more concentrated than the more reactive Ru(III) species.

Hydrogen atoms generated by eq 13 can be depleted from solution by various pathways, e.g.

$$2H\cdot \longrightarrow H_2 \quad (14)$$

$$H\cdot + CH_3CN \longrightarrow (CH_3CHN)\cdot \quad (15)$$

$$H\cdot + Ru(NH_3)_5L^{2+} \longrightarrow Ru(NH_3)_5(\dot{L}H)^{2+} \text{ or } Ru(NH_3)_5L^+ + H^+ \quad (16)$$

$$H\cdot + Ru(NH_3)_5L^{3+} \longrightarrow Ru(NH_3)_5(\dot{L}H)^{3+} \text{ or } Ru(NH_3)_5L^{2+} + H^+ \quad (17)$$

$$H\cdot + \text{impurity} \longrightarrow (\text{impurity})H \quad (18)$$

Furthermore, in the presence of isopropyl alcohol the following scavenging process is likely[15]

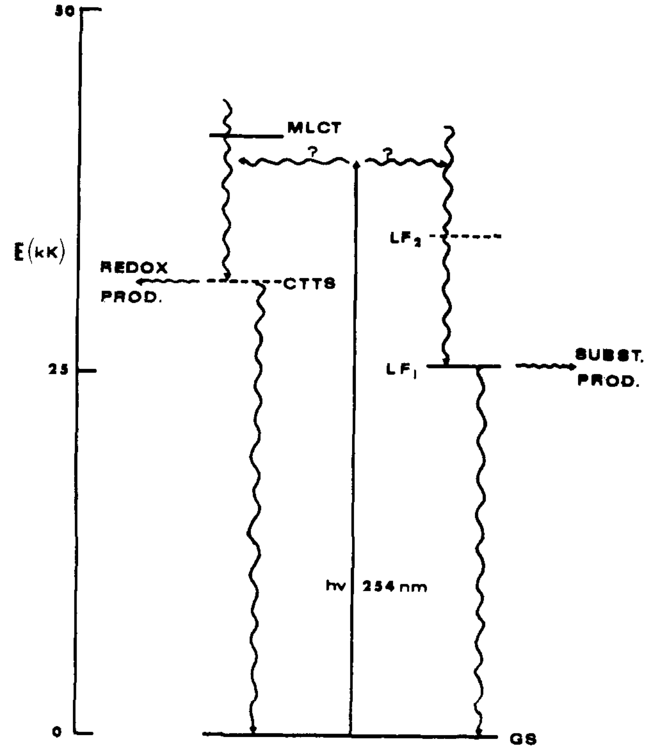
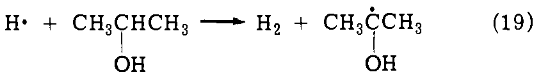


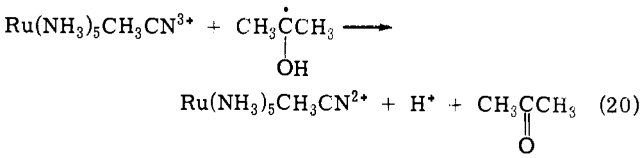
Figure 2. Proposed order of singlet excited states of aqueous $Ru(NH_3)_5CH_3CN^{2+}$.



$$H\cdot + CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \longrightarrow H_2 + CH_3\underset{\displaystyle OH}{\underset{|}{\dot{C}}}CH_3 \quad (19)$$

A complicating feature is that many of these reactions lead to intermediates which are also very reactive. Hydrogen quantum yields (Φ_{H_2}) were measured for 254-nm irradiation as this was the only wavelength for which hydrogen quantum yields for the ferrocyanide actinometer have been determined. At this wavelength both oxidation and aquation reactions have prominent roles in the photochemistry of $Ru(NH_3)_5CH_3CN^{2+}$. In the absence of added scavenger, quantum yields for H_2 formation were small (~0.005), and if one assumes that H_2 is produced by eq 14 then Φ_{H_2} represents only 5–10% ($2\Phi_{H_2}/\Phi_{Ru(III)}$) of the reducing equivalents needed to balance $\Phi_{Ru(III)}$. The fate of the remainder is not obvious, although reduction of Ru(III) species to Ru(II) (eq 17) will not contribute since the evaluation is based on net formation of Ru(III) product. However, it should be pointed out that Φ_{H_2} values were measured by sampling the reaction solution after ~30% disappearance of the starting material. The $\Phi_{Ru(III)}$ value quoted in Table I for 254 nm is an initial value obtained by extrapolation, and a more realistic comparison would be to $\Phi_{Ru(III)}$ measured overall for the 30% conversion (~0.1 mol/einstein). Even then, recovered H_2 represents less than 20% of the reducing equivalents produced in the photooxidation. One might speculate that the remaining equivalents may have been consumed in reactions with solution impurities or in the reduction[30] of free acetonitrile released in the photoaquation reaction.

Photolysis in the presence of isopropyl alcohol leads both to substantial increases in Φ_{H_2} and to decreases in $\Phi_{Ru(III)}$. These observations suggest that isopropyl alcohol is scavenging the hydrogen atoms produced and the resultant isopropyl radical is reducing Ru(III) (eq 20). The analogous reduction of $Ru(NH_3)_6^{3+}$ with isopropyl radical occurs with a rate constant,[31] $k = 1.8 \times 10^6\ M^{-1}\ sec^{-1}$. In 2 M isopropyl alcohol, $\Phi_{Ru(III)}$ is virtually zero whether measured as an extrapolated value or at the conclusion of the photolysis period at which H_2 is sampled. Of particular interest is the fact that Φ_{H_2} measured under these conditions is equal to the $\Phi_{Ru(III)}$ value determined in the absence of the trapping agent. Since Φ_{H_2} is the same in pH 2 and pH 3 solution, it appears that H^+ efficiently captures the e^-_{aq} produced and that the 2 M isopropyl alcohol effectively traps H·, giving a net of one H_2 for each photochemical event represented by eq 12. Thus, we conclude the value 0.15 represents the primary quantum yield for photoredox processes at 254 nm.



$$Ru(NH_3)_5CH_3CN^{3+} + CH_3\underset{\displaystyle OH}{\underset{|}{\dot{C}}}CH_3 \longrightarrow Ru(NH_3)_5CH_3CN^{2+} + H^+ + CH_3\underset{\displaystyle O}{\underset{\|}{C}}CH_3 \quad (20)$$

For an overall view of the $Ru(NH_3)_5CH_3CN^{2+}$ photochemistry, the following should be considered. (1) Direct excitation of the lowest ligand field absorption band leads exclusively to substitution reactions, a pattern consistent with the expected reactivity of a ligand field excited state for a low spin, d^6 hexacoordinate complex. (2) The photoaquation quantum yields as reflected by Φ_{CH_3CN} are relatively independent of excitation wavelength over the range 366–254 nm, but drop to small values at wavelengths less than 254 nm. (3) Photooxidation of Ru(II) to Ru(III) is observed over the wavelength region where charge transfer absorption is significant and becomes increasingly important over the range 313–214 nm. (4) Although the dominant feature of the $Ru(NH_3)_5CH_3CN^{2+}$ electronic spectrum is a MLCT absorption band at 226 nm, both the spectrum and photoredox behavior of the hexaammine complex[8] and of $Ru(NH_3)_5CH_3CN^{2+}$ itself suggest that a CTTS state is the reactive excited state toward oxidation. (5) Direct excitation of the MLCT absorption band at 228.8 and 213.9 nm leads to relatively efficient interconversion to the excited state(s) responsible for oxidation processes and little or no interconversion to the excited state(s) responsible for substitution reactions. Since the $\Phi_{Ru(III)}$ is ~0.50 under these conditions, nonradiative deactivation directly to ground state (i.e., by-passing the ligand field excited state manifold) must operate to account for much of the remaining 50% of excited molecules produced.

Figure 2 illustrates the excited state order which would be consistent with the above summary. LF_1 and MLCT are easily identified from absorption spectra and are shown with energies corrected for an assumed Stokes shift of 3 kK from the absorption maximum to the thermally equilibrated excited state. The states CTTS and LF_2 are shown as dashed lines because their existence is indicated indirectly, the former because of the redox photochemistry the latter because of the curve analysis of the absorption spectrum and analogy to the $Ru(NH_3)_6^{2+}$ spectrum. Singlet states are the only ones shown although states of different multiplicities may in fact be responsible for part of the photoreactivity. The CTTS "state" is shown as having a discrete energy; however, it must be very diffuse given the uncertainty and variety of the many solvent complex configurations possible in the excited states. This variety of structure and the rapid relaxation of different configurations with respect to each other no doubt provide ample opportunity for the MLCT excited state to interconvert to an isoenergetic CTTS state. The quantum yield data can be rationalized according to a simple model. In this model excitation at any wavelength would lead to competitive population of states in the charge transfer or ligand field manifolds. Ligand field states would rapidly undergo interconversion to a common (lowest energy?) LF state from which aquation or nonradiative deactivation to the ground state occurs. Molecules in upper charge transfer states would undergo internal conversion to the lower energy CTTS state where metal oxidation or deactivation directly to the ground state occurs. Internal conversion to the ligand field manifold would be inefficient relative to these other processes. As an illustration, the photooxidation and photosubstitution paths resulting from 254-nm excitation may be explained by competitive population of the ligand field and charge transfer manifolds which do not interconvert rapidly.

The 254-nm photolysis of the dinitrogen complex shows a pattern somewhat different from that of the acetonitrile complex. Photooxidation of Ru(II) to Ru(III) occurs concurrently with H_2 formation but the only significant N_2 aquation observed is a consequence of the photooxidation pathway. The observation of H_2 formation is in direct contrast to the previous qualitative study by Sigwart and Spence[11] who reported Ru(III) but not H_2 among the products resulting from the irradiation of aqueous $Ru(NH_3)_5N_2^{2+}$ with an unfiltered high-pressure mercury lamp. These workers did detect traces of O_2 in the mass spectra of product gases from their photolyses, and it is conceivable that their reaction solution may have contained sufficient O_2 to trap any hydrogen atoms formed. The Φ_{H_2} value (0.035) reported here for 254-nm irradiation represents approximately 40% of the reducing equivalents produced in the photooxidation if it is assumed that eq 14 is the principal H_2 source. The Φ_{H_2} value (0.1) determined in the presence of 0.5 M isopropyl alcohol represents an approximately 20% increase in the reducing equivalents produced as H_2 if eq 19 is the principal source of H_2 under these conditions. The fate of the reducing equivalents unaccounted for as H_2 is unclear. One possibility previously suggested[11] was that dinitrogen is perhaps being reduced under these conditions; however, this possibility is not particularly attractive given the observation by Baxendale and Mulazzani[22] that not even reaction of the solvated electron with $Ru(NH_3)_5N_2^{2+}$ leads to dinitrogen reduction but leads to metal ion reduction instead.

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