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SOME ASPECTS OF THE PHOTOCHEMISTRY OF COORDINATION COMPOUNDS

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ABSTRACT

The results of some investigations in this Laboratory on the photochemistry of Cr^{III} and Co^{III} complexes are summarized. Cr^{III} complexes undergo only photosubstitution reactions, but not necessarily the ones that predominate in their thermal reaction chemistry. Co^{III} complexes not only show the same type of photochemistry as do the Cr^{III} ones, but also can undergo photoredox decompositions yielding Co^{II} and oxidized ligand. Another kind of photoredox reaction, so far only observed with certain cyano complexes, is that of photoelectron production.

A given complex may show one or another type of reaction, depending on the wave-length of light used, and one can generally account for the reaction mode in terms of the kind of excited state involved. Thus irradiation of *d-d* absorption bands tends to produce photosubstitution, and that of charge transfer bands, to give redox decomposition or photoelectrons. Often, more than one kind of substitution reaction is possible, and in the case of Cr^{III} complexes the reaction chemistry of the excited quartet state supposed to be involved can be described with some success by means of empirical rules. The situation is complicated by competing radiationless deactivation processes, and by the likelyhood that the various excited states may have a different geometry from, *i.e.* be distorted relative to the ground state.

INTRODUCTION

The field of coordination compound photochemistry is an emerging one. While scattered reports of photosensitivity can be found in the literature of a hundred years ago, and excellent, detailed studies were made on certain specific systems in the twenties and thirties, it is only following the renaissance of inorganic chemistry after World War II that interest in photochemistry has started to become serious. Work is still confined to relatively few laboratories. The field has considerable depth and scope, however, and there is no doubt that it is on its way to becoming a major one.

The intention, in the writing of this paper, is to give primary emphasis to work in this Laboratory, but with recognition given to other currently active groups. Our interest has been mainly in those transition metal complexes of the Werner type, and primarily in those having a well characterized stoichiometry and some degree of kinetic stability. Also, it has been mainly confined to the study of primary photochemical processes insofar as they can be defined, as opposed to the study of the subsequent reactions of reactive fragments photolytically produced. We believe that this emphasis is essentially an emphasis on the chemical nature of the various excited states involved.

This paper, as well as much of our work, has been confined to two families of complexes: those of chromium and cobalt. Additional studies on molybdenum and on platinum species will not be reported on. There is a reason for this concentration of interest. In studies of the chemistry of an excited state of a complex, it is necessary to anticipate and to be able to identify possible products, and, frequently, to correct for the dark reaction. A photochemical investigation, then, if it is not to be quite empirical, must be able to draw on a fairly complete knowledge of the ordinary reaction chemistry of the system. It is natural to select for initial study those systems for which such information already exists. Further, the excited state whose chemistry is to be studied should be one of definite spectroscopic description; again, it is only for a few families of complexes that reliable assignments have been worked out.

The background of thermal reaction chemistry and of spectroscopic assignments relevant to Cr^{III} and Co^{III} complexes will not be specifically reviewed here; the reader is referred to monographs on the subject, as for example that by Basolo and Pearson[1]. Some review of the photochemistry of coordination compounds is given in reference 1 and also by Wehry[2].

EQUIPMENT AND PROCEDURES

It is perhaps worthwhile to make some very brief comments about equipment and procedures; details can be found in an excellent monograph by Calvert and Pitts[3]. Current light sources consist mainly of Xe, Kr, or Hg arcs of various designs, and giving either line or highly pressure broadened emission. The arc can be quite small so that good collimation optics are possible. Wave-length selection may be by means of filter solutions, or by conventional monochromaters, but it is very common to used interference filters because of their convenience and high transmission.

Since the quantum yield, ϕ, is given by the ratio of moles of reaction to einsteins (*i.e.* moles of light quanta) absorbed, the measurement of this last quantity, E, is central to photochemistry. In determining E, it is not satisfactory to rely on a manufacturer's description of the output of his lamp, and some independent measure of the absorbed intensity is necessary. This may be done by bolometry, but chemical actinometry is the usual choice. The two most widely used actinometers are the ferrioxalate[4] and uranyl oxalate[5] ones. These are suited for light in the near ultra-violet; for visible light a system calibrated in this Laboratory is suggested[6]. This makes use of a standard reagent, Reinecke's salt, which yields the easily detected thiocyanate ion on photolysis.

As a final comment, a frequent complication in the photochemistry of coordination compounds is that the products of photolysis may have a very similar absorption spectrum to that of the reactant and may themselves be comparably photosensitive. Secondary photolysis is thus often a problem; it can be minimized by photolyzing to only a few percent reaction. As an example of what can happen otherwise, Fig. 1 shows the sequence of spectra found on extended photolysis of aqueous $Cr(CN)_6{}^{3-}$, using 370 mμ light[7]. Here a succession of aquocyano complexes dominate the light absorption in turn, and a quantum yield based on average light absorption and amount of free cyanide ion produced would be rather useless.

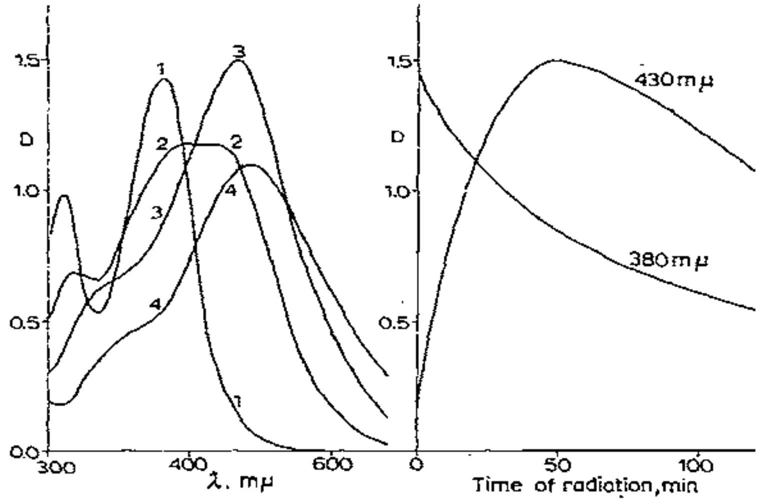


Fig. 1. Photolysis of $Cr(CN)_6{}^{3-}$ (25° C, 277 mμ, pH 6.85)
1,initial; 2,20 min; 3,50 min; 4,120 min irradiation.

CHROMIUM(III) COMPLEXES

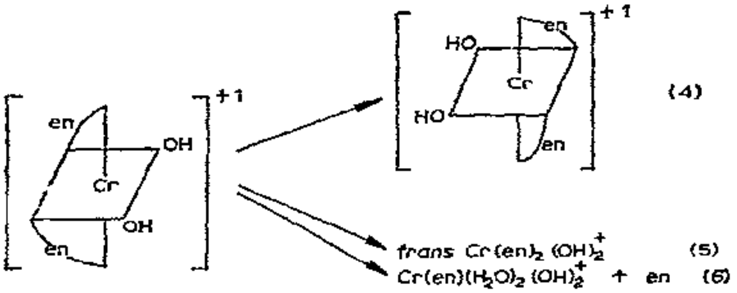
General behavior.—This best studied family of complexes provides a good illustration of the points made in the Introduction. A large number have been characterized and their reaction kinetics studied. In aqueous solution, the typical reaction is that of aquation:

$$Cr(NH_3)_6{}^{3+} + H_2O = Cr(NH_3)_5(H_2O)^{3+} + NH_3 \tag{1}$$

$$Cr(NH_3)_5(NCS)^{2+} + H_2O = Cr(NH_3)_5(H_2O)^{3+} + NCS^- \quad (2)$$

$$\text{or } \textit{cis} \text{ or } \textit{trans}\ Cr(NH_3)_4(H_2O)(NCS)^{2+} + NH_3 \quad (3)$$

Reaction (3) has not generally been reported to occur as a thermal process, but does occur photochemically. Racemization and isomerization may also take place:



(where *en* denotes ethylenediamine). Reactions (4) and (5) are probably not intramolecular, but involve an intermediate in which one end of the ethylenediamine ligand has aquated; reattachment to the chromium is then accompanied by racemization or isomerization. Anation reactions (the reverse of reaction (2)) probably occurs through an encounter or ion-pair complex as intermediate; in fact all of these substitution reactions can be regarded as having the common rate determining step of an outer-inner coordination sphere ligand exchange.

Turning next to the visible absorption spectra, these are well understood; a typical appearence is that illustrated in Fig. 2. The transitions involved may be depicted in various ways. Fig. 3a, a crystal field diagram, illustrates that in an octahedral (O_h) symmetry field, the 3-*d* orbitals are split into a t_{2g} and an e_g set,

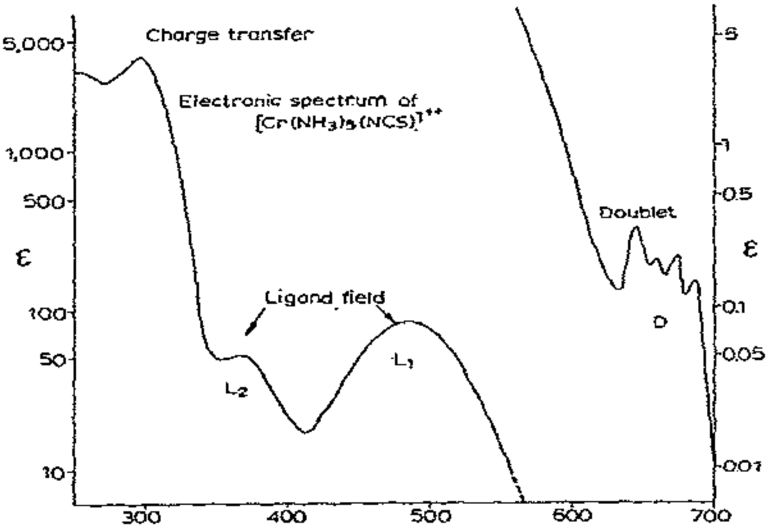


Fig. 2. Absorption spectrum of $Cr(NH_3)_5(NCS)^{2+}$ in 0.1 *N* H_2SO_4.

with an energy spacing of 10 *Dq*. The three *d* electrons of Cr^{III} half fill the t_{2g} set, and the L_1 band of Fig. 2 represents promotion of an electron to an e_g orbital. The term diagram of Fig. 4 gives necessary further detail; the L_1 and L_2 bands are seen to correspond to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, respectively (in O_h symmetry), the $^4T_{1g}$ state having more interelectronic repulsion energy than the $^4T_{2g}$ one. The weak, structured band labelled D corresponds to $^4A_{2g} \rightarrow {}^2E_g$, *i.e.* to spin pairing within the t_{2g} set. Finally, the L_1 band maximum gives directly the crystal field strength, 10 *Dq*, in the case of O_h complexes, and its position for various ones provides the spectrochemical series of increasing ligand field strength: $Br^- < Cl^- < OH^- < H_2O < NCS^- < NH_3 <$ en $< CN^-$. This brief review serves to establish the framework in which Cr^{III} photochemistry will be discussed; the reader is referred to texts (such as reference 1) for details.

Cr^{III} complexes are in general quite photosensitive, with quantum yields of 0.1–0.5 for light in the visible region. The photoreaction is always one of ligand substitution, ordinarily aquation, and one observation is that quantum yields increase with position in the spectrochemical series. The exception of $Cr(CN)_6^{3-}$ may be related to the high degree of π bonding present. For the mainly σ bonded ligands a tentative rationalization is that in a quartet excited state an electron occupies a σ antibonding orbital. The resulting bond weaking may simply be greater the higher the energy of the L_1 transition.

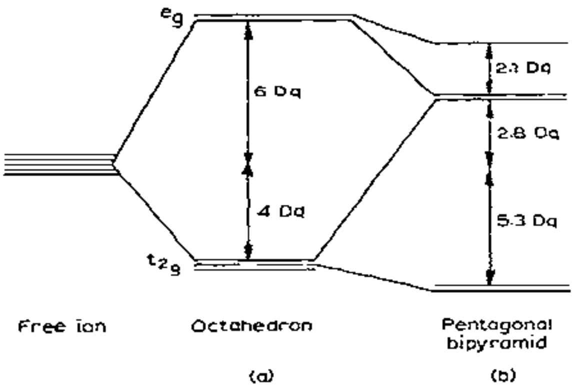
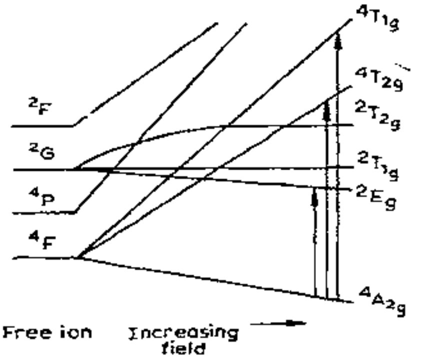


Fig. 3. Crystal field splitting diagram.
(a) Octahedral field; (b) Pentagonal bipyramidal field.

The behavior of the O_h complexes could be explained on the basis of a prompt heterolytic bond fission, following excitation, but further studies indicate that not only are specific excited states probably involved, but that they have a reaction chemistry that is not necessarily the same as the thermal one. That is, the photoreactions are not just catalyses of thermal processes. Thus in the case of $Cr(NH_3)_5(NCS)^{2+}$, reaction (2) is the predominant thermal process, while (3) is the predominant photochemical one, as detailed[8] in Table II. Note that while the



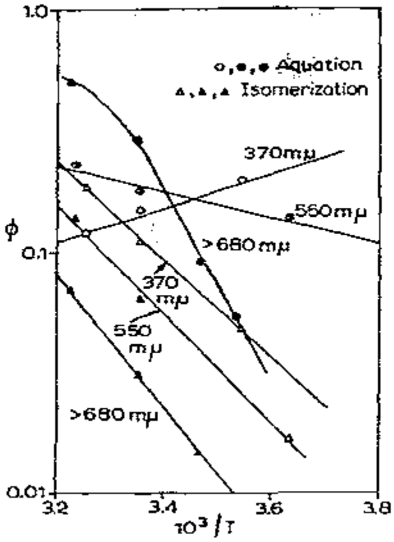


Fig. 4. Term diagram for a d^3 octahedral complex.

Fig. 5. Quantum yields for photoaquation and isomerization of *cis* $Cr(en)_2(OH)_2^+$.

ratio of quantum yields for the two reaction modes is about the same for irradiation of the L_1 or L_2 bands, it changes to a value more like that of the thermal reaction on irradiation of the D band. Similar, although less complete results have been reported for $Cr(NH_3)_5Cl^{2+}$, as noted in Table 1.

With less symmetric complexes, more drastic photospecificities appear; for example, the dominant thermal reaction of *cis* $Cr(en)_2(OH)_2^+$ is that of isomerization, reaction (5), while both reactions (5) and (6) are important photochemically[9]. As shown in Fig. 5, not only does the ratio of quantum yields vary according to whether the L_2, L_1, or D band is irradiated, but the yields are quite temperature dependent, with apparent activation energies of 10–15 kcal/mole.

The diagnostic nature of the experiments just cited should perhaps be emphasized. A mere variation of quantum yield with wave-length of irradiation does not necessarily indicate that different excited states are direct precursors to chemical reaction. Here, however, the *ratio* of reaction modes is wave-length dependent so that *different* immediate precursors to reaction must be involved. These are presumed here to be different excited states.

Photolysis rules.—Altogether perhaps twenty mixed ligand type complexes have been studied, and some useful empirical rules have emerged[17]. These are:

Rule 1: Represent the coordination octahedron by three mutually perpendicular axes, each having two ligands. On irradiation, that axis having the weakest average ligand field strength will be the one labilized.

Rule 2: If the labilized axis contains two different ligands, then the one preferentially photoactivated will be that of higher ligand field strength.

TABLE 1

PHOTOLYSIS BEHAVIOR OF SELECTED Cr^{III} COMPLEXES

Complex and absorption maxima (L_2, L_1, D in mμ)	*Band irradiated*	*Quantum yield at 250° C*	*Ligand[a] aquated*	*Ref.*
	O_h Complexes			
$Cr(urea)_6^{3+}$	L_2	0.10	urea	6
(444,620,697)	L_1	0.10		
	D	0.095		
$Cr(H_2O)_6^{3+}$	L_2	0.06–0.18	H_2O	10
(408,574,669)	L_1	0.12–0.18	(exchange)	
$Cr(NCS)_6^{3-}$	L_2	0.26	NCS^-	6
(420,567,—)	L_1	0.27		
$Cr(NH_3)_6^{3+}$	L_1L_1	0.32	NH_3	11
(354,466,656)	L_1	0.26		6
	D	0.29		6
$Cr(en)_3^{3+}$	L_2	0.55	en	12
(350,462,659)	L_1	0.47		
$Cr(CN)_6^{3-}$	L_2	*ca.* 0.1	CN^-	7
(307,376,530)	L_1	*ca.* 0.1		
	Non-O_h Complexes			
$Cr(NH_3)_5(H_2O)^{3+}$	L_1L_2	0.17–0.20	NH_3	13
(360,484,655)	L_1	0.15		
$Cr(NH_3)_2(H_2O)_4^{3+}$	L_1L_2	0.0018	NH_3	13
(384,525,660)	L_1	0.0017		
$Cr(NH_3)_5Cl^{2+}$	L_2	0.39	NH_3; trace	14, 15
(375,512,673)	L_1	0.35	Cl^-	
$Cr(H_2O)_5(NCS)^{2+}$	L_2	6×10^{-5}	NCS^-	16
(410,570,—)	L_1	2×10^{-5}		

[a] Unless otherwise specified, only aquation of the indicated ligand was looked for.

As examples, consider first the complex *trans* $Cr(NH_3)_2(NCS)_4^-$, known as Reinecke's salt (if the ammonium salt). The weaker field axes are the SCN-NCS ones, and by Rule 1, one expects (and finds) the only reaction to be that of photoaquation of the thiocyanate[6]. $Cr(NH_3)_5(NCS)^{2+}$ provides the second illustration. Here the weaker field axis is the NH_3-NCS one, and by application of Rule 2, photoaquation of ammonia is predicted to be favored over that of thiocyanate, again as is found experimentally (Table 2). Rule 2, moreover, suggests that the *trans* rather than the *cis* isomer of $Cr(NH_3)_4(H_2O)$ $(NCS)^{2+}$ is likely to be the one formed, and this prediction is tentatively confirmed by current work in this Laboratory. Rule 2 is not required to imply stereochemical consequences, however, and exceptions may well exist. Wasgestian[14], in the case he studied, believed the product to be *cis* $Cr(NH_3)_4(H_2O)Cl^{2+}$; both isomers were not prepared, however, and his isomer identification was tentative.

Rule 1 can be accounted for by the following qualitative ligand field picture[18]

TABLE 2

PHOTOLYSIS OF $Cr(NH_3)_5(NCS)^{2+}$ IN 0.1 *N* H_2SO_4[a]

Temperature	*370 mμ*		*490 mμ*		*643 mμ*	
°C	NCS^-	NH_3	NCS^-	NH_3	NCS^-	NH_3
5.0	0.024	0.39	0.019	0.42		
25.0	0.030	0.46	0.021	0.48	0.018	0.15
45.0	0.040	0.53	0.024	0.53		
E[b]	2.2	1.4	1.0	0.8		

[a] The quantities given are the quantum yields for photoaquation of the indicated ligand, with light of indicated wave-length. The three wave-lengths correspond to the L_2, L_1, and D bands; the results for the latter have been obtained since the publication cited.

[b] Apparent activation energy in kcal/mole.

Unsymmetrical complexes are approximated as still having three mutually perpendicular axes, but now of unequal average ligand field strength. Roughly speaking, the L_1 band then splits as though each axis were producing independently its quartet excited state. Thus a greater splitting of the L_1 band is often observed for a *trans* CrA_4X_2 complex than for a *cis* one, where A denotes an ammine group, and X, a halogen. The splitting is determined by the difference in average ligand field strength between the two kinds of axes, and it follows that the difference between the A–A and X–X axes in the *trans* compound should be twice that between the A–A and A–X axes in the *cis* one. From the spectrochemical series, the X–X and A–X axes are the weaker field ones; thus the long wave-length component of the composite L_1 band corresponds to the anti-bonding electron being in an orbital directed along the weaker field axis. Rule 1 then follows, if it is assumed that regardless of the irradiation wave-length, a rapid conversion occurs to leave the complex in the lowest excited quartet state. Rule 2 may be justified slightly by analogy to the O_h complexes, for which quantum yields tend to increase with ligand field strength, which suggests that the presence of an antibonding electron has a greater labilizing effect the greater the field strength of the ligand involved.

Excited state distortion.—The rationalization of Rule 1 leads to a further question: since the D band lies at a lower energy than does the L_1 band, should not inter-system crossing occur to leave the complex in the $^2E_{2g}$ state, with chemical reaction occurring only at this point? This sequence has in fact been proposed[19,20]; it is attractive in several ways. First, the doublet state, like the triplet states of organic photochemistry, should be long-lived relative to quartet states insofar as emission life-times are concerned, and hence likely to make a good reaction intermediate; second, the spin-pairing has freed an orbital so that ligand substitution *via* a seven coordinated intermediate should require little activation energy (see also Ref. 19). Finally, the near wave-length independence of quantum yields for the O_h complexes is explained if all interstate conversion efficiencies are high.

While the doublet intermediate mechanism may well be important for the

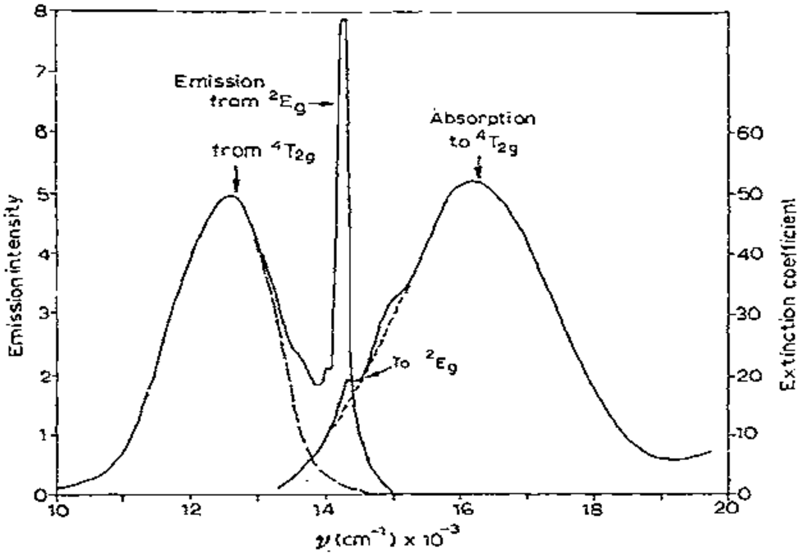


Fig. 6. Emission and absorption spectra for $Cr(urea)_6^{3+}$ in a low temperature glass. (from ref. 12).

O_h family, it does appear necessary to suppose that reaction occurs from excited quartet states in the case of at least some of the unsymmetric complexes, *i.e.* in the instances where the ratio of two reaction modes is wave-length dependent. This in turn implies that the inter-system quartet to doublet crossing is not always fast compared to chemical reaction of the excited doublet state).

An explanation for this last conclusion may be developed as follows. First, it has been found, in the now classic case of $Cr(urea)_6{}^{3+}$, that the low temperature fluorescence emission from the $^4T_{2g}$ state is shifted to the red by some 10 kcal/mole over the position of the absorption band[12], as shown in Fig. 6. Evidently, the geometry of the $^4T_{2g}$ state is sufficiently different from that of the ground state that in a Franck-Condon transition, the former is produced at a high vibrational level (see Ref. 19). If the $^4T_{2g}$ state thermally equilibrates before emission, then, similarly, emission would be to a high vibrational level of the ground state. As illustrated in Fig. 7, this explains both the broadness of the absorption and emission bands, and the red shift of the latter. The $^2E_{2g}$ state, however, involves no anti-bonding electrons, and should not be very distorted relative to the ground state; corresponding, both absorption and emission are fairly sharp (although vibronic coupling is still involved in the transition[21]).

The net of the above analysis is that, first, the thermally equilibrated $^4T_{2g}$ state may actually lie below the ^2E_g one, and, second, a Franck–Condon transition $^4T_{2g}$(equilibrated) $\rightarrow$ ^2E_g would center at high vibrational levels of the latter. For both reasons, then, it is entirely possible for the $^4T_{2g}$ state to be the practical terminus of the cascade from higher quartet levels[22].

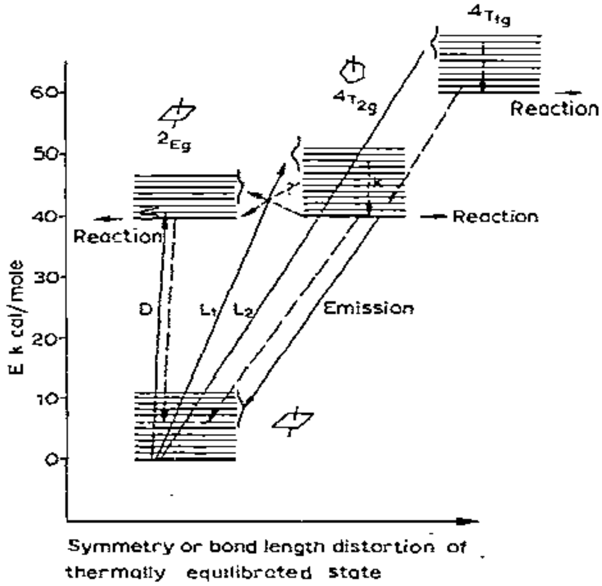


Fig. 7. Various deactivation processes for Cr^{III} excited states. (Radiationless processes shown as dashed lines.)

To emphasize the matter of excited state distortion, the $^4T_{2g}$ state is shown in Fig. 7 as a pentagonal pyramid. If it is assumed that a solvent molecule is coordinated during the thermal equilibration, to give a pentagonal *bi*pyramidal geometry, then a simple crystal field calculation is available. Figure 3b shows the splitting for this geometry[1], and for a d^3 system, the stabilization energy is 5.8 *Dq*, as compared to 2 *Dq* for the first excited state in octahedral geometry. On this very simple basis, the distorted state is the more stable one by 3.8 *Dq* (or 17 kcal/mole in the case of $Cr(urea)_6{}^{3+}$). The Jahn–Teller theorem provides another basis for predicting that, in principle, some excited state distortion *must* occur[1].

The full situation is yet more complicated; at room temperature Cr^{III} complexes do *not* emit, so that the photochemical reaction must be in competition with radiationless deactivation processes. Some studies in this Laboratory[17] and in Arizona[23] on the aquation and phosphorescence yields when a mixed solvent solution of Reinecke's salt is cooled from room temperature down to 77 °K have suggested that the radiationless deactivation which *competes* with the phosphorescence (*i.e.* emission from the ^2E_g state), *leads* to the photolytically active state, *i.e.* corresponds to process *k* in Fig. 7. There is thus another, although tentative, line of support to the conclusion that quartet excited states can be direct precursors to chemical reaction.

Another approach is to examine what happens if the D band is irradiated directly. The experiment is sufficiently difficult (because of the weak absorption) that few results exist. We found[6] no significant change in quantum yield in the case of $Cr(NH_3)_6^{3+}$, but a drop in yield and the highly significant change in the ratio of reaction modes, in the cases of $Cr(NH_3)_5(NCS)^{2+}$ (Table 2) and *cis* $Cr(en)_2(OH)_2^{+}$[9]. In other instances, as with Reinecke's salt, the D band is only a weak feature on the tail of the L_1 band, and the lack of change in quantum yield is probably not significant.

In summary, while there is a good deal of controversy about the exact sequence of events leading to Cr^{III} photolyses and in particular about the nature of the states undergoing chemical reaction, our own conclusions are the following.

(a) O_h complexes for which the thermally equilibrated $^4T_{2g}$ state lies above the ^2E state may photolyze primarily through the latter, with $Cr(NH_3)_5^{3+}$ as a likely example.

(b) Other O_h complexes, and possibly all of the less symmetric ones photolyze largely through excited quartet states, with different quartet states providing different photochemical paths in the case of very unsymmetric complexes.

Photoanation.—A particularly interesting reaction is that of photoanation, or the reverse of reaction (2). In the particular case studied, quantum yields were very low, but were first order in anion concentration, and it appeared that it was actually the ion-pair that was being photoactivated to an inner-outer sphere exchange of ligands[16]:

$$Cr(H_2O)_6^{3+} + NCS^- \xrightleftharpoons{K_{ip}} [Cr(H_2O)_6 \cdot NCS]^{2+} \tag{7}$$

$$[Cr(H_2O)_6 . NCS]^{2+} \xrightarrow{h\nu} Cr(H_2O)_5(NCS)^{2+} + H_2O \tag{8}$$

The alternative path of direct reaction between the anion and an excited state of the complex is unlikely in view of what is known about the rates of radiationless deactivation processes. These should be too fast for an excited state to retain its activation long enough to make an encounter with a dilute solvent species.

The general conclusion is that probably all photoreactions of complexes, if not merely prompt bond fission, are confined to reactions with a component of the solvent cage, *i.e.* with some species immediately available for reaction. This has led to some similar conclusions concerning the detailed mechanism of bimolecular thermal reactions of complexes[9,24].

COBALT(III) COMPLEXES

There is about the same diversity of Co^{III} complexes as of Cr^{III} ones, and the principal reaction chemistry is again one of ligand substitution, and probably by essentially the same mechanism. However, Co^{II} rather than Co^{III} is the stable valence state of the aqueous ion; $Co(H_2O)_6^{3+}$ is reduced by water, and complexes with easily oxidizable ligands can undergo thermal redox decompositions. Thus

$Co(C_2O_4)_3^{3-}$ decomposes in hot solution to give CO_2 and Co^{II}[25], and $Co(NH_3)_5I^{2+}$ gives Co^{II} and I_3^- in an iodide ion catalyzed reaction[26].

Spectra for a number of Co^{III} acidopentammine complexes are given in Fig. 8. A pure ligand field spectrum, as for $Co(NH_3)_5F^{2+}$, is rather similar in appearance to that for Cr^{III} complexes, and the transitions are similar in nature. Fig. 9 gives the term system; since Co^{III} has six *d* electrons, these pair in the ground state to give diamagnetic complexes, and the low lying excited states must all involve promotion of an electron to an e_g orbital. The main bands are due to the transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, in O_h symmetry. In addition, a spin forbidden transition to ${}^3T_{1g}$ is predicted, but is not observable in the absorption spectrum, possibly because it lies under one of the more intense bands. The hexacyano complex is exceptional in that phosphorescent emission (in the *red*) has been observed, presumably due to ${}^3T_{1g} \rightarrow {}^1A_{1g}$[27].

Returning to Fig. 8, it is seen that many of the complexes exhibit an intense absorption in the region of the L_2 band; this is attributed to a charge transfer (CT) process in which electron density shifts towards the cobalt, possibly to a *p* antibonding orbital[18]. In the charge transfer excited state, the Co-X bond may be more nearly Co^{II}-X than Co^{III}-X^-; that some such change in bond character occurs is suggested by the fact that the wave-length of the CT band is longer the lower the expected potential for the process $X^- = X + e^-$.

In view of this qualitative description of the excited states involved, it is not

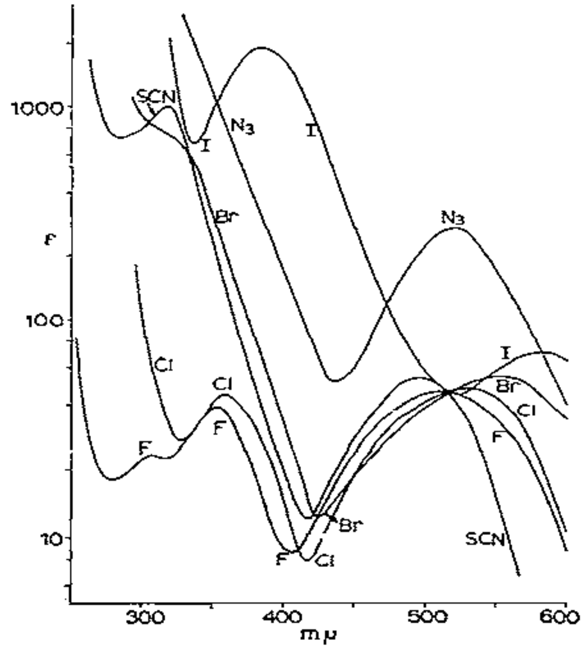
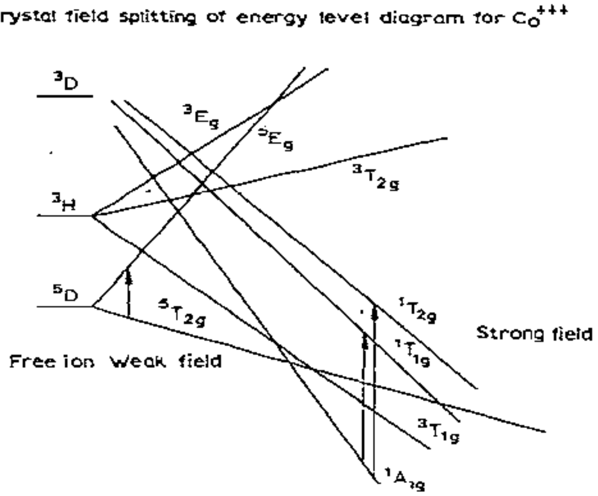


Fig. 8. Absorption spectra of $Co(NH_3)_5X^{2+}$ complexes.



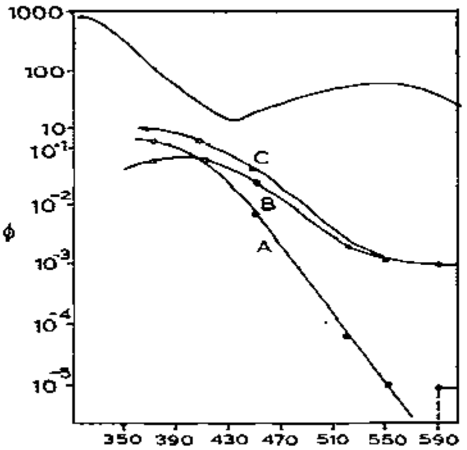


Fig. 9. Term diagram for a d_6 system in an octahedral complex.

Fig. 10. Photolysis of Cr(NH$_3$)$_5$Br^{2+}.
Upper section: absorption spectrum; lower section: quantum yield for Co^{II} (curve A), for aquation (curve B), and total quantum yield (curve C) (from ref. 31).

surprising that irradiation of a CT band tends to produce photoredox decomposition, *i.e.* Co^{II} and oxidized ligand. Data for Co(NH$_3$)$_5$Br^{2+} are shown in Fig. 10. Flash photolysis studies have confirmed that homolytic bond fission does occur[28] —a bromine atom transient is observed. In the deeper ultra-violet (254 mμ), pure ammine complexes, such as Co(NH$_3$)$_6$$^{3+}$ similarly undergo photoredox decompositions[29]. Here, small but complex pH dependencies of the quantum yields were found and explained in terms of excited state acid–base equilibria. In the presence of added iodide ion, so that the ion-pair [Co(NH$_3$)$_6$ · I]$^{2+}$ is present, a photoredox reaction occurs at the longer wave-lengths with which this paper is concerned (> 350 mμ), but now with I$_3$$^-$ the oxidation product[30]; evidently, redox partners need not be bonded directly to each other.

Not only do Co^{III} complexes differ from Cr^{III} ones in showing easy photoredox decompositions, but the photoaquation behavior is also different. Thus Co(NH$_3$)$_6$$^{3+}$, Co(NH$_3$)$_5$Cl^{2+}, and other ions not having low lying CT bands are quite stable to visible light; what little reaction occurs is one of aquation, but with quantum yields of 0.01 or much less. Even for those ions, such as Co(NH$_3$)$_5$Br^{2+}, whose L$_2$ band is covered by a CT one, irradiation of the apparently unaffected L$_1$ band again leads to very low quantum yields (and no redox decomposition). It is perhaps equally curious that while irradiation of the CT band understandably produces an efficient photoredox decomposition, there may now be a high quantum yield for aquation as well.

Some data for representative systems are collected in Table 3. Note that the cyano complexes are again exceptional; while the visible absorption bands show no CT character, and no photoredox behavior seems to occur, quite high photoaquation quantum yields are found.

Excited state chemistry.—Considering first the ligand field excited states, it is not clear why they appear to be so unreactive. Schläfer[19] has noted that there would be no crystal field contribution to the activation energy of reaction (by either a square pyramid or a pentagonal bipyramid intermediate) if, in the case of Cr^{III} the reacting state were $^4T_{2g}$ or ^2E_g, but that there would be in the case of Co^{III} reacting from the $^3T_{1g}$ (but not the $^1T_{1g}$) state. He considers Cr^{III} complexes always to react from the $^2E_{2g}$ state, and, if analogously, Co^{III} ones react from the $^3T_{1g}$ level, the presence of an activation energy would make chemical reaction highly unfavored relative to radiationless deactivation.

Again, there may be an alternative explanation. If Fig. 3 is applied to the d^6 case, the crystal field stabilization of the pentagonal bipyramid becomes 15.6 *Dq*, as compared to 14 *Dq* for the first singlet excited state in octahedral symmetry; the difference is about half of that in the Cr^{III} case. Possibly, then, geometric or

TABLE 3

PHOTOLYSIS BEHAVIOR OF SELECTED CO^{III} COMPLEXES

Complex	*Band irradiated, wave-length used (mμ)*	*Total quantum yield*	*Reaction mode*[a]	*Ref.*
$Co(NH_3)_5Cl^{2+}$	CT (254)	0.2^b	100% R	29
	L_2 (370)	0.01	A	31
	L_1 (550)	0.002	A	
$Co(NH_3)_5(NCS)^{2+}$	CT (370)	0.05	30% A, 70% R	31
	L_1 (550)	7×10^{-4}	80% A, 20% R	31
$Co(NH_3)_5N_3^{2+}$	CT (370)	0.4	100% R	31
	? (550)	0.01	100% R	
$Co(NH_3)_5I^{2+}$	CT (370)	0.7	100% R	31
	? (370)	0.1	100% R	
$Co(C_2O_4)_3^{3-}$	CT (313)	0.7	100% R	32
	CT (370)	0.4	100% R	33
	L_1 (550)	0.002	100% R	33
$Co(CN)_6^{3-}$	L_1 (365)	0.9^c	A	30
		0.3	A	34
$Co(CN)_5Cl^{3-}$	L_1 (370)	0.3	A	30
$Co(CN)_5I^{3-}$	L_1 (550)	0.7	A	30
trans $Co(eo)_2Br_2^+$	CT (370)	0.07	90% A, 10% R	35
	L_1 (550)	6×10^{-4}	97% A, 3% A	
cis $Co(en)_2Br_2^+$	CT (370)	0.1	95% A, 5% R	35
	L_1 (550)	0.004	93% A, 7% R	
$Co(NH_3)_6^{3+}$	CT (254)	0.7^d	100% R	29

[a] A: aquation; R: redox decomposition. [b] In 0.044 *N* $HClO_4$. [c] The lower quantum yield is probably correct. [d] In 0.044 *M* $HClO_4$.

symmetry distortion is not energetically favored in the case of Co^{III} excited states, so that the thermally equilibrated $^1T_{1g}$ state remains essentially octahedral, and as a consequence, its radiationless deactivation to the ground state should be much faster than the corresponding process in the Cr^{III} system. Distortion must still be present, judging from the broadness of the absorption bands, but would now be supposed to be more of the nature of an average bond lengthening.

None of the above helps to explain the high aquation quantum yields for the cyano complexes. Here, however, the cobalt electrons are undoubtedly heavily involved in π-bonding, so that the L_1 excited state corresponds to taking an electron from a π-bonding to a σ-antibonding state. Possibly this double bond weakening effect is what is important. Alternatively, in view of the observed phosphorescence[27], photoaquation for these complexes may be occurring from the first triplet state. Yet another possibility is that the species $Co(CN)_5{}^{2-}$ is unusually stable and capable of relatively prolonged independent existence. Wilmarth and co-workers[36] find that the assumption of such an intermediate explains their kinetic data on rates of anation of $Co(CN)_5(H_2O)^{2-}$. We find that irradiation of either aqueous $Co(CN)_6{}^{3-}$ or $Co(CN)_5(H_2O)^{2-}$ at 350 mμ in the presence of 1 to 3 M iodide leads to a direct photoanation[7]. Alternatively, irradiation of $Co(CN)_5I^{3-}$ at 500 mμ leads to photoaquation, but in quantum yield which decreases from 0.2 to 0.02 as the concentration of added iodide ion is increased from zero to 2 M. Qualitatively, all of these results are explainable in terms of a photolytic production of $Co(CN)_5{}^{2-}$, which is then scavenged competitively by water and iodide. Quantitatively, there are indications that scavenging occurs within the solvent cage of the parent complex. These complexities are cited to illustrate that a great deal of work remains to be done on the cyanide complex systems.

Proceeding to the case of irradiation of low lying CT bands, *i.e.* ones which appear to overlap an L_2 band, it seems quite general that homolytic bond fission of the Co–X bond occurs. The corresponding radicals have been observed directly, in flash photolysis experiments, with X = Br, I, and SCN, and, indirectly, with $X = N_3$. The really striking feature is that while photoaquation quantum yields are low for a ligand field band, they can be quite high, along with the redox decomposition, on irradiation of a CT band. Thus at 370 mμ, the photoaquation and photoredox quantum yields for $Co(NH_3)_5Br^{2+}$ are each 0.1 (15 °C), and the former shows a small *negative* temperature dependence. The suggested explanation[30] is that the two modes of reaction are competitive:

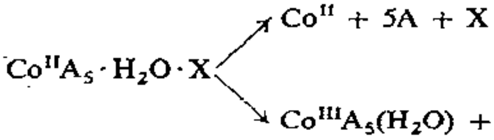
first stage: homolytic bond fission

$$Co^{III}A_5X \xrightarrow{h\nu} Co^{II}A_5 \cdot X \tag{9}$$

second stage: diffusional separation of fragments

$$Co^{II}A_5X \rightarrow Co^{II}A_5 \cdot H_2O \cdot X \tag{10}$$

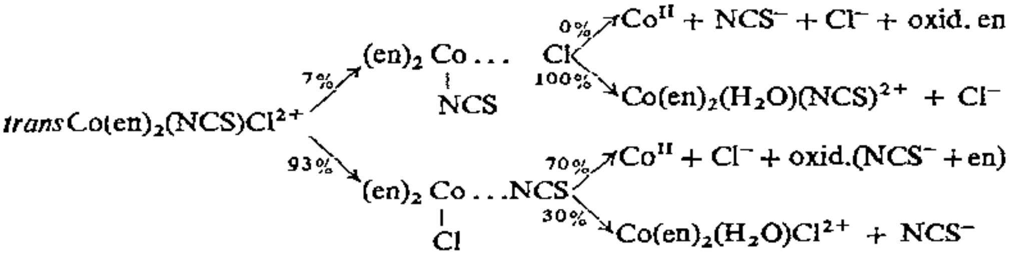
third stage: escape of X, with or without electron return



$$\begin{tikzcd}[row sep=small] & \mathrm{Co^{II} + 5A + X} \quad (11) \\ \mathrm{Co^{II}A_5\cdot H_2O\cdot X} \arrow[ur] \arrow[dr] & \\ & \mathrm{Co^{III}A_5(H_2O) + X^-} \quad (12) \end{tikzcd}$$

The picture is that irradiation loads to homolytic bond fission, but that electron return may occur as a cage reaction during the diffusional escape of the X radical. If, at this point, water coordinates, the product would be the aquopentammine or aquated complex. The sequence with the cyano complexes may be very similar, except that the first step would then be that of a heterolytic bond fission.

According to the above mechanism, the photoaquation path should be entirely different for a CT *vs.* a ligand field band. This conclusion cannot be tested so long as only one photoaquation process occurs; if, however, two or more photoaquation reactions can occur, then it would be expected that the *ratio* of aquation modes should vary according to which band was irradiated. As the potentially diagnostic experiment, we are studying the photolysis behavior of *trans* $\mathrm{Co(en)_2(NCS)Cl^{+}}$[37]. For this complex the thermal reaction is entirely one of chloride aquation[38]. Irradiation of the L_1 band (556 mμ) leads to no detectable redox decomposition but only to photoaquation, with a quantum yield of 1.1×10^{-4} for chloride release and 1.8×10^{-4} for thiocyanate release (22 °C, 0.1 *M* acetic acid solution). The ratio of chloride to thiocyanate aquation is then 0.6. If however, the irradiation is at 385 mμ, or in the CT region, the quantum yield for $\mathrm{Co^{II}}$ is 0.087, and analyses for $\mathrm{Cl^-}$, $\mathrm{SCN^-}$, $\mathrm{Co(en)_2(H_2O)Cl^{2+}}$ and $\mathrm{Co(en)_2(H_2O)(NCS)^{2+}}$ yield the photolytic scheme assuming the cage mechanism:



$$\begin{tikzcd}[row sep=small, column sep=small] & & \mathrm{Co^{II} + NCS^- + Cl^- + oxid.\,en} \\ & \mathrm{(en)_2Co\ldots Cl}\ (\mathrm{NCS}) \arrow[ur, "0\%"] \arrow[dr, "100\%"'] & \\ \textit{trans}\,\mathrm{Co(en)_2(NCS)Cl^{2+}} \arrow[ur, "7\%"] \arrow[dr, "93\%"'] & & \mathrm{Co(en)_2(H_2O)(NCS)^{2+} + Cl^-} \\ & \mathrm{(en)_2Co\ldots NCS}\ (\mathrm{Cl}) \arrow[r, "70\%"] \arrow[dr, "30\%"'] & \mathrm{Co^{II} + Cl^- + oxid.(NCS^- + en)} \\ & & \mathrm{Co(en)_2(H_2O)Cl^{2+} + NCS^-} \end{tikzcd}$$

As might be expected from its greater electronegativity, homolytic fission of the Co—Cl bond occurs only 7% of the time, and then with 100% electron return. Less based on interpretation and very significant is the fact that the ratio of chloride to thiocyanate aquation is now 0.2; this result strongly indicates that a different photoaquation mechanism is indeed present when the CT band is irradiated.

Another type of excited state behavior appears to be present with complexes of the type $\mathrm{Co(NH_3)_5(OOCR)^{2+}}$. The spectra for a series of these are shown in

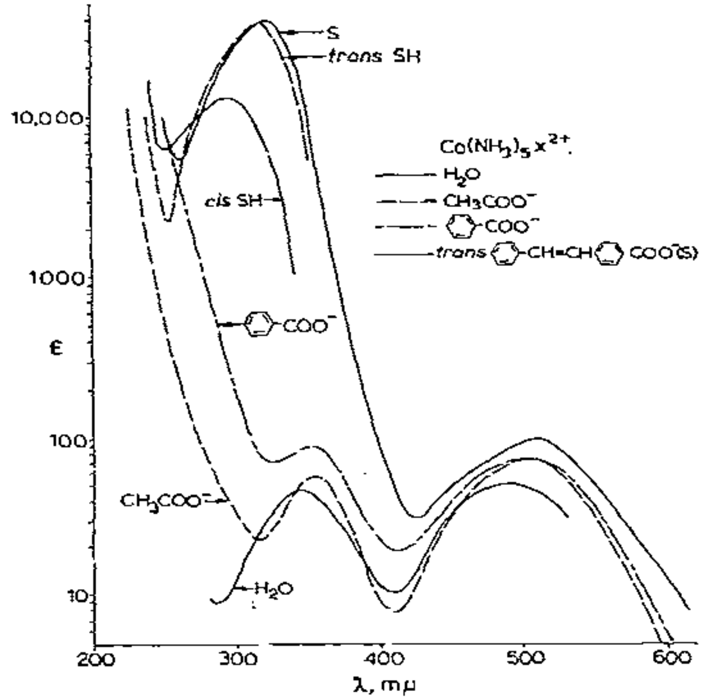
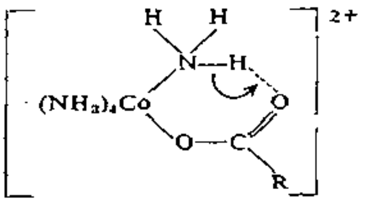


Fig. 11. Absorption spectra for complexes of the type $Co(NH_3)_5X^{2+}$.

Fig. 11; all have an absorption band around 350 mμ, although probably only coincidentally. That for $R = CH_3$ may simply be an 2 band, while that for R = *trans* stilbene is probably largely derived from a toluenic singlet state[39]. Photolysis results at 350 mμ indicate that all three carboxylic complexes give Co^{II} and the free acid[40], with ammonia (or possibly solvent) oxidized. The point of interest is that an absorption band mainly centered within the ligand, as it appears to be particularly in the case of the stilbene complex, leads to photolysis involving the cobalt center. Possibly a cyclic hydrogen bonded structure is present:



so that, upon excitation, hydrogen atom transfer from the ammonia group occurs, with an electron shift to leave Co^{II}, free RCOOH, and NH_2 as the immediate products. In any event, some form of intramolecular energy transfer seems to have occurred. More generally, the Co^{III} systems, with their singlet and triplet excited states, offer some analogies to organic photochemistry, suggesting a number of potentially interesting experiments. These involve testing to see whether inter- or intramolecular energy transfer can occur between a Co^{III} moiety and an organic one whose photochemistry is known. Results in this area are sparse; Hammond and co-workers have reported certain metal chelates to quench organic triplet states[41].

PHOTOELECTRON PRODUCTION

The discovery that flash photolysis of the CT band of $Fe(CN)_6^{4-}$ leads to production of a photoelectron transient (and $Fe(CN)_6^{3-}$) [42] provided a useful generating system for those interested in the subsequent reaction chemistry of hydrated electrons. It also made it clear that a different kind of photoredox reaction from that of Co^{III} complexes could occur. The general prerequisites for photoelectron production seem to be that:

(a) a CT band be irradiated,

(b) the complex have a reasonably stable one electron higher oxidation state of the same stoichiometry, and

(c) the complex not have a stable one electron lower oxidation state of the same stoichiometry (which makes electron scavenging by the parent compound less favorable).

Ferrocyanide ion meets the above specifications; so do $Mo(CN)_6^{4-}$, $W(CN)_6^{4-}$, and $Ru(CN)_6^{4-}$, and support was given to the predictive value of the above rules by the finding that the two octacyano complexes did indeed show photoelectron production, as did also the ruthenium one[43].

The finding of photoelectron production helped better to understand the photochemistry of $Fe(CN)_6^{4-}$; depending on whether the irradiation is at 254 mμ or further towards the visible, the photolysis product is $Fe(CN)_6^{3-}$ or $Fe(CN)_5(H_2O)^{3-}$. In the presence of oxygen, scavenging of the electron yields O_2^-, which can react further with the various complex ion species; also, depending on pH, $Fe(CN)_6^{3-}$ can undergo probably both photoredox decomposition (to $Fe(CN)_5(H_2O)^{3-}$ and cyanogen radical) and photoaquation.

There has similarly been a complicated history of publication on the photochemistry of $Mo(CN)_5^{4-}$ [44,45,46]. The final product is an aquo (or oxo[47]) tetracyano complex, but a transient red form appears in the early stages of the photolysis, of a minute or so lifetime, and flash photolysis shows both the presence of photoelectrons and of another transient of a millisecond lifetime. It is entirely possible that rather involved redox reaction sequences occur.

Photoelectron production may prove to be a much more common process for coordination compounds than now realized. It represents an alternative redox mode to that involving reduction of the central metal ion. In fact, the determination of which mode occurs for a given system should provide a chemical diagnosis of whether the CT excited state is ligand-to-metal or ligand-to-solvent in type of electron displacement involved.

SUMMARY AND CONCLUSIONS

It should again be emphasized that this paper is not intended to constitute a general review of coordination compound photochemistry. It is first of all limited mainly to Cr^{III} and Co^{III} complexes in aqueous media, and then primarily to that work in this Laboratory, past and in progress, which seems to be informative as to the nature of the primary processes.

The general points on which we feel we have good, although not conclusive, evidence are the following. First, quite a variety of photochemical reactions are found to occur with irradiation in the wave-length region of ligand field bands, and of a nature understandable not so much in terms of the thermal reaction chemistry of the complex, as in terms of the electronic structure and bonding in the excited state. The second general point is that the excited state reaction is not necessarily a prompt one; it may be activated, and it may be in competition with other chemical processes or with spectroscopic ones.

Finally, it seems important to recognize that the traditional octahedral, square planar, etc. geometries of complex ions are not necessarily those of the excited states. Alfred Werner established the ground state geometries; the coordination photochemist must try to do so for excited states. May he be as successful!

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