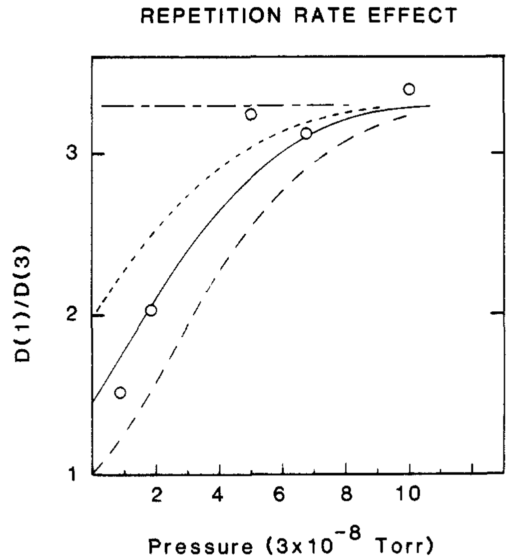

Figure 4. Ratio of dissociation at pulse rates of 3 and 1 s^{-1}. Calculated curves are shown for assumed radiative rates of 0 (– –), 1.5 (—), and 3 (–––) s^{-1}, as well as the cascade-model prediction (– — –) for radiative rates faster than 3 s^{-1}.

sorption measurements[11] (5 s^{-1}) but this is not unexpected, since the IR-excited ions probably have on the average much less than 2.5 eV of internal energy to start with. It is not seriously different from the rate of approximately 2 s^{-1} calculated for the neutral molecule from IR absorption intensity measurements (as in ref 2). The recent theoretical work of Rosmus and Werner[14] suggests that in diatomic ions radiation is likely to be much faster than in the neutral, but it is not clear whether this expectation will carry over to large, charge-delocalized polyatomic ions like this one.

Determination of this rate in previous photodissociation work with continuous light sources seems to have been unreliable. Some problems are inherent in these kinetic analyses. The analysis is sensitive to deviations from pure two-photon kinetics as described by eq 1, and use of more elaborate kinetics, as in ref 9, carries the danger that the assumed complex mechanism may be incorrect. A similar uncertainty is whether the rate-process picture of relaxation is correct: assuming a different relaxation picture can significantly affect the plots, extrapolations, and fits involved in these analyses. The alternative cascade-model kinetics explored above illustrate, but do not exhaust, these possibilities. Other kinetic complications are easily imagined but not easily modeled: for instance, the Franck–Condon factors and hot-band intensities involved in the σ_2 photon absorption presumably change as the ion relaxes, so that treating the σ_2 process as a rate process may not be accurate; or again, excited electronic states may participate in ways similar to, or more complicated than, van Velzen and van der Hart's mechanism for bromobenzene ion.[9] In general, there are enough possibilities for complications and deviations that such analyses should be somewhat circumspect.

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Photochemistry of $[Co(NH_3)_5Br]^{2+}$: Wavelength, Pressure, and Medium Dependence of Redox and Aquation

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The ratio of redox to aquation of $[Co(NH_3)_5Br]^{2+}$ has been shown to be constant at about 2 for irradiation wavelengths (nm) of 254, 275, 313, and 365, falling close to zero at 514.5. With increasing pressure, quantum yields for redox and aquation decrease, the former somewhat faster, and in a wavelength-dependent fashion, so that the apparent volumes of activation (mL mol^{-1}) for redox and aquation are respectively 6.0 ± 0.6 and –0.4 ± 3.2 at 365 nm and 4.8 ± 0.3 and 2.5 ± 2.7 at 313 nm. At ordinary pressure the redox yield falls 8-fold and the aquation yield increases 50% in 40 wt % glycerol/water. The equations relating volumes of activation for individual reaction steps to the overall apparent volumes of activation for the lifetime and quantum yield are derived. It is shown that all of the above observations are supportive of a mechanism involving generation of a caged radical pair which has no "memory" of the excitation energy of its progenitor.

Introduction

In a recent article on mechanism and high pressure, Swaddle[1] remarked on the "curiously refractory problem" of the assignment of mechanism in the substitution reactions of octahedral transition-metal complexes in solution. Even more refractory has proved to be that of the corresponding photochemical reaction mechanisms, where only rarely has the electronically excited species responsible for reaction been identified.

One useful approach to the assignment of mechanism has been the study of the pressure dependence of the rate

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constant. The interpretation of such effects in photochemistry can be made in terms of an apparent volume of activation for either the quantum yield, Φ, or the reciprocal lifetime, τ^{-1}:

$$\Delta V^\ddagger_{\phi,\mathrm{app}} = -RT\frac{\partial \ln \Phi}{\partial P}\bigg|_T$$
$$\Delta V^\ddagger_{\tau,\mathrm{app}} = -RT\frac{\partial \ln \tau^{-1}}{\partial P}\bigg|_T \tag{1}$$

evaluated at zero pressure if $\Delta V^\ddagger$ is a function of the pressure.

Van Eldik and Kelm[2] have reviewed the mechanistic interpretation of apparent volumes of activation of inorganic reactions, considering particularly the differing role of changes of bond angle and length between reactant and transition state and of effects due to solvation. Further, LeNoble[3] reminds us that the transition state in a reaction is determined by an energy profile maximum, and that the volume of activation is the volume difference between the "energy determined" transition state and the reactants; this, unlike the activation energy, may be either positive or negative. Hence reactions with activation energies similar to their endothermicities will have volumes of activation close to the volume change, ΔV^0, of the reaction, because of the similarity of transition state and the products. Conversely, very fast reactions with necessarily small activation energies can be expected to have volumes of activation that are small compared with ΔV^0. A number of important photochemical reactions will fall in this latter category. This point was illustrated by an earlier study which revealed only small pressure effects on lifetimes and quenching for some inorganic complexes.[4]

The application of high-pressure techniques to inorganic complexes has been illustrated by a series of articles by Angermann et al.[5-7] They found that acidopentamminechromium(III) complexes photoaquate with a negative $\Delta V^\ddagger$, while some ML_6 complexes (M = Co or Cr) photoaquate with a positive $\Delta V^\ddagger$. The interpretation of such findings is made difficult, first because of the uncertainty surrounding the mechanisms of these reactions, and also since the quantum yield for photoaquation represents a composite of several rate constants. For the Cr(III) complexes, Angermann et al.[5,6] assumed reaction via the quartet state, and hence argued that their results supported an associative, I_a, mechanism for the acidopentammines of Cr(III) and dissociative, I_d, mechanism for the ML_6 photoaquations.

For $[Cr(bpy)_3]^{3+}$, where photoaquation in basic medium occurs via the doublet state,[8] a recent study of the pressure dependence[9] similarly implies that the intermediate proposed in this reaction[8] is generated in a dissociative process.

With this background, it was of interest to extend the photochemical pressure dependence studies to a different class of reaction, that of redox photochemistry, and to compare this mode with photoaquation in the sample complex. $[Co(NH_3)_5Br]^{2+}$ has been extensively studied, particularly by Endicott and associates.[10] Photolysis in the intense LMCT bands at about 320 and 250 nm led[10] to formation of Co(II) with a constant quantum yield, 0.30, at wavelengths below about 330 nm. Concomitant photoaquation of Br^- was reported[10] to have a quantum yield maximum of 0.09 at 420 nm, decreasing to near zero at 330 nm and to about 10^{-3} in the ligand field bands. The photoredox quantum yield decreased in viscous solvents.[11] No data concerning the nature or the kinetics of the excited states formed on irradiation have been reported, mainly since no luminescence can be detected.

We report here the results of our studies on the photochemical reactions of $[Co(NH_3)_5Br]^{2+}$ as a function of pressure, and on the ratio of aquation to redox as a function of wavelength in water and in 40 wt % glycerol/water.

Experimental Section

Preparation of Materials. $[Co(NH_3)_5Br]Br_2$ was prepared by a literature method.[12] The UV/visible spectrum was in agreement with published data.[13] The chloride salt was prepared by precipitation from a 40 °C, pH 4 aqueous solution of the bromide by sodium chloride, reprecipitation, and recrystallization from pH 4 water. The UV/visible spectrum for the chloride matched that for the bromide.

Pressure Dependence of Redox Quantum Yield. $[Co(NH_3)_5Br]Cl_2$, at a concentration of about 5×10^{-3} M in a pH 4 acetic acid solution, was photolyzed at 20 °C at an exciting wavelength of 365 nm as a function of applied pressure up to 2.8 kbar, and at 313 nm and pressures of 1 bar and 2.7 kbar. The high-pressure cell previously described was used.[14] Co^{2+} in the reacted solution was measured by the method of Kitson[15] as modified by Caspari et al.[16] Runs at ordinary pressure and at elevated pressures were made under otherwise identical conditions. Light intensities at 313 and 365 nm were measured by ferrioxalate actionometry; the light power was of the order 5×10^{-8} einstein s^{-1}.

Aquation/Redox Ratio. The quantum yield ratio for aquation to redox was measured by combining a direct measurement[15,16] of Co(II) in the reacted solution with a computer fitting of the post-photolysis spectrum to the spectra of Co(II), $[Co(NH_3)_5Br]^{2+}$, and $[Co(NH_3)_5H_2O]^{2+}$ over the spectral range 400–650 nm. In all experiments, the calculated concentrations summed within 10% to the known starting concentration of $[Co(NH_3)_5Br]^{2+}$, providing a material balance confirmation of the computer fit.

Results

Aquation/Redox. In aqueous acidic solution at 1 atm pressure, the ratio of the aquation quantum yield to the redox quantum yield is independent of excitation wavelength for $\lambda \leq 365$ nm. The ratio found, 0.46 ± 0.06, is of the order of that given by Adamson,[15] namely, 1.05 at $340 < \lambda < 400$ nm, but in disagreement with results of Endicott

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et al.,[10] who could find no evidence for the aquation mode for λ ≤ 334 nm.

Some care was taken to confirm this ratio at 365, 313, 275, and 254 nm (see Table I). As only the ratio of aquation to redox was to be determined in this set of experiments, conversions were carried out to extents of 50 to 95%. Although this is normally a photochemical sin, it is appropriate here since the molar absorptivity of $[Co(NH_3)_5Br]^{2+}$ at all of these wavelengths greatly exceeds those of the observable products: $[Co(NH_3)_5H_2O]^{3+}$ and $Co^{2+}(aq)$. Such large conversions permit precise analyses, with material balances better than 10%. It is rather unlikely that the ratio would be influenced by percent conversion and no evidence for this was found (Table I). The spectral changes unambiguously show aquation as a major mode of photolysis at all wavelengths, including ultraviolet.

Pressure Dependence of Redox and Aquation Quantum Yields. The effects of pressure on the quantum yield of redox and on the ratio of aquation to redox were determined in separate experiments because the former requires small, and the latter large, conversions. At 365 nm Φ_{redox} shows a linear decrease of ln Φ with increasing pressure, within experimental error (±15%). The slope corresponds to an apparent volume of activation $\Delta V^{\ddagger}_{app,red,365} = 6.0 \pm 0.6$ mL mol^{-1}; e.g., $\Phi_{redox} = 0.181$ at 1 atm, 0.100 at 2300 atm. At 313 nm Φ_{redox} decreases by a factor of 1.7 at 2700 atm (0.162) relative to its value at 1 atm (0.274). The apparent volume of activation, $\Delta V^{\ddagger}_{app,red,313}$, $= 4.8 \pm 0.3$ mL mol^{-1}. The ratio of aquation to redox is also a function of pressure. The data (Table I) obtained in the high-pressure cell exhibit more scatter than those from conventional cells used at 1 atm. However, there is a definite increase of aquation relative to redox at high pressure. At 365 nm the increase in the ratio at 2850 atm is 2.1 ± 0.6, at 313, it is 1.3 ± 0.4. Thus, $\Delta V^{\ddagger}_{app,aqn} - \Delta V^{\ddagger}_{app,redox} = -6.4 \pm 2.6$ and -2.3 ± 2.4 mL mol^{-1} for these wavelengths, respectively; $\Delta V^{\ddagger}_{app,aqn,365} = -0.4 \pm 3.2$, $\Delta V^{\ddagger}_{app,aqn,313} = 2.5 \pm 2.7$.

Medium Effect on Aquation/Redox. In glycerol/water solution (40 wt % glycerol), although the material balances were poorer (±20%) than in water, the ratio of aquation to redox was found to increase to 6 ± 2 at both 365 and 313 nm. Endicott, Ferraudi, and Barber[10] found that the redox quantum yield is decreased in 50% glycerol/water solution to about 40% of its value in water.

In this work, precise quantum yield determinations were not carried out in glycerol/water, but the data of Table I, together with the irradiation times and other conditions, showed that at 313 and 365 nm the total reaction yield in mixed solvent falls to 65% of that in water. Together with the percentage aquation, this yields for the mixed solvent $\Phi_{red,365,glycerol} = 0.02$, $\Phi_{red,313,glycerol} = 0.04$, $\Phi_{aqn,365,glycerol} = 0.13$, and $\Phi_{aqn,313,glycerol} = 0.22$. For both wavelengths aquation increases 50% and redox decreases 8-fold in the viscous solvent. Thus the decreases in redox found here are twice as large as reported earlier;[10] the increase in aquation found is a new result.

Discussion

Before considering in detail the results of this investigation, it is necessary to discuss the general problem of the pressure dependence of excited-state lifetimes and of photochemical quantum yields.

The lifetime of an excited-state intermediate is the reciprocal of the sum of the rate constants for all processes removing that intermediate from the system:

$$\tau^{-1} = \sum k_i \tag{2}$$

Pressure dependence data will yield an apparent volume of activation via the logarithmic derivative of $1/\tau$ with respect to applied pressure as in eq 1. Hence

$$\Delta V^{\ddagger}{}_{\tau,\mathrm{app}} = -RT\frac{\partial \ln \sum k_i}{\partial P}\bigg|_T = \frac{-RT}{\sum k_i}\frac{\partial \sum K_{\mathrm{i}}}{\partial P}\bigg|_T \tag{3}$$

$$= \frac{-RT}{\sum k_i}\sum \frac{\partial k_{\mathrm{i}}}{\partial P}\bigg|_T = \frac{-RT}{\sum k_i}\sum\left(k_i\frac{\partial \ln k_{\mathrm{i}}}{\partial P}\bigg|_T\right) \tag{4}$$

Introducing the efficiency, η_{i},[18] where

$$\eta_i = k_i\tau \quad \text{and} \quad \Delta V^{\ddagger}{}_i = -RT\frac{\partial \ln k_{\mathrm{i}}}{\partial P}\bigg|_T \tag{5}$$

we arrive at

$$\Delta V^{\ddagger}{}_{\tau,\mathrm{app}} = \sum \eta_i \Delta V_i^{\ddagger} \tag{6}$$

That is, the apparent volume of activation for the decay lifetime of an intermediate is the sum of the individual volumes of activation for the reactions which remove the intermediate from the system, weighted by their efficiencies.

The expression for the quantum yield of a photoproduct X (or an emission quantum yield) may be considerably more complex but is given in the simplest circumstances by the product of efficiences[17-19] of reaction of the n intermediates comprising the reaction path leading to product X:

$$\Phi_X = \prod_n \eta_n \tag{7}$$

Derivation of an activation volume now requires a double summation over the i possible fates of each of the n intermediates comprising the path to product. Thus

$$\Delta V^{\ddagger}{}_{\mathrm{X,app}} = -RT\frac{\partial \ln \Phi_{\mathrm{x}}}{\partial P}\bigg|_T = -RT\sum_n \frac{\partial \ln \eta_{\mathrm{n}}}{\partial P}\bigg|_T \tag{8}$$

For each of the n individual reaction steps the efficiency will be of the form $\eta_n = k_n\tau_n$ where k_n is the rate constant for that reaction and τ_n the lifetime of the intermediate:

$$\Delta V^{\ddagger}{}_{n,\mathrm{app}} = -RT\frac{\partial \ln \eta_n}{\partial P}\bigg|_T = -RT\frac{\partial \ln k_n\tau_n}{\partial P}\bigg|_T \tag{9}$$

$$= -RT\frac{1}{k_{\mathrm{n}}}\frac{\partial k_n}{\partial P}\bigg|_T + \frac{RT}{\sum k_n}\sum\frac{\partial k_{\mathrm{n}}}{\partial P}\bigg|_T$$

$$= \Delta V^{\ddagger}{}_n - \sum_i \eta_i \Delta V^{\ddagger}{}_i \tag{10}$$

where now the summation in eq 10 is the same kind of summation as in eq 6. From eq 8 and 10, the overall apparent activation volume is

$$\Delta V^{\ddagger}{}_{\mathrm{X,app}} = \sum_n \Delta V^{\ddagger}{}_n - \sum_n\sum_i \eta_i \Delta V^{\ddagger}{}_i \tag{11}$$

The double summation in eq 11, taken over all reactions in the system of intermediates involved in production of X, shows that they *all* contribute to the apparent volume of activation associated with photochemical production of X. We emphasize that it is a mistake to arbitrarily leave out contributions from steps subsequent to rate-determining steps.

The formats of eq 6 and 11, applying to the reciprocal lifetime and the quantum yield, respectively, are of general

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TABLE I

$\lambda_{exc}{}^n$, nm	medium^a	press., atm	$[[CoA_5Br]_i{}^{2+}]$, mM	$[[CoA_5Br]_f{}^{2+}]$, mM	$[[CoA_5H_2O]^{3+}]$, mM	$[Co^{2+}]$, mM	% dec^n	% aquation^b	material balance^c
514.5	H_2O	1	8.63	4.93	3.93	1.37×10^{-3}	43	>99	1.03
365	H_2O	1	1.63	0.55	0.39	0.80	66	32.7	1.07
365	H_2O	1	2.42	0.37	0.59	1.34	85	30.6	0.95
365	H_2O	1	2.68	0.74	0.55	1.38	72	28.5	1.00
365	H_2O	1	2.81	0.37	0.77	1.70	87	31.1	1.01
365	H_2O	1	5.84	1.19	1.34	3.19	80	29.8	0.98
365	H_2O	1	6.62	3.22	1.07	2.37	51	31.1	1.01
								30.6 ± 1.41	
365	H_2O	2850	1.94	0.85	0.64	0.67	56	48.9	1.11
365	H_2O	2850	2.45	0.39	0.77	1.06	84	43.1	0.91
365	H_2O	2850		0.63	1.27	1.08	79	54.0	
								48.3 ± 6.0	
313	H_2O	1	1.18	0.30	0.35	0.64	75	35.4	1.09
313	H_2O	1	2.48	0.39	0.64	1.44	84	30.8	1.00
313	H_2O	1	1.93	0.20	0.59	1.18	90	33.3	1.02
313	H_2O	1	5.89	2.78	0.81	2.19	53	27.0	0.98
								31.6 ± 3.6	
313	H_2O	2850		0.09	0.64	1.14	95	36.0	
313	H_2O	2850	2.27	1.01	0.49	0.83	56	37.1	1.03
313	H_2O	2850	2.34	1.09	0.58	1.11	54	34.3	1.19
313	H_2O	2850	2.38	0.77	0.65	0.94	68	40.9	0.99
								37.1 ± 2.8	
275	H_2O	1	2.45	0.99	0.52	1.07	60	32.7	1.05
254	H_2O	1	2.31	1.20	0.45	0.80	48	36.0	1.06
365	40% glycerol/	1		1.58	0.57	0.068	29	89	
	H_2O	1	6.16	4.06	0.85	0.139	34	86	0.82
313	40% glycerol/	1	5.96	3.99	1.01	0.138	33	88	0.86
	H_2O	1		0.53	0.77	0.187	64	80	

[a] All runs were in acetic acid/acetate buffer at pH 4. [b] Calculated as $100[[CoA_5H_2O]^{3+}]/\{[[CoA_5H_2O]^{3+}] + [Co^{2+}]\}$. [c] Calculated as $\{[[CoA_5Br]_f{}^{2+}] + [[CoA_5H_2O]^{3+}] + [Co^{2+}]\}/[[CoA_5Br]_i{}^{2+}]$.

application to other activation parameters, the activation energy being another of particular interest.

Two limiting cases are of special interest with regard to eq 6 and 10, and the latter affects eq 11. Consider, for example, the circumstance that one of the processes involving an intermediate is dominant, i.e., some $\eta_n \rightarrow 1$. From eq 6, it follows that the apparent volume of activation for τ^{-1} is just the true volume of activation for that dominant step, i.e.

$$\Delta V^{\ddagger}_{\tau,\mathrm{app}} \rightarrow \Delta V^{\ddagger}_{n} \qquad (12)$$

In contrast, eq 10 shows that, for a quantum yield, the contribution to the apparent volume of activation of a unit efficiency step becomes zero. That is, the reaction of an intermediate for which there are no competing steps *can make no contribution to the overall apparent volume of activation* (*or the overall apparent activation energy*).

For the opposite limiting case, in which a particular process is a minor one, as, for example, in the familiar case of many phosphorescence emissions, $\eta_{\mathrm{phos}} \ll 1$, eq 12 still governs the pressure effect on the lifetime. However, from eq 10, assuming that only one other process n dominates that step of the mechanism, the contribution to the overall volume of activation is

$$\Delta V^{\ddagger}_{\mathrm{phos,app}} = \Delta V^{\ddagger}_{\mathrm{phos}} - \Delta V^{\ddagger}_{n} \qquad (13)$$

If the true activation volume, $\Delta V^{\ddagger}_{\mathrm{phos}}$, is close to zero,[4] then the volume of activation for τ^{-1} and efficiency of the emission are equal and opposite in sign for that step, although there may be other contributions to the apparent overall volume of activation for emission efficiency, compare eq 10 and 11.

Returning to the specific example under consideration, one finds that the important features of the data on the photochemistry of $[Co(NH_3)_5Br]^{2+}$ to be satisfied in the formulation of a mechanism are the following:

(i) The quantum yields of bromide aquation and of redox are 0.14 and 0.30, respectively, independent of excitation wavelength at and below 313 nm; that is, the total reaction quantum yield in this limiting region is constant at appreciably less than unity.

(ii) At 365 nm, the ratio of aquation to redox is the same as at the shorter wavelengths, but the quantum yields are decreased to about 65% of their short wavelength limiting values.

(iii) In the visible (ligand field band) region, the quantum yields are small and the ratio of equation to redox is much larger than in the ultraviolet.

(iv) At 313 and 365 nm in a 40% glycerol–water mixture, aquation increases 6-fold in importance relative to redox while the overall yield drops to about 65% at both wavelengths.

(v) the apparent volume of activation associated with redox is small but positive and changes only slightly from 313 to 365 nm; that for aquation is uncertain, probably very small but positive.

These data make certain demands on the character of a mechanism designed to fit them. First of all, the basic mechanism must be different for excitation in the UV, where charge transfer (CT) bands dominate the absorption, and for excitation in the visible ligand field (LF) bands, with some overlap in the spectral region between, in which the absorption is mixed between CT and LT. We shall be concerned here with the UV region only. We accept the conventional view that the LF photochemistry occurs by a different mechanism.

The effect of increased viscosity implies that aquation and redox arise from a common intermediate, one for which diffusion apart of two species is required for redox to be consummated. It is also required that this species, once formed, has no "memory" of its origin, as we observe that the reaction mode ratio is excitation wavelength independent.

That the limiting quantum yield is less than unity may arise in two different ways: (1) either a third reaction, e.g., of nonradiative crossing to the ground state, occurs from the intermediate leading to aquation and redox, or (2) there must be an earlier branching involving a prior intermediate that also has lost its "memory" of excitation. The observed volumes of activation put certain restrictions on the nature of these intermediates and their reactions.

Finally, there must be competition early in the mechanism in which, for at least a certain minimum excitation energy corresponding to a wavelength between 313 and 365 nm, a particular intermediate is formed with unit efficiency. For excitation energies less than this minimum, the efficiency of formation of this same intermediate is reduced without changing its subsequent reaction pattern.

These considerations lead us to two simplest mechanisms, A and B, that differ only in the means of satisfying the requirement for a short wavelength photoreaction yield sum less than unity.

For mechanism A, we choose two intermediates, X and Y, both of which are subject to competitions:

$$Co(NH_3)_5Br^{2+} \xrightarrow{\lambda \leq 313\ \mathrm{nm}} X \qquad \alpha(\lambda) \simeq 1 \qquad (14)$$

$$Co(NH_3)_5Br^{2+} \xrightarrow{\lambda > 313\ \mathrm{nm}} X \qquad \alpha(\lambda) < 1 \qquad (15)$$

$$Co(NH_3)_5Br^{2+} \xrightarrow{\lambda > 313\ \mathrm{nm}} Co(NH_3)_5Br^{2+} \qquad 1 - \alpha(\lambda) \qquad (16)$$

$$X \xrightarrow{k_1} Co(NH_3)_5Br^{2+} \qquad (17)$$

$$X \xrightarrow{k_2} Y \qquad (18)$$

$$Y \xrightarrow{k_3} Co^{2+} + 5NH_3 + Br\cdot \qquad (19)$$

$$Y \xrightarrow{k_4} Co(NH_3)_5H_2O^{3+} \qquad (20)$$

According to this mechanism, the quantum yields are given by

$$\Phi^{A}_{\mathrm{aq}} = \alpha(\lambda)\eta_2\eta_4 \qquad (21)$$

$$\Phi^{A}_{\mathrm{redox}} = \alpha(\lambda)\eta_2\eta_3 \qquad (22)$$

in which only the efficiency of X production, $\alpha(\lambda)$, is a function of excitation as indicated in eq 14–16. The limiting photoreaction yield of 0.44 fixes this to be the value of η_2, while the reaction yields ratio calls for $\eta_3 = 1 - \eta_4 = 0.68$.

In mechanism B, the limiting quantum yield sum less than unity arises from a three-way competition among aquation, redox, and deactivation to the original ground-state ion. Reactions 14–16 are followed by

$$X \xrightarrow{k_5} Z \qquad (23)$$

$$Z \xrightarrow{k_6} Co^{2+} + 5NH_3 + Br\cdot \qquad (24)$$

$$Z \xrightarrow{k_7} Co(NH_3)_5H_2O^{3+} + Br^- \qquad (25)$$

$$Z \xrightarrow{k_8} Co(NH_3)_5Br^{2+} \qquad (26)$$

In this mechanism, the quantum yields are

$$\Phi^{B}_{\mathrm{aq}} = \alpha(\lambda)\eta_7 \qquad (27)$$

$$\Phi^{B}{}_{redox} = \alpha(\lambda)\eta_6 \tag{28}$$

and the efficiencies are simply equal to the limiting quantum yields at $\lambda = 313$ nm, that is, $\eta_6 = 0.30$, $\eta_7 = 0.14$, and therefore $\eta_8 = 1 - \eta_6 - \eta_7 = 0.56$.

When eq 11 is used, the apparent volumes of activation for each of the quantum yields at < 313 nm in terms of the two mechanisms can be evaluated as follows (remember that $\alpha(\lambda) = 1$ and can therefore not contribute):

$$\Delta V^{\ddagger}{}_{app,aq,A} = (1 - \eta_2)(\Delta V^{\ddagger}{}_2 - \Delta V^{\ddagger}{}_1) + \eta_3(\Delta V^{\ddagger}{}_4 - \Delta V^{\ddagger}{}_3) \tag{29}$$

$$\Delta V^{\ddagger}{}_{app,redox,A} = (1 - \eta_2)(\Delta V^{\ddagger}{}_2 - \Delta V^{\ddagger}{}_1) - \eta_4(\Delta V^{\ddagger}{}_4 - \Delta V^{\ddagger}{}_3) \tag{30}$$

$$\Delta V^{\ddagger}{}_{app,aq,B} = (1 - \eta_7)\Delta V^{\ddagger}{}_7 - \eta_6\Delta V^{\ddagger}{}_6 - \eta_8\Delta V^{\ddagger}{}_8 \tag{31}$$

$$\Delta V^{\ddagger}{}_{app,redox,B} = (1 - \eta_6)\Delta V^{\ddagger}{}_6 - \eta_7\Delta V^{\ddagger}{}_7 - \eta_8\Delta V^{\ddagger}{}_8 \tag{32}$$

With the data presented here, we find

$$\Delta V^{\ddagger}{}_{app,aq,A} - \Delta V^{\ddagger}{}_{app,redox,A} = \Delta V^{\ddagger}{}_4 - \Delta V^{\ddagger}{}_3 = \Delta V^{\ddagger}{}_7 - \Delta V^{\ddagger}{}_6 = -2.1 \pm 2.4 \text{ mL mol}^{-1}$$

whence, from eq 29 or 30

$$\Delta V^{\ddagger}{}_2 - \Delta V^{\ddagger}{}_1 = 7.3 \pm 2.2 \text{ mL mol}^{-1}$$

and from eq 30, substituting $1 - \eta_7$ by $\eta_6 + \eta_8$ yields

$$\Delta V^{\ddagger}{}_7 - \Delta V^{\ddagger}{}_8 = 5.7 \pm 3.8 \text{ mL mol}^{-1}$$

Both mechanisms assume that the only parameter that depends on wavelength of excitation is $\alpha(\lambda)$. Thus the apparent volume of activation associated with eq 15 in both mechanisms is given by the difference between the volumes of activation of the redox quantum yields at 365 and at 313 nm:

$$\Delta V^{\ddagger}{}_{app,\alpha} = \Delta V^{\ddagger}{}_{app,redox,365} - \Delta V^{\ddagger}{}_{app,redox,313} = 1.2 \pm 0.9 \text{ mL mol}^{-1} \tag{33}$$

In terms of the volumes of activation for eq 15, $\Delta V^{\ddagger}{}_{\alpha}$, and for eq 16, $\Delta V^{\ddagger}{}_{1-\alpha}$, putting the value $1 - \alpha = 0.33$ into eq 10 gives

$$\Delta V^{\ddagger}{}_{\alpha} - \Delta V^{\ddagger}{}_{1-\alpha} = 3.6 \pm 2.7 \text{ mL mol}^{-1}$$

These alternate mechanisms have a number of features in common. The intermediate Y in mechanism A and the corresponding intermediate Z in mechanism B very probably represent a caged radical pair consisting of a bromine atom and a cobalt(II) species, $[Co(NH_3)_5]^{2+}$. Diffusion apart of this radical pair (reactions 19 or 24) would correspond with consummation of redox since bulk recombination is likely too slow to compete with other processes such as the irreversible loss of ammonia from the Co(II) species. A radical pair intermediate of this nature is supported by the results for glycerol/water mixtures which show that the redox to aquation ratio is decreased in the viscous solvent relative to water. This aspect of the mechanism, required by our data, has been included in almost all treatments of the photochemistry of acidopentaamminecobalt(III) ions.[19]

The mechanisms both lead to the same value for the difference in volume of activation between aquation and redox reaction, -2.1 ± 2.4 mL mol^{-1}. Although the individual values cannot be separated, we observe that this difference is in a direction that is intuitively reasonable. Dissociative processes are expected to have positive volumes of activation and therefore decrease their yield with pressure increase. If we accept that successful redox requires greater pair separation than aquation, and therefore greater positive $\Delta V^{\ddagger}$, then redox will decrease faster than aquation with pressure, consistent with the direction of the observed effects.

And finally, for both mechanisms, the intermediate X is most likely a vibrationally equilibrated singlet or triplet ligand–metal charge transfer state ion (since there is no wavelength effect beyond this state).

The two mechanisms otherwise diverge. Mechanism A involves a wavelength-independent competition between formation of the caged pair Y (reaction 18) and deactivation to the ground state ion (reaction 17). In contrast, in mechanism B, the formation of the intermediate X is always followed by formation of the cage pair Z (reaction 23), then the return to the ground state ion (required since the sum of quantum yields for redox and aquation is less than one) is a step competitive with the other cage reactions (reactions 24 and 25).

The pressure dependence data do not allow us to choose between these alternatives, but the data for 40% glycerol/water do have some relevance. For irradiation at 313 and 365 nm, aquation increased 2.3-fold, while redox decreased 8-fold in the mixed solvent. This finding is suggestive that mechanism B operates, with a dramatic decrease in redox, a marked increase in aquation, and a small increase in return to the ground state with increase in viscosity, the effect being the same at both wavelengths. These grounds support a mild preference for mechanism B.

It is unfortunate that experimental difficulties would probably preclude success in another potential test to distinguish these two mechanisms; scavengers for bromine atom should increase the yield of redox potentially to the limit value of unity at short wavelengths in mechanism B, but should leave the total yield unaltered if mechanism A were operative.

Although our data do not permit a definite resolution of this uncertainty, they do show that the wavelength dependence of the system is simpler than earlier suggested[19] and that the effect of excitation energy, pressure, and solvent viscosity can all be explained in terms of a simple, if not unique mechanism, involving a radical pair species bearing no memory of its original excitation energy. The volumes of activation observed in the work are completely consistent with and suggestive of such a mechanism. The observation that the precursor to reaction has no memory of its excitation, giving rise to the same division of redox and aquation at all CT wavelengths is a new result and supports the suggestion that reaction may occur via an equilibrated CT singlet or triplet state.

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Registry No. $[Co(NH_3)_5Br]^{2+}$, 14970-15-1; $[Co(NH_3)_5H_2O]^{2+}$, 22045-50-7; Co^{II}, 22541-53-3.