

Photosensitized Aquation Reactions of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ *

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Biacetyl and acridinium ion but not Michler's ketone sensitize the aquation of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ in 0.1 N sulfuric acid solution. Phosphorescence quenching occurs in first system, and the kinetics of this and of the sensitized reaction in the presence and absence of oxygen indicate that transfer of excitation energy occurs from the biacetyl first triplet state. The reaction is entirely one of ammonia aquation, indicating that the first quartet excited state of the complex is populated.

Acridinium ion sensitizes both ammonia and thiocyanate aquation, the presence of oxygen affecting the latter but not the former mode. The kinetics of the fluorescence quenching by the complex and that of the sensitized ammonia aquation indicate that the latter process is induced by the first singlet excited state of acridinium ion, along with a small component of thiocyanate aquation. The oxygen dependence results indicate that the remainder of the thiocyanate aquation is induced by the first triplet excited state of the donor. It is concluded that, in this system, the singlet excited state of acridinium ion populates the first quartet excited state of the complex ion while the triplet state populates the doublet excited state of the complex. Some of the complexities of excited state processes of Cr(III) complexes are discussed.

Das Biacetyl und das Acridinium, nicht aber Michler's Keton sensibilisieren die Aquotisierung von $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ in 0,1 n-Schwefelsäure-Lösung. Phosphoreszenzlöschung tritt im erstgenannten System auf und seine Kinetik, sowie die der sensibilisierten Reaktion, in Gegenwart sowie unter Ausschluß von Sauerstoff weist darauf hin, daß der Übergang der Anregungsenergie vom ersten Triplettzustand des Biacetyls stattfindet. Die Reaktion führt anschließend zur Aquotisierung von Ammoniak. Diese Tatsache weist darauf hin, daß der erste angeregte Quartettzustand des Komplexes besetzt wird. Das Acridinium sensibilisiert sowohl die Ammoniak- als auch die Thiocyanat-Aquotisierung, wobei die Gegenwart von Sauerstoff zwar letztere, jedoch nicht erstere beeinflusst. Die Kinetik der Fluoreszenzlöschung durch den Komplex sowie die der sensibilisierten Ammoniak-Aquotisierung deuten darauf hin, daß letzterer Prozeß durch den ersten angeregten Singulettzustand des Acridiniums induziert wird, zusammen mit einem kleinen Teil der Thiocyanat-Aquotisierung. Die Sauerstoffabhängigkeit zeigt, daß der Rest der Thiocyanat-Aquotisierung durch den ersten angeregten Triplettzustand des Donors induziert wird. Daraus wird der Schluß gezogen, daß in diesem System der angeregte Singletzustand des Acridiniums zur Besetzung des ersten angeregten Quartettzustands des Komplexes führt, wohingegen die Energie des Triplettzustands auf den angeregten Dublettzustand des Komplexes übertragen wird. Einige Probleme der Prozesse zwischen angeregten Zuständen von Cr(III)-Komplexen werden diskutiert.

Les ions biacétyle et acridinium, mais non pas la cétone de Michler, sensibilisent l'hydratation de $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ dans une solution d'acide sulfurique 0,1 N. L'extinction de la phosphorescence se produit dans le premier système; sa cinétique ainsi que celle de la réaction sensibilisée en présence et en l'absence d'oxygène indiquent que le transfert d'énergie d'excitation se produit à partir du premier état triplet du biacétyle. La réaction est totalement celle de l'hydratation de l'ammoniac, ce qui indique que le premier quartet excité du complexe se trouve peuplé.

L'ion acridinium sensibilise l'hydratation de l'ammoniac et du thiocyanate seule cette dernière réaction étant sensible à l'oxygène. La cinétique de l'extinction de fluorescence par le complexe ainsé

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que celle de l'hydratation sensibilisée de l'ammoniac indiquent que ce dernier processus est induit par le premier état excité singulet de l'ion acridinium, avec parallèlement une faible hydratation du thiocyanate. Les résultats sur le rôle de l'oxygène montrent que le restant de l'hydratation du thiocyanate est induit par le premier triplet excité du donneur. On en conclue que dans ce système l'état excité singulet de l'ion acridinium peuple le premier quartet excité de l'ion complexe tandis que l'état triplet peuple l'état excité doublet du complexe. On discute certains détails complexes des processus d'excitation des complexes de Cr (III).

Introduction

The photochemistry of Cr(III) complexes is perhaps the best studied of any family of transition metal coordination compounds. It is summarized in several review articles [1-3]. Absorption of light in the visible or near ultraviolet leads to photosubstitution reactions in relatively high quantum yield in the case of O_h complexes, and in rather variable quantum yield if more than one type of ligand is coordinated. In this last case, the photolysis product is not necessarily that observed in the thermal reaction, but is governed by certain empirical rules [4]. Their nature suggests that reaction occurs primarily from the lowest ligand field quartet excited state (${}^4T_{2g}$ in O_h symmetry) and only secondarily from the first doublet excited state (2E_g) as reached by intersystem crossing.

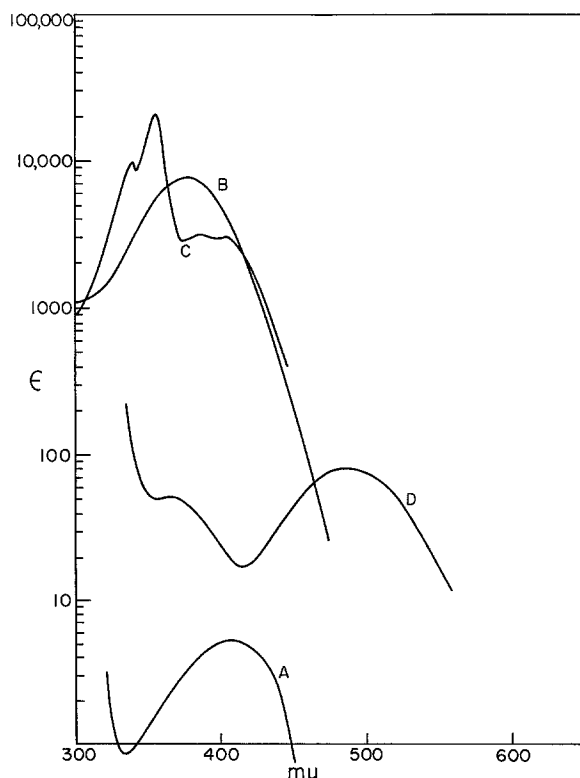


Fig. 1. Absorption spectra in aqueous media at 25° C; A: Biacetyl; B: Michler's ketone; C: Acridinium ion; D: $\text{Cr}(\text{NH}_3)_5(\text{NCS})_2^{2+}$

The above conclusion is supported by a study of the photochemistry of aqueous $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ [5]. The finding was that while the thermal reaction is exclusively one of thiocyanate aquation, the photoreaction consists primarily of ammonia aquation and that the ratio of the two reaction modes is 15.3:1, 22.2:1, and 8.2:1, on irradiation of the second and first ligand field bands, L_2 and L_1 , and the doublet band, D , respectively. These bands are shown in Fig. 1; in O_h symmetry the corresponding ligand field transitions would be designated ${}^4A_{2g} \rightarrow {}^4T_{1g}$, ${}^4A_{2g} \rightarrow {}^4T_{2g}$, and ${}^4A_{2g} \rightarrow {}^2E_g$, again respectively. Further splitting occurs on the descent of symmetry to C_{4v} , and the terms 4L_1 and 2D will be used to denote the lowest ligand field quartet and doublet states, respectively.

These results made it clear that at least two excited states are direct precursors to chemical reaction in this system, and, in fact, they could be explained on the basis that only ammonia aquation occurred from the first quartet excited state and only thiocyanate aquation from the doublet state. The appearance of some of the latter reaction mode on irradiation of the L_2 or L_1 bands then reflects the degree of intersystem crossing, and the ammonia aquation component in the photochemistry of the D band is explained as due to absorption in the tail of the L_1 band. Similar results have been reported for $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ [6, 7].

A complication that may be special to transition metal complexes is that of the high degree of distortion in the spin allowed ligand field excited states. In the case of Cr(III) complexes the fluorescence, where observed, is at longer wave lengths than the phosphorescence [8]. As illustrated in Fig. 2, the L_1 band

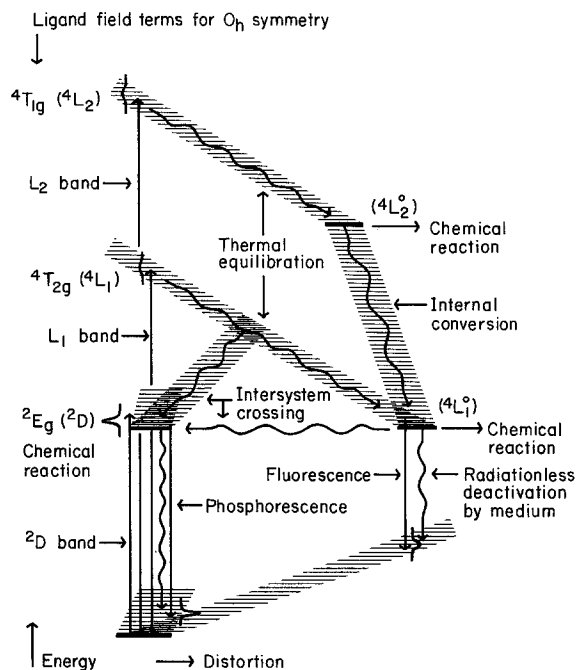


Fig. 2. Energy level-distortion diagram for Cr(III) complexes

Table 1. *Excited state energies (kcal/mole)*

Species	Singlet	Triplet	4L_1	2D
Acridinium ion	62.2 ^a	49.8 ^b , 45.5 ^c		
Biacetyl	61.5 ^a	56.1 ^a		
Michler's ketone		62 ^d		
Cr(NH ₃) ₅ (NCS) ²⁺			58.7 ^e	41.8 ^e

^a Emission band maxima in 0.1 N H₂SO₄.

^b Value for 3,6 diamino acridinium ion (96% ethanol, 20° C), from Zanker, V., Körber, W.: *Z. angew. Phys.* **14**, 32 (1962).

^c Acridine molecule (*S*→*T* absorption in CHCl₃ under 75 atm oxygen), from Evans, D. F.: *J. chem. Soc. (London)* **1957**, 1351.

^d Value for ethanol-propane-ether solvent at 90° C, from Lewis, G. N., Kasha, M.: *J. Amer. chem. Soc.* **66**, 2100 (1944).

^e Absorption band maxima in 0.1 N H₂SO₄. The $^4L_1^0$ energy appears to be close to the 2D energy, as judged from the tailing of the L_1 band.

maximum corresponds to a high vibrational level of the 4L_1 state, and the true (non vibrationally excited) state, $^4L_1^0$, may be close to or below the 2D state. The distortion indicated by the abscissa of Fig. 2 may be one of bond length changes or may be to a point group not contained by that of the ground state, which is a reason for using the designation $^4L_1^0$ rather than a representation of the C_{4v} group. As indicated in the figure, vibrational excitation may carry the nuclear positions along one or another distortion path, depending on the vibrational coordinate or mode (see Discussion).

Because of the distortion aspect, there is a distinct possibility that intersystem crossing to the 2D state occurs more readily from the 4L_1 than from the $^4L_1^0$ region of states. A direct population of $^4L_1^0$ might therefore yield a cleaner photochemistry than that by absorption at the L_1 band maximum. Also, direct population of the 2D state would avoid the ambiguity in direct photolysis that part of the absorption in the region of the *D* band is into the tail of the L_1 band. The indicated alternative approach is thus one of excitation energy transfer.

We have communicated a preliminary finding that it is possible to photosensitize reactions of Cr(III) complexes [9], and the present paper details the results for aqueous Cr(NH₃)₅(NCS)²⁺. The two principal sensitizers used are acridinium ion and biacetyl, both water soluble. Acridinium ion shows only fluorescence, but the energies of its triplet and first singlet excited states are known; biacetyl both fluoresces and phosphoresces, again from known energy states. As shown in Table 1, there is a degree of matching between these energies and those of the 4L_1 and 2D states of the complex. Some results are also reported using Michler's ketone as sensitizer, data for which are included in the Table. It was hoped that use of these sensitizers would allow the identification of specific excited state chemistries for the complex.

Experimental

Materials. The complex Cr(NH₃)₅(NCS)(ClO₄)₂ was prepared by a described procedure [5]; its visible absorption spectrum agreed well with that reported. Acridine (Aldrich Chemical Co., A2360-9) was recrystallized re-

peatedly from ethanol until a white solid was obtained, mp. 110–111° C. Biacetyl (Matheson, Coleman, and Bell Co., BX1660) was distilled in nitrogen atmosphere (bp. 89° C) and stored in the dark. Michler's ketone, 4,4' bis-(dimethylamino)benzophenone (Eastman Organic Chemicals 243) was recrystallized twice from methanol.

Analytical Procedures. Free thiocyanate ion was determined essentially as previously described [5]. An aliquot of either the dark or the irradiated solution was diluted at least 4:1 with a solution 0.1 M in $\text{Fe}(\text{NO}_3)_3$ and 0.5 N in HClO_4 . The optical density was then determined at 450 nm where the iron-thiocyanate complex which forms has an optical density of $4.30 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

Released ammonia was determined indirectly through a procedure suggested by the previous work [5]. The complex $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCS})^{2+}$ undergoes a base catalyzed aquation of the thiocyanate ion, in contrast to $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$, which does not. An aliquot of solution was neutralized with 1 N NaOH and then diluted two fold with a pH 7 phosphate buffer. The mixture was allowed to stand for two and one half hours in the dark at room temperature to allow the thiocyanate aquation to go to completion, and then analyzed for thiocyanate ion as described above. Correction was made for the amount of thiocyanate ion already present.

Photolysis Equipment and Procedures. Photolyses were carried out either using an AH-6 lamp in a configuration previously described [5], or a 202 high pressure mercury lamp in a 911 lanphousing (PEK Inc.). Monochromatization was effected by means of a BL-410 (Bausch and Lomb) interference filter and a CS-O-51 (Corning) blocking filter, which passed a band whose peak was 410 nm with a half width of 10 nm.

Solutions to be irradiated were placed in a water jacketed pyrex cell held at the desired temperature and bubbled with an appropriate gas, Ar for oxygen removal, O_2 or air if a known O_2 content was desired. The respective oxygen concentrations were 1.3×10^{-8} M, 1.6×10^{-4} M, and 1.3×10^{-3} M; these values were estimated from the Henry's Law constant for oxygen, the first value reflecting the manufacturers statement of maximum impurity in the argon gas used. The bubble train was so located as not to intercept the light beam. The gassing procedure, which was begun 45 minutes prior to an irradiation procedure, also served to keep the solution mixed. A companion dark solution was always present, at the same temperature, to allow correction for thermal aquation.

Ferrioxalate actinometry was used [10]; variation in lamp intensity during a run was about one percent, the actual value of the adsorbed intensity being about 3×10^{-8} einstein/sec. The total extent of photolysis of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ varied from about 4% (runs labelled short) to about 20% (runs labelled long). The "long" irradiations were needed if thiocyanate aquation was to be measured because of the low quantum yield for this reaction mode.

All solutions were 0.1 N in sulfuric acid. This choice of medium was made for the same reason as in the previous work [5] as well as to allow comparison of ordinary and sensitized behaviour. Acridine was present entirely as acridinium ion ($pK_a = 5.45$) [11]. The total optical densities of the solutions irradiated were generally between 1.20 and 1.26, with the concentrations of

sensitizer and of complex adjusted so that their ratio of light absorption was at least 70:1. The sensitizer concentrations were 4.6×10^{-4} M for acridine and 0.23 M for biacetyl; that of the complex was less than about 10^{-3} M. The absorption spectra for the sensitizers are included in Fig. 1. The fluorescence of acridinium ion, while fairly pronounced, did not appear to perturb the measured absorption spectrum as this was found to be independent of the positioning of the solution with respect to the slit system of the Cary Model 14R spectrophotometer used.

Emission studies. Emission quantum yields were determined by means of an Aminco emission spectrophotometer using quinine sulfate as standard [12]. Fluorescence lifetimes were determined with a TRW nanosecond lifetime apparatus (Model 75A Decay Time Fluorimeter, Model 31A Nanosecond Spectral Source with nitrogen lamp, and Model 32A Decay Time Computer). Biacetyl fluorescence lifetimes were measured as follows. Excitation was effected with a Strobolume lamp (type 1532C, General Radio Co.) operated in the low intensity range with flashes triggered manually. The exciting light passed through a Corning blocking filter CS-7-70, and the emitted light was filtered by a combination Corning CS-3-71 filter and Bausch and Lomb 520 interference filter, which gave a peak transmission at 520 nm, or close to the phosphorescence peak for biacetyl. An RCA 931A photomultiplier tube (760 V, 33 k Ω load resistor) detected the emission, and the signal was displayed on a Tektronix 564 storage oscilloscope with Type 3A1 dual trace amplifier. The flash as monitored with a blank showed no trace in the 50 to 180 μ sec decay interval of the phosphorescence.

Our findings, along with relevant literature values, are summarized in Table 2.

Correction for Reabsorption of Acridinium Ion Fluorescence. The large quantum yield for acridinium ion fluorescence, 0.77, and the fact that the fluorescence spectrum nearly coincides with the L_1 absorption band of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ necessitated a correction for direct photolysis of the

Table 2. *Emission characteristics of biacetyl and acridine*

Donor	Solvent	ϕ_f^0	τ_f (sec)	ϕ_p^0	τ_p (sec)	Ref.
Biacetyl	0.1 N H_2SO_4	7.5×10^{-4}	8×10^{-9}	2.7×10^{-3}	6.2×10^{-5}	a
	Water				0.23×10^{-3}	b
Acridinium ion	0.1 N H_2SO_4	0.77	4.3×10^{-8}			a
	Water		3.8×10^{-8}			c
Acridine	Ethanol	0.80	3.6×10^{-8}			d
	Water		3.8×10^{-9}			c
3,6 diamino acridinium ion	Ethanol	0.16	2×10^{-9}			d
	96% ethanol	0.74		0.03	1.44(77°K)	e

^a This work.

^b Bäckström, H. L. J., Sandros, N.: Acta chem. scand. **12**, 823 (1958).

^c Bennett, R. G.: Rev. Sci. Inst. **31**, 1275 (1960).

^d Zanker, V., Rammensee, H.: Z. angew. Phys. **12**, 237 (1960).

^e — Körber, W.: Z. angew. Phys. **14**, 43 (1962).

complex by this path. An analytical treatment is in principle possible, but is rather difficult. For example, some experiments were made in which the angular distribution of the fluorescence was determined by means of a Brice-Phoenix Universal Lightscattering Photometer (Model 1000-D). The fluorescence was viewed through a filter combination which essentially eliminated the stimulating light at 436 nm, but passed light at the wavelength of the fluorescence maximum; there was a several fold greater intensity in the forward direction over that at 90° ; the effect is undoubtedly due to the angular variation of the fluorescing volume as seen by the scanning photomultiplier [13]. The same effect was observed using fluorescein as the emitter.

The effective directional anisotropy of the fluorescent light was confirmed by two qualitative experiments. In the first, three 1 cm radius \times 1 cm cells were placed in series, the first and last containing a solution of acridinium and complex ions, and the middle one, aqueous FeCl_4^- of concentration such as to intercept the stimulating light at 410 nm, but to pass the 460 nm fluoresced light from the first cell. Appreciable ammonia aqutation of the complex occurred in the third cell. On the other hand, if the configuration was one of two concentric cells, both filled with the solution of acridinium and complex ions, but only the center one irradiated, then the fluorescence induced photolysis of the solution in the other or concentric cell was negligible in comparison to that produced in the central one.

The actual correction for fluorescence induced photolysis was determined empirically as follows. Experiments were carried out on solutions 1×10^{-3} and 5×10^{-4} M in complex, 4.6×10^{-4} M in acridinium ion, and 0.1 N in sulfuric acid, including cells of the same size (ca. 2 cm radius) as in the rest of the sensitization experiments, but of various depths. The results, shown in Fig. 3, allow extrapolation to zero cell depth and hence to zero fluorescence in-

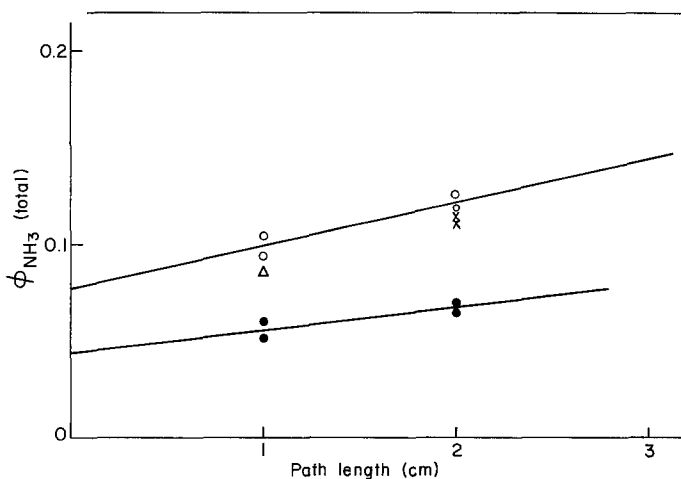


Fig. 3. Fluorescence photolysis of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ by acridinium ion; 10^{-3} M complex; cell radius: \circ 1 cm, \times 2 cm, Δ 2.8 cm. 5×10^{-4} M complex; cell radius: \bullet 1 cm

duced photolysis. The remaining sensitization experiments were all performed with a 2 cm path length cell, and the correction for fluorescence induced photolysis was interpolated from the data of Fig. 3; it amounted to 30% to 37% of the total ammonia photolysis. The same concentration of acridine was used in all the experiments, so no adjustments for variation in this factor were needed.

The observed ammonia and thiocyanate aquations were corrected in the following manner. The ammonia release was reduced by an amount Δ_{NH_3} , due to fluorescence photolysis, and then further by the amount calculated to have been formed by direct photolysis due to the fraction of incident 410 nm light directly absorbed by the complex, using the quantum yield of 0.46 from the previous study [5]. The released thiocyanate was corrected for dark reaction, for fluorescence photolysis by the amount $\Delta_{\text{NH}_3}/22$ (this being the previously determined quantum yield ratio at around 500 nm), and then for direct photolysis, using a quantum yield figure of 0.026. The effect of these series of corrections was to make the ammonia and thiocyanate release due to sensitized reaction about half of the total observed values.

Results

Quenching of Luminescence by $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$. Addition of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ to aqueous deaerated solutions 0.1 N in H_2SO_4 and containing either biacetyl or acridine resulted in phosphorescence and fluorescence quenching, respectively. The effect is illustrated in the case of biacetyl by Fig. 1 of Ref. [9], and the results for a typical series of experiments with acridine are shown in Fig. 4. Relative fluorescence and phosphorescence yields were determined by fitting the emission spectra with a gaussian curve analyser (DuPont Model 310), which then gave the areas. The procedure is not of the highest accuracy, partly because each determination made use of a separately prepared solution, and partly because the spectra are not exactly gaussian in shape.

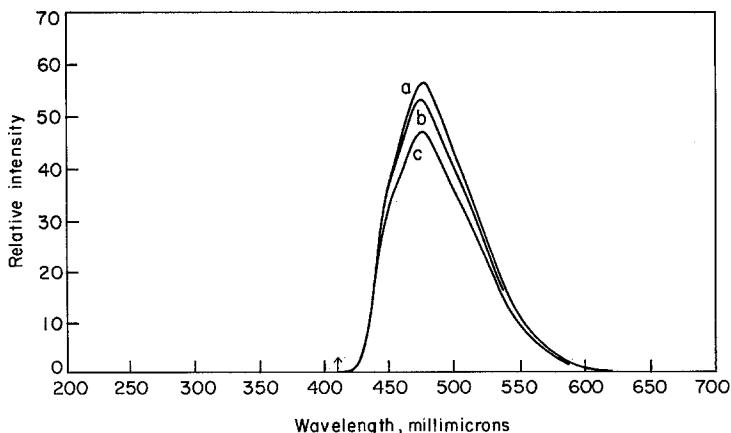


Fig. 4. Quenching of acridinium ion fluorescence by $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$; a) no added complex; b) 5.13×10^{-4} M; c) 6.65×10^{-4} M (all solutions 4.6×10^{-4} M in acridine and 0.1 N in H_2SO_4)

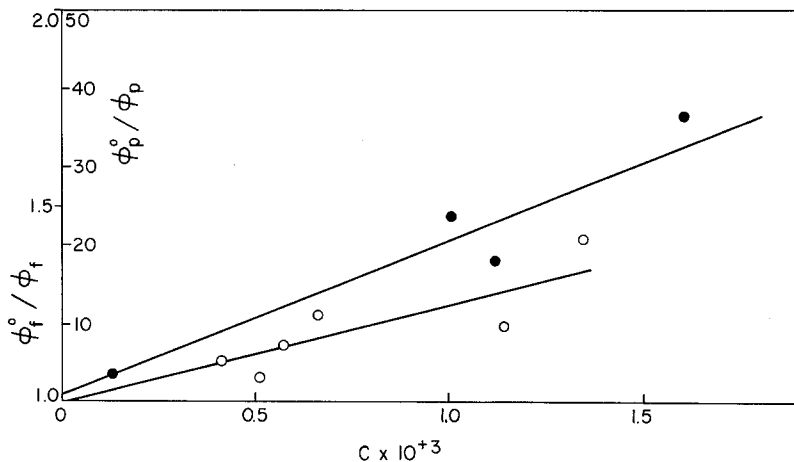


Fig. 5. Emission quenching by $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$; ○ acridinium ion fluorescence (outer scale); ● biacetyl phosphorescence (inner scale)

The results, plotted in Fig. 5 according to the Stern-Volmer equations,

$$\phi_p^0/\phi_p = 1 + \beta_p C_0, \quad (1)$$

$$\phi_f^0/\phi_f = 1 + \beta_f C_0, \quad (2)$$

show approximately linear behaviour. The least squares values for the slopes are given in Table 3 (C_0 denotes the complex concentration, ϕ , quantum yield, and the subscripts f and p refer to fluorescence and phosphorescence respectively).

Photosensitization Results. Photosensitized aquation was observed with biacetyl and acridinium ion as sensitizers, but no effect could be detected when Michler's ketone was used (although some ammonia aquation was observed when an acetone-water medium was used [9]). As noted in a previous publication [14], photosensitized reactions are expected to obey an equation of the form

$$1/\phi_c = \alpha_c + \beta_c \beta / C_0 \quad (3)$$

if sensitization is in simple competition with other deactivation processes. The quantity β is the function $[C_0/(C_0 - C)] \ln(C_0/C)$, which allows for consumption of the acceptor, and was generally less than 1.1 in our experiments; ϕ_c is the quantum yield for a given sensitized reaction.

The data for sensitization by biacetyl obeyed Eq. (3) well and, as shown in Fig. 2 of Ref. [9], the slope β_c increased with increasing oxygen content. Only ammonia aquation occurred, there being less than one percent of a thiocyanate aquation component. Acridinium ion sensitization led to both ammonia and thiocyanate aquation, however, and the values for ϕ_{NH_3} are plotted in Fig. 6 according to Eq. (3). While a small temperature dependence is indicated, the results at 25°C were essentially invariant to time of irradiation ("long" or "short", see Experimental) and to oxygen content. A single least squares intercept and slope is therefore reported in Table 3 for each temperature.

Table 3. Results of quenching and sensitization experiments

Sensitizer	Values of indicated constants			
	Oxygen concentration, M			
	10°	25°		
	1.3×10^{-8}	1.3×10^{-8}	2.6×10^{-4}	1.3×10^{-3}
	M	M	M	M
Biacetyl				
β_p, M^{-1}		4×10^4		
α_{NH_3}		4.9	4.9	5.0
β_{NH_3}, M		ca. 10^{-4}	2.1×10^{-3}	5.6×10^{-3}
Acridinium ion				
β_f, M^{-1}		260		
α_{NH_3}	3.8	4.9	(4.9)	(4.9)
β_{NH_3}, M	0.013	0.010	(0.010)	(0.010)
α_{NCS}	160	140	110	113
β_{NCS}, M	0.21	0.13	0.18	0.23

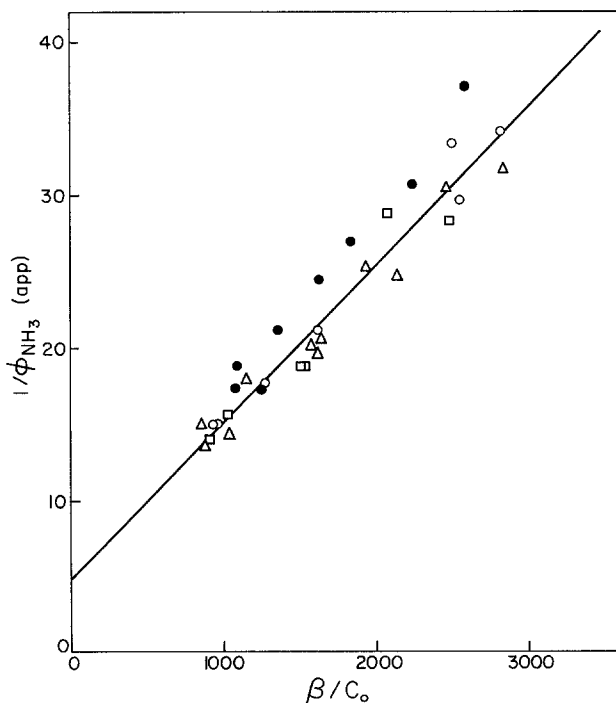


Fig. 6. Acridinium ion sensitized ammonia aequation of $Cr(NH_3)_5(NCS)^{2+}$ in 0.1 N H_2SO_4 ; \circ argon bubbled, 25° C, short irradiation; Δ argon bubbled, 25° C, long irradiation; \square oxygen bubbled, 25° C, long irradiation; \bullet argon bubbled, 10° C, long irradiation. (See Experimental for explanation)

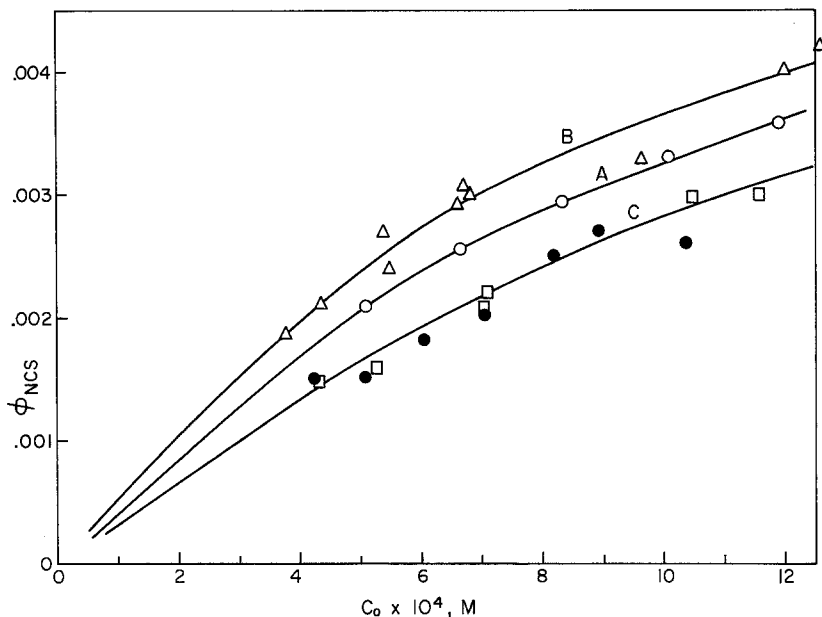


Fig. 7. Acridinium ion sensitized thiocyanate aquation of $\text{Cr}(\text{NH}_3)_5(\text{NCS})^{2+}$ in 0.1 N H_2SO_4 , long irradiations (see Experimental); Δ argon bubbled, 25° C; \circ air bubbled, 25° C; \square oxygen bubbled, 25° C; \bullet argon bubbled, 10° C

Sensitized thiocyanate aquation also occurred, in ten to twenty fold smaller yield, as shown in Fig. 7. The plot is of ϕ_{NCS} vs. C_0 ; while Eq. (3) is theoretically not applicable, the data showed essentially linear behaviour when so plotted, and the results of least squares fitting to this equation are included in Table 3. By either presentation it is evident that there is now a significant effect of dissolved oxygen. It should be emphasized that each point represents a separate experiment and this as well as the large corrections for direct and fluorescence photolysis are undoubtedly responsible for the considerable degree of scatter in Figs. 6 and 7.

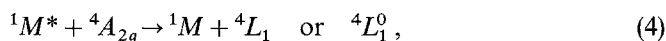
There is always a question in sensitization experiments as to whether chemical reaction has occurred between the sensitizer and the acceptor. In the case of acridine, the total sensitizer concentration was comparable to that of *reacted* complex. Since no spectral changes occurred in the irradiated solutions other than those ascribable to ammonia (and some thiocyanate) aquation, we conclude that no consumption of sensitizer occurred. It is consistent with our observations that acridine does not show a photochemical reaction with dissolved oxygen [15], although more highly condensed homologues may [16].

The spectral test was less applicable in the case of biacetyl sensitizations since this sensitizer was present in large excess, although the change in absorption in the L_1 region indicated that only ammonia aquation occurred on irradiation of the mixtures. However, any chemical reaction with $\text{Cr}(\text{NH}_3)_5 \cdot (\text{NCS})^{2+}$ would lead to either oxidized or reduced chromium. In either case,

the result would have been a shedding of the ligands which in turn means that (a) appearance of thiocyanate ion would have been observed and (b) no secondary release of thiocyanate would have occurred on bringing the irradiated solutions to pH 7. Both predictions are contrary to fact, and we, therefore, conclude that no chemical attack on the complex was involved.

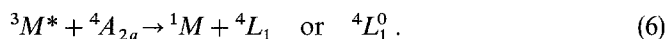
Discussion

Qualitative Conclusions. We consider first sensitization by acridinium ion as the donor molecule, M. It is to be expected that the triplet excited state, $^3M^*$, but not the singlet excited state, $^1M^*$, would be quenched by oxygen. In view of the observation that ϕ_{NCS} but not ϕ_{NH_3} was sensitive to oxygen, it appears that the latter sensitization mode does not involve $^3M^*$ and that the former does to at least a major extent. The direct photolysis studies [5] strongly suggested that thiocyanate aquation is the major if not exclusive reaction from the 2D state, and ammonia aquation, that of the 4L_1 (or $^4L_1^0$) state, and the present results are well explained by the processes



Eq. (4), which calls for sensitization by $^1M^*$ to give primarily ammonia aquation, is supported by the observation that the complex does quench the fluorescence emission of acridinium ion.

Turning to biacetyl as sensitizer, the fact that it leads only to ammonia aquation suggests that it is the 4L_1 state of the complex that is populated. It is now the $^3M^*$ state of biacetyl that is involved, however, in view of the phosphorescence quenching results. The excitation energy transfer reaction thus appears to be

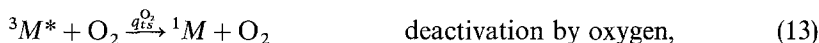
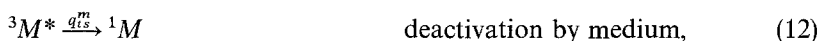
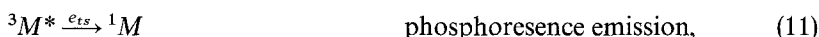
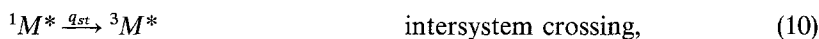
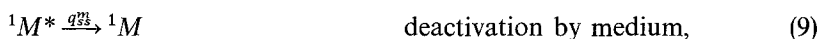
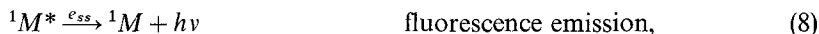
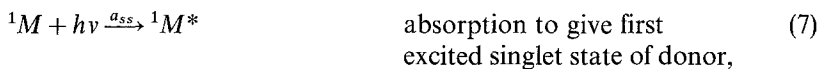


Eqs. (4), (5), and (6) violate the spin conservation rule only in the sense that a change in number of unpaired electrons occurs; no fundamental violation need be present. During the encounter between a donor and an acceptor species some association complex presumably forms whose net spin may be any of the possible combinations, $|J_1 + J_2|$, $|J_1 + J_2| - 1$, ... $|J_1 - J_2|$, of the spin angular momenta of the partners. In all of the above cases there exists a combination for the reactant species which is also possible for the product ones. There is thus an intimate reaction path for which net spin is conserved. Nor do the above processes seem unreasonable on energetic grounds. Referring to Table 1, the biacetyl triplet state has sufficient energy to populate the first quartet excited state of the complex between 4L_1 and $^4L_1^0$, and the singlet and triplet state energies of acridinium ion are reasonably suited to the 4L_1 and 2D energies of the complex. The failure of Michler's ketone as a sensitizer may simply be a consequence of too rapid deactivation by the medium.

Kinetic Analysis of Biacetyl Sensitization. We will use the following symbolism to designate the various rate processes. Small letters a , e , q , and k

will denote rate constants for absorption, emission, quenching or radiationless processes, and chemical reactions, respectively. Subscripts give the initial and terminal electronic state of the donor, and superscripts, additional information such as the quenching agent (*m* for medium, C for complex, O_2 for oxygen).

Considering the biacetyl system first, the processes are as follows,



Eq. (14) corresponds to deactivation by the complex, the fraction $\phi_{ts}^{\text{NH}_3}$ of such processes leading to chemical reaction, in this case ammonia aquation. The usual assumption of a steady state in ${}^1M^*$ and ${}^3M^*$ concentrations leads to the expression

$$\phi_p^0/\phi_p = 1 + \beta_p C_0, \quad (15)$$

where ϕ_p^0 is the quantum yield for phosphorescence in the absence of complex, and

$$\beta_p = \frac{q_{ts}^c}{q_{ts}^m + e_{ts} + q_{ts}^{\text{O}_2}(\text{O}_2)}. \quad (16)$$

The ammonia quantum yield is given by

$$1/\phi_{\text{NH}_3} = \alpha_{\text{NH}_3} + \beta_{\text{NH}_3}/C_0 \quad (17)$$

(the last term containing the additional factor β if appreciable reaction occurs) where

$$\alpha_{\text{NH}_3} = \frac{q_{ss}^m + e_{ss} + q_{st}}{\phi_{ts}^{\text{NH}_3} q_{st}} \quad (18)$$

and

$$\beta_{\text{NH}_3} = \frac{(q_{ts}^m + e_{ts} + q_{ts}^{\text{O}_2}(\text{O}_2))(q_{ss}^m + e_{ss} + q_{st})}{q_{ts}^c \phi_{ts}^{\text{NH}_3} q_{st}}. \quad (19)$$

Our results are reasonably consistent with the above scheme. Eq. (17) is obeyed with β_{NH_3} increasing with increasing oxygen concentration and α_{NH_3} constant. The ratio $\alpha_{\text{NH}_3}/\beta_{\text{NH}_3}$ is found from Table 3 to be about 5×10^4 in the absence of oxygen, and, by the above analysis, this should equal β_p , or 4×10^4 ; the agreement is fair. Further, the product $\beta_{\text{NH}_3} \phi_p^0$ should be equal to $e_{ts}/(q_{ts}^c \phi_{ts}^{\text{NH}_3})$, and from the data of Tables 2 and 3 $q_{ts}^c \phi_{ts}^{\text{NH}_3}$ is calculated to be

ca. $6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. This is somewhat high for a diffusion controlled rate constant, but not wildly so; the Smoluchowski relationship, $8 RT/3000 \eta$ gives about $8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. An incidental point is that since $\phi_p^0 \gg \phi_f^0$, q_{st} is probably the largest term in the numerator of Eq. (18), so $1/\alpha_{\text{NH}_3} \sim \phi_{is}^{\text{NH}_3}$.

Finally, the values of β_p as given by $\alpha_{\text{NH}_3}/\beta_{\text{NH}_3}$ allow a calculation of $q_{is}^{O_2}$ from Eq. (16). The slope of the plot of $1/\beta_p$ vs. (O_2) is about 0.7, so that $q_{is}^{O_2}$ is about $0.7 q_{is}^c$.

Kinetic Analysis of Acridinium Ion Sensitization. The preceding scheme must now be extended to include sensitization from the first singlet excited state of acridinium ion



where $\phi_{ss}^{\text{NH}_3}$ and ϕ_{ss}^{NCS} now give the fractions of such processes leading to ammonia and thiocyanate aquation. We then obtain

$$\phi_f^0/\phi_f = 1 + \beta_f C_0, \quad \beta_f = \frac{q_{ss}^c}{q_{ss}^m + e_{ss}} \quad (21)$$

and

$$1/\phi_{\text{NH}_3} = \alpha_{\text{NH}_3} + \beta_{\text{NH}_3}/C_0, \quad (22)$$

where

$$\alpha_{\text{NH}_3} = 1/\phi_{ss}^{\text{NH}_3} \quad \text{and} \quad \beta_{\text{NH}_3} = \frac{q_{ss}^m + e_{ss}}{\phi_{ss}^{\text{NH}_3} q_{ss}^c}. \quad (23)$$

The data do obey Eq. (22), including the predicted lack of dependence on dissolved oxygen. It is interesting that the value of $1/\alpha_{\text{NH}_3}$ is the same as for biacetyl sensitization, and about half of ϕ_{NH_3} for direct irradiation of the L_1 band of the complex. The discrepancy may reflect quenching of the donor by the complex without excitation of the latter. An auxiliary relationship is

$$\alpha_{\text{NH}_3}/\beta_{\text{NH}_3} = \frac{q_{ss}^c}{q_{ss}^m + e_{ss}} = \beta_f. \quad (24)$$

The ratio $\alpha_{\text{NH}_3}/\beta_{\text{NH}_3}$ is found from Table 3 as 490 M^{-1} in the absence of oxygen, now in somewhat poor agreement with the experimental β_f of 260 M^{-1} . While there is some uncertainty in the slope and especially the intercept in Fig. 6, β_f is perhaps an equally suspect quantity, since it was obtained by gaussian fitting to a rather non gaussian emission spectrum. The product $q_{ss}^c \phi_{ss}^{\text{NH}_3}$ is given by $e_{ss}/\beta_{\text{NH}_3} \phi_f^0$, and the value $3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ may be calculated from the data of Tables 2 and 3. This is to be compared with the estimate of $2.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ using the Smoluchowski equation as modified by a Debye-Hückel correction for repulsion between like charged ions, $\exp\left[-\frac{z_1 z_2 e^2}{D \kappa r T} (1 - \kappa r)\right]$, r being taken to be 5 \AA .

We next apply the scheme to ϕ_{NCS} , assuming that thiocyanate aquation may be sensitized either from the acridinium ion singlet or triplet excited states. Omitting e_{is} as evidently negligible, the resulting expression is

$$\phi_{\text{NCS}} = \frac{q_{is}^c \phi_{is}^{\text{NCS}} q_{st} C}{(q_{is}^m + q_{is}^{O_2} (O_2) + q_{is}^c C) (q_{ss}^m + e_{ss} + q_{ss}^c C)} + \frac{q_{ss}^c \phi_{ss}^{\text{NCS}} C}{q_{ss}^m + e_{ss} + q_{ss}^c C}. \quad (25)$$

Analysis is made manageable by defining $r = \phi_{\text{NCS}}/\phi_{\text{NH}_3}$; combination of Eq. (25) and (22) gives

$$r = \frac{(q_{ts}^c \phi_{ts}^{\text{NCS}} q_{st})}{(q_{ts}^m + q_{ts}^{\text{O}_2}(\text{O}_2) + q_{ts}^c C) (q_{ss}^c \phi_{ss}^{\text{NH}_3})} + r_{ss}, \quad (26)$$

where $r_{ss} = \phi_{ss}^{\text{NCS}}/\phi_{ss}^{\text{NH}_3}$. Eq. (26) is of the form

$$r = \frac{a}{b + c(\text{O}_2)} + r_{ss}, \quad (27)$$

which gives

$$\frac{1}{r_0 - r} = b/a + \frac{b^2}{ac} 1/(\text{O}_2), \quad (28)$$

where r_0 is the ratio for $(\text{O}_2) = 0$. The smoothed data of Figs. 6 and 7 were plotted in this manner, for several values of β/C^0 . From the respective intercepts and r_0 values, $\phi_{ss}^{\text{NH}_3}/\phi_{ss}^{\text{NCS}}$ is 33 ± 3 . This is to be compared with the ratio of 22.2 on direct irradiation of the L_1 band of the complex.

Summary Conclusions. The principal conclusions have been stated, but the overall picture can be reviewed at this point. It does appear that, as surmised from the direct photolysis study, the reaction chemistry of the doublet excited state of the complex is entirely one of thiocyanate aquation. That of the first excited quartet state is then largely one of ammonia aquation, the thiocyanate aquation component being smaller in the sensitized systems than on direct photolysis. Thus the reaction is 100% ammonia aquation under biacetyl sensitization, 97% under acridinium ion sensitization, and 95.5% on direct photolysis. In view of the first result in particular, it may be that the 4L_1 state undergoes only ammonia aquation and that the small thiocyanate component reflects varying degrees of intersystem crossing.

This last conclusion can be rationalized on the basis that the various means of populating the first excited quartet state may do so at different levels of the ${}^4L_1 - {}^4L_1^0$ separation as indicated in Fig. 2. For intersystem crossing to be competitive with thermal equilibration of the 4L_1 state, the latter should be somewhat hindered. This could be the case if the geometries of the 4L_1 and ${}^4L_1^0$ states are sufficiently different that considerable readjustment of the solvent cage is required. (See Ref. [4] for further discussion of this picture.)

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