Photochemistry of Complex Ions. VI. Aqueous Thiocyanatopentaamminechromium(III)

Edoardo Zinato, Robert D. Lindholm, and Arthur W. Adamson

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received September 3, 1968*

Abstract: The quantum yield ratios ϕ_2/ϕ_1 for photoaquation of the ion $Cr(NH_3)_5(NCS)^{2+}$ are found to be 15.3, 22.2, and 8.2 at 25° and for the wavelengths 373, 492, and 652 mμ, respectively, where ϕ_1 and ϕ_2 denote the yields for photoaquation of thiocyanate and of ammonia, again respectively. The wavelengths are those of the L_2, L_1, and D (doublet) ligand field bands. The photolysis was thus spectrospecific, and this is taken to indicate that various quartet excited states as well as probably a doublet excited state are direct precursors to chemical reaction. The results also confirm the predictive value of a set of empirical photolysis rules for Cr(III) complexes, which affirm that ammonia photoaquation should predominate, and more so on irradiation of the L_1 than the L_2 band. The ammonia *trans* to the thiocyanate ligand is the one predicted to be photolabilized, and the photolysis appears to be stereospecific since the product is concluded to be *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$. Thermal aquation studies confirm that thiocyanate aquation is the predominant thermal reaction. Ammonia release also occurs but is attributed to formation of $Cr(NH_3)_4(H_2O)_2^{3+}$ and related species. Such secondary reactions are accelerated in neutral and basic solution and the photolyses and most of the thermal rate studies were made in 0.1 *N* H_2SO_4. A sulfate ion effect was found on the rate of thermal release of thiocyanate, but not on the photolysis quantum yields. The effect is concluded to arise not from ion pairing, but from competition of sulfate with thiocyanate in secondary reanation reactions.

The photochemistry of the coordination compounds of Cr(III) has perhaps been better studied than that of any other family of transition metal complexes. While the subject has been reviewed recently,[1-4] two aspects of direct concern to the present investigation should be outlined here. First, irradiation of Cr(III) complexes with light in the visible leads only to substitution or to substitution-type reactions. Since the thermal reactions are also substitutional in nature, the question arises as to whether the photochemistry of Cr(III) species may amount to no more than a photocatalysis of existing thermal processes. This question is not answered by the several published studies with CrA_6-type complexes since for these only one kind of substitution process is possible and, perforce, the photo and thermal reactions must be the same. The study of a complex having two potential modes of reaction becomes more diagnostic, however, since it can now be determined whether the ratio of the reaction modes is the same for the thermal and the photolytic systems. Thus, in the case of *cis*-$Cr(en)_2(OH)_2^+$, it was found that photoaquation was the preferred reaction mode, while the predominant thermal reaction was one of isomerization.[5] However, it is unlikely that these reactions are single-step processes; they could, for example, represent alternative sequels to the detachment of one end of an ethylenediamine group.

The behavior of non-O_h complexes having only monodentate groups would not be subject to such mechanistic complexities, but until recently reports on complexes of this type were not directly informative on this question of the degree of specificity of photoreactions. The preferred photo- and thermal aquation modes either were the same, as with *trans*-$Cr(NH_3)_2(NCS)_4^-$ (Reineckate ion),[6] or the alternative mode to the thermal reaction was not looked for, as in the cases of $Cr(H_2O)_5(NCS)^{2+}$,[7] and the series $Cr(NH_3)_a(H_2O)_{6-a}{}^{3+}$.[8]

An analysis of such then available results led, however, to the formulation of a set of photolysis rules for Cr(III) complexes which implied that there was in fact a specific reaction chemistry of Cr(III) excited states.[9] The complex was regarded as consisting of three pairs of ligands located on the three mutually perpendicular axes of an octahedron, and, in brief, it was proposed that (1) the photochemically labilized axis should be primarily that one of weakest average ligand field strength, and (2) that if the labilized axis contained two different ligands, then the one of greater ligand field strength would be preferentially aquated. In the case of an acidopentaammine complex, the prediction is thus that photoaquation of ammonia should predominate. This prediction has been confirmed in the case of $Cr(NH_3)_5Cl^{2+}$, for which the ammonia quantum yield was 0.35 to 0.38 in the region of 500–375 mμ,[10] while that of chloride was estimated to be only about 0.01.[11]

A similar prediction would be made for $Cr(NH_3)_5(NCS)^{2+}$. While this complex had been reported to photoaquate thiocyanate,[12] other investigators had noted spectral shifts during exposure to light, of a nature which suggested that ammonia aquation occurred as well.[13] The system seemed better suited than the chloropentaammine one for an accurate investigation of the quantum yields for both ammonia and thiocy-

---

(1) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).

(2) E. L. Wehry, *Quart. Rev.* (London), 21, 213 (1967).

(3) D. Valentine, *Advan. Photochem.*, 6, 124 (1968).

(4) A. W. Adamson, *Coord. Chem. Rev.*, 3, 169 (1968).

(5) A. W. Adamson, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 237.

(6) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, 88, 394 (1966).

(7) A. W. Adamson, *J. Inorg. Nucl. Chem.*, **13**, 275 (1960).

(8) M. R. Edelson and R. A. Plane, *Inorg. Chem.*, 3, 231 (1964).

(9) A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

(10) H. F. Wasgestian and H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), 57, 282 (1968).

(11) L. Moggi, F. Bolletta, and V. Balzani, *Ric. Sci.*, **36**, 1228 (1966).

(12) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

(13) W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *ibid.*, 81, 2958 (1959).

anate aquation. The present paper gives the results of this investigation, a preliminary report on which has been published.[14] We noted, in that report, that ammonia photaquation predominated, and gave quantum yield ratios for the two reaction modes, for two wavelengths of irradiating light.

Aquation of the acido group is the preferred and may be the exclusive thermal reaction mode for both the chloropentaammine[15] and the thiocyanatopentaammine complexes.[16,17] We felt therefore that a detailed study of this latter complex was warranted as a potential model system for the demonstration that Cr(III) complexes do exhibit an excited-state chemistry which is different from that of the ground state.

A second area in which a question has existed is that of photolysis mechanism. The two principal absorption bands for Cr(III) complexes, which lie in the visible wavelength region, correspond to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, in O_h symmetry; these will be designated here as the L_1 and L_2 bands, respectively. One supposition has then been that reaction may occur either separately from each excited quartet state, or at least from the lower lying $^4T_{2g}$ one, following internal conversion from the $^4T_{1g}$ state (see ref 9). In addition, however, Cr(III) complexes show a weak absorption around 650–700 mμ, attributed to the transition $^4A_{2g} \rightarrow {}^2E_g$, again in O_h symmetry. Low-temperature emission studies have shown that the ^2E_g state can be populated by intersystem crossing, following irradiation in the region of the L_1 or L_2 bands.[18,19] An alternative proposal has therefore been that a doublet excited state is similarly produced in room-temperature aqueous media, and is always the immediate precursor state to chemical reaction.[20,21]

It has been difficult to distinguish between these alternative mechanisms on the basis of quantum yield data for systems showing only one photolysis mode. The variation of such quantum yields with wavelength has not, for example, yielded information of a decisive nature (see ref 1 and 9). If, however, two substitutional reaction modes can be observed, then the presence or absence of a major wavelength dependence of the *ratio* of the quantum yields for the two reactions should be diagnostic. Thus if, irrespective of the irradiating wavelength, all reactions occur from a doublet excited state, no wave-length dependence of this ratio should occur. Contrariwise, such dependence is expected if quartet and doublet excited states can separately function as immediate precursors to chemical change.

The investigation on which we report here has thus had two major purposes. The first has been to establish in detail a case in which the principal mode of photosubstitution is significantly different from that of the thermal aquation reaction, and the second has been to determine accurately the degree of wavelength dependence of the quantum yield ratio. In addition some thermal aquation rate studies are reported. While these were undertaken as a necessary adjunct to the photolysis work, the results have some interest in their own right.

Experimental Section

A. Preparation of Complexes. Aquopentaamminechromium(III) Ammonium Nitrate. This salt was prepared by the method of Mori.[22]

Thiocyanatopentaamminechromium(III) Nitrate and Perchlorate. A 15-g amount of aquopentaamminechromium(III) ammonium nitrate was dissolved in 50 ml of water, and the mixture was added to a solution containing 30 g of sodium thiocyanate in 20 ml of water. The solution was heated at 60–65° for 5 min and then cooled in an ice bath and the precipitate filtered off. This was then washed with ethanol and ether. The yield was 59%. The product was recrystallized from an aqueous solution by the addition of ammonium nitrate. *Anal.* Calcd for $[Cr(NH_3)_5(NCS)](NO_3)_2$: Cr, 16.29; NH_3, 26.67; NCS, 18.06. Found: Cr, 16.47; NH_3, 26.34; NCS, 18.06.

The nitrate salt was converted to the perchlorate by dissolving 2 g of the former in 200 ml of water at 50° and adding dropwise an excess of 0.2 *M* sodium perchlorate and then cooling the mixture in an ice bath. The product was filtered and washed with alcohol and ether and then recrystallized. *Anal.* Calcd for $[Cr(NH_3)_5(NCS)](ClO_4)_2$: Cr, 13.20; NH_3, 21.61; NCS, 14.74. Found: Cr, 13.50; NH_3, 21.43; NCS, 14.70.

The absorption spectrum of this complex is shown in Figure 1. The principal absorption maxima and corresponding extinction coefficients are 224 mμ (ε 10,500), 255 (2750), 298 (3630) (characteristic of the thiocyanate ligand), 363 (53), and 487 (84), in agreement with literature values.[23] In addition, the following features associated with the transition to the first doublet excited state are observed: 644 mμ (ε 0.32), 658 (0.20), 673 (0.21), and 685 (0.15).

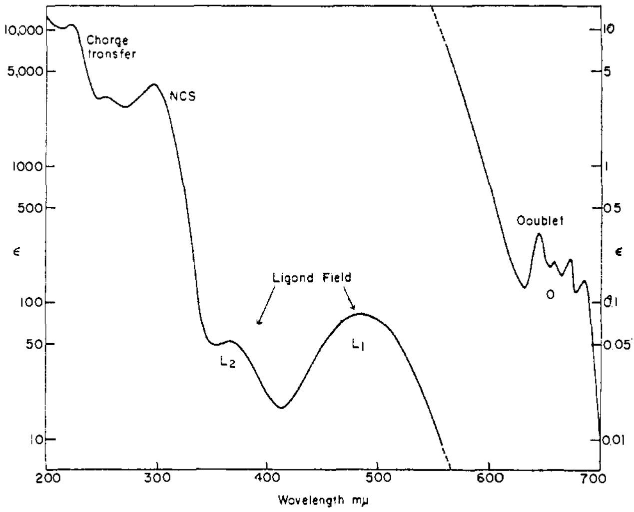


Figure 1. Visible and uv absorption spectrum of $Cr(NH_3)_5NCS^{2+}$ ion in 5×10^{-3} *N* $HClO_4$.

Oxalatotetraamminechromium(III) Nitrate. This compound was prepared by the method of Pfeiffer.[24]

***cis*-Chloroaquotetraamminechromium(III) Chloride.** This salt was prepared by treating the above oxalato complex with concentrated hydrochloric acid for 15 min at 50°.[25] The product was filtered, washed with ice-cold water, ethanol, and ether, and then air-dried.

---

(14) R. D. Lindholm, E. Zinato, and A. W. Adamson, *J. Phys. Chem.*, 71, 3713 (1967).

(15) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, 83, 2453 (1961).

(16) A. W. Adamson and R. G. Wilkins, *ibid.*, 76, 3379 (1954).

(17) D. L. Gay and G. C. Lalor, *J. Chem. Soc.*, 1179 (1966).

(18) G. B. Porter and H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), 38, 227 (1963).

(19) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, 19, 1687 (1963).

(20) H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), 11, 65 (1957).

(21) R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.*, 79, 3343 (1957).

(22) M. Mori, *Inorg. Syn.*, 5, 132 (1957).

(23) M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Allgem. Chem.*, 278, 287 (1955).

(24) P. Pfeiffer, *Ber.*, 38, 3592 (1905).

(25) A. Benrath and H. Steinrath, *Z. Anorg. Allgem. Chem.*, 194, 351 (1930).

***cis*-Dithiocyanatotetraamminechromium(III) Perchlorate.** The preparation followed closely a published procedure[26] and consisted of treating the complex with excess sodium thiocyanate. The resulting chloride salt was converted to the perchlorate in the usual manner. The final product was washed with ethanol and ether and air-dried. *Anal.* Calcd for $[Cr(NH_3)_4(NCS)_2]ClO_4$: Cr, 15.49; NH_3, 20.29; NCS, 34.60. Found: Cr, 14.79; NH_3, 19.77; NCS, 34.28. The visible absorption spectrum, which seems not to have previously been reported, shows the L_1 and L_2 bands to be at 501 mμ (ε 92.3) and 377 mμ (ε 56.8), respectively.

***cis*-Thiocyanatoaquotetraamminechromium(III) Ion.** This apparently not previously reported species was obtained by controlled aquation of the corresponding dithiocyanato complex, followed by isolation by means of cation-exchange chromatography. A 0.15-g portion of the parent compound was dissolved in 50 ml of 0.1 *M* perchloric acid and allowed to aquate in the dark for 30 min at 70°; the extent of aquation was checked by analysis for free thiocyanate and was limited to 10–15% so as to minimize the formation of diaquo product. After cooling, a 20-ml portion of the solution was adsorbed on a 4 cm × 0.4 cm column of Dowex 50W-X4 resin (50–100 mesh) which had previously been treated with 0.1 *M* perchloric acid. The unreacted orange-pink parent compound was eluted by means of 50 ml of 0.4 *M* perchloric acid; the next 20-ml portion of acid yielded a colorless fraction. The orange band remaining at the top of the column was then eluted by means of 30 ml of 0.8 *M* perchloric acid.

It was not possible to isolate a solid product, but analysis of the solution gave the following metal to ligand ratios: $Cr:NH_3:NCS = 1:4.13:0.95$. The absorption maxima for the L_1 and L_2 bands are at 497 mμ (ε 64.2) and 372 mμ (ε 41.1), respectively.

B. Analytical Procedures. Two types of situations were encountered. In the first, a preparation of a complex was to be analyzed, which might either be in the form of the solid salt or as the supposedly sole component of a column eluent fraction. In either case, the sample was decomposed by heating with an excess of 2 *M* sodium hydroxide, and the evolved ammonia was determined by means of a standard Kjeldahl method. The residual mixture was then analyzed for chromium and for free thiocyanate as described below. In the second situation, it was desired to determine the amount of free ammonia and thiocyanate formed by thermal or photolytic reaction. The latter could be determined directly, but the more elaborate procedure for ammonia analysis described below became necessary.

Thiocyanate. The free thiocyanate content of a solution was determined by diluting, at least 4:1, the aliquot into a reagent consisting of 0.1 *M* ferric nitrate in 0.5 *M* perchloric acid, and measuring the optical density at 450 mμ. If the sample contained thiocyanatopentaamminechromium(III) ion, partial precipitation of the perchlorate salt sometimes occurred; this was filtered off before making the spectrophotometric measurement.

The extinction coefficient of the iron–thiocyanate complex so formed is 4.30×10^3.[6] In the presence of sulfate ion, however, the apparent extinction coefficient decreases; it is 4.15×10^3 with 0.25 *M* sulfate present, and 3.55×10^3 with 1 *M* sulfate.

Chromium. Samples containing chromium hydroxide were acidified; the chromium was oxidized and determined spectrophotometrically by means of a published procedure (see ref 6). The species formed with the 1,5-diphenylcarbohydrazide reagent has an absorption maximum at 546 mμ (ε 4.20×10^4).

Ammonia. The colorimetric method used for the determination of free ammonium ion involved highly alkaline solutions which decomposed any complex present. Accordingly, it was necessary first to obtain a solution containing only the free ammonia. This was done as follows. A 5-ml aliquot of the solution was adsorbed on a 4–5 cm × 1 cm column of the above-described cation exchanger which had been washed with 0.5 *M* perchloric acid. The ammonium ion was then eluted by means of a 45-ml portion of 0.5 *M* perchloric acid (which did not move di- and tripositively charged complexes). The pH of the eluate was adjusted to near neutrality by the addition of aqueous sodium hydroxide; a 4-ml portion of sodium phenate reagent and 1 ml of 5% sodium hypochlorite solution were then added, and the mixture was made up to 100 ml with water. A characteristic blue color develops, due to an absorption at 610 mμ[27] whose intensity reaches a maximum after 50–70 min at room temperature. The entire procedure was carried out under dim red illumination.

It might be noted that the sodium phenate reagent ages and is best prepared the day of its use. Its preparation consists of mixing 20 ml each of solutions a and b below, and diluting to 100 ml with water. Solution a consists of 62.5 g of phenol and 18 ml of acetone made up to 100 ml with ethanol (and is indefinitely stable if kept cool). Solution b consists of 27 g of sodium hydroxide in 100 ml of water. In practice, the extinction coefficient of the 610-mμ band characteristic of the presence of ammonia was sensitive to the age and exact method of preparing the reagent, and was found to vary between 2800 and 3800. This variation was allowed for by a parallel standardization whereby a solution containing a known amount of ammonium hydroxide was put through the same ion-exchange separation and determination procedure. Separate tests showed that Beer's law was obeyed in any given series of parallel measurements. Because of its complexity, the entire procedure gave results reproducible only to 5–10%.

C. Equipment and Procedures. The photolysis equipment employed was essentially that described in a previous publication.[6] The following combinations of Bausch and Lomb interference and glass blocking filters were used to obtain the indicated wavelengths of irradiation. For irradiation of the L_2 region, the combination BL-730 + CS-760 gave a window at 373 mμ of half-width 40 mμ; for the L_1 region, BL-730 + CS-372 + CS-496 gave a window at 492 mμ with 30-mμ half-width; and for the D region, the combination BL-650 + CS-366 gave a window at 652 mμ of 20-mμ half-width. When the L_1 or L_2 bands were irradiated, absorption was greater than 99%, and the absorbed intensity was determined by Reineckate actinometry.[6] It was not practical to have complete absorption at the wavelength of the D band, and here the absorbed intensity was determined by differential bolometry, in the manner described in the previous work.[6] Light-intensity measurements were generally made both before and after the actual photolytic run, and the variation was usually less than 3%. The average intensity was used in calculating quantum yields.

The solutions were usually photolyzed in 10-cm spectrophotometer cells, mounted in a hollow wall holder thermostated to within 0.2°. In each case a companion aliquot of the solution was kept at the same temperature and in the dark; the irradiated and dark solutions were then analyzed in parallel so that correction for any dark reaction could be made. The irradiated solution was stirred at intervals corresponding to not more than 2–3% reaction, to avoid the occurrence of appreciable secondary photolysis or inner filter effects.

The kinetic studies were carried out with the same general precautions used for the dark solutions in the photolysis experiments. Also we report concentrations to one significant figure only where there is no need to give the exact value.

Results

A. Photolyses in Acid Solution. General Results. The net photolysis behavior of $Cr(NH_3)_5(NCS)^{2+}$ is different for pH's below about 2.5 and those above about 6.5. The complication that enters is one of increasingly rapid secondary reactions with increasing pH, and for this reason the results in acid solution are presented first. These are largely at pH 1, using sulfuric acid as the acidifying agent; the otherwise first choice of perchloric acid was inconvenient because of the relative insolubility of the perchlorate salt of the complex.

The general spectrophotometry of photolyzed solutions is shown in Figure 2. The presence of crossing points at 370, 423, and 505 mμ which are isosbestic makes it clear that up to about 15% photolysis only a single product or ratio of products is involved. Further, the result that the absorption maximum of irradiated solutions shows a bathochromic shift of the L_1 band suggests strongly that ammonia rather than thiocyanate photoaquation predominates. Were the reverse true, so that $Cr(NH_3)_5(H_2O)^{3+}$ was the principal product, the maximum would have shifted toward shorter wavelengths, as evidenced by the spectrum of this compound, included in Figure 2. Note also in this figure the rather slow change that occurs due to thermal reaction.

---

[26] P. Pfeiffer and M. Tilgner, *Z. Anorg. Chem.*, **55**, 361 (1907).

[27] A. Crowther and R. Large, *Analyst*, 81, 64 (1956).

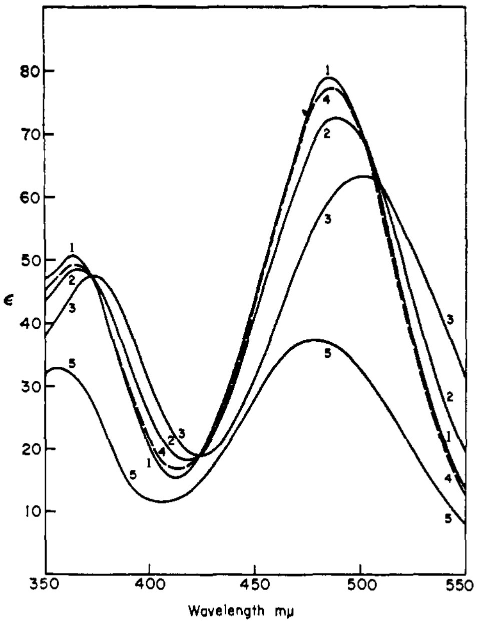


Figure 2. Spectral changes during irradiation of a $Cr(NH_3)_5NCS^{2+}$ solution at pH 1: curve 1, initial solution; curves 2 and 3, 1-hr and 3-hr irradiations; curve 4, after thermal aquation for 1 day a 25°; curve 5, spectrum of aqueous $[Cr(NH_3)_5(H_2O)](ClO_4)_3$.

The quantitative results, summarized in Table I, show that in the photolytic situation reaction 2 predominates over reaction 1.

$$Cr(NH_3)_5(NCS)^{2+} + H_2O \xrightarrow{\phi_1,\ k_1} Cr(NH_3)_5(H_2O)^{3+} + NCS^- \quad (1)$$

$$Cr(NH_3)_5(NCS)^{2+} + H_2O \xrightarrow{\phi_2,\ k_2} Cr(NH_3)_4(H_2O)(NCS)^{2+} + NH_3 \quad (2)$$

The solutions employed were 0.1 N in sulfuric acid and were around 0.01 M in complex if the L_1 or L_2 band was to be irradiated, and about 0.02 M if the D band was to be irradiated. We found the quantum yields to be independent of both light intensity and of irradiation time, the latter up to at least 15% reaction. The analytical methods allowed a precision such that average deviations for ϕ_1 and ϕ_2 were less than about 5 and 10%, respectively. Furthermore, no post-reaction occurred; the product analysis remained constant for at least a 24-hr post-irradiation standing of the solutions. Finally, the absolute quantum yields for photolysis in the doublet region of wavelength were significantly less precise, perhaps by a factor of 2, than those for the L bands, because of the generally greater difficulty of the experiments. However, the ratio ϕ_2/ϕ_1 retains the same precision as in the other runs. For example, fluctuations in light intensity could occur in the 12–17-hr irradiation times required for the doublet band irradiations, so that some added uncertainty would be present in the separate ϕ values, although not in their ratio.

The apparent activation energies for ϕ_1 and ϕ_2 were 1.0 and 0.8 kcal/mole, respectively, for irradiation of the L_1 band. The values became 2.2 and 1.4 kcal/mole, again respectively, on irradiation of the L_2 band.

Confirmation that the principal photolysis product was indeed $Cr(NH_3)_4(H_2O)(NCS)^{2+}$ was obtained as follows. An excess of solid sodium tetraphenylborate was added to a portion of photolyzed solution, and the precipitated ammonium salt filtered off. The filtrate was then passed through an anion-exchange column (Bio-Rad AG1-X4) in the perchlorate form to remove the free thiocyanate ion. An equal volume of 8 M sodium perchlorate was then added to the column effluent to precipitate the parent complex (as well as the small amount of aquopentaammine species present), and the material remaining in the filtrate was decomposed and analyzed for chromium, ammonia, and thiocyanate by the procedures described in the Experimental Section.

The particular concentrations found were 4.77 × 10^{-5}, 19.3 × 10^{-5}, and 4.65 × 10^{-3} M, respectively, corresponding to the ratios 1.00:4.04:0.98, and thus confirming that the product was a thiocyanatoaquotetraammine species. As a qualitative confirmatory indication, the spectral features of the solution containing this product material underwent an instantaneous shift to longer wavelengths upon raising the pH to 8. (There then followed a developing cloudiness as precipitation of $Cr(OH)_3$ took place.) In acid solution, the complex is quite stable; its spectrum showed no change over 48 hr, nor, as noted above, did any detectable dark release of ammonia or of thiocyanate occur in 24 hr.

In summary, we believe the photoproduction of thiocyanate and of ammonia to be due to reactions 1 and 2, respectively (and not to either subsequent thermal or photolytic reactions). Further, the variation of ϕ_1 between the L_1 and L_2 band irradiations is considered to be real, although possibly that of ϕ_2 is within experimental error. Similarly, the change in ϕ_2 between the L and D bands is well beyond experimental error, although that of ϕ_1 probably is not. The apparent activation energies for ϕ_1 and ϕ_2 are quite small, and differences between them are probably not of sufficient significance to warrant any attempts at interpretation.

Finally, as a point of significance in relation to the thermal aquation studies, the special effort was made in one case to obtain results for an acid solution which was free of sulfate. No significant change in behavior was found (see Table I).

Characterization of the Product $Cr(NH_3)_4(H_2O)(NCS)^{2+}$. An interesting further question is whether the $Cr(NH_3)_4(H_2O)(NCS)^{2+}$ produced by photoreaction 2 had the *cis* or *trans* configuration. The photolysis experiments produced this compound only in concentrations too low to allow its isolation as a pure crystalline salt, but an indirect procedure allowed the determination of its absolute absorption spectrum.

Some photolyzed solution was mixed with an equal volume of 8 M sodium perchlorate, so that the excess initial complex was precipitated quantitatively, along with the small amount of $Cr(NH_3)_5(H_2O)^{3+}$ present. The solution after filtration then contained only $Cr(NH_3)_4(H_2O)(NCS)^{2+}$. The absorption spectrum of this solution was measured and corrected for the small residual absorption found after the same treatment of a nonphotolyzed solution. Analysis of this filtrate for chromium then allowed the calculation of extinction coefficients; the resulting spectrum is included in Figure 3, and its features are detailed in Table II.

It was hoped originally to prepare authentic samples of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$ and to compare their spectra with that of the photolysis product. Neither isomer appears to have been prepared previously, and a search of the literature failed to indicate a

Table I. Photoaquation Quantum Yields for $Cr(NH_3)_5(NCS)^{2+}$ in Acid Solution[a]

Band irradiated[b]	Temp, °C	Photolysis yields[c]: NCS^- %	ϕ_1	NH_3 %	ϕ_2	ϕ_2/ϕ_1
L_2 (373)	5.0	0.29	0.0255	4.14	0.410	
		0.46	0.0240			
				5.72	0.362	
			Av 0.025 ± 3%		Av 0.39 ± 6%	15.5
	25.0	0.32	0.0293	5.13	0.467	
		0.33	0.0314	4.66	0.462	
		0.49[d]	0.0282[d]			
		0.57[d]	0.0304[d]			
			Av 0.030 ± 4%		Av 0.46 ± 0.6%	15.3
	45.0	0.40	0.0386	5.21	0.505	
		0.49	0.0418	6.55	0.562	
			Av 0.040 ± 4%		Av 0.53 ± 5%	13.2
L_1 (492)	5.0	0.32	0.0195	7.04	0.427	
		0.49	0.0193	9.74	0.384	
		0.50	0.0181	14.84	0.456	
		0.74	0.0174			
		0.75	0.0199			
		0.88	0.0213			
		0.93	0.0196			
			Av 0.019 ± 5%		Av 0.42 ± 6%	21.8
	25.0	0.26	0.0197	7.67	0.426	
		0.29	0.0227			
		0.38[e]	0.0222[e]	8.03[e]	0.470[e]	
		0.43	0.0219			
		0.45	0.0205	11.07	0.505	
		0.49	0.0213			
			Av 0.021 ± 3%		Av 0.47 ± 9%	22.2
	45.0	0.41	0.0237	9.06	0.528	
		0.42	0.0251	8.80	0.526	
			Av 0.024 ± 3%		Av 0.53 ± 0.2%	21.6
D (652)	25.0	0.13	0.0173	1.13	0.155	
		0.28	0.0172	2.43	0.150	
		0.28	0.0188	2.23	0.132	
			Av 0.018 ± 4%		Av 0.15 ± 6%	8.2

[a] All solutions were 0.1 N in sulfuric acid unless specifically indicated to be otherwise and were varied around 0.01 M in $[Cr(NH_3)_5(NCS)](ClO_4)_2$, except that 0.02 M $[Cr(NH_3)_5(NCS)](NO_3)_2$ was used for the experiments at 652 mμ. The order of the experiments was not that of the table, but was essentially random. [b] The actual irradiation wavelength is given in parentheses, in mμ. [c] The photolyis yields are given both as per cent of compex actually photolyzed according to the indicated reaction mode and the corresponding quantum yield. [d] Light of 358 mμ was used in this case. [e] The solution was 5×10^{-3} M in perchloric acid and was sulfate free.

Table II. Spectral Features of Various Acidoammine Complexes of Cr(III)

Species	L_2 λ, mμ	L_2 ε	L_1 λ, mμ	L_1 ε	Ratio L_1/L_2	Ref
Photoproduced $Cr(NH_3)_4(H_2O)(NCS)^{2+}$	382	43.3	513	55.7	1.29	This work
cis-$Cr(NH_3)_4(NCS)_2^+$	377	56.8	501	92.3	1.62	This work
cis-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$	372	41.1	497	64.2	1.56	This work
cis-$Cr(NH_3)_4(H_2O)_2^{3+}$	368	26.5	494	36.5	1.38	29
cis-$Cr(en)_2(H_2O)(NCS)^{2+}$	370	57	486	105	1.84	28
trans-$Cr(en)_2(H_2O)(NCS)^{2+}$	392	46	527	74	1.61	28

reliable synthetic route for the preparation of the *trans* species. That of the *cis* isomer appeared to be feasible, however, since there existed a method for obtaining the analogous *cis*-chloroaquotetraamminechromium(III) complex;[25] also, a compound believed to be the *cis* isomer of dithiocyanatotetraamminechromium(III) is known.[26] Of some help, in addition, was the reported preparation of *cis*- and *trans*-$Cr(en)_2(H_2O)(NCS)^{2+}$ through the thermal aquation of the corresponding dithiocyanato complexes.[28]

Following the above guides, a solution containing *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$ was prepared by means of a controlled aquation of *cis*-$Cr(NH_3)_4(NCS)_2^+$ and ion-exchange isolation of the product as described in the Experimental Section. There was no doubt that the reaction was one of aquation of the thiocyanate group, as free thiocyanate ion was formed during the reaction; also the general elution procedure in the ion-exchange separation was that which was successful in isolating *cis*-$Cr(en)_2(H_2O)(NCS)^{2+}$.[28] As shown in Table II and Figure 3, the spectral characteristics of this product fall nicely in between those of the known compounds *cis*-Cr-

(28) J. M. Veigl and C. S. Garner, *Inorg. Chem.*, 4, 1569 (1965).

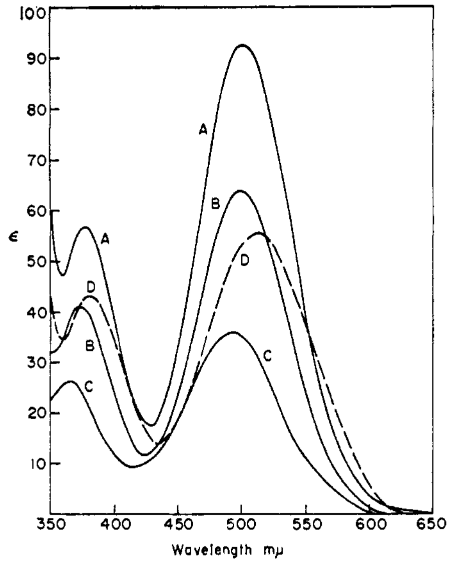


Figure 3. Visible absorption spectra for some chromium(III)–ammine complexes containing H_2O and NCS ligands: A, *cis*-$Cr(NH_3)_4(NCS)_2^+$; B, *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$; C, *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$; D, photoproduced $Cr(NH_3)_4(H_2O)(NCS)^{2+}$.

$(NH_3)_4(H_2O)_2^{3+}$ and *cis*-$Cr(NH_3)_4(NCS)^{2+}$. Finally, analysis of the components present in the eluent fraction gave Cr:NH_3:NCS = 1.00:4.13:0.95, or close to the required ratios. We feel therefore reasonably sure of the authenticity of this preparation. Our conclusions as to isomer characterization follow in the next main section. *cis*-Thiocyanatoaquotetraamminechromium(III) is a fairly stable ion in aqueous acidic solution, since only a 1–2% change in the absorption maxima occurred on 3 days standing at room temperature.

Photolytic Behavior of *cis*-$Cr(NH_3)_4(NCS)_2^+$. A photolysis run was made on a solution which was 0.01 *M* in this complex and 0.1 *N* in sulfuric acid, using light of 492 mμ. The quantum yields for ammonia and for thiocyanate release were 0.6 and 0.04, at 25°, respectively. On a more qualitative level the bathochromic shift in the spectral features that occurred on irradiation confirmed that the predominant photoreaction was one of ammonia aquation, while the small ipsochromic shift that occurred if the aquation took place in the dark indicated that the thermal reaction was primarily one of thiocyanate release.

To the extent that the photolysis rules mentioned in the introductory section are valid, the above behavior is correct for the *cis* isomer; were the complex the *trans* isomer, only thiocyanate photoaquation should have been observed. Since the isomeric configuration for the compound claimed to be *cis*-$Cr(NH_3)_4(NCS)_2^+$ is not actually fully proven in the literature, the photolysis behavior provides a confirmation that the assignment is correct.

B. Photolyses in Neutral and Basic Solutions. Secondary Thermal Reactions. Some photolysis studies were made on aqueous $Cr(NH_3)_5(NCS)^{2+}$ at its natural pH of about 6.5. The pH rose during the photolysis, as a result of the ammonia release, and, further, the quantum yields ϕ_{NCS} and ϕ_{NH_3} were found to depend both on the time of irradiation and on the interval between the end of the irradiation and the analysis. If the interval was sufficiently long, some precipitation of $Cr(OH)_3$ would occur. In a more controlled study, the same effect was found with solutions buffered at pH 5 or higher. However, for short irradiations, the quantum yields were independent of the pH of the solution during the irradiation. The primary photochemical processes were thus not pH dependent, but, evidently, the photolysis products could undergo fairly rapid further thermal reaction in neutral and basic solution.

The results of a typical experiment are reported in Table III. A solution 0.01 *M* in $Cr(NH_3)_5(NCS)^{2+}$ and 0.1 *N* in sulfuric acid was photolyzed at 492 mμ in the usual manner. The pH was then adjusted to 7 by partial neutralization with concentrated aqueous sodium hydroxide followed by the addition of a phosphate buffer mixture. The amount of free thiocyanate and of ammonia, expressed as apparent quantum yields, are given in Table III for various times after effecting the change in pH. It seems clear that the $Cr(NH_3)_4(H_2O)(NCS)^{2+}$ formed in the photolysis underwent complete thermal aquation of thiocyanate, since $\phi_{NCS}/\phi_{NH_3}{}^0$ approached unity. Further, it appears that both photolysis products eventually completely aquated their coordinated ammonia, since $\phi_{NH_3}/\phi_{NH_3}{}^0$ approached 5. Other experiments showed a similar behavior, with final ratios around the two values of 1 and 5; there was some scatter, perhaps because of the increasing presence of $Cr(OH)_3$ in the solution to be analyzed.

Table III. Photolysis of $Cr(NH_3)_5(NCS)^{2+}$. Post-Irradiation Effects on the Apparent Quantum Yields[a]

Post-irrad time, min	ϕ_{NCS}	ϕ_{NH_3}	$\phi_{NCS}/\phi_{NH_3}{}^0$	$\phi_{NH_3}/\phi_{NH_3}{}^0$
0	0.019	0.42	0.04	1.00
5	0.069	0.46	0.16	1.09
37	0.28	0.81	0.66	1.91
123	0.44	1.14	1.02	2.69
1500	0.48	2.05	1.12	4.81

[a] Irradiation conditions: 492 mμ, pH 1, 25°; post-irradiation condition: pH 7, 25°.

C. Thermal Aquation Behavior of $Cr(NH_3)_5(NCS)^{2+}$. Reaction 1, or thiocyanate aquation, is the dominant thermal reaction. The reaction was found to be first order in complex up to at least 30% reaction, and the pseudo-first-order rate constants, k_1, in 0.1 *N* sulfuric acid were 0.17×10^{-6}, 0.75×10^{-6}, and 2.58×10^{-6} at 25.0, 35.0, and 45.0, respectively, in units of sec^{-1}. The corresponding activation enthalpy and entropy values are 25.6 kcal/mole and −5.6 eu, respectively. The activation enthalpy is in good agreement with the previously reported figure of 24.9 kcal/mole[16] (see also ref 17), but the activation entropy is somewhat more positive; *i.e.*, the absolute values of our rate constants are somewhat larger than those found earlier. The probable reason for this is considered further below.

Thermal release of ammonia also occurred. The first-order plots were curved, however, corresponding to a gradually increasing apparent first-order rate constant. Extrapolation of these slopes or corresponding rate constants to zero time yielded an apparent k_2 for reaction 2 of about half of the k_1 value at each temperature. The apparent activation enthalpy for reaction 2 was thus the same as for reaction 1.

A rather different interpretation of the data is possible, however. The product of reaction 1, $\mathrm{Cr(NH_3)_5(H_2O)^{3+}}$, is reported to aquate at 40° in 0.4 *M* nitric acid solution with a rate constant of 2.4×10^{-5} sec^{-1}.[29] The reaction is fast enough that our entire observed ammonia release could be occurring as a result of the reaction 1 followed by reaction 3. As shown in Figure

$$\mathrm{Cr(NH_3)_5(H_2O)^{3+} + H_2O \xrightarrow{k_3} Cr(NH_3)_4(H_2O)_2{}^{3+} + NH_3} \quad (3)$$

4, the ammonia production at 25° could be quite well accounted for using k_1 and k_3 values of 0.16×10^{-6} and 2×10^{-5} sec^{-1}, respectively. The k_1 value is close to the directly measured one, although that for k_3 is appreciably higher than might be expected from the literature value at 40°, assuming the activation energy to be about 25 kcal/mole. First, the product of reaction 3 undergoes further and rather rapid aquation, which would make the apparent k_2 value high. There is another factor, however, discussed below.

The photolysis runs were made in 0.1 *N* aqueous sulfuric acid, as were the above thermal rate studies, and while there was no sulfate ion effect on the photochemical behavior, one might exist for the thermal one. Accordingly, a series of thermal aquation rate measurements was made at 45° for solutions 0.01 *M* in $\mathrm{Cr(NH_3)_5(NCS)^{2+}}$, 4×10^{-3} *M* in perchloric acid (the maximum value allowed by the solubility of the complex), and having increasing amounts of added sodium sulfate. These results are summarized in Table IV and show an approximate doubling of the apparent k_1 value as the sulfate ion content was varied from 0 to 1 *M*. The rate constant for zero sulfate is now fairly close to that given by the literature.[16,17]

There are several possible explanations for this dependence of k_1 on the sulfate concentration. First, there was inevitably a large variation in ionic strength, which could well have an important effect, although not in terms of simple interionic attraction theory since reaction 1 is between a charged and a neutral species. On a more sophisticated level, there would seem to be an excellent chance that an important degree of ion pairing occurred at the higher sulfate ion concentrations, and that the species $\mathrm{Cr(NH_3)_5(NCS)\cdot SO_4}$ had a greater aquation rate constant than the non-ion-paired one. Ion pairing constants between sulfate and tripositive complexes can be quite large; that with $\mathrm{Co(NH_3)_6{}^{3+}}$ is about 10^3, for example.[30,31] No values are available for dipositive complexes, however. We could find only minor spectral changes on increasing the sulfate content of solutions of $\mathrm{Cr(NH_3)_5(NCS)^{2+}}$, over the range from 200 mμ through the visible, and could not therefore evaluate to what extent ion-pair formation might actually be occurring.

A further line of approach suggested yet another explanation of the sulfate effect on k_1, however. Included in Table IV are the equilibrium degrees of aquation, as determined from the free thiocyanate ion present after six to seven reaction half-lives, along with the spectral features of these final solutions. First, a general bathochromic shift occurred, along with a decrease in extinction coefficients, as the sulfate content of the medium increased. The shifts are presumably due to increasing ammonia aquation; that of thiocyanate would not be apparent because of the closeness of thiocyanate and water in the spectrochemical series. However, the steady decrease in the apparent extinction coefficient of the 295-mμ band, characteristic of coordinated thiocyanate, indicates that the degree of thiocyanate aquation was also increasing with increasing sulfate content. As another observation, the spectrum of system 1 is close to that assigned to *cis*-$\mathrm{Cr(NH_3)_4(H_2O)(NCS)^{2+}}$, while systems 7 and 8 have spectra close to that of $\mathrm{Cr(H_2O)_6{}^{3+}}$. The degree of aquation of system 8 is indicated by another result. If this system was treated with concentrated sodium perchlorate solution after about one half-life, the 50% of unreacted starting material was precipitated and the filtrate then showed the spectrum of $\mathrm{Cr(NH_3)(H_2O)_5{}^{3+}}$ (L_1 and L_2 bands at 545 and 395 mμ, respectively). This observation is consistent with the report that the aquopentaammine complex is a relatively stable one.[29]

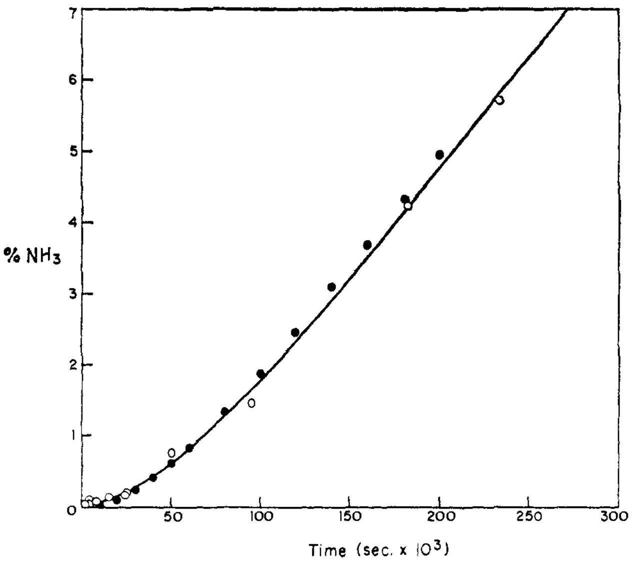


Figure 4. Ammonia release by aqueous $\mathrm{Cr(NH_3)_5NCS^{2+}}$ at 25°: ○, experimental values; ●, values calculated assuming reaction 1 followed by reaction 3, with $k_1 = 0.16 \times 10^{-6}$ sec^{-1} and $k_3 = 2 \times 10^{-5}$ sec^{-1}.

The thrust of this last series of observations, considered in more detail in the Discussion, is that in the presence of sulfate ion the nature of the reaction sequence and of the products is affected. The sulfate effect on the thermal reaction kinetics thus appears to be more than a medium or ion-pairing effect on the rate of reaction 1.

Discussion

Photochemical Results. The present results seem clearly to provide answers to the two questions presented in the introductory section, at least in terms of one specific system. Photolysis of $\mathrm{Cr(NH_3)_5(NCS)^{2+}}$ produces mainly ammonia aquation, or reaction 2, while the thermal aquation is largely and perhaps exclusively of the thiocyanato group. It seems reasonable if not in fact unavoidable to speak of a chemistry of excited states which is, in this case, different from that of the ground state. Certainly, the photolyses cannot be regarded a mere photocatalysis of the thermal reaction.

---

(29) E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958).

(30) S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, 3343 (1963).

(31) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, 78, 15 (1956).

Table IV. Effect of Sulfate Ion Concentration on the Aquation Behavior of Aqueous $Cr(NH_3)_5(NCS)^{2+}$ at 45°[a]

Expt	$[SO_4^{2-}]$, *M*	k_1(app) × 10^6, sec^{-1}	% free NCS^- at equil	Equilibrium spectral characteristics					
				L_1		L_2		NCS band	
				λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
1	0	2.05	48.7	500	52.5	373	34.8	295	2100
2	0.0002	2.05							
3	0.0005	2.05							
4	0.001	2.08	52.0	507	38.7	377	27.6	294	1890
5	0.01	2.33	73.3	550	24.3	400	23.6	293	1510
6	0.05	2.58	94.9	565	21.7	410	21.0	291	830
7	0.25	3.37	100	565	21.0	412	19.7	290	510
8	1.0	4.40	100	568	20.4	412	19.0	288	275

[a] All solutions were also 4×10^{-3} *M* in perchloric acid.

The ratio ϕ_2/ϕ_1 is about 15 for irradiation of the L_2 band, 22 for that of the L_1 band, and 8 for that of the D band. Also the total ϕ value drops on going from the L_1 to the D region. Thus it is difficult to see how chemical reaction could be occurring solely from a doublet excited state. We propose instead that significant amounts occur from the quartet excited states associated with the L_1 and L_2 bands, that is, that such states are direct precursors to chemical change. In C_{4v} symmetry, the $^4T_{2g}$ state of an O_h complex of Cr(III) is split into the components $^4B_{2g}$ and ^4E_g;[32] the latter involves the average ligand field strength along the *z* axis and is the lower lying of the two states. Possibly, then, rapid internal conversion following absorption in the region of the L_1 band places the complex in the ^4E_g state, which then exhibits the observed 22:1 preference for ammonia over thiocyanate aquation.

The $^4T_{1g}$ state of O_h symmetry is similarly split, into $^4A_{2g}$ and $^4E_{2g}$, and the 15:1 reaction ratio might be characteristic of the lower one of these two states. On the other hand, ϕ_2 is essentially independent of which L band is irradiated, and another possibility is that some 90% of the time internal conversions generate the ^4E_g state, which then undergoes only ammonia aquation. Thiocyanate aquation, whose quantum yield is higher for the L_2 than for the L_1 band, might then be due to less probable reaction from one or another of the other quartet excited states.

A further thought is that since thiocyanate aquation is relatively more important for the D than for the L bands, this might in fact be the principal reaction for a doublet excited state. The ϕ_2 of 0.15 would then be attributed to that component of the absorption which was due to the tail of the L_1 band. Some part of the ϕ_1 for the L_1 band might then be due to reaction from a doublet state, produced by intersystem crossing. These are merely examples of possible situations; quite evidently, there are more processes potentially present than independent variables which are determined.

A further complication that might be mentioned is that higher doublet states exist, which could still be low enough in energy to be populated by intersystem crossing, particularly from the $^4T_{1g}$ level. One could then assign the observed spectrospecificity to variations in the degree of such population with irradiating wavelength, assuming that different doublet-excited states had different reaction chemistries. However, emission from higher doublet states has not been observed (see ref 18 and 19), so that such population is not important even at low temperatures, and the above alternative mechanism remains a speculative possibility. As another point, it may be possible to make a direct determination of the reaction chemistry of doublet excited states if the photolysis of Cr(III) complexes can be sensitized, as with Co(III) complexes.[33]

Finally, radiationless deactivation of a thermally equilibrated quartet excited state produces a highly vibrationally excited ground state, the most direct evidence being the broadness of the fluorescent emission, where this can be observed.[18] Chemical reaction could then be attributed to hot ground-state molecules, and the difference between the photolytic and thermal modes explained as being due to differences in the way high vibrational levels were populated in the various situations. It is hard to make an experimental distinction between this mechanism and one which considers the thermally equilibrated excited states as reacting chemical entities. However, the presence of even the small apparent activation energies observed here, and certainly that of the much larger values found for other systems (ref 5, for example), seems awkward to explain in terms of the hot ground-state mechanism.

To turn to a more empirical aspect, the present study satisfactorily confirms the photolysis rules mentioned in the introductory section. The reaction mode predicted to be favored is indeed the dominant one, and the preference for it is greater on irradiation of the L_1 than on irradiation of the L_2 band. There is a further point of interest. The specific prediction is that the ammonia *trans* to the thiocyanate group should be the one aquated. To the extent that the photolytic reaction is stereospecific, the product should be *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$.

As detailed in the Results section, it was not possible to make an unequivocal determination of the isomeric nature of the ammonia photoaquation product. We feel, however, that the evidence that it is largely or entirely the *trans* isomer is persuasive. First, of course, its spectrum differs significantly from that of the *cis* form, which was prepared. Further, the nature of this difference is consistent with the photoproduct being the other isomer. Thus the L_1 band of the photoproduct is at a longer wavelength than that of the *cis* isomer, and such a red shift holds for known *trans*–*cis* pairs (see Table II).

Two possible objections to our assignment of the

---

(32) See A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).

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

trans configuration to the photoproduct are the following. First, the L_1 band of a *trans* complex is often split, as for example, with $Cr(en)_2(H_2O)Cl^{2+}$,[34] while that of the photoproduct is not. However, such a splitting does not occur and is in fact not expected to occur in the present case. Water is sufficiently close to ammonia in ligand field strength that the difference between the *z* and *x,y* axes in *trans*-$Cr(NH_4)_4(H_2O)(NCS)^{2+}$ is not as great as that in *trans*-$Cr(en)_2(H_2O)Cl^{2+}$. Even the spectra of *cis*- and *trans*-$Cr(en)_2(H_2O)(NCS)^{2+}$ are quite similar, the L_1 band of the latter not being obviously split (see Table II).

A second point is that extinction coefficients for *cis* isomers are often considerably larger than those for the corresponding *trans* ones, while those for the photoproduct are close to those for *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$. However, the related cases where such extinction coefficient differences are observed all involve complexes with coordinated ethylenediamine rather than ammonia, so that the effect need not be expected in the present case.

A remaining possibility is that the aquation product of the *cis*-$Cr(NH_3)_4(NCS)_2{}^+$ was *trans* rather than *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$, so that we were mistaken as to the isomer with which we were comparing the photoproduct. This seems unlikely since such substitution reactions are generally stereospecific. Thus in the analogous aquation of *cis*-$Cr(en)_2(Cl)(NCS)^+$, the products are reported to be 96% *cis*- and 4% *trans*-$Cr(en)_2(H_2O)(NCS)^{2+}$.[28]

Next, it is interesting that in the case of $Cr(NH_3)_5Cl^{2+}$, the ammonia photoaquation product is reported to be *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$.[10] It is, of course, not necessary that photoaquations be stereospecific, and this last system may simply be different in this respect from ours. However, the isomer assignment in the case of the chloropentaammine complex appears to be tentative. Both isomers of the photoproduct were not prepared, and, moreover, the spectrum of the photoproduct was inferred from the over-all spectral changes during irradiation and could have been subject to some uncertainty.

In summary of this section, we believe the present investigation has provided evidence that quartet and probably also doublet excited states of Cr(III) complexes can be direct precursors to chemical reaction, and that the various excited states have a specific reaction chemistry which is not necessarily the same as that for the ground state. The results also give further support to the empirical photolysis rules and indicate that these rules can be useful in predicting the stereochemistry of photoaquation reactions as well as in confirming whether a given complex is the *cis* or *trans* isomer, as in the case of *cis*-$Cr(NH_3)_4(NCS)_2{}^+$ mentioned under Results.

Thermal Reaction Studies. Our studies on the thermal aquation of $Cr(NH_3)_5(NCS)^{2+}$ largely confirm and agree with the literature data. We conclude that reaction 1 predominates, the ammonia release being entirely explainable in terms of a rapid aquation of the product of reaction 1. Allowing for experimental error, we place an upper limit to the contribution of reaction 2 of perhaps 10%.

While the secondary reactions were not studied in any detail, reaction 3 is probably followed not only by further ammonia steps, but also by reanation, reaction 4.

$$Cr(NH_3)_4(H_2O)_2{}^{3+} + NCS^- \xrightarrow{k_4} Cr(NH_3)_4(H_2O)(NCS)^{2+} \quad (4)$$

While we did not isolate $Cr(NH_3)_4(H_2O)(NCS)^{2+}$ from thermally aquated systems, this type of reaction sequence has been reported in a thermal aquation study with $Cr(NH_3)_5F^{2+}$.[35] It was found in this last case that the amount of free fluoride ion in solution was consistently less than that of disappeared starting complex, and $Cr(NH_3)_4(H_2O)F^{2+}$ was present. The presence of reaction 4 then means that the equilibrium concentration of free thiocyanate reported in Table IV (expt 1) is not a measure of the amount of reacted $Cr(NH_3)_5(NCS)^{2+}$. The entire coordinated thiocyanate may in this case have been present in the form of thiocyanatoaquoammine complexes. Also k_1 should be reported as $k_{1(\mathrm{app})}$.

The above considerations have a bearing on the sulfate ion effect. We are inclined to believe that this effect is not due to ion pairing. This is partly because no spectroscopic evidence for association could be found, partly because the presence of sulfate had no effect on the photolysis behavior, and partly because the variation of k_1 with sulfate ion concentration could not be fitted to an ion-pairing reaction scheme. The alternative explanation is that sulfate ion takes part in sulfate anation reactions analogous to reaction 4, thus inhibiting the reentry of thiocyanate ion and increasing the apparent k_1 value, as well as the equilibrium concentration of free thiocyanate. The data of Table IV could not be fitted to any simple algebraic analysis, however, so that this explanation is tentative. Complications to any detailed treatment include the problem of assigning activity coefficients, and the likelihood that at the highest sulfate concentrations some ion pairing might be present.

Some concluding remarks might be made regarding post-irradiation thermal reactions. Both in the present investigation and in those on *trans*-$Cr(NH_3)_2(NCS)_4{}^-$,[36] it has been found that thermal aquation of the acido group is not base catalyzed, in contrast to the behavior of Co(III) acidoammines.[37] However, once a solvent molecule is present in the coordination sphere, either through ammonia photoaquation in the present case or through photo or thermal aquation of one thiocyanate in the case of Reinecke salt, then solvolytic loss of additional acido groups becomes base catalyzed. Thus, in the case of Reinecke salt, neither the primary quantum yield nor the rate of first step thermal aquation was affected by making the solution alkaline, but a rapid secondary release of thiocyanate would then occur. In the photoreaction, the effect was to increase the apparent quantum yield for thiocyanate aquation by a factor of 4.[6]

The quite analogous behavior observed in the present study can be summarized by the reaction scheme of eq 5, where the reaction labeled k_5 is base catalyzed. While step 5 is referred to as base catalyzed, its acceleration

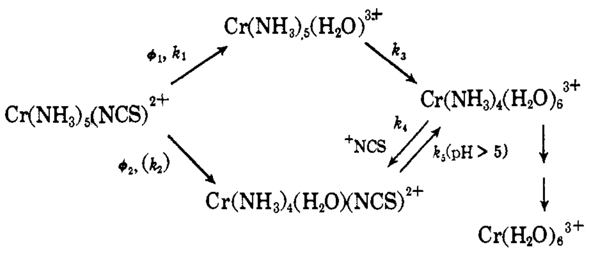
---

[34] D. J. McDonald and C. S. Garner, *J. Am. Chem. Soc.*, 83, 4152 (1961).

[35] T. P. Jones and J. K. Phillips, *J. Chem. Soc., A*, 674 (1968).

[36] A. W. Adamson, *J. Am. Chem. Soc.*, 80, 3183 (1958).

[37] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 177.



(5)

becomes noticeable at pH's as low as 5. Quite possibly the mechanism is one involving the formation of a hydroxy complex; it could be quite analogous to the counter base mechanism that has been proposed and largely accepted for the base hydrolysis of Co(III) acidoammine complexes.[37] Apparently, then, ammonia coordinated to Cr(III) is only very weakly acidic, and in order for the counter base mechanism to become important the more acidic coordinated water is required.

Acknowledgments. These investigations have been supported in part by Contract AT(11-1)-113 between the University of Southern California and the U. S. Atomic Energy Commission. In addition, E. Z. wishes to thank the National Science Foundation for assistance through Grant Gp-5725 and also the National Research Council of Italy.

Primary Quantum Yields in Photodissociation of Isopropyl Nitrite

Barbara E. Ludwig and G. R. McMillan

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received August 16, 1968*

Abstract: Illumination of isopropyl nitrite in the banded region at 3660 Å results in formation of isopropoxy radicals and nitric oxide with a primary quantum yield of 0.36 at 26°, inconsistent with the usual assumption that the primary yield is unity in nitrite photolysis. The *cis* and *trans* conformers apparently decompose with the same quantum efficiency. The primary yield for photodetachment of HNO or NOH is less than 0.06 and probably near zero. Excitation of the $^1(n,\pi^*)$ state with a few quanta in the terminal N═O stretching vibration leads to no more efficient decomposition than does excitation of the vibrationless state. On the basis of observed changes in the product distribution, this is not due to vibrational deactivation before decomposition.

The principal photodissociative process for simple alkyl nitrites at all wavelengths so far studied is a scission of the RO–NO bond to form an alkoxy radical and nitric oxide.[1] The primary quantum yield of this process is generally assumed to be unity,[2] but only for *t*-butyl nitrite[3] has the primary yield been measured in the banded region lying between 3200 and 4000 Å. A molecular split of the type $R_2CHONO + h\nu \rightarrow R_2CO + HNO$ (or NOH) has often been suggested, but Calvert and Pitts conclude that no unambiguous evidence is available on its importance.[4] The photolysis of isopropyl nitrite was studied to test the assumption of unit quantum efficiency for photodissociation; to determine the importance of the photodetachment of HNO; to try to detect differences, if any, in the photochemistry of the *cis* and *trans*-nitrite rotamers; and to test for coupling between excited vibrational levels in the (n,π^*) state and the decomposition mode. Photolysis of isopropyl nitrite has been previously studied both in the vapor phase and in solution.[5]

Experimental Section

Isopropyl nitrite was prepared by reaction of isopropyl alcohol with nitrous acid. The product was treated with anhydrous K_2CO_3 and mercury, distilled at atmospheric pressure, and stored at −78° on the vacuum line. Nitric oxide from the Matheson Co. was passed over silica gel cooled to −78° and finally fractionally distilled on the vacuum line. All illuminations were carried out in a quartz vessel of diameter 5 cm and volume 240 cm³. The Osram XBO 150 high-pressure xenon lamp was used in conjunction with a Bausch and Lomb grating monochromator. A Hanovia 673A medium pressure mercury arc was used with two filter systems to isolate 3660-Å radiation. The first filter system consisted of a 10-cm optical path of a 5 g/100 ml aqueous solution of $CuSO_4 \cdot 5H_2O$, followed by 1 cm of a 0.01 g/100 ml aqueous solution of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate, and 0.5 cm of Corning glass 7-37. The transmission and stability of this filter have been recorded.[6] The second filter system consisted of the Corning glass 7-37 alone. Quantum yields were based on light intensities measured with the potassium ferrioxalate actinometer. The intensities were checked by measuring the quantum yield of nitrogen in photolysis of azomethane vapor. The yield was 1.05;

---

(1) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 480.

(2) P. Kabasakalian and E. R. Townley, *J. Amer. Chem. Soc.*, **84**, 2711 (1962); M. Akhtar, *Advan. Photochem.*, 2, 263 (1964); R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 236; ref 1, p 481.

(3) G. R. McMillan, *J. Phys. Chem.*, **67**, 931 (1963).

(4) Reference 1, p 482.

(5) H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, **33**, 1546 (1937); P. Tarte, *Bull. Soc. Roy. Sci. Liege*, **22**, 226 (1953); P. Kabasakalian, E. R. Townley, and M. D. Yudis, *J. Amer. Chem. Soc.*, **84**, 2718 (1962).

(6) Reference 1, pp 734–735.