

Reaction Dynamics and Hydroxide Ion Quenching of Rhodium(III) Ligand Field Excited States: Photoreactions of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$

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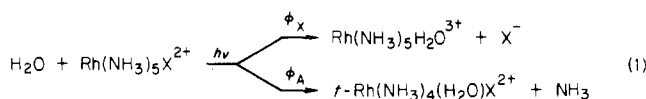
Received July 25, 1983

Comparison of the photosubstitution reactions of the $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ ion in acidic and alkaline aqueous solutions resulting from ligand field excited states shows that, while hydroxide ion quenches NH_3 labilization, it also enhances I^- labilization substantially. These results demonstrate that the previous observation of partial quenching by Brønsted bases of the $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ photosubstitution reactions can best be interpreted in terms of OH^- acting as a "noninnocent" quencher. It is proposed that OH^- quenches the ligand field excited state reactively giving a new chemical species that can undergo halide labilization or decay to the ground-state starting complex. In addition, the emission lifetime of the $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ ligand field excited state is reported to be 1.3 ± 0.1 ns in 25 °C acidic aqueous solution, and this value has been used to calculate excited-state reaction rate constants for this rhodium(III) complex.

Introduction

The ability to measure both photoreaction and photoemission properties of the halopentaamminerhodium(III) complex $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) under equivalent solution conditions has provided the opportunity for examining the reaction dynamics of the ligand field (LF) excited states (ES) of d^6 complexes.^{4,5} As the result of such studies, it was argued that the ligand field photochemistry of these and related rhodium(III) complexes can be attributed mostly to the lowest energy excited state, a triplet LF ES, formed rapidly and efficiently by internal conversion/intersystem crossing from states populated initially upon excitation.⁴ A corollary of this argument is that reactions that give different products occur as competitive processes from a vibrationally relaxed, lowest energy LF state or from states in equilibrium with this lowest energy ES. Competitive processes are emission and nonradiative deactivation to the ground state.⁶⁻⁸ Most experimental observations relative to the photoreaction properties of these complexes are consistent with this model;⁴ however, significant modifications to the model have recently been proposed^{9,10} to account for the photochemical and photophysical properties noted in alkaline solution.⁹⁻¹¹

In dilute acid aqueous solution, the photoreactions resulting from LF excitation of the $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ ions include both ammine and halide aquation⁴ (eq 1). Under the same con-



ditions, these complexes ($\text{X} = \text{Cl}^-, \text{Br}^-$) were found to luminesce, giving broad Gaussian emission bands and emission lifetimes of 14 and 12 ns, respectively.⁶ These emissions have been attributed to phosphorescence from LF triplet states. In alkaline solution these LF emissions are quenched by OH^- in

a manner consistent with Stern-Volmer kinetics.^{9,10} However, the photosubstitution chemistry, while largely quenched by OH^- , is not entirely suppressed. Furthermore, it has been reported¹⁰ that, at least for the $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ ion, the two photoreaction quantum yields ϕ_A and ϕ_X are affected differently by base; ammine loss is fully quenched, but Br^- aquation is apparently unaffected by base. In this context, it has been suggested¹⁰ that the two photoreactions originate from at least two distinct low-lying excited states, one of which is the emitting state and is subject to hydroxide quenching and the other which neither emits nor is subject to quenching by OH^- . If this were the case, the populations of these states could not be in equilibrium.

This interpretation¹⁰ of the quenching experiments represents a substantial revision of the earlier photoreaction model. An alternative explanation is that hydroxide may be acting as a "noninnocent" quencher for the excited state,^{9,12} i.e., that new reaction patterns may be the result of a chemical process depleting the emitting ES. This possibility has prompted the present further investigation of the OH^- quenching of the LF photochemistry of the $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ ion in aqueous solution and the extension of such studies to the iodo complex $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$. Reported here are results for the latter complex ion that substantiate the view that the hydroxide ion is acting as a noninnocent quencher in these cases and obviate the need to postulate the existence of noncommunicating LF states having nearly identical energies but different chemical and photophysical properties. Also reported are ES emission lifetimes for the $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ ion in aqueous solution at ambient temperature.

Experimental Section

Materials and Synthesis. Reagent grade compounds were used for all preparations described in this work. Water used for syntheses and experimental determinations was deionized and then distilled.

The complexes $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ and $[\text{Rh}(\text{NH}_3)_5\text{I}](\text{ClO}_4)_2$ were synthesized according to procedures described elsewhere.^{14,15} The purity of these complexes was established by comparison of the electronic absorption spectra with published values.^{6,13,16,17} Electronic spectra were recorded on a Cary 118 spectrophotometer.

A Radiometer PHM 84 pH meter was used for all pH and hydroxide ion measurements. Sodium hydroxide stock solutions were freshly prepared from boiling water to minimize carbonate impurities from atmospheric carbon dioxide.

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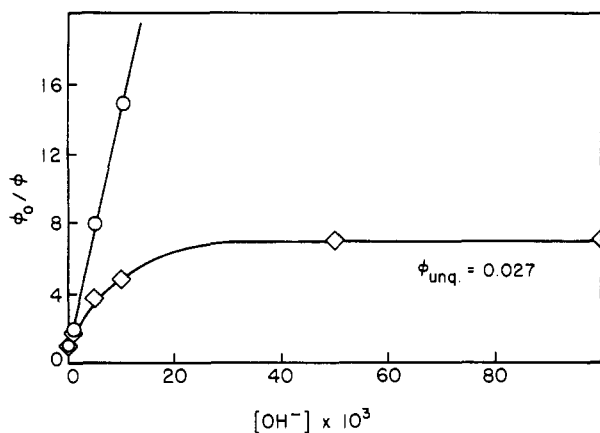


Figure 1. Stern-Volmer type plots for the OH^- quenching of the photosubstitution reactions of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in aqueous solution: \diamond , ϕ_0/ϕ ; \circ , $\phi_0/(\phi - 0.027)$.

Photolysis and Luminescence. Photolyses were carried out by the same methods and by using the photolysis apparatus previously described.^{6,18} The $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ complex (having a lowest energy LF band at λ_{max} 347 nm) was irradiated at 366 nm, and the $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ complex (λ_{max} 416 nm) was irradiated at 404 nm. Spectral changes were monitored at the wavelength of irradiation, at the λ_{max} of the starting material, and at the λ_{max} of the major photoproduct. Measurements continued until the reactions were approximately 25% complete. The emission lifetimes of the $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ and $\text{Rh}(\text{ND}_3)_5\text{I}^{2+}$ complexes were measured in dilute acidic aqueous solutions (10^{-3} M HClO_4) at 298 K by single-photon correlation techniques with a mode-locked argon ion laser as described previously.¹⁹

Results and Discussion

The present investigation confirms the reported⁹ photo-reaction behavior of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in alkaline aqueous solution. At high hydroxide ion concentrations, the LF emission from $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ is apparently quenched; yet, a residual photoreaction quantum yield of 0.027 mol/einstein remains at high base concentration. This value constitutes about 14% of the acidic solution photosubstitution quantum yield. A Stern-Volmer (SV) plot of ϕ_0/ϕ vs. $[\text{OH}^-]$ is nonlinear (Figure 1), consistent with an unquenched contribution to the total quantum yield. Moreover, the quantity $\phi_0/(\phi - 0.027)$ does give a linear SV plot with a slope (K_{SV}) of 1390 M^{-1} . (It should be noted that while Cl^- aquation is the predominant photosubstitution pathway in acidic solution, modest NH_3 aquation also has been observed.²⁰ Although spectral changes are consistent with Cl^- hydrolysis being the principal unquenched photoreaction, spectral differences between the products are sufficiently small that we are unable to assign the unquenched photoreaction to Cl^- loss exclusively.)

The above results plus the previous findings that Br^- photolabilization is the exclusive unquenched reaction of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ in alkaline solution¹⁰ can be rationalized by a mechanism such as Scheme I. In Scheme I, a single lowest energy LF ES (or a collection of low-energy excited states in thermal equilibrium) reacts with OH^- (a noninnocent quencher) to give an intermediate (I) that can react further to give halide labilization or return to the starting complex. The partitioning between these two pathways would be determined by the relative values of k' and k_x' so that a fortuitous ratio of these two rate constants could give a ϕ_{Br} value in

Scheme I

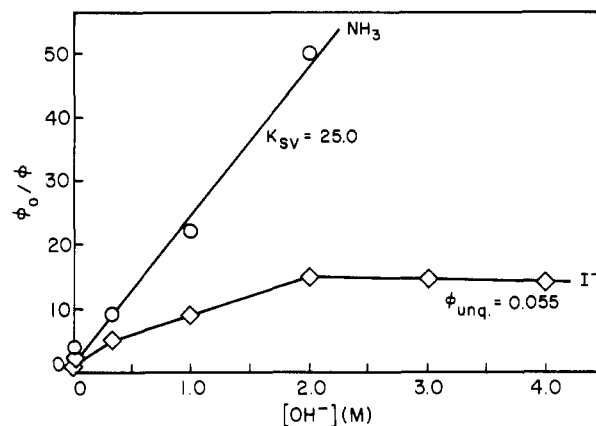
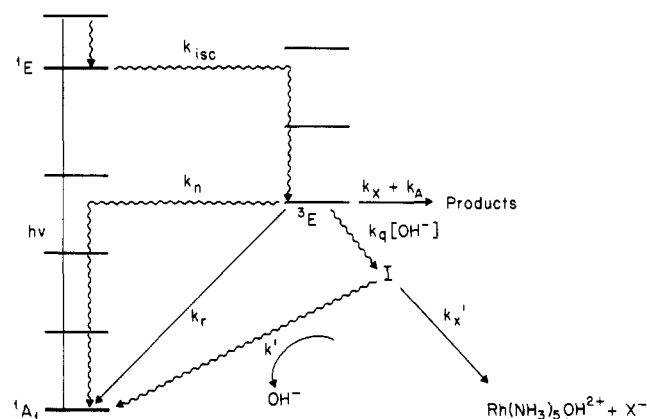


Figure 2. Stern-Volmer type plots for the photosubstitution reactions of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ in alkaline solution: \diamond , ϕ_1^0/ϕ_1 ; \circ , $\phi_{\text{NH}_3}^0/\phi_{\text{NH}_3}$.

alkaline solution comparable to that seen in acidic solution. We would suggest I to be a species such as $\text{Rh}(\text{NH}_3)_4(\text{NH}_2)\text{X}^+$ (the product of proton transfer to the Brønsted base OH^-); however, associative OH^- addition to give a seven-coordinate intermediate cannot be excluded.

If a mechanism such as Scheme I were operable, then there should be conditions for which base "quenching" of the excited state is accompanied by enhanced values of ϕ_x . In contrast, simple (innocent) quenching should never give this result. In order to test for this possibility, the iodo complex should be ideal, given that LF photolysis of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ in acidic solution leads to no detectable halide labilization ($\phi_{\text{I}} \leq 0.01$) but to extensive ammine aquation ($\phi_{\text{NH}_3} = 0.79$).

The photochemistry of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ in alkaline solution is easily monitored spectrally because the LF absorption bands for the starting material at 416 nm and for the expected primary photoproduct *trans*- $\text{Rh}(\text{NH}_3)_4(\text{OH})\text{I}^+$ at 480 nm are well resolved. The NH_3 labilization pathway to give the latter ion (monitored at 485 nm) is fully quenched by hydroxide as illustrated by the linear ϕ_0/ϕ_{485} SV plot with $K_{\text{SV}} = 25.0 \text{ M}^{-1}$ (Figure 2). In contrast, disappearance of starting material (monitored at 416 nm) is not fully quenched under conditions of high $[\text{OH}^-]$, but a limiting unquenched quantum yield of 0.055 mol/einstein is given. Acidifying the solution and adding I^- regenerates the starting complex nearly quantitatively, thus confirming that the photochemically induced spectral changes indeed represent iodide aquation. The crucial finding is that the limiting value of ϕ_1 in alkaline solution is more than fivefold larger than that found in acidic solution. Thus, the proposal that hydroxide is acting as a "noninnocent" quencher in a manner such as that described in Scheme I is fully consistent with the experimental observations. The alternative explanation, which assumes several noncommunicating low-energy LF states, is incompatible with the enhanced ϕ_1 values in the

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(20) (a) From our investigation of $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ in acidic solution, $\phi_{\text{Cl}} = 0.15$ and $\phi_{\text{NH}_3} = 0.04$ mol/einstein. (b) Kelm and co-workers have separately determined for $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ $\phi_{\text{Cl}} = 0.20$ and $\phi_{\text{NH}_3} = 0.036$ mol/einstein. These results combined with the earlier studies done by Bergkamp conclusively show ammonia photoaquation occurring in significant amounts for the $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ complex.

alkaline solution photochemistry of the $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ ion, since population of these states would be independent of $[\text{OH}^-]$.

Another aspect of the quenching studies is the possibility of extracting kinetic information from the linear Stern–Volmer plots. The Stern–Volmer constant is related to the excited-state lifetime according to

$$K_{\text{SV}} = k_a \tau_0 \quad (2)$$

where τ_0 is the measured lifetime in the absence of quencher and k_a is the second-order quenching constant. In 25 °C aqueous solution the K_{SV} value for the hydroxide ion quenching of the $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ photosubstitution reactions was measured as 1390 M^{-1} from Figure 1. Given the τ_0 value of 14.2 ns measured previously in acidic solution,⁶ a k_a value of $9.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ can be calculated under these conditions. These values can be compared to those determined previously from the OH^- quenching of the $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ phosphorescence lifetimes at 4 °C: $K_{\text{SV}} = 645 \text{ M}^{-1}$, $\tau_0 = 30.1 \text{ ns}$, $k_a = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. (Hydroxide ion quenching of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ phosphorescence at 5 °C gave the values $K_{\text{SV}} = 625 \text{ M}^{-1}$, $\tau_0 = 24.1 \text{ ns}$, and $k_a = 2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The k_a values are remarkably large in both cases, are comparable to the fastest proton-transfer rate constants measured in aqueous solution,²¹ and approximate the diffusion control limit. This implies the quenching process occurs at nearly every encounter between OH^- and the excited complex, a feature compatible with either proton transfer or energy transfer but unlikely if OH^- coordination were the mechanism. Since energy transfer is unlikely owing to the absence of low-energy OH^- excited states, we conclude the quenching process to involve some form of proton transfer.

For the iodo complex, the K_{SV} value of 25 M^{-1} is much smaller than that found for the chloro complex under analogous conditions. In an earlier report,²² we estimated k_a to fall in the range $(2 - 10) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ and used eq 2 to then estimate the previously unmeasured τ_0 therefore to fall in the approximate range 0.25–1.3 ns. We have now measured the triplet LF lifetime directly by picosecond pulse laser techniques. In acidic aqueous solution, $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ displays an emission decay lifetime of $1.3 \pm 0.1 \text{ ns}$, in reasonable agreement with the above estimate. The deuterated analogue $\text{Rh}(\text{ND}_3)_5\text{I}^{2+}$ in D_2O has a slightly longer lifetime of $2.0 \pm 0.1 \text{ ns}$, consistent with deuteration effects noted earlier.⁶ This highly sensitive instrumentation also detected a small fluorescence component ($\tau_f = 40 \text{ ps}$) comparable to those noted earlier for other Rh(III) complexes.²³ Quenching of the phosphorescence from $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ by NaOH in H_2O solutions gave linear τ_0/τ vs. $[\text{OH}^-]$ plots with a K_{SV} value of 26 M^{-1} in agreement with that noted for photoreaction quenching.

From the $\tau_0 = 1.3 \text{ ns}$ value, k_a for the OH^- quenching of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ is calculated from eq 2 as $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

Table I. Experimental Results Concerning the Photochemical and Photophysical Characteristics of $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ Complexes in Aqueous Solution^a

complex	ϕ_{X}^b	$\phi_{\text{NH}_3}^b$	$\tau_0, \text{ ns}$	$k_{\text{X}}, \text{ s}^{-1}$	$k_{\text{NH}_3}, \text{ s}^{-1}$
$\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$	0.15	0.04	14.2 ^c	10.5×10^6	2.8×10^6
$\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$	0.02 ^d	0.18 ^d	12.4 ^c	1.6×10^6	14.5×10^6
$\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$	≤ 0.01	0.79	1.3	$\leq 8 \times 10^6$	6.1×10^8

^a At 25 °C in acidic aqueous solution (10^{-3} M HClO_4). ^b Units of mol/einstein. ^c Reference 6. ^d Reference 13.

This is less than the k_a value measured for the chloro analogue. One rationalization for the difference is that the iodo complex is less acidic in its LF excited state than the chloro complex owing to the greater ability of the coordinated iodide to donate π electrons²⁴ into the vacancy formed in the π -symmetry metal-centered orbitals by LF excitation.²⁵

Table I summarizes some lifetime and rate data for the $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ LF excited states calculated according to⁶

$$\phi_i = k_i \tau \quad (3)$$

which assumes that internal conversion/intersystem crossing to the lowest energy LF ES has an efficiency near unity.¹³ From these data, it can be seen that the variation in the $\phi_{\text{X}}/\phi_{\text{A}}$ ratio by several orders of magnitude can be largely attributed to changes in the NH_3 labilization rate constant k_{NH_3} , while k_{X} is less variable. Given that the ammonia labilized probably originates from the position trans to the halide, these differences denote a strong kinetic trans effect by the halogens on the k_{NH_3} values.

In summary, the significant conclusion of the above experiments is the demonstration that ES quenching in the halopentaammine systems by hydroxide is probably not “innocent”; i.e., there are chemical consequences above and beyond simple quenching of the LF excited state. This conclusion really should not be surprising given the apparent absence of low-lying electronic states in OH^- to which energy transfer might occur. Thus, it is likely that the quenching mechanism involves a chemical process such as Brønsted proton transfer, a step likely to have other consequences. We have attempted to demonstrate alternative “innocent” energy-transfer quenching with transition-metal cations Ni^{2+} (0.5 M), Cr^{2+} (1.0 M), Cr^{3+} (2.0 M), Mn^{2+} (1.0 M), Cu^+ (1.0 M), Co^{2+} (2.0 M), and Eu^{3+} (2.0 M) but as yet have not found such a system where k_a is sufficiently large to intercept the short-lived LF excited states of the Rh(III) complexes.

Acknowledgment. This research was supported by grants from the National Science Foundation to P.C.F. and to D.M. The rhodium used in these studies was provided on loan from Johnson-Matthey, Inc.

Registry No. $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, 15379-09-6; $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$, 15337-81-2; $\text{Rh}(\text{ND}_3)_5\text{I}^{2+}$, 50513-51-4; *trans*- $\text{Rh}(\text{NH}_3)_4(\text{OH})\text{I}^+$, 73085-25-3; OH^- , 14280-30-9.

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