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Photochemical and spectral properties of the sulfito rhodium(III) complexes *trans*-$Rh(NH_3)_4(SO_3)CN$ and Na(*trans*-$Rh(NH_3)_4(SO_3)_2$)

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Abstract

The aqueous solution UV spectra of the aqueous Rh(III) sulfito complexes *trans*-$Rh(NH_3)_4(SO_3)(X)^{n-}$ ($X=CN^-$ (I) or SO_3^{2-} (II) are dominated by intense ($\epsilon_{max} \sim 10^4$ M^{-1} s^{-1}) absorption bands at λ_{max} 226 (I) and 266 (II) nm attributed to ligand to metal charge transfer (LMCT) transitions. Both compounds are photoactive. Photolysis of **II** at 313 nm leads to $Rh(NH_3)_4(SO_3)(H_2O)^+$ formation with a quantum yield (0.16±0.01) independent of light intensity (I_a) and of air, behavior consistent with excitation to a substitution labile ligand field excited state. More complicated behavior was observed with 254 nm photolysis of both **I** and **II** which indicates the possible contributions of photoredox pathways originating in the LMCT state(s). The luminescence spectra and lifetimes at 77 K of **I** and **II** and of the two cyano complexes $[Rh(NH_3)_5CN]Cl_2$ and [*trans*-$RhNH_3)_4CNCl]Cl$ are also reported. Each of these compounds displays broad bands attributed to emission from ligand field triplet states. Also described is the equilibrium constant for reaction of *trans*-$Rh(NH_3)_4(SO_3)(H_2O)^+$ with Cl^- in aqueous solution ($K=0.053\pm0.007$ M).

Introduction

The photochemical and photophysical properties of d^6 metal complexes have received considerable attention over the past several decades [1, 2]. One goal has been to examine systematically complexes of different metal/ligand combinations to establish both the generalities and discontinuities in the excited state behavior of homologous systems. In this context, penta- and tetraammine complexes of rhodium(III), $Rh(NH_3)_5X^{n+}$ and $Rh(NH_3)_4XY^{m+}$ have been extensively studied [3–5]. The large majority of such complexes have been ones where X (and Y) are weaker field ligands than NH_3, although several cyano complexes including $Rh(NH_3)_5CN^{2+}$ have been investigated [5]. The present investigation extends these spectral and photochemical studies to several Rh(III) ammine complexes of the S-bound sulfito [6] ligand, known to be strongly *trans* labilizing in thermal substitution reactions of d^6 complexes [7].

Experimental

Analytical grade chemicals and doubly distilled water were used for all experiments. The sulfito ammine-rhodium(III) complexes used in the photochemical studies *trans*-$Rh(NH_3)_4(SO_3)CN$ (**I**) and Na(*trans*-$Rh(NH_3)_4(SO_3)_2$) (**II**) were synthesized from $(Rh(NH_3)_5(H_2O))(ClO_4)_3$ by the route reported by Baranovskii and Babaeva [8]. Correct elemental analyses confirmed the compound compositions. The cyano complexes $(Rh(NH_3)_5CN)Cl_2$ (**III**) and (*trans*-$Rh(NH_3)_4$-$(CN)Cl)Cl$ (**IV**) were prepared as previously described [5a].

Photolysis experiments were carried out at 25 °C in 1.0 cm pathlength quartz cells capped with a rubber septum for studies under deaerated conditions. The magnetically stirred aqueous solutions (10^{-4} M initial complex concentration) either were air saturated or were deoxygenated by entraining with dinitrogen. Certain experiments were carried out in the presence of ferrous sulfate (1×10^{-4} M) and sodium ethylenediaminetetraacetate (1×10^{-4} M) in a phosphate buffer (pH 6.8).

Irradiation at 313 nm was carried out on an optical train utilizing a PEK 200-W high pressure mercury short arc lamp as a light source, a 313 nm interference filter (Oriel) for wavelength selection with an IR filter (Oriel) and water cell to protect the interference filter

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from excessive IR, and a thermostated cell holder [9]. Irradiation at 254 nm was carried out on an optical train utilizing a low pressure mercury lamp (Oriel) [10]. Irradiation beam intensities were determined by ferrioxalate actinometry. Spectroscopic quantum yields for the disappearance of starting material were obtained by plotting interval quantum yields as a function of percent reaction and extrapolating the roughly linear plot to zero percent reaction [11]. Concurrent dark reactions were carried out to correct for potential thermal reactions.

Electronic absorption spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. Diffuse reflectance (DR) spectra were recorded versus $MgCO_3$ reference on a Cary 14 UV–Vis spectrophotometer equipped with an integrating sphere and an On-Line Instrument Systems (OLIS) computer control system. The *trans*-$Rh(NH_3)_4(SO_3)CN$ sample was a pure solid, but Na[*trans*-$Rh(NH_3)_4(SO_3)_2$] was diluted by 1:20 in $MgCO_3$ to insure better reproducibility of the data. The emission lifetimes and spectra were measured as solids in a KBr pellet or in 4/1 CH_3OH/H_2O glass at 77 K on a Nd/YAG laser system ($\lambda_{\text{excitation}} = 266$ nm) using techniques described previously [3].

Results and discussion

Absorption and reflectance spectra

The aqueous solution absorption spectra of the sulfite complexes I and II and other complexes relevant to this investigation are summarized in Table 1. Notably the spectra of the cyano aquo species [5a] *cis* and *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ (potential photolysis products) both show ligand field bands of the type seen [11] for $Rh(NH_3)_6{}^{3+}$ with typical extinction coefficients $\sim 10^2$ M^{-1} cm^{-1}. In contrast, coordination of $SO_3{}^{2-}$ results in very strong bands ($\epsilon \sim 10^4$ M^{-1} cm^{-1}) (Fig. 1), which must be attributed to charge transfer transitions. The analogous cobalt sulfito complexes $Co(NH_3)_5(SO_3)^+$ and *trans*-$Co(NH_3)_4(SO_3)_2{}^-$ show similarly intense bands at λ_{max} 278 nm ($\epsilon = 1.95 \times 10^4$ M^{-1} cm^{-1}) and 327 nm (3.0×10^4), respectively, in aqueous solution [12] as do the cobalt(III) complexes *trans*-$Co(CN)_4(SO_3)(H_2O)^{3-}$ and *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ at 263 nm (1.03×10^4) and 317 nm (3.2×10^4), respectively [13]. These bands have been assigned as ligand-to-metal charge transfers (LMCT) [13]. The lower energies of the LMCT bands in the Co(III) amine complexes can be rationalized in terms of the relationship proposed by Jørgensen [14] for LMCT energies of an octahedral d^6 complex MX_6 (i.e. $E^{ct} = 30(\chi(X) - \chi(M)) + 10Dq - D$, where $\chi(M)$ and $\chi(X)$ are the optical electronegativities of metal ion M and ligand X, respectively, $10Dq$ the ligand field splitting energy and D the 'spin pairing parameter') [15]. Although proposed for a homoleptic complex, this relationship provides a basis for comparing the spectra of closely analogous complexes. Therefore, since the optical electronegativities of low spin Co(III) and Rh(III) are virtually the same, the larger E^{ct} value for the Rh(III) complexes can be attributed to the $10Dq$ contribution, which should be considerably larger for Rh, and to D, which should be smaller. It is more difficult to rationalize the λ_{max} order of this transition

TABLE 1. Electronic absorption spectra of various Rh(III) amine complexes

Compound	λ_{max} (nm) ($\epsilon_{max}(M^{-1}\ cm^{-1})$)[a]	Reference
$Rh(NH_3)_5(H_2O)^{3+}$	316(106), 266(99)	5
$Rh(NH_3)_5CN^{2+}$	287(146), 246(139)	5
trans-$Rh(NH_3)_4(H_2O)(CN)^{2+}$	296(160), 253(138)	5
cis-$Rh(NH_3)_4(H_2O)(CN)^{2+}$	291(119), 251(133)	5
Na(*trans*-$Rh(NH_3)_4(SO_3)_2$)	264 (1.30×10^4)[b]	this work
trans-$Rh(NH_3)_4(SO_3)CN$	226 (1.81×10^4)	this work
trans-$Rh(NH_3)_4(SO_3)Cl$	232 (1.03×10^4)	this work
trans-$Rh(NH_3)_4(SO_3)(H_2O)^+$	218 (0.73×10^4)	this work

[a] Aqueous solution (pH 3.8 in $HClO_4$) except where noted.
[b] Neutral aqueous solution (pH 6.5).

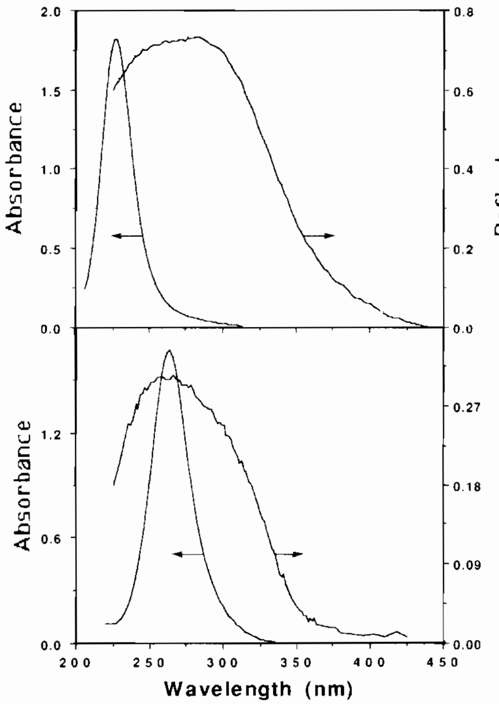

Fig. 1. (top) Absorption spectrum of *trans*-$Rh(NH_3)_4(SO_3)CN$ (I) (1.01×10^{-4} mol l^{-1}) in aqueous solution and reflectance spectrum of solid *trans*-$Rh(NH_3)_4(SO_3)CN$ (referenced to solid $MgCO_3$). (bottom) Absorption spectrum of Na(*trans*-$Rh(NH_3)_4(SO_3)_2$) (II) (1.28×10^{-4} mol l^{-1}) in aqueous solution and reflectance spectrum of solid Na(*trans*-$Rh(NH_3)_4(SO_3)_2$) (referenced to solid $MgCO_3$).

for the various X of *trans*-$Rh(NH_3)_4(SO_3)X$ ($H_2O < CN^- < Cl^- \ll SO_3^{2-}$), although this may be the result of the crossing of states owing to the different effects of the ligand X on orbital energies. For example, given a proposed σ-donor strength for the sulfito ligand comparable to that of NH_3 [14], the lowest unoccupied orbital would be the d_{z^2} in the case of $X = Cl^-$ or H_2O, but the $d_{x^2-y^2}$ for $X = CN^-$.

Diffuse reflectance (DR) spectra of **I** and **II** are also shown in Fig. 1. For solid *trans*-$Rh(NH_3)_4(SO_3)CN$, the reflectance spectrum indicates absorption at a much longer wavelength than the LMCT band. (The DR spectra have been corrected versus a $MgCO_3$ reference, but sensitivity falls off seriously below 250 nm). It is our experience that weak transitions on the long wavelength edge of much stronger transitions are often enhanced in DR spectra relative to the apparent intensities of these bands in solution absorption spectra, while bands with very high extinction coefficients are attenuated. In this context, it is noteworthy that the apparent maximum at ~285 nm in the reflectance spectrum of **I** occurs at the same wavelength as a weak shoulder ($\epsilon \sim 400$ M^{-1} cm^{-1}) in solution. This λ_{max} is comparable to that of the lower energy ligand field band of $Rh(NH_3)_5CN^{2+}$ (Table 1); thus, a similar assignment would be reasonable for this band in **I**. For solid Na(*trans*-$Rh(NH_3)_4(SO_3)_2$), the DR spectrum indicates a broad poorly resolved band at a λ comparable to the intense LMCT band seen in the absorption spectrum although tailing to longer wavelength. This tailing may be an artifact due to the unavoidable attenuation of the LMCT band in the DR mode, but may suggest the presence of a LF band at ~300 nm, as expected for a *trans*-tetraammine rhodium(III) complex with ligands having σ-donor strengths comparable to NH_3.

Emission spectra and lifetimes

The luminescence properties of *trans*-$Rh(NH_3)_4(SO_3)CN$ and Na(*trans*-$Rh(NH_3)_4(SO_3)_2$) in KBr pellets at 77 K were briefly examined as were such properties for $[Rh(NH_3)_5CN]Cl_2$ (Table 2). In each case the emission was a broad unstructured band with the respective ν_{max} (and $\Delta\nu_{1/2}$, defined as full width at half the maximum height) values of 1.67 ± 0.05 (0.41), 1.72 ± 0.05 (0.41) and 1.63 (0.47) μm^{-1}. These data allow estimation of the respective excited state energies, E^{00}, as 2.20 ± 0.15, 2.25 ± 0.15 and 2.25 ± 0.15 μm^{-1}, according to the assumption of Gaussian band shape [11]. Lifetime measurements gave exponential decays with the τ values of 11.5, 20 ± 1 and 21 ± 1 μs, for **I**, **II** and **III**, respectively. Fluid aqueous solutions were not luminescent at 298 K.

The luminescence properties of **I**, **II** and **III** are quite similar to those of the hexaammine complex $(Rh(NH_3)_6)(ClO_4)_3$, which displays a broad unstructured emission band with a calculated E^{00} value 2.20 ± 0.10 μm^{-1} and lifetime 27 ± 1 μs under comparable conditions [11, 16]. The luminescence properties of the latter complexes have been attributed to emission from lowest energy, triplet ligand field (^3LF) excited states; an analogous assignment would be logical for the emitting states of **I**, **II** and **III**. The close similarities in the emission energies of these complexes can be attributed to two features. The apparent ligand field strengths of SO_3^{2-} and NH_3 are reported to be close [14]; therefore, the lowest LF excited states of **II** would be predicted to be similar in energy to that of $Rh(NH_3)_6^{3+}$. Furthermore, the lowest ligand field state for a *trans* tetraammine complex with strong field ligands such as CN^-, or possibly SO_3^{2-}, would be $^3A_2$ with an energy principally determined by the four equatorial ammines.

Equilibrium studies

In an attempt to verify the spectral properties of suspected products of the photoreactions described below, it was discovered that aqueous solutions prepared from *trans*-$Rh(NH_3)_4(SO_3)Cl$ (10^{-4} M, pH 6.8, $\mu = 1.0$ M, $NaClO_4$) displayed spectra which were markedly dependent on the Cl^- concentration. At very low $[Cl^-]$, the aqueous solutions displayed a strong LMCT band at λ_{max} 218 nm which shifted to 232 nm as additional Cl^- (in the form of NaCl) was added. This observation would be consistent with a labile equilibrium, i.e.

$$trans\text{-}Rh(NH_3)_4(SO_3)Cl + H_2O \rightleftharpoons Rh(NH_3)_4(SO_3)(H_2O)^+ + Cl^- \quad (1)$$

TABLE 2. Luminescence data for some tetraamminerhodium(III) complexes at 77 K

Compound[a]	ν_{max}[b]	$\Delta\nu_{1/2}$[b]	E^{00}[b, c]	τ (μs)
$(Rh(NH_3)_5CN)Cl_2$	16.3 ± 0.5	4.7 ± 0.5	22.5 ± 1.5	21 ± 1
(*trans*-$Rh(NH_3)_4CNCl)Cl$	16.0 ± 0.5	4.4 ± 0.5	21.0 ± 1.5	14 ± 1
trans-$Rh(NH_3)_4(SO_3)CN$	16.7 ± 0.5	4.1 ± 0.5	22.0 ± 1.5	11.5 ± 1
Na(*trans*-$Rh(NH_3)_4(SO_3)_2$	17.2 ± 0.5	4.1 ± 0.5	22.5 ± 1.5	20 ± 1

[a] In KBr pellets (1–4% sample/KBr), $\lambda_{excitation} = 266$ nm. [b] In 10^3 cm^{-1}. [c] Excited state energy (0–0 energy) calculated according to the assumption of Gaussian band shape, $E^{00} = \nu_{max} + 1.29\ \Delta\nu_{1/2}$ [15].

In order to determine the equilibrium constant, the optical spectra were recorded for a series of solutions at constant [Rh] but different [Cl^-] (10^{-5} to 1.00 M), and the ratio Abs_{232}/Abs_{218} was plotted versus log [Cl^-]. Reproducible runs gave the K_{eq} value 0.053 ± 0.007 M. The same equilibrium constant was determined in the absence of the $NaClO_4$ added to maintain constant ionic strength. These results indicate that in the 10^{-4} M solutions made up from *trans*-$Rh(NH_3)_4(SO_3)Cl$, dissociation to give $Rh(NH_3)_4(SO_3)(H_2O)^+$ is nearly complete.

Addition of excess Na_2SO_3 to a neutral aqueous solution of *trans*-$Rh(NH_3)_4(SO_3)Cl$ resulted in rapid formation of the *trans*-bis(sulfite) ion **II**, but the equilibrium constant was too large to measure in the manner used for eqn. (1).

Photolysis of trans-$Rh(NH_3)_4(SO_3)_2^-$

Photolysis of aqueous **II** (1×10^{-4} M in neutral solution) with 313 nm light led to depletion of the characteristic absorption band at 266 nm (Fig. 2) and appearance of a new strong band at 218 nm identical to that of *trans*-$Rh(NH_3)_4(SO_3)(H_2O)^+$ (**V**). Formation of **V** was nearly quantitative as determined from relative spectral changes at 218 and 264 nm, and the quantum yield for the disappearance of **II** (Table 3) was the same under N_2 ($\Phi_d = 0.159 \pm 0.014$) as in aerated solution (0.166 ± 0.011) and was independent of added Fe^{3+} and of absorbed light intensity (I_a) (see below). No pH changes were observed during these photolyses, thus NH_3 aquation must be, at most, a minor reaction. Attempts were made to separate the photoproducts by chromatography, but decomposition of sulfite complexes on all ion exchange resins tried invalidated this technique. Addition of excess Na_2SO_3 to exhaustively photolyzed solutions did regenerate the absorption band at 264 nm characteristic of **II**. The extent of regeneration of the *trans* bis(sulfito) complex was >80%; however, this analytical technique may not be fully quantitative*. These experiments support assignment of *trans*-$Rh(NH_3)_4(SO_3)(H_2O)^+$ as the principal photoproduct of 313 nm excitation in neutral aqueous solution, i.e.

$$trans\text{-}Rh(NH_3)_4(SO_3)_2^- + H_2O \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(SO_3)(H_2O)^+ + SO_3^{2-} \quad (2)$$

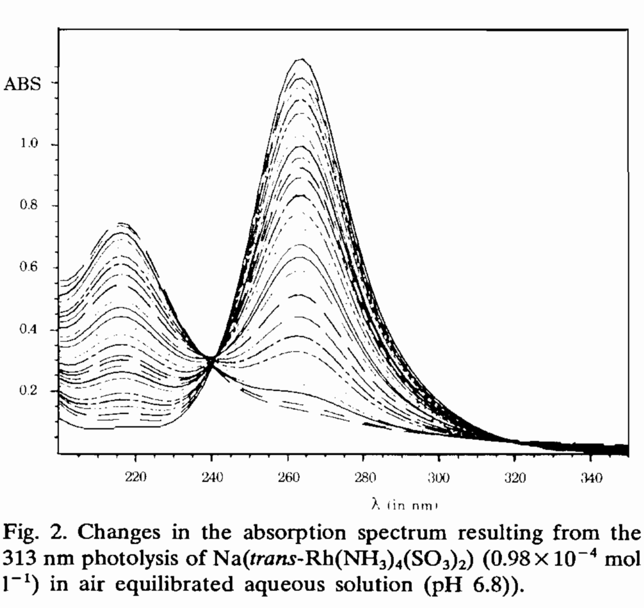

Fig. 2. Changes in the absorption spectrum resulting from the 313 nm photolysis of Na(*trans*-$Rh(NH_3)_4(SO_3)_2$) (0.98×10^{-4} mol l^{-1}) in air equilibrated aqueous solution (pH 6.8)).

Similar spectral changes were noted for the 254 nm photolysis of aqueous **II**; however, the relative yield of **V** estimated spectrally was smaller, 70%, although addition of sodium sulfite to the product solutions generated most of the original *trans*-$Rh(NH_3)_4(SO_3)_2^-$. Furthermore, 254 nm photolysis gave significantly higher Φ_d values in aerated solution (0.28 ± 0.01) than under N_2 (0.17 ± 0.01) (Table 3), an observation which suggests the possible mechanistic role of radical intermediates (see below). In this context, it is notable that higher I_a values led to moderately smaller quantum yields in the presence of O_2 but had no effect in its absence (Table 3) and that when photolysis under O_2 was undertaken with Fe(II) added as a radical scavenger [18], the value of Φ_d dropped to that seen under N_2 (Table 3).

These photoreactions would appear to be best explained in terms of a scheme such as Fig. 3. The 313 nm photolysis corresponds to excitation at the long wavelength edge of the LMCT band. However, given the apparent similarity of the ligand field strengths of SO_3^{2-} and NH_3, 313 nm is also close to the predicted λ_{max} of the lowest energy spin allowed LF absorption band (for $Rh(NH_3)_6^{3+}$, λ_{max} (LF) = 306 nm) [15]. Thus, 313 nm excitation should lead to population of singlet LF excited states followed by rapid internal conversion/intersystem crossing to the lowest energy triplet ligand field state ($^3LF^*$) in analogy to other Rh(III) ammine complexes [3–5]. It is the $^3LF^*$ state to which the low temperature luminescence has been attributed. Labilization along the axis of the weaker σ-donor ligands would be expected. Thus, the S-bound SO_3^{2-} would appear to be a weaker σ-donor than is NH_3, since eqn. (2) is the only observed photoreaction. Notably, longer

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*As control experiments, both *cis*- and *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ were prepared as described in ref. 17 and excess $Na_2(SO_3)$ was added to the solution. After a few minutes the spectrum of the solution indicated the formation of >80% **II** (but <100%) according to the charge transfer band at 264 nm. Thus, this technique proved to be less than quantitative and also appeared not to differentiate between *cis* and *trans* photoproducts since the reaction with SO_3^{2-} appeared to force the complexes into the *trans* configuration.

TABLE 3. Disappearance quantum yields for the photolysis of *trans*-$Rh(NH_3)_4XY^{n+}$

Complex	λ_{irr} (nm)	$I_a \times 10^{10}$ [a] (einstein/(L·s))	Φ_d (mol/einstein)[b]	
			in air	under N_2
trans-$Rh(NH_3)_4(SO_3)CN$[c]	254	4.6	0.104±0.013	0.102±0.011
	313	4.3	0.166±0.006	0.159±0.005
		2.0	0.155±0.001	0.164±0.003
		1.0	0.166±0.003	0.155±0.006
trans-$Rh(NH_3)_4(SO_3)_2^-$ [d]	254	7.0	0.280±0.010	0.170±0.011
		4.8	0.328±0.004	0.148±0.003
		1.1	0.343±0.020	0.159±0.001

[a] I_a = intensity of light absorbed. [b] The quantum yield values were each the results of at least four independent measurements. [c] $[Rh(III)] = 1.0 \times 10^{-4}$ M, aqueous solution (pH 3.8 in $HClO_4$), $T = 25$ °C. [d] $[Rh(III)] = 1.0 \times 10^{-4}$ M, aqueous solution (pH 6.5), $T = 25$ °C.

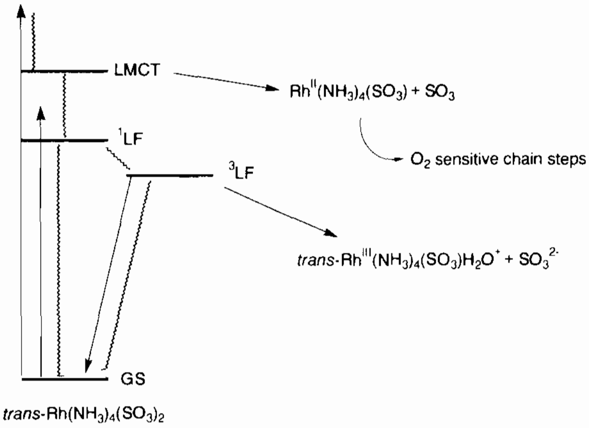

Fig. 3. Proposed excited state reaction scheme for the photolysis of *trans*-$Rh(NH_3)_4(SO_3)_2^-$ in aqueous solution.

wavelength photoexcitation of *trans*-$Co(CN)_4(SO_3)_2^{5-}$ also leads to *z*-axis labilization [9].

With 254 nm excitation, the situation is more complex since Φ_d values were enhanced by the presence of air, under which conditions they were also dependent on the irradiation intensity and were affected by addition of Fe(II). One explanation consistent with these observations is that 254 nm excitation leads to population of a LMCT state, followed by rapid internal conversion to LF states from which labilization of SO_3^{2-} occurs with an efficiency about 16%. However, the LMCT ES may also undergo homolytic fragmentation of the metal–sulfur bond to give a Rh(II) species plus the $\cdot SO_3^-$ radical (eqn. (3)) in analogy to the photoredox processes which have been reported for LMCT excitation of Rh(III) halo-pentaammine complexes [19]. The role of O_2 could be interception of Rh(II) and/or $\cdot SO_3^-$ (both Rh(II) and $\cdot SO_3^-$ are known to react very rapidly with O_2 to form new radicals) [20, 21] thereby preventing a rapid back reaction to give **II** and/or the generation of new species capable of initiating a chain reaction leading to depletion of **II**. Radical recombination as a termination step of a chain reaction would certainly be consistent with the decrease in Φ_d on increasing I_a (Table 3) and the role of Fe(II) in sharply reducing Φ_d for the photolyses carried out in aerated solution. The fact that Φ_d values observed under dinitrogen and in air with the Fe(II) radical trap added are about equal to those measured for 313 nm photolysis suggests that radical formation is a very minor primary photoreaction even for $\lambda_{irr} = 254$ nm and that the principal deactivation pathway of the initial LMCT state is internal conversion to a common reactive state, presumably the $^3LF^*$ ES to which ligand photolabilization was attributed. A competing, but minor, deactivation pathway leading to the formation of some radicals which, in the presence of O_2, can initiate a chain reaction with numerous turnovers but bimolecular chain terminating steps could account for the effect of O_2 on Φ_d seen for 254 nm excitation.

$$II^* \longrightarrow Rh^{II}(NH_3)_4(SO_3) + \cdot SO_3^- \qquad (3)$$

Photolysis of trans-Rh(NH$_3$)$_4$(SO$_3$)CN

The 254 nm photolysis of **I** in aqueous solution ($[Rh] = 1.0 \times 10^{-4}$ M), pH 3.8 in $HClO_4$, 25 °C) led to depletion of the strong LMCT band at 226 nm (Fig. 4). The measured Φ_d was 0.104±0.013 mol einstein^{-1} in aerated solution and the same spectral changes and Φ_d (0.102±0.011) were observed under N_2 (Table 3). Since the absorption bands of the aquo cyano complexes are several orders of magnitude less intense than the LMCT band of **I** (Table 1), one possible explanation of the spectral changes would be simple SO_3^{2-} photoaquation to give $Rh(NH_3)_4(H_2O)CN^{2+}$. In order to test this hypothesis, the photolysis was carried out at higher [*trans*-$Rh(NH_3)_4(SO_3)CN$] (1.0×10^{-3} M, pH 3.8 in $HClO_4$, 25 °C). Excess Na_2SO_3 was added to the exhaustively photolyzed solution. After a few minutes, the resulting spectrum displayed a strong band at 228

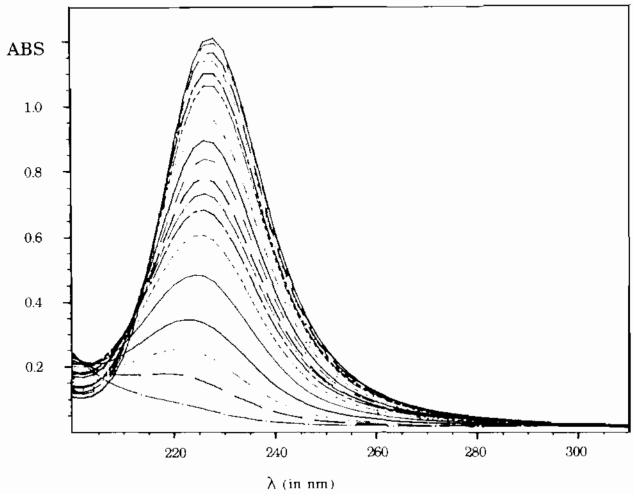

Fig. 4. Changes in the absorption spectrum resulting from the 254 nm photolysis of *trans*-$Rh(NH_3)_4(SO_3)CN$ (0.67×10^{-4} mol l^{-1}) in air equilibrated aqueous solution (pH 3.8, $HClO_4$).

nm characteristic of **I** but corresponding to only ~20% regeneration. A second stronger band at 264 nm indicated the presence of **II** corresponding to about 78% of the rhodium in solution. Since the addition of excess Na_2SO_3 to aqueous *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$ prepared thermally led to nearly quantitative formation of **I**, one must conclude that no more than ~20% of the Rh(III) product formed by the photolysis of **I** is *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$. The remainder is apparently the diaquo tetraammine $Rh(NH_3)_4(H_2O)_2{}^{3+}$ ion, and the most likely source of this product is a photoredox process*, since neither *cis*- nor *trans*-$Rh(NH_3)_4$-$(H_2O)CN^{2+}$ is labile toward CN^- photoaquation [5].

Conclusions

The absorption spectra of the rhodium(III) sulfito complexes *trans*-$Rh(NH_3)_4(SO_3)X$ ($X = SO^{2-}$, CN^-, H_2O, or Cl^-) are dominated by intense absorption bands ($\epsilon \sim 10^4$ M^{-1} cm^{-1}) which are attributed to ligand-to-metal charge transfer transitions. In contrast, the 77 K luminescence spectra are quite similar to those of analogs such as $Rh(NH_3)_6{}^{3+}$ and $Rh(NH_3)_5CN^{2+}$ and are assigned to emission from the lowest energy ligand field excited states. Corresponding LF bands were not observable in the solution phase absorption spectra given the dominance of the LMCT bands; however, the diffuse reflectance spectra of the solids suggest LF transitions on the low energy shoulders of the charge transfer bands. Photolysis of the bis(sulfito) complex **II** on the low energy edge of the LMCT band (313 nm) led exclusively to sulfite photoaquation, and this pathway is attributed largely to the population of a substitution-labile, lowest energy ligand field excited state. Ligand photoaquation remains the principal overall result of higher energy LMCT photolysis (254 nm) of **I** and **II**, however, for both complexes, redox pathways appear to play significant roles in this case.

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*While CN^- labilization is an unlikely pathway for ligand field irradiation of *cis*- or *trans*-$Rh(NH_3)_4(H_2O)CN^{2+}$, this process may result from a photoredox decomposition of the LMCT excited state to give a Rh(II) species, i.e. $I^* \rightarrow Rh^{II}(NH_3)_4CN^+ + SO_3{}^-$. Pentacoordinate Rh(II) tetraammines complexes such as $Rh^{II}(NH_3)_4CN^+$ been shown to undergo rapid axial ligand labilization [20]; hence such an intermediate may be responsible for the eventual formation of diaquo species as one result of 254 nm irradiation of **I**.

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