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Flash Photolysis Studies of Ruthenium(II)–Ammine Complexes. 1. Transient Intermediates in the Photolysis of Ru(NH₃)₅py-X²⁺ and Their Relationship to Photosubstitution Pathways

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Conventional flash photolysis of the ruthenium(II) complexes Ru(NH₃)₅py-X²⁺ (where py-X is a substituted pyridine or related aromatic heterocycle) in aqueous solution leads to the formation of relatively long-lived transients for those species also showing net photoaquation of py-X. Since only those species which undergo significant photoaquation ($\phi_L > 0.01$ mol/einstein) display measurable transient formation and since these complexes are those previously concluded to have a ligand field (LF) state as the lowest energy excited state, it is concluded that this LF state is the immediate precursor of this transient. In this context, it is proposed that the transient is an intermediate (not an excited state) with the pyridine ring π bonded to the Ru(II) species Ru(NH₃)₅²⁺ in a manner making the nitrogen lone pair free to be reversibly protonated. Rates of relaxation of the intermediate to starting material and to products are markedly pH dependent, indicating that the protonated intermediate is particularly long-lived but decays largely to form aquation products. A reaction scheme for formation and decay of these transients is proposed, and comparisons are made with relaxation rates and with quantum yields for net photoaquation.

Introduction

The quantitative photochemistry of ruthenium(II)–amine complexes in aqueous solution is a continuing research interest of these laboratories.[2-13] Although the majority of these studies have involved continuous photolysis techniques, preliminary flash photolysis studies have indicated[8,9,14] a rich chemistry of species produced transiently in these systems. In general, the phenomena resulting from flash photolysis can be separated into two categories. The first involves intermediates apparently related to the photosubstitution reactions of the hexacoordinate complexes, while the second involves intermediates derived from photoredox reactions in the presence of oxidants added to the reaction solutions. The latter reaction types have received considerable attention with regard to the excited-state chemistry of tris(bipyridyl)ruthenium(II) and analogues,[15] encouraged in part by the proposition that such species are possible mediators in the conversion of solar energy to chemical potential energy.[16] Clearly, these excited-state reaction types are interrelated, at least in the context that deactivation by substitution decreases the role of redox pathways and leads to decomposition. For example, even the relatively stable Ru(bpy)₃²⁺ ion displays some photolability[17] which may diminish its usefulness in photocatalytic applications where long-term stability is desired.

This paper is concerned with the kinetic behavior of intermediates generated "unimolecularly" in the flash photolysis of the Ru(II) complexes Ru(NH₃)₅py-X²⁺ in aqueous solution (where py-X is a substituted pyridine or a related aromatic nitrogen heterocycle). These species display intense metal-to-ligand charge-transfer (MLCT) absorption bands in their visible spectra, but the only reaction resulting from visible photolysis is ligand photoaquation. Understanding the be-

havior of the transient intermediates seen under flash irradiation is essential to the explanations of two features of the photoreaction behavior: first, the marked pH dependence on the pyridine aquation quantum yields for certain complexes in acidic solution,[4] and second, the discovery that the photoreactivities can be "tuned" by the choice of the substituent X.[10] The kinetic behavior of intermediates generated by flash photolysis of Ru(NH₃)₅py-X²⁺ in the presence of added oxidants will be described separately.[11]

Experimental Section

Materials. The recrystallized [Ru(NH₃)₅py-X](BF₄) salts were prepared from [Ru(NH₃)₅Cl]Cl₂ according to published procedures.[10,18] Aqueous solutions for photolysis were prepared from redistilled water with reagent sodium chloride used to maintain ionic strength. Solutions were deaerated with argon which had been passed through a chromous bubbler. Reinecke's salt used in actinometry was purchased from Eastman as (NH₄)[Cr(NH₃)₂(SCN)₄] and converted to the potassium salt by recrystallizing from KNO₃ solution.
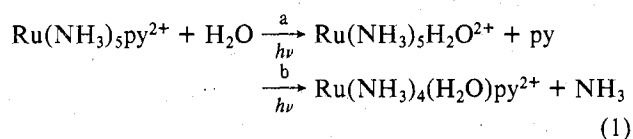
Flash Photolysis Procedures. Flash photolyses were carried out on a kinetic flash photolysis apparatus based on a Xenon Corp. Model A micropulser and a Model C trigger system. Filtered flash pulses of various energies (100–500 J) were used. Absorbance vs. time data were obtained using a high-stability analyzing light beam (from a 75-W Xenon Corp. source powered by a PEK Model 401 power supply) passed through appropriate light baffles, filters, and monochromators. The data were collected with an EMI 6256B photomultiplier tube and recorded with either a Tektronix Model 564 storage oscilloscope or a Biomation 805 transient waveform recorder coupled with a Hewlett-Packard 7035B XY recorder. Instrumental dead time was approximately 35 μs under typical conditions. Sample cells were concentric jacketed quartz cells 1 cm in diameter and either 12 or 20 cm in length. Cutoff filter solutions were placed in an outer jacket for wavelength selection of flash irradiation. All ruthenium(II) substrate solutions (10⁻⁵ M in substrate, 0.2 M NaCl/HCl) were

rigorously deoxygenated in the dark prior to photolysis. The flash apparatus and procedures are reported in greater detail elsewhere.[1a]

The transient absorbance changes subsequent to flash irradiation generally were simple first-order processes giving linear plots of $-\ln (A_\infty - A_t)$ vs. time t (where A_∞ is the long-term absorbance after the flash and A_t is the absorbance at time t). However, several runs appear to have involved a minor additional pathway which was much slower and much less sensitive to pH. Since most runs did not show this behavior, the "slow" process is likely due to an impurity in solution. In these cases plots of $-\ln (A_\infty - A_t)$ vs. t for the decay of the "fast" portion of the trace are curved when the "final" A_∞ is used but are linear for at least 3 half-lives when an "apparent" A_∞ calculated by the Kezdy–Swinebourne method (similar to Guggenheim method) is used.

Results

A. Flash Photolysis of $Ru(NH_3)_5py^{2+}$. Flash irradiation into the visible region MLCT band of $Ru(NH_3)_5py^{2+}$ in fluid aqueous solution results in efficient "instantaneous" (i.e., less than 35 μs, the instrument dead time) bleaching of the CT absorption followed by partial regeneration of the original band. Net bleaching is observed, consistent with the continuous photolysis observations made on this compound,[4,7,10] and this can be attributed largely to the photoaquation of pyridine (eq 1a). In the visible region, both the transitory

$$Ru(NH_3)_5py^{2+} + H_2O \xrightarrow[h\nu]{a} Ru(NH_3)_5H_2O^{2+} + py$$

$$\xrightarrow[h\nu]{b} Ru(NH_3)_4(H_2O)py^{2+} + NH_3$$

$$(1)$$

and net spectral changes parallel the substrate spectrum, and maximum bleaching is observed at the MLCT maximum at 407 nm. In several experiments the flash intensity was sufficient to cause ~90% temporary bleaching of the MLCT absorbance. Thus, the transient has little visible-range absorbance, and its extinction coefficient can be estimated to be ≤ 700 M^{-1} cm^{-1} at 407 nm (vide infra) and even smaller at longer wavelengths. However, UV monitoring shows a transient *increase* over the substrate's absorbance. The UV absorption begins at 350 nm and increases to a maximum at about 280 nm where it has an apparent extinction coefficient of approximately 600 M^{-1} cm^{-1}. Spectral changes observed are independent of whether the reaction medium is aqueous $HClO_4/LiClO_4$ solution or aqueous $HCl/NaCl$ solution. For the dynamic processes observed subsequent to the flash radiation, the rate of the transient disappearance monitored at 300 nm is identical with that of substrate regeneration monitored at 407 nm under identical conditions.

The partial regeneration of the aqueous $Ru(NH_3)_5py^{2+}$ MLCT absorption occurs in a period of milliseconds after flash irradiation at $\lambda_{irr} > 405$ nm. Plots of $-\ln (A_\infty - A_t)$ vs. t are linear, indicating a first-order process. Calculated first-order rate constants k_{obsd} are listed in Table I for various acid concentrations, and log k_{obsd} is plotted vs. pH in Figure 1. These rate constants are independent of the initial $Ru(NH_3)_5py^{2+}$ concentration but are markedly affected by the solution pH, increasing by more than 2 orders of magnitude as the pH is raised from 0.71 to above 3.0. The variation of k_{obsd} with temperature was also investigated briefly in 0.2 M HCl and values of 14.6 and 1.39 × 10^3 s^{-1} were measured at 15 and 45 °C, respectively, giving the apparent activation parameters $\Delta H^{\ddagger} = 27 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = 40 \pm 6$ eu at 25 °C.

The quantum yields ϕ_0 for the instantaneous bleaching were obtained by extrapolating the linear kinetics plots to time zero to give the intercept A_0. The ratio of the instantaneous absorbance change, $A_i - A_0$ (A_i is the solution absorbance before the flash), to the net change, $A_i - A_\infty$, is equal to the ratio $\phi_0/\phi_L(\text{spec})$, where $\phi_L(\text{spec})$ is the spectroscopic quantum yield for photoaquation of the ligand L determined by continuous

Table I. Quantum Yields for Transient Bleaching and Rate Constants for Substrate Regeneration in the Flash Photolysis of $Ru(NH_3)_5L^{2+}$ ^{a}

pH	L = py		L = py-3-Cl	
	ϕ_0 ^{b}	$10^{-2}k_{obsd}$ ^{c}	ϕ_0 ^{b}	$10^{-2}k_{obsd}$ ^{c}
0.0				0.63
0.45				1.0
0.71	0.15	0.57		
0.78			0.13	3.6
1.00		0.96	0.11	9.4
1.16	0.14	1.16		
1.53		1.59	0.12	29
1.99		3.3	0.14	91
2.16	0.16	5.6		
2.56		13.0		
3.01	0.17	41.5		150
3.50		100.0		
4.0		~190.0		
7.6		≥250.0		

^{a} Observations in deaerated aqueous solution: $\mu = 0.20$ M NaCl/HCl, $\lambda_{irr} > 405$ nm, $\lambda_{max} = 407$ nm, $T = 21.6$ °C, $[Ru(II)]_i = 1.3 \times 10^{-5}$ M; solutions were discarded after a single flash. A Biomation 805 transient recorder and an XY plotter were used to obtain output transmittance vs. time curve rates. Rate constants were measured 2–4 times in each case with a reproducibility of better than ±10%. ^{b} Quantum yield for the instantaneous flash-induced bleaching. ^{c} In s^{-1}.
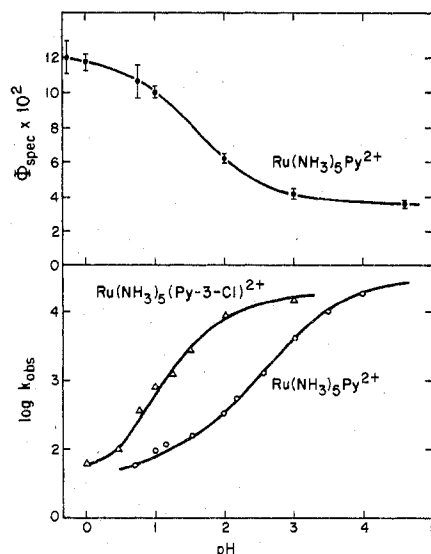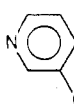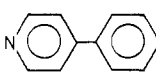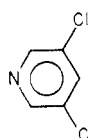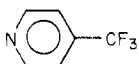

Figure 1. Upper: plot of $\phi_L(\text{spec})$ vs. pH for the photoaquation of py from $Ru(NH_3)_5py^{2+}$ in 25 °C aqueous solution (405-nm irradiation). The data are from ref 4. Lower: plots of log k_{obsd} vs. pH for the relaxation rates of the transients produced in the flash photolyses of $Ru(NH_3)_5py^{2+}$ and $Ru(NH_3)_5py$-3-Cl^{2+} in aqueous solution.

photolysis studies.[10] From these data ϕ_0 can be calculated as having the value 0.16 ± 0.02 mol/einstein for $Ru(NH_3)_5py^{2+}$ independent of the solution pH over the range 0.71–3.01.

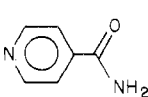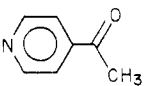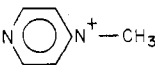**B. Flash Photolysis of $Ru(NH_3)_5py$-X^{2+}.** Table II summarizes the qualitative but reproducible observations made when the pentaammineruthenium(II) complexes of various substituted-pyridine and related pyrazine complexes were flash photolyzed in aqueous solution. The pattern parallels closely the observations made by Malouf[10] in continuous photolysis experiments under comparable solution conditions. Systems displaying $\phi_L(\text{spec})$ values greater than 0.01 mol/einstein undergo flash-induced net bleaching of the reaction solution MLCT absorbance. In each of these cases, flash photolysis at low pH also leads to transient bleaching greater than the net bleaching followed by partial regeneration of the MLCT absorbance. *In no case did $Ru(NH_3)_5py$-X^{2+} complexes shown*

Table II. Summary of Qualitative Spectroscopic Observations[a] for the Flash Photolysis of Selected Ru(NH₃)₅L²⁺ Complexes

L	λ_{max} (MLCT),[b] nm	ϕ_L(spec)[c]	pH	λ_{irr},[d] nm	λ_{mon},[e] nm	transient[f] absorbance change	net absorbance[g] change
(pyridine)	407	0.045	0.7–7.4	>405	407 280	TB[h] TA	NB
(3-chloropyridine)	426	0.048	0.0–3.5	>405	426	TB[h]	NB
(4-phenylpyridine)	446	0.033	0.28 1.28 2.02 3.04 4.0	>405	446	TB (87) TB (430) TB (1.6 × 10³) TB (1.2 × 10⁴) TB (~1.3 × 10⁴)	NB NB NB NB NB
(3,5-dichloropyridine)	447	0.042	0.00 0.28 3.00	>405	447	TB (650) TB (~1.4 × 10³) none	NB NB NB
(4-CF₃-pyridine)	454	0.022	0.05	>405	454	TB (~10³)	NB
(pyrazine)	472	1 × 10⁻³	5.7	>405	472 510 330	none none none	none none none
(isonicotinamide)	479	1 × 10⁻³	0.05	>405	479 425	none none	very small NB
(4-acetylpyridine)	523	3 × 10⁻⁴	1–3.4	≥405	240–523	none	none
(pyrazinium)	508	1 × 10⁻⁴	0–1.5	>405	290–600	none	none
(N-methylpyrazinium)	540	4 × 10⁻⁵	1–2	≥439 ≥320	240–572 240–572	none none	none none

a In deaerated aqueous solution; $T = 23 \pm 2$ °C. Results described for several flash experiments in each case where solutions were discarded after the first flash if a net reaction was observed. *b* λ_{max} of the MLCT absorption band. *c* Spectroscopic quantum yield measured at pH 3 and 25 °C for aqueous solution, except L = pyrazine (pH 7) and L = pzH⁺ (pH 1); $\lambda_{irr} = \lambda_{max}$(MLCT).[10] *d* Wavelength range of flash irradiation. *e* Monitoring wavelength. *f* Time-dependent absorbance changes observed for k_{obsd} (s⁻¹): 40 μs; TB, transient bleaching; TA, transient absorption increase. Rate constants for first-order transient decay are given in parentheses. *g* Nature of overall absorbance change $(A_i - A_\infty)$ for a single flash: NB, net bleaching; none, no change. *h* See Table I.

to have smaller ϕ_L(spec) values display measurable net bleaching or transient bleaching as the result of a single flash. (The failure to see any net bleaching for those systems where ϕ_L(spec) values are very small reflects the sensitivity limitations of the kinetic flash photolysis spectrometer; i.e., absorbance changes of less than 0.5% were lost in the noise.)

Some kinetics studies were carried out to determine the rates of substrate regeneration for those complexes which display bleached transients. In each case the transient decay process is markedly pH dependent (Tables I and II). However, the quantum yield for transient bleaching ϕ_0 was shown to be pH independent (0.12 ± 0.02 mol/einstein); this was also true for the 3-chloropyridine complex (Table I).

Discussion

The qualitative flash photolysis observations in Table II show a definite parallel with the continuous photolysis studies of aqueous Ru(NH₃)₅py-X²⁺. Transient bleaching (TB) of the Ru^II py-X MLCT absorption band is seen only for those complexes also showing detectable net reaction when flash photolyzed, i.e., only for those "reactive" complexes displaying relatively large (>0.01 mol/einstein) quantum yields of photoaquation.[10] The lifetimes of these transient phenomena are markedly pH dependent and, in some cases, TB was not detected within the limitations of the flash apparatus for several reactive complexes at high pH. However, TB is seen under conditions of low pH for each "reactive" complex studied but not for any "unreactive" complex at analogously low pH's. Notably, the pH effects on TB lifetimes fall in approximately the same pH range that the similar effects on ϕ_L(spec) have also been noted for Ru(NH₃)₅py²⁺ and other "reactive" complexes[3,4] (Figure 1). Thus, for the various substituted-pyridine complexes, those factors determining whether a long-lived bleached transient will be formed are closely interrelated to the factors determining the relative photolability of the complexes.

Under continuous photolysis, it was shown that the Ru(NH₃)₅py-X²⁺ complexes having MLCT band maxima longer than 460 nm in aqueous solution are relatively photoinert toward ligand substitution while those with shorter λ_{max} generally are much more active. These observations led Malouf[5,10] to propose that the "reactive" complexes were those

with their lowest energy excited state having ligand field (LF) character while, in contrast, the lowest energy excited state of the "unreactive" complexes is a MLCT state. Since the energies of the MLCT absorption band and presumably of the thermally relaxed MLCT states are quite sensitive to X, judicious choice of pyridine substituent can be used to "tune" the photochemistry of these systems.[10] Similar models have also been used to interpret the photosubstitution behavior of various py-X complexes of pentacarbonyltungsten(0), W-(CO)$_5$py-X,[19] and of pentacyanoferrate(II),[20] Fe(CN)$_5$py-X^{3-}. In a similar vein, the fact that TB is seen in the flash photolysis only of complexes having λ_{max}(MLCT) $\lesssim$460 nm indicates that *a MLCT state is unlikely to be the immediate precursor to whatever intermediate responsible for this behavior.* This conclusion directly contradicts the proposal that the transient species is a pyridine radical anion coordinated to Ru(III) and is produced by a distortion of the MLCT excited state.[21] Thus the strong parallels between the continuous and flash photolysis results strongly support the argument that the immediate precursor of the TB and photosubstitution is a common lowest energy state, LF in character.
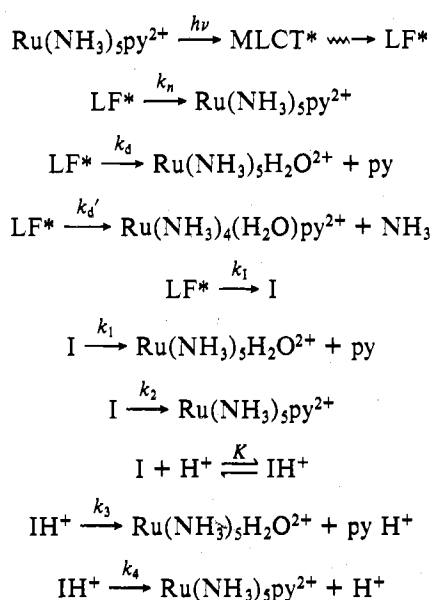
Scheme I is a modification of the sequence originally proposed[4] to explain the pH effects noted for the continuous photolysis quantum yields. In this scheme, MLCT* is the electronic state formed in the initial charge-transfer excitation, LF* is the lowest LF state populated by efficient internal conversion/intersystem crossing from MLCT*, I is a long-lived intermediate formed from LF* and has very little absorption in the visible, and IH$^+$ is the protonated form of I. Direct aquation of py from LF* and formation of I would have the respective quantum yields

$$\phi_d = k_d/(k_n + k_d + k_d' + k_I)$$

$$\phi_I = k_I/(k_n + k_d + k_d' + k_I)$$

Here ϕ_I has been measured as 0.16 ± 0.02 for Ru(NH$_3$)$_5$py^{2+} and 0.12 ± 0.02 for Ru(NH$_3$)$_5$py-3-Cl^{2+}. Unlike pyridine, ammonia is depicted as aquating only from LF* and not from I since ϕ_{NH_3} has been shown to be insensitive to solution pH in contrast to ϕ_{py}.[4]

Scheme I

$$Ru(NH_3)_5py^{2+} \xrightarrow{h\nu} MLCT^* \rightsquigarrow LF^*$$

$$LF^* \xrightarrow{k_n} Ru(NH_3)_5py^{2+}$$

$$LF^* \xrightarrow{k_d} Ru(NH_3)_5H_2O^{2+} + py$$

$$LF^* \xrightarrow{k_d'} Ru(NH_3)_4(H_2O)py^{2+} + NH_3$$

$$LF^* \xrightarrow{k_I} I$$

$$I \xrightarrow{k_1} Ru(NH_3)_5H_2O^{2+} + py$$

$$I \xrightarrow{k_2} Ru(NH_3)_5py^{2+}$$

$$I + H^+ \xrightleftharpoons{K} IH^+$$

$$IH^+ \xrightarrow{k_3} Ru(NH_3)_5H_2O^{2+} + py\ H^+$$

$$IH^+ \xrightarrow{k_4} Ru(NH_3)_5py^{2+} + H^+$$

When the photoreactions are monitored spectroscopically at wavelengths corresponding to λ_{max}(MLCT) of the starting material, NH$_3$ aquation has very little effect on the solution absorbance.[4,10] Thus ϕ_{py}(spec) is indicative of the total pyridine labilization by direct aquation from LF* (ϕ_d) and by indirect

reaction via intermediate formation of I:

$$\phi_{py}(spec) = \phi_{indirect} + \phi_d \qquad (2)$$

$\phi_{indirect}$ has the form

$$\phi_{indirect} = \phi_I \frac{k_1 + k_3K[H^+]}{k_1 + k_2 + (k_3 + k_4)K[H^+]} \qquad (3)$$

These relationships suggest that ϕ_L(spec) should follow a reverse S curve with pH-independent plateaus at low and high pH as was indeed shown by Chaisson et al.[4] (Figure 1). The limiting values should be

$$\lim_{[H^+]\to 0} \phi_{py}(spec) = \phi_I \frac{k_1}{k_1 + k_2} + \phi_d \qquad (4)$$

$$\lim_{[H^+]\to \infty} \phi_{py}(spec) = \phi_I \frac{k_3}{k_3 + k_4} + \phi_d \qquad (5)$$

The ϕ_{py}(spec) data plotted in Figure 1 indicate these limiting values to be ~0.036 and 0.125 mol/einstein, respectively.

The time-dependent absorbance changes followed in the flash experiments correspond to the first-order partial regeneration of starting material. A straightforward derivation shows that the slope (k_{obsd}) of the $-\ln (A_\infty - A_t)$ vs. t plots would, according to Scheme I, be

$$k_{obsd} = \frac{k_1 + k_2 + (k_3 + k_4)K[H^+]}{1 + K[H^+]} \qquad (6)$$

Thus the k_{obsd} should also show limiting values at low and high pH's as suggested by Figure 1:

$$\lim_{[H^+]\to \infty} k_{obsd} = k_3 + k_4 \qquad (7)$$

$$\lim_{[H^+]\to 0} k_{obsd} = k_1 + k_2 \qquad (8)$$

At high pH, k_{obsd} is very large, falling close to the instrumental capabilities, and the limiting rates for Ru(NH$_3$)$_5$py^{2+} and Ru(NH$_3$)$_5$py-3-Cl^{2+} are approximately 2.5 × 10^{-4} and 1.5 × 10^{-4} s^{-1}, respectively.

Equation 6 suggests another manner of data analysis. At acid concentrations where $K[H^+] \gg 1$, k_{obsd} has the form

$$k_{obsd} = (k_3 + k_4) + (k_1 + k_2)K^{-1}[H^+]^{-1} \qquad (9)$$

Thus, at sufficiently low pH, plots of k_{obsd} vs. $[H^+]^{-1}$ should be linear with slopes of $(k_1 + k_2)K^{-1}$ and intercepts of $(k_3 + k_4)$. (This type of analysis would be consistent with the earlier report[14] of k_{obsd} for Ru(NH$_3$)$_5$py^{2+} having the form $a + b$-[H$^+$]$^{-1}$.) For the data in Table I, a plot of k_{obsd} vs. [H$^+$]$^{-1}$ gives a very good line for Ru(NH$_3$)$_5$py^{2+} with a slope of 4.1 ± 0.3 M s^{-1} and intercept of 36 ± 3 s^{-1}.[22] Similar treatment of the Ru(NH$_3$)$_5$py-3-Cl^{2+} data is less satisfactory but gives a slope of 77 ± 15 M s^{-1} with an intercept of about 0. However, the curvature of the log k_{obsd} vs. pH plot for the latter complex at the low pH range indicates that this intercept should be nonzero with a value in the range of 10–50 s^{-1}.

Division of lim$_{[H^+]\to 0}$ k_{obsd} (eq 8) by the slope of the k_{obsd} vs. [H$^+$]$^{-1}$ plots (eq 9) gives the equilibrium constants K equal to ~6.1 × 10^3 and ~2 × 10^2 M^{-1} for Ru(NH$_3$)$_5$py^{2+} and Ru(NH$_3$)$_5$py-3-Cl^{2+}, respectively. Thus, there is a modest substituent effect on the basicity of I, the electron-withdrawing 3-Cl substituent reducing the basicity about 30-fold, as reflected by the shift of the log k_{obsd} vs. pH plots to lower pH's.

Despite the complexity of Scheme I, there is sufficient information available for the Ru(NH$_3$)$_5$py^{2+} system to estimate rate constants for the proposed steps by which I is depleted. A key problem is found in eq 2 since ϕ_{py}(spec) may have contributions both from pathways directly from LF*(ϕ_d) and

indirectly via formation of I and subsequent product formation ($\phi_{indirect}$). In the absence of an independent measurement of ϕ_d, two limiting assumptions can be made: $\phi_d = 0$ and $\phi_d = 0.036$ mol/einstein (the high pH limit of ϕ_{py}).

If $\phi_d = 0$, then eq 4 gives

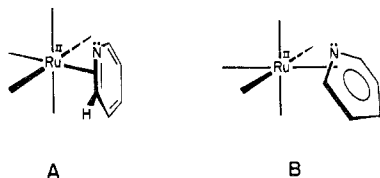$$\phi_1 \frac{k_1}{k_1 + k_2} = \lim_{[H^+] \to 0} \phi_{py}(spec) = 0.036$$

Therefore $k_1/(k_1 + k_2) = 0.036/0.16$, which rearranges to give $k_1 = 0.30 k_2$. Since according to eq 8 $(k_1 + k_2) = \sim 2.5 \times 10^4$ s^{-1}, the values $k_1 = \sim 6 \times 10^3$ s^{-1} and $k_2 = \sim 1.9 \times 10^4$ s^{-1} result. Equation 5 gives

$$\lim_{[H^+] \to \infty} \phi_{py}(spec) = \phi_I \frac{k_3}{k_3 + k_4} = 0.125$$

This can be rearranged to give $k_3 = 3.6 k_4$. From eq 8 we obtain $k_3 + k_4 = 36$ s^{-1}, which gives the values $k_3 = 28$ s^{-1} and $k_4 = 8$ s^{-1}.

If the assumption $\phi_d = 0.036$ mol/einstein is made, a similar treatment gives $k_1 << k_2 = \sim 2.5 \times 10^4$ s^{-1}, $k_3 = 20$ s^{-1}, and $k_4 = 16$ s^{-1}.

We envision the intermediate I as a π-bonded complex between pyridine and the Ru(II) species Ru(NH$_3$)$_5$$^{2+}$. One possibility would be A, in which the pyridine has turned 90°


A   B

from the normal Ru–N bond axis and involves a Dewar–Chatt-type π bond between the Ru(II) and one double bond of a bond-localized cyclic triene. An alternative configuration would be B where the pyridine ring remains aromatic and the plane of this ring is at an oblique angle to the normal Ru–N bond axis. Notably, both species maintain the Ru(II) oxidation state and can be formed by simple rearrangement from the LF* state consistent with the continuous and flash photolysis results discrediting the lowest MLCT configuration as the immediate precursor either to ligand aquation products or to I. Also in both cases, the pyridine nitrogen lone pair is available for protonation. The decreased basicity relative to free ligand (pK_a = 5.3 for py,[23] 3.8 for I) might be expected given the proximity of a cationic charge as would be the effects due to the ring substituents (e.g., pK_a of 3-Cl-py is 2.8;[23] pK_a of the intermediate from Ru(NH$_3$)$_5$py-3-Cl^{2+} is 2.3).

Such π complexes of Ru(NH$_3$)$_5$$^{2+}$ have precedence in the report that Ru(NH$_3$)$_5$H$_2$O^{2+} in acetone reacts with acetylene and olefins to form characterizable complexes.[24] We have also noted that a deaerated aqueous solution of the aromatic cation C$_6$H$_5$CH$_2$N(CH$_3$)$_3$$^+$ plus Ru(NH$_3$)$_5$H$_2$O^{2+} displays a broad absorption band at 329 nm which is not seen in solutions of either Ru(NH$_3$)$_5$H$_2$O^{2+} or C$_6$H$_5$CH$_2$N(CH$_3$)$_3$$^+$ individually. UV absorption increases noted for the flash-induced transient from Ru(NH$_3$)$_5$py^{2+} are consistent with electronic spectra noted for such π complexes.[4] In addition, π complexes are logical candidates for the intermediates observed or inferred in the linkage isomerization[25] of the dinitrogen of Ru(NH$_3$)$_5$^{15}N≡N^{2+} and in the substitution reactions of Ru(NH$_3$)$_5$H$_2$O^{2+} plus pyH$^+$,[26] 2,6-dimethylpyridine,[26] or the N-methylpyrazinium ion.[27] Notably, the flash photolysis of Fe(CO)$_5$ in benzene is also reported to give a long-lived transient which may be a π complex of Fe(CO)$_4$ and benzene.[28]

Formation of I can be reconciled to the one-electron description proposed by Malouf[10] for the lowest energy LF state of Ru(NH$_3$)$_5$py^{2+}. This is the $^3B_1$ configuration $(d_{yz})^2$

$(d_{xy})^2(d_{xz})^1(d_{z^2})^1(d_{x^2-y^2})^0$. Upon relaxation, such a Franck–Condon state is expected to result in distortion along the z axis, which in its limit leads to ligand dissociation. However, the relatively large, pH-independent ϕ_I values argue strongly against a mechanism where the pyridine first passes into the bulk solvent then recombines with Ru(II) to form I. A distortion involving both lengthening of the Ru–N bond and twisting of the pyridine ring upward so that it is no longer coplanar with the Ru(II) center has the attractive feature that this motion is counterparallel to the angular redistribution of electron density on the metal ion suggested by formation of $^3B_1$ excited state from the $^1A_1$ ground state.

Regardless of the specific configuration of I, it is obvious from the observation that the protonated form IH$^+$ is more stable than I toward either dissociation to products (k_3 vs. k_1) or regeneration of Ru(NH$_3$)$_5$py^{2+} (k_4 vs. k_2) that the bonding between the metal and the pyridine rings in these intermediates must involve considerable π back-bonding. Such back-bonding is implicit in the Dewar–Chatt model for a species such as A. For B one can see that the tilted configuration of the pyridine places the unoccupied a_2 orbital in position to act as a π-acceptor from the d_{xz} metal orbital (assuming I to be in a singlet electronic ground state) and perhaps places the unoccupied b_1 ligand orbital in a position appropriate to act as a σ-acceptor from the filled d_{yz} orbital.

b$_1$ a$_2$
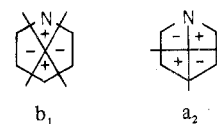
Summary

The studies described here clearly demonstrate a one-to-one correspondence between those Ru(NH$_3$)$_5$py-X^{2+} complexes showing significant quantum yields for photoaquation of py-X and those giving flash-photolysis-induced bleached transients. Since these complexes all have relatively high-energy MLCT absorption bands, we conclude that the lowest energy excited state for the reactive complexes is LF in character and that this state is the precursor of the intermediates formed. Notably, those complexes displaying relatively long-wavelength MLCT absorption maxima do not give bleached transients upon flash photolysis. Since a LF state of Ru(II), not a MLCT state, is apparently the precursor of the bleached transient, it is suggested that this intermediate consists of the Ru(II) moiety Ru(NH$_3$)$_5$$^{2+}$ π bonded to the pyridine ring in a manner freeing the ring-nitrogen lone pair for protonation.

Rates of relaxation of the flash-induced intermediate to products and starting material are markedly pH dependent and are very rapid at high pH's and relatively slow at low pH's. The kinetic pH effect parallels pH effects on photoaquation quantum yields noted previously[4] thus indicating that the pathways for intermediate relaxation are influenced differently by pH. Thus, the protonated intermediate decays largely by aquation but is less labile toward relaxation than its conjugate base.

Registry No. Ru(NH$_3$)$_5$py^{2+}, 21360-09-8; Ru(NH$_3$)$_5$py-3-Cl^{2+}, 19471-60-4; Ru(NH$_3$)$_5$py-4-Ph^{2+}, 52544-48-6; Ru(NH$_3$)$_5$py-3,5-Cl$_2$$^{2+}$, 52544-49-7; Ru(NH$_3$)$_5$py-4-CF$_3$$^{2+}$, 52544-50-0; Ru(NH$_3$)$_5$pz^{2+}, 19471-65-9; Ru(NH$_3$)$_5$py-4-C(O)NH$_2$$^{2+}$, 19471-53-5; Ru(NH$_3$)$_5$py-4-C(O)CH$_3$$^{2+}$, 52544-51-1; Ru(NH$_3$)$_5$pzH^{3+}, 19441-21-5; Ru(NH$_3$)$_5$pzCH$_3$$^{3+}$, 48135-76-8.

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Photoaquation of *trans*-[Cr(en)$_2$NCSF]$^+$

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On photolysis in aqueous solution in the wavelength range 366–578 nm and temperatures of 10 and 20 °C, *trans*-[Cr(en)$_2$NCSF]$^{2+}$ aquates mainly thiocyanate (ϕ = 0.22–0.28) with a small yield of ethylenediamine (ϕ = 0.05–0.11). No observable aquation of fluoride occurs (ϕ < 0.005). The ratio of the two modes of photoreaction varies with wavelength, particularly at 10 °C, at wavelengths longer than 436 nm. These results support reaction via at least two excited states which are not in thermal equilibrium. The various models of chromium(III) photochemistry are considered briefly and the results shown to agree best with a recent semiempirical molecular orbital theory. The wavelength and temperature-dependence data, the theory, and general considerations are suggestive that both ^4E and $^4B_2$ states may be photoreactive in complexes of this type.

Introduction

In the last decade a number of models, empirical and theoretical, for chromium(III) photochemistry have appeared,[1-7] the most recent being a semiempirical molecular orbital approach.[8,9] This study of *trans*-[Cr(en)$_2$NCSF]$^+$ was undertaken to compare its behavior with the reported photochemistry of *trans*-[Cr(en)$_2$F$_2$]$^{+2}$ and *trans*-[Cr(en)$_2$(NCS)$_2$]$^{+10}$ and to provide a further test of the models then existing. In particular we anticipated from the σ-donor model[2] that the ratio of ethylenediamine to thiocyanate or fluoride aquation should be intermediate to the values of >5 for [Cr(en)$_2$F$_2$]$^+$ and ~0.5 for [Cr(en)$_2$(NCS)$_2$]$^+$.

The molecule was also of interest as it emits phosphorescence at 719 nm from room-temperature aqueous solution and can be quenched by [Cr(ox)$_3$]$^{3-}$ and [Cr(CN)$_6$]$^{3-}$. It therefore represented an opportunity to study both the quenching of emission and multiple reaction modes under identical conditions. The investigation of this aspect of the photochemistry has been rendered difficult by analytical problems and by the high absorbance of the available quenchers and is therefore not reported here.

Experimental Section

trans-[Cr(en)$_2$NCSF]ClO$_4$ was prepared as previously described.[11] The purity of the compound was confirmed by analysis[11] and by ion-exchange chromatography[12] and was at least 99% pure with respect to elutable complexes including *cis*-[Cr(en)$_2$NCSF]$^+$.

The UV/visible spectrum of the compound is shown in Figure 1.

Photolysis was carried out in the apparatus previously described.[12] Proton uptake measurements[13] were used to determine amounts of

Table I. Apparent Quantum Yield for *trans*-[Cr(NH$_3$)$_2$(NCS)$_4$]$^-$ at Various Wavelengths and Temperatures

wavelength, nm	temp, °C					
	30	23	15	10	5	1
578		0.269	0.244	0.220	0.205	0.195
546	0.311	0.281	0.256	0.228	0.219	
436		0.310	0.276		0.239	

ethylenediamine released. These measurements were performed at pH 3 so that about 50% of any released fluoride would also have been included in the measurement. Fluoride was not measured directly; instead ion-exchange chromatography to detect *cis*-[Cr(en)$_2$H$_2$ONCS]$^{2+}$ was used to determine the extent of fluoride loss. Thiocyanate was measured by the method of Wegner and Adamson.[14]

Ion-exchange chromatography was carried out on a 20 cm long, 8 mm diameter column of either Baker Analyzed CGC 241 or Hamilton HC8X cation-exchange resin, eluted with gradients (0.2–1.0 M) of ammonium sulfate solution. A modified Technicon AutoAnalyser was used to react the eluted complexes with 1 M sodium hydroxide and 0.5% (w/v) hydrogen peroxide. By monitoring the chromate absorbance at 370 nm a complete chromatogram[12] could be recorded.

Depending on the wavelength of interest, both ferrioxalate[15] and reineckate[14] actinometry were employed for measurement of the incident light flux. The latter actinometer exhibited temperature dependence of its photolysis yield. Consequently calibration was required. For this purpose the light flux was monitored continuously by a Phillips 150 CV phototube observing 8% of the incident beam and the relative yield of thiocyanate measured for various temperatures and wavelengths. The temperature dependence of photolysis yield observed could be due partly to a change in solution absorbance with