Sensitized Photoaquation of Thiocyanatopentaamminechromium(III) and Chloropentaamminechromium(III) Ions by Excited Singlet Riboflavin

E. L. Wehry

Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916. *Received August 26, 1972*

Abstract: In aqueous media (pH 3.2), the first excited singlet state of riboflavin sensitizes photoaquation of $Cr(NH_3)_5X^{2+}$ ($X^- = NCS^-, Cl^-$). For both complexes, the dominant sensitized reaction mode is ammonia release. From a comparison of fluorescence quenching and sensitized aquation data, it is concluded that quenching of the riboflavin excited singlet by the complexes proceeds by two competitive paths of approximately equal efficiency, one of which involves electronic energy transfer to form excited quartet states of the complexes. Qualitative evidence for energy transfer from triplet riboflavin to the doublet manifold of $Cr(NH_3)_5Cl^{2+}$ is also presented.

The ability of transition metal complexes to act as quenchers of triplet excited states of organic molecules by intermolecular energy transfer is well established.[1] Singlet quenching by coordination compounds has, however, received little attention until very recently,[1a,g,h] and electronic energy transfer from excited organic singlets to coordination compounds is a virtually unexplored area. In a study of quenching of fluorescence of riboflavin (6,7-dimethyl-9-(D-1′-ribityl)-isoalloxazine) by aquo metal ions,[2] we unexpectedly observed that $Cr(H_2O)_6^{3+}$ was an effective quencher of singlet riboflavin, as were several other Cr(III) species. In one specific case, $Cr(NH_3)_5NCS^{2+}$, the quenching action of the complex was accompanied by sensitized photoaquation.[2] In this paper we describe in detail the sensitized photoaquation of $Cr(NH_3)_5NCS^{2+}$ and $Cr(NH_3)_5Cl^{2+}$ by the first excited singlet state of riboflavin.

Experimental Section

Materials. Purification of riboflavin[2] and methyl methacrylate[3] has been described. Preparation and purification of $[Cr(NH_3)_5NCS](ClO_4)_2$ and $[Cr(NH_3)_5Cl](ClO_4)_2$ followed literature procedures.[4] Water was distilled in a borosilicate-glass apparatus and stored in polyethylene containers. In all solutions containing riboflavin and chromium complexes, the pH was adjusted to the desired value by addition of reagent grade $HClO_4$; no buffer salts were employed.

Methods. Instrumentation employed in *fluorescence quenching* studies has been described.[5] Unless otherwise noted, all solutions contained 1.20×10^{-5} *M* riboflavin at pH 3.2. All spectra were measured at 25.0 ± 0.1° in rectangular cells by right-angle illumination. Methods for correction of fluorescence spectra and determination of fluorescence quantum yields have been described.[2,5] Though the corrected fluorescence maximum for riboflavin was 543 nm (Figure 1), Stern-Volmer quenching plots for the chromium complexes were based on measurements made at other wavelengths (570 nm for $Cr(NH_3)_5NCS^{2+}$, 585 nm for $Cr(NH_3)_5Cl^{2+}$) to minimize corrections for absorption of riboflavin fluorescence by quencher; when necessary, such corrections were made by literature procedures.[6] As described previously,[2] precautions were exercised to minimize errors caused by direct photolysis of either riboflavin or quencher or thermal reactions of quencher with riboflavin. Fluorescence decay times were obtained with a TRW "Nanosecond Spectral Source;" mathematical procedures,[7] rather than the analog computer associated with the instrument, were used to extract decay times from the data.

The general procedures employed in *photosensitization* experiments have been described.[3] Light from a Hanovia 975C98 2500-W xenon lamp was dispersed by a Schoeffel GM 250 grating monochromator; use of this intense lamp made it possible to achieve moderate intensities (*ca.* 5×10^{15} photons sec^{-1}) with small half-bandwidths (5 nm). Photolyses were carried out at 25.0 ± 0.1° in rectangular 1-cm cells. Solutions were magnetically stirred during photolysis. The initial pH was 3.2 ± 0.1, the initial riboflavin concentration was 1.20×10^{-4} *M*, and, unless otherwise indicated, the initial concentration of chromium complex was 5.00×10^{-3} *M*. All irradiations were performed at a nominal wavelength of 430 nm; when corrected[8] for the nonmonochromaticity of the incident light, the fractions of incident light absorbed by the solutes in solutions of the above composition were riboflavin, 0.89, and $Cr(NH_3)_5NCS^{2+}$, 0.07; or riboflavin, 0.89, and $Cr(NH_3)_5Cl^{2+}$, 0.03.

Ferrioxalate actinometry[9] was employed. For determination of free NCS^- or Cl^-, the irradiated solution was passed over a column of Dowex 1-X8 anion resin in the ClO_4^- form. The NCS^- or Cl^- retained by the resin was displaced by 3.5 *M* aqueous $HClO_4$. The solution was then adjusted to near neutrality. Thiocyanate was determined spectrophotometrically by reaction with Fe^{3+};[10] Cl^- analyses were performed by chloride-electrode potentiometry.[11] Free ammonia was determined by coulometric titration with electrogenerated hypobromite employing amperometric endpoint detection.[12] The photolyzed solution (volume 4 ml) was adjusted to pH 2.0 and passed over a column of Dowex 50W-X8 cation resin in the H^+ form; the resin retained NH_4^+ and the chromium complexes

---

(1) Recent references include: (a) H. D. Gafney and A. W. Adamson, *J. Phys. Chem.*, **76**, 1105 (1972); (b) T. L. Kelly and J. F. Endicott, *ibid.*, **76**, 1937 (1972); (c) M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, **94**, 1805 (1972); (d) V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *ibid.*, **93**, 339 (1971); (e) H. F. Wasgestian and G. S. Hammond, *Theor. Chim. Acta*, 20, 186 (1971); (f) E. Zinato, P. Tulli, and P. Riccieri, *J. Phys. Chem.*, **75**, 3504 (1971); (g) J. E. Martin and A. W. Adamson, *Theor. Chim. Acta*, 20, 119 (1971); (h) M. A. Scandola, F. Scandola, and V. Carassiti, *Mol. Photochem.*, **1**, 403 (1969).

(2) A. W. Varnes, R. B. Dodson, and E. L. Wehry, *J. Amer. Chem. Soc.*, **94**, 946 (1972).

(3) (a) S. Sundararajan and E. L. Wehry, *J. Phys. Chem.*, **76**, 1528 (1972); (b) E. L. Wehry and R. A. Ward, *Inorg. Chem.*, 10, 2660 (1971).

(4) E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Inorg. Nucl. Chem.*, **31**, 449 (1969).

(5) M. Goldman and E. L. Wehry, *Anal. Chem.*, **42**, 1178 (1970).

(6) C. A. Parker and W. J. Barnes, *Analyst (London)*, **82**, 606 (1957).

(7) J. N. Demas and A. W. Adamson, *J. Phys. Chem.*, **75**, 2463 (1971).

(8) E. L. Wehry in "Analytical Photochemistry and Photochemical Analysis," J. M. Fitzgerald, Ed., Marcel Dekker, New York, N. Y., 1971, p 174.

(9) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(10) L. R. Morrow, Jr., M.S. Thesis, Indiana University, 1969.

(11) S. Sundararajan and E. L. Wehry, *J. Inorg. Nucl. Chem.*, **34**, 3699 (1972).

(12) (a) A. F. Krivis, G. R. Supp, and E. S. Gazda, *Anal. Chem.*, **35**, 2216 (1963); (b) G. D. Christian, E. C. Knoblock, and W. C. Purdy, *ibid.*, **35**, 2217 (1963).

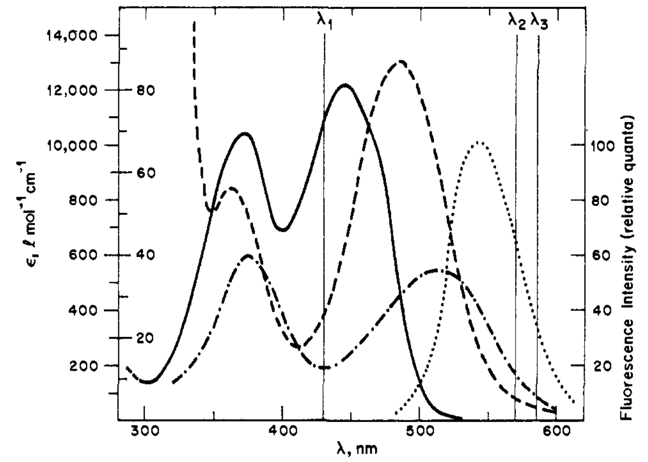

Figure 1. Electronic spectra in aqueous media (pH 3.2): (—), absorption spectrum of riboflavin (left outer ordinate); (- - -) absorption spectrum of Cr(NH$_3$)$_5$NCS^{2+} (left inner ordinate); (— · —) absorption spectrum of Cr(NH$_3$)$_5$Cl^{2+} (left inner ordinate); (· · · · ·) corrected fluorescence spectrum of riboflavin (right ordinate). Vertical lines denote wavelengths: λ$_1$, excitation wavelength for sensitized aquations; λ$_2$, wavelength for measurement of riboflavin fluorescence quenching by Cr(NH$_3$)$_5$NCS^{2+}; λ$_3$, wavelength for measurement of fluorescence quenching by Cr(NH$_3$)$_5$Cl^{2+}.

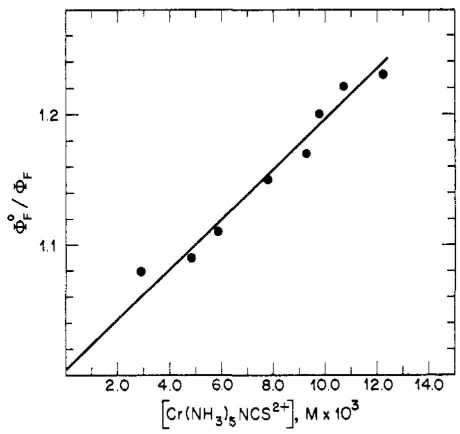

Figure 2. Stern–Volmer plot for quenching of riboflavin fluorescence by Cr(NH$_3$)$_5$NCS^{2+}.

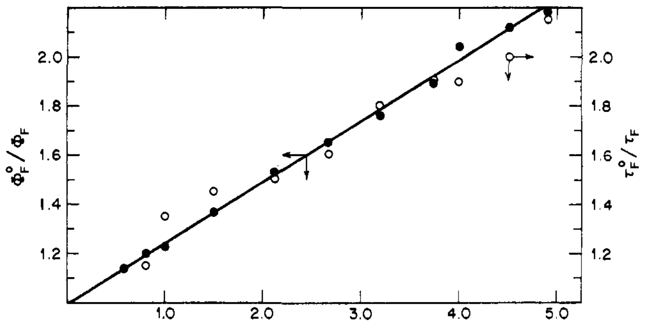

Figure 3. Quenching of riboflavin fluorescence by Cr(NH)$_5$Cl^{2+}: (●) quantum-yield data (left ordinate), (○) lifetime data (right ordinate).

but passed riboflavin (pK_a ~ 0[13]). The ammonia was then eluted with 0.3 M HClO$_4$.[14] The pH of the eluate was adjusted to near neutrality; to the resulting solution was added 30 ml of a solution containing 22 g of sodium tetraborate and 400 g of KBr/l. The pH of the resulting solution was adjusted, if necessary, to fall in the range 8.2–8.6. The coulometric titration[12] was then performed. The procedure was calibrated by standard addition of NH$_4$F; the standard deviation of the procedure was ±1.1%.

Photolysis times were always 15 min or less; thus, corrections for thermal aquation of the chromium complexes were negligible. In all cases in which quantum yields for ammonia release were measured, decomposition of chromium complex was held at <6%. When necessary, solutions were degassed by freeze–thaw cycles.[5] All quantum yields were corrected for direct photolysis of the complex *via* both absorption of incident light[6] and absorption of riboflavin fluorescence.[1g] All runs in which detectable decomposition of riboflavin occurred were rejected.

Results

Fluorescence Quenching. Both Cr(NH$_3$)$_5$NCS^{2+} and Cr(NH$_3$)$_5$Cl^{2+} strongly quenched riboflavin fluorescence. Solubility limitations hindered determination of a reliable value for the rate constant for quenching of singlet riboflavin by Cr(NH$_3$)$_5$NCS^{2+}. The quenching data for this complex (Figure 2), when fitted to the Stern–Volmer equation (1), yield for K a value of 19.7

$$\frac{\Phi_F^0}{\Phi_F} - 1 = K[Q] = k_Q\tau_0[Q] = \frac{\tau_0}{\tau} - 1 \qquad (1)$$

± 0.8 M^{-1}. Taking for τ_0 a value[2] of 4.7 ± 0.4 × 10^{-9} sec, one obtains k_Q = 4.2 ± 0.6 × 10^9 M^{-1}. Because of the restriction to low values of [Q], no attempt was made to determine k_Q for Cr(NH$_3$)$_5$NCS^{2+} from fluorescence decay times. For Cr(NH$_3$)$_5$Cl^{2+} (Figure 3), K from quantum-yield data (24.4 ± 0.2 M^{-1}) yields for k_Q a value of 5.2 ± 0.5 × 10^9 M^{-1} sec^{-1}. From lifetime data (Figure 3), a value for k_Q of 4.8 ± 0.9 × 10^9 M^{-1} sec^{-1} is obtained, which agrees satisfactorily with that determined from fluorescence yields. For both complexes, the singlet quenching rate constants were comparable to those observed for Cr(H$_2$O)$_6$$^{3+}$ (and other aquo–metal ions) with riboflavin as substrate.[2]

Direct Photoaquation of Chromium Complexes. Quantum yields for direct photoaquation of Cr(NH$_3$)$_5$NCS^{2+} and Cr(NH$_3$)$_5$Cl^{2+} are compared with reported values in Table I.

Sensitized Aquation of Cr(NH$_3$)$_5$NCS^{2+}. Upon excitation (430 nm) of solutions (pH 3.2), 1.20 × 10^{-4} M in riboflavin and ≥1.0 × 10^{-3} M in Cr(NH$_3$)$_5$NCS^{2+}, ammonia release by the complex was detected. No dark reaction between the complex and riboflavin was detected. Spectral changes[2] indicated that the direct and sensitized photolysis formed the same product (presumably *cis*-Cr(NH$_3$)$_4$(H$_2$O)NCS^{2+} [15]). The quantum yield, $\Phi_{NH_3}{}^{obsd}$, for ammonia release varied with initial concentration of complex as shown in Figure 4. No detectable quantity of NCS$^-$ was released unless exposure was continued for a sufficiently long time that appreciable direct photolysis occurred.[16] Degassing had no discernible effect upon observed quantum yields for ammonia release. No postphotolysis effects were noted.

---

(13) L. Michaelis, M. P. Schubert, and C. V. Smythe, *J. Biol. Chem.*, 116, 587 (1936).

(14) E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, 91, 1076 (1969).

(15) E. Zinato and P. Riccieri, *ibid.*, in press; *cf.* ref 37 in E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, *Inorg. Chem.*, 11, 1746 (1972).

(16) Excessive significance should not be ascribed to this result, because the exposure duration was necessarily minimized to decrease corrections for direct photoaquation of the complex. Since the thiocyanate yields are very small under direct photolysis conditions, it is conceivable that in our system, the thiocyanate yield was finite but undetectable due to the rather poor sensitivity of the colorimetric thiocyanate analyses.

Table I. Quantum Yields for Direct Photoaquation[a]

Compound	λ, nm	Φ_{NH_3}	Φ_{NCS^-}	Φ_{Cl^-}	Ref
$Cr(NH_3)_5NCS^{2+}$	430[b]	0.44 ± 0.02[d]	0.023 ± 0.006		This work
	487[c]	0.42 ± 0.01[e]	0.020 ± 0.004		This work
	492	0.47 ± 9%	0.024 ± 3%		14
$Cr(NH_3)_5Cl^{2+}$	430[b]	0.40 ± 0.03[d]		0.004 ± 0.002	This work
	511[c]	0.37 ± 0.02[e]		0.004 ± 0.001	This work
	425	0.377 ± 0.008			*g*
	500	0.353 ± 0.010			*g*
	406	0.38		0.0072	*h*
	546	0.37		0.0045	*h*
	503	0.35[f]		0.01[f]	1f

[a] Temperature = 25.0 ± 0.1°. Initial concentration of complex: 1.00×10^{-2} *M* for $Cr(NH_3)_5NCS^{2+}$, 5.00×10^{-2} *M* for $Cr(NH_3)_5Cl^{2+}$. [b] Wavelengths used in riboflavin-sensitized aquations. [c] Maximum in "L_1" d–d absorption band. [d] Mean of five determinations. [e] Mean of seven determinations. [f] Measured in 50% aqueous ethanol. [g] H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem.* (*Frankfurt am Main*), **57**, 282 (1968). [h] H. F. Wasgestian and H. L. Schläfer, *ibid.*, **62**, 127 (1968).

Sensitized Aquation of $Cr(NH_3)_5Cl^{2+}$. Exposure of solutions of 1.20×10^{-4} *M* riboflavin and $\geq 2.0 \times 10^{-3}$ *M* in $Cr(NH_3)_5Cl^{2+}$ to 430-nm light resulted in release of both NH_3 and Cl^-. The spectral changes observed upon irradiation, determined as difference spectra between photolyzed and unexposed solutions, very closely resembled those previously reported[17] for the direct photoaquation of $Cr(NH_3)_5Cl^{2+}$ to *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. The observed quantum yield for formation of NH_3 varied with initial concentration of complex as shown in Figure 4. In solutions of 3.0×10^{-3} *M* in $Cr(NH_3)_5Cl^{2+}$, the observed quantum yield for Cl^- release was of the order of 0.03 in degassed solutions but decreased to *ca.* 0.002 in solutions containing air.[18] In degassed solutions $>3.0 \times 10^{-3}$ *M* in $Cr(NH_3)_5Cl^{2+}$, the chloride yield appeared to decrease slightly with increasing complex concentration; *e.g.*, at $[Cr(NH_3)_5Cl^{2+}] = 6.00 \times 10^{-3}$ *M*, $\Phi_{Cl}^{obsd} = 0.016 \pm 0.006$. The ammonia yields were unaffected by degassing. No detectable release of either NH_3 or Cl^- occurred in unexposed solutions containing riboflavin and $Cr(NH_3)_5Cl^{2+}$ for periods of 30 min; the longest exposure durations employed in sensitized photolyses were 12 min. No postphotolysis effects were detected.

Discussion

Sensitized aquation of $Cr(NH_3)_5X^{2+}$ ($X^- = Cl^-$, NCS^-) by riboflavin produces predominantly ammonia, rather than X^-, release. There appears to be an emerging pattern of data which implies that, in acidopentaamminechromium(III) complexes, the excited quartet states exhibit principally, and perhaps exclusively, ammonia aquation,[1f,1g,14,19,20] while X^- release is the dominant (but very inefficient) reaction mode of the doublet manifold.[1f,1g,14] Hence, the present observations may suggest that riboflavin-sensitized ammonia release from $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5NCS^{2+}$ proceeds *via* energy transfer from singlet riboflavin to excited quartet states of the complexes. The following scheme is suggested to account for the observations (R = riboflavin).

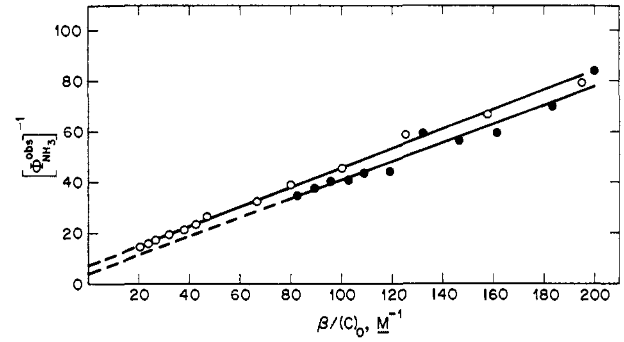

Figure 4. Variation of observed ammonia yield with initial concentration of complex: (●) $Cr(NH_3)_5NCS^{2+}$, (○) $Cr(NH_3)_5Cl^{2+}$.

$$h\nu + R \longrightarrow {}^1R^* \tag{2}$$

$$^1R^* \longrightarrow {}^3R^* \tag{3}$$

$$^1R^* \longrightarrow R\ (+\ h\nu_F) \tag{4}$$

$$^1R^* + Cr(NH_3)_5X^{2+} \longrightarrow R + {}^4[Cr(NH_3)_5X^{2+}]^* \tag{5}$$

$$^1R^* + Cr(NH_3)_5X^{2+} \longrightarrow R + Cr(NH_3)_5X^{2+} \tag{6}$$

$$^4[Cr(NH_3)_5X^{2+}]^* \longrightarrow Cr(NH_3)_4(H_2O)X^{2+} + NH_3 \tag{7}$$

It is quite improbable that ammonia aquation is a consequence of thermal reactions of $Cr(NH_3)_5X^{2+}$ with intermediates formed in photodecomposition of riboflavin. Inasmuch as the photochemistry of riboflavin involves principally reduction processes[21] proceeding by intra- or intermolecular hydrogen atom abstractions resulting in formation of a flavin semiquinone radical,[22] reactions of the chromium complex with intermediates in riboflavin photolysis would almost certainly result in oxidation or reduction of chromium, with rapid release of both NH_3 and X^-, and probably also in the production of transients resulting from oxidation or reduction of the ligands. Such occurrences were not observed. It is worth reemphasizing that care was exercised in rejecting all quantum-yield runs in which detectable decomposition of riboflavin occurred.

It has previously been suggested[1d,h] that excited states of organic molecules which are effective hydrogen atom abstractors (*e.g.*, biacetyl) may abstract a hydrogen from a coordinated ammonia molecule in an

---

(17) M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, 10, 207 (1971).

(18) These values were not detectably decreased by decreasing the temperature from 25 to 5°, so it is unlikely that the chloride was formed by thermal aquation[1f] of product $Cr(NH_3)_4(H_2O)Cl^{2+}$.

(19) H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem.* (*Frankfurt am Main*), 57, 282 (1968).

(20) H. F. Wasgestian and H. L. Schläfer, *ibid.*, 62, 127 (1968).

(21) (a) W. L. Cairns and D. E. Metzler, *J. Amer. Chem. Soc.*, **93**, 2772 (1971); (b) W. M. Moore and C. Baylor, Jr., *ibid.*, **91**, 7171 (1969); (c) P. S. Song and D. E. Metzler, *Photochem. Photobiol.*, **6**, 691 (1967); (d) W. E. Kurtin, M. A. Latino, and P. S. Song, *ibid.*, **6**, 247 (1967).

(22) (a) M. Green and G. Tollin, *ibid.*, 7, 129 (1968); (b) B. Holmstrom, *ibid.*, **3**, 97 (1964).

ammine complex, eventually effecting ammonia release from the complex. Excited states (particularly the lowest triplet[23]) of riboflavin are well known for their proclivity to abstract hydrogen atoms from hydroxylic solvents as well as from the ribityl side chain of the molecule itself. If hydrogen atom abstraction from $Cr(NH_3)_5X^{2+}$ by $^1R^*$ occurred to a significant extent, the production of flavin semiquinone radicals at an appreciable rate would almost certainly result in redox decomposition of the chromium complexes (which, as noted above, is not observed), and it is also highly probable that the observed ammonia yields would be affected by the presence of radical scavengers. In fact, as previously noted, the observed ammonia yields are unaffected by the presence of O_2, and they are also unchanged in the presence of 0.3 *M* methyl methacrylate, an effective scavenger in systems of this type.[3,8] Consequently, all subsequent discussion assumes the formation of quartet excited states of $Cr(NH_3)_5X^{2+}$ by energy transfer from $^1R^*$.[24]

The variation of the observed quantum yield for a singlet-sensitized photoreaction varies with acceptor concentration according to the equation[25]

$$[\Phi_{NH_3}{}^{obsd}]^{-1} = [\Phi_{NH_3}{}^{lim}]^{-1}\left[1 + \frac{\beta}{k_S\tau_R{}^{\circ}[C]}\right] \qquad (8)$$

where k_S is the bimolecular rate constant for sensitization, [C] is the quencher (complex) concentration, $\tau_R{}^{\circ}$ is the lifetime of singlet riboflavin in the absence of quencher, and β is a correction[26] for consumption of acceptor during the experiment. For both $Cr(NH_3)_5NCS^{2+}$ and $Cr(NH_3)_5Cl^{2+}$, $[\Phi_{NH_3}{}^{obsd}]^{-1}$ varies linearly with $[C]^{-1}$ (Figure 4), as predicted by eq 8. In the simplest case, wherein fluorescence quenching produces, with unit efficiency, the "same" excited state formed by direct excitation of the chromium complex, k_S should equal the quenching rate constant, k_Q, and $\Phi_{NH_3}{}^{lim}$ should equal $\Phi_{NH_3}{}^{direct}$. Actually, for $Cr(NH_3)_5Cl^{2+}$, $\Phi_{NH_3}{}^{lim} = 0.18 \pm 0.02$ (from the intercept of Figure 4), whereas $\Phi_{NH_3}{}^{direct} \cong 0.4$ (Table I). The value of k_S, evaluated[25] from the slope/intercept ratio of Figure 4, is $2.7 \pm 0.3 \times 10^9$ M^{-1} sec^{-1}, while $k_Q = 5.2 \pm 0.5 \times 10^9$ M^{-1} sec^{-1}. Similarly, for $Cr(NH_3)_5NCS^{2+}$, $\Phi_{NH_3}{}^{lim} = 0.24 \pm 0.04$, but $\Phi_{NH_3}{}^{direct} = 0.44$ and $k_S = 2.6 \pm 0.4 \times 10^9$ M^{-1} sec^{-1} while $k_Q = 4.2 \pm 0.6 \times 10^9$ M^{-1} sec^{-1}.

The rate of sensitization is smaller than the rate of quenching for both complexes, and, under limiting conditions, the direct photoaquation of each complex is about a factor of 2 more efficient than the sensitized aquation. These two results, considered together, indicate the occurrence of two independent quenching processes, only one of which produces excited quartet $Cr(NH_3)_5X^{2+}$.[27] This "nonenergy-transfer" quenching pathway is denoted by process 6. We then write

$$\frac{k_S}{k_Q} = \delta \qquad (9)$$

where δ denotes the fraction of quenching events resulting in excitation of quencher. For $Cr(NH_3)_5Cl^{2+}$, $\delta = 0.5$ while $\Phi_{NH_3}{}^{lim}/\Phi_{NH_3}{}^{direct} = 0.6$; for $Cr(NH_3)_5NCS^{2+}$, $\delta = 0.6$ while $\Phi_{NH_3}{}^{lim}/\Phi_{NH_3}{}^{direct} = 0.5$. The self-consistency of the two ratios for each complex reinforces the hypothesis of a simple scheme in which quenching occurs by two pathways of approximately equal efficiency, with only one of the quenching processes effecting excitation of the quencher. The nature of the presumed "nonenergy-transfer" path cannot presently be specified.[28]

In agreement with earlier work,[1g,30] sensitized thiocyanate release from $Cr(NH_3)_5NCS^{2+}$ is an inefficient process, though we cannot, in this case, be certain that it is less efficient, relative to ammonia release, in the sensitized than in the direct reaction. However, for $Cr(NH_3)_5Cl^{2+}$, sensitized Cl^- release is definitely detected; $\Phi_{Cl^-}{}^{obsd}$ is sensitive to the presence of O_2, and $\Phi_{Cl^-}{}^{obsd}/\Phi_{NH_3}{}^{obsd}$ is, in degassed solutions, larger for the riboflavin-sensitized case than for direct excitation of the complex.[18] If one assumes that the photodecomposition mode of $Cr(NH_3)_5Cl^{2+}$ in the lowest doublet state is Cl^- aquation, these results *may* indicate sensitization of the doublet excited states of the complex by riboflavin triplet

$$^1R^* \xrightarrow[\text{intersystem crossing}]{} {}^3R^* + Cr(NH_3)_5Cl^{2+} \longrightarrow R + {}^2[Cr(NH_3)_5Cl^{2+}]^* \qquad (10)$$

Indeed, the efficiency of intersystem crossing in unperturbed riboflavin is *ca.* 0.7[31] and the riboflavin triplet is reported[32] to be highly susceptible to oxygen quenching. Although the riboflavin triplet is very short lived[33] in solution (it could not be detected by a flash-photolysis apparatus capable of 10-μsec time resolution[2]), it appears susceptible to quenching by a variety of metal complexes.[34] Consistent with this picture is the qualitative observation that $\Phi_{NH_3}{}^{obsd}/\Phi_{Cl^-}{}^{obsd}$ increases as the initial concentration of $Cr(NH_3)_5Cl^{2+}$ is increased, which is the expected result if process 5 competes effectively with process 3. Unequivocal evidence for sensitization of doublet $Cr(NH_3)_5Cl^{2+}$ is not available, owing (*inter alia*) to the absence of useful direct photolysis studies in the doublet absorption region of the complex. That the oxygen-inhibited sensitized chloride aquation occurs *via* a

---

(23) P. S. Song and W. E. Kurtin, *Mol. Photochem.*, 1, 1 (1969).

(24) Slopes of Stern–Volmer plots were unaffected by changes in the riboflavin concentration, in contrast to what would be predicted[25] if reverse energy transfer occurred with appreciable efficiency or if hydrogen atom abstraction from coordinated NH_3 by $^1R^*$ were an important quenching process.

(25) P. J. Wagner in "Creation and Detection of the Excited State," Vol. 1A, A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 4.

(26) A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, 90, 5943 (1968).

(27) It could be argued that the excited state populated by energy transfer from $^1R^*$ is less reactive than that formed by direct excitation. In addition to being entirely speculative, this argument fails to rationalize the observed differences between k_S and k_Q.

(28) If the "non-energy-transfer" singlet-quenching process involved enhancement of the singlet-triplet intersystem-crossing efficiency[29] of riboflavin, one might expect the efficiency of its anaerobic photobleaching to be enhanced by the chromium complexes. Meaningful studies of this effect cannot be made because, as noted previously, radicals produced in the riboflavin photobleaching tend to destroy the chromium complexes.

(29) (a) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 66, 199 (1966); (b) B. Brocklehurst, *Radiat. Res. Rev.*, 2, 149 (1970); (c) P. Yuster and S. I. Weissman, *J. Chem. Phys.*, 17, 1182 (1949).

(30) A. W. Adamson, J. E. Martin, and F. D. Camessei, *J. Amer. Chem. Soc.*, 91, 7530 (1969).

(31) (a) P. S. Song in "Flavins and Flavoproteins," H. Kamin, Ed., University Park Press, Baltimore, Md., 1971, p 37; (b) B. Nathanson, M. Brody, S. S. Brody, and S. B. Broyde, *Photochem. Photobiol.*, 6, 177 (1967).

(32) T. A. Moore and P. S. Song, *ibid.*, 10, 13 (1969).

(33) L. Tegner and B. Holmstrom, *ibid.*, 5, 223 (1966).

(34) A. W. Varnes, Ph.D. Thesis, Indiana University, 1970.

second quartet excited state[35] of $Cr(NH_3)_5Cl^{2+}$ is an unattractive postulate, due to the lack of oxygen quenching of the flavin singlet,[2] the low energy of the flavin triplet,[31] and the absence of efficient Cl^- release brought about by direct photolysis of the complex.

Three general implications of these results are stressed. First, while there are several well-documented examples[1a, 1f, 1g, 36] in which coordination compounds do not quench excited singlet states of aromatic molecules, it is clear[1g,h] that energy transfer from organic singlets to "spin-allowed" excited states of metal complexes can be highly efficient. Thus, the application of quenching and sensitization experiments to inorganic photochemistry is not always restricted to "spin-forbidden" excited states. Second, energy transfer quenching of excited organic molecules by metal complexes may in many instances be competitive with quenching processes not producing excited states of the quencher. We presently know virtually nothing about the factors responsible for the greatly varying susceptibility of different photoexcited aromatic molecules to quenching by transition metal complexes or about the detailed nature of "non-energy-transfer" quenching. Finally, the ability of flavins to act as singlet energy donors in metal-containing systems may have important implications for flavin-dependent photobiology.[37] Additional studies of interactions of photoexcited flavins with metal complexes are in progress in this laboratory.

Acknowledgment. This work was assisted by financial support from the National Science Foundation (Grant GP-26109).

---

(35) There is evidence for involvement of two reactive excited quartet states, exhibiting different reaction modes, in some mixed-ligand Cr(III) complexes: M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, **94**, 7152 (1972).

(36) M. A. Scandola and F. Scandola, *ibid.*, **92**, 7278 (1970).

(37) P. Hemmerich, G. Nagelschneider, and C. Veeger, *Fed. Eur. Biochem. Soc. Lett.*, **8**, 69 (1970).

Spectroscopic and Structural Characterization of Ruthenium(II) Carbonyl–Porphine Complexes

J. J. Bonnet,[1] S. S. Eaton,[2] G. R. Eaton,[2] R. H. Holm,[2] and James A. Ibers*[1]

Contribution from the Departments of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Northwestern University, Evanston, Illinois 60201. *Received October 11, 1972*

Abstract: Reaction of $Ru_3(CO)_{12}$ with tetraphenylporphine and tetra-*p*-isopropylphenylporphine affords ruthenium(II) carbonyl–porphine complexes which in past investigations have been formulated as the monocarbonyls Ru(CO)(TPP) and Ru(CO)(*i*-Pr-TPP), respectively. A recent X-ray study of the tetraphenylporphine reaction product recrystallized from chloroform–ethanol has led to reformulation of this product as the *dicarbonyl* $Ru(CO)_2(TPP)$, containing markedly bent (154°) Ru–C–O bonds. The nature of these compounds after recrystallization from chloroform–ethanol has been reinvestigated. Chemical and spectroscopic experiments show (i) no CO evolution when monopyridinates are formed with excess pyridine, (ii) no mass spectral peaks due to dicarbonyl ions such as $Ru(CO)_2TPP^+$, (iii) an ABCD pattern of phenyl *o*-H and *m*-H pmr signals (*i*-Pr-TPP complex) which collapses to an AA′BB′ pattern at elevated temperatures, (iv) methyl and methylene pmr signals (*i*-Pr-TPP complex) whose chemical shifts are indicative of axially coordinated ethanol. These observations are incompatible with the dicarbonyl description but are consistent with the formulations Ru(CO)(TPP)(EtOH) and Ru(CO)(*i*-Pr-TPP)(EtOH). The composition and structure of the TPP reaction product has been confirmed by an X-ray determination. The compound Ru(CO)(TPP)(EtOH) crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system in a cell of dimensions a = 10.078 (4), b = 11.819 (5), c = 8.883 (4) Å; α = 101.37 (5), β = 106.12 (4), and γ = 65.91 (3)°. A density of 1.416 g cm^{-3} calculated for one molecule in the unit cell agrees with that of 1.39 (1) g cm^{-3} observed by flotation of the crystals in aqueous $ZnCl_2$. The structure has been solved and refined by standard methods, based on 2906 unique reflections collected by counter methods using monochromatized Mo Kα radiation. The final agreement index is 7.5%. The molecule has crystallographically imposed $\bar{1}$ symmetry and hence the CO and EtOH groups are disordered and the RuN_4 portion of the molecule is planar. The overall deviations from planarity of the porphinato core are very small. The distances within the porphinato core are in good agreement with those reported for other metalloporphyrins. The Ru–O(Et) distance is 2.21 (2) Å, and the EtOH group has its expected geometry. The Ru–C (of CO) distance is 1.77 (2) Å and the Ru–C–O bond is essentially linear, the bond angle being 175.8 (1.9)°.

In recent years the range of metalloporphine and porphyrin complexes has been expanded by the synthesis of species containing second- and third-row transition metal ions,[3] including ruthenium(II, III).[4–11] Ruthenium(II) carbonyl–porphine or –porphyrin complexes undergo inter- and intramolecular ligand exchange reactions at rates which allow the study of these

---

(1) Northwestern University.

(2) Massachusetts Institute of Technology.

(3) P. Hambright, *Coord. Chem. Rev.*, **6**, 247 (1971).

(4) E. B. Fleischer, R. Thorp, and D. Venerable, *Chem. Commun.*, 475 (1969).

(5) B. C. Chow and I. A. Cohen, *Bioinorg. Chem.*, **1**, 57 (1971).

(6) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.*, **93**, 1820 (1971).

(7) M. Tsutsui, D, Ostfeld, J. N. Francis, and L. M. Hoffman, *J. Coord. Chem.*, **1**, 115 (1971).

(8) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.*, **32**, C52 (1971).

(9) S. S. Eaton, G. R. Eaton, and R. H. Holm, *ibid.*, **39**, 179 (1972).

(10) D. Cullen, E. Meyer, Jr., T. S. Srivastara, and M. Tsutsui, *J. Chem. Soc., Chem. Commun.*, 584 (1972).

(11) G. W. Sovocool, F. R. Hopf, and D. G. Whitten, *J. Amer. Chem. Soc.*, **94**, 4350 (1972).