PHOTOCHEMISTRY OF TRANSITION-METAL COORDINATION COMPOUNDS

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I. INTRODUCTION

The photosensitivity of coordination compounds has been appreciated since the earliest literature in the field of inorganic chemistry. This subject has drawn attention as an interesting area for qualitative study and now, increasingly, for quantitative investigations; as having valuable applications to preparative chemistry; and, of course, as a nuisance aspect to thermal kinetics, especially with the advent of fluorescent lighting. There has been a considerable recent expansion of the literature on inorganic photochemistry, a growth that promises to continue not only along established lines but also with increasing interrelations with the now extensive subject of organic photochemistry.

We have attempted to be reasonably definitive in literature coverage; *Chemical Abstracts* was searched

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through 1967, as well as a number of leading journals individually. Early literature is not cited in great detail; where possible the reader is directed to papers having good bibliographies of such material. There are some recent, less extensive summaries in the field.[2,3]

It is desirable to define closely the intended scope. Coordination compounds are taken to be "those compounds formed by the union in stoichiometric ratio of otherwise saturated molecules, themselves capable of independent existence."[4] Excluded are ionic solids (and thus silver halides and the field of photography), oxide entities (such as the molybdates, but, as an exception, not MnO_4^-), and metal–organic compounds. Also excluded are chelates of biological origin, such as the porphyrins.

Secondly, we have concerned ourselves mainly with primary photochemical processes, so that detailed considerations of the subsequent reactions of radicals or other fragments are omitted, as are reports of qualitative observations on poorly defined systems. A borderline area is that of the radiolytic and photolytic chemistry of aqueous ions; some relevant material is included, but the reader also is referred to reviews for further aspects.[5] Lastly, any discussion of photochemistry requires some consideration of the nature of the excited states involved. Excited-state assignments are therefore summarized, with some criticality, but without attempting actually to review what is a large body of literature in its own right. The general framework of excited-state systems important to coordination chemistry, their transitions, and the various general types of photolysis mechanisms are discussed briefly.

The material has been organized according to two principles. Generally, the sequence of transition-metal groups in the periodic table is followed. However, certain families of complexes (cyanides, oxalates, etc.) have been investigated so often as a group that these are so treated here. Such groupings are largely historical. Thus $Cr(C_2O_4)_3^{3-}$ is closer in behavior to other Cr(III) complexes than to the oxalato family, and the photochemistry of $Co(CN)_6^{3-}$ could as well have been included with Co(III), and, furthermore, has resemblances as much to $Cr(CO)_6$ as to other cyanides. Finally, the tables of data are selective rather than comprehensive, and the papers cited often contain additional results.

A. ELECTRONIC STATES OF COORDINATION COMPOUNDS

The ligand–metal bonding system of a coordination compound is so mutually interacting that generally one must consider excited states of the molecule rather than those of isolated bonds or groups. In crystal-field theory, the point group symmetry of the complex (considering only those atoms directly bound to the central metal atom) determines the extent to which the metal d orbitals lose degeneracy. Crystal-field excited states typically involve promotion of a d electron from an orbital directed away from the ligand positions (a t_{2g} orbital in octahedral or O_h complexes) to one directed more toward them (an e_g orbital in O_h complexes). The characteristic colors of coordination complexes are often due to transitions to these low-lying electronic levels. Individual electronic configurations are described by spectroscopic terms, and a frequent representation is that of the variation of the energy of the various term states with crystal-field strength, as illustrated for Cr(III) in Figure 4. In this case, the energy of the transition ${}^4A_{2g} \rightarrow {}^4T_{2g}$ gives directly the crystal-field parameter $10Dq$. The spectrum of a typical Cr(III) complex is shown in Figure 5.

Where bonding aspects are recognized, the treatment is called ligand-field theory, and the corresponding transitions, ligand-field ones. As a matter of convenience, the principal ligand-field bands will be labeled L_1, L_2, etc., in order of increasing energy, as shown in Figure 5. Bands corresponding to transitions involving a change in multiplicity will be given a different label, such as D (for doublet) in the case of ${}^4A_{2g} \rightarrow {}^2E_g$ for Cr(III).

The electronic states of structures having an inversion center have parity designations "g" or "u." Transitions between states of the same parity are Laporte forbidden, with extinction coefficients around 100 M^{-1} cm^{-1}. Transitions between states of differing multiplicity are spin forbidden and are therefore usually even less intense.

Ligand-field theory provides correlations between metal, ligand, and molecular orbitals. A generalized (and simplified) diagram for a first-row transition metal complex of O_h symmetry is given in Figure 1.[6] Here, π as well as σ bonding is indicated, and the ligand-field transition is shown by the solid arrow to be from a π molecular orbital to the first σ antibonding one. In the absence of any interaction, the transition would be that given by the dotted arrow, *i.e.*, from the unperturbed metal t_{2g} or σ nonbonding orbital. With strongly π-bonded complexes, such as the carbonyls, some transitions in the ligand-field range of energy have been assigned as being to ligand π antibonding orbitals, or CTTL (see below).

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(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

(3) (a) E. L. Wehry, *Quart. Rev.* (London), 21, 213 (1967) (45 references); (b) J. Szychlinsky, *Wiadomosci Chemi.*, 16, 607 (1962) (250 references); (c) V. Balzani, L. Moggi, F. Scandola, and V. Corassiti, *Inorg. Chim. Acta Rev.*, 1, 7 (1967).

(4) H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1944, p 79.

(5) (a) R. F. Gould, Ed., "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965; (b) F. S. Dainton and D. G. L. James, *Trans. Faraday Soc.*, 54, 649 (1958).

(6) P. J. Stephens, private communication.

There is a second type of absorption band, usually occurring at higher energies than the ligand-field ones, but often overlapping partly with the L_2 band. The transition is an allowed one (g to u in O_h complexes) and therefore of high extinction coefficient (10^3–10^5 M^{-1} cm^{-1}). Such transitions are called *charge-transfer* ones since electron density has moved radially rather than angularly as in ligand-field excitations. Charge-transfer (CT) transitions are of two basic types: those in which electron density has moved toward the central metal atom (CTTM, charge transfer to metal), and those in which the density has moved outward. The transfer may be from the metal to a ligand (CTTL, charge transfer to ligand) or from either a ligand or the complex as a whole to the solvent (CTTS). In addition, of course, absorptions due to internal ligand transitions may be present, as in the case of the thiocyanato complexes. We will adopt the usage of naming excited states by the process of excitation, *e.g.*, d–d, CT, etc. states. In addition to the specific papers cited in the individual sections, there is a number of standard references which treat crystal- and ligand-field theory as well as that of CT transitions.[2,7–13]

B. EXCITED-STATE PROCESSES

There are several processes which a molecule in an excited state can undergo. Figure 7 gives an illustration of the situation with Cr(III). The excited state, when first generated by absorption of a light quantum, may be in a high vibrational state. This is usually the case with coordination compounds, as evidenced by the broadness of the absorption and emission bands and, where observable, the red shift of the latter relative to the former. The accepted explanation is that the transitions obey the Franck–Condon principle in that the most favored transition is to vibrational levels such that the most probable nuclear positions are not much different from those in the ground state. If a transition terminates on a high vibrational level of the excited state, the implication is that the zero vibrational level is one of significantly different geometry from that of the ground state (note ref 14).

A preliminary and very rapid process is then the *thermal equilibration* of the excited state to vibrational equilibrium with the medium; this probably occurs within a few vibrational periods. The equilibrated excited state may then return to the ground state by *emission*, or by *radiationless deactivation* (*internal conversion*). The energy released presumably appears as phonon waves in the medium; the process has been discussed theoretically.[15,16] Either form of return is usually to some high vibrational level of the ground state. Alternatively, the internal conversion may be to a lower state of the same multiplicity. Emission and radiationless deactivation may be somewhat hindered in the case of complexes, and suggested lifetimes have been around 10^{-7} sec,[17] while internal conversion to a lower excited state is considered to be very fast. Thus excitation is thought normally to be followed by a rapid cascade down to the lowest excited state of the same multiplicity. It has been suggested, however, that this may not always be the case, especially with asymmetric complexes.[14] Returning to the emission process, this is called *fluorescence* if the excited state and ground states are of the same multiplicity, and *phosphorescence* otherwise.

The excited state may also undergo a radiationless transition to a lower state of different multiplicity, *i.e.*, *intersystem crossing* may occur, and this process is

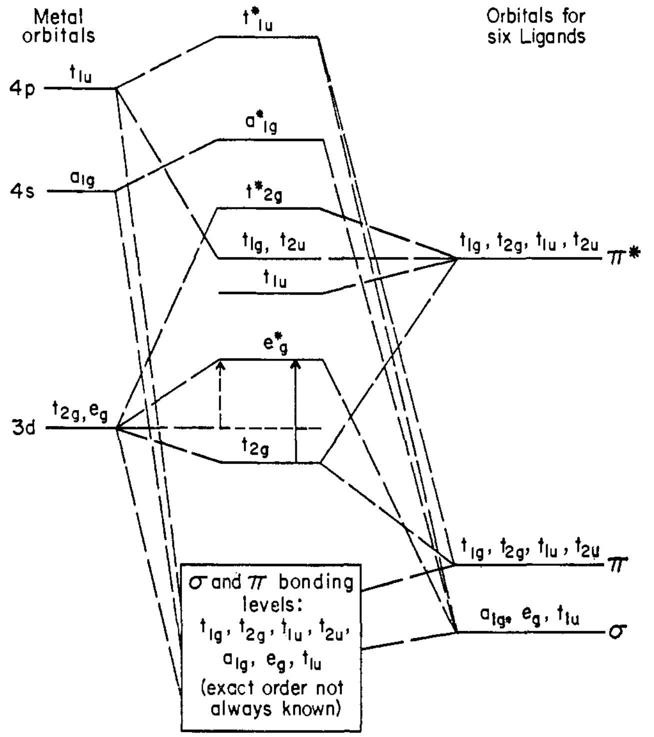

Figure 1.—Molecular orbital diagram for a transition-metal complex of O_h symmetry. The σ and π bonding levels have been left as a block, since, while the former generally lie below the latter, the two kinds of levels may be partially interspersed in the case of certain strongly π bonding ligands.

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(7) T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 229

(8) C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

(9) L. E. Orgel, "An Introduction to Transition-Metal Chemistry and Ligand Field Theory," Methuen and Co., Ltd., London, 1960.

(10) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

(11) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(12) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1966.

(13) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966.

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

(15) G. W. Robinson, *J. Mol. Spectry.*, **6**, 58 (1961).

(16) M. Gouterman, *Chem. Rev.*, **65**, 413 (1965).

(17) H. L. Schläfer, *J. Phys. Chem.*, **69**, 2201 (1965).

thought to have about the same probability as that of radiationless deactivation to the ground state, at least in the case of Cr(III).[17,18] The new state so reached may now have a relatively small emission probability since the phosphorescent return to the ground state is hindered by the multiplicity change. The triplet states of organic molecules and the doublet state of Cr(III) are examples of such potentially long-lived states.

Finally, of course, an excited state may undergo chemical reaction, as discussed in detail below. Such reaction as well as radiationless deactivations, but not emissions, may be temperature dependent.

In the photochemical investigations considered here, excited states have so far always been produced by the absorption of a light quantum. An alternative possibility is that of intermolecular energy transfer

$$A^* + B \longrightarrow A + B^* \qquad (1)$$

where A* and B* are excited-state molecules. The process is well known in organic photochemistry,[19] usually involving triplet states, but only two reports involving coordination compounds seem extant.[20]

C. PHOTOCHEMICAL MECHANISMS

Photochemical change can occur at or during any of the stages or processes mentioned above. If some particular bond is highly distorted in the nascent excited state, fairly prompt or predissociative cleavage would be a possibility (and not necessarily with any appreciable concomitant broadening of the absorption band[12]). A thermally equilibrated excited state may, alternatively, be able to undergo a rapid but otherwise essentially ordinary chemical reaction. In either situation, the nature of the chemical process should show some correlation with that of the excited state, and such correlations are in fact found. Thus excitation to a ligand-field state tends to lead to heterolytic reactions, usually an aquation in which water replaces some ligand in the coordination sphere. Charge-transfer excited states, if CTTM, tend to give redox decompositions in which the metal is reduced and either a ligand or solvent is oxidized; CTTS states tend to lead to oxidation of the metal or of the complex as a unit, accompanied either by reduction of the solvent or production of a solvated electron. Photochemistry thus means to some extent the chemistry of excited states.

Alternatively, reaction can occur during or immediately after a transition back to the ground state. The nascent ground-state molecule will generally be highly vibrationally excited, or "hot," and may thus in some degree resemble the transition state of a thermal reaction path. A pursuit of this mechanism led to the equation[21]

$$\phi = k(1 - E^0/E)^n \qquad (2)$$

where ϕ is the quantum yield, E^0 is the threshold energy for reaction, E is the energy of the light quantum absorbed, and n is related to the number of vibrational modes excited. Such a model predicts a sharply dropping ϕ with increasing wavelength, which, however, is not the usual observation in the case of coordination compounds. This mechanism appears to require that the energy of the absorbed light quantum be entirely or at least proportionately converted to ground-state vibrational energy, so that an implicit assumption is that no equilibration of the excited state occurs before radiationless deactivation. Where equilibration does occur, quantum yields should not be wavelength dependent, and the same would be true if internal conversion or intersystem crossing were involved, so that the reactive excited state was not the one produced by the absorption.

On the other hand, the observation of a quantum yield which shows a sharp decrease with increasing wavelength of irradiation does not necessarily confirm that the mechanism of eq 2 is operating. Frequently such drops in quantum yield can just as well be attributed to an overlap of two absorption bands, only the shorter wavelength one of which is photoactive. This appears to be the situation with many Co(III) complexes, for example. We emphasize that while hot molecule reactions certainly can occur, the presence or absence of a wavelength dependence of the quantum yield is not diagnostic.

As another point, it might be thought that a hot ground-state molecule should react like the ordinary activated molecule of thermal kinetics, so that the photochemical reaction should be the same as the thermal one. It is always possible, however, that the distribution of vibrational energy in the hot molecule is different enough from that in the transition state for the photochemical and thermal reactions not to take the same course.

Thus neither the nature of the chemical reaction nor the wavelength dependence of its quantum yield provides a certain indication of the immediately antecedent excited state. Concurrent studies of any fluorescent or phosphorescent emission can be of help. Also, we do assume that if two different kinds of photochemical reactions occur, and the *ratio* of the quantum yields for the two reaction modes varies with wavelength, then there are at least two different paths, involving different excited-state precursors.

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

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

(20) (a) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4781 (1966); (b) L. Lindquist, *Acta Chem. Scand.*, **20**, 2067 (1966).

(21) G. Zimmerman, *J. Chem. Phys.*, **23**, 825 (1955).

Photochemical reactions observed with coordination compounds often appear to be photoaccelerations of existing thermal reactions. The thermal reaction may be irreversible, particularly in the case of photoredox decompositions, or, as is often the case with photosubstitution processes, the dark reaction may be reversible. If it is reversible, then the phenomenon of *photochromism* appears. This is discussed in section XIV, but the essential requirement is that the photochemical reaction be complemented by a reverse thermal process, so that color changes induced by radiation revert in the dark.[22]

It is inherent in a photochromic system that a photostationary state exist, in which the photochemical (plus thermal) forward and thermal back-reaction rates balance. This state will be displaced toward the products if the back-reaction is slow, and toward the reactants if it is fast, relative to the photolysis rate. Thus, it seems likely that many of the substitutionally labile complexes appear to be insensitive to light simply because the photostationary state corresponds to very little net reaction. Also, it is perhaps for this reason that while both photoredox and photosubstitution reactions have been observed for the nonlabile complexes, only the former have been reported so far for the labile ones (with the possible exception of $Ni(CN)_4^{2-}$).

II. EXPERIMENTAL

The scope of this review is not such as to include the literature on experimental methods in photochemistry, much of which is summarized in a current monograph.[19] Some very recent papers deserve mention, however. Also, several are directed toward experimental aspects of special importance to the photochemistry of coordination compounds.

A. ACTINOMETRY

A quantum yield, ϕ, is defined by

$$n = E\phi \quad (3)$$

where n denotes the moles of reactant photolyzed, and E is the number of einsteins of light quanta absorbed by the reactant molecules. The determination of E can be by absolute photometry, but it is extremely convenient to be able to use a previously calibrated chemical system. Two such actinometric systems are the ferrioxalate and the uranyl oxalate ones, whose photochemistry is discussed in section III. Other actinometers are available,[19] but ferrioxalate actinometry has gained wide use because of its sensitivity and convenience. Its usual region of applicability is between 250 and 450 mμ. The uranyl oxalate actinometer, useful over about the same wavelength region, has traditionally been calibrated in terms of the disappearance of oxalate, with the consequence that E must be fairly large for reasonable accuracy to be obtained. However, a micromethod based on the measurement of the evolved carbon monoxide now allows a greatly increased sensitivity, up to about a 1000-fold more than usual.[23,24] A recently proposed actinometer, also for use in the ultraviolet, is based on the electrochemical detection of photoproduced chloride ions from *p*-chloroaniline.[25]

The study of the photochemistry of coordination compounds has been hampered by the fact that ligand-field excited states are generally produced by light in the visible range of wavelengths, for which the common actinometers are not applicable. Recently, however, a new system has been made available.[26] The sensitive compound is the Reineckate ion, *trans*-$Cr(NH_3)_2(NCS)_4^-$, which absorbs throughout the visible to give a nearly wavelength-independent quantum yield of about 0.3 (see Table V). The product, free thiocyanate ion, is easily detected, and the useful wavelength range is from 316 to 600 mμ. An alternative complex, $Cr(urea)_6^{3+}$, while less convenient to use, provides an actinometric range of 450–735 mμ. Also, the complex $Mn(C_2O_4)_3^{3-}$ has been proposed for use in actinometry,[27,28] for the range 313–550 mμ, although the thermal instability of this compound will probably limit its usefulness. It is noteworthy that all of the principal actinometers in use involve coordination compounds.

Recent apparatus descriptions include two designs capable of absolute quantum yield measurements[29,30] and a brief review on flash photolysis.[31]

B. INCOMPLETE ABSORPTION AND SECONDARY PHOTOLYSIS

The photochemical study of coordination compounds, particularly of those which undergo photosubstitution reactions, can be subject to certain complications which often are not present in other areas of photochemistry. In many instances, the extinction coefficient of the reactant species is low, so that it may not be practicable to ensure that complete absorption of the incident light takes place. The initial absorption by a reactant species A is then given by

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[22] G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.*, 11, 2 (1961).

[23] K. Porter and D. H. Volman, *J. Am. Chem. Soc.*, **84**, 2011 (1962).

[24] D. H. Volman and J. R. Seed, *ibid.*, **86**, 5095 (1964).

[25] T. Latowski and J. Biedrzycki, *Zeszyty Nauk. Mat. Fiz. Chem. Wyzsza Szkol. Pedagog. Gdansk.*, **6**, 91 (1966); *Chem. Abstr.*, **66**, 80756*b* (1967).

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

[27] B. Rackow, *Z. Physik. Chem.* (Leipzig), **233**, 103, 110, 113 (1966).

[28] B. Rackow, *Z. Chem.*, **5**, 397 (1965).

[29] H. P. Wolf, J. J. Bohning, P. A. Schnieper, and K. Weiss, *Photochem. Photobiol.*, **6**, 321 (1967).

[30] F. Wasgestian and H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **51**, 208 (1966).

[31] A. B. Callear, *Endeavor*, **97**, 9 (1967).

$$\mathrm{d}\bar{E}_{\mathrm{A}}/\mathrm{d}t \cong I_0(1 - e^{-k_{\mathrm{A}}lC_{\mathrm{A}}^0}) \qquad (k_{\mathrm{A}} = \epsilon_{\mathrm{A}}/2.303) \quad (4)$$

Here, I_0 is the incident light intensity in moles of quanta per second, l is the path length, C_A^0 is the initial concentration of reactant, and k_A and ϵ_A are the absorption and molar extinction coefficients of A, respectively; solvent absorption has been neglected. As the irradiation progresses, C_A diminishes in time (and in space, depending on the degree of convection and stirring) so that the total absorbed light, $E_A = \int_0^t (\mathrm{d}E_A/\mathrm{d}t)\mathrm{d}t$, can be a complicated function of the system variables. The situation, while not new, has been treated recently.[32,33]

The further complication that is fairly common in the case of coordination compounds is that the product of the photolysis may also absorb the irradiating light. Often, in fact, the reactant and product absorption spectra are somewhat similar. As a consequence, an increasing proportion of the incident light is absorbed by the product as the photolysis proceeds. The phenomenon is known as the *inner filter effect* and has been treated for the simple reaction A → B.[34] The problem is to determine the integrated amount of absorption due to the reactant only, as this is the quantity that must be used in eq 4 in determining the quantum yield. An extreme situation of this type occurs in the ultraviolet irradiation of $Fe^{2+}(aq)$, since the extinction coefficient of the product $Fe^{3+}(aq)$ may be several hundred times larger than that of the reactant.[35]

It may further happen that the photolysis product not only absorbs similarly to the original complex, but is itself similarly photosensitive. As an example, aqueous $Cr(CN)_6^{3-}$ apparently photolyzes to $Cr(CN)_5(H_2O)^{2-}$, but this species is so light sensitive that the first observed product is $Cr(CN)_4(H_2O)_2^-$. The tetracyano complex in turn is photosensitive, and, since only relatively minor progressive shifts in the ligand field bands occur as aquation proceeds, each product in succession tends to dominate the light absorption. The net result is that irradiation of $Cr(CN)_6^{3-}$ leads to a photolysis cascade to more and more highly aquated products.[36] Eventually a photostationary state is reached as the back-reaction develops in importance.

Alternatively, a back-reaction may assume importance at a very early stage in the photolysis. This is true, for example, in the case of carbonyl complexes, and the problem is a serious one.[34,37,38] While all of these situations can, in principle, be handled mathematically, in practice the most reliable general procedure has been to extrapolate apparent quantum yields to zero time of irradiation.

III. OXALATO COMPLEXES

Photochemical studies on oxalato complexes have produced a fairly large and diverse body of literature. Two review papers[3a,39] cover much of this, and the presentation here is intended as a supplement to them. A classical system is that known as Eder's reaction[40]

$$2HgCl_2 + C_2O_4^{2-} \xrightarrow{h\nu} Hg_2Cl_2 + 2CO_2 + 2Cl^- \quad (5)$$

The active species is probably $Hg_2Cl_2(C_2O_4)_2^{2-}$, and the primary step very likely produces Hg^+ and $C_2O_4^-$ ions.[41] Another well-known example of oxalate photochemistry is the uranyl ion catalyzed decomposition of oxalate ion, discussed in section III.G. Both systems illustrate the general tendency for oxalato complexes to undergo photoredox decompositions.

The absorption spectra of oxalato complexes typically show a strong CT band in the 400-mμ region or below and one or more weak bands at $\geqslant 500$ mμ, attributable to d–d transitions. The more stable oxalato complexes are those of the trivalent transition metals, and the typical over-all reaction following irradiation of the CT band is

$$2M(C_2O_4)_3^{3-} \xrightarrow{h\nu} 2M^{II} + 5C_2O_4^{2-} + 2CO_2 \quad (6)$$

The CT band thus appears to be CTTM in nature. A correlation has been noted between decreasing energy of the CT band, increasing ease of thermal decomposition, and increasing quantum yield for photodecomposition in the series M = Cr, Co, Mn, and Fe, except that the thermal stability for M = Mn is less than that for M = Fe.[42]

Irradiation of a d–d band might be expected to produce photosubstitution or related reactions, judging from the general behavior of Cr(III) complexes, *i.e.*, reactions of the type

$$M(C_2O_4)_x{}^{n-2x} + 2H_2O \xrightarrow{h\nu} M(C_2O_4)_{x-1}(H_2O)_2{}^{n-2x-2} + C_2O_4^{2-} \quad (7)$$

where n is 2 or 3. This is essentially the case with $Cr(C_2O_4)_3^{3-}$, but reactions of type 7 are relatively uncommon; thus the M(III) trisoxalato complexes tend to show reaction 6 even with irradiations well into a d–d band region. A suggested explanation has been that even a small degree of overlap of the CT and d–d bands is sufficient to allow a conversion from the latter to the former state (they being of the same symmetry); irradiation of a d–d band would then still lead primarily

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[32] H. Shaw and S. Toby, *J. Chem. Educ.*, **43**, 408 (1966).

[33] H. Mauser, *Z. Naturforsch.*, **22b**, 569 (1967).

[34] O. Kling, E. Nikolaiski, and H. L. Schläfer, *Ber. Bunsenges. Physik. Chem.*, **67**, 883 (1968).

[35] J. Jortner and G. Stein, *J. Phys. Chem.*, **66**, 1258, 1264 (1962).

[36] A. Chiang and A. W. Adamson, unpublished work.

[37] W. Strohmeier and K. Gerlach, *Chem. Ber.*, **94**, 398 (1961).

[38] W. Strohmeier, *Ber. Bunsenges. Physik. Chem.*, **67**, 892 (1963).

[39] K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, **61**, 213 (1961).

[40] J. Eder, *Chem. Ber.*, **13**, 166 (1880).

[41] G. H. Cartledge, *J. Am. Chem. Soc.*, **63**, 906 (1941).

[42] G. B. Porter, J. G. W. Doering, and S. Karanka, *ibid.*, **84**, 4027 (1962).

to reaction 6.[42] The primary step may then always be of the type

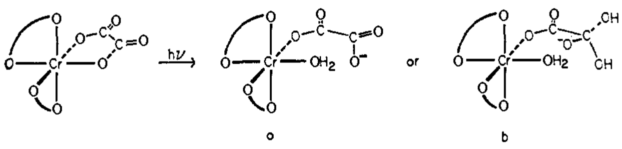
$$M(C_2O_4)_3^{3-} \xrightarrow{h\nu} M(C_2O_4)_2^{2-} + C_2O_4^- \qquad (8)$$

with variations in detail from one metal to another. It is also possible that in some cases reaction 7 does occur, but that the aquated product then undergoes a rapid redox decomposition. In the case of M(II) oxalates, the apparent absence of reaction 7 could simply be due to the general lability of such complexes, that is, to the speed of the thermal back-reaction.

The subsections that follow take up the oxalato complexes of trivalent Cr, Mn, Fe, Co, Rh, and UO_2^{2+}; with the exception of rhodium, no work seems to have been done on 4d and 5d transition metals. A scattering of work on some other metal oxalates is covered in a previous review.[39]

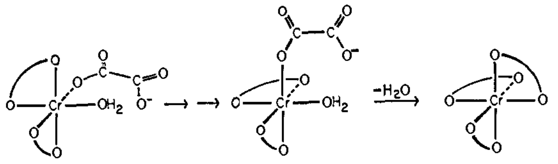
A. CHROMIUM

Aqueous $Cr(C_2O_4)_3^{3-}$ undergoes a nearly wavelength independent photoracemization with light in the visible region; quantum yields are about 0.1 (see Table I), with an apparent activation energy of 2.1 kcal/mole.[43] Both the thermal and photoracemization rates decrease by 25% in D_2O. The proposed primary step was of the type shown in eq 7, involving aquation of one end of a bidentate oxalato group (eq 9). The suggested sequence



(9)

leading to inversion was then that shown in eq 10.



(10)

Evidence for this sequence, as opposed to an intramolecular twist, was that a concomitant photoexchange with solvent oxygen was found to occur, using ^{18}O labeling. The proposed mechanism was one of *o*-carboxylate formation (product b in reaction 9). The thermal racemization rate is greatly reduced in water–acetone, methanol, and ethanol mixtures, and the photoyields likewise, but to a lesser extent. The quantum yield for photoaquation is small.[44]

The quantum yield in 30% ethanol dropped by 20% on irradiation in the region of the doublet band, as compared to shorter wavelengths; see also section VII.

Investigators generally have found no indication of any photoredox decomposition;[42–44] no transients appear under flash photolysis conditions where such are observed[45] with $Fe(C_2O_4)_3^{3-}$. The finding is consistent with the general behavior of Cr(III) complexes, but it has been claimed[46] that redox decomposition does in fact occur, with $\phi = 0.16$ at 254 mμ and pH 5.4.

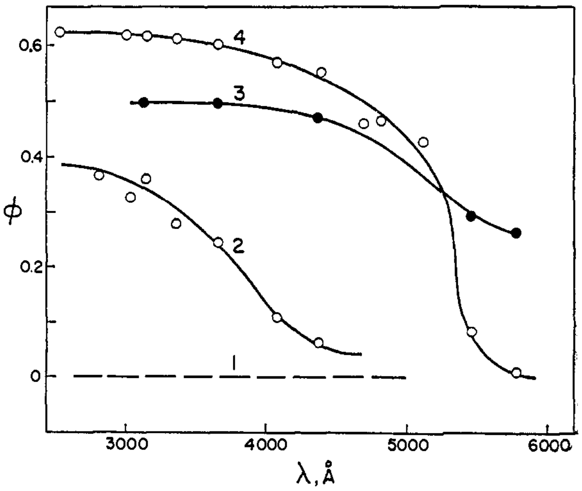


Figure 2.—Photolysis quantum yields for oxalato complexes: (1) $Cr(C_2O_4)_3^{3-}$, (2) $Co(C_2O_4)_3^{3-}$, (3) $Mn(C_2O_4)_3^{3-}$, (4) $Fe(C_2O_4)_3^{3-}$ (after ref 42).

B. MANGANESE

The complex $Mn(C_2O_4)_3^{3-}$ is both thermally[47,48] and photochemically unstable toward redox decomposition (reaction 6). The wavelength dependence of the quantum yield is shown in Figure 2;[42] a value of $\phi = 0.30$ also has been reported (for white light).[27]

The quantum yield remains high, even at 500 mμ or in the region of a presumed d-d band; as noted in the introduction to this section, a possible explanation is that of an intersystem crossing to the CT excited state. However, in view of the thermal instability of $Mn(C_2O_4)_3^{3-}$ (13-min half-life at 25°),[42] the alternative possibility cannot be entirely discounted, namely that the primary process is one of photoaquation, with the product then immediately decomposing thermally to give the observed net redox reaction. The mechanism generally assumed, however, is that discussed in section III.D.

$K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ photolyzes in the solid state[49] under ultraviolet irradiation, according to

$$2K_3[Mn(C_2O_4)_3]\cdot 3H_2O \xrightarrow{h\nu} 2K_2[Mn(C_2O_4)_2] + K_2C_2O_4 + 2CO_2 + 6H_2O \qquad (11)$$

In view of the stoichiometry, it would appear that two adjacent manganese ions must interact, possibly

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[43] S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).

[44] A. W. Adamson and A. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

[45] C. Parker and C. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959).

[46] M. A. Malati and M. W. Rophael, *J. Inorg. Nucl. Chem.*, **28**, 915 (1966).

[47] H. Taube, *J. Am. Chem. Soc.*, **70**, 1216 (1948).

[48] G. H. Cartledge and W. P. Ericks, *ibid.*, **58**, 2061 (1936).

[49] E. L. Simmons and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **27**, 2325 (1965).

through some form of oxalate bridging. The same decomposition occurs thermally, at 85°.

Aqueous Mn(II) appears also to be photosensitive in the presence of oxalate ion.[50] On irradiation with a low-pressure mercury lamp, spectral changes occurred and the solution showed reducing power toward then added Hg(II). The photoreaction was thought to be

$$\mathrm{Mn(C_2O_4)} \xrightarrow{h\nu} \mathrm{Mn(O\text{-}\dot{C}\text{-}O)_2} \qquad (12)$$

C. IRON

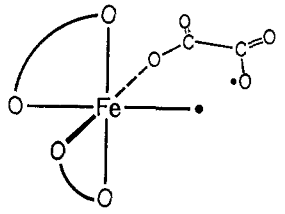
The redox photolysis of aqueous $\mathrm{Fe(C_2O_4)_3^{3-}}$ according to eq 6 has been extensively and accurately investigated, with several independent absolute quantum yield determinations available.[26,45,51–59] The wavelength variation of the quantum yield is shown in Figure 2 and summarized in Table I. The system is widely used for chemical actinometry in the blue and ultraviolet (section II). It should be mentioned that $\mathrm{Fe(C_2O_4)^+}$ or $\mathrm{Fe(C_2O_4)_2^-}$ may have been present in some of the systems studied.

Irradiation of dilute solutions frozen in liquid nitrogen produced radicals detected by esr,[60] presumably $\mathrm{CO_2^-}$ or $\mathrm{C_2O_4^-}$, but also possibly the formyl radical HCO.[61] Flash photolysis[45] of room-temperature aqueous solutions produced a transient absorbing at about 420 mμ and which decayed with a first-order rate constant of about 200 $\mathrm{sec^{-1}}$. These observations, plus the fact that the quantum yields for Fe(II) production can exceed unity, are consistent with the general reaction scheme[45]

$$\mathrm{Fe(C_2O_4)_3^{3-}} \xrightarrow{h\nu} \mathrm{Fe(C_2O_4)_2^{2-}} + \mathrm{C_2O_4^-} \qquad (13)$$

$$\mathrm{C_2O_4^-} + \mathrm{Fe(C_2O_4)_3^{3-}} \longrightarrow \mathrm{Fe(C_2O_4)_2^{2-}} + \mathrm{C_2O_4^{2-}} + 2\mathrm{CO_2} \qquad (14)$$

(the radical may decompose to $\mathrm{CO_2}$ and $\mathrm{CO_2^-}$, with the latter then involved in eq 14). However, the first-order, *i.e.*, ferrioxalate independent, decay of the transient precludes $\mathrm{C_2O_4^-}$ as the species, so eq 13 is probably not the correct primary process. It has been proposed, accordingly, that the transient is either a metastable excited state of $\mathrm{Fe(C_2O_4)_3^{3-}}$, a radical complex such as



or some complex between $\mathrm{C_2O_4^-}$ and ground state $\mathrm{Fe(C_2O_4)_3^{3-}}$.[45,60]

Dissolved oxygen has no effect under the usual actinometric conditions of low pH and light intensity. Under flash photolysis conditions, however, the quantum yield falls, and some new product appears, possibly $\mathrm{FeO_4^{2-}}$.[45] There is a scattering of other studies involving iron(III) oxalates.[62,63]

The solid salt undergoes both a thermal and a photolytic decomposition (using a low-pressure mercury lamp)[64]

$$2\mathrm{K_3[Fe(C_2O_4)_3]\cdot 3H_2O} \xrightarrow{h\nu} 2\mathrm{Fe(C_2O_4)} + 3\mathrm{K_2C_2O_4} + 2\mathrm{CO_2} + 6\mathrm{H_2O} \qquad (15)$$

The reaction is essentially analogous to that for the manganese and cobalt complexes. Finally, a Mössbauer study of the photolytic decomposition of $\mathrm{K_3[Fe(C_2O_4)_3]}\cdot n\mathrm{H_2O}$ has been reported.[65]

D. COBALT AND RHODIUM

The ion $\mathrm{Co(C_2O_4)_3^{3-}}$ is extremely robust or nonlabile; exchange with free oxalate ion is negligible.[66] It does undergo a thermal redox decomposition for which a proposed mechanism is[67]

$$\mathrm{Co(C_2O_4)_3^{3-}} \overset{h\nu}{\rightleftarrows} \mathrm{Co(C_2O_4)_2^{2-}} + \mathrm{C_2O_4^-} \qquad (16)$$

$$\mathrm{Co(C_2O_4)_2^{2-}} + \mathrm{C_2O_4^{2-}} = \mathrm{Co(C_2O_4)_3^{4-}} \quad \text{(rapid equilibrium)} \qquad (17)$$

$$\mathrm{Co(C\ O_4)_3^{3-}} + \mathrm{C_2O_4^-} \longrightarrow \mathrm{Co(C_2O_4)_2^{2-}} + \mathrm{C_2O_4^{2-}} + 2\mathrm{CO_2} \qquad (18)$$

Process 16 was required to be reversible to account for the Co(II)–Co(III) exchange which occurred during the decomposition. The extensive earlier literature has already been covered.[39]

The complex is quite photosensitive, with several early studies[68–71] reporting also some rather obscure salt and solvent effects. A detailed and more recent investigation gave results consistent with the primary step

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(50) S. Sakuraba and S. Ikeya, *Bull. Chem. Soc. Japan*, **30**, 662, 748 (1957).

(51) A. J. Allmand and W. W. Webb, *J. Chem. Soc.*, 1518, 1531 (1929).

(52) E. Baur, C. Oullet, and E. Wäckerlin, *Z. Wiss. Phot., Photophysik. Photochem.*, **30**, 88 (1933).

(53) G. Kornfeld, *J. Phys. Chem.*, 44, 949 (1940).

(54) R. Livingstone, *ibid.*, 44, 601 (1940).

(55) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953).

(56) C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956).

(57) C. A. Parker, *Trans. Faraday Soc.*, **50**, 1213 (1954).

(58) J. Lee and H. H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964).

(59) J. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

(60) D. J. Ingram, W. E. Hodgson, C. A. Parker, and W. T. Rees, *Nature*, **176**, 1227 (1955).

(61) G. A. Shagisultanova, L. N. Neokladnova, and A. L. Poznyak, *Dokl. Akad. Nauk SSSR*, **162**, 1333 (1965); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **162**, 491 (1965).

(62) T. Mukaibo and S. Tsujimura, *J. Chem. Soc. Japan*, **56**, 144, 244 (1953); *Chem. Abstr.*, **48**, 8096*c*, 9243*d* (1954).

(63) J. Pound, *J. Phys. Chem.*, **43**, 955 (1939).

(64) W. W. Wendlandt and E. L. Simmons, *J. Inorg. Nucl. Chem.*, **28**, 2420 (1966).

(65) N. Saito, H. Sano, T. Tominaga, and F. Ambe, *Bull. Chem. Soc. Japan*, **38**, 681 (1965).

(66) F. A. Long, *J. Am. Chem. Soc.*, **63**, 1353 (1941).

(67) A. W. Adamson, H. Ogata, J. Grossman, and R. Newbury, *J. Inorg. Nucl. Chem.*, **6**, 319 (1958).

(68) J. Vrânek, *Z. Elektrochem.*, **23**, 336 (1917).

(69) I. G. Murgulescu, *Bul. Soc. Stiinte Cluj*, **8**, 193 (1935); *Chem. Abstr.*, **30**, 4402⁹ (1936).

(70) F. M. Jaeger and G. Berger, *Proc. Acad. Sci. Amsterdam*, **23**, 84 (1920); *Chem. Abstr.*, **15**, 1470 (1921).

(71) F. M. Jaeger and G. Berger, *Rec. Trav. Chim.*, **40**, 153 (1921).

TABLE I

PHOTOCHEMISTRY OF OXALATO COMPLEXES (SELECTED DATA)

Complex (absorption max, mμ/extinction coeff)[a]	Wavelength, mμ	Quantum yield[b]	Remarks	Ref
$Cr(C_2O_4)_3^{3-}$ (698/5.1; 571/77; 417/96)[78]	697	0.012	Racemizn, 30% ethanol	43
	420	0.090	Racemizn, 15°	43
	420	0.071	Racemizn, −2°	43
	420	0.015	Racemizn, 30% ethanol	43
$Mn(C_2O_4)_3^{3-}$ (~510/~330; ~260 sh/~7000)[79]	547	0.30	*c*	42
	366	0.49	*c*	42
	313	0.50	*c*	42
$Fe(C_2O_4)_3^{3-}$ (436/20.2; 405/125; 365/722; 313/1600)[51]	577	0.013	*c*	56
	546	0.15	*c*	56
	436	1.11	*c*	56
	365	1.26, 1.20	*c* (concn dependent)	58
	365	1.21	*c*	56
	254	1.25	*c*	56, 51
$Co(C_2O_4)_3^{3-}$ (596/165; 420/218; 245/21,400)[72]	530	0.0017	*c*	43
	450	0.12	*c*	43
	435	0.15	*c*	42
	435	0.12	*c*	72
	410	0.24	*c*	43
	405	0.20	*c*	42
	405	0.16	*c*	72
	355–385	0.44	*c*	43
	370	0.46	*c*	42
	365	0.69	*c*	72
	313	0.74	*c*	42
	313	0.73	*c*	72
$Rh(C_2O_4)_3^{3-}$ (~520/~10; 398/~230; ~330/~400; ~280/~3000)[80]	546	4.3×10^{-3}	Racemizn	43
	546	7.6×10^{-4}	Decompn	43
$UO_2^{2+} + C_2O_4^{2-}$	435	0.58	*d*	77
	406	0.56	*d*	77
	366	0.49	*d*	77
	313	0.56	*d*	77
	255	0.60	*d*	77

[a] Values given as approximate are taken from graphs. [b] These are the observed quantum yields, *i.e.*, for disappearance of complex, or, in the case of UO_2^{2+}, of oxalate. [c] Unless otherwise specified, the reaction is one of redox decomposition at about 25°. [d] 0.01 *M* uranyl sulfate and 0.05 *M* oxalic acid.

being a reaction analogous to eq 13, followed by eq 18.[72] The yield was unaffected by 0.05 *M* acid, oxygen, complex concentration, light intensity, and extensive dilution by ethanol or acetone. Heavy metal ions such as Cu^{2+} and Hg^{2+} had some effect, however. These data are included in Figure 2; they were confirmed by subsequent work,[42,43] which also showed a negligible temperature dependence except at 605 mμ.[43] The results are summarized in Table I.

The sharp drop in quantum yield is close to, but at a definitely longer wavelength than the minimum between the intense CT band in the ultraviolet and the L_2 band, whose maximum is at 420 mμ. This last band is relatively intense, however, with ϵ_{max} 218. The appearance of photoredox behavior on irradiation of an intense ligand-field band, close to a CT band, is found with various Co(III) ammines (section X). That some greater complexity is present than given by eq 13 and 18 is suggested by the presence of three stages on flash photolysis of $Co(C_2O_4)_3^{3-}$ solutions: an instantaneous rise in absorption, a rapid decrease, and then a slow decrease.[45]

Other oxalato complex ions have been examined. $Co(en)_2(C_2O_4)^+$ is photolytically stable,[43,73] while $Co(en)(C_2O_4)_2^-$ photoracemizes with some photodecomposition.[74] Finally, solid $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ is both thermally and photochemically unstable.[75] The thermal decomposition produces KHC_2O_4 and $KHCO_3$ among the products, however, while the photodecomposition proceeds according to eq 11. Solid $K[Co(en)(C_2O_4)_2]$ is also photosensitive.[74]

$Rh(C_2O_4)_3^{3-}$ ion undergoes both photoracemization and decomposition.[43]

E. URANIUM

The photochemistry of uranium oxalato complexes is almost entirely that of the uranyl ion catalyzed decomposition of oxalate ion. The approximate concurrent reactions are

$$H_2C_2O_4 \xrightarrow{h\nu} H_2O + CO_2 + CO \qquad (19)$$

$$H_2C_2O_4 \xrightarrow{h\nu} HCOOH + CO_2 \qquad (20)$$

and, especially in the absence of oxygen

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(72) T. Copestake and N. Uri, *Proc. Roy. Soc.* (London), **A228**, 252 (1955).

(73) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).

(74) F. Dwyer, I. Reid, and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 1285 (1961).

(75) W. W. Wendlandt and E. L. Simmons, *J. Inorg. Nucl. Chem.*, **27**, 2317 (1965), and preceeding papers.

$$H_2C_2O_4 + U^{VI} \xrightarrow{h\nu} U^{IV} + 2CO_2 + 2H^+ \qquad (21)$$

The system has been accurately calibrated for use in chemical actinometry in the blue and near-ultraviolet (see section II) and representative quantum yields are given in Table I.

The literature through 1959 has already been reviewed.[39] The quantum yields used in the actinometric application are those based on the amount of oxalate decomposed, and a recent redetermination of these has been made,[76] with results in good agreement with the earlier ones.[77] Other work gives the fractional contributions of reactions 19–21, assuming these to be correct, and based on CO and CO_2 analyses.[23,24]

The complete series of reactions occurring is not yet fully understood. The proportions of products depend on pH and the primary process may be the photoactivation of $UO_2(HC_2O_4)^+$, $UO_2(C_2O_4)$, and UO_2^{2+} to respective excited states which then undergo hydrolytic and redox reactions.[39]

Selected values for various transition-metal oxalate complexes are given in Table I. Included for convenience are literature data on the absorption spectra.[78–80]

IV. CYANIDE COMPLEXES

The photosensitivity of transition-metal cyanide complexes has been recognized since the middle of the last century, and this area has been the subject of extensive photochemical studies, primarily of the iron family, but more recently also of those of the chromium group and cobalt. There are two recent reviews of the chemistry of cyano complexes.[81,82]

Before proceeding to the photochemical results, it should be noted that a number of attempts have been made to give spectroscopic assignments to the various excited states of cyano complexes. The absorption spectra typically consist of weak bands or shoulders in the near-ultraviolet; these are in a general way attributed to ligand-field transitions, and their short wavelength location gives cyanide ion its high position in the spectrochemical series and accounts for the usual off-white color of such complexes. Further in the ultraviolet (200–300 mμ) are more intense bands, evidently of a CT character. The cases of d^0, d^1, and d^2 electron or hole configurations have been treated in ligand-field theory.[83–86] Three examples of CT bands may be cited. Treinin[87] accepted earlier assignments of the absorption by $Fe(CN)_6^{4-}$ below 300 mμ as CTTS, and proposed a continuum model treatment, and this assignment has been accepted by later authors.[88–90] Alternatively, the transition has been thought to be d–π* (CN)[91] or CTTL in type. This assignment is supported by Ohno,[92] mainly on the ground that no blue shift occurs on reducing the water activity of aqueous ferrocyanide. The intense absorptions of $Fe(CN)_6^{3-}$ at 415, 305, and 260 mμ have been assigned as CTTM in nature,[93] and certain bands in nitrosylpentacyano complexes as CTTL.[94]

As might be expected from the different types of transitions that must be considered, several photolysis modes have been observed. These are substitution (usually aquation), reduction of the metal with oxidation of the ligand, and photoelectron production. It is tempting to assign the former as indicating a d–d type of excitation, and the latter two as suggesting that irradiation has been in CTTM and CTTS or CTTL bands, respectively. Some representative results are summarized in Table II. We find no photochemical information for the higher homologs of Mn and of Co, or for Os. $Ni(CN)_4^{2-}$ is inactive to 254-, 313-, and 365-mμ light, and $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ are inactive to 254-mμ light, as evidenced by the lack of any pH change on irradiation.[95] On the other hand, a transient has been observed for $Ni(CN)_4^{2-}$ under flash photolysis conditions.[96] $Pt(CN)_4^{2-}$ is reported to fluoresce both in aqueous solution and in the solid phase.[97] No photochemistry seems to have been reported for the Sc, Ti, and V families, nor for the lanthanide or actinide series. No specific reports were found for Cu, Ag, or Au; however, this as well as the zinc group tend to

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(76) C. A. Discher, P. F. Smith, I. Lippman, and R. Turse, *J. Phys. Chem.*, **67**, 2501 (1963).

(77) W. G. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

(78) A. W. Adamson, *J. Inorg. Nucl. Chem.*, **28**, 1955 (1966).

(79) S. J. Adler and R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2036 (1955).

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

(81) B. M. Chadwich and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 84 (1966).

(82) M. H. Ford-Smith, "The Chemistry of Complex Cyanides," Her Majesty's Stationery Office, London, 1964.

(83) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

(84) R. M. Golding and A. Carrington, *Mol. Phys.*, **5**, 377 (1962).

(85) E. König, *Theoret. Chim. Acta* (Berlin), 1, 23 (1962).

(86) Z. Stasicka, A. Samotus, and W. Jakób, *Roczniki Chem.*, **40**, 967 (1966).

(87) A. Treinin, *J. Phys. Chem.*, **68**, 893 (1964).

(88) M. Shirom and G. Stein, *Nature*, **204**, 778 (1964).

(89) G. Stein, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, pp 238–240.

(90) P. L. Airey and F. S. Dainton, *Proc. Roy. Soc.* (London), **A291**, 340, 478 (1966).

(91) J. J. Alexander and H. B. Gray, *Coord. Chem. Rev.*, **2**, 29 (1967).

(92) S. Ohno, *Bull. Chem. Soc. Japan*, **40**, 1765, 1770, 1776, 1779 (1967).

(93) (a) C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961); (b) P. N. Schatz, A. J. McCaffery, W. Suetka, G. N. Henning, A. B. Ritchie, and P. J. Stephens, *ibid.*, **45**, 722 (1966).

(94) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).

(95) L. Moggi, F. Bolletta, V. Balzani, and F. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).

(96) P. Fleischauer, Ph.D. Dissertation, University of Southern California, 1968.

(97) W. E. Ohnesorge, "Fluorescence and Phosphorescence Analysis," D. M. Hercules, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 160.

show photosensitivity or photosensitizations as the halide salts,[98] and the cyano complexes may merely be insufficiently investigated. The photolysis of $Hg(CN)_2$ in various organic solvents has been reported to give cyanide radical as the primary step.[99]

A. CHROMIUM

An important early paper[100] reported that $Cr(CN)_6^{3-}$ was photolyzed by visible and near-ultraviolet light to give free cyanide ion. The process is one of photoaquation.[95] The reverse thermal reaction presumably accounts for the report of photoexchange at a rate independent of the cyanide ion concentration.[101] The situation can easily be complicated by secondary photolysis, however. Work in this laboratory,[36] using recently available spectra for the various aquocyano complexes,[102] indicates that the primary photoaquation quantum yield at 370 mμ is *ca.* 0.1, but with efficient, further photoaquation of $Cr(CN)_5(H_2O)^{2-}$ to give $Cr(CN)_4(H_2O)_2^{-}$ as the first observed product. This, and the tricyano complex are in turn about as photosensitive as the hexacyanide. Flash photolysis in the quartz ultraviolet gives some other product, possibly derived from redox decomposition.[96]

B. MOLYBDENUM

1. $Mo(CN)_8^{3-}$

Photochemical work on Mo cyanides has been confined to the two species: $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$. The former undergoes photoredox decomposition to Mo(IV), reportedly with the evolution of cyanogen,[103] indicating the mechanism to be

$$Mo(CN)_8^{3-} \xrightarrow{h\nu} Mo(CN)_7^{3-} + CN \qquad (22)$$

$$Mo(CN)_7^{3-} + H_2O \longrightarrow Mo(CN)_7(H_2O)^{3-} \qquad (23)$$

with anation to $Mo(CN)_8^{4-}$ in the presence of cyanide ion. However, detailed studies by other workers[104,105] led to the proposed sequence

$$Mo(CN)_8^{3-} \xrightarrow{h\nu} [Mo(CN)_8^{3-}]^* \text{ (photoexcitation)} \qquad (24)$$

$$[Mo(CN)_8^{3-}]^* + H_2O \longrightarrow Mo(CN)_8^{4-} + OH + H^+ \qquad (25)$$

$$[Mo(CN)_8^{3-}]^* + OH^- \longrightarrow Mo(CN)_8^{4-} + OH \qquad (26)$$

$$Mo(CN)_8^{8-} + OH \longrightarrow Mo(CN)_8^{4-} + O + H^+ \qquad (27)$$

$$Mo(CN)_8^{3-} + H_2O + OH \longrightarrow Mo(CN)_8^{4-} + 2OH + H^+ \qquad (28)$$

$$2OH \longrightarrow H_2O + O \qquad (29)$$

The over-all reaction proposed was thus

$$2Mo(CN)_8^{3-} + H_2O \longrightarrow 2Mo(CN)_8^{4-} + 2H^+ + {}^1/_2O_2 \qquad (30)$$

The excited species, $[Mo(CN)_8^{3-}]^*$, has been thought, alternatively, to first give $Mo(CN)_7^{2-}$, which would then be the reactant in processes 25 and 26, or $Mo(CN)_8(H_2O)^{3-}$. The addition of water would be facilitated by the promotion of the sole d electron out of its lowest level in $[Mo(CN)_8^{3-}]^*$.[95] Returning to the over-all observations, quantum yields based on the disappearance of $Mo(CN)_8^{3-}$ increased from 1.9 to 4.4 in the pH range 4.0–7.0, and varied between 3.2 and 4.1 for various water–methanol, ethanol, and propanol mixtures.

Analyses in the above studies were spectrophotometric, and complications included the expected presence of $Mo(CN)_7(H_2O)^{3-}$ from secondary photolysis of the assumed product, $Mo(CN)_8^{4-}$, and possible mechanistic complexities resulting from the use of permanganate for the *in situ* preparation of the starting complex from $Mo(CN)_8^{4-}$, so that Mn^{2+} was also present. The discrepancy between the mechanisms corresponding to eq 22 and 23 and 24–29 is of some importance, since the former implies CTTM character to the excited state involved, while the latter suggests that the transition is mainly d–d in nature, particularly if the intermediate is actually $Mo(CN)_8(H_2O)^{4-}$. Of relevance to these alternative mechanisms are the results given in section IV.C on the behavior of the analogous tungsten compounds.

2. $Mo(CN)_8^{4-}$

The complex $Mo(CN)_8^{4-}$ is extremely stable in either acidic or basic media,[101,106–109] although it has been suggested that a small equilibrium concentration of $Mo(CN)_7(H_2O)^{3-}$ and possibly $Mo(CN)_6(H_2O)_2^{2-}$ may be present.[106–108] On the other hand, the general photosensitivity of $Mo(CN)_8^{4-}$ has long been recognized.[110–112] More recently, an efficient photoexchange with cyanide ion has been reported,[109] and a number of papers have appeared to the general effect that the photoreaction at 370 mμ is substitutional (as

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[98] J. Kosar, "Light-Sensitive Systems," W. Clark, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, pp 14–40.

[99] K. Yoshida and S. Tsutsumi, *J. Org. Chem.*, **31**, 3635 (1966).

[100] R. Schwarz and K. Tede, *Chem. Ber.*, **60B**, 69 (1927).

[101] A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, **75**, 5204 (1953); **76**, 4222 (1954).

[102] R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

[103] J. R. Perumareddi, Ph.D. Dissertation, University of Southern California, 1962, p 83.

[104] V. Carassiti and V. Balzani, *Ann. Chim.* (Rome), **51**, 518 (1961).

[105] V. Balzani and V. Carassiti, *ibid.*, **52**, 432 (1962).

[106] V. Carassiti and M. Claudi, *ibid.*, **49**, 1674 (1959); *Chem. Abstr.*, **54**, 16130e (1960).

[107] V. Carassiti and V. Balzani, *Ann. Chim.* (Rome), **50**, 630 (1960).

[108] A. Bertoluzza, V. Carassiti, and A. M. Marinangeli, *ibid.*, **50**, 645 (1960).

[109] A. W. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950).

[110] A. Chilesotti, *Gazz. Chim. Ital.*, **34**, 497 (1904).

[111] A. Rosenheim, A. Garfunkel, and F. Kohn, *Z. Anorg. Allgem. Chem.*, **65**, 166 (1909).

[112] O. Collenberg, *ibid.*, **136**, 245 (1924).

opposed to redox) in type.[44,101,103,113–126] This yellow complex on prolonged irradiation in aqueous solution yields a blue product generally agreed to be a tetracyanide, whose formula now seems to be established as $Mo(O)(OH)(CN)_4^{3-}$,[124,125] *i.e.*, hexacoordinated. The formation of the blue species is reported to be facilitated by irradiating at high pH.[112,114,123,126] Intermediate degrees of photolysis give a green solution which, however, is merely a mixture of the original and terminal species.[103]

During the initial stages of irradiation, a red species of a transient nature is formed; if the irradiated solution is placed in the dark, the red product disappears in a few minutes at room temperature. Its absorption spectrum is similar to that of $Mo(CN)_8^{4-}$ except for a peak at 510 mμ;[103,113] it may be photosensitive itself. The nature—even the general nature—of the species is disputed. It has not been isolated as a simple salt, but Jakób and coworkers[116–118,120–122] report the isolation of insoluble, reddish substances on irradiating $Mo(CN)_8^{4-}$ in concentrated ammonia or hydrazine solutions. The analyses corresponded to the general formula $M_2[Mo(CN)_8R_2]\cdot xH_2O$, where $M = Cd^{2+}$ or Mn^{2+}, and $R = NH_3$ or N_2H_4. The transient red species described initially is then proposed to be $Mo(CN)_8(H_2O)_2^{4-}$, *i.e.*, to be decacoordinated. Adamson and Perumareddi[103,113] and also Carassiti and coworkers[106–108] have considered the formulation to be $Mo(CN)_7(H_2O)^{3-}$ (or $Mo(CN)_7(OH)^{4-}$), *i.e.*, have proposed the red species to be the product of a first-step photoaquation. The latter supposition is plausible in that the terminal product is tetraaquated, so that photoaquation is occurring; in addition, iodine titration of free cyanide showed one cyanide per original complex photolyzed.[103,113] The formation of the red species was found to be inhibited by added cyanide ion, presumably by return to $Mo(CN)_8^{4-}$ through anation of the $Mo(CN)_7(H_2O)^{3-}$.[103,113] The second group of authors reached their conclusions through studies of the changes in pH and spectral absorption during irradiation. From symmetry considerations, they further suggested that the formation of a nine-coordinated intermediate stage may be involved in the reaction of the photoexcited ion $[Mo(CN)_8^{4-}]^*$ to give $Mo(CN)_7(H_2O)^{3-}$.

Jakób and coworkers found additional support for the proposed decacoordinated species in the similarity of the absorption spectra of the red transient and the $M_2[Mo(CN)_8R_2]$ products. They further cite as consistent with their proposal the observation that the conductivity decreased as the red product appeared and consider the above cited iodine titration to have given results made spurious by the probable presence of some terminal product (see ref 122 for a detailing of these arguments). Perumareddi has added the point that the decacoordination geometry should give paramagnetic rather than the observed diamagnetic insoluble red products,[114] but this argument is also disputed.[122]

The above results pertain to irradiation of aqueous $Mo(CN)_8^{4-}$ with light around 370 mμ, and the excited state(s) produced appears to be mainly ligand field in nature.[83] However, in the region around 250 mμ, there are intense CT bands[83] and the photolysis takes on a different character. Flash-photolysis experiments have indicated that photoelectron production occurs.[127]

$$Mo(CN)_8^{4-} \xrightarrow{h\nu} Mo(CN)_8^{3-} + e^-(aq) \qquad (31)$$

The same behavior is observed with $W(CN)_8^{4-}$ (see below), and the implication in both cases is that the excited state is CTTS or CTTL in nature.

C. TUNGSTEN

The photochemistry of tungsten cyanides parallels that of molybdenum closely. $W(CN)_8^{3-}$ undergoes photoredox decomposition with light in the 370-mμ region and a reaction sequence similar to eq 24–29 has again been proposed.[105,128] Additional information for the tungsten system is that exchange with cyanide ion is photoinduced;[129] this would be consistent with the mechanism analogous to eq 22 and 23 but could also be explained by the alternative sequence, since the product $W(CN)_8^{4-}$ of the reaction corresponding to eq 30 would in turn undergo a photoexchange reaction

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(113) A. W. Adamson and J. R. Perumareddi, *Inorg. Chem.*, **4**, 247 (1965).

(114) J. R. Perumareddi, *Z. Naturforsch.*, **21b**, 22 (1966).

(115) S. Ašperger, I. Murati, and D. Pavlović, *J. Chem. Soc.*, 730 (1960).

(116) W. Jakób and Z. Jakób, *Roczniki Chem.*, **26**, 492 (1952); **36**, 593, 601 (1962).

(117) Z. Jakób and W. Jakób, *Zeszyty Nauk. Uniw. Jagiel, Ser. Nauk. Mat.-Przyrod., Mat., Fiz., Chem.*, **2**, 49 (1959); *Chem. Abstr.*, **52**, 17981*h* (1958).

(118) W. Jakób, A. Kosinska-Samotus, and Z. Stasicka, Proceedings of the 7th International Conference on Coordination Chemistry, Stockholm and Uppsala, Sweden, June 25, 1962, p 238.

(119) W. Jakób, A. Kosinska-Samotus, and Z. Stasicka, *Roczniki Chem.*, **36**, 611 (1962).

(120) Z. Stasicka and A. Samotus, "Absorption Spectra in Ultraviolet and Visible Region," Vol. IV, L. Lang, Ed., Academic Press Inc., New York, N. Y., 1963, p 21.

(121) W. Jakób, A. Samotus, and Z. Stasicka, "Theory and Structure of Complex Compounds," B. Jeżowska-Trzebiatowska, Ed., The Macmillan Co., New York, N. Y., 1964, p 211.

(122) W. Jakób, A. Samotus, Z. Stasicka, and A. Golebiewski, *Z. Naturforsch*, **21b**, 819 (1966).

(123) W. Jakób, A. Samotus, and Z. Stasicka, *Roczniki Chem.*, **40**, 1383 (1966).

(124) S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, 118 (1967).

(125) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **6**, 1943 (1967).

(126) V. Carassiti, A. M. Marinangeli, and V. Balzani, *Ann. Chim.* (Rome), **50**, 790 (1960).

(127) W. L. Waltz, A. W. Adamson, and P. D. Fleischauer, *J. Am. Chem. Soc.*, **89**, 3912 (1967).

(128) V. Balzani and V. Carassiti, *Ann. Chim.* (Rome), **51**, 533 (1961).

(129) E. L. Goodenow and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 5268 (1955).

(see next paragraph). The observation that the pH falls during the irradiation[129] is consistent with eq 30. The complex in solid state is reported to be photosensitive.[129,130]

Irradiation of aqueous $W(CN)_8^{4-}$ in the 370-mμ region leads to a terminal violet colored solution,[95,107,116,119,123–126] probably due to $W(O)(OH)(CN)_4^{3-}$.[124,125] Again, Jakób and coworkers report an intermediate transient product and the isolation of insoluble materials of the formula $M_2[W(CN)_8R_2] \cdot xH_2O$ on irradiation in the presence of aqueous ammonia or hydrazine[119] (see section IV.B.2). Very likely the same general questions pertain here as do to the molybdenum system.

Finally, again as with $Mo(CN)_8^{4-}$, flash photolysis in the 250-mμ region leads to photoelectron production, and in larger yield.[127]

D. MANGANESE

Aqueous $Mn(CN)_6^{3-}$ has been reported to be photosensitive,[100] although cyanide exchange studies showed no light acceleration.[131] $Mn(CN)_6^{4-}$ is apparently not photosensitive.[101]

E. IRON

The iron cyanide complexes form an important group in photochemistry, both historically and industrially. According to Baur,[132] a light-induced color change of ferrocyanide solutions was reported as early as 1846. Further citations to the early work have been given.[100,132–134] Although these complexes are of considerable importance to the blue-printing industry, this subject will not be covered here; the book by Kosar[98] constitutes a useful reference on this aspect.

1. $Fe(CN)_6^{4-}$

Irradiation of aqueous $Fe(CN)_6^{4-}$ at wavelengths greater than about 250 mμ appears to lead primarily to photoaquation (eq 32) as might be expected from the assignment of the absorption bands to d–d transitions (note ref 91). The pH of the solution rises during the irradiation[101,115,134–138] and tends to decrease on standing in the dark,[101,115,134,135] and the appearance of the aquopentacyano complex has been followed by means of nitrosobenzene or azide ion as reagents.[92,133,139–141] Exchange with cyanide ion is light accelerated[101] and free cyanide is detected,[92] as is also Fe^{2+} under conditions of low pH and absence of oxygen.[92,133,142] Irradiation either in the presence of oxygen, or sufficiently prolonged, leads to the formation of ferric hydroxide.[115,133,137]

$$Fe(CN)_6^{4-} + H_2O \xrightarrow{h\nu} Fe(CN)_5(H_2O)^{3-} + CN^- \quad (32)$$

The first step of the thermal decomposition appears also to be reaction 32,[135,141,143–145] but the decomposition proceeds in a complex way to further products,[134,135,141,142,145] and the photolytic situation is similarly complicated. It is pH dependent, possibly due to the protonation of $Fe(CN)_6^{4-}$ to give $HFe(CN)_6^{3-}$ as the especially photosensitive species;[141,143,146] also, $Fe(CN)_5(H_2O)^{3-}$ is involved in acid–base equilibria and is itself photosensitive (see below).

Representative quantum yields are given in Table II; it should be noted that the photolyzed species is not always exactly known. However, at pH's of 1, 3, and 10, the major species should be $H_2Fe(CN)_6^{2-}$, $HFe(CN)_6^{3-}$, and $Fe(CN)_6^{4-}$, respectively. The yields are insensitive to temperature or to light intensity[92,134,135,139,141,142] but vary with complex concentration as well as with pH. They are also wavelength dependent, and it has been suggested that this aspect can be related to the lifetimes of the various excited states.[139]

$Fe(CN)_6^{4-}$ exhibits a strong charge-transfer band at 218 mμ,[91] and irradiation of this band leads to photoelectron production (eq 33), both under steady illumination,[88–90,93] and in flash-photolysis experiments.[127,147] The same reaction occurs with $HFe(CN)_6^{3-}$, but in smaller yield and possibly including hydrogen atom formation.[90] The ferrocyanide system is a difficult one to study, and some quantum yield discrepancies may be noted in Table II.

$$Fe(CN)_6^{4-} \xrightarrow{h\nu} Fe(CN)_6^{3-} + e^-(aq) \quad (33)$$

The occurrence of reaction 33 is consistent with the assignment of the 218-mμ band as CTTS in type,[88–90] although Ohno[92] has suggested the transition to be d–π*(CN) or CTTL. Qualitatively, it has been noted that the yields for photoelectron production are in the order $Fe(CN)_6^{4-} > W(CN)_8^{4-} > Mo(CN)_8^{4-}$, which is also the order of increasing oxidizing potential.[127]

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(130) O. Olssen, *Chem. Ber.*, 47, 917 (1914).

(131) A. W. Adamson, J. P. Welker, and W. B. Wright, *J. Am. Chem. Soc.*, 73, 4786 (1951).

(132) E. Baur, *Helv. Chim. Acta*, 8, 403 (1925).

(133) O. Baudisch, *Chem. Ber.*, 62, 2706 (1929), and earlier papers.

(134) V. Carassiti and V. Balzani, *Ann. Chim.* (Rome), 50, 782 (1960).

(135) A. Ašperger, *Trans. Faraday Soc.*, 48, 617 (1952).

(136) G. D'Amore and A. Bellomo, *Atti Soc. Peloritana Sci. Fis. Mat. Nat.*, 5, 449 (1958); *Chem. Abstr.*, 54, 17004e (1960).

(137) H. Lecoq, *Bull. Soc. Roy. Sci. Liège*, 14, 268 (1945); *Chem. Abstr.*, 42, 7139a (1948).

(138) G. Rossi and C. Bocchi, *Gazz. Chim. Ital.*, 55, 876 (1925); *Chem. Abstr.*, 20, 1357^5 (1926).

(139) G. Emschwiller and J. Legros, *Compt. Rend.*, 261, 1535 (1965).

(140) G. Emschwiller and J. Legros, *ibid.*, 239, 1491 (1954).

(141) A. Ašperger, I. Murati, and O. Čupahin, *J. Chem. Soc.*, 1042 (1953).

(142) V. Karas-Gašparec and T. Pinter, *Z. Physik. Chem.* (Leipzig), 220, 327 (1962).

(143) G. Emschwiller, *Compt. Rend.*, 236, 72 (1953).

(144) G. Emschwiller and J. Legros, *ibid.*, 241, 44 (1955).

(145) J. Legros, *J. Chim. Phys.*, 61, 909 (1964).

(146) J. Jordan and G. J. Ewing, *Inorg. Chem.*, 1, 587 (1962).

(147) M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, 67, 2613 (1963).

Finally, some of the complexities of the photolysis results at longer wavelengths could be due to the presence of some of the photoelectron reaction mode. A similar complication could be present in the results reported for $Mo(CN)_8^{4-}$.

2. *Substituted Ferrocyanides*

$Fe(CN)_5(H_2O)^{3-}$ is reported to undergo photoaquation; irradiation at 365 mμ leads to pH increase and eventually to Fe^{2+},[95,115] but the situation is complicated by thermal reactions which also make difficult the interpretation of $Fe(CN)_6^{4-}$ photolyses (note ref 148 on post-irradiation reactions with hydrogen peroxide). Photoexchange with cyanide ion is reported to occur.[101]

$Fe(CN)_5CO^{3-}$, by contrast, is remarkably stable both photolytically and thermally.[149] The species $Fe(CN)_4(AA)^{2-}$ and $Fe(CN)_2(AA)_2$ (where AA is 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)) may be formed by 365-mμ irradiation of $Fe(CN)_6^{4-}$ in the presence of AA. The reactions probably occur through aquocyano intermediates.[150] The apparent quantum yields are about 10^{-3} and 2×10^{-4} for the bipy and phen complexes, respectively. The ammine products are themselves photosensitive. Irradiation of $Fe(CN)_4(AA)^{2-}$ in the presence of free AA, with light of 365 mμ, gives $Fe(CN)_2(AA)_2$, with $\phi = 10^{-3}$ and 10^{-4} for bipy and phen, respectively.[151] In highly acidic media, $Fe(CN)_2(bipy)_2$ undergoes further decomposition with $\phi = 1.3 \times 10^{-3}$.[152] These relatively low quantum yields may be characteristic of systems for which the light absorption is primarily a delocalized one of a chelate ring containing the metal ion, in this case the Fe(AA) ring.

3. *$Fe(CN)_6^{3-}$*

When solutions of $Fe(CN)_6^{3-}$ are irradiated in the 254–405-mμ region, the pH rises to approach a constant value of around 8,[95,100,101] with spectral changes suggesting that $Fe(CN)_5(H_2O)^{2-}$ is the first product.[95,153,154] Also, a photoexchange with cyanide ion has been reported.[109] However, the following products have also been identified: Fe^{2+},[95] $(CN)_2$,[95,100] $Fe(CN)_6^{4-}$,[95,109,153] $Fe(CN)_5(H_2O)^{3-}$,[95,153] and $Fe(OH)_3$.[95,100] In acid solution, prussian blue forms eventually.[155] Some recent quantum yield values[153] for production of $Fe(CN)_6^{4-}$ and $Fe(CN)_5(H_2O)^{2-}$ are given in Table II; it is not clear what the reaction sequence is that produced $Fe(CN)_6^{4-}$. Some of these products may arise from the thermal or the photolytic decomposition of $Fe(CN)_5(H_2O)^{2-}$.[95] Finally, the oxidation of $N_2H_5^+$ by $Fe(CN)_6^{3-}$ reported is accelerated by light,[156] as is the formation of $Fe(CN)_5N_3^{3-}$ in the presence of azide ion.[157]

F. RUTHENIUM

$Ru(CN)_6^{4-}$ is photolyzed by ultraviolet light to a product, presumably $Ru(CN)_5(H_2O)^{3-}$, which gives an orange color on reaction with nitrosobenzene.[158] In further parallel to the iron system, flash photolysis (with light including the 250-mμ region) leads to photoelectron production.[159]

G. COBALT

$Co(CN)_6^{3-}$ photoaquates in aqueous solution.[100,101] Detailed studies with light in the 300–370-mμ region indicate that $Co(CN)_5(H_2O)^{2-}$ is the sole and terminal product,[44,95] particularly because of the presence of a clean isosbestic point in the spectral changes that occur during irradiation.[95] These changes as well as the quantum yields are essentially independent of pH and of wavelength used.[95]

The above photolysis appears to be merely a particular case of the general reaction

$$Co(CN)_5X^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5(H_2O)^{2-} + X^- \quad (34)$$

where X = CN, Cl, Br, I, and probably H_2O.[44] All of these complexes appear to give $Co(CN)_5(H_2O)^{3-}$ as the terminal product; the photolytic reaction may thus be used for preparative purposes (for example, ref 160). The thermal reverse of reaction 34, or anation, is slow, and the proposed kinetics involve $Co(CN)_5^{2-}$ as the reaction intermediate.[161] Possibly the same intermediate is produced in the photolysis of $Co(CN)_5X^{3-}$. Thus irradiation at 340–370 mμ of $Co(CN)_6^{3-}$ or of $Co(CN)_5(H_2O)^{2-}$ in 1–3 *M* iodide ion leads to direct photoanation, to give $Co(CN)_5I^{3-}$. Further, irradiation of $Co(CN)_5I^{3-}$ at 500 mμ leads to photoaquation which is reduced in yield by added iodide ion. Detailed results suggest a cage mechanism, rather than a mechanism involving $Co(CN)_5^{2-}$ as an ordinary chemical intermediate.[36] The similarity of behavior to $Cr(CO)_6$ is discussed in section V. D.

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(148) B. B. Lal, *Proc. Indian Acad. Sci.*, **38A**, 522 (1953); *Chem. Abstr.*, **48**, 7441*d* (1954), and earlier papers.

(149) D. J. Kenney, T. P. Flynn, and J. B. Gallini, *J. Inorg. Nucl. Chem.*, **20**, 75 (1961).

(150) V. Balzani, V. Carassiti, and R. Soto Loos, *Ann, Chim.* (Rome), **54**, 103 (1964).

(151) V. Balzani, V. Carassiti, and L. Moggi, *ibid.*, **54**, 251 (1964).

(152) V. Balzani, V. Carassiti, and L. Moggi, *Inorg. Chem.*, **3**, 1252 (1964).

(153) J. Legros, *Compt. Rend.*, **265**, 225 (1967).

(154) M. Rákoš and E. Tarabčáková, *Collection Czech. Chem. Commun., Suppl.*, **25**, 2265 (1960).

(155) R. P. Mitra, D. V. Jain, A. K. Bannerjee, and K. V. Raghavachari, *Nature*, **200**, 163 (1963).

(156) E. C. Gilbert, *J. Phys. Chem.*, **35**, 3631 (1931).

(157) D. J. Kenney, G. G. Clinckemaillie, and C. L. Michiels, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967; see also G. G. Clinckemaillie, *Dissertation Abstr.*, **B28** (4), 1402 (1967).

(158) G. Emschwiller, *Compt. Rend.*, **248**, 959 (1959).

(159) W. L. Waltz and A. W. Adamson, unpublished results.

(160) J. H. Bayston, R. N. Beale, N. K. King, and M. E. Winfield, *Australian J. Chem.*, **16**, 954 (1963).

(161) A. Haim, R. J. Grassi, and W. K. Wilmarth, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31.

TABLE II

PHOTOCHEMISTRY OF CYANO COMPLEXES (SELECTED DATA)

Complex (absorption max or sh, mμ/extinction coeff)	Wavelength, mμ	Quantum yield	Reaction mode[a]/conditions[b]/method[c]	Ref
$Cr(CN)_6^{3-}$ (377/85.9; 307/59.5)[102]	370	0.1	A/nat pH, 25°/Sp	36
$Mo(CN)_8^{4-}$ (510 sh/2.7; 431 sh/69; 367.6/170; 308.2 sh/262; 267.4 sh/1350; 240.0/15,540)[83]	436	0.28	A/0.01 *M* OH^-, 20°/Sp	126
	405	0.42	A/0.01 *M* OH^-, 20°/Sp	126
	365	0.49	A/0.01 *M* OH^-, 20°/Sp	126
	365	0.14	A/nat pH, 25°/Sp	113
	365	0.12	A/nat pH, 20°/pH	107
$Mo(CN)_8^{3-}$ (387.7/1350; 312.5 sh/800; 271.7/2000; 251.3/1900)[83]	365	2.6	R/pH 5.5, 20°/Sp	104
	365	4.4	R/pH 7, 20°/Sp	104
	365	3.9	R/pH 7, 20% ethanol, 20°/Sp	105
$W(CN)_8^{4-}$ (625.0 sh/1.9; 502.4 sh/4.8; 434.8/111.0; 370.3/251.0; 303.1 sh/520; 273.7 sh/3000; 249.0/25,060)[83]	436	0.14	A/0.01 *M* OH^-, 20°/Sp	126
	405	0.29	A/0.01 *M* OH^-, 20°/Sp	126
	365	0.54	A/0.01 *M* OH^-, 20°/Sp	126
	365	0.08	A/nat pH, 20°/pH	107
$W(CN)_8^{3-}$ (357.0/1790; 296.8 sh/810; 259.0/2120; 239.2/2170)[83]	365	1.6	R/pH 5.5, 20°/Sp	128
	365	1.6	R/pH 7.0, 20°/Sp	128
	365	1.4	R/pH 7.0, 20% ethanol, 20°/Sp	105
$Fe(CN)_6^{4-}$ (422/4.73; 322.5/302.0; 270 sh/~1000; 218/24,200; 200/23,700)[91]	366	0.52	A/pH 0.65, 25°/Chem	92
	366	0.89	A/pH 4.0, 25°/Chem	92
	366	0.36	A/pH 10, 20°/Chem	139
	365	0.0	E/nat pH, rt/Chem	88, 89
	313	0.35	A/pH 10, 20°/Chem	139
	313	0.26	E/nat pH, rt/Chem	89
	254	0.14	A/pH 6.8, 20°/Chem	139
	254	1.0	E/nat pH, rt/Chem	88, 89
	254	0.66	E/nat pH, 25°/Chem	90
	254	0.35	E/nat pH, 25°/Chem, Sp	92
$Fe(CN)_6^{3-}$ (550/0.287; 415/1050; 320 sh/1200; 304/1590; 280 sh/1000; 260/1260; ~227 sh/~2500)[e]	366	0.009	A/pH 4, rt/Chem, Sp	153
	366	0.014	R/pH 4, rt/Chem	153
	366	0.0065	A/pH 10, rt/Chem	153
	366	0.018	R/pH 10, rt/Chem	153
$Co(CN)_6^{3-}$ (313/243.0; 260/180.0; 202/35,400)[91]	370	0.89[d]	A/nat pH, rt/Chem, Sp	44
	365	0.31	A/pH 5.5, 7.5, 25°/Sp	95
	313	0.31	A/pH 5.5, 7.5, 25°/Sp	95
	254	0.31	A/pH 5.5, 25°/Sp	95
	254	0.38	A/pH 5.5, 75°/Sp	95
$Co(CN)_5Cl^{3-}$ (380/44; 310/128)[44]	370	0.25[d]	A/nat pH, rt/Sp	44
$Co(CN)_5Br^{3-}$ (395/170)[44]	370	0.69[d]	A/nat pH, rt/Sp	44
$Co(CN)_5I^{3-}$ (500/87; 330/2630)[44]	550	0.67[d]	A/nat pH, rt/Sp	44
	500	0.20	A/nat pH, rt/Sp	36
	370	0.95[d]	A/nat pH, rt/Sp	44

[a] A, aquation; R, redox; E, electron production. [b] nat pH, the natural pH of the sodium or potassium salt; rt, room temperature. [c] Sp, reaction followed spectrophotometrically; pH, reaction followed by pH change; Chem, reaction followed by chemical tests or titrations. [d] These values appear to be high by a factor of *ca.* 3, probably due to an error in actinometry. [e] A, V. Kiss, J. Abraham, and I, Hegediis, *Z. Anorg. Allgem. Chem.*, **244**, 98 (1940).

Irradiation of $Co(CN)_6^{3-}$ in the 250-mμ region may lead to different or to further reactions,[95] and, in acidic methanol solution, evolution of hydrogen has been reported.[92] This suggests that photoelectron production may result from irradiation of the CT band. Finally, the complexes $K[Co_2(CN)_{10}]\cdot 2H_2O$ and $K_5[Co_2(CN)_{10}O_2]$ are photosensitive; the latter gives $Co(CN)_5(H_2O)^{2-}$.[160,162,163]

H. PENTACYANONITROSYL COMPLEXES

Complexes of the type $M(CN)_5(NO)^{n-}$ are treated as a group because of certain common features and difficulties in their chemistry and photochemistry. The photosensitivity of nitroprusside ion, the best known member, has long been known,[164] and a recent review is available.[165] The absorption spectra of a number of these complexes have been presented recently, along with a molecular orbital interpretation of the transitions, which are considered to be d–d, d–π*(NO), and d–π*(CN) in type.[94] The latter two absorptions are CTTL in nature. In the odd-electron case (Mn(II)), CTTM transitions exist.[94]

1. *Mo(CN)₅(NO)⁴⁻*

The compound $K_4[Mo(CN)_5(NO)]\cdot 2H_2O$ may be photosensitive, according to some indirect indications.[166]

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(162) L. Cambi and E. Paglia, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **26**, 326 (1959); *Chem. Abstr.*, **53**, 21339*g* (1959).

(163) E. Paglia, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **26**, 794 (1959); *Chem. Abstr.*, **54**, 6382*f* (1960).

(164) A. Overbeck, *Arch. Pharm.*, **124**, 189 (1853).

(165) V. N. Bernshtein and V. G. Belikov, *Usp. Khim.*, **30**, 532 (1961); *Russ. Chem. Rev.*, **30**, 227 (1961).

(166) R. F. Riley and L. Ho, *J. Inorg. Nucl. Chem.*, **24**, 1121 (1962).

2. $Mn(CN)_5(NO)^{2-,3-}$

The manganese nitrosylpentacyano complexes are photosensitive, in apparent contrast to the hexacyano species. The photoreactions have been difficult to interpret, however, partly because of an uncertainty as to whether NO is released as such or as NO^+. Thus photolysis of aqueous $Mn(CN)_5(NO)^{2-}$ gives Mn^{2+}, if the pH is below 4, whereas otherwise the initially yellow solution becomes violet, with a spectrum characteristic of $Mn(CN)_5(NO)^{3-}$, and a concomitant pH decrease occurs.[167] This last product is also formed with near-infrared irradiation, corresponding to $d-\pi^*(NO)$ excitation.[94] The potential for the couple $Mn(CN)_5(NO)^{2-,3-}$ is 0.6 V,[167] and it is possible that the photoreaction is always one of aquation, but with oxidation of cyanide ion occurring at pH's such that $Mn(CN)_5(NO)^{3-}$ would be a stable product. $Mn(CN)_5(NO)^{3-}$ is insensitive to irradiation at 570 mμ, which involves the $d-\pi^*(NO)$ transition at 550 mμ, but with light of 254 and 365 mμ ($d-\pi^*(CN)$ and d–d transitions, respectively), photodecomposition occurs.[168] The sensitivity is three times greater at 254 mμ than at 365 mμ. The actual reaction is not certain, but the polarographic presence of Mn^{2+} and of NO is reported; further, a photoexchange with radiocyanide ion is claimed.[169]

3. $Fe(CN)_5(NO)^{2-}$

Two somewhat disparate reactions are suggested by the literature on the photolysis of nitroprusside ion. On the one hand, photoexchange (white light) with cyanide ion has been reported,[101,169] in fact, preferentially of the cyanide ligand *trans* to the NO group.[169] However, the release of NO and NO^+ has been reported,[170–172] and the eventual formation of prussian blue occurs.[171–174] Finally, the photochemical formation of $Fe(CN)_5(NO)^{3-}$ has been reported to be detected by esr in nonaqueous media.[175]

4. $Co(CN)_5(NO)^{3-}$

$Co(CN)_5(NO)^{3-}$ behaves somewhat differently from $Fe(CN)_5(NO)^{2-}$ in aqueous solution. Irradiation with white light again leads to cyanide ion exchange,[169] but apparently preferentially at the *cis* position. The pH effects are different.[169]

V. CARBONYL AND ARENE COMPLEXES

The carbonyl and arene complexes form a rather closely knit group, with respect both to their general chemistry and to their photochemical behavior. There are a number of reviews on the compounds,[176–184] which also make clear the great value of photochemical preparative procedures in ensuring clean reactions in good yield. On the other hand, the literature on photochemical studies *per se*, that is, investigations concerned with the nature of primary photolysis processes, is more limited. Much of it has been reviewed recently.[184,185]

For the most part, specific photochemical studies have been confined to the simple carbonyls of the type $M(CO)_n$ and their monosubstituted derivatives, $M(CO)_{n-1}A$, where A denotes some Lewis base. The electronic absorption spectra of such compounds tend to lie in the blue and ultraviolet, and consist primarily of fairly intense bands of a CT character. Occasional shoulders and separated peaks of lower intensity are assigned to d–d transitions. A typical spectrum is shown in Figure 3 (after ref 186).

A molecular orbital treatment for metal hexacarbonyls and substituted carbonyls of the type $M(CO)_5A$ which accounts for the main spectral features is available.[186,187] The first d–d transition is given as $^1A_{1g} \rightarrow {}^1T_{1g}$ or $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$, in O_h symmetry, and $^1A_1 \rightarrow {}^1E$, or $e(\pi,d_{xz}d_{yz}) \rightarrow a_1(\sigma^*,d_{z^2})$, in C_{4v} symmetry. The first CT absorption (CTTL) is described as $^1A_{1g} \rightarrow {}^1T_{1u}$ or $t_{2g}(\pi) \rightarrow t_{1u}(\pi^*)$, and $^1A_1 \rightarrow {}^1E$ or $b_2(\pi^*,d_{xy}) \rightarrow e(\pi^*,CO(axial))$, for the two geometries. The d–d transition is thus from π bonding to σ antibonding, and the CTTL one is from a metal–ligand π orbital to an antibonding π orbital on the carbonyl group. With respect to excited-state chemistry, one would expect that in the case of $M(CO)_5A$ complexes absorption into the d–d band would weaken the bonding on the *z*

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(167) W. Jakób, A. Goliewski, and T. Senkowski, "Theory and Structure of Complex Compounds," B. Jeżowska-Trzebiatowska, Ed., The Macmillan Co., New York, N. Y., 1964, pp 381–386.

(168) W. Jacób and T. Sensowski, *Roczniki Chem.*, **40**, 1601 (1966).

(169) B. Jeżowska-Trzebiatowska and J. Ziotkowski, "Theory and Structure of Complex Compounds," B. Jeżowska-Trzebiatowska, Ed., The Macmillan Co., New York, N. Y., 1964, pp 387–392.

(170) R. P. Mitra, D. V. A. Jain, A. K. Banerjee, and K. V. R Chari, *J. Inorg. Nucl. Chem.*, **25**, 1263 (1963).

(171) L. E. Kapatos, E. Voyatsakis, and D. Yanoukakis, *Chim. Chronika* (Athens, Greece), **23**, 72 (1958); *Chem. Abstr.*, **52**, 17950*f* (1958).

(172) O. Baudisch, *Science*, **108**, 443 (1948).

(173) T. Pavolini, *Chem. Zentr.*, I, 259 (1931).

(174) T. Pavolini, *Giorn. Farm. Chim.*, **79**, 119 (1930).

(175) E. F. Hockings and I. Bernal, *J. Chem. Soc.*, 5029 (1964).

(176) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, 1, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, pp 1–124.

(177) E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, 1, 55 (1959).

(178) E. O. Fischer and H. P. Fritz, *Angew. Chem.*, **75**, 353 (1961).

(179) P. L. Pauson, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 346.

(180) E. O. Fischer and H. Werner, *Angew. Chem. Intern. Ed. Engl.*, 2, 80 (1963).

(181) R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, 4, 78 (1962).

(182) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(183) W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1960).

(184) G. R. Dobson, I. W. Stoltz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

(185) W. Strohmeier, *Angew. Chem. Intern. Ed. Engl.*, **3**, 370 (1964).

(186) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

(187) H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, *Can. J. Chem.*, 41, 1281 (1963).

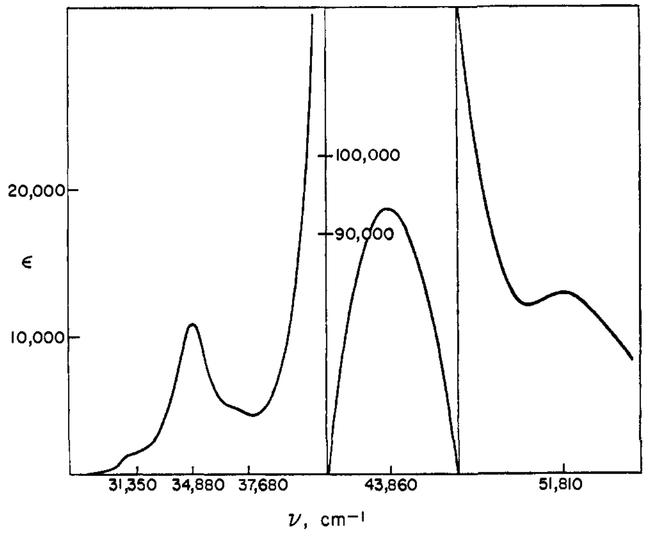

Figure 3.—Absorption spectrum of $Mo(CO)_6$ (after ref 186).

axis and hence tend to labilize both the A ligand and the *trans* or axial carbonyl. Absorption into the CTTL band could labilize primarily the axial carbonyl.

The spectra are medium sensitive in that the CTTL bands tend to shift toward the blue in polar solvents;[186,187] otherwise the solution spectra are essentially the same as in the gas phase. The photochemical behavior need not be phase independent, however, but so far all work on primary quantum yields has been done with solutions. The most striking general observation is that photochemical efficiencies appear always to be unity; the primary photolysis step is simply the loss of a molecule of carbon monoxide, as was proposed as early as 1934.[188,189] No luminescence is observed, nor, evidently, does radiationless deactivation appear to be an important competing process to the photochemistry.

Finally, in view of the two quite different types of absorption bands present, some spectrospecificity of photolysis behavior might be expected. This aspect has been given but little attention; in fact, most irradiations have been on the long-wavelength side of the first absorption feature and probably have involved the tails of both the first d-d and the first CTTL absorptions.

Some representative data are given in Table III.

A. SIMPLE CARBONYLS

The photochemistry can be understood in terms of the primary step

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1} + CO \qquad (35)$$

The definite existence of the intermediate of reduced coordination has been established elegantly in the cases of $Cr(CO)_6$, $W(CO)_6$, and $Mo(CO)_6$.[190,191] Irradiation of solutions in isopentane–methylcyclohexane at 77°K produced a species whose infrared spectrum corresponded to square-pyramidal $M(CO)_5$; on warming to around the glass point, the spectrum changed to that for a trigonal-bipyramidal geometry. The presence of $M(CO)_{n-1}$ has also clearly been demonstrated by other means[37,184] and has been shown to be responsible for photochromic behavior in the absence of bases.[192]

For net photochemical reaction to occur, some base must be present.

$$M(CO)_{n-1} + B \longrightarrow M(CO)_{n-1}B \qquad (36)$$

The base may be the solvent itself, or it may be present as a solute in isopentane or some other noncoordinating solvent; bases used include a variety of amines, such as propylamine or pyridine, nitriles, sulfoxides, etc. (see ref 185). In the case of $Fe(CO)_5$ the base is found to be exclusively in the axial position.[193] The carbon monoxide from eq 35 competes increasingly with any other base present as photolysis proceeds, with a consequent steady diminution of the apparent quantum yield for net reaction. The quantum yield decrease with time is also a function of light absorption by products and secondary photolyses. Both the thermal return of reaction 35 and secondary photolysis may be discounted by extrapolating the apparent quantum yields to zero time; as already noted, such limiting yields are essentially unity.[34,37,38,194] Irradiations have generally been at 365 or 436 mμ.

In contrast to the foregoing observations, it has been reported that flash photolyses of $Fe(CO)_5$ and $Ni(CO)_4$ yield appreciable amounts of elemental iron and nickel.[195]

B. SUBSTITUTED CARBONYLS

Carbonyls of the type $M(CO)_{n-1}A$ appear to photolyze according to the scheme[196]

$$M(CO)_{n-1}A \xrightarrow{h\nu,\ \phi_1} [M(CO)_{n-1}A]^* \qquad (37)$$

$$\begin{tikzcd} & M(CO)_{n-2}A + CO \quad (38) \\ {[M(CO)_{n-1}A]^*} \arrow[ur, "\phi_2"] \arrow[dr, "\phi_3"'] & \\ & M(CO)_{n-1} + A \quad (39) \end{tikzcd}$$

In the presence of base B, the further reactions are

$$M(CO)_{n-2}A + B \xrightarrow{\phi_4} M(CO)_{n-2}AB \qquad (40)$$

$$M(CO)_{n-1} + B \xrightarrow{\phi_5} M(CO)_{n-1}B \qquad (41)$$

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(188) H. W. Thompson and A. P. Garratt, *J. Chem. Soc.*, 524 (1934).

(189) H. W. Thompson and A. P. Garratt, *ibid.*, 1817 (1934).

(190) I. W. Stoltz, G. R. Dobson, and R. K. Sheline, *J. Am. Chem. Soc.*, **84**, 3589 (1962).

(191) I. W. Stoltz, G. R. Dobson, and R. K. Sheline, *ibid.*, **85**, 1013 (1963).

(192) M. A. El-Sayed, *J. Phys. Chem.*, **68**, 433 (1964).

(193) E. H. Schubert and R. K. Sheline, *Inorg. Chem.*, **5**, 1071 (1966).

(194) W. Strohmeier and D. von Hobe, *Chem. Ber.*, **94**, 761 (1961).

(195) A. B. Callear and R. J. Oldman, *Nature*, **210**, 730 (1966).

(196) W. Strohmeier and D. von Hobe, *Chem. Ber.*, **94**, 2031 (1961).

where B may include the carbon monoxide released in reaction 38. The systems so far studied (except for the special case of the cyclopentadienyl carbonyls) are those for which A and B have been the same; in this case only reaction 40 leads to net chemical change. The quantum yield for this reaction, ϕ_4, has been found to vary from 0.05 to about 0.3, depending on the nature of the base.[185] The defect from unity then corresponds to ϕ_5, assuming the total quantum yield ($\phi_2 + \phi_3$) still to be unity, as with the simple carbonyls. This assumption has not been verified experimentally, however.

The values of ϕ_4 decrease in the order py > THF > $(C_2H_5)_3N$ > $CH_3COOC_2H_5$ > CH_3COCH_3, or in the order of decreasing M–A bond energy, for M = Cr, W, or Mo.[197] In addition, ϕ_4 increases on going from 436- to 365-mμ radiation, corresponding to an increasing ratio of M–CO to M–A bond breaking. It has been inferred from this that the M–CO bond is the stronger of the two.[198] Although this conclusion was not elaborated on, possible grounds for it might be that $[M(CO)_{n-1}A]^*$ in reactions 38 and 39 represents a hot ground-state molecule and that decreasing the wavelength of the radiation used increased the amount of excess energy available for bond breaking. Alternatively, however, the d–d and CTTL excited states may have different chemistries. The assignment for the CTTL state as π^*(CO(axial)) suggests that M–CO bond breaking might follow, while, as discussed previously, the d–d transition will weaken both the axial M–CO bond and the M–A bond, the excited state being (σ^*, d_{z^2}). The variation in ϕ_4 could then be due to a variation in the population of the two types of states with the wavelength employed. An interesting point is that, in the case of $M(CO)_5A$, the excited state assignments suggest that it should be the carbonyl *trans* to A that is labilized. Thus the stereochemistry of the photoreaction could differ from that of the thermal process in which exchange of carbon monoxide with $M(CO)_5A$ complexes is reported to occur preferentially with the *equatorial* carbonyls.[199]

A number of more complex secondary reactions can occur on irradiation of metal carbonyls. These include (a) the formation of polynuclear metal carbonyls involving both metal–metal bonds[200,201] and bridging groups,[193] (b) organic condensation reactions which may include the incorporation of carbonyl groups,[202,203] (c) ligand isomerization reactions,[204] (d) polymerization reactions,[205,206] and (e) the oxidation of the metal by the ligand (as in the case of the base acetylacetone (HAA)[207] in the formation of $Fe(AA)_3$). Finally, photochemical techniques have been most useful in producing ^{14}C-labeled carbonyls.[208,209]

C. ARENE COMPLEXES

The photochemistry of arene complexes is essentially limited to that of mixed arene–carbonyl species, for which the primary step is again one of dissociation of a carbonyl group.[185,198] Compounds studied include $(C_5H_5)Mn(CO)_3$, $(C_6H_6)Cr(CO)_3$, $(C_5H_5)Co(CO)_2$, and related species (see ref 185, 210). However, in the flash photolysis of $(C_4H_4)Fe(CO)_3$, the major photochemical step appears to be the production of $[C_4H_4]^*$ and $Fe(CO)_3$.[211]

Ferrocene like the carbonyls (above) has been found to photocatalyze isomerization and polymerization reactions.[212]

D. COMPARISON OF CARBONYL AND CYANO COMPLEXES

There is a number of well-established similarities between the chemistries of the carbonyl and the cyano complexes, and it is interesting that some tentative parallels appear to exist in their photochemistries. Most striking in this respect is the isoelectronic pair $Cr(CO)_6$ and $Co(CN)_6^{3-}$ and their monosubstituted derivatives $Cr(CO)_5A$ and $Co(CN)_5X^{3-}$, where X is a halogen. There are similarities both in the spectra and in the excited-state assignments. The d–d transitions for $Co(CN)_6^{3-}$ are similar in type to those for $Cr(CO)_6$, and the CTTL band for the former has similarly been described as involving a π^*(CN) configuration (see section IV.G).

As noted in section IV,G, the primary photolysis step for $Co(CN)_6^{3-}$ appears to be

$$Co(CN)_6^{3-} \xrightarrow{h\nu} Co(CN)_5^{2-} + CN^- \qquad (42)$$

or the analog of eq 35. Similarly, too, the $Co(CN)_5^{2-}$ fragment then reacts competitively with available bases, in the manner of eq 36. In the case of $Co(CN)_5I^{3-}$, the first d–d band (at 500 mμ) is well separated from the

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(197) W. Strohmeier, D. von Hobe, G. Schönauer, and H. Laporte, *Z. Naturforsch.*, **17b**, 502 (1962).

(198) W. Strohmeier and D. von Hobe, *Z. Physik. Chem.* (Frankfurt), **34**, 393 (1962).

(199) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

(200) J. K. Ruff, *Inorg. Chem.*, **6**, 1502 (1967).

(201) G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Commun.*, 186 (1967).

(202) H. W. Sternberg, R. Markley, and I. Wender, *J. Am. Chem. Soc.*, **80**, 1009 (1958).

(203) W. Strohmeier, H. Laporte, and D. von Hobe, *Chem. Ber.*, **95**, 455 (1962).

(204) F. Asinger, B. Fell, and K. Schrage, *ibid.*, **98**, 372 (1965).

(205) W. Strohmeier and H. Grubel, *Z. Naturforsch.*, **22b**, 115 (1967).

(206) C. H. Bamford, J. Hobbs, and R. P. Wayne, *Chem. Commun.*, 469 (1965).

(207) J. Goan, G. Huether, and H. Podall, *Inorg. Chem.*, **2**, 1078 (1963).

(208) W. Strohmeier and R. Müller, *Z. Physik. Chem.* (Frankfurt), **28**, 112 (1961).

(209) W. Strohmeier and D. von Hobe, *Z. Naturforsch.*, **18b**, 770 (1963).

(210) W. Strohmeier, C. Barbeau, and D. von Hobe, *Chem. Ber.*, **96**, 3254 (1963).

(211) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(212) J. J. Dannenberg and J. H. Richards, *J. Am. Chem. Soc.*, **87**, 1626 (1965).

TABLE III

PHOTOCHEMISTRY OF CARBONYL AND ARENE COMPLEXES (SELECTED DATA)

Complex[a]	Wavelength, mμ	Quantum yield	Process or product	Ref
$Cr(CO)_6$	366	1.0	Eq 35	198
$W(CO)_6$	366	1.0	Eq 35	198
$Mo(CO)_6$	366	1.0	Eq 35	198
$(C_5H_5)Mn(CO)_3$	436	1.0	Eq 35	198
	366	1.0	Eq 35	198, 210
$Cr(CO)_5(py)$	436	0.133	$Cr(CO)_4(py)_2$[b]	198
	366	0.21	$Cr(CO)_4(py)_2$[b]	198
$Mo(CO)_5(py)$	436	0.11	$Mo(CO)_4(py)_2$[b]	198
	366	0.16	$Mo(CO)_4(py)_2$[b]	198
$W(CO)_5(py)$	436	0.078	$W(CO)_4(py)_2$[b]	198
	366	0.11	$W(CO)_4(py)_2$[b]	198

[a] py =pyridine. [b] In benzene solution.

first CT band, and, on irradiation of it, only breaking of the Co–I bond appears to occur. The inference is that corresponding irradiation of $Cr(CO)_5A$ might lead primarily to Cr–A bond breaking.

Cobalt(III) complexes are not generally very sensitive to irradiation of d–d bands; as discussed in section X, photoaquation quantum yields for the largely or purely σ-bonded ammines are low (as small as 10^{-4}). It is thus also significant to the present comparison that the Co(III) cyano complexes as a group show photoaquation quantum yields in the range of 0.2–0.6 (see Table II), or close to the value of unity observed for $Cr(CO)_6$. Since the aqueous cyano complexes are undoubtedly strongly solvated, it is to be expected that some reduction in quantum yield might occur owing to radiationless deactivation.

VI. SCANDIUM, TITANIUM, AND VANADIUM GROUPS

The inclusion of this section is essentially *pro forma* in view of the very limited number of observations to report. First, we find nothing on the scandium group within the scope of this review, bearing in mind that the rare earths are treated in section XIII.

Some photolyses at 254 mμ have been reported for $V^{2+}(aq)$, $V^{3+}(aq)$, $VO^{2+}(aq)$, and $Ti^{3+}(aq)$ in acidic solutions;[213] irradiation leads to sensitized polymerization. For $V^{2+}(aq)$ and $Ti^{3+}(aq)$ at least, the basic photochemistry is probably the same as for $Fe^{2+}(aq)$ (section IX.A), namely photoelectron production. Also, $V^{2+}(aq)$ like $Fe^{2+}(aq)$ forms a complex with acrylonitrile, which absorbs in the visible. Irradiation of solutions containing this complex, at wavelengths longer than the CT band of $V^{2+}(aq)$ does not lead to polymerization of the acrylonitrile.[213] Aqueous titanium(IV) lactate is photoreduced to Ti(III) in the presence of methylene blue, using white light.[214] The photoreduced dye was considered to be the reducing agent. While important, the photoproperties of TiO_2 are not relevant to this review.

Some photochemistry of the niobium halides, $NbCl_5$, $NbCl_4$, and $NbCl_3$, in hydrochloric acid solution has been reported.[215] Also, some substituted niobium carbonyl complexes have been studied,[216] with results fitting the general pattern discussed in section V.

VII. CHROMIUM, TUNGSTEN, AND MOLYBDENUM

The photochemistry of Cr(III) complexes has been better investigated than that of any other group of coordination compounds. Not only is there a considerable literature on the carbonyl, oxalato, and cyano complexes, discussed in those sections, but numerous nitrogen and oxygen coordinated complexes exist, generally well characterized as to structure and thermal reaction chemistry and hence relatively easy to prepare and to study. With a few possible exceptions involving light of 254 mμ or shorter wavelength (see sections III.A and IV.A), photolysis always consists of substitution or substitution related reactions uncomplicated by redox processes, and quantum yields are generally large. There are two recent reviews,[2,3a] which include aspects of Cr(III) photochemistry.

It is very convenient, in presenting the photochemistry of this group, to consider first those complexes having O_h symmetry. Since only one kind of coordinated atom is present, only one kind of substitution reaction is possible, and studies of such complexes are therefore limited to determinations of the wavelength and temperature dependence of quantum yields.

Complexes of lower symmetry perforce have more than one kind of ligand atom; consequently, two or more modes of substitution reaction are possible. Important additional information may then be gained from a study of the variation of the *ratio* of reaction modes with wavelength and temperature. The behavior of CrO_4^{2-} is mentioned in section VIII.

The spectra of Cr(III) complexes are understood theoretically in some detail, and relevant aspects are discussed in the subsections that follow. In addition, there is much information on fluorescent and phosphorescent emission.

For the rest, a few observations have been made on aqueous Cr(II) but virtually none on tungsten and molybdenum complexes, other than those covered in the sections on carbonyls and cyanides. As an isolated report, aqueous colloidal MoO_3 photolyzes in the ultra-

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(213) F. S. Dainton and D. G. L. James, *Trans. Faraday Soc.*, 54, 649 (1958).

(214) G. K. Oster and G. Oster, *J. Am. Chem. Soc.*, 81, 5543 (1959).

(215) J. Wojtczak, *Poznan. Towarz. Przyjaciol Nauk, Wydzial Mat. Przyrod. Proc. Komisji Mat.-Przyrod.*, 12, 25 (1967); *Chem. Abstr.*, 67, 77860 (1967).

(216) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Pasynski, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 744, 2231 (1966); *Chem. Abstr.*, 65, 8229c (1966).

violet, in the presence of hydrogen or carbon monoxide, to give molybdenum blue.[217]

A. CHROMIUM(II)

The photochemistry of Cr(II) consists entirely of observations on the labile aquo species and is rather similar to that of aqueous Fe(II) (section IX.A).[213,218] The absorption spectrum of the blue $Cr^{2+}(aq)$, $Cr(H_2O)_6{}^{2+}$, ion in acidic solutions shows a CTTS band as a shoulder at 270 mμ on a more intense allowed band still deeper in the ultraviolet, and a minor peak at 420 mμ (ϵ *ca.* 0.1), followed by a broad band around 700 mμ (ϵ *ca.* 10).[213]

On irradiation with 200–350-mμ light, evolution of hydrogen occurs and production of Cr(III).[213,218–220] The primary steps have been formulated as[220]

$$\mathrm{Cr^{2+}(aq)} \xrightarrow{h\nu} [\mathrm{Cr^{3+}H_2O^-}] \longrightarrow \mathrm{Cr^{3+}(aq)} + \mathrm{OH^-} + \mathrm{H} \quad (43)$$

However, in view of more recent developments, the primary act may well be one of photoelectron production (see section IX.A). A detailed study using 254- and 265-mμ light gave a quantum yield of 0.13 for hydrogen production at pH 1.0 to pH 2.5, independent of light intensity and of Cr(II) concentration.[220] The yield increased slightly with added hydrochloric or sulfuric acids (up to 1 *N*) and decreased with added acrylamide, or alcohols. These effects could be largely accounted for in terms of various radical reactions following process 43, but it was necessary to suppose that species such as $CrCl^+$ and $Cr(SO_4H)^+$ were also photosensitive.

B. CHROMIUM(III) COMPLEXES OF O_h SYMMETRY

1. *Absorption and Emission*

The term states for an O_h, d^3 system, as given by crystal-field theory, are shown in Figure 4.[7] There is a series of quartet excited states, the two lowest of which are $^4T_{2g}$ and $^4T_{1g}$, and a low-lying doublet state, ^2E_g. Accordingly, Cr(III) complexes typically show at least two quartet–quartet transitions, usually in the visible, and at least one spin-forbidden transition, sometimes not resolved. A typical spectrum is shown in Figure 5, and the doublet and first two quartet transitions are designated D, L_1, and L_2. The energy of the first quartet–quartet transition, $^4A_{2g} \rightarrow {}^4T_{2g}$, gives directly the crystal-field parameter, $10Dq$, and thus the position of the ligand in the spectrochemical series: $CN^- >$ en $> NH_3 > NCS^- > H_2O \sim C_2O_4{}^{2-} >$ urea $> Cl^-$ (ref 2, 7, 10, 11, for example). The molecular orbital treatment shows the electron in the first two excited quartet states to be in a σ antibonding orbital.[2,7,10,11]

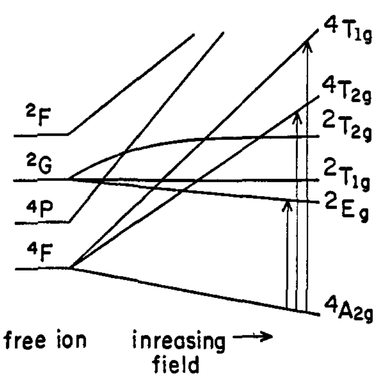

Figure 4.—Schematic crystal-field diagram for an octahedral Cr(III) complex (after ref 7).

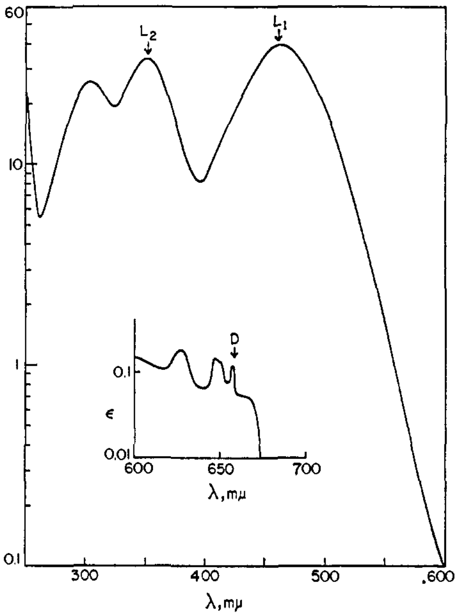

Figure 5.—Absorption spectrum for aqueous $Cr(NH_3)_6{}^{3+}$, pH 3 (after ref 221 and also unpublished work from this laboratory).

The lowest doublet state, ^2E_g, involves only spin pairing within a nonbonding set of orbitals, and, understandably, the transition $^4A_{2g} \rightarrow {}^2E_g$ is relatively insensitive in energy to the type of ligand, although some correlation has been noted;[78] the doublet band typically occurs in the region 650–700 mμ. It is fairly narrow but may be structured, indicative of vibronic coupling.[221–224]

Finally, a CT band is usually found in the ultraviolet, often below 250 mμ. No detailed treatment seems to be available, but such bands are presumably CTTM in

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(217) N. Ya. Dodonova, *Zh. Fiz. Khim.*, **39**, 3033 (1965); **40**, 1543 (1966); *Chem. Abstr.*, **64**, 9131*a* (1966); **65**, 11591*h* (1966).

(218) F. S. Dainton and D. G. L. James, *J. Chim. Phys.*, **48** C17 (1951); *Chem. Abstr.*, **49**, 9996*i* (1952).

(219) B. Ya. Dain and E. Liberzon, *Acta Physicochim. URSS*, **19**, 410 (1944); *Chem. Abstr.*, **39**, 3203⁹ (1945).

(220) E. Collinson, F. S. Dainton, and M. A. Malati, *Trans. Faraday Soc.*, **55**, 2096 (1959).

(221) A. W. Adamson and T. M. Dunn, *J. Mol. Spectry.*, **18**, 83 (1965).

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

(223) G. B. Porter and H. L. Schläfer, *ibid.*, **40**, 280 (1964).

(224) H. L. Schläfer, H. Gausmann, H. F. Wasgestian, and H. U. Zander, *ibid.*, **51**, 274 (1966).

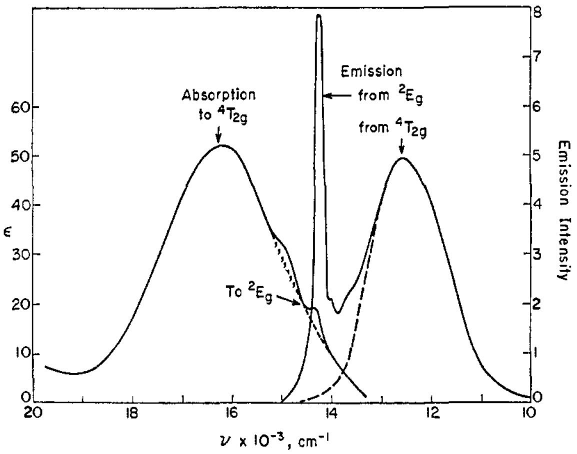

Figure 6.—Absorption (25°) and emission (−195°) spectra of 0.03 *M* $[Cr(urea)_6](ClO_4)_3$. The dotted and dashed lines indicate the approximate resolution of the absorption and emission spectra into the different bands. Emission intensity is on a relative scale (after ref 225).

type. Thiocyanate containing complexes show a strong absorption at 305 mμ, but this is attributed to a transition within the thiocyanate group.[7]

Low-temperature emission studies characteristically show a phosphorescence in the red, of half-life about 10^{-3} sec, and due to emission from the doublet state.[18,222–229] As illustrated in Figure 6 (after ref 225), the emission is but little shifted in position from that of the doublet absorption band. The implication is that the geometry of the two states is about the same,[225] as would be expected since the transition involves only a rearrangement of nonbonding electrons.

A few Cr(III) complexes have exhibited fluorescent emission, attributed to the $^4T_{2g} \rightarrow {}^4A_{2g}$ transition,[225–227] as also illustrated in Figure 6. The emission is broad and considerably shifted to the red relative to the absorption band. The $^4T_{2g}$ state is thus strongly distorted,[17,230,231] possibly to another symmetry point group.[14] Emission, after thermal equilibration, would then be to high vibrational levels of the ground state, hence the large red shift. It has been suggested that to observe fluorescence the equilibrated $^4T_{2g}$ state should lie below the ^2E_g state[226] and that this is more apt to be true of ligands low in the spectrochemical series.[227]

Treatments of the intensity of the transitions are given in various monographs (for example, ref 7, 10, 11). Quartet–quartet transitions, nominally Laporte forbidden, probably gain intensity through vibronic coupling to higher, *ungerade* states,[232,233] and the spin-forbidden quartet–doublet ones, through spin–orbit coupling with states of differing multiplicity.

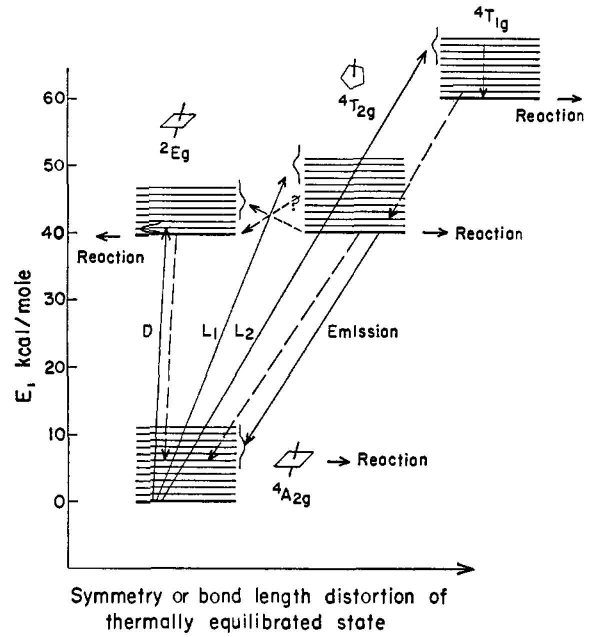

Figure 7.—Processes that may occur following excitation of a Cr(III) complex. Dashed lines indicate radiationless processes. The octahedral figures are inserted to indicate that little change in geometry occurs on excitation to the ^2E_g state, and the pentagonal pyramidal one, to suggest that a major change in geometry could occur in the thermally equilibrated ^4T states. The term symbols are for O_h symmetry, but the diagram is intended to serve as a generalized one for any Cr(III) complex.

Both phosphorescent and, where observed, fluorescent emission decrease rapidly as the temperature is raised past the glass point of the medium used,[225,228,234] and none has been observed in aqueous media at room temperature. Quantum yields for photolysis behave reciprocally, increasing from very low values at 77°K to, usually, several tenths at room temperature; this is true of $Cr(urea)_6^{3+}$ [235] and of $Cr(NH_3)_2(NCS)_4^-$.[14,235] Emission plus photolysis yields do not total unity, however, and radiationless deactivation processes must also be important. The general scheme of possible processes is shown in Figure 7, and estimates of the various rates have been made.[14,17,18,229] The rate constant for internal conversion, $^4T_{1g} \rightarrow {}^4T_{2g}$, has been taken to be very large, *ca.* 10^{11} sec^{-1}, and that for intersystem crossing, $^4T_{2g} \rightarrow {}^2E_g$, about 10^7 sec^{-1} (ref 17; see also ref 18, 229), but such estimates are rather uncertain. Where no emission is observed, radiationless deactivation

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(225) G. B. Porter and H. L. Schläfer, *Z. Physik. Chem.* ((Frankfurt), **37**, 109 (1963).

(226) H. L. Schläfer, H. Gausmann, and H. U. Zander, *Inorg. Chem.*, **6**, 1528 (1967).

(227) H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967).

(228) H. L. Schläfer, H. Gausmann, and H. Witzke, *Z. Physik. Chem.* (Frankfurt), **56**, 55 (1967).

(229) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964).

(230) C. Furlani, *Coord. Chem. Rev.*, **1**, 51 (1966).

(231) V. Balzani, V. Carassiti, and F. Scandola, *Gazz. Chim. Ital.*, **96**, 1213 (1966).

(232) G. Herzberg and E. Teller, *Z. Physik. Chem.*, **B21**, 410 (1933).

(233) A. D. Liehr and C. J. Ballhausen, *Phys. Rev.*, **106**, 1161 (1957).

(234) T. J. Wisk, "Luminescence of Reinecke Salt as a Function of Temperature," M.S. Thesis, The University of Arizona, 1967.

(235) R. D. Lindholm, Ph.D. Dissertation, University of Southern California, 1968.

must, of course, then be faster by orders of magnitude than the radiative process, but the latter is now not measurable. It cannot safely be assumed to be given by application of the Lewis–Kasha relationship[236] to the area under the absorption band.[14]

2. *Photochemistry*

The available data for O_h complexes are collected in Table IV; the photoreactions are all aquations, *e.g.*

$$Cr(NH_3)_6^{3+} + H_2O \xrightarrow{h\nu} Cr(NH_3)_5(H_2O)^{3+} + NH_3 \quad (44)$$

The quantum yields are high and increase with increasing ligand-field strength, with the exception of $Cr(CN)_6^{3-}$. The yields are nearly wavelength independent in the region of the quartet bands, and in the three cases studied this constancy extends to the doublet region. The doublet absorption is quite pronounced in the case of $Cr(NH_3)_6^{3+}$, so that absorption due to the tail of the adjacent L_1 band is not dominant, and here it appears that no change in the photoaquation yield occurs,[26] although an earlier report indicated a high value.[237] Furthermore, the yields are generally nearly temperature independent, although the photoexchange of $Cr(H_2O)_6^{3+}$ with solvent water appears to be an exception.[238]

Some solid-state photolyses have been reported. Radiation from a xenon flash tube converted solid $[Cr(en)_3]X_3$ to $[Cr(en)_2X_2]X$.[239] With X = Cl and Br the *cis* product was obtained, whereas with X = NCS the *trans* one resulted; no effect occurred with X = I. Ultraviolet irradiation of $[Cr(en)_3]_2(S_2O_8)_3$ led to products which exploded on heating.[240]

The lack of wavelength dependence at first observed for the photolysis of aqueous Cr(III) complexes, along with parallels drawn to organic systems, stimulated the suggestion that the photochemical reactions occurred primarily from the ^2E_g state.[238,241] This state should contain sufficient energy and be of long enough life for reaction,[241] should have an electronic configuration which makes it substitutionally labile,[238] and should have zero crystal-field activation energy for reaction.[17] As an empirical correlation, it appeared at first that the smaller the separation between the L_1 and D bands, the lower the quantum yield. The explanation was offered that quantum yield loss occurred by thermal activation from the doublet back to the nearest quartet state, and thence by radiationless deactivation to the ground state. The smaller this energy difference, the more probable would be the sequence.[237] The correlation fails badly if applied to Cr(III) complexes generally[242] (but does hold for the O_h group, excepting $Cr(CN)_6^{3-}$).

C. CHROMIUM(III) COMPLEXES OF NON-O_h SYMMETRY

1. *Absorption and Emission*

The complexes of lower symmetry that have been studied photochemically are primarily those of the type $Cr(NH_3)_5X^{2+}$, or C_{4v}, and *cis*- and *trans*-$Cr(en)_2X_2^+$, which are C_{2v} and D_{4h}, respectively. The descent in symmetry leads to a further splitting of the d orbital levels; various semiquantitative treatments have been carried out.[10,102,243,244] A useful approach is described by Ballhausen.[245] The complex is assumed to retain the three mutually perpendicular axes of the octahedron, but allowance is made for differing ligand-field strengths along each axis. In the above cases, two axes are the same, and the third is different. The $^4T_{2g}$ state in O_h symmetry is then split, and by an amount related to the difference in average field strength between the two kinds of axes. The splitting for a *trans* compound can be shown to be twice that for a *cis* in this approximation. A similar splitting of the $^4T_{1g}$ state occurs, but as might be expected the first doublet state is not much affected, and as a practical observation the doublet absorption band remains at about the same wavelength.

Both fluorescent[223,226] and phosphorescent emission[18,223,226,228,229] have been observed for complexes of reduced symmetry, in low-temperature glasses, and the emission spectra and phosphorescent lifetimes are similar to those of the O_h complexes. In the case of *trans*-$Cr(NH_3)_2(NCS)_4^-$, emission yields and lifetimes have been determined as a function of temperature.[234]

2. *Photochemistry*

The available results are summarized in Table V. It will be noted that quantum yields are now extremely variable, ranging from near unity to below 10^{-4}. They are more often wavelength and temperature dependent than those in the case of the O_h family. Finally, where two reaction modes have been studied, the ratio of their quantum yields may be wavelength and temperature dependent.

A good deal of systematization is provided by a set of empirical rules.[14]

Rule 1. Consider the six ligands to lie in pairs at the ends of three mutually perpendicular axes. That axis having the smallest average crystal field will be the one

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[236] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **67**, 994 (1945).

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

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

[239] C. H. Stembridge and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **27**, 129 (1965).

[240] S. E. Beacom, *Nature*, **183**, 38 (1959).

[241] H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **11**, 65 (1957).

[242] A. W. Adamson, *J. Inorg. Nucl. Chem.*, **13**, 275 (1960).

[243] A. B. P. Lever, "Werner Centennial," Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 430.

[244] A. B. P. Lever, *Coord. Chem. Rev.*, in press.

[245] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 107.

labilized, and the total quantum yield will be about that for an O_h complex of the same average field.

Rule 2. If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates. This may be a type of *trans* effect.

Rule 3. The discrimination implied by rules 1 and 2 will occur to a greater extent if it is the L_1 rather than the L_2 band that is irradiated.

The data of Table V are consistent with these rules. Thus the low quantum yield for photoaquation[237] of ammonia in $Cr(NH_3)_2(H_2O)_4^{3+}$ is explained on the basis that the $H_2O–OH_2$ axis is the weak field one, so that the principal photolysis reaction should be water exchange rather than ammonia aquation. Conversely, *trans*-$Cr(NH_3)_2(NCS)_4^-$ should undergo primarily thiocyanate aquation, as is found to be the case.[26,44] The behavior of *cis*- and *trans*-$Cr(en)_2(OH)_2^+$, for which both photoaquation and photoisomerization occurred,[246] again appears to be consistent with the above rules.[14]

A simple example of the application of rules 1 and 2 occurs in the case of $Cr(NH_3)_5X^{2+}$ for which the two possible reactions are

$$\mathrm{Cr(NH_3)_5X^{2+} + H_2O} \begin{array}{ll} \xrightarrow{h\nu} \mathrm{Cr(NH_3)_5(H_2O)^{3+} + X^-} & (45) \\ \xrightarrow{h\nu} \mathrm{Cr(NH_3)_4(H_2O)X^{2+} + NH_3} & (46) \end{array}$$

Ammonia aquation is predicted to be dominant if X = Cl or NCS, and this is confirmed experimentally. For $Cr(NH_3)_5Cl^{2+}$, ϕ_{NH_3} is about 0.4 and ϕ_{Cl^-} about 0.01.[247,248] For $Cr(NH_3)_5(NCS)^{2+}$, photoaquations both of ammonia[249] and of thiocyanate[44] have been reported, and a more recent study[250] gives both quantum yields as a function of temperature and wavelength. The ratio ϕ_{NH_3}/ϕ_{NCS^-} at 25° is 15 and 23 at 370 and 490 mμ, respectively (note rule 3).

An interesting question is whether photosubstitution reactions are stereospecific. If they are, then a further prediction of the rules is that the above ammonia aquation products should be *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ and *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$. The actual product was inferred to be *cis* in the first case, from the nature of the spectral change in photolysis,[248] but definitely appears to be *trans* in the second case.[235,251]

There are now several instances in which the preferred photochemical reaction is not the preferred thermal one. Thus for *cis*- and *trans*-$Cr(en)_2(H_2O)_2^{3+}$, $Cr(en)_2(H_2O)(OH)^{2+}$, and $Cr(en)_2(OH)_2^+$, the dominant thermal reaction is isomerization, while, in the photolysis, aquation is of major importance.[246] $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5(NCS)^{2+}$ show primarily, if not exclusively, thermal aquation of the acido group, while, as noted above, the photolysis is largely one of ammonia aquation. Again in DMSO (dimethyl sulfoxide) the thermal reaction[252] of *cis*-$Cr(en)_2Cl_2^+$ produces *cis*-$Cr(en)_2(DMSO)Cl^{2+}$, intially, while the photolytic product[253] is *trans*-$Cr(en)_2Cl_2^+$, both reactions studied with equimolar chloride.

Finally, several of the above systems show spectrospecificity, *i.e.*, wavelength dependence of the ratio of reaction modes, extending to the region of the doublet band (see Table V). In the case of $Cr(NH_3)_5(NCS)^{2+}$, for example, the ratio ϕ_{NH_3}/ϕ_{NCS^-} at 25° is 8.3 at 652 mμ,[235,251] in contrast to the high values at shorter wavelengths.

Additional observations are that *trans*-$Cr(en)_2Cl_2^+$ photoaquates to $Cr(en)_2(H_2O)Cl^{2+}$ in white light,[254] and, similarly, $Cr(H_2O)_4Cl_2^+$ is aquated to $Cr(H_2O)_6^{3+}$.[255,256] Several photoanations have been studied, involving the coordination of either NCS^- or Cl^-.[242] Quantum yields were quite low, and it was felt that the actual species photolyzed was the ion pair of the complex with the entering anion. Paramagnetic ions apparently do not influence Cr(III) quantum yields; thus the photoaquation quantum yield for *trans*-$Cr(NH_3)_2(NCS)_4^-$ was not affected by the presence of 1 *M* Mn^{2+}.[26]

D. PHOTOLYSIS MECHANISMS

Figure 7 illustrates the complexity of the situation that potentially exists on irradiation of a Cr(III) complex. First, the chemical reaction may occur directly from one or another excited state. One early proposal that prompt bond fission occurred[44,257] is now too simple to account for the various observations.[231] Another, discussed in section VII.B.2, was that intersystem crossing was rapid so that, regardless of wavelength used, the complex terminated in the lowest doublet excited state, from which reaction occurred. This mechanism continues to find strong support,[17] but it is disappointing that, particularly in the case of $Cr(NH_3)_6^{3+}$, no increase in photolysis quantum yield appears to occur on irradiation of the doublet band.[26,235,251] A more recent proposal is that reaction may occur from the first excited quartet state, and even from higher ones.[14] This was thought to be particularly likely for the non-O_h complexes, for which the equilib-

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(246) A. W. Adamson, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 237.

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

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

(249) W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Am. Chem. Soc.*, **81**, 2958 (1959).

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

(251) E. Zinato, R. D. Lindholm, and A. W. Adamson, unpublished work.

(252) D. A. Palmer and D. W. Watts, *Inorg. Chem.*, in press.

(253) D. W. Watts and A. W. Adamson, unpublished results.

(254) D. J. McDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

(255) V. V. Kurilow, *J. Russ. Phys. Chem. Soc.*, **47**, 469 (1915); *Chem Abstr.*, **10**, 146^4 (1916).

(256) D. S. Datar and M. Qureshi, *J. Osmania Univ.*, **8**, 6 (1940); *Chem. Abstr.*, **35**, 5392^6 (1941).

(257) A. W. Adamson and A. H. Sporer, *J. Inorg. Nucl. Chem.*, **8**, 209 (1958).

TABLE IV

PHOTOCHEMISTRY OF CHROMIUM(III) COMPLEXES OF O_h SYMMETRY (SELECTED DATA)

Complex (band/wavelength, mμ/extinction coeff)[a]	Wavelength, mμ	Quantum yield	Reaction mode[b]/conditions/method[c]	Activation energy, kcal/mole	Re
$Cr(urea)_6^{3+}$ (D/697/4.7; L_1/620/46.9; L_2/444/38.4)[26,225]	696[d]	0.095	A/nat pH 4.0, 22°/Chem		26
	628	0.10	A/nat pH 4.0, 22°/Chem	3.0	26
	452	0.10	A/nat pH 4.0, 22°/Chem		26
$Cr(H_2O)_6^{3+}$ (D/669/-; L_1/574/13.4; L_2/408/15.6; L_3/261/∼5)[237,238]	540–730	0.12–0.18[e]	$H_2^{18}O$/0.1 N H^+, 27°/Chem	∼13	238
	350–480	0.06–0.18[e]	$H_2^{18}O$/0.1 N H^+, 27°/Chem	∼13	238
	254	∼0.12[e]	$H_2^{18}O$/0.1 N H^+, 27°/Chem	∼13	238
$Cr(C_2O_4)_3^{3-}$ (D/698/5.1; L_1/571/77; L_2/417/96)[78]	697	0.011[f]	Rac/30% mole EtOH, 4°/Opt act		43
	570	0.09	Rac/nat pH, 15°/Opt act		43
	570	0.014[f]	Rac/30% mole EtOH, 4°/Opt act		43
	420	0.09	Rac/nat pH, 15°/Opt act	2.1	43
	420	0.015[f]	Rac/30% mole EtOH, 4°/Opt act	3.2	43
$Cr(NCS)_6^{3-}$ (D/-/-; L_1/564/159; L_2/420–129)[261]	600	0.27	A/pH 1.2, 23°/Chem		26
	545	0.26	A/pH 1.2, 23°/Chem		26
$Cr(NH_3)_6^{3+}$ (D/659/∼0.05; L_1/462.5/38.9; L_2/350/33.5)[g,78,221]	652	0.29	A/pH 5.2, 23°/Chem		26
	630–665	1.3	A/0.05 N H^+, 25.6°/Sp		237
	452	0.26	A/pH 5.2, 23°/Chem		26
	320–600	0.32	A/0.05 N H^+, 25°/Sp	∼0	259
$Cr(en)_3^{3+}$ (D/671.5/0.29; L_1/452/69; L_2/350/55)[78]	L_1	0.47			260
	L_2	0.55			260
$Cr(CN)_6^{3-}$ (D/530/0.44; L_1/377/85.9; L_2/307/59.5)[102,262]	370	∼0.1	A/nat pH, 25°/Sp		36

[a] The wavelength for the doublet band is that of the longest feature of that band; values indicated to be approximate were taken from graphs. [b] A, photoaquation of the ligand; $H_2^{18}O$, exchange of ^{18}O with the solvent; Rac, photoracemization. [c] Chem, reaction followed by chemical analysis; Sp, reaction followed spectrophotometrically; Opt act, reaction followed by measuring the optical activity. [d] Selected wavelengths; others reported in ref 26. [e] The values of ref 238 are multiplied by 6 so as to be consistent with those of the rest of the table. [f] Interpolated results. [g] Also unpublished work, A. W. Adamson.

rium excited-state geometries might be sufficiently different from the ground-state one that the various radiationless electronic transitions would be hindered. Support for these conclusions came from various reasonings. The photolysis rule 1 could be accounted for if reaction occurred primarily from the lowest excited quartet state for which ligand-field considerations would place an antibonding electron in an orbital on the z or weak-field axis (section VII.C.1). Analysis of the relative behavior of aquation and phosphorescence quantum yields for *trans*-$Cr(NH_3)_2(NCS)_4^-$ in glass-forming media, over the temperature range 25 to −195°, indicated that the radiationless process which *competed* with emission from the doublet state *led* to chemical reaction.[14,235] This implies that chemical reaction did not occur from the doublet state but was probably due to reaction of the equilibrated first quartet state. Finally, the cases of spectrospecificity of the ratio of reaction modes require two paths, only one of which could involve the doublet state as the reactant; the inference is that at least one if not both must occur through reacting quartet states.[14]

A rather different proposal is that the reacting species may be a vibrationally excited or hot ground-state molecule.[231] Such a mechanism had earlier been discounted on the grounds that the expected decrease in quantum yield with increasing wavelength did not occur.[238] (see Introduction). The more recent proposal,[231] however, is that, where two reaction modes are observed, one may be from the doublet state, and the other, from a hot ground state produced by radiationless deactivation of the doublet state itself. It was pointed out that one of the two modes has so far always been that of the thermal reaction; this could be coincidental, however, since if only two reaction modes are possible, the thermal reaction will have to correspond to one of them. It seems more likely that the reactions all occur from excited states.[3a]

As a somewhat different line of thought, it has been suggested that, irrespective of the electronic state of the excited species, Cr(III) photochemistry is essentially that of cage reactions. That is, the reactants involved must be in a diffusional encounter when the quantum of radiation is absorbed.[246,258]

Tables IV and V give selected data of the photochemistry of Cr(III) complexes of O_h and non-O_h symmetry, respectively,[259,260] along with their spectral features.[261–264]

VIII. MANGANESE GROUP

The only significant photochemistry in this group is for manganese, and primarily for the carbonyls, cya-

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(258) A. W. Adamson, "Alcuni Aspetti della Chimica dei Complessi Ottaedrici," National Research Council Publication, Rome, 1966.

(259) M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63**, 327 (1959).

(260) E. Nikolaiski, Thesis, University of Frankfurt am Main, 1962.

(261) J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956).

(262) R. Krishnamurthy and W. B. Schaap. *Inorg. Chem.*, **2**, 605 (1963).

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

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

TABLE V

PHOTOCHEMISTRY OF CHROMIUM(III) COMPLEXES NOT OF O_h SYMMETRY (SELECTED DATA)

Complex (band/wavelength, mμ/extinction coeff)[a]	Wavelength, mμ	Quantum yield	Reaction mode[b]/conditions/method[c]	Activation energy, kcal/mole	Ref
$Cr(NH_3)_5(H_2O)^{3+}$ (D/655/0.25; L_1/484/35.0; L_2/360/29.0)[237]	430–700	0.15	NH_3/0.05 *N* H^+, 25.6°/Sp		237
	320–700	0.20	NH_3/0.05 *N* H^+, 25°/Sp	~0	237
$Cr(NH_3)_4(H_2O)_2^{3+}$ (D/657/1.1; L_1/494/31.4; L_2/368/23.1)[237]	320–700	0.16	NH_3/0.05 *N* H^+, 25.6°/Sp	~0	237
	320–410	0.15	NH_3/0.05 *N* H^+, 25.6°/Sp		237
$Cr(NH_3)_3(H_2O)_3^{3+}$ (D/657/0.66; L_1/508/27.0; L_2/378/25.9)[237]	430–700	0.019	NH_3/0.05 *N* H^+, 25.6°/Sp		237
	320–700	0.014	NH_3/0.05 *N* H^+, 25.6°/Sp	~0	237
	340–485	0.015	NH_3/0.05 *N* H^+, 25.6°/Sp		237
$Cr(NH_3)_2(H_2O)_4^{3+}$ (D/660/1.5; L_1/525/21.4; L_2/384/24.3)[237]	430–700	0.0017	NH_3/0.05 *N* H^+, 25.6°/Sp		237
	320–700	0.0019	NH_3/0.05 *N* H^+, 25.6°/Sp	~0	237
	340–485	0.0015	NH_3/0.05 *N* H^+, 25.6°/Sp		237
$Cr(NH_3)_5(NCS)^{2+}$ (D/685/0.15; L_1/487/82.8; L_2/363/51.8)[250,251,263]	652	0.15	NH_3/0.1 *N* H^+, $\mu = 0.17$, 25°/Chem		235, 251
	652	0.018	NCS^-/0.1 *N* H^+, $\mu = 0.17$, 25°/Chem		235, 251
	490	0.48	NH_3/0.1 *N* H^+, $\mu = 0.17$, 25°/Chem	0.8	250
	490	0.021	NCS^-/0.1 *N* H^+, $\mu = 0.17$, 25°/Chem	1.0	250
	370	0.46	NH_3/0.1 *N* H^+, $\mu = 0.17$, 25°/Chem	1.4	250
	370	0.030	NCS^-/0.1 *N* H^+, $\mu = 0.17$, 25°/Chem	2.2	250
$Cr(NH_3)_5Cl^{2+}$ (D/673/~0,7; L_1/512/36; L_2/375/39)[248,264]	500, 525	0.35	NH_3/10^{-3} *N* H^+, $\mu = 0.5$, 20°/Chem, pH	0 ± 3	248
	530	~0.01	Cl^-/10^{-3} *N* H^+, 5°/Chem		247
	375	0.38	NH_3/10^{-3} *N* H^+, $\mu = 0.5$, 20°/Chem, pH	0 ± 3	248
	365	~0.01	Cl^-/10^{-3} *N* H^+, 5°/Chem		247
$Cr(H_2O)_5(NCS)^{2+}$ (D/685/-; L_1/570/31.1; L_2/410/32.8)[242]	575	2.1×10^{-5}	NCS^-/0.01 *N* H^+, $\mu = 0.4$, 25°/Chem	6.1	242
	400	6.0×10^{-5}	NCS^-/0.01 *N* H^+, $\mu = 0.4$, 25°/Chem	8.3	242
trans-$Cr(NH_3)_2(NCS)_4^-$ (D/746.3/0.40; L_1/518/102; L_2/390/88)[78]	750[d]	0.27	NCS^-/nat pH 5.3, 23°/Chem		26
	520	0.29	NCS^-, no NH_3/nat pH 5.3, 23°/Chem	1.3	26
	452	0.32	NCS^-, traces NH_3?/nat pH 5.3, 23°/Chem		26
cis-$Cr(en)_2(OH)_2^+$ (D/692 sh/1.4; L_1/528/65; L_2/377/69)[246]	>680	0.24	en/pH 10.5 (added en), 25°/Chromat	20	246
	>680	0.025	I/pH 10.5 (added en), 25°/Chromat	13	246
	550	0.18	en/pH 10.5 (added en), 25°/Chromat	3	246
	550	0.065	I/pH 10.5 (added en), 25°/Chromat	10	246
	370	0.15	en/pH 10.5 (added en), 25°/Chromat	−3	246
	370	0.10	I/pH 10.5 (added en), 25°/Chromat	9	246
trans-$Cr(en)_2(OH)_2^+$ (D/685sh/1.4; L_1/505/34; L_2/398/33)[246]	500	0.003	en/pH 10.5 (added en), 18°/Chromat	9	246
	500	0.01	I/pH 10.5 (added en), 18°/Chromat	0	246
cis-$Cr(en)_2(H_2O)(OH)^{2+}$ (D/681sh/1.4; L_1/515/72; L_2/392/47)[246]	550	0.04	en/pH 5.5 (AcO^-–AcOH), 25°/Chromat		246
	550	0.05	I/pH 5.5 (AcO^-–AcOH), 25°/Chromat		246
trans-$Cr(en)_2(H_2O)(OH)^{2+}$ (D/680/2.1; L_1/495/38; L_2/398/49)[246]	680	0.05	I only/pH 5.5 (AcO^-–AcOH), 25°/Chromat		246
	500	0.3	I only/pH 5.5 (AcO^-–AcOH), 25°/Chromat		246
	370	0.4	I only/pH 5.5 (AcO^-AcOH), 25°/Chromat		246
cis-$Cr(en)_2(H_2O)_2^{3+}$ (D/667/0.95; L_1/485/70; L_2/368/48)[246]	370	0.17	en/pH 2.0 (HCl), 25°/Chromat		246
	370	0.15	I/pH 2.0 (HCl), 25°/Chromat		246
trans-$Cr(en)_2(H_2O)_2^{3+}$ (D/-/-; L_1/445/32; L_2/365/43)[246]	White light	~0.04	en + I/pH 2.0 (HCl), 25°/Chromat		246

[a] The wavelength for the doublet band is that of the longest feature of that band; values indicated to be approximate were taken from graphs. [b] The ligand indicated is that whose photoaquation was studied; unless specified, no other process was looked for. I, photoisomerization. [c] Chem, reaction followed by chemical analysis; Sp, reaction followed spectrophotometrically; pH, reaction followed by pH change; Chromat, reaction products determined chromatographically. [d] Selected wavelengths; others reported in ref 26.

nides, and oxalates, discussed in those sections. The remaining literature relates mainly to MnO_4^-, which photolyzes to MnO_2 and O_2 in solutions of pH 7–14, and to MnO_4^{2-}, in acid solutions.[21] The situation with regard to acid solutions, however, appears in doubt.[265]

The spectrum of MnO_4^- consists of three highly structured and intense band systems evidently due to strongly vibrationally coupled electronic transitions, and which center at about 550, 340, and below 200 mμ. Theoretical interpretation has been difficult, but the transitions appear to be to π antibonding states.[266,267]

The photodecomposition of aqueous MnO_4^- has been investigated quantitatively between 254 and 578 mμ, and the primary reaction was considered to be[21]

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[265] E. K. Rideal and R. G. W. Norrish, *Proc. Roy. Soc.* (London), A103, 342 (1923).

[266] S. L. Holt and C. J. Ballhausen, *Theoret. Chim. Acta* (Berlin), 7, 313 (1967).

[267] A. Viste and H. B. Gray, *Inorg. Chem.*, 3, 1113 (1964).

$$MnO_4^- \xrightarrow{h\nu} (MnO_2 + O_2^-) \text{ or } (MnO_2^- + O_2) \quad (47)$$

The central observation was that the evolved oxygen had not exchanged with solvent oxygen and must therefore have been produced by some concerted fission of two oxygen atoms; a similar process has been postulated for $PtBr_6^{2-}$ (section XI.C). Other studies, in a rigid system at 77°K, also showed that molecular oxygen was produced directly.[268] Returning to the aqueous photolysis, the quantum yield decreased from about 0.1 to 10^{-5} with increasing wavelength. The decrease occurred in somewhat discrete stages corresponding to the traversing of the three band systems, but there was also a decrease within each stage, particularly the longest wavelength one. It is concluded in both of the above papers that the photodecomposition should be attributed to vibrationally excited or hot ground-state molecules, produced by a rapid radiationless deactivation of the excited state.

According to a proposed model,[21] if a minimum energy, E^0, were needed for the reaction, then the excess over this which a hot molecule would possess would diminish rapidly with increasing wavelength of excitation, and hence likewise the quantum yield (see Introduction). However, strongly wavelength-dependent quantum yields can occur if the band irradiated is not itself photoactive but contains some absorption from the tail of an adjacent one which is active; this seems to be the situation in the case of the photoredox decomposition of Co(III) complexes (section X). The primary step may be more complex than eq 47. As a possible indication of this, irradiation of the solid alkali metal permanganates yields MnO_2 and O_2, but through a process thought to involve an electron transfer[269]

$$2MnO_4^- \xrightarrow{h\nu} MnO_4^{2-} + MnO_4 \quad (48)$$

The primary act might thus be one of photoelectron production

$$MnO_4^- \xrightarrow{h\nu} MnO_4 + e^- \quad (49)$$

Also somewhat surprising, in terms of the hot ground-state mechanism, is the observation that MnO_4^{2-} and MnO_4^{3-} are photochemically inert.[268] These ions, like MnO_4^-, are thermodynamically unstable to reduction by water, and E^0 might therefore be supposed to be small. Explanations have been offered, however, based either on expected variations in the activation energy for oxygen release, or on related estimates of the thermodynamic stabilities of the immediate products, MnO_2^-, MnO_2^{2-}, and MnO_2^{3-}.[268]

The photochemical stability of CrO_4^{2-} to 300-mμ light[268,270] is consistent with the hot ground-state mechanism. Unlike MnO_4^-, the ion is stable to reduction by water to Cr(III), and E^0 would therefore be expected to be large. On the other hand, chromate photosensitizes the decomposition of electron donors, such as alcohols, which are oxidized to aldehydes with quantum yields of unity.[270] Alkyl chromates are also readily photolyzed with 365-mμ light.[271]

The above observations give some support for a primary reaction such as eq 49, in which case the lack of net photolysis of CrO_4^{2-} in the absence of scavengers would be attributed to a rapid thermal return. However, the actual photolytic species may be different in the presence of an alcohol, and CrO_4^{2-} *per se* may be truly light insensitive. While the excited-state assignments for CrO_4^{2-} and MnO_4^- are the same,[267] the transitions for the former are shifted by approximately 8500 cm^{-1} toward the blue. Purely on this basis, CrO_4^{2-} would not be expected to photolyze until much deeper in the ultraviolet than does MnO_4^-.

IX. IRON, RUTHENIUM, AND OSMIUM

The photochemistry of coordination compounds of iron finds a natural division into Fe(II) and Fe(III) complexes, each then subdivided into the labile (mainly aquo) ions and the nonlabile or robust species. It should be remembered that iron carbonyl, cyanide, and oxalate complexes have already been treated, under these ligand group headings. No photochemistry appears to have been reported for ruthenium or osmium complexes, except for $Ru(CN)_6^{4-}$.

A. IRON(II)

1. *Labile Systems*

In the case of Fe(II) the work on labile systems seems entirely confined to Fe(II) ion in acidic aqueous media. The spectrum of $Fe(H_2O)_6^{2+}$ consists essentially of a strong shoulder around 240 mμ on an even more intense band deeper in the ultraviolet, both evidently CTTS.[35,272a] The effect of 254-mμ radiation is to produce hydrogen and ferric iron, along with secondary reactions of a free-radical nature;[35,272] thus a polymerization of various monomer species can be induced.[5b]

The primary process was for many years considered to be

$$Fe^{2+}(aq) \xrightarrow{h\nu} [Fe^{3+}H_2O^-] \longrightarrow Fe^{3+}(aq) + OH^- + H \quad (50)$$

where the brackets denote a solvent cage, but more re-

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[268] U. Kläning and M. C. R. Symons, *J, Chem. Soc.*, 3269 (1959).

[269] V. V. Boldyrev, A. N. Oblivantsey, A. M. Raitsimling, and E. M. Uskov, *Dokl. Akad. Nauk SSSR*, 166, 891 (1966); *Chem. Abstr.*, 64, 15058*f* (1966).

[270] E. J. Bowen and J. E. Chatwin, *J. Chem. Soc.*, 2081 (1932); 2353 (1927).

[271] U. Kläning, *Acta Chem. Scand.*, 12, 807 (1958).

[272] (a) E. Hayon and J. Weiss, *J. Chem. Soc.*, 3866 (1960); (b) J. J. Weiss, "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 17.

cent work[90] has suggested the reaction to be one of photoelectron production (but see see ref 272b).

$$\mathrm{Fe^{2+}(aq)} \xrightarrow{h\nu} \mathrm{Fe^{3+}(aq)} + \mathrm{e^-(aq)} \tag{51}$$

Reaction 51 had been suggested as a possibility in 1938,[273] on the basis of a thermodynamic calculation which gave the energy requirement as about 4.5 eV (corresponding to 275-mμ radiation), but had been generally rejected on grounds that later proved to be spurious. The quantum yield for eq 51 at 254 mμ has been given as 0.069 at pH 3.0,[90] although higher yields, presumably for the same primary process, have been reported in earlier publications.[272,274] The situation can be complicated by cage and secondary reactions that must be allowed for; such subsequent reaction chemistry is not treated here and the reader is referred to a recent monograph.[5a] In high sulfuric acid (or sulfate) concentrations, association may introduce different or at least modified primary processes.[274]

Esr signals attributed to free hydrogen production have been observed in sulfuric and phosphoric acid solids at 77°K. Presumably, hydrogen atoms are produced by the capture of photoelectrons by protons.[275]

2. Nonlabile Complexes

The Fe(II) complexes of the type $\mathrm{Fe(AA)_3^{2+}}$, where AA denotes 1,10-phenanthroline or 2,2′-bipyridine, appear to be stable to irradiation, but partially substituted ones may not be. The series $\mathrm{Fe(CNCH_3)_{6-2n}(AA)_n^{2+}}$ has been studied for the cases of $n = 0$, 1, and 2 at 365 and 254 mμ.[276,277] The two wavelengths correspond to d–d transitions in the $n = 0$ case. In the other two cases, they correspond to d → π* and to AA bands,[278] although the same d–d bands may still be present but covered by these more intense ones. The photoreactions are aquations of the $\mathrm{CNCH_3}$ group. Thus $\mathrm{Fe(CNCH_3)_6^{2+}}$ gives $\mathrm{Fe(CNCH_3)_4(H_2O)_2^{2+}}$ as the product,[276] and $\mathrm{Fe(CNCH_3)_4(AA)^{2+}}$ and $\mathrm{Fe(CNCH_3)_2(AA)_2^{2+}}$ give mixed aquated species and $\mathrm{Fe^{2+}(aq)}$ ion, respectively.[277] Quantum yields are reported as being in the range 0.1–0.01 and to decrease with increasing wavelength and increasing n value (see Table VI).

B. IRON(III)

1. Labile Systems

As with Fe(II), there is an extensive photochemistry of aqueous ferric ion. Now, however, the existence of complexes of the type $\mathrm{FeX^{2+}}$ (or probably $\mathrm{Fe(H_2O)_5X^{2+}}$) is sufficiently well characterized that much of the photochemistry is described in terms of photolyses of such individual species. The absorption spectra characteristically include a CT band in the blue or ultraviolet, attributed to the primary process

$$\mathrm{FeX^{2+}} \xrightarrow{h\nu} [\mathrm{Fe^{2+}X}] \tag{52}$$

where X may be a halogen, hydroxide, or water itself.[279] These topics have been reviewed;[280,281] some significant recent results are the following.

In the case of ferric perchlorate solution, *i.e.*, in the absence of other scavenging or associating species, the immediate reaction sequence has been supposed to be

$$\mathrm{Fe^{3+}(aq)} \xrightarrow{h\nu} [\mathrm{Fe^{3+}H_2O}]^* \longrightarrow [\mathrm{Fe^{2+}H_2O^+}] \longrightarrow \mathrm{Fe^{2+}(aq)} + \mathrm{H^+} + \mathrm{OH} \tag{53}$$

A study using ^{59}Fe(III) so that the appearance of labeled Fe(II) provided the measure of reaction 53 gave 0.05 for the primary quantum yield in 0.5 *M* perchloric acid and with 254-mμ radiation.[282] The dependence on added Fe(II) was, however, not explainable in terms of sequence 53, and it was proposed that $[\mathrm{Fe^{3+}H_2O}]^*$ converted to a second excited state of now sufficient lifetime to undergo a bimolecular exchange reaction

$$[\mathrm{^{59}Fe^{3+}H_2O}]^* \xrightarrow{8\%} [\mathrm{^{59}Fe^{3+}H_2O}]^{**} \tag{54}$$

$$[\mathrm{^{59}Fe^{3+}H_2O}]^{**} + \mathrm{Fe^{2+}(aq)} \longrightarrow \mathrm{^{59}Fe^{2+}(aq)} + \mathrm{Fe^{3+}(aq)} \tag{55}$$

The detailed nature of this second excited state was not discussed.

A number of studies have been made where X = OH or Cl, using scavengers such as polymerizable monomers, benzene, and benzene derivatives, and giving quantum yields of about 0.1 at 313 mμ.[283-288] For X = $\mathrm{N_3}$, the yield is 0.5 at about 300 mμ and drops to a low value at around the 470-mμ band.[284] For X = SCN, a recent investigation gives a yield of 0.035 (acid solution, 436 mμ), decreasing with increasing wavelength, and the

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(273) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1113 (1938).

(274) L. J. Heidt, M. G. Mullin, W. B. Martin, Jr., and A. M. J. Beatty, *J. Phys. Chem.*, **66**, 336 (1962).

(275) N. N. Bubnov, V. V. Voevodskiĭ, N. V. Fok, and B. N. Shelimov, *Opt. i Spektroskopiya*, 11, 78 (1961); *Chem. Abstr.*, **55**, 25479g (1961).

(276) V. Carassiti, G. Condorelli, and L. L. Condorelli-Costanzo, *Ann. Chim.* (Rome), **55**, 329 (1965).

(277) G. Condorelli and L. L. Condorelli-Costanzo, *ibid.*, **56**, 1140, 1159 (1966).

(278) G. Condorelli, L. L. Condorelli, and V. Carassiti, *ibid.*, **56**, 298 (1966).

(279) E. Rabinowitch. *Rev. Mod. Phys.*, 14, 112 (1942).

(280) N. Uri, *Chem. Rev.*, **50**, 375 (1952) (p 413).

(281) F. S. Dainton, Special Publication No. 1, The Chemical Society, London, 1954, p 18.

(282) M. G. Adamson, D. L. Baulch, and F. S. Dainton, *Trans. Faraday Soc.*, **58**, 1388 (1962).

(283) M. G. Evans and N. Uri, *Nature*, **164**, 404 (1949).

(284) M. G. Evans. M. Santappa, and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

(285) J. H. Baxendale and J. Magee, *Trans. Faraday Soc.*, **51**, 205 (1955).

(286) F. S. Dainton and M. Tordoff, *ibid.*, **53**, 666 (1957).

(287) H. G. C. Bates, M. G. Evans, and N. Uri, *Nature*, **166**, 869 (1950).

(288) H. G. C. Bates and N. Uri, *J. Am. Chem. Soc.*, **75**, 2754 (1953).

paper summarizes much of the earlier work on this system.[289] Finally, in the case of X = HO_2 (obtained with moderately high concentrations of H_2O_2), irradiation of the CT band around 350 mμ gives HO_2 and, ultimately, oxygen.[290] A summary of data is given in Table VI.

The photooxidation of carboxylic acids has long been known to be sensitized by Fe(III),[291,292] but only relatively recently has attention been paid to just what coordination species might be involved. Thus, in the case of formic acid,[59] tartaric acid,[293,294] and citric acid,[293,295,296] the active species is the 1:1 complex; with lactic [293,297] and mandelic[293] acids, it is 1:2. The proposed primary process is the analog of eq 52

$$(\mathrm{Fe^{3+}RCOO^-}) \xrightarrow{h\nu} [\mathrm{Fe^{2+}RCOO\cdot}] \longrightarrow \mathrm{Fe^{2+}} + \mathrm{RCOO\cdot} \longrightarrow \mathrm{Fe^{2+}} + \mathrm{R\cdot} + \mathrm{CO_2} \quad (56)$$

where R· is H for formic acid[59] and $\mathrm{R\dot{C}HOH}$ for the hydroxy acids.[293,294,297] The behavior of the oxalato complex, treated in section III.C, is entirely analogous.

There is a moderate body of early literature on the photolysis of Fe(III), usually $FeCl_3$, in organic solvents such as methanol, ethanol, ether, or acetone. The typical reaction produces Fe(II) and not always well-identified oxidation products. One specific sequence for $FeCl_4^-$ in ethanol is

$$\mathrm{FeCl_4^-}\ (\mathrm{ethanol}) \xrightarrow{h\nu} [\mathrm{FeCl_4^{2-}\text{-}H^+, CH_3\dot{C}HOH}] \longrightarrow \mathrm{FeCl_4^{2-}} + \mathrm{H^+} + \mathrm{CH_3\dot{C}HOH} \quad (57)$$

This is followed in part by reduction of $FeCl_4^-$ by the radical, which is oxidized to the aldehyde.[298,299] The presence of free radicals has been confirmed by esr spectroscopy in methanol and ethanol.[300] Hydrocarbon solvents are also photosensitized by $FeCl_3$, the primary reaction being

$$\mathrm{FeCl_3(R)} \xrightarrow{h\nu} \mathrm{FeCl_3^-} + \mathrm{R^+} \quad (58)$$

where R may be benzene, toluene, or *p*-xylene.[301] The CT band at around 340 mμ in the case of benzene shifts to longer wavelengths with increasing number of methyl groups, symbatic with the decreasing ionization potential of the hydrocarbon.

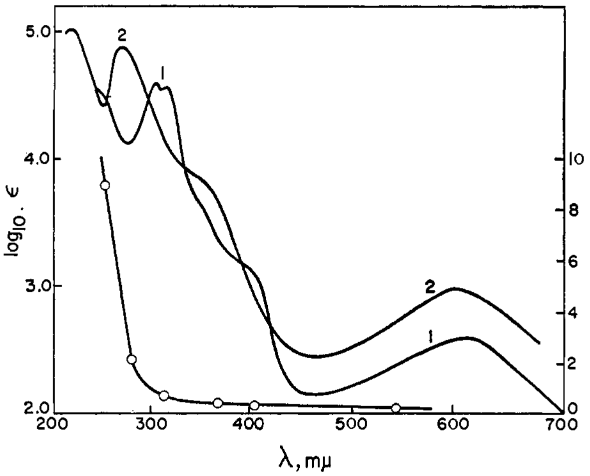

Figure 8.—Absorption spectra of $Fe(AA)_3^{3+}$ complexes: (1) AA = 2,2′-bipyridine; (2) AA = 1,10-phenanthroline. Quantum yields (○) for photoreduction of 10^{-4} *M* $Fe(phen)_3^{3+}$ in solution of 0.10 *N* H_2SO_4 and 0.50 *M* formic acid (after ref 59).

2. Nonlabile Complexes

Relatively few even moderately robust complexes of Fe(III) are known (other than the ones considered in sections III.C and IV.E), and photochemical studies have concentrated on the $Fe(AA)_3^{3+}$ species, where AA = 1,10-phenanthroline or 2,2′-bipyridine. The two complexes have similar spectra, as shown in Figure 8. The complexes photolyze to the $Fe(AA)_3^{2+}$ ion (in the presence of formic acid), but with quantum yields which are very low until the region of the intense band around 300 mμ is reached, as illustrated in Figure 8 for the 1,10-phenanthroline case.[59] The explanation offered for the low yields was that an efficient radiationless deactivation competed with the chemical reaction, although it is evident that the wavelength region studied traversed different bands and hence that different excited states of differing chemistry could well have been involved. In view of the lack of any destruction of the ligand, the sequence proposed was then

$$\mathrm{Fe(AA)_3^{3+}} \underset{\text{deactn}}{\overset{h\nu}{\rightleftarrows}} [\mathrm{Fe(AA)_3^{3+}}]^* \quad (59)$$

$$[\mathrm{Fe(AA)_3^{3+}}]^* + \mathrm{Red} \longrightarrow \mathrm{Fe(AA)_3^{2+}} + \mathrm{Oxid} \quad (60)$$

where Red might be either the formic acid or the Fe(III) complex. Others, however, have suggested a sequence analogous to reaction 53.[302]

Partially chelated species of the type $Fe(AA)_n^{3+}$, with the average *n* value between 1 and 2.5, behave similarly to the *n* = 3 complexes.[59,303] Chelates of

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(289) K. J. Ellis and G. S. Laurence, *Trans. Faraday Soc.*, **63**, 91 (1967).

(290) B. Behar and G. Stein, *Science*, **154**, 1012 (1966).

(291) J. M. Eder, *Monatsh.*, 1, 755 (1880).

(292) H. De Vries, *Rec. Trav. Chim.*, 3, 365 (1884).

(293) G. V. Bakore and S. D. Bhardwaj, *Proc. Natl. Inst. Sci. India*, **A29**, 90 (1963); *Chem. Abstr.*, **60**, 154*b* (1964).

(294) T. S. Glikman, V. A. Kalibabchuk, and V. P. Sosnovskaya, *Zh. Obshch. Khim.*, **35**, 1530 (1965); *Chem. Abstr.*, **63**, 17838*d* (1965).

(295) O. E. Lanford and J. R. Quinan, *J. Am. Chem. Soc.*, **70**, 2900 (1948).

(296) J. L. Frahn, *Australian J. Chem.*, 11, 399 (1958).

(297) G. V. Bakore and S. D. Bhardwaj, *Z. Physik. Chem.* (Leipzig), **227**, 26 (1964).

(298) G. J. Brealey, M. G. Evans, and N. Uri, *Nature*, **166**, 959 (1950).

(299) G. J. Brealey and N. Uri, *J. Chem. Phys.*, **20**, 257 (1952).

(300) A. I. Kryukov, L. V. Nazarova, and B. Ya. Dain, *Ukr. Khim. Zh.*, **29**, 812 (1963); *Chem. Abstr.*, **60**, 2457*g* (1964).

(301) A. I. Kryukov and B. Ya. Dain, *Dokl. Akad. Nauk SSSR*, **138**, 153 (1961); *Chem. Abstr.*, **56**, 8207*h* (1962).

(302) T. S. Glikman and M. E. Podlinyaeva, *Ukr. Khim. Zh.*, **21**, 211 (1955); *Chem Abstr.*, **50**, 1472*f* (1956).

(303) J. Novak, *Talanta*, 12, 649 (1965); *Chem. Abstr.*, **63**, 9280*f* (1965).

TABLE VI

PHOTOCHEMISTRY OF IRON-CONTAINING SYSTEMS (SELECTED DATA)

System (absorption max, mμ/extinction coeff)[a]	Wavelength, mμ	Quantum yield	Photoreaction or product	Ref
Fe^{2+}(aq) (239/20)[35]	254	0.069	e$^-$(aq), pH 3.0	90
Fe(CNCH$_3$)$_6$$^{2+}$ (315/320; 263/340)[276]	365	0.03	Aquation	276
	254	0.09	Aquation	276
Fe(CNCH$_3$)$_4$(phen)$^{2+}$ (365/2640; 328/4790; 290 sh/10,000; 270/26,400; 252/20,000; 225/45,800)[278]	365	0.003	Aquation	277
	254	0.005	Aquation	277
Fe(CNCH$_3$)$_4$(bipy)$^{2+}$ (350/2820; 312/12,900; 300/10,300; 274/16,000; 236/15,400)[278]	365	0.004	Aquation	277
	254	0.009	Aquation	277
Fe(CNCH$_3$)$_2$(phen)$_2$$^{2+}$ (415/5480; 380/5810; 310 sh/3320; 290 sh/26,400; 263/72,580; 225/66,100)[278]	365	0.0013	Aquation	277
	254	0.0043	Aquation	277
Fe(CNCH$_3$)$_2$(bipy)$_2$$^{2+}$ (416/4470; 310 sh/9130; 285/38,100; 242/19,100)[278]	365	0.0013	Aquation	277
	254	0.0066	Aquation	277
Fe^{3+}(aq) (700/0.062; 550/0.097; 407/0.334; 238/4520)[308]	254	0.05	Eq 53	282
	Uv	~0.001	O$_2$	307
FeOH^{2+} (~300/~5000)[308]	365, 313	0.05	Fe^{2+}	284
	313	0.13	OH	285
	313	0.19	OH	286
FeCl^{2+} (336/1980)[309]	365, 313	0.13	Fe^{2+}	284
FeN$_3$$^{2+}$ (460/3680)[310]	~300	0.5	Fe^{2+}	284
FeSCN^{2+} (447/4700)[311]	546	0.015	SCN	289
	436	0.035	SCN	289
	366	0.062	SCN	289
Fe^{3+} + HCOO$^-$ (~280/~5500)[59]	365	~0.24[a]	Fe^{2+}	59
	300–250	~0.55[a]	Fe^{2+}	59
FeCl$_4$$^-$ (ethanol) (365/~7600; 310/~7000; 244/~11,800)[299]	365	0.31	Fe(II)[b]	299
	313	0.49	Fe(II)[b]	299
	254	0.58	Fe(II)[b]	299
FeCl$_3$ (benzene) (340/6700)[301]	365	0.061	Fe(II)[b]	301
FeCl$_3$ (toluene) (~345/6200)[301]	365	0.14	Fe(II)[b]	301
FeCl$_3$ (*p*-xylene) (~350/5600)[301]	365	0.19	Fe(II)[b]	301
Fe(phen)$_3$$^{3+}$ (~600/~950; ~350 sh/~6900; ~270/~80,000; ~220/~107,000)[59]	546	0.001	Fe(phen)$_3$$^{2+}$	59
	365	0.005	Fe(phen)$_3$$^{2+}$	59
Fe(bipy)$_3$$^{3+}$ (~615/~380; ~400 sh/~1320; ~320/~36,000; ~308/~41,000)[59]	546	0.006	Fe(bipy)$_3$$^{2+}$	59
	365	0.0078	Fe(bipy)$_3$$^{2+}$	59
Fe(phen)$_n$$^{3+}$ (~360/~4100)[312]	365	~0.007	Fe(II)	59
Fe(bipy)$_n$$^{3+}$	365	~0.03	Fe(II)	59

[a] Values indicated to be approximate were taken from graphs. [b] In the indicated organic solvent.

Fe(III) with EDTA (ethylenediaminetetraacetic acid) and analogous ligands also give Fe(II) on irradiation with visible or ultraviolet light.[304,305] The ligand is oxidized, presumably through the sequence corresponding to reaction 56.[304] The same photoreduction is reported to be photosensitized by the lowest excited triplet state of dyes, such as fluorescein[306] and by methylene blue, in the presence of excess EDTA.[214]

As a final note, the temperature dependence of photolysis yields has rarely been explored in any of the above reactions, but where mention is made the dependence has been found to be very slight.[59,282,289]

See Table VI for selected data of the photochemistry (and spectra) of iron-containing systems.[307–312]

X. COBALT, RHODIUM, AND IRIDIUM

The compounds of Co(III) are the most studied group of coordination chemistry; a great number of the ones known today were first prepared by S. M. Jørgensen and A. Werner around 1900,[313] and there are many incidental early observations of photosensitivity. Several papers of the period 1920–1940 established that cobalt(III) ammines, oxalates, and related complexes underwent photoredox decompositions and, in some cases, photoaquation reactions.[314–320] Linhard and Weigel, in a series of publications around 1950, established that the photoredox decompositions of acidoammine complexes were primarily associated with the

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(304) S. S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).

(305) D. G. Hill-Cottingham, *Nature*, **175**, 347 (1955).

(306) L. Lindquist, *Acta Chem. Scand.*, **20**, 2067 (1966).

(307) B. Ya. Dain and A. A. Kachan, *Dokl. Akad. Nauk SSSR*, **61**, 471 (1948); *Chem. Abstr.*, **42**, 8659*b* (1948).

(308) E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942).

(309) R. N. Heistand and A. Clearfield, *ibid.*, **85**, 2566 (1963).

(310) R. M. Wallace and E. K. Dukes, *J. Phys. Chem.*, **65**, 2094 (1961).

(311) H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.*, **69**, 1321 (1947).

(312) A. E. Harvey, Jr., and D. L. Manning, *ibid.*, **74**, 4744 (1952).

(313) G. B. Kauffman, Ed., "Werner Centennial," Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967.

(314) G. Berger, *Rec. Trav. Chim.*, **44**, 47 (1925).

(315) R. Schwarz and K. Tede, *Chem. Ber.*, **60B**, 63 (1927).

(316) R. Schwarz and H. Weiss, *ibid.*, **58B**, 746 (1925).

(317) R. Luther and H. Frieser, *Z. Elektrochem.*, **36**, 141 (1930).

(318) I. Lifschitz and W. Froentjes, *Rec. Trav. Chim.*, **60**, 225 (1941).

(319) A. K. Bhattacharya and N. R. Dhar, *Z. Anorg. Allgem. Chem.*, **175**, 357 (1928); *Chem. Abstr.*, **23**, 340^9 (1929).

(320) O. K. H. Burger, *Proc. Chem. Soc.*, **27**, 160 (1911); *Chem. Abstr.*, **6**, 2043^6 (1912).

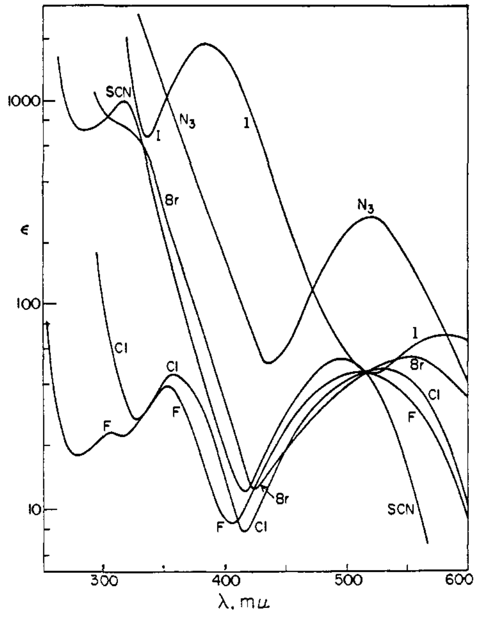

Figure 9.—Absorption spectra for $Co(NH_3)_5X^{2+}$ complexes (unpublished work from this laboratory).

more intense short wavelength bands;[321] the main effect of much subsequent work has been to make their observations more quantitative. The present review centers on this more recent work and complements two existing summaries;[2,3a,c] it also covers the not very extensive literature on rhodium and iridium photochemistry.

The spectra of several complexes of the type $Co(NH_3)_5X^{2+}$ are shown in Figure 9 and are seen to consist of ligand-field bands more or less covered by a first CT one. The first two CT bands have been assigned to transitions in which an electron is transferred from a molecular orbital mainly localized in the X or acido group, to one mainly localized on the cobalt, or CTTM in type.[7,8,321,322] The lowest energy and intensity CT band is considered to correspond to the transfer of a π electron, and the higher energy and more intense one, to that of a σ electron, in both cases to the d_{z^2} σ antibonding orbital.[323] The energy of the first CT band decreases symbatically with the energy for the process

$$X^- = X + e^- \qquad (61)$$

and, with compounds such as $Co(NH_3)_5I^{2+}$, the second ligand-field band may be entirely overlaid by the first CT one.

The ligand-field excited states have been treated theoretically (see, for example, ref 7, 10, 11). As shown in Figure 10,[324] the ground and first excited states are $^1A_{1g}$ and $^1T_{1g}$ and $^1T_{2g}$, respectively, in O_h symmetry, and the two excited states are split on descent to C_{4v} or D_{4h} symmetry. There is also a set of triplet excited states, of which the lowest is $^3T_{1g}$.[7] All of these excited states have an electron in a σ antibonding orbital.

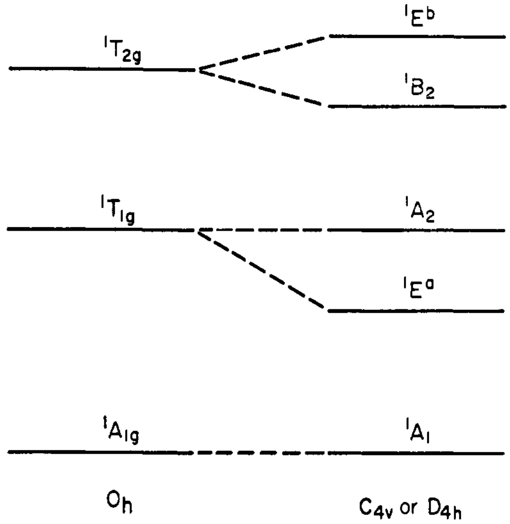

Figure 10.—Tetragonal splitting of the excited states of Co(III). The "g" symbol is retained in D_{4h} symmetry, but parity designations are not applicable in C_{4v} symmetry (after ref 324).

Some comparisons with Cr(III) are inevitable. While Cr(III) photochemistry consists almost entirely of substitution reactions, that of Co(III) is largely one of photoredox decompositions. This major difference is ascribable to the much longer wavelength position of the first CT band in Co(III) complexes as compared to Cr(III) ones. It is surely significant in this respect that Cr(III) complexes are in general stable to thermal redox decomposition, both kinetically and thermodynamically, while Co(III) ones are generally unstable thermodynamically and often kinetically as well. Also, while irradiation of d–d bands of Co(III) complexes may produce only photoaquation, it is then in very low quantum yield, in distinct contrast to the behavior of Cr(III) compounds. A general summary of quantum yields is given in Table VII.

While much is known concerning various excited-state processes for Cr(III) species, from fluorescent and phosphorescent emission studies, no such information appears to be available for Co(III) ones, with the exception of $Co(CN)_6^{3-}$.[325]

A. COBALT(III) AMMINES

The photochemistry of the cobalt(III) ammines consists almost entirely of redox decompositions produced by ultraviolet light. Photolysis yields at longer wavelengths are small. Thus for $Co(NH_3)_6^{3+}$, φ is less than 2×10^{-3} for either 340-, 400-, or 500-mμ

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(321) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266**, 49 (1951); **267**, 114, 121 (1951); **271**, 101 (1953), and earlier papers.

(322) L. Moggi, N. Sabbatini, and V. Balzani, *Gazz. Chim. Ital.*, **97**, 980 (1967).

(323) H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

(324) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(325) (a) M. Mingardi and G. B. Porter, *J. Chem. Phys.*, **44**, 4354 (1966); (b) G. A. Crosby, *J. Chim. Phys.*, **64**, 160 (1967)

light.[326] No definitive evidence for any photoaquation of this complex, nor of $Co(en)_3^{3+}$, with 254-mμ light has been found.[327,328]

Redox photolysis yields are fairly high, however, at 254 mμ. These have been reported for a number of ammine complexes, based on the production of Co(II).[327–329] There may be a variety of oxidation products. In the case of $Co(NH_3)_5(H_2O)^{3+}$, nitrogen is produced,[327] while with $Co(en)_3^{3+}$ ammonia and formaldehyde were found,[328] but no nitrogen.[327] The photolysis of the tris-1,2-propanediamine and tris-2,3-butanediamine complexes is more complicated.[329] It was concluded from the distribution of products that the primary step involved the transfer of an electron to the cobalt, leaving a positive nitrogen atom, following which the C–C bond β to that nitrogen underwent cleavage. The type of reaction sequence proposed was

$$Co(en)_3^{3+} \underset{}{\overset{h\nu}{\rightleftarrows}} [Co(en)_3^{3+}]^* \longrightarrow Co(en)_2(en')^{3+} \quad (62)$$

$$Co(en)_2(en')^{3+} \longrightarrow Co(en)_3^{3+} \quad (63)$$

$$Co(en)_2(en')^{3+} + H_2O \longrightarrow Co(en)_2(NH_2CH_2\cdot)^{2+} + NH_4^+ + CH_2O \quad (64)$$

where $en' = H_2NCH_2CH_2\dot{N}H_2^+$. In the case of $Co(en)_3^{3+}$, the quantum yield for Co(II) is 0.070 at 254 mμ and about 0.0005 at 366 mμ. At this last wavelength, most of the absorption was in the second ligand-field band, assumed to be inactive, and the low quantum yield was taken merely to reflect the small proportion of absorption which occurred into the tail of the CT band.

Quantum yields for Co(II) production were found to be somewhat pH dependent for the above and other ammine complexes,[327] and this was ascribed to the protolytic equilibrium

$$[Co(en)_3^{3+}]^* = [Co(en)_2(H_2NCH_2CH_2NH)^{2+}]^* + H^+ \quad (65)$$

The excited state first produced was further suggested to involve Co(II) in the $t_{2g}^6e_g$ configuration, with subsequent conversion, possibly in conjunction with reaction 65, to the normal $t_{2g}^5e_g^2$ configuration. However, there is not really a sufficient basis for deciding on such specifics.[2] Other observations were that the effects of ionic strength, temperature, or light intensity were small. There are some further, more qualitative studies with $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$.[330–333]

Some solid-state photolyses have been reported for $[Co(en)_3]X_3$ salts, using 254-mμ radiation.[334] The products were Co(II), possibly in the form of a polynuclear complex with Co(III), and oxidized amine. The photosensitivity was in the order F > Cl > Br > I; also, for X = Cl, $Co(NH_3)_6^{3+} > Co(en)_3^{3+} > Co(pn)_3^{3+}$. Apparently similar effects were found for $[Co(en)_3]Cl_3$ and $[Co(NH_3)_6]Cl_3$,[335] and irradiation of $[Co(en)_3]_2(S_2O_8)_3$ led to potentially explosive products.[240] Various Co(III) ammines and chelates were found to photoexchange with labeled Co(II) when the mixed salts, spread as a thin film, were irradiated with a tungsten lamp.[336]

B. COBALT(III) ACIDOAMMINES

The behavior of complexes of the type $Co(NH_3)_5X^{2+}$ presents an interesting and fairly consistent picture. As illustrated in Figure 9, all of this family show a first ligand field, or L_1 band, at around 500–550 mμ, and a second one at around 350 mμ, unless hidden by a CT band. This last band extends rather far into the visible in the case of X = I or N_3, and in both these cases the L_1 band is higher in intensity than normal (note the introduction to section III).

The photochemistry is found to correlate well with the ease of oxidation of the X ligand, *i.e.*, with the energy of reaction 61.[44,257,326,337] Thus, around 370 mμ, no redox photolysis occurs with X = NH_3, SO_4, and Cl, while with X = Br, NO_2, NCS, N_3, and I, the proportion of photoredox reaction increases from 50 to 100%, with a trend toward increasing quantum yields (see Table VII). This sequence coincides with the movement of the first CT band into the visible, and it seems clear that the CT excited state is responsible for the photolysis, as would be expected from the molecular orbital analysis mentioned earlier.

Irradiation of the L_1 band, however, in most cases leads primarily to aquation of the acido group, with quantum yields of about 10^{-3}. Thus the excited state is not very photochemically active. With X = N_3 or I, however, relatively high quantum yields were found, but now exclusively for redox decomposition. Significantly, it is just for these complexes that incursion of CT character into the L_1 band seems to have occurred, judging from its intensity.

The first generalization from the above results is that ligand-field excited states photoaquate, in low quantum yield, and that CT excited states undergo photoredox decomposition, in high quantum yield. The second observation is that the aquation quantum yields can be

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(326) A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960).

(327) J. F. Endicott and M. Z. Hoffman, *J. Am. Chem. Soc.*, **87**, 3348 (1965).

(328) D. Klein and C. W. Moeller, *Inorg. Chem.*, **4**, 394 (1965).

(329) W. C. Taylor, Jr., and C. W. Moeller, *ibid.*, **4**, 398 (1965).

(330) L. N. Neokladnova and G. A. Shagisultanova, *Dokl. Akad. Nauk SSSR*, **149**, 1084 (1963); *Proc. Acad. Sci. USSR*, **149**, 329 (1963).

(331) L. N. Neokladnova and G. A. Shagisultanova, *Radiokhimiya*, **6**, 305 (1964); *Chem. Abstr.*, **61**, 9083*f* (1964).

(332) S, R. Veljković, *Bull. Inst. Nucl. Sci., "Boris Kidrich"* (Belgrade), **2**, 93 (1953).

(333) S. R. Veljković, *ibid.*, **4**, 63 (1954).

(334) D. Klein, C. W. Moeller, and R. Ward, *J. Am. Chem. Soc.*, **80**, 265 (1958).

(335) J. Balog, J. Csaszar, and L. Kiss, *Acta Chim. Acad. Sci. Hung.*, **33**, 77 (1962); *Chem. Abstr.*, **58**, 3085*b* (1963).

(336) A. Nath and S. Khorana, *J. Chem. Phys.*, **46**, 2858 (1967).

(337) N. Shinozuka and S, Kikuchi, *Nippon Kagaku Zasshi*, **87**, 413 (1966).

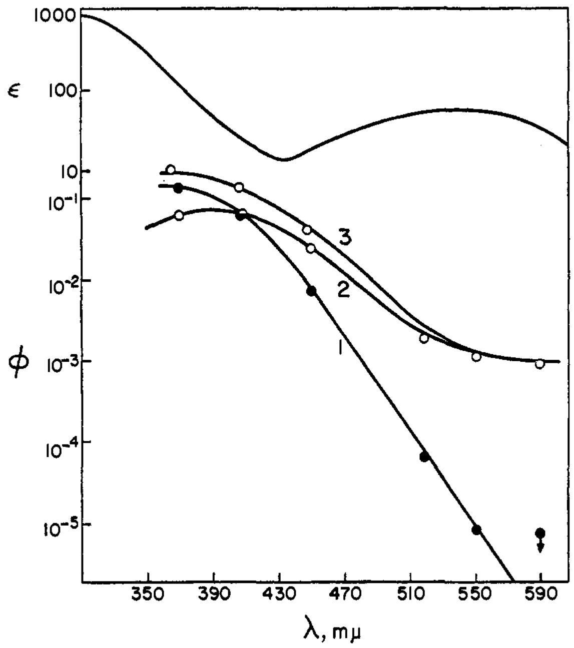

Figure 11.—Photolysis of $Co(NH_3)_5Br^{2+}$: upper section, absorption spectrum; lower section, quantum yield for Co(II) (1), for aquation (2), and total quantum yield (3) (after ref 326).

fairly high on irradiation of a CT band. Both characteristics are illustrated by the case of $Co(NH_3)_5Br^{2+}$, as shown in Figure 11.

The photoaquation yield for this last compound shows a negative temperature coefficient, suggesting that the aquation and redox modes of reaction are directly competitive.[326] The mechanism leading to aquation is thus suggested to be different for the CT and L_1 excited states, and a confirmation of this conclusion comes from the finding that for *trans*-$Co(en)_2(NCS)Cl^+$, the ratio of photoaquation of chloride to that of thiocyanate is 0.6 at 550 mμ, and 0.2 at 370 mμ.[338]

The above redox photolyses evidently involve a homolytic fission of the Co–X bond

$$Co(NH_3)_5X^{2+} \xrightarrow{h\nu} Co(II) + 5NH_3 + X \qquad (66)$$

since, for X = I or Br, the respective halogen atom transient was found in flash photolysis studies,[339] and similarly with *trans*-$Co(en)_2Br_2^+$.[96] With $X = N_3$, no transient was observed, but, in the presence of added iodide ion, the iodine atom transient appeared. It had previously been noted that in the photolysis of $Co(NH_3)_5N_3^{2+}$, nitrogen evolution was inhibited and iodine produced instead, if added iodide ion was present. Similarly, iodine production was observed in the cases of $X = SO_4$ and Br.[326] Also, in neutral or alkaline solution, $Co(OH)_2$ would be expected, but, as a further example of scavenging of X radicals, one finds instead that the net photolysis reaction gives $Co(OH)_3$ and X^-. This was true for $X = N_3$[321] and for $Co(NH_3)_3(NO_2)_3$.[317] Finally, in the case of $Co(NH_3)_5I^{2+}$, a quantum yield of 1.94 was found for Co(II) production (at 254 mμ), explainable on the basis that the iodine atom of reaction 66 was scavenged by a second molecule of the complex.[340] As would be expected from the above mechanism, the quantum yield is light-intensity dependent.[327] The same is true for 254-mμ irradiation of $Co(NH_3)_5Br^{2+}$.[327]

An interesting further observation is that irradiation of $Co(NH_3)_6^{3+}$ in 0.08 *M* KI solution also leads to iodine production, with quantum yields of about 0.2 and 0.0005 at 370 and 500 mμ, respectively.[44] As confirmed by later work,[341] the proposed mechanism was that of photolysis of the ion pair ($Co(NH_3)_6^{3+}I^-$). Iodine is also produced with irradiation at 254 mμ, however, where now the absorption is primarily by iodide ion, and it was proposed that in this case photoelectrons were produced which then reduced the complex.[327,342] In acid solution, hydrogen atoms are produced by the reaction $H^+ + e^-(aq) \rightarrow H$, which then act as the reducing agent.

To turn to another aspect, the irradiation of acidoammines at wavelengths shorter than 370 mμ gives predominately photoredox decompositions. This is true for the irradiation of $Co(NH_3)_5Br^{2+}$,[327] and for $Co(NH_3)_5Cl^{2+}$ and *cis*- and *trans*-$Co(en)_2Cl_2^+$.[322,327] In the case of *cis*- and *trans*-$Co(en)_2(H_2O)Cl^{2+}$, again only redox photolysis occurs at 254 mμ, while for *cis*-$Co(NH_3)_4(H_2O)Cl^{2+}$ nearly half of the photolysis yield is considered to be *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$.[322] Small but significant proportions of aquo products were reported for several of the above complexes, using 313-mμ light,[322] although the products were not actually isolated.

No chlorine production is observed with the chloro complexes,[322,327] but with the iodo ones iodine is formed.[44,326,327] In the case of $Co(NH_3)_5Br^{2+}$, photoredox decomposition has been asserted to yield[327] and not to yield[326] bromine (under somewhat different conditions). Also, irradiation of $Co(NH_3)_5Cl^{2+}$ at 254 and 313 mμ is thought to give *trans*-$Co(NH_3)_4(H_2O)Cl^{2+}$ as the aquation component of the photolysis.[322]

A few additional Co(III) systems have been studied. Irradiation of *cis*-$Co(en)_2Cl_2^+$ in methanol solution led to isomerization,[343] but only if the first CT, rather than the L_1 band, was involved. The mechanism, however, appears to be one involving photolytically produced Co(II) which then acts as a catalyst for the isomerization. The production of Co(II) appears to dominate

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[338] A. Vogler and A. W. Adamson, Abstracts of Pacific Conference on Chemistry and Spectroscopy, American Chemical Society Western Regional Meeting, Anaheim, Calif., Oct 30–Nov 1, 1967.

[339] S. A. Penkett and A. W. Adamson, *J. Am. Chem. Soc.*, **87**, 2514 (1965).

[340] A. Haim and H. Taube, *ibid.*, **85**, 495 (1963).

[341] G. C. Stirling, Ph.D. Thesis, University of Melbourne, 1967.

[342] J. F. Endicott and M. Z. Hoffman, *J. Phys. Chem.*, **70**, 3389 (1966).

[343] S. Kawaguchi and H. Fujioka, *Bull. Chem. Soc. Japan*, **40**, 802 (1967).

the photochemical behavior in dipolar aprotic solvents, such as dimethyl sulfoxide, dimethylformamide, and dimethylacetamide.[253] The tris(amino acid) complexes of glycine, alanine, valine, and glutamine photodecompose to Co(II) with light of 254 and 313 mμ, corresponding to the CT band but are insensitive to light of 546 mμ (L_1 band).[344] The complexes with aspartic acid also photodecompose.[318] An interesting observation is that the peroxo complex, $(H_3N)_5Co(O_2)Co(NH_3)_5{}^{5+}$, photolyzes to give $Co(NH_3)_5{}^{3+}$ as one primary product, whose scavenging reactions can then be studied.[345]

Photoinduced linkage isomerization of $Co(NH_3)_5(NO_2)^{2+}$ to $Co(NH_3)_5(ONO)^{2+}$ has been reported both in solution[337,346] and in the solid state.[347,348] Compounds of the series $Co(NH_3)_n(NO_2)_{6-n}{}^{n-3}$ have been reported to undergo photoredox decomposition,[315,316,321] and apparently also to undergo photoaquation of the ammonia.[349] $Co(NH_3)_4(H_2O)(NO_2)^{2+}$ has been reported to be photosensitive.[350] Aqueous $Co(NO_2)_6{}^{3-}$ photolyzes with a tungsten lamp at a rate proportional to the square root of the light intensity.[319] Finally, the solids $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_5(NCS)](NCS)_2$, and $[Co(NH_3)_5Br]Cl_2$ are reported to be photosensitive.[335]

C. PHOTOLYSIS MECHANISMS FOR COBALT(III) COMPLEXES

The straightforward generalization has been expressed that CT excited states lead to redox decomposition, and ligand-field ones lead to substitution, and that the presence of both reaction modes simply reflects the degree of overlap of the two types of bands.[231] This view does not seem tenable, in that irradiation of either L_I or L_2 bands leads to very little photoaquation, if they are well separated from the nearest CT one. The ligand-field excited states of Co(III) seem inherently to be but little photoactive, and the large aquation quantum yields observed in those cases where low-lying CT bands are irradiated need further explanation.

One of the first detailed mechanisms for Co(III) photolyses recognized this problem.[44,257] The primary act was considered to be a homolytic bond fission, and in terms of an acidopentaammine, the process was

$$Co(NH_3)_5X^{2+} \xrightarrow{h\nu} [Co(NH_3)_5{}^{2+}X] + \Delta \qquad (67)$$

where Δ represents excess energy, which is supposed to be dissipated rapidly into the medium. Cage reactions then followed, in which X could be recoordinated, with further release of energy, or could begin to diffuse away.

$$[Co(NH_3)_5{}^{2+}X] \longrightarrow Co(NH_3)_5X^{2+} \quad (\text{favored if } \Delta \text{ small}) \qquad (68)$$

$$[Co(NH_3)_5{}^{2+}X] \longrightarrow Co(NH_3)_5{}^{2+}(H_2O)X] \quad (\text{favored if } \Delta \text{ large}) \qquad (69)$$

Final escape of X would lead to net redox decomposition, but, as an alternative, X might regain an electron without itself being able to coordinate, so that aquation would result

$$[Co(NH_3)_5{}^{2+}(H_2O)X] \longrightarrow Co^{II} + 5NH_3 + X \qquad (70)$$

$$[Co(NH_3)_5{}^{2+}(H_2O)X] \longrightarrow Co(NH_3)_5(H_2O)^{3+} + X^- \qquad (71)$$

The empirically observed connection between photoredox decomposition and photoaquation on irradiation of a CT band was thus accounted for, as well as the high aquation quantum yields for the $Co(CN)_5X^{3-}$ series of complexes (see sections IV.G and V.D, however). The cage mechanism would predict that decreasing the wavelength of the irradiation would increase the proportion of redox *vs.* aquation reaction, as is observed experimentally. The occurrence of redox decomposition on irradiation of the nominally L_1 bands of $Co(NH_3)_5I^{2+}$ and $Co(NH_3)_5N_3{}^{2+}$ suggested that the nature of the absorption band was not important. Subsequent considerations, however, indicate that heterolytic rather than homolytic bond fission probably occurs on irradiation of L_1 bands, provided the nearest CT band is well removed.

It has been noted with respect to this last point[351] that the energy requirement for eq 67 is probably not met at a wavelength much longer than that of the first CT band, and that correlation diagrams suggest that excitation to the L_1 excited state should lead to heterolytic bond fission. Experiments[338] with *trans*-$Co(en)_2(NCS)Cl^+$ tend to substantiate this conclusion in that, as noted earlier, the ratio of photoaquation modes changes drastically if the L_1 rather than the CT band is irradiated. Otherwise, the results conform well with the cage mechanism. Complete analysis for the products of irradiation at 385 mμ (Co(II), Cl^-, NCS^-, and aquo products) leads to the mechanism of Scheme I. As might be expected from the relative energies of reaction 61 for X = Cl *vs.* X = NCS, homolytic fission of the Co–Cl bond occurs only 7% of the time, and then with 100% return of the electron. As a further comment, the likelihood that the competition reactions of the cage mechanism would be largely diffusion controlled perhaps accounts for the apparently generally small temperature coefficients of quantum yields for Co(III) complexes.[317,326,344]

A remaining question is why the ligand-field excited states of Co(III) are so much less chemically active than those of Cr(III). The broadness of the absorption

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(344) V. Balzani, V. Carassiti, L. Moggi, and N. Sabbatini, *Inorg. Chem.*, **4**, 1247 (1965).

(345) D. Valentine and J. Valentine, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967.

(346) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, private communication.

(347) B. Adell, *Z. Anorg. Allgem. Chem.*, **279**, 219 (1955).

(348) W. W. Wendlandt and J. H. Woodlock, *J. Inorg. Nucl. Chem.*, **27**, 259 (1965).

(349) Y. Tsunoda and A. Ouchi, *Nippon Kagaku Zasshi*, **83**, 447 (1961); *Chem. Abstr.*, **57**, 5505*d* (1962).

(350) U. D. Gomwalk and A. McAuley, *J. Chem. Soc.*, 1692 (1966).

(351) Z. Simon, *Can. J. Chem.*, **38**, 2373 (1960).

TABLE VII

PHOTOCHEMISTRY OF COBALT(III) AND RHODIUM(III) COMPLEXES (SELECTED DATA)

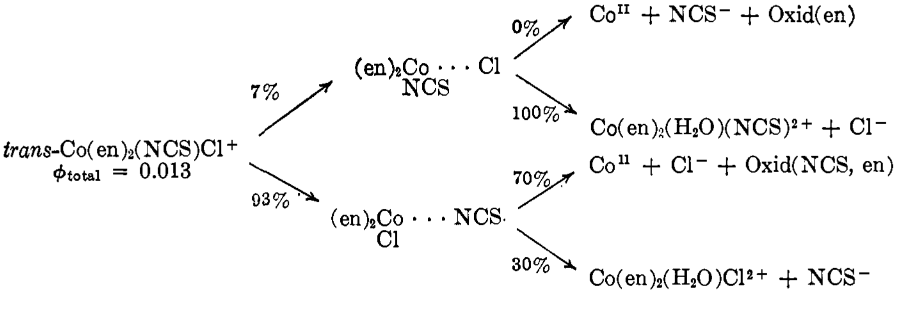
Complex[a] (absorption max, mμ/extinction coeff)[b]	Wavelength, mμ	Quantum yield	Reaction mode[c]/conditions[d]/method[e]	Ref
$Co(NH_3)_6^{3+}$ (475/55; 340/49; 200/20,000)[8,44]	550	$<10^{-3}$	R/pH 4, 25°/Chem	326
	370	$<10^{-3}$	R/pH 4, 25°/Chem	326
	254	1.1	R/pH 11.0, 37°/Chem	327
	254	0.89	R/pH 6.5, 37°/Chem	327
	254	0.62	R/0.19 *M* H^+, 37°/Chem	327
$Co(NH_3)_5SO_4^+$ (500/50; 351/58)[359]	550	$\sim 10^{-3}$	R/pH 4, 25°/Chem	326
	370	$\sim 10^{-3}$	R/pH 4, 25°/Chem	326
$Co(NH_3)_5Cl^{2+}$ (530/48; 360/45; 228/20,000)[8,257]	550	0.0015	A of Cl^-, trace of R/pH 4, 25°/Chem	326
	370	0.011	A of Cl^-, trace of R/pH 4, 25°/Chem	326
	365	0.0003	R/acidic, rt/Chem	337
	313	0.16	R/0.1 *M* H^+, 25°/Chem	322
	254	0.17	R/0.2 *M* H^+, 37°/Chem	327
	254	0.34	R/4.4×10^{-3} *M* H^+, 37°/Chem	327
cis-$Co(NH_3)_4(H_2O)Cl^{2+}$ (~530/~50; ~380/~40; ~230/>15,000)[322]	313	0.23	R/0.1 *M* H^+, 25°/Chem	322
	254	0.1	A/0.1 *M* H^+, 25°/Sp	322
	254	0.24	R/0.1 *M* H^+, 25°/Chem	322
$Co(NH_3)_5Br^{2+}$ (542/48; 370 sh/630; 253/18,500)[8,359]	550	0.0014	A/pH 4, 25°/Chem	326
	370	0.067	A/pH 4, 25°/Chem	326
	370	0.15	R/pH 4, 25°/Chem	326
	365	0.29	R/acidic, rt/Chem	337
	254	0.19	R/0.19 *M* H^+, 37°/Chem	327
$Co(NH_3)_5(NO_2)^{2+}$ (458/90; 325/~1600; 239/~14,000)[346]	442	0.035	L-isom/0.1 *M* H^+, 25°/Sp, Chem	346
	442	0.12	R/0.1 *M* H^+, 25°/Chem	346
	370	1.0	35% A, 65% R/pH 4, 25°/Chem	326[f]
	365	0.055	L-isom/0.1 *M* H^+, 25°/Sp, Chem	346
	365	0.32	R/acidic, rt/Chem	337
	365	0.31	R/0.1 *M* H^+, 25°/Chem	346
	313	0.11	L-isom/0.1 *M* H^+, 25°/Sp, Chem	346
	313	0.41	R/0.1 *M* H^+, 25°/Chem	346
	254	0.13	L-isom/0.1 *M* H^+, 25°/Sp, Chem	346
	254	0.51	R/0.1 *M* H^+, 25°/Chem	346
$Co(NH_3)_3(NO_2)_3$ (437/160; 345/2800)[359]	366	0.2	R/acidic, 15°/Sp	317
$Co(NH_3)_5(NCS)^{2+}$ (500/170; 330/1000)[44]	550	6.7×10^{-4}	80% A, 20% R/pH 4, 25°/Chem	326
	370	0.045	30% A, 70% R/pH 4, 25°/Chem	326
	365	0.1	R/acidic, rt/Chem	337
$Co(NH_3)_5N_3^{2+}$ (518/260; 302/7700)[321]	550	0.011	<1% A, 100% R/pH 4, 25°/Chem	326
	370	0.44	<1% A, 100% R/pH 4, 25°/Chem	326
$Co(NH_3)_5I^{2+}$ (585/75; 380/1880; 287/16,500)[8,44]	550	0.10	<1% A, 100% R/pH 4, 25°/Chem	326
	370	0.66	<1% A, 100% R/pH 4, 25°/Chem	326
	365	0.47	R/acidic, rt/Chem	337
	254	1.94	R/0.1 *M* H^+, rt/Chem	340
	254	0.5, 1.0	R/0.2 *M* H^+, 37°/Chem	327
$Co(NH_3)_5(H_2O)^{3+}$ (487/42; 343/42; 192/25,000)[8,359]	254	0.28	R/0.22 *M* H^+, 37°/Chem	327
$Co(en)_3^{3+}$ (465/86.5; 340/79.7; 211/21,200)[328]	366	$\sim 5 \times 10^{-4}$	R/12 *M* HCl, rt/Chem	328
	254	0.06	R/pH 11.0, 37°/Chem	327
	254	0.07	R/pH 6.5, 37°/Chem	327
	254	0.12	R/0.19 *M* H^+, 37°/Chem	327
	254	0.07	R/12 *M* HCl, rt/Chem	328
cis-$Co(en)_2Cl_2^+$ (537/89; 392 sh/69; 312 sh/590; ~240/19,000)[8,321]	~600	0.0033	A/nat pH, 1°/Chem	43
	~600	6.9×10^{-5}	R/nat pH, 1°/Chem	43
	~360	3.1×10^{-4}	R/nat pH, 1°/Chem	43
	313	~0.01	A/0.001 *M* H^+, 18°/Sp	322
	313	0.02	R/0.001 *M* H^+, 18°/Chem	322
	254	0.09	R/0.0022 *M* H^+, 37°/Chem	327
	254	0.10	R/1 *M* H^+, 37°/Chem	327
trans-$Co(en)_2Cl_2^+$ (620/41; 444 sh/29); 386 sh/31; 307 sh/1300; 248/27,000)[321]	313	~0.01	A/0.001 *M* H^+, 18°/Sp	322
	313	0.04	R/0.001 *M* H^+, 18°/Chem	322
	254	~0.01	A/0.001 *M* H^+, 18°/Sp	322
	254	0.08	R/0.003 *M* H^+, 37°/Chem	327
	254	0.07	R/0.22 *M* H^+, 37°/Chem	327
cis-$Co(en)_2(H_2O)Cl^{2+}$ (~510/~90; ~380/~70; ~230/~8000)[322]	~600	0.0035	Racem/nat pH, 1°/Sp	43
	313	~0.05	A/0.001 *M* H^+, 18°/Sp	322
	313	0.07	R/0.001 *M* H^+, 18°/Chem	322
	254	0.07	R/0.01 *M* H^+, 18°/Chem	322
trans-$Co(en)_2(H_2O)Cl^{2+}$ (~540/~40; ~440 sh/~35; ~380 sh/40; ~300 sh/~1000; ~240/~9000)[322]	313	~0.01	A/0.001 *M* H^+, 18°/Sp	322
	313	0.04	R/0.001 *M* H^+, 18°/Chem	322
	254	~0.01	A/0.001 *M* H^+, 18°/Sp	322
	254	0.04	R/0.001 *M* H^+, 18°/Chem	322
cis-$Co(en)_2Br_2^+$ (553/110; ~380 sh/~800; ~290 sh/~800; ~253/~20,000)[321]	550	0.004	93% A, 7% R/nat pH, rt/Chem	360
	370	0.1	95% A, 5% R/nat pH, rt/Chem	360

TABLE VII (*Continued*)

Complex[a] (absorption max, mμ/extinction coeff)[b]	Wavelength, mμ	Quantum yield	Reaction mode[c]/conditions[d]/method[e]	Ref
trans-$Co(en)_2Br_2^+$ (655/54; 485 sh/310; 357 sh/2200; 280/22,000)[321]	550	6×10^{-4}	97% A, 3% R/nat pH, rt/Chem	360
	370	0.07	90% A, 10% R/nat pH, rt/Chem	360
$Co(pn)_3^{3+}$ (465/95; 340/100; 230/21,000)[329]	254	0.11	R/3 *M* HCl/Chem	329
$Co(tn)_3^{3+}$	254	0.07	R/0.93 *M* H^+, 37°/Chem	327
	254	0.11	R/0.22 *M* H^+, 37°/Chem, Sp	327
	254	0.03	R/1.1 × 10^{-4} *M* H^+, 37°/Chem	327
$Co(bn)_3^{3+}$ (470/110; 333/120; 217/17,000)[329]	254	0.18	R/3 *M* HCl/Chem	329
$Co(cn)_3^{3+}$	254	0.059	R/0.24 *M* HCl, 37°/Chem	327
	254	0.052	R/4.8 × 10^{-4} *M* HCl, 37°/Chem	327
$Co(trien)(en)^{3+}$	254	0.13	R/1.86 *M* H^+, 37°/Chem	327
	254	0.24	R/0.088 *M* H^+, 37°/Chem	327
	254	0.18	R/4.8 × 10^{-4} *M* H^+, 37°/Chem	327
$Co(den)_2^{3+}$ (463/112; 339/88; 219/~20,000)[361]	254	0.017	R/1.12 *M* H^+, 37°/Chem	327
	254	0.029	R/0.22 *M* H^+, 37°/Chem	327
	254	0.026	R/pH 6.5, 37°/Chem	327
α-$Co(gly)_3$ (542/93; 373/140; 220/44,000)[362]	365	~10^{-3}	R/0.1 *N* H_2SO_4, 25°/Sp	344
	313	0.25	R/0.1 *N* H_2SO_4, 25°/Sp	344
	254	0.35	R/0.1 *N* H_2SO_4, 75°/Sp	344
	254	0.25	R/0.1 *N* H_2SO_4, 25°/Sp	344
	254	0.20	R/0.001 *N* H_2SO_4, 25°/Sp	344
β-$Co(gly)_3$ (520/145; 377/120; 214/28,000)[362]	365	~10^{-3}	R/0.1 *N* H_2SO_4, 25°/Sp	344
	313	0.19	R/0.1 *N* H_2SO_4, 25°/Sp	344
	254	0.17	R/0.1 *N* H_2SO_4, 25°/Sp	344
α-$Co(alan)_3$ (540/90; 371/145; 221/22,000)[362]	365	~10^{-3}	R/0.1 *N* H_2SO_4, 25°/Sp	344
	313	0.21	R/0.1 *N* H_2SO_4, 25°/Sp	344
	254	0.31	R/0.1 *N* H_2SO_4, 25°/Sp	344
α-$Co(val)_3$ (~535/~95; ~370/~140; ~230/~20,000)[363]	365	0.01	R/0.1 *N* H_2SO_4, 25°/Sp	344
	313	0.16	R/0.1 *N* H_2SO_4, 25°/Sp	344
	254	0.47	R/0.01 *N* H_2SO_4, 75°/Sp	344
	254	0.44	R/0.1 *N* H_2SO_4, 50°/Sp	344
	254	0.33	R/0.1 *N* H_2SO_4, 25°/Sp	344
α-$Co(glut)_3^{3-}$ (~535/~80; ~380/~125; ~240/~8000)[363]	365	$\ll 10^{-3}$	R/0.1 *N* H_2SO_4, 25°/Sp	344
	313	0.28	R/0.1 *N* H_2SO_4, 25°/Sp	344
	254	0.33	R/0.1 *N* H_2SO_4, 25°/Sp	344
β-$Co(glut)_3^{3-}$ (~520/~140; ~375/~130; ~230/~13,000)[363]	365	~10^{-3}	R/0.1 *N* H_2SO_4, 25°/Sp	344
	313	0.21	R/0.1 *N* H_2SO_4, 25°/Sp	344
	254	0.31	R/0.1 *N* H_2SO_4, 25°/Sp	344
$Rh(NH_3)_5Cl^{2+}$ (349/93; 277/144; CT < 220)[353]	365	0.14	A of Cl^- only/nat pH and 0.001 *M* H^+, 15°/Sp	353
	254	0.11	A of Cl^- only/nat pH and 0.001 *M* H^+, 15°/Sp	353

[a] Abbreviations: en, ethylenediamine; pn, 1,2-propanediamine; tn, 1,3-propanediamine; bn, 2,3-butanediamine; cn, *trans*-1,2-cyclohexanediamine; trien, triethylenetetramine, den, diethylenetriamine; gly, glycinato; alan, alaninato; val, valinato; glut, glutamato. [b] Values indicated to be approximate were taken from graphs. [c] R, redox; A, aquation; Racem, racemization; L-isom, linkage isomerization. [d] nat pH, natural pH; rt, room temperature. [e] Chem, chemical analysis for products; Sp, spectrophotometric analysis for products. [f] The reported aquation may well have been linkage isomerization.

SCHEME I



bands of Co(III) complexes suggests that, as with Cr(III), the ligand-field transitions terminate around high vibrational states of the excited state. Rapid thermal equilibration presumably then occurs, followed either by chemical reaction or by radiationless deactivation. The lower quantum yields could then be due either to slower chemical reaction or faster deactivation, relative to Cr(III) complexes. Support for the first possibility can be provided on the basis that in Cr(III) excited states a t_{2g} orbital has been freed for additional bonding by an entering group, while this is not the case with Co(III).

It has also been suggested that singlet–singlet radiationless deactivations may be inherently very fast.[351]

As a related point, it has been postulated that the equilibrium geometry of the first excited quartet state for Cr(III) compounds may be sufficiently different from that of the ground state for deactivation to be hindered.[14] The likelihood of such excited-state distortion is supported by crystal-field stabilization arguments, and these same arguments would predict that Co(III) in the first excited singlet state is more likely to retain the same symmetry as the ground state[352] so that deactivation could now be very fast. Considerations of the possible role of singlet–triplet crossing to give Co(III) triplet excited states seem not to have been explored as yet, although it has been noted that various Co(III) chelates quench organic triplet states.[20a] An example of intramolecular energy transfer is discussed in section XIV.

D. RHODIUM AND IRIDIUM

The reported photochemistry of rhodium and iridium complexes is mostly qualitative. As an exception, $Rh(NH_3)_5Cl^{2+}$ photoaquates chloride with quantum yields of 0.11 and 0.14 at 254 and 365 mμ, respectively, the wavelengths of the first two d–d transitions.[353] The *increase* in quantum yield with increasing wavelength is attributed to the σ antibonding electron of the lower d–d state being in a d_{z^2} orbital, while in the higher excited state it is in a $d_{x^2-y^2}$ orbital. Since the z axis is the one containing the chloride ligand, the first d–d state should give a greater bond weakening. $Ir(NH_3)_5NO_2^{2+}$ has been reported to photoisomerize,[354] and $IrCl_6^{2-}$, to photoaquate.[231]

A series of pyridine-containing complexes of rhodium and iridium has been shown to be photosensitive (to sunlight).[355] *cis*- and *trans*-$Rh(py)_2Cl_4^-$ and *cis*- and *trans*-$Ir(py)_2Cl_4^-$ undergo photoaquation of a chloride in aqueous solution; in the case of *trans*-$Ir(py)_2Cl_4^-$, the isomer obtained was not the same as that for the thermal reaction. $Ir(py)_3Cl_3$ photolyzes to give $Ir(py)_2(H_2O)Cl_3$ or its polymerization products. In chloroform and other solvents, pyridine is lost and polymeric products are formed, and it was suggested that the immediate photolysis product is $Ir(py)_2Cl_3$. The photolysis reactions of $Rh(py)_3Cl_3$ are similar,[355,356] as are those of $Rh(py)_3Br_3$ and $Ir(py)_3Br_3$.[355] Finally, *cis*- and *trans*-$Ir(py)_4Cl_2^+$ appear to convert to $Ir(py)_3(H_2O)(OH)Cl^+$ on irradiation, and $Rh(py)_4Cl_2^+$ gives $Rh(py)_3Cl_3$.[357] As another series of observations, the Rh(III) EDTA complex photoracemizes in sunlight, and the complex of *l*-propylenediaminetetraacetic acid mutarotates.[358a]

Some interesting recent observations concern aqueous *trans*-$M(en)_2X_2^+$ with M = Rh or Ir, and X = Cl, Br, or I.[358b] These complexes undergo stereospecific photoaquation to the corresponding $M(en)_2(H_2O)X^{2+}$ species. Thus the photolysis rules for Cr(III) complexes (section VII.C) appear to apply to these systems.

See Table VII for selected data on the photochemistry of Co(II) and Rh(III) complexes.[359–363]

XI. NICKEL, PALLADIUM, AND PLATINUM

The general coordination chemistry of nickel, palladium, and platinum consists largely of that of the M(II) complexes, and of Pd(IV) and Pt(IV), in addition to the various carbonyls and cyanides of low oxidation number. However, the photochemistry so far reported is confined to the less labile members of these families, and, in fact, primarily to Pt(II) and Pt(IV) complexes.

The spectra of the square-planar M(II) compounds typically consist of d–d transitions close to and often appearing as shoulders on a strong first CT band. There is a general shift of the d–d features toward shorter wavelengths in the order Ni, Pd, Pt, with a consequent compression of these transitions into the region of the CT absorption. Figure 12 gives the spectrum of $PtCl_4^{2-}$. In the figure, the bands labeled 1 and 2 were assigned as singlet–singlet transitions from d_{xz}, d_{yz}, and d_{xy}, respectively, to $d_{x^2-y^2}$, while bands 3 and 4 were taken to be the corresponding singlet–triplet transitions.[364] Other treatments show some variation in detail,[365–368] but there is general agreement that the first d–d transitions are to σ and π antibonding levels and that singlet–triplet transitions and singlet–singlet transitions can occur with somewhat comparable intensities, presumably because of the greater degree of spin–orbit coupling in the case of the heavy transition metal elements, as compared to the first-row ones (*e.g.*, ref 365). There does not appear to be any detailed

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(352) (a) A. W. Adamson, A. Chen, and W. L. Waltz, Proceedings of Nara Meeting on the Synthetic and Stereochemical Aspects of Coordination Chemistry, Nara, Japan, Sept 20–22, 1967; (b) A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).

(353) L. Moggi, *Gazz. Chim. Ital.*, **97**, 1089 (1967).

(354) F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

(355) M. Delépine, *Compt. Rend.*, **233**, 1533, 1156 (1951); **234**, 1721 (1952); **236**, 1713 (1953); **238**, 27 (1954); **240**, 2468 (1955); **242**, 27 (1956).

(356) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1224 (1964).

(357) F. Larèze, *Compt. Rend.*, **259**, 2438 (1964).

(358) (a) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961); **82**, 4823 (1960); (b) R. A. Bauer and F. Basolo, *ibid.*, **90**, 2437 (1968).

(359) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388 (1938).

(360) A. W. Adamson, unpublished results.

(361) H. H. Schmidtke, *Z. Physik. Chem.* (Frankfurt), **38**, 177 (1963).

(362) M. Mori, M. Shibata, E. Kyuno, and M. Kanaya, *Bull Chem. Soc. Japan*, **34**, 1837 (1961).

(363) V. Carassiti and A. M. Marinangeli, *Ann. Chim.* (Rome), **50**, 593 (1960).

(364) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

(365) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 386 (1958).

(366) (a) V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, **4**, 1243 (1965); (b) F. Scandola, O. Traverso, V. Balzani, G. L. Zucchini, and V. Carassiti, *Inorg. Chim. Acta*, **1**, 76 (1967).

(367) J. R. Perumareddi and A. W. Adamson, *J. Phys. Chem.*, **72**, 414 (1968).

(368) E. König and H. Schläfer, *Z. Physik. Chem.* (Frankfurt), **26**, 371 (1960).

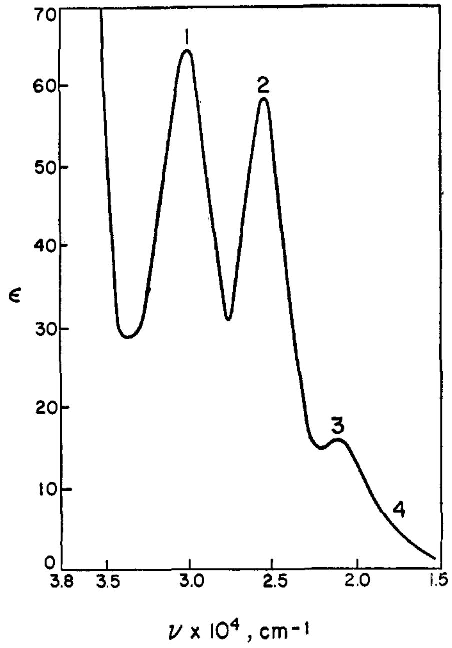

Figure 12.—Absorption spectrum of $PtCl_4^{2-}$ (after ref 364).

analysis available of the intense ultraviolet bands, but they are presumed to be CT in nature (and could then be CTTM or CTTS).

Ni(II) complexes are either diamagnetic (square planar) or paramagnetic (octahedral or tetrahedral) and their spectra are different. Assignments have been made for the spectrum of diamagnetic $Ni(CN)_4^{2-}$.[83,369] Again, there is variation in detail, but the first singlet–singlet transition appears to be to a π antibonding configuration and some low-intensity transitions are assigned as singlet–triplet. A particularly interesting suggestion, however, is that one of the singlet–singlet transitions may terminate on a state having D_{2d} equilibrium geometry.[369] The labile tetrahedral and octahedral paramagnetic complexes appear not to have been studied photochemically; their spectra have been treated in various papers,[370–372] as well as in texts and monographs listed in the Introduction.

Pt(IV) complexes, as d^6 systems, nominally have the same electronic structure as Co(III) complexes, but the spectra show the compression of d–d transitions into the region of the first CT band, again as a manifestation of the generally higher effective ligand-field strength exhibited by ligands coordinated to heavy transition metals. As with Pt(II) compounds, singlet–singlet and singlet–triplet transitions occur relatively close to each other and with somewhat comparable intensity.[373] The spectrum of $PtBr_6^{2-}$ is shown in Figure 13; the CT bands were assigned as due to π electrons from the ligands, which are transferred to platinum d orbitals, *i.e.*, CTTM in type.[373,374]

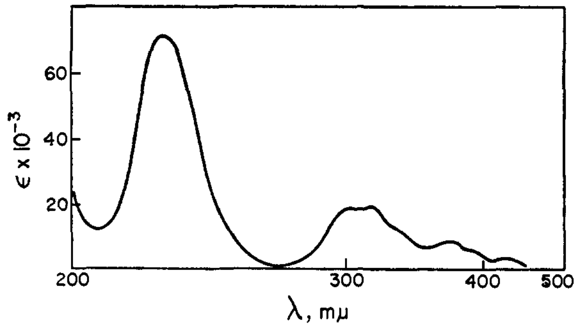

Figure 13.—Absorption spectrum of $PtBr_6^{2-}$ (after ref 374).

The general photochemistry is one of substitution or isomerization in the case of square-planar complexes, and of substitution and redox reactions in the case of Pt(IV) species. Representative data are given in Table VIII.

A. NICKEL AND PALLADIUM

There are only a few entries in the literature—all for the divalent metals. *trans*-Ni(glycine)$_2$ (square planar) is not photosensitive to 365-mμ light;[366] the same is true for Pd(glycine)$_2$ at 313 mμ.[366] These wavelengths correspond to the region of the first d–d transition of the complex in question. However, this last complex did undergo photodecomposition (to palladous oxide) with 254-mμ light, which corresponds to the first CT band.[366] The Ni(II) EDTA complex is reported not to be photosensitive.[305] Ni(II) appears to play an interesting role in the photocatalytic production of amino acids.[375,376]

B. PLATINUM(II)

The photochemistry of Pt(II) complexes appears to consist primarily of substitution and isomerization reactions, regardless of whether d–d or adjacent allowed bands are irradiated. Quantum yields may be wavelength dependent, however.

Members of the family $Pt(NH_3)_nX_{4-n}^{n-2}$ photoaquate as a rule. This is reported to be the case for $PtCl_4^{2-}$,[103] but apparently is not so for $PtBr_4^{2-}$.[377] *cis*-$Pt(NH_3)_2Cl_2$ yields the aquation product, $Pt(NH_3)_2(H_2O)Cl^+$, with a quantum yield of several tenths, which is both wavelength and temperature dependent[367] (see Table VIII). The *trans* isomer also photoaquates, but with a much lower quantum yield. It has been reported that with light below 200 mμ or between 250 and 300 mμ both

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[369] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4**, 514 (1965).

[370] F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

[371] G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

[372] A. D. Liehr and C. J. Ballhausen, *Ann. Physik.*, **6**, 134 (1959).

[373] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

[374] C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

[375] K. Issieib and R. B. Srivastava, *Indian J. Appl. Chem.*, **27**, 77 (1964); *Chem. Abstr.*, **61**, 12831*e* (1964).

[376] K. Bahadur and R. B. Srivastava, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1070 (1963); *Chem Abstr.*, **59**, 7767*e* (1963).

[377] A. A. Grinberg, L. E. Nikoleskaya, and G. A. Tsagesultanova, *Dokl. Akad. Nauk SSSR*, **101**, 1059 (1955).

TABLE VIII

PHOTOCHEMISTRY OF PLATINUM COMPLEXES (SELECTED DATA)

Complex (absorption max or sh,mμ/extinction coeff)[a]	Wavelength, mμ	Quantum yield	Reaction mode[b]/conditions/method[c]	Ref
cis-$Pt(NH_3)_2Cl_2$ (417 sh/12; 367/28; 302/128; 269 sh/92)[103]	410	0.25	A–Cl^-/nat pH, 25.5°/Cond	367
	363	0.39[d]	A–Cl^-/nat pH, 26°/Cond	367
	350	0.46	A–Cl^-/nat pH, 24°/Cond	367
trans-$Pt(NH_3)_2Cl_2$ (450 sh/8; 370/33; 312/68; 266/78)[103]	363	0.01	A–Cl^-/nat pH, 25°/Cond	367
cis-$Pt(NH_3)_2(H_2O)_2^{2+}$ (425 sh/9; 325 sh/87); 260 sh/280)[103]	363	0.13	I/0.1–0.12 *M* $HClO_4$, 26°/Sp	367
cis-$Pt(P(C_2H_5)_3)_2Cl_2$ (~315/~671; ~265 sh/~2013; ~240/~6720; ~220/11,000)[381]	315	0.01–0.02	I/benzene/Sp	381
trans-$Pt(P(C_2H_5)_3)_2Cl_2$ (~315 sh/~753; ~270/~1000; ~250/~1070; ~220/~400)[381]	315	0.01–0.02	I/benzene/Sp	381
cis-$Pt(gly)_2$ (~325/~27.5; ~260 sh/~200)[366]	313	0.13	I/nat pH, ~25°/Sp	366
	254	0.12	I/nat pH, ~25°/Sp	366
$PtCl_6^{2-}$ (453/50; 353 sh/490; 262/24,500)[373]	546	40	Br^- exch/1 *M* HBr, 25°/*Cl^-	393
	436	50	Br^- exch/0.1 *M* HBr, 25°/*Cl^-	393
	366	30	Br^- exch/1 *M* HBr, 25°/*Cl^-	393
$PtBr_6^{2-}$ (525/140; 435 sh/1500; 364 sh/7400; 311/17,800; 226/70,000)[373,374]	540	10–500	Br^- exch[e]/nat pH, ~25°/*Br^-	44
	313–530	0.4	A/μ = 1, pH 6–6.9, 25°/pH, Sp	395
trans-$Pt(NH_3)_4Br_2^{2+}$ (~370 sh/~210; 318/1150; 235/41,300)[96]	380–280	0.03–0.06	R/nat pH, 0.01 *M* Br^-, 10% methanol, 22°/Chem, Sp	96
	350	0.06	A–Br^-/nat pH, 22°/Chem, Sp	96
	305	0.1	A–Br^-/nat pH, 22°/Chem, Sp	96

[a] Values given as approximate are taken from graphs. [b] A, photoaquation of the ligand indicated; I, isomerization (*cis–trans*); R, oxidation–reduction reaction; exch, photoexchange of anion indicated. [c] Cond, reaction followed conductimetrically; Sp, reaction followed spectrophotometrically; *Cl^-, reaction followed by determination of released $^{36}Cl^-$; *Br^-, reaction followed by determination of released $^{80}Br^-$; Chem, reaction followed by chemical test; pH, reaction followed by pH change. [d] At 363 mμ, the temperature dependence corresponded to an activation energy of 2.4 kcal/mole. [e] Dependent on light intensity.

species give polynuclear Pt(II)–Pt(IV) substances.[378] $Pt(NH_3)_3Cl^+$ photolyzes to give both ammonia and chloride aquation with 305-mμ light.[379] Solid *trans*-$Pt(NH_3)_2(NO_3)_2$ is photosensitive, as evidenced by darkening in sunlight, but the solid *cis* isomer is not.[367] Finally, *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ photoisomerizes to *trans* with a quantum yield of about 0.1 at 363 mμ, but on long irradiation there is also some additional photoreaction which may be ammonia aquation.[367] The appearance of two reaction modes in some of the above cases suggests that further studies may reveal empirical photolysis rules of the type found for Cr(III) complexes (section VII.C).

Photoisomerizations have been reported for several compounds of the type PtB_2Cl_2. An early study found that with B = $(C_2H_5)_3P$ or $(C_2H_5)_3As$, *cis* to *trans* photoisomerization occurred in ether solution, but not the reverse.[380] It was later found that, for the former complex, the photoisomerization occurred in both directions, in a variety of solvents. Essentially white light was used, but not below 304 mμ, so that only d–d absorptions were involved, and it was postulated that the singlet excited state produced on irradiation decayed to a triplet state which could rearrange to a tetrahedral configuration and thus lead to isomerization.[381] Somewhat similar results were found for B = pyridine, methylamine, and isoquinoline, with the additional observation that shorter wavelength irradiation tended to produce decomposition.[382] There is a possibility that photoaquation occurs as well in these systems; spectral changes on replacing chloride by water are sometimes small with Pt(II) complexes so that such a reaction might go unnoticed. In the case of $Pt(glycine)_2$, *cis* to *trans* photoisomerization occurs, but not the reverse.[366] Again, it was postulated that isomerization took place through a tetrahedral triplet excited state. The photochemistry of platinum(II) dithizonate is mentioned in section XIV.

C. PLATINUM(IV)

The hexahalide complexes have been studied fairly extensively. Early work with $PtCl_6^{2-}$ indicated that both the thermal and photoreactions were aquations.[383–387]

$$PtCl_6^{2-} + H_2O \xrightarrow{h\nu} PtCl_5(OH)^{2-} + H^+ + Cl^- \qquad (72)$$

Either sunlight or unfiltered lamps emitting from about 250 to 550 mμ were used, and the reaction was followed either by titration of the aquo product, or conducti-

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(378) A. V. Babaeva and M. A. Mosyagina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 205 (1953).

(379) P. Natarajan and A. W. Adamson, unpublished work.

(380) I. Lifschitz and W. Froentjes, *Z. Anorg. Allgem. Chem.*, **233**, 1 (1937).

(381) P. Haake and T. A. Hylton, *J. Am. Chem. Soc.*, 84, 3774 (1962).

(382) P. Haake and S. H. Mastin, private communication.

(383) E. H. Archibald, *J. Chem. Soc.*, 1104 (1920).

(384) M. Boll, *Compt. Rend.*, **156**, 138, 691 (1913); *Chem. Abstr.*, **7**, 1324, 2152 (1913).

(385) M. Boll, *Compt. Rend.*, **157**, 115 (1913); *Chem. Abstr.*, **7**, 3706 (1913).

(386) M. Boll, *Ann. Phys.*, **2**, 226 (1915); *Chem. Abstr.*, **9**, 1270 (1915).

(387) M. Boll and P. Job, *Compt. Rend.*, **154**, 881 (1913); *Chem. Abstr.*, **7**, 1133 (1913).

metrically. The various aquated species, $H_2[PtCl_n(OH)_{6-n}]$, were also found to be photosensitive, releasing up to all but one of the coordinated chlorides, at a rate proportional to light intensity and increasing with decreasing wavelength.[384–387] More recent work confirms the general observations and reports further on the aquation equilibria at various pH's.[388] In 3 M hydrochloric acid only $PtCl_6^{2-}$ is present, while in 0.01 M acid both $PtCl_5(OH)^{2-}$ and $PtCl_4(OH)_2^{2-}$ are important, and a 0.1 M sodium hydroxide solution contains $PtCl(OH)_5^{2-}$ and $Pt(OH)_6^{2-}$ ions.

On the other hand, a detailed study of the thermal and photochemical exchange of chloride ion with $PtCl_6^{2-}$ (in 0.08 M acid) led to the conclusion that a photoredox reaction occurred (in sunlight) to generate a Pt(III) species which then catalyzed the exchange.[389] The suggested reactions included

$$PtCl_6^{2-} \xrightarrow{h\nu} PtCl_5^{2-} + Cl \qquad (73)$$

$$PtCl_5^{2-} + Cl^{-*} = PtCl_5^{2-*} + Cl^- \qquad (74)$$

$$PtCl_5^{2-*} + PtCl_6^{2-} = PtCl_6^{2-*} + PtCl_5^{2-} \qquad (75)$$

The presence of a chain mechanism was confirmed by quantum-yield measurements for the exchange, as a function of wavelength, temperature, and chloride ion concentration,[390] which gave yields ranging from 15 to 1000. The apparent activation energy was reported to vary from 2.5 to 12 kcal/mole, depending on wavelength (and on chloride ion concentration).

The exchange of other halide ions with $PtCl_6^{2-}$ has also been studied. That of iodide ion was first reported not to be photoinduced,[391] but later work showed that if traces of $IrCl_6^{2-}$ were removed, then photoexchange did occur, and it was concluded that the exchange involved a photoproduced Pt(III) intermediate.[392] A study of the photoexchange of bromide ion with $PtCl_6^{2-}$ yielded wavelength-dependent quantum yields ranging from 30 to 1000; the apparent activation energies were 5, 6, and 13 kcal/mole at 366, 436, and 546 mμ, respectively.[393] Again, there appeared to be a chain reaction involving lower valent platinum complexes.

$PtBr_6^{2-}$ is also photosensitive. Early work indicated that, as with $PtCl_6^{2-}$, a photoaquation occurred, which could be followed by the pH change. On irradiation, the acidity rose initially, presumably as a consequence of the analog of eq 72 occurring, but then went through a maximum and decreased. These latter acidity changes were thought to be associated with second stage and further aquation.[394] Later investigations indicated that only photoaquation occurred, again reversible in the dark and inhibited by added bromide ion.[395] This and other studies have also confirmed that the photoaquation could proceed to give $PtBr_4(H_2O)_2$.[96] The reported quantum yield for the first aquation step was 0.4, independent of wavelength from 313 to 530 mμ, and it was proposed that the reaction occurred after conversion from a singlet to a triplet excited state, which either then reacted or which deactivated to a vibrationally excited and hence reactive ground-state molecule.[395]

The photoexchange of bromide ion with $PtBr_6^{2-}$ appears to involve a chain reaction, just as in the chloride system. Quantum yields at 540 mμ were found to vary from 10 to 500, depending on light intensity, and a mechanism analogous to eq 73–75 was proposed.[44] The photoacceleration of bromide ion exchange was confirmed by other studies.[396] Flash photolysis of aqueous $PtBr_6^{2-}$ gives a transient absorbing between 400 and 450 mμ and decaying with a 0.1-sec half-life,[96] but not the bromine atom production predicted by the analog of eq 73.[339] An alternative primary process was therefore proposed.[339]

$$PtBr_6^{2-} \xrightarrow{h\nu} [PtBr_4^{2-}] + Br_2 \qquad (76)$$

A similar process of molecular elimination of adjacent coordinated atoms has been shown to occur in the case of MnO_4^- (section VIII). It was further proposed that the photolytically produced $[PtBr_4^{2-}]$ remained in an unstable geometry, to act as an intermediate in the chain reaction leading to exchange, before being reoxidized by bromine (or its hydrolysis product).

It is interesting that both with $PtCl_6^{2-}$ and $PtBr_6^{2-}$ the net photoreactions correspond to photoaquation as the primary step, while the exchange studies seem to require a redox process. Evidently both processes either occur as alternative modes, or the photoaquation might actually be a terminal result of some complex reaction sequence also leading to exchange (note reaction 77).

The thermal exchange of iodide ion with PtI_6^{2-} was found to be immeasurably fast (by ordinary mixing techniques), which precluded any photochemical observations, and, in contrast to the other hexahalide complexes, no detectable photoaquation was found.[397] However, a later study reports photoaquation with 254, 313, 365, and 530 mμ light; these wavelengths involved CT rather than d–d absorptions.[395] Flash photolyses of PtI_6^{2-} solutions containing iodide ion produce a 0.1-sec half-life transient absorbing at 410 mμ but not otherwise identified.[339]

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(388) E. Blasius, W. Preetz, and R. Schmitt, *J. Inorg. Nucl. Chem.*, **19**, 115 (1961).

(389) R. L. Rich and H. Taube, *J. Am. Chem. Soc.*, **76**, 2608 (1954).

(390) R. Dreyer, K. König, and H. Schmidt, *Z. Physik. Chem.* (Leipzig), **227**, 257 (1964).

(391) A. J. Poë and M. S. Vaidya, *Proc. Chem. Soc.*, 118 (1960).

(392) A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 2981 (1961).

(393) R. Dreyer and K. König, *Z. Chem.*, **6**, 271 (1966).

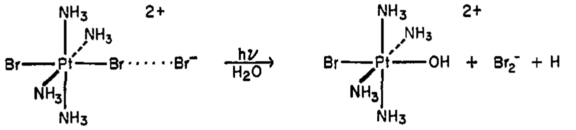
(394) E. H. Archibald and W. A. Gale, *J. Chem. Soc.*, 2849 (1922).

(395) V. Balzani, F. Manfrin, and L. Moggi, *Inorg. Chem.*, **6**, 354 (1967).

(396) G. Schmidt and W. Herr, *Z. Naturforsch.*, **16a**, 748 (1961).

(397) A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 187 (1960).

A few other Pt(IV) complexes have been studied. The exchange of chloride ion with $Pt(en)_2Br_2^{2+}$ is reported to be photoinduced.[398] The *trans* form of $Pt(NH_3)_4Br_2^{2+}$ photoaquates with a quantum yield of 0.06 at 350 mμ, and 0.1 at 305 mμ.[96] No other reactions, such as reduction of the platinum, or ammonia release appeared. However, if added bromide ion was present, flash photolysis studies showed that Br_2^- radicals were produced, along with hydrogen atoms. There was spectral evidence for ion pairing, and the suggested reaction was eq 77, which provides an example



$$\mathrm{Br{-}Pt(NH_3)_4{-}Br\cdots Br^-}\ ^{2+} \xrightarrow[\mathrm{H_2O}]{h\nu} \mathrm{Br{-}Pt(NH_3)_4{-}OH}\ ^{2+} + \mathrm{Br_2^-} + \mathrm{H} \qquad (77)$$

of photoaquation occurring as the net reaction of the complex even though a redox process is involved. *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$ shows a similar photochemistry,[96] with respect both to production of transients and to the net photolysis reaction.

The various isomers of $Pt(NH_3)_2(NO_2)_2X_2$, X = Cl or Br, are photosensitive. Isomerization, substitution, and redox reactions are reported, using light which probably was mainly 254 mμ.[399,400] It was suggested that a redox path through Pt(II) was involved. Finally, $H_2[Pt(malonate)_3]$ is reported to undergo a photochemical redox reaction, with a quantum yield of unity for Pt(II) formation.[401]

XII. COPPER AND ZINC GROUPS

A. COPPER, SILVER, AND GOLD

There are very few reports that fall within the scope of this review. The photochromic behavior of the dithizonates is discussed in section XIV. Photoredox decomposition is reported for $[Cu(en)_2]SO_4$, $[Cu(en)(H_2O)_2]SO_4$, and $Na_2[Cu(C_2O_4)_2]$[402] and other copper compounds.[403] A photoreduction of copper phthalocyanine occurs in aqueous amine solutions and an intermolecular energy transfer is postulated between the excited dye molecule and the amine.[404] Cuprous halides are reported to catalyze the photopolymerization of norbornene, by a mechanism involving an excited norbornene complex with CuX.[405]

The complex $Ag(bipy)_2^{2+}$ undergoes a photoredox decomposition with light of 254, 313, and 436 mμ, with quantum yields of 0.1, 0.04, and 10^{-3}, respectively.[406] The first two wavelengths correspond to ligand absorptions, while the third is characteristic of the complex. The photolysis (at 365 and 405 mμ) is enhanced by alcohol.[407]

The quantitative literature on gold compounds is very sparse, in spite of their notorious photosensitivity, which finds some application in photography.[408–410] The salt $Na[AuCl_4]\cdot 2H_2O$ acts as a sensitizer in the photopolymerization of N-vinylcarbazole,[411,412] and it is suggested that the mechanism involves a photoreduction to Au(II).[412] There is some evidence for the existence of this valence state.[413,414] Dilute aqueous $H[AuCl_4]$ is also reported to undergo some form of photoredox decomposition.[415] Quite possibly, these systems will prove to have a behavior similar to those involving Pt(IV) complexes.

B. ZINC, CADMIUM, AND MERCURY

The photochemistry of this group is also rather limited; some of the halides act as sensitizers in photographic processes. $Hg(CN)_2$ is photosensitive, as mentioned in section IV.A, and the dithizonates have been studied (section XIV). The gas-phase photolysis of $Hg(CH_3)_2$ proceeds with quantum yield unity according to the equation[416–419]

$$Hg(CH_3)_2 \xrightarrow{h\nu} HgCH_3 + CH_3 \qquad (78)$$

followed by various free-radical reactions.

The aqueous halides $HgCl_2$, $HgCl_4^{2-}$, $HgBr_2$, $HgBr_4^{2-}$, and HgI_4^{2-} all undergo redox photolysis on irradiation of the first CT band;[420,421] flash photolysis of these systems produces transients identified as X_2^-.[420]

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(398) F. Basolo, A. F. Messing, P. H. Wilks, R. G. Wilkins, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **8**, 203 (1958).

(399) I. I. Chernyaev, G. S. Muraveiskaya, and L. S. Korablina, *Russ. J. Inorg. Chem.*, 10, 395, 567 (1965).

(400) I. I. Chernyaev, G. S., Muraveiskaya, and L. S. Korablina, *ibid.*, 11, 714, 728 (1966).

(401) T. Banerjee, H. Chakravorty, and S. Sacker, *J. Indian Chem. Soc.*, 20, 207 (1943).

(402) G. A. Shagisultanova and L. A. Il'yikevich, *Zh. Neorgan. Khim.*, 11, 945 (1966); *Chem. Abstr.*, **65**, 200*h* (1966).

(403) G. A. Shagisultanova, *Russ. J. Inorg. Chem.*, 11, 510 (1966).

(404) G. Eigenmann, *Helv. Chim. Acta*, **46**, 855 (1963).

(405) D. J. Trecher, R. S. Foote, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **88**, 3021 (1966).

(406) V. Carassiti, G. Condorelli, and L. L. Costanzo, *Ann. Chim.* (Rome), **54**, 303 (1964).

(407) V. Balzani, A. Bertoluzza, and V. Carassiti, *Bull. Soc. Chim. Belges*, 71, 821 (1962).

(408) F. Evva, *Z. Wiss. Phot., Photophysik Photochem.*, **52**, 64 (1957).

(409) A. Narath and A. Tiilikka, *J. Phot. Sci.*, **9**, 303 (1961).

(410) P. Faelens and C. F. van Veelen, *Photo. Korr.*, **99**, 185 (1963).

(411) C. E. H. Bawn, A. Ledwith, and S. L. Yang, *Chem, Ind.* (London), 769 (1965).

(412) S. Tazuke, M. Asai, S. Ikeda, and S. Okamura, *Polymer Letters*, **5**, 453 (1967).

(413) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

(414) J. H. Waters and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3534 (1965).

(415) (a) H. Witzmann and A. Helmshaub, *Z. Physik. Chem.* (Leipzig), 213, 1 (1960); (b) R. Sriram and A. W. Adamson, unpublished results.

(416) R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **31**, 631 (1953); *J. Chem. Phys.*, 21, 1723 (1953).

(417) B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc.* (London), **A218**, 269 (1953).

(418) R. A. Holroyd and W. A. Noyes, *J. Am. Chem. Soc.*, **76**, 1583 (1954).

(419) R. E. Rebbert and P. Ausloos, *ibid.*, **85**, 3086 (1963).

(420) M. E. Langmuir and E. Hayon, *J. Phys. Chem.*, **71**, 3808 (1967).

(421) A. A. Nosonovich, I. I. Dilung, and B. Cain, *Ukr. Khim. Zh.*, **32**, 1280 (1966); *Chem. Abstr.*, **66**, 70839*s* (1967).

There is some conflict in the reports, particularly with respect to the presence of Cl_2^-. The primary act could be one of halogen atom production, but it seems likely that the primary steps are

$$HgX_2 \xrightarrow{h\nu} [Hg^+X_2^-] \longrightarrow Hg^I + X_2^- \qquad (79)$$

and

$$HgX_4^{2-} \xrightarrow{h\nu} [HgX_2^-X_2^-] \longrightarrow Hg^I + X_2^- + 2X^- \qquad (80)$$

The concerted departure of two atoms is known to occur in the case of MnO_4^- (section VIII), and a process analogous to the above has been postulated for certain Pt(IV) complexes (section XI.C).

Process 79, if correct, is rather interesting, as it would imply considerable bending of the X–Hg–X bond, either in the ground or in the excited state. It may be significant that photolysis of aqueous HgI_2 (for which such bending is least likely) does not produce the transient I_2^-. One is led to postulate that $HgCl_2$ and $HgBr_2$ may have coordinated solvent so that the actual species are tetrahedral or octahedral. It is significant that $CdBr_3^-$ is known,[422] and aqueous $ZnCl_2$ is octahedral, from Raman studies.[423] As a final comment, CdX_2 crystals are reported to be photosensitive only in the presence of water;[424] the phenomenon could be due to adsorbed water entering the coordination sphere of surface cadmium ions to give a surface layer having bent X–Cd–X bonds. Previous work on these systems produced no acceptable mechanism and has been reviewed.[425]

XIII. LANTHANIDES AND ACTINIDES

The nature of the electronic spectra of the rare earth and actinide complexes is rather different from that of the transition-metal coordination compounds. The coordinate bonds are often ionic in character, as judged partly from their very small perturbing effect on the well-shielded 4f and 5f electrons, whose excitations are the ones involved in the visible and near-ultraviolet absorption spectra. Because of this lack of perturbation by the environment of the central metal ion and the dipole-allowed character of the transitions ($\Delta L = 1$), very sharp, nearly line spectra are observed. A trait critical to the photochemistry of transition-metal complexes is thus missing, namely interaction and mixing of states on the metal with those on the ligand. Further, where new spectral features do appear on coordination, these typically are associated with a chelate ring acting as a chromophoric center; delocalized electron configurations appear to be involved rather than ones antibonding to specific bonds.

Perhaps for these reasons, but in any event the rare earth and actinide complexes show very little photochemistry of a substitutional nature. This is true even where major intramolecular energy transfers must be occurring, as evidenced by luminescence studies. Thus, absorption may be in the chelate chromophore and emission from the rare earth excited state system, without photodecomposition;[426] the energy transfer may even be from a triplet state of a sensitizer to the chelate triplet level, with emission then occurring from the rare earth ion, as is the case with tris(hexafluoroacetylacetonato)europium(III).[427] Such emission studies are not directly within the province of this review and are cited here only to illustrate the apparent lack of any chemical reactivity of a substitutional nature for the various excited states. There is a useful recent review on such emission studies.[428]

Those rare earth and actinide ions having more than one reasonably stable valence state may exhibit photoredox behavior, however, and the rest of this section is devoted to these cases. The bulk of the literature concerns cerium and uranium, which are treated in the first two subsections, with the scattering of other results collected in the third. In most instances ion pairs or in general labile ion clusters of not clearly known stoichiometry or structure function as the photoactive species. Since this review is concerned mainly with the photochemistry of definite coordination compounds, the material that follows is intended to be illustrative rather than definite in coverage.

A. CERIUM

Ce(IV) probably does not exist in solution as a 4+ ion but is always to some degree hydrolyzed or associated with anions in labile complexes. For this reason, while the general photolytic process is of the type

$$Ce^{IV}(aq) \xrightarrow{h\nu} Ce^{III}(aq) + OH \text{ or oxidized anion} \qquad (81)$$

it is difficult to assign accurate quantum efficiencies to specific species. Thus the photoreduction of Ce(IV) in sulfuric and perchloric acid solutions has been studied by several groups,[429–433] with two suggested mechanisms, namely the photoreduction of Ce(IV) dimers[429] and the photoproduction of hydroxyl radical from the

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[422] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 607.

[423] D. E. Irish, B. McCaroll, and T. F. Young, *J. Chem. Phys.*, **39**, 3436 (1963).

[424] J. A. Hedvall, P. Wallgren, and S. Mansson, *Svensk Kem. Tidskr.*, **52**, 98 (1940); *Chem. Abstr.*, **34**, 7180^3 (1940).

[425] C. Ellis and A. S. Wells, "Chemical Action of Ultra-Violet Rays," Reinhold Publishing Corp., Inc., New York, N. Y., 1941, p 367.

[426] G. A. Crosby and R. E. Whan, *J. Chem. Phys.*, **36**, 863 (1962), and preceeding papers.

[427] M. L. Bhaumik and M. A. El-Sayed, *J. Phys. Chem.*, **69**, 275 (1965).

[428] K. K. Rohatgi, *J. Sci. Ind. Res.* (India), **24**, 456 (1965).

[429] L. J. Heidt and M. E. Smith, *J. Am. Chem. Soc.*, **70**, 2476 (1948).

[430] L. J. Heidt, Proceedings of the World Symposium on Applied Solar Energy, Phoenix Ariz., 1955, p 275.

[431] T. J. Sworski, *J. Am. Chem. Soc.*, **79**, 3655 (1957).

[432] M. G. Evans and N. Uri, *Nature*, **166**, 602 (1950).

[433] T. J. Sworski, *J. Am. Chem. Soc.*, **77**, 1074 (1955).

solvation sphere of a single Ce(IV).[431–433] This last interpretation seems the better substantiated and is further supported by recent results in acidic sulfate or nitrate-containing solutions.[434] Also esr studies on irradiated Ce(IV) in ice indicate that with 254-mμ light the primary step is[435]

$$\mathrm{Ce^{IV}(aq)} \xrightarrow{h\nu} [\mathrm{Ce^{III}H_2O^+}] \qquad (82)$$

By way of illustration, the quantum yield for Ce(III) production in 0.4 M sulfuric acid solution, with 254-mμ irradiation, increased from about 0.03 to 0.2 on addition of Tl^+, the effect being negated if Ce(III) was initially present.[431] The interpretation was that Ce(III) and Tl^+ competed for reaction with hydroxyl radical produced in the primary step.

Three studies are reported which do involve specific coordination species. $Ce(NO_3)_6^{2-}$ (in 6 M nitric acid solution) yields nitrate radicals on flash photolysis.[434,436] A related complex, $Ce(NO_3)_4(OCOCH_3)_2^{2-}$, photolyzes in glacial acetic acid with light of 280–465 mμ, under both flash and steady irradiation conditions, to give a variety of organic products ascribable to redox reactions of the acetate ligand, plus some Ce(III).[437] An intramolecular energy transfer from cerium to acetate was suggested, followed by reaction of the acetate molecule with the medium. Quantum yields for Ce(III) production were about 0.4 at 50°.

Ce(III) excited states may be relatively analogous to those of transition metal ions; with only one f electron, no allowed f-orbital transitions are observed, and the absorption bands are weak and broad as a probable reflection of interaction between metal and ligand orbitals. However, no substitutional photochemistry seems to have been reported. Charge-transfer-type bands occur in the ultraviolet, and the photochemical behavior with 254-mμ irradiation, for example, suggests that these are of the CTTS type.

The photolysis of aqueous Ce(III) follows the over-all reaction

$$2\mathrm{Ce^{3+}(aq)} \xrightarrow{h\nu} 2\mathrm{Ce(OH)^{3+}} + \mathrm{H_2} \qquad (83)$$

The quantum yield at 254 mμ is concentration dependent and may be represented as[438]

$$1/\phi = 700 + 2/[\mathrm{Ce^{3+}}] + 5/[\mathrm{H^+}] + 0.13/[\mathrm{H^+}]\,[\mathrm{Ce^{3+}}] \qquad (84)$$

at 25°; the largest actual value of ϕ obtained was 0.0014. The supporting mechanism is that an excited Ce(III) reacts with hydronium ion to give Ce^{IV}–OH–H_2, which then reacts with a second Ce(III) to give the products.[438,439] Alternatively, the primary step may be the production of a hydrogen atom,[440,441] although this does not account for the dependence of ϕ on $[Ce^{3+}]$. Since acidic solutions are involved, it is also possible that the primary process is actually one of photoelectron production, with subsequent scavenging by aqueous protons. It may be significant in this respect that irradiation at room temperature of glasses containing Ce(III) leads to electron-associated color centers.[442,443]

B. URANIUM

Most of the photochemistry of uranium concerns the various reactions of uranyl ion, either complexed or as an aquo ion; this has been well reviewed through 1960.[444] While the exact assignment of excited states of uranyl ion is unclear, it is thought that the transitions in the visible and near-ultraviolet involve excitation of a π bonding electron to a nonbonding orbital.[444] Since the photochemistry is primarily redox in nature to give U(IV), the nonbonding orbital may then be one largely localized on the uranium atom. Uranyl ion forms a variety of complexes of the chelate type; these show enhanced intensity of the absorption bands and often enhanced photoredox quantum yields.

The material of this section will be limited to work since 1960 (with oxalate containing systems covered in section III). Some further work on the photoreduction of uranyl ion has been reported,[445,446] and several papers relate to the photosensitivity of uranyl ion in phosphate, especially tributyl phosphate media.[447–449] In nitrate-containing systems, photolytically produced U(IV) appears to be oxidized by oxygen, so that in the presence of tributyl phosphate the net reaction is that of a uranyl ion catalyzed photooxidation of the phosphate ester.[448] However, it is possible that the primary photochemical act in these various systems produces U(V), which then disproportionates; there is some recent evidence on the generation of U(V) intermediates.[450,451]

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(434) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, **71**, 3802 (1967).

(435) J. J. Weiss, *J. Chem. Phys.*, 42, 3127 (1965).

(436) T. W. Martin, A. Henshall, and R. C. Gross, *J. Am. Chem. Soc.*, **85**, 113 (1963).

(437) T. W. Martin, J. M. Burk, and A. Henshall, *ibid.*, **88**, 1097 (1966).

(438) L. J. Heidt and A. F. McMillan, *ibid.*, **76**, 2135 (1954).

(439) L. J. Heidt, *Proc. Am. Acad. Arts Sci.*, **79**, 228 (1951).

(440) F. H. C. Edgecombe and R. G. W. Norrish, *Nature*, **197**, 282 (1963).

(441) F. Hussain and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A275**, 161 (1963).

(442) A. J. Cohen and H. L. Smith, *Science*, **137**, 981 (1962).

(443) J. S. Stroud, *J. Chem. Phys.*, **35**, 844 (1961).

(444) E. Rabinowitch and R. L. Belford, Ed., "Spectroscopy and Photochemistry of Uranyl Compounds," Vol. 1, "Monographs on Nuclear Energy, Chemistry Division," The Macmillan Co., New York, N. Y., 1964.

(445) J. L. Carroll, R. E. Burns, and H. D. Warren, U. S. Atomic Energy Commission, Report HW-70543, 1961.

(446) J. Sobkowski, NASA Accession No. N65-36638, Report No. 359/64, 1964; *Chem. Abstr.*, **66**, 80741*t* (1967).

(447) A. S. Kertes and M. Halpern, *J. Inorg. Nucl. Chem.*, **19**, 359 (1961).

(448) J. Brzeski, *Nukleonika*, **6**, 649 (1961).

(449) V. G. Knyaginina and O. G. Nemkova, *Radiokhimiya*, **1**, 665 (1959); *Chem. Abstr.*, **54**, 17135*e* (1960).

(450) B. J. Masters and L. L. Schwartz, *J. Am. Chem. Soc.*, **83**, 2620 (1961).

(451) C. H. Brubaker and J. D. Hoeschele, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967.

Probably related to the photochemistry of oxalate- and carboxylate-containing systems (sections III and IX.B) is the uranyl ion sensitized photodecomposition of carboxylic acids. Some recent work indicates that specific complexes (1:1 for malonic acid and 1:1 and 2:1 for succinic and glutaric acids) are the photosensitive species.[452] As a case where U(IV) production is observed, the following over-all reaction has been found to take place.[453]

$$UO_2^{2+} + (CH_3)_2C(OH)(COOH) + 2H^+ \xrightarrow{h\nu} U^{IV} + (CH_3)_2CO + CO_2 + 2H_2O \quad (85)$$

Some U(IV) photochemistry has been reported recently. The 1:1 U(IV)–citrate complex, taken to be $U(OH)_2(H\text{–}cit)^-$, is photooxidized to U(VI) in the presence of oxygen;[454] U(V) and a hydrogen atom are proposed as the primary photolysis products. Again, a possibility not eliminated is that photoelectron production occurs instead. Photoreduction of U(IV) is reported to occur when UCl_4 is photolyzed at $\lesssim 300$ mμ in a low-temperature glass; the product is the intensely colored UCl_3.[455]

C. LANTHANIDES OTHER THAN CERIUM

There is evidence that lanthanides, which, like cerium, have more than one stable oxidation state, also show photoredox behavior. Photolysis of aqueous Eu^{2+} at 366 mμ leads to Eu^{3+} and hydrogen,[456] with a quantum yield of 0.20; the primary process could be one of photoelectron production. Perhaps similarly, Eu^{2+} and Sm^{3+} interact in the crystalline state to give Eu^{3+} and Sm^{2+}, under irradiation at 366 mμ.[457] Irradiation at 254 mμ of Tm^{3+} in liquid $BaBr_2$ leads to Tm^{2+} production[458] and similarly, photoreduction of Nd^{3+} to Nd^{2+} has been reported to occur in crystalline CaF_2.[459]

XIV. PHOTOACTIVE LIGAND CHROMOPHORES. PHOTOCHROMISM

A. PHOTOACTIVE LIGAND CHROMOPHORES

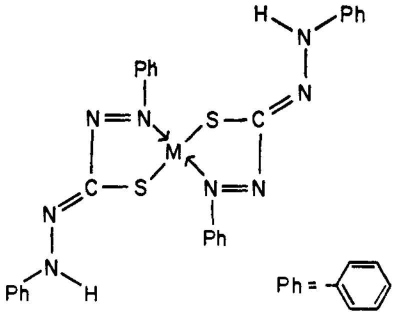
There is a large number of coordination compounds in which a ligand forms a ring containing the metal atom. Ligands which form such chelate complexes are, for example, β-diketone (such as acetylacetone), maleonitriledithiolate (MNT), and related ligands,[460,461] the familiar bidentate and polydentate amines, such as ethylenediamine, ethylenediaminetetraacetate, phenanthroline, and the various macrocyclic coordination compounds.[462] In a number of cases, the formation of the coordinate ring system is accompanied by the appearance of intense absorption, assigned to transitions involving delocalized excited states of the ring. In the case of the iron(II) phenanthroline type complexes, for example, the intense color is attributed to a CTTL charge-transfer excitation[463] (see section IX.A.2). Similar interpretations have been made for the excited states of the MNT and related families of complexes.[460,461]

Intense absorption, if coupled with photosensitivity, can provide dramatic effects, but unfortunately it appears that chelate ring chromophores typically are not very photoactive. The iron phenanthroline and related chelates are essentially insensitive to light[464] (note also Table VI), and likewise the MNT[464] and diketone complexes.

A recently studied system provides an apparent exception to the above rule. The complexes involved are formed according to the reaction

$$M^{n+} + nH_2Dz = M(HDz)_n + 2H^+ \quad (86)$$

where $HDz^- = (C_6H_5N{=}NC(S){=}NNHC_6H_5)^-$. The metal, M, may be divalent Mn, Co, Ni, Pd, Pt, Cu, Zn, Cd, Hg, Pb, or Ag^+, Tl^+, or Bi^{3+}.[465] The structure for Hg^{2+} and Cu^{2+} is square planar.[466,467]



All of these chelates have an intense absorption in the 450–550-mμ region (ε 10^5–10^6) and are typically rather insoluble in solvents generally, and very insoluble in water. The complexes with divalent Pd, Pt, Zn, Cd, Hg, or Pb, and with Ag^+ and Bi^{3+} are sensitive to irradiation in the region of the intense band; the characteristic color change is from a yellow, orange, or green to a blue or violet.

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(452) G. E. Heckler, A. E. Taylor, C. Jensen, D. Percival, R. Jensen, and P. Fung, *J. Phys. Chem.*, **67**, 1 (1963).

(453) K. Pan and W. K. Wong, *J. Chinese Chem. Soc.* (Taiwan), **8**, 1 (1961); **7**, 20 (1960).

(454) A. Adams and T. D. Smith, *J. Chem. Soc.*, 4846 (1960).

(455) S. Freed and K. M. Sancier, *J. Chem. Phys.*, **22**, 928 (1954).

(456) D. L. Douglas and D. M. Yost, *ibid.*, **17**, 1345 (1949); **18**, 1687 (1950).

(457) P. P. Feofilov, *Opt. i Spectroskopiya*, **12**, 531 (1962); *Opt. Spectry.* (USSR), **12**, 296 (1962).

(458) H. L. Pinch, *J. Am. Chem. Soc.*, **86**, 3167 (1964).

(459) A. A. Kaminskii, V. V. Osiko, and M. M. Fursikov, *Zh. Eksperim. i Teor. Fiz., Pis'ma v Redaktsiyu*, **4**, 92 (1966); *Chem. Abstr.*, **66**, 24385*t* (1967).

(460) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(461) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(462) D. H. Busch, "Alfred Werner 1866–1919," Verlag Helvetica Chimica Acta, Basel 7, Switzerland, 1967, p 174.

(463) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

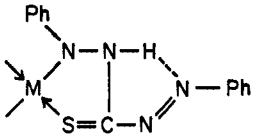
(464) A. W. Adamson and P. Fleischauer, unpublished work.

(465) L. S. Meriwether, E. C. Breitner, and C. L. Sloan, *J. Am. Chem. Soc.*, **87**, 4441 (1965).

(466) M. M. Harding, *J. Chem. Soc.*, 4136 (1958).

(467) R. F. Bryan and P. M. Knopf, *Proc. Chem. Soc.*, 203 (1961).

The photosensitive systems are photochromic, reverting in the dark, and it appears that the reaction is one of a tautomeric change in the ligand structure.[468]



Half-lives for the dark return range from about 1 min for $Hg(HDz)_2$ to less than 1 sec for $Zn(HDz)_2$; in the case of the former, the rate in benzene or tetrahydrofuran solution is first order in complex (and in added water). The apparent lack of photosensitivity of the other metal complexes could have been merely because the back-reaction was fast enough to give a photostationary state corresponding to negligible net reaction (see below).

The dithizonates are perhaps not an exception to the observation that chelate ring chromophoric centers are not photoactive. The reaction in this case involves a change in the ligand rather than any direct change in the state of the metal. This is evidenced by the fact that the behavior of this family of complexes is relatively insensitive to the nature of the metal.

It is possible, however, by irradiation of a ligand chromophore to produce changes at the central metal ion. The complex $Co(NH_3)_5(TSA)^{2+}$, where TSA denotes *trans*-stilbene-4-carboxylate, shows an absorption spectrum which has a d–d band at about 500 mμ, which is normal and characteristic for acetatopentaamminecobalt(III) complexes, and an intense band at about 350 mμ, which is essentially that of the free TSA ligand.[469] Irradiation at 350 mμ, or in the stilbene absorption region, leads to photoredox decomposition of the complex. The products include Co(II), free TSA, and either oxidized ammonia or water. The chromophore in this case is intrinsic to the ligand (and the transition has been assigned on the basis of a molecular orbital analysis[470]), so that an intramolecular energy transfer has occurred.

B. PHOTOCHROMISM

Photochromism or phototropism has been observed in a large number of systems; so far, however, these are mostly either organic or solid-state inorganic. The subject has been reviewed recently.[22] As mentioned in the Introduction, the essential requirement is that the photochemical reaction be complemented by a reverse thermal process, so that the color change induced by light reverts in the dark. The prototype reaction is thus

$$A \underset{k_{-1}}{\overset{h\nu,\,k_1}{\rightleftarrows}} B \tag{87}$$

If a system is photochromic, it must be possible to reach a photostationary state in which the photochemical forward reaction is balanced by the reverse dark reaction. The thermodynamic equilibrium constant, $K = k_1/k_{-1}$, can then be compared to a corresponding pseudo-equilibrium constant for the photostationary state. The forward rate is now

$$d[A]/dt = k_1(\text{app})[A] = k_1[A] + (dE_A/dt)\phi_A/V \tag{88}$$

where dE_A/dt is the rate of light absorption by A in einsteins per second, and V is the volume of the solution irradiated. The photostationary constant is then

$$K_s = k_1(\text{app})/k_{-1} \tag{89}$$

In the limiting case where the incident light is not appreciably attenuated by absorption, dE_A/dt will be equal to $\alpha I_0\epsilon_A[A]$, where the constant α is determined by the irradiation geometry, and I_0 is the incident intensity in einsteins/second. If, further, the forward thermal rate is negligible, then

$$K_s = (\alpha\epsilon_A\phi_A I_0/V)/k_{-1} \tag{90}$$

Thus labile systems for which k_{-1} is large cannot be expected to show appreciable net reaction at photostationary equilibrium; that is, irradiation of A will appear to produce no B.

A further possibility, fairly common with coordination compounds, is that the back-reaction may also be photoaccelerated, and, in the limiting case in which this dominates over the thermal back-reaction, eq 90 becomes

$$K_s = \epsilon_A\phi_A/\epsilon_B\phi_B \tag{91}$$

As a simple example, $Cr(C_2O_4)_3^{3-}$ photoracemizes, and, if a racemic solution were to be irradiated with circularly polarized light, a photostationary state would be reached which would have a net optical activity.[471] Here $K_s = \epsilon_A/\epsilon_B$, since the quantum yields would be expected to be identical.

Since the photostationary state differs from the equilibrium one, a free-energy difference exists, defined as $\Delta G_s = RT \ln (K_s/K)$,[471] and this can be written as a sum of enthalpic and entropic contributions

$$\Delta G_s = \Delta H_s - T\Delta S_s \tag{92}$$

While the photostationary state is a dissipative one to which simple second-law equations do not apply, the above formulation allows some distinctions to be made between various types of photochromic systems. Thus the example above of $Cr(C_2O_4)_3^{3-}$ is one for which ΔG_s

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(468) L. S. Meriwether, E. C. Breitner, and N. B. Colthup, *J. Am. Chem. Soc.*, **87**, 4448 (1965).

(469) A. W. Adamson, A. Vogler, and I. R. Lantzke, unpublished results.

(470) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(471) A. W. Adamson, A. Chen, and W. L. Waltz, Proceedings of the Xth International Conference on Coordination Chemistry, Tokyo and Nikko, Japan, Sept 12–16, 1967.

derives entirely from the entropy term; that is, the difference between a racemic and a nonracemic mixture is in the entropy rather than the enthalpy content.

Several systems involving coordination compounds have been found to be photochromic[36,192,242] in addition to the dithizonate family. Thus irradiation of 0.01 M $Cr(CN)_6^{3-}$ in 0.1 M cyanide ion at about 10^{-4} einstein/(l. sec) produces a photostationary state corresponding to mainly $Cr(CN)_3(H_2O)_3^{2-}$, and in the dark the system reverts to mainly $Cr(CN)_4(H_2O)_2^-$.[36] Similarly, $Co(CN)_5I^{3-}$ in concentrated iodide solution photolyzes largely to $Co(CN)_5(H_2O)^{2-}$ at 500 mμ and returns almost completely to the starting material in the dark.[36] Since heats of substitution tend to be rather small for coordination compounds,[1] ΔG_s for these systems must be mainly entropic in nature.[471] Also again $K_s \simeq \epsilon_A/\epsilon_B$ since the photostationary displacement from equilibrium is due primarily to extinction coefficient differences at the irradiating wavelength and not to quantum yield differences.

The matter of energy production from photochromic systems is of potential interest. Clearly, it would be desirable to find cases where ΔG_s was due primarily to energy rather than to entropy storage. This is not likely to be the case with photosubstitution reactions but could be so with photoredox systems. As an example, there exists the possibility of a cycle of the type

$$A \xrightarrow{h\nu} A^+ + e^-(aq) \qquad (93)$$

$$\text{Oxid} + e^-(aq) \longrightarrow \text{Red} \qquad (94)$$

where Oxid and Red denote the oxidized and reduced forms of some nonphotolytic redox couple. If the reaction between A^+ and Red is slow, then the possibility of a photochemical cell exists. So far none involving coordination compounds seems to have been established, although systems in which A is $Fe(CN)_6^{4-}$ and Oxid is a redox dye such as methylene blue have shown some indications of conforming to the desired pattern.[472]

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[472] A. Kirk and A. W. Adamson, unpublished work.