eter at 70 eV. Microanalysis was performed by Galbraith Laboratory, Knoxville, Tenn.

Preparation. A solution of diphenylselenium dichloride (1.52 g, 0.0050 mol) in 35 ml of spectrograde methanol was treated with a solution of sodium acetylacetonate (1.25 g, 0.0102 mol) in 15 ml of methanol at room temperature. Instant color change of solution from yellow to orange was observed. After being stirred for 3 hr the solvent was removed and the remaining solids were extracted with chloroform and filtered to remove unreacted materials and sodium chloride. Addition of petroleum ether to the filtrate and cooling the solution gave the crude product. Recrystallization of the crude product from chloroform–petroleum ether gave 0.98 g (60% yield) of light orange crystals of diacetylmethylenediphenylselenurane, **1**; mp 125–126.5°; ir (KBr pellet) 3035 (m), 2960 (m), 1950 (w), 1560 (s, shoulder), 1520 (s, broad), 1450 (m), 1428 (m), 1400 (m), 1350 (s), 1320 (s), 1300 (s), 1270 (s), 1175 (m), 1060 (m), 1010 (m), 990 (m), 930 (s), 838 (w), 740 (s), 685 (s), 600 (s), 585 (s), 450 (s), 325 (m), 305 (m); ^{1}H nmr (CDCl$_3$) δ 2.43 (s, 6 H), 7.41–7.65 (m, 10 H); mass spectrum m/e 332 (M$^+$), 317 (M$^+$ − CH$_3$), 290, 239, 234 (Ph$_2$Se$^+$), 223, 211, 195, 175, 157 (C$_6$H$_5$Se$^+$), 154 ((C$_6$H$_5$)$_2$$^+$), 132, 117, 94, 77 (C$_6H_5$$^+$).

Anal. Calcd for $C_{17}H_{16}O_2Se$: C, 61.63; H, 4.86. Found: C, 62.02; H, 4.83.

X-Ray Analysis. A small crystal 0.10 × 0.20 × 0.15 mm was mounted along the b axis (0.20 mm). Cell data (from a least-squares fit to the settings for 12 reflections, Cu Kα, λ 1.54178 Å) are $C_{17}H_{16}O_2Se$, mol wt = 335.25, monoclinic, a = 13.297 (7), b = 13.418 (6), c = 9.112 (5) Å, β = 111.7 (1)°; V = 1510 × 10^{-24} cm^3, Z = 4, D_{calcd} = 1.475 g cm^{-3}, μ = 37.6 cm^{-1} (Cu Kα), space group $P2_1/c$.

Intensity data were collected as described previously.[26,27] A total of 2680 intensities was measured, 2370 of which were considered above background at the 2σ level based on counting statistics. The structure was solved by the heavy-atom method. The model including positional and anisotropic thermal parameters for the nonhydrogen atoms was refined to an R factor of 0.099 on all nonzero reflections. A difference map calculated at this stage in the analysis provided positions for all the hydrogen atoms. However, some of these atoms moved to rather unreasonable positions where they were included in the refinement process and were subsequently constrained at the positions found from the difference map. After convergence of the least-squares refinement, the final R factor on all nonzero reflections was 0.088. The list of atomic coordinates is given in Table II. The final thermal parameters and the observed and calculated structure factors will appear in the microfilm edition.[28] A weighting scheme based on that proposed by Corfield, Doedens, and Ibers[29] was used in the refinement. The scattering curves for Se, C, and O were from the compilation by Cromer and Mann,[30] that from hydrogen being the one calculated by Stewart, *et al.*[31]

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Supplementary Material Available. The final thermal parameters and the values of h, k, l, $|F_o|$, and F_c for **1** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-4099.

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Short-Wavelength, Ultraviolet Photolysis of Metal Complexes. Substantial Photoreduction of Ruthenium Complexes

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Abstract: Unlike previous investigations at 185 nm which have been characterized by the photolysis of water and not the solute, this report centers upon the solute (the metal complexes) absorbing most of the light at 185 nm. Photolysis of $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5OH_2^{3+}$, and $Ru(NH_3)_5Cl^{2+}$ at 185 nm has been investigated. Substantial photoreduction ($\Phi_r \sim 0.65$) of $Ru(NH_3)_6^{3+}$ was observed in the presence of small amounts of 2-propanol, methanol, or ethanol. Photolysis at 254, 229, and 214, while resulting in some photoreduction, gave no apparent indication of the enhanced photoreduction observed at the higher energy. The rapid rise in Φ_r in the low uv corresponds to the onset of the charge-transfer band of the ruthenium complex. On the contrary, photoaquation is not similarly enhanced on going from 254 to 185 nm. A mechanism is proposed in which the 2-propanol serves as a radical scavenger of photoexcited ruthenium radical. The 2-propanol radical which results (free or coordinated) undergoes hydrogen abstraction to produce a mole of acetone and 0.5 mol of hydrogen. ($\Phi_r = \Phi_{acetone} = 2\Phi_{H_2}$.)

As compared with the large number of reports at 254 nm, low uv photolysis of metal complexes at 185 nm has received little attention.[1] It has readily been demonstrated that 254-nm photolysis of metal complexes can activate a molecule coordinated to a metal center.[2,3] Recent investigators[4,5] have concentrated on 229- and 214-nm irradiation of inorganic salts. In the past, photochemistry below 200 nm has

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[1] Photolysis of SO_4^{2-}: J. Barrett, M. Fox, and A. L. Mansell, *J. Phys. Chem.*, **69**, 2996 (1965).

[2] A. Vaudo, E. Kantrowitz, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, *J. Amer. Chem. Soc.*, **74**, 6655 (1972).

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been characterized by the generation of H· and $\dot{O}H$ from the photolysis of water,[6] because water has been one of the primary absorbing species in the solution. However, many coordination complexes exhibit intense charge-transfer transitions between the metal and the ligand (or the solvent) in this spectral region.[7] In particular, we have observed extremely intense absorption bands for some ruthenium complexes which do not appear until one scans below 210 nm. Thus, while there may be some photochemistry above 210 nm, one may not observe significant photochemistry unless one searches further into the low uv. Previous investigations at 254 nm concluded that $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ undergo photoaquation with rather low quantum yields.[8] However, we shall demonstrate that the characteristics of the spectrum of $Ru(NH_3)_6^{3+}$ dictate that when studies are extended to lower wavelengths substantial quantum yields for photoreduction of Ru(III) in aqueous solution are observed. These results indicate *significant* photochemistry of ruthenium complexes and demonstrate the utility of 185-nm irradiation and the importance of extending more photochemical experiments below 200 nm.

Experimental Section

Unless otherwise noted all reagents used were of the highest quality available. The alcohols used for scavengers were of spectral grade. For the acetone analyses, carbonyl free 2-propanol was prepared after the method of Lappin and Clark.[9] Water was doubly distilled with the last distillation from alkaline permanganate. Deuterated ethanol-d_6 and 99.8% D_2O were purchased from Stohler Isotope Chemicals.

$[Ru(NH_3)_6](TFMS)_3$. The $TFMS^-$ salt (trifluoromethylsulfonate anion) was prepared by the dropwise addition of concentrated HTFMS to a solution of recrystallized $[Ru(NH_3)_6]Cl_3$. The white solid was washed with acetone and ether, redissolved in a minimum volume of water, reprecipitated with HTFMS, and washed again with acetone and ether.

$[Ru(NH_3)_5OH_2](TFMS)_3$. $[Ru(NH_3)_5Cl]Cl_3$ (0.1 g) was dissolved in a minimum of hot water (using the steam bath). With a continual flow of argon, aqueous ammonia was added dropwise. The solution was immediately cooled in an ice bath and reacidified with HTFMS. Excess HTFMS precipitated the $TFMS^-$ salt. The procedure was repeated once again to ensure the absence of chloride. The solid was washed with acetone and ether.

Preparation of Solutions. In most cases the ruthenium complex was weighed out and dissolved in the appropriate solvent and then degassed with argon (Matheson, 99.99%). Argon was purified through a Cr^{2+} tower and passed through a 0.1 *M* NaCl tower before reaching the reaction solution. The argon line was of all-glass construction. In addition, when solutions containing alcohols were to be degassed, an excess of the alcohol-containing liquid mixture (minus only the ruthenium complex) was prepared and used to presaturate the gas which entered the flask containing the reaction solution. Rigorous methods of handling air-sensitive solutions were employed from the beginning of the work. All solutions were transferred using fitted, all-glass syringes and platinum needles. In order to cover the reaction flasks, heavy-walled serum caps were used and, where necessary, sealed with wax.

Ru(II) was specifically analyzed as $Ru(NH_3)_5OH_2^{2+}$ using isonicotinamide[10] as a complexing agent (λ_M 480, ϵ 1.17 × 10^4 M^{-1} cm^{-1}) by injecting the photolyzed solution into a sealed, degassed spectrophotometer cell containing solid isonicotinamide. The concentration of $Ru(NH_3)_6^{2+}$ was determined by using Fe^{3+} and analyzing for the Fe^{2+} produced as the *o*-phenanthroline complex.[11]

The spectra of the products of photoreduction are somewhat different from the oxidized forms. Slight increases in absorbance at 268 and 275 nm were observed, as expected, for the production of $Ru(NH_3)_5OH_2^{2+}$ and $Ru(NH_3)_6^{2+}$, respectively. Most of our solutions were irradiated so as to reduce less than 5% of the available ruthenium. When very low concentrations of the complex were used to test for ruthenium dependence, the photochemical conversion was allowed to proceed to 10–15% of the available ruthenium.

HTFMS. Concentrated HTFMS was purchased from the 3M Co. and purified by fractional distillation under vacuum (bp 88°, (50 mm)). The distillate was diluted immediately in order to prolong its stability.

NaTFMS. HTFMS was neutralized with Na_2CO_3 in an ice bath. The solution was heated until NaTFMS began to crystallize out. Upon cooling, the solid was filtered and washed with a minimum of acetone. The solid was recrystallized by dissolving it in a minimum volume of acetone, filtering, and evaporating until NaTFMS crystals began to appear. After cooling, the solid was washed with ether and dried at 110°. Its purity was checked by its mp at 248°.[12]

Photolysis at 185 nm. Irradiation (185 nm) was obtained from a low-pressure Hg-resonance lamp of suprasil construction (Hanovia Lamp Division). The flat spiral of the lamp was fixed into one end of an aluminum box (coated on the inside with black paint). A slit of ~2 cm in diameter was placed between the water cooled (25°) cell holder and the lamp. A narrow space between the slit and the cell holder was allotted to permit the insertion of glass filters. On one side, the aluminum box was fitted with a rubber cushion to permit sealing of the box so that it could be continually purged with nitrogen. In addition, the box was also fitted with aluminum cooling coils to dissipate the heat generated inside the box. Since the large platinum electrodes of the lamp were situated outside the aluminum box, the entire photolysis setup was placed inside a larger wooden box fitted with a fan to dissipate the heat and the ozone. Cylindrical, suprasil spectrophotometer cells (1-cm path length) were used in all runs at 185 nm. The cells contained a micro stirring bar to provide for continued stirring during the photolysis. Outside the aluminum box a heavy duty magnetic stirrer was placed directly below the cell. The cell was fitted with a heavy-wall septum cap covered with wax. A typical exposure time was 4.0 min.

Photolysis at 254 nm. A spectrophotometer cell was sealed with a serum cap and the cell irradiated on one face. A low-intensity Hg-vapor lamp (U-shaped low-pressure Hg lamp from Hanovia Lamp Division) was used with a Corning filter (No. 7910) to remove any other emission lines below 240 nm.

Photolysis at 214 and 229 nm. Irradiation at 229 nm was performed with a 25-W Phillips Cadmium spectral lamp (No. 93107). Under the conditions employed, the only spectral line being absorbed by the solution was that at 229 nm. Irradiation at 214 nm was obtained from a 25-W Phillips Zinc spectral lamp (No. 93106). Both lamps were warmed for 20 min prior to irradiation. The lamps were encased in a blackened housing with a circular opening (~2 cm in diameter). A 1-cm cell containing 1.0 *M* NaCl was placed immediately in front of the circular opening and before the solution to be irradiated to ensure the elimination of other emission lines of <208 nm.[4] For the preliminary studies at these wavelengths, the cells were cooled by a stream of air directed at the cells ($T = 26 \pm 2°$).

Actinometry. Solutions used to determine the intensity of the lamps were placed in the same cells used for photolyses of the ruthenium complexes. At 185 nm a 5 *M* solution of aqueous C_2H_5OH was used as a chemical actinometer ($\Phi_{H_2} = 0.63$).[13] The H_2 was analyzed by fitting the cell with bulb to increase the gas volume of the cell. The gas was analyzed using a F and M gas chromatograph (6 ft molecular sieve, 5A column at 50° with nitrogen as a carrier gas). A standard curve of peak height *vs.* micromoles of H_2 was used to calibrate the gas chromatograph. The 185-nm lamp stabilized within the 10 min allotted for warm-up time. Actinometry was performed every time that a ruthenium solution was photolyzed. At 254 nm, actinometry was performed by analysis of the Co^{2+} produced on irradiation[14] of $Co(NH_3)_5OAc^{2+}$ ($\Phi_{Co^{2+}} = 0.19$). Co^{2+} was determined spectrophotometrically after complexing the Co^{2+} produced with excess SCN^- in 50%

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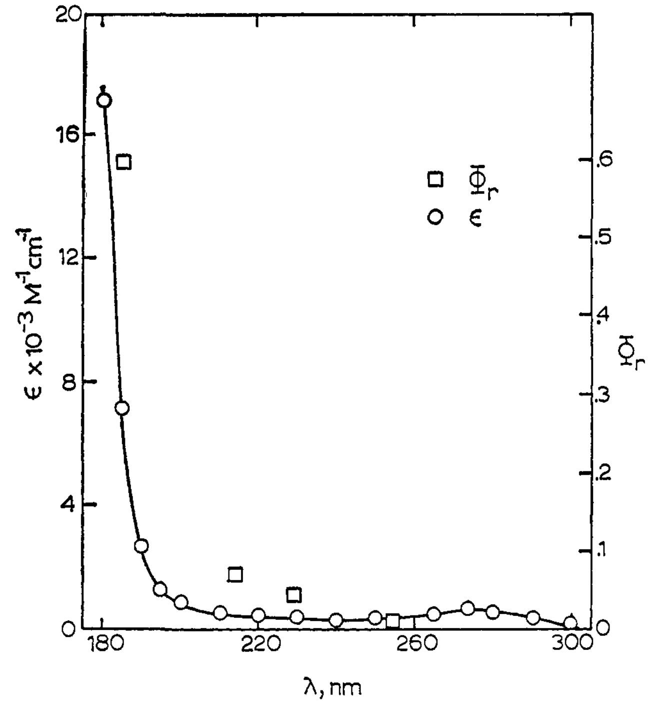

Figure 1. Comparison of uv and action spectrum of $[Ru(NH_3)_6](TFMS)_3$. Photolysis corresponds to $[Ru(NH_3)_6^{3+}] = 1.8 \times 10^{-3}\ M$, pH 2 with HTFMS, $T = 25°$, [2-propanol] = 0.05 at 185 and 0.5 M elsewhere. At the 2-propanol concentrations used for photolysis, the ruthenium complex is the primary absorbing species.

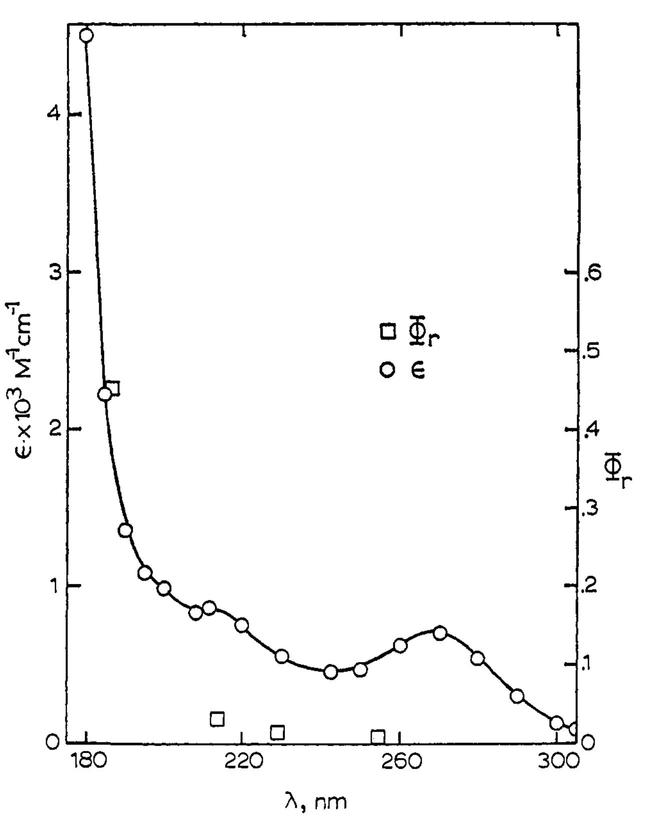

Figure 2. Comparison of uv and action spectrum of $[Ru(NH_3)_5OH_2](TFMS)_3$. Photolysis corresponds to $[Ru(NH_3)_5OH_2^{3+}] = 1.8 \times 10^{-3}\ M$, pH 2 with HTFMS, $T = 25°$, [2-propanol] = 0.05 M at 185 and 0.5 M elsewhere. At the 2-propanol concentrations used for photolysis, the ruthenium complex is the primary absorbing species.

acetone.[15] Actinometry at 214 and 229 nm was obtained[4] upon photolysis of NaN_3 solutions buffered to pH 7.7 (with HPO_4^{2-} at $10^{-3}\ M$). The N_3^- depletion was monitored spectrophotometrically at 235 nm (ϵ 420 M^{-1} cm^{-1}).[16] Values of $\Phi_{-N_3^-} = 0.32 \pm 0.1$ at 214 nm ($10^{-3}\ M$ NaN_3) and $\Phi_{-N_3^-} = 0.31 \pm 0.01$ at 229 nm ($2 \times 10^{-3}\ M$ NaN_3) were used to obtain intensities of 8.8×10^{-5} einstein/(l. min) at 214 nm and 1.5×10^{-4} einstein/l. min) at 229 nm. In addition, the NH_2OH produced upon photolysis of NaN_3 was also analyzed ($\Phi_{-N_3^-} = \Phi_{NH_2OH}$)[4,5] spectrophotometrically by forming the *p*-nitrobenzaldoxine.[17]

Filters. A Corning filter, No. 7910, was used to remove light of <240-nm wavelength, and a Pyrex plate was used to filter out light of <320-nm wavelength. A LiF disk (previously γ irradiated with a ^{60}Co γ-ray source)[18] was used to remove 254-nm radiation. In order to minimize the amount of 254-nm radiation getting through the LiF disk, the absorbance of the filter at 254 nm was maintained above 4.0 absorbance units,[19] while the absorbance of the filter itself at 190 nm was <0.65 absorbance units.

Acetone Analyses. Acetone was analyzed spectrophotometrically[20] by treating the photolyzed solution with 2,4-dinitrophenylhydrazine. Appropriate standard solutions with acetone and ruthenium were prepared to obtain the concentration of acetone produced upon photolysis. For the aqueous solutions in this work, the method of analysis was insufficient, beyond indicating the presence of a significant amount of acetone. Gas chromatographic analysis[21] using a Perkin-Elmer 990 gas chromatograph fitted with a flame ionization detector (using a 12 ft × 1/8 in. 20% FFAP on Chromosorb 60–80 mesh column) specifically indicated the presence of acetone. A standard curve was prepared using solutions containing known amounts of ruthenium, 2-propanol, HTFMS, and acetone.

Spectra. All spectra above 200 nm were recorded on a Cary 14 recording spectrophotometer. Below 200 nm, spectra were obtained using a Cary 16 recording spectrophotometer appropriately modified for low uv spectra. These spectra were recorded for us by Professor Malcolm Fox.[22]

γ Radiolysis. ^{60}Co γ radiolysis of the ruthenium solution was performed at 25° in septum-stoppered vials. All radiolyses were performed under an inert atmosphere, and the analyses were performed as described above. The dose of the source corresponded to 5.9×10^{16} eV/(ml min).

Results

Spectra. Figures 1 and 2 describe the spectra of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5OH_2^{3+}$, respectively. The values of ε at 275 and 268 nm, respectively, agree with previously published values in the literature.[23,24] However, a new band appears at 212 nm (ϵ 850 M^{-1} cm^{-1}) for $Ru(NH_3)_5OH_2^{3+}$ which has not been observed in the past. The failure of previous investigators to observe this band at 212 nm may have been due to the difficulty in preparing solid salts of the aquo complex. In the past, the counterion of the complex absorbed intensely below 240 nm (such as the Br^- salt). Addition of a very small amount of solid NaCl to the solution of $Ru(NH_3)_5OH_2^{3+}$ in HTFMS obscures this new peak completely. Thus, one could not observe this weak band at 212 nm under the charge-transfer

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[15] Spectrophotometric analysis for Co^{2+} as the SCN^- complex in 50% acetone: M. V. Olson, Ph.D. Thesis, Stanford University, August, 1969.

[16] I. Burak and A. Treinen, *J. Chem. Phys.*, **39**, 189 (1963).

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[19] R. A. Holroyd and T. E. Pierce, *J. Phys. Chem.*, **68**, 1392 (1964).

[20] For the sensitivity required to detect small amounts of acetone, it was necessary to reflux 2-propanol with 2,4-DNP according to the method used in ref 9.

[21] We wish to thank Ms. Lorraine McDonald for her technical assistance with the instrument.

[22] Professor Fox was on sabbatical leave from the School of Chemistry, City of Leicester Polytechnic, Leicester, U. K.

[23] J. N. Armor, Ph.D. Thesis, Stanford University, May, 1970.

[24] J. N. Armor, H. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, 90, 5928 (1968).

(CT) band due to Br^-. This brings out an important feature of our anion of choice, $TFMS^-$. Besides being both a poor complexing agent[25] and a poor oxidizing agent, $TFMS^-$ absorbs very little light above 180 nm (ϵ_{185} 1.5 M^{-1} cm^{-1}). This makes $TFMS^-$ a highly desirable anion to work with when photolyzing at very low wavelengths in the uv. Upon 185-nm irradiation of 0.1 M $TMFS^-$ for extended periods of time, no major absorbance changes were observed. Returning to Figure 1, one observes that both the ruthenium complexes studied absorb intensely at 185 nm. (At 185 nm: $\epsilon_{Ru(NH_3)_6^{3+}}$ 7.11 × 10^3 M^{-1} cm^{-1}, $\epsilon_{Ru(NH_3)_5OH_2^{3+}}$ 2.20 × 10^3 M^{-1} cm^{-1}, and ϵ_{H_2O} 1.46 cm^{-1}.) One does note the marked onset of these CT bands for the ruthenium complexes below 210 nm. The spectrum of 0.05 M 2-propanol (ϵ 48 at 185 nm) is too weak to be designated in Figure 2. The other alcohols used in this study absorb[26] even less at 185 nm. (At 185 nm: $\epsilon_{methanol}$ 8.8 M^{-1} cm^{-1} and $\epsilon_{ethanol}$ ~15 M^{-1} cm^{-1}.)

Table I. 185-nm Photolysis of $Ru(NH_3)_6^{3+}$ [a]

$[Ru(NH_3)_6^{3+}]$, $\times 10^3$ M	[2-Propanol], M	pH	Φ_r[b]
0.071	0.50	2.0	0.14
0.14	0.50	2.0	0.19
0.38	0.10	2.0	0.54
0.38	0.50	2.0	0.49
0.95	0.50	2.0	0.56
1.8	0.50	2.0	0.65
3.6	0.50	2.0	0.61
6.0	0.50	2.0	0.78
7.7	0.50	2.0	0.49
7.7	0.10	2.0	0.48
9.1	0.50	2.0	0.71
20.3	0.50	2.0	0.82
1.8	0	2.0	0.05
1.8	5.0 × 10^{-5}	2.0	0.02
1.8	5.0 × 10^{-4}	2.0	0.04
1.8	1.6 × 10^{-4}	2.0	0.17
1.8	5.0 × 10^{-3}	2.0	0.31
1.8	1.6 × 10^{-2}	2.0	0.35
1.8	5.0 × 10^{-2}	2.0	0.59
1.8	0.10	2.0	0.62
1.8	0.50	2.0	0.65
1.8	2.0	2.0	0.72
1.8	0.50	1.0	0.67
1.8	0.50	3.6	0.72
1.8	0.50	5.1	0.57
1.8	0.50	9.5	0.62
1.8	0.50	10.5	0.64
1.8	0	5.1	0.04

[a] $T = 25°$, av $I_a = 1.7 \times 10^{-6}$ einstein/(l. min), Φ_r independent of intensity. [b] For $\Phi_r > 0.1 \pm 10\%$ or $\phi_r < 0.1 \pm 20\%$.

Table II. 185-nm Photoreduction of $Ru(NH_3)_6^{3+}$ with Other Added Alcohols[a]

[Ethanol], M	[Methanol], M	[*tert*-Butyl alcohol], M	Φ_r[d]
5.0 × 10^{-4}			0.26
1.0 × 10^{-3}			0.17
5.0 × 10^{-3}			0.43
5.0 × 10^{-2}			0.52
6.4 × 10^{-2}			0.75
0.10			0.74
0.13			0.67
0.50			0.60
0.64			0.78
2.0			0.62
5.0			0.78
0.50			0.85[b]
	5.0 × 10^{-3}		0.16
	5.0 × 10^{-2}		0.27
	0.10		0.59
	0.50		0.59
		0.10	0.07
		0.50	0.12
		0.10[c]	0.70

[a] $(Ru(NH_3)_6^{3+}] = 1.80 \times 10^{-3}$ M, $T = 25°$, pH 2.0, $I_a \sim 1.7 \times 10^{-6}$ einstein/l. min). [b] Deuterated alcohol and D_2O. [c] Plus 0.1 M 2-propanol. [d] ±10%.

Table III. 185-nm Photoreduction of $Ru(NH_3)_5OH_2^{3+}$ [a]

$[Ru(NH_3)_5$-$OH_2^{3+}]$, $\times 10^3$ M	[Alcohol][b]	$[Cl^-]$[c]	Φ_r[h]
0.9	4.0 × 10^{-4}		0.14
0.9	1.0 × 10^{-3}		0.27
0.9	2.5 × 10^{-3}		0.60
0.9	0.10		0.56[d]
0.9	0.50		0.58
0.9	1.0		0.77
0.9	2.0		0.60
1.5	0.50		0.57
1.8	0.020		0.45
1.8	0.050		0.61,[e] 0.62[f]
1.8	0.20		0.69, 0.48[g]
0.9	2.5 × 10^{-3}	2.0 × 10^{-3}	0.37
0.9	2.5 × 10^{-3}	5.0 × 10^{-3}	0.15
0.9	2.5 × 10^{-3}	1.0 × 10^{-2}	0.048
0.9	2.5 × 10^{-3}	2.0 × 10^{-2}	0.045
1.8	0.50		0.52
5.4	0.50		0.45

[a] $T = 25°$, pH 2.0, $I_a \sim 1.7 \times 10^{-6}$ einstein/(l. min). [b] Except for the last two entries, which are ethanol, 2-propanol was the alcohol used. [c] NaCl added. [d] In D_2O. [e] $I_a = 1.1 \times 10^{-5}$ einstein/(l. min). [f] $I_a = 4.7 \times 10^{-5}$ einstein/(l. min). [g] 2.0 × 10^{-4} M acetone added. [h] ±10%.

Photolyses. Tables I, II, and III summarize some of the quantum yields for the photoreduction (Φ_r) of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5OH_2^{3+}$ to yield $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5OH_2^{2+}$, respectively. The isonicotinamide analysis is specific for $Ru(NH_3)_5OH_2^{2+}$. ($Ru(NH_3)_4(OH_2)_2^{2+}$ would give rise to a noticeably different spectrum.)[27] Also, analyses of the product solution from the photolysis of $Ru(NH_3)_6^{3+}$ with isonicotinamide gave no indication of substantial $Ru(NH_3)_5OH_2^{2+}$ production ($\Phi_{aquation} < 0.07$).[8,28]

From Tables I, II, and III it is apparent that substantial photoreduction occurs when alcohols are added to the ruthenium-containing solutions. It appears that the behavior of methanol, ethanol, and 2-propanol is similar. However, *tert*-butyl alcohol gives a much lower value for Φ_r. Using ClO_4^- as the counterion, significant photoreduction was apparent, despite the added absorption due to ClO_4^- in the solution ($\epsilon_{ClO_4^-}$ 20 M^{-1} cm^{-1} at 180 nm).[29] (Oxidation of Ru(II) by ClO_4^- is not significant at the level of ClO_4^-

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(27) R. G. Gaunder and H. Taube, *Inorg. Chem.*, 9, 2629 (1970).

(28) This work, Table VII.

(29) M. J. Blandauer and M. Fox, *Chem. Rev.*, 70, 59 (1970).

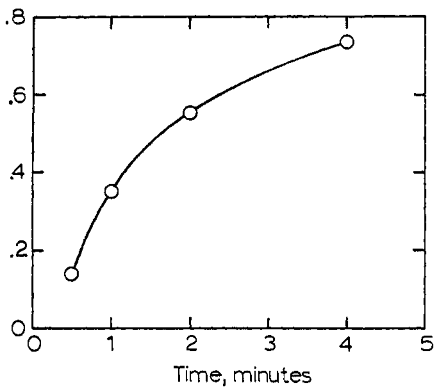

Figure 3. Apparent photoreduction of $Ru(NH_3)_5Cl^{2+}$. Formation of $Ru(NH_3)_5OH_2^{2+}$ with time of 185-nm irradiation. $[Ru(NH_3)_5Cl](TFMS)_2 = 1.6 \times 10^{-3}$ *M*, pH 2 with HTFMS, [2-propanol] = 0.1 *M*, *T* = 25°. Note $\epsilon_{Ru(NH_3)_5Cl^{2+}}$ 1.18×10^4 at 185 nm. Each point corresponds to a single experiment and not to a Φ_r determined by measuring photochemical yields over several time intervals.

employed in this experiment.) This confirms that $TFMS^-$ is not uniquely involved in the primary photochemical process.

In all our experiments, filters were used to specifically test for the interference of stray light. Substantial photoreduction ($\Phi_r < 0.001$) is not observed (1) when a Pyrex filter is used, (2) when both LiF and the Corning No. 7910 filters are used, or (3) when the Corning No. 7910 filter is used alone.

The behavior of $Ru(NH_3)_5Cl^{2+}$ (Table IV) in Cl^- free medium under the conditions employed above for $Ru(NH_3)_5OH_2^{3+}$ and $Ru(NH_3)_6^{3+}$ is unique. (Note: the $Ru(NH_3)_5Cl^{2+}$ is still absorbing most of the 185-nm light.) The analysis indicates that $Ru(NH_3)_5OH_2^{2+}$ is produced, but the lability of $Ru(NH_3)_5Cl^+$ does not permit one to readily differentiate between the direct photoreduction of $Ru(NH_3)_5Cl^{2+}$ (followed by rapid aquation) and $Ru(NH_3)_5OH_2^{2+}$. In an effort to separate these two alternatives, photolyses were carried out for progressively shorter exposure times. It is apparent from Figure 3 that while considerable Ru(II) may be present after photolyzing for several minutes, the production of $Ru(NH_3)_5OH_2^{2+}$ is due to the photolysis of $Ru(NH_3)_5OH_2^{3+}$. The latter species must be produced from photoaquation of $Ru(NH_3)_5Cl^{2+}$. Photoaquation of $Ru(NH_3)_5Cl^{2+}$ at 254 nm has already been reported.[8] At 185 nm, the Φ_r for $Ru(NH_3)_5Cl^{2+}$ is close to zero, but the production of the first traces of Ru(II) can catalyze[30] the aquation of $Ru(NH_3)_5Cl^{2+}$ to $Ru(NH_3)_5OH_2^{3+}$. Since there is no external chloride present in the medium, the equilibrium

Table IV. Apparent Photoreduction of $Ru(NH_3)_5Cl^{2+}$ at 185 nm[a,c]

[2-Propanol]	Φ_r[b]
2.5×10^{-3}	0.19
5.0×10^{-3}	0.21
1.0×10^{-2}	0.29
2.0×10^{-2}	0.26
0.10	0.50
0.50	0.60
1.0	0.51
2.0	0.40

[a] *T* = 25°, 1.5×10^{-3} *M* $[Ru(NH_3)_5Cl](TFMS)_2$, pH 2 with HTFMS, $I_a \sim 1.7 \times 10^{-6}$ einstein/(l. min). [b] By isonicotinamide method of analysis. [c] ϵ_{185} of $Ru(NH_3)_5Cl^{2+}$ $1.18 \times 10^4\ M^{-1}\,cm^{-1}$.

$$Ru(NH_3)_5Cl^{2+} + H_2O \xrightleftharpoons{Ru(II)} Ru(NH_3)_5OH_2^{3+} + Cl^-$$

lies far to the right.[30] Thus, while we know that $Ru(NH_3)_5OH_2^{3+}$ is the primary species being photolyzed in $Ru(NH_3)_5Cl^{2+}$ solutions, we cannot ascertain how much $Ru(NH_3)_5OH_2^{2+}$ initially arises from direct photoreduction of $Ru(NH_3)_5Cl^{2+}$.

We became concerned about the small contribution made by the alcohol to the absorbance of our solutions at 185 nm. Tables V and VI summarize the Φ_r for $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5OH_2^{3+}$ at 254, 229, and 214 nm. It is apparent that the Φ_r's at 254 approach those obtained in the absence of 2-propanol. At 229 and 214 nm the Φ_r's show some increase but do not serve to indicate the substantial value of Φ_r which we observe at 185 nm. The action spectra for $Ru(NH_3)_5OH_2^{3+}$ and $Ru(NH_3)_6^{3+}$ are incorporated into Figures 1 and 2. These spectra demonstrate the intense band for ruthenium below 210 nm is directly coupled with the sharp increase in Φ_r below 210 nm.

Table V. Photoreduction at 229 and 214 nm[a]

λ, nm	$[Ru(NH_3)_6^{3+}]$, $\times 10^3$ *M*	$[Ru(NH_3)_5OH_2^{3+}]$, $\times 10^3$ *M*	[2-Propanol], *M*	Φ_r[b]
214	1.8		0	<0.001
	1.8		0.50	0.068
		1.8	0	<0.002
		1.8	0.50	0.056
229	1.8		0	<0.003
	1.8		0.50	0.041
		1.8	0	<0.006
		1.8	0.50	0.030

[a] pH 2 with HTFMS, *T* = 25°, $I_a \sim 1.5 \times 10^{-4}$ einstein/(l. min) at 229 nm and $I_a \sim 8.8 \times 10^{-5}$ einstein/(l. min) at 214 nm. [b] ±10%.

Table VI. Photoreduction at 254 nm[a]

$[Ru(NH_3)_6^{3+}]$, $\times 10^3$ *M*	$[Ru(NH_3)_5OH_2^{3+}]$, $\times 10^3$ *M*	[2-Propanol]	Φ_r[d]
1.8		0	<0.001
1.8		0.50	0.013[b]
	1.8	0	<0.001
	1.8	0.5	0.008[c]

[a] pH 2.0 with HTFMS, *T* = 25°, $I_a \sim 1.5 \times 10^{-4}$ einstein/(l. min). [b] Φ_r = 0.005 using isonicotinamide analysis. [c] Φ_r = 0.004 using Fe analysis (±20%). [d] ±10%.

Our values for Φ_r at 254 nm are significantly higher than those values previously reported.[8] These new values were obtained using a much more sensitive and specific analytical technique. Further, the increased amounts of Ru(II) which we now report at 254 nm substantiate the suggestions of the previous investigators[8] that some Ru(II) must be produced.

The values for photoaquation of $Ru(NH_3)_6^{3+}$ at 185 nm have been inserted in Table VII for two reasons: (1) earlier investigators[8] indicated that similar values of

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(30) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, 84, 4984 (1962).

Table VII. Photoaquation of $Ru(NH_3)_6^{3+}$ at 185 nm[a]

[Ru-$(NH_3)_6^{3+}$], $\times 10^3$ *M*	pH	[Cl^-]	Other conditions	$\Phi_{aquation}$[e]
0.83	2			0.13
1.5	2			0.17,[b] 0.10,[c] 0.14[d]
2.8	2			0.19
1.5	0			0.10
1.5	1.0			0.14
1.5	3.0			0.16
1.5	4.2			0.077
1.5	5.5			0.12
1.5	2		0.10 *M* 2-propanol	0.15
1.5	2		1.0 *M* 2-propanol	0.12
1.5	2	0.11	0.50 *M* 2-propanol	0.094, 0.026[c]
1.5	1	0.90		0.070
1.5	2		H_2SO_4 to control pH	0.12
1.5	2		$HClO_4$ to control pH	0.13
1.5	2	0.1		0.038,[c] 0.038[d]

[a] $T = 25°$, $I_a \sim 1.7 \times 10^{-6}$ einstein/(l. min). [b] 5 and 15 min $h\nu$. [c] O_2 saturated. [d] N_2O saturated. [e] ±10%.

$\Phi_{aquation}$ were obtained at 254 nm (thus, while photoreduction increases with decreasing wavelength, $\Phi_{aquation}$ does not) and (2) the addition of Cl^- to the medium lowers the value for $\Phi_{aquation}$, which is also consistent with the fact that Cl^- is now absorbing most of the light[31] and competing with the photoaquation pathway.

Radiolyses. It became apparent in the course of our work that alcohol radicals were possible candidates for reduction of Ru(II) ammines. A nonphotochemical test for the possibility of radicals being capable of reducing $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5OH_2^{3+}$ can be offered. γ radiolyses of water produces primarily e_{aq}^- (2.8), $\dot{O}H$ (2.8), and $\dot{H}$ (0.6) (where the values in parentheses represent the *G* values[32]). In 0.1 *M* 2-propanol, the conditions of the radiolyses of argon saturated solutions of 10^{-3} *M* HTFMS and 9×10^{-4} *M* $Ru(NH_3)_5OH_2^{3+}$ are such that $\dot{O}H$ reacts with 2-propanol to produce 2-propanol radicals ($G = 2.8$). Analyses of the irradiated solutions gave G[Ru(II)] = 5.2. This indicates that 2-propanol radicals reduce $Ru(NH_3)_5OH_2^{3+}$. This is not surprising in light of the fact that 2-propanol radicals are also known to reduce $Ru(NH_3)_6^{3+}$.[33]

Acetone and Hydrogen Analyses. Although standard solutions of the ruthenium complex and acetone were prepared, some difficulty was initially encountered in obtaining accurate product analyses. Analysis for acetone using the colorimetric 2,4-dinitrophenylhydrazone derivative indicated that acetone (at approximately the same level of Ru(II) generated) was also produced. Liquid phase gas chromatographic separation indicated that 1 mol of acetone was produced per mole of Ru(II) produced. Since large values of Φ_r were obtained under conditions whereby the absorbance of the ruthenium complex is more than 20 times that of 2-propanol, the acetone could not have arisen from direct photolysis of the 2-propanol.[34] In addition, photolysis in the presence of added acetone does not alter Φ_r.

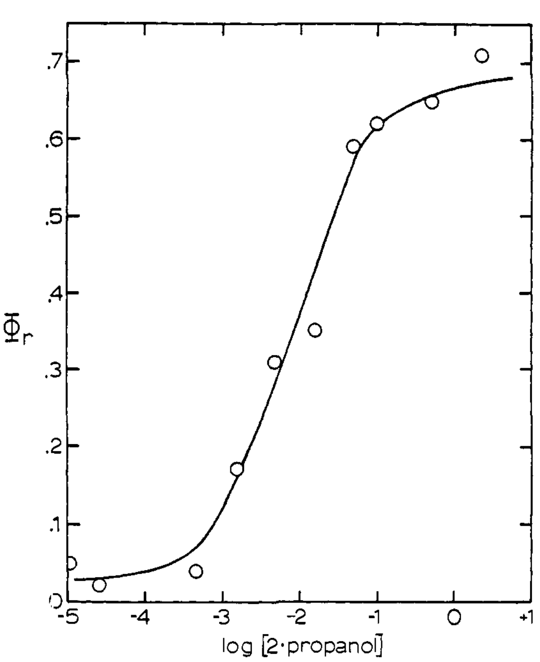

Figure 4. Photoreduction of $Ru(NH_3)_6^{3+}$ at 185 nm as a function of 2-propanol concentration. [$Ru(NH_3)_6^{3+}$] = 1.8×10^{-3} *M*, pH 2, $T = 25°$, all TFMS⁻ medium.

At this stage, it occurred to us that an additional product might arise on photolysis of our ruthenium–alcohol solutions. Analysis of the gas phase above the solution indicated that the quantum yield of H_2 production was about one-half that of Φ_r ($\Phi_{H_2} = 0.25$ at 0.02 *M* 2-propanol and 1.8×10^{-3} *M* $Ru(NH_3)_6^{3+}$) or $\Phi_{acetone}$. In the presence of either methanol or ethanol, H_2 was also produced when either $Ru(NH_3)_6^{3+}$ or $Ru(NH_3)_5OH_2^{3+}$ was used ($\Phi_{H_2} \sim {}^1/_2\Phi_r$).

Discussion

The data of Tables I, II, and III reveal that the quantum yields for photoreduction (Φ_r) of both $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5OH_2^{3+}$ are comparable. Both reactants display little if any dependence upon pH. Recalling the spectrum of the individual components of the solutions (Ru(III), alcohol, and TFMS⁻), the value of Φ_r is virtually independent of $Ru(NH_3)_6^{3+}$ from 9.5×10^{-4} to 2.0×10^{-2} *M*. At lower levels of Ru(III) the value of Φ_r drops off as one might expect, since the other species in the solution begin to absorb increasing amounts of the light.

A plot of Φ_r *vs.* log [2-propanol] gives a sigmoidal curve indicative of a radical being formed and scavenged by the 2-propanol. The first three steps of the following mechanism would explain the scavenging curve in Figure 4.

Mechanism I

$$Ru(NH_3)_6^{3+} \xrightarrow{h\nu} R^0 \qquad (1)$$

$$R^0 \longrightarrow Ru(NH_3)_6^{3+} \qquad (2)$$

$$R^0 + (CH_3)_2\overset{H}{C}OH \longrightarrow Ru(NH_3)_6^{2+} + (CH_3)_2\dot{C}OH + H^+ \qquad (3)$$

$$(CH_3)_2\dot{C}OH + Ru(NH_2)_6^{3+} \longrightarrow Ru(NH_3)_6^{2+} + (CH_3)_2C{=}O + H^+ \qquad (4)$$

$$(CH_3)_2\dot{C}OH \xrightarrow[\text{Ru cat}]{} (CH_3)_2C{=}O + {}^1/_2H_2 \qquad (5)$$

We are not in a position to define the composition of the radical, R^0. For $Ru(NH_3)_6^{3+}$ as the reactant, R^0

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(31) L. E. Orgel, *Quart. Rev.*, 8, 422 (1954).

(32) M. Anbar in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968, p 65.

(33) H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, 94, 6944 (1972).

(34) M. Fox and E. Hayon, *J. Phys. Chem.*, 76, 2703 (1972).

might be a coordinated radical [*e.g.*, $Ru^{II}(NH_3)_6{}^{2+}$, $\dot{O}H$]. A similar mechanism can be devised for $Ru(NH_3)_5OH_2{}^{3+}$ as the reactant. For the latter reactant, the radical may resemble $[Ru^{II}(NH_3)_5O^+H_2]^{3+}$ or $Ru^{II}(NH_3)_5OH_2{}^{2+}$, $\dot{O}H$. Some preliminary flash photolysis experiments were performed on a solution of 3.4×10^{-5} *M* $Ru(NH_3)_5OH_2{}^{3+}$ (argon saturated) and 0.1 *M* 2-propanol (pH 2). Using a xenon flash of 50 J output with a dead time of 50 μsec (the intensity of the flash drops off markedly below 200 nm)[35] while purging the area of the flash lamps with N_2, no transients were observed.

Step 2 in the above mechanism is included to account for the absence of substantial photoreduction at very low levels of 2-propanol. The R^0 species may be scavenged by the alcohol; the R^0 can decompose resulting in reoxidation of the Ru(II). Step 3 accounts for the saturation in Φ_r which is achieved at high levels of 2-propanol. Step 4 is inserted separately to account for the observation that the 2-propanol radical (as generated by ^{60}Co γ irradiation) is also capable of reducing Ru(II).

The similarity of the values of Φ_r for 2-propanol, methanol, and ethanol would be expected for such a mechanism since these alcohols are known to act as effective radical scavengers.[36] The low value of Φ_r observed when *tert*-butyl alcohol is present is consistent with the low reactivity associated with the *tert*-butyl alcohol radical.

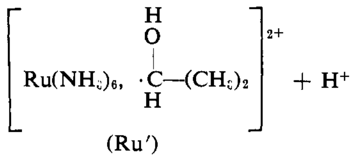
When 2-propanol was used as the alcohol scavenger, acetone was specifically observed in the product mixture. The high yield of acetone is not compatible with only the first four steps of the above mechanism. Step 5 gives both acetone and H_2 as products. The rate of step 4 has been previously determined[33] as 9.2×10^8 M^{-1} sec^{-1} at 25°. At the low radical concentrations[37] generated during steady state photolysis, dismutation of the 2-propanol radical ($k = 1.4 \times 10^9$ M^{-1} sec^{-1} at 25°)[38] into 2-propanol and acetone is not an important component in the total mechanism. Getoff[39] has observed that 10^{-3} *M* Fe^{3+} catalyzes the 185-nm photoformation of oxalate from formate. Thus, we may also be observing (*via* step 5) a ruthenium-sensitized decomposition of the 2-propanol radical. Reaction 4 would produce more acetone. However, step 4 also results in the production of Ru(II), reducing the product ratio of acetone/Ru(II) to 1:2. Step 5 gives both acetone and H_2 as products without producing additional ruthenium(II). Recalling that our results dictate $\Phi_{H_2} = {}^1/_2\Phi_{acetone}$, one concludes that steps 1, 3, and 5 are important in the presence of added 2-propanol. This mechanistic sequence would also explain the low Φ_r observed in the presence of *tert*-butyl alcohol (H abstraction would not be expected to be a facile process). The similarity in the saturation effect of 2-propanol, ethanol, or methanol upon Φ_r and the production of 0.5 mol of H_2 per mole of Ru(II) suggest that a similar mechanism also occurs in the presence of ethanol and methanol.

An alternative mechanism also exists which accounts for the product yields observed above. In mechanism II Ru′ represents a radical-containing

Mechanism II

$$Ru(NH_3)_6{}^{3+} \xrightarrow{h\nu} [Ru(NH_3)_6{}^{3+}]^*$$

$$[Ru(NH_3)_6{}^{3+}]^* + (CH_3)_2\overset{H}{C}OH \longrightarrow$$



$$\left[Ru(NH_3)_6,\ \cdot\overset{\overset{H}{O}}{\underset{H}{C}}-(CH_3)_2\right]^{2+} + H^+$$

(Ru′)

$$Ru' \longrightarrow Ru(NH_3)_6{}^{2+} + (CH_3)_2C{=}O + {}^1/_2H_2$$

species, possibly seven coordinate, arising from the photolysis of the CT band of the Ru ammine. The excited Ru ammine, $[Ru(NH_3)_6{}^{3+}]^*$, reacts with 2-propanol to produce the radical adduct, Ru′, which can then proceed to undergo direct collapse into acetone and $^1/_2H_2$. The possibility of a seven-coordinate or adduct species on Ru(II) ammine is not without precedent.[23,40,41] The saturation effect exhibited by 2-propanol is explained by the reaction of 2-propanol with the photoexcited $Ru(NH_3)_6{}^{3+}$. In the absence of sufficient 2-propanol, the $[Ru(NH_3)_6{}^{3+}]^*$ undergoes deactivation *via* internal decay to the reactants. If $[Ru(NH_3)_6{}^{3+}]^*$ had interacted with the water, in the absence of 2-propanol, the Ru(II) on Ru′ would be expected to be readily reoxidized by the $\dot{O}H$ radical.[33] On the other hand, the 2-propanol adduct incorporates a much poorer oxidizing radical, the 2-propanol radical. Mechanism II differs from the first mechanism in one important feature: the 2-propanol radical remains coupled to the ruthenium complex and is not generated in sufficiently high concentrations in solution for step 4 to become competitive.

The results of Table VII indicate that photoreduction increases with decreasing wavelengths while photoaquation does not. This is to be expected since 185-nm photolysis more closely approximates the energy of the charge-transfer band[42] of the ruthenium complex. Photolysis of the charge-transfer band might be expected to result in photoredox behavior as opposed to photoaquation. Recently, Endicott[43] has observed enhanced photoredox behavior upon photolysis of the CTTM band of $Co(EDTA)^-$ ($\lambda > 214$ nm).

Conclusion

Photolysis at 185 nm often is complicated by the fact that other components of the solution absorb strongly at this wavelength. The spectra of Figures 1 and 2 indicate that this is not the case in our system. In addition several other facts are consistent with the ruthenium complex absorbing most of the light: (1) lowering the [Ru(III)] lowers Φ_r; (2) photolysis in D_2O does not affect Φ_r (D_2O absorbs much less than H_2O

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at 185 nm);[44] (3) adding Cl^- lowers Φ_r (Cl^- absorbs strongly at 185 nm);[31] (4) photolysis in deuterated alcohol does not alter Φ_r (deuterated alcohols absorb even less than the hydrogen-containing alcohols at 185 nm);[45] and (5) the action spectrum indicates that the increase in Φ_r parallels the primary absorbing species, the ruthenium complex.

We have demonstrated the utility of 185-nm radiation to uncover enhanced photoredox behavior which would not be observed by simply photolyzing at 214 or 229 nm. Mechanisms have been proposed to account for the absence of photoreduction in the absence of alcohol. Further, we have evidence to suggest an unusual "hydrogen-abstraction" reaction of the 2-propanol radical, catalyzed by ruthenium.

The instability of the radicals involved in this study prevents their further identification at this stage. It is our intention to demonstrate further evidence of the enhanced photoredox behavior of metal complexes at 185 nm by choosing complexes which are capable of producing stable one-electron reduction products of the ligands.

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Ion Cyclotron Resonance Photodissociation Spectroscopy Spectra of Substituted Benzenes

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Abstract: The first extensive series of photodissociation spectra are reported for a group of mono- and disubstituted benzene compounds between 0.2 and 0.8 μ. For each ion at least two distinctive and relatively sharp photodissociation peaks are observed. Comparison of the photodissociation spectra with their corresponding photoelectron spectra suggests that the two techniques are comparable in the expected way and that the ions observed by the two techniques are structurally similar. Substantial differences in the spectra produced by the two techniques are observed. These differences can be of potential value in interpreting both types of spectra.

Since observation of the photodissociation of CH_3Cl^+ by ion cyclotron resonance spectroscopy,[2] examinations of light-induced dissociation and reactions of a number of gas phase ions have been reported.[2-7] Icr spectroscopy has proved to be a convenient method for observing these processes under low pressure (10^{-9}–10^{-7} Torr) steady state conditions where photon-induced processes can readily compete with other ion–molecule reactions.

Early work in this area has indicated that the cross section for photodissociation of gas phase cations is energy dependent.[2] A study of isomeric $C_7H_8^+$ ions by Dunbar and Fu[6] confirms that dissociation maxima may occur in the visible region of the spectrum for some ionic species. This has prompted the present study of the photodissociation spectroscopy (pds) of a wide range of substituted benzene cations in the near uv and visible regions of the optical spectrum.

Previous studies of ions produced by electron impact and trapped for long periods in the icr spectrometer have been interpreted as indicating that the ion energy is probably near thermal.[7] Thus, addition of an unreactive quenching gas such as N_2 or CH_4 has no effect on the photodissociation rate constant (other than that produced by pressure changes) in a number of systems.[4,7] The absorption of near uv or visible light by ions in these photodissociation experiments can reasonably be assumed to involve excitation of the ion from the thermalized electronic ground state to some excited electronic energy level, probably with vibrational excitation within that level. A photodissociation spectral peak indicates an optical absorption peak for the cation and is governed in part by the Franck–Condon overlap of the two electronic energy states, as in other electronic excitation processes.

A fruitful comparison may be made between photodissociation spectroscopy and uv photoelectron spectroscopy, in which the thermal neutral molecule is excited *directly* to an excited electronic energy level of the *ion*

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