Quenching of Emission and of Photochemistry for Aqueous $Rh(NH_3)_5Cl^{2+}$

ARTHUR W. ADAMSON, ROBERT C. FUKUDA, MARINA LARSON, HELMUT MÄCKE and JEAN PIERRE PUAUX

Department of Chemistry, University of Southern California, Los Angeles, Calif. 90007, U.S.A.

Fig. 1. Temperature dependence of emission and ESA lifetimes for aqueous $Rh(NH_3)_5Cl^{2+}$. ○ Emission; △ ESA; ● datum from Ref. 4. Numbers in parentheses give the number of separate experiments.

Fig. 2. Stern–Volmer plot of OH^- and CO_3^{2-} quenching of aqueous $Rh(NH_3)_5Cl^{2+}$ at 4 °C. △ OH^- quenching of emission. ○ CO_3^{2-} quenching of emission. ● Test of effect of $[HCO_3^-]$, see text. Numbers in parentheses give the number of separate experiments.

Both ordinary and sensitized photochemistry have been reported for various Rh(III) ammine complexes, from several laboratories [1, 2]. The reactivity has been attributed to the lowest triplet thexi state, T_1^0 [1a]. Low temperature emission, also assigned to T_1^0, has been known for sometime [3], but has only recently been observed in room temperature, aqueous solution for $Rh(NH_3)_5X^{n+}$, for X = NH_3, ND_3, Cl, Br [4], and for X = Cl, Br, and H_2O [5, 6]. In the case of $Rh(NH_3)_5Cl^{2+}$, the room temperature emission spectrum shows a maximum at 640 nm [5], and generally resembles the low temperature spectrum [7]. There is also a transient absorption, with a maximum at 500 nm, $\epsilon_{max} > 100 \, M^{-1} \, cm^{-1}$, and assigned to T_1^0 since the decay time is the same as that of emission [5].

The ability to observe emission and excited state absorption (ESA) under photochemical conditions should provide leverage for excited state studies, much as has been possible for Cr(III) complexes [2, 8]. We have been examining the possibility, and report here some results for aqueous $Rh(NH_3)_5Cl^{2+}$. Figure 1 shows the temperature dependence of the (presumed) T_1^0 lifetime, τ^0, as obtained from emission and ESA*. The two sets of data lie on the same Arrhenius plot, of slope corresponding to 5.4 ± 0.3 kcal mol^{-1} apparent activation energy. The interpolated τ^0 value for 25 °C, 14.8 nsec, agrees well with the reported value of 14.2 nsec [4]; our value at 4 °C, of importance below, is 30.1 ± 0.7 nsec.

We find that the emission is quenched by OH^- and by CO_3^{2-} ions (that the behavior is the same for ESA was checked in the case of OH^-), and the Stern–Volmer type plots for 4 °C are shown in Fig. 2. Carbonate ion has not previously been reported as a
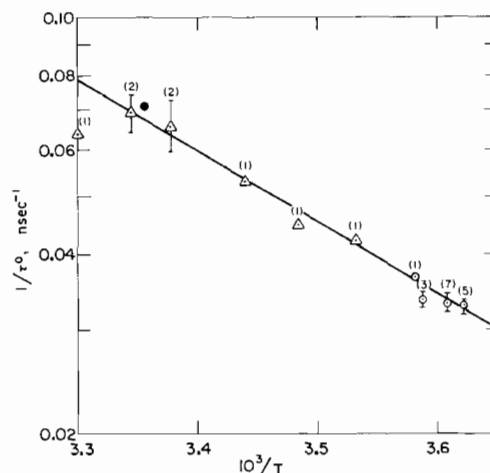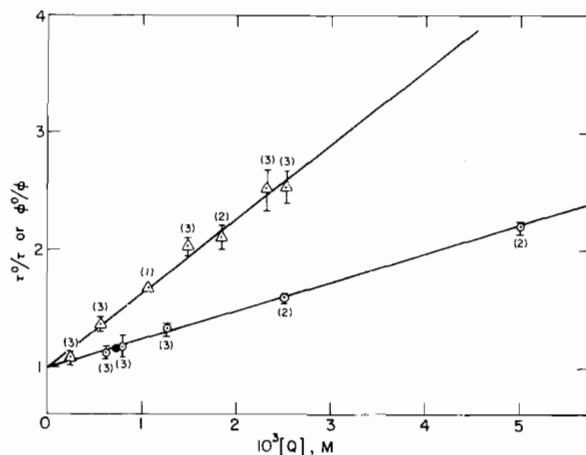
quencher for an excited state of a coordination compound*. The slopes of the two Stern–Volmer plots yield bimolecular quenching rate constants, k_q,

---

---

*As a cautionary note, CO_3^{2-} may easily be present as adventitious impurity in basic solutions; its quenching ability was discovered as a result of investigating the source of irreproducibilities in preliminary experiments. In subsequent ones, care was taken to use A.R. or 'super pure' grade sodium hydroxide, which was water washed and immediately made up to a stock solution. Dilutions were made with care to minimize absorption of atmospheric CO_2, and irradiations, in sealed cells. Hydroxide ion concentration was calculated from the measured pH at 25 °C. The carbonate solutions were equiformal in $NaHCO_3$ and Na_2CO_3, and had a pH of 10.08.

of 2.1×10^{10} and 8.3×10^9 M^{-1} sec^{-1} for OH^- and CO_3^{2-}, respectively. These k_q values correspond to about the diffusion encounter rates expected for the two quenchers. That the quenching is due to CO_3^{2-} rather than to HCO_3^-, is indicated by the agreement of the dark circle point of Fig. 2, for $[CO_3^{2-}] = 7.5 \times 10^{-4}$ M, $[HCO_3^-] = 9.0 \times 10^{-3}$ M, with the adjacent open circle point, for $[CO_3^{2-}] = [HCO_3^-] = 8.0 \times 10^{-4} M$.

An important aspect that may now be tested is the degree to which emission quenching leads to reduction in photochemical quantum yield. The 25 °C yields for chloride and for ammonia photoaquation are reported to be 0.16 and $< 10^{-3}$, respectively [1a]. Our procedure, in testing for OH^- quenching, was to carry out paired irradiations, one in pH 2 perchloric acid solution, and one at the desired OH^- concentration, and to compare the spectrophotometrically determined degrees of photolysis*. The results, in terms of ϕ/ϕ^0, where ϕ is reaction quantum yield, *vs.* τ/τ^0, are shown in Fig. 3 [11]. The intercept gives the unquenchable yield, 13% in this case. Photolysis quenching was also observed qualitatively, in the case of CO_3^{2-} solutions, but with indication of complexity in that some prompt formation of $Rh(NH_3)_5(CO_3)^+$ occurred.

It has been suggested, from deuteration effects on emission lifetime and photochemical quantum yield,

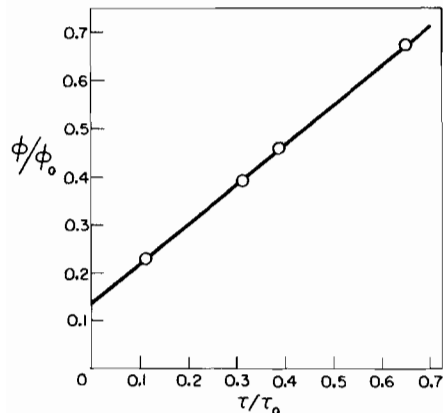that the photoaquation and emission are competitive [4]. Our results tend to confirm this conclusion in that emission quenching is indeed accompanied by quenching of photochemistry. The 13% unquenchable portions could be due either to reaction from an excited state not populated via T_1^0, or to some anation during a quenching encounter.

Results of tests for other quenchers are that we detect no emission quenching by acetate, formate, or oxalate ions, or by the species present in 0.05 f borate at pH 9.2. Cyanide ion is a weak quencher, with 25% lifetime quenching in 0.05 f cyanide at pH 9.3. The three quenching species, OH^-, CO_3^{2-}, and CN^-, have the common property of being good proton acceptors; it may be that there is a common quenching mechanism of proton transfer from T_1^0 to base, B^-, during a quenching encounter. The immediate product, $[Rh(NH_3)_4(NH_2)Cl \cdot HB]^+$, should be substitution labile, and might in part convert to $Rh(NH_3)_5B^{n+}$. Such behavior would account for our results with OH^- and for the component of prompt anation in the case of CO_3^{2-}.

If the proton transfer hypothesis is correct, a complex with no acidic protons should not show hydroxide quenching. This test was made with *cis*-$Rh(bipyr)_2Cl_2^+$ [15]. Emission has been reported at 77 K and assigned as d–d phosphorescence for the lowest triplet [16]. As a new observation, we find emission in room temperature aqueous solution, 52.3 ± 2.5 nsec at 11 °C. Consistent with the hypothesis, there is no OH^- quenching; $k_q < 10^7$ M^{-1} sec^{-1}.

Fig. 3. Test for unquenchable photolysis of $Rh(NH_3)_5Cl^{2+}$ in OH^- solutions.

---

*It was first verified that no different photochemistry occurred in the alkaline solutions. The solution was acidified after photolysis, and the spectrum found to correspond to that for a stage in the acid photolysis. Also, since the absorption spectra for $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5(H_2O)^{3+}$, and $Rh(NH_3)_5(OH)^{2+}$ are known [12, 13], independent (and agreeing) determinations of the course of photolysis in either acid or alkaline solution could be made by suitable plotting (see Ref. 14) of optical density changes at various wavelengths. Photolyses of the 0.003 M $Rh(NH_3)_5Cl^{2+}$ were 10% to 20% reaction and some pH decrease of the OH^- solutions occurred; the points in Fig. 2 are for the average OH^- concentration during the photolysis.

References

1 (a) T. L. Kelly and J. F. Endicott, *J. Phys. Chem., 76*, 1937 (1972); J. F. Endicott and G. J. Ferraudi, *J. Phys. Chem., 80*, 849 (1976). (b) M. M. Muir and W. L. Huang, *Inorg. Chem., 12*, 1831 (1973). (c) C. Kutal and A. W. Adamson, *Inorg. Chem., 12*, 1454 (1973). (d) P. C. Ford and J. D. Petersen, *Inorg. Chem., 14*, 1404 (1975). See also references cited in the above.

2 (a) V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds', Academic Press, New York (1970). (b) A. W. Adamson and P. D. Fleischauer, eds., 'Concepts of Inorganic Photochemistry', Wiley, New York (1975).

3 T. R. Thomas, R. J. Watts and G. A. Crosby, *J. Chem. Phys., 59*, 2123 (1973), and references therein.

4 M. A. Bergkamp, R. J. Watts, P. C. Ford, J. Brannon and D. Magde, *Chem. Phys. Lettr., 59*, 125 (1978).

5 A. W. Adamson, *Pure and Applied Chem., 51*, 313 (1979). Note: the uncorrected emission spectrum using a photomultiplier rather than the vidicon detector has a maximum at 670 nm.

6 Unpublished work in this laboratory.

7 T. R. Thomas and G. A. Crosby, *J. Molec. Spectr., 38*, 118 (1971).

8 (a) A. W. Adamson, R. T. Walters, R. Fukuda and A. R. Gutierrez, *J. Am. Chem. Soc., 100*, 5241 (1978). (b) A. R. Gutierrez and A. W. Adamson, *J. Phys. Chem., 82*, 902 (1978). (c) R. T. Walters and A. W. Adamson, *Acta Chem. Scand.*, in press.

9 G. W. Bushnell, G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc. A*, 719 (1966).

10 D. A. Palmer and G. M. Harris, *Inorg. Chem., 13*, 965 (1974).

11 See, for example: R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi and V. Balzani, *J. Phys. Chem., 77*, 2947 (1973).

12 P. E. Hoggard and H. Schmidke, *Ber. Bun. Ges., Physik. Chemie, 59*, 2123 (1973).

13 C. K. Jørgensen, *Acta Chem. Scand., 10*, 500 (1956).

14 P. S. Sheridan and A. W. Adamson, *J. Am. Chem. Soc., 96*, 3032 (1974).

15 The complex was prepared according to R. D. Gillard, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.*, 1951 (1965).

16 J. N. Demas and G. A. Grosby, *J. Am. Chem. Soc., 92*, 7262 (1970).