in all the solvents tried. It did not melt below 320° and was paramagnetic, with a magnetic moment of 4.5 Bohr magnetons at 24°.

Anal. Calcd. for $C_{20}H_{20}N_4O_4S_2Fe$: C, 48.0; H, 4.0; Fe, 11.2. Found: C, 47.7; H, 4.2; Fe, 11.0.

Bis-(α-pyridylmethylene)-ethylene-bis-(thioglycolic Hydrazide (XXVII).—Freshly distilled pyridine-2-aldehyde (2.2 g.) was added to a warmed suspension of ethylene bis-thioglycolic hydrazide (2.4 g.) in ethanol (20 ml.). The solid soon dissolved and then after a few minutes the crystalline product separated. It was recrystallized from much ethanol and thus obtained as a white powder, m.p. 190°.

Anal. Calcd. for $C_{18}H_{20}N_6O_2S_2$: C, 51.9; H, 4.8. Found: C, 51.7; H, 4.9.

Bis-(α-pyridylmethylene-(ethylene-bis-(thioglycolic Hydrazide) Iron(II) Thiocyanate Dihydrate (XXX).—A solution of iron(II) sulfate heptahydrate (0.2 g.) in a little water was added to a solution of XXVII (0.3 g.) in dimethylformamide (10 ml.). Addition of saturated aqueous potassium thiocyanate solution (5 ml.) to the intensely red colored solution led to precipitation of a solid which was recrystallized from ethanol and thus obtained in dark red needles, m.p. 210°.

Anal. Calcd. for $C_{20}H_{20}N_8O_2S_4Fe{\cdot}2H_2O$: C, 38.5; H, 3.8; Fe, 9.0. Found: C, 38.3; H, 3.5; Fe, 8.6.

Ethylene-bis-(thioglycolic-α-pyridylmethylamide) (XXXI).—Ethyl thioglycolate (5.32 g.) and 2-aminomethylpyridine (4.32 g.) were heated together at 180° for 6 hours. The solid which separated on cooling (80%) was recrystallized several times from ethanol and obtained in colorless needles, m.p. 155°.

Anal. Calcd. for $C_{18}H_{22}N_4O_2S_2$: C, 55.4; H, 5.6. Found: C, 55.4; H, 5.8.

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SYDNEY, AUSTRALIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Photochemistry of Complex Ions. I. Some Photochemical Reactions of Aqueous $PtBr_6^{-2}$, $Mo(CN)_8^{-4}$ and Various Co(III) and Cr(III) Complex Ions

BY ARTHUR W. ADAMSON AND A. H. SPORER

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Studies have been made of the photochemistry of aqueous $Co(NH_3)_6^{+3}$, $Co(NH_3)_5X^{+2}$ (X = SCN, Cl, I), $Co(CN)_5X^{-3}$ (X = CN, Cl, Br, I), $Co(C_2O_4)_3^{-3}$, $Cr(NH_3)_5SCN^{+2}$, $Cr(NH_3)_2(SCN)_4^{-}$, $Cr(C_2O_4)_3^{-3}$, $Mo(CN)_8^{-4}$, and the exchange system $PtBr_6^{-2}$–Br^-. Quantum yields were obtained for the oxidation–reduction decompositions, aquation, racemization or exchange reactions that occurred, usually for two wave lengths, one in the ligand field band region and one in the electron transfer band region of the absorption spectra. The results are interpreted to indicate that the chemical nature of the excited state is qualitatively independent of the wave length of the light used. On the other hand, the net consequence of light absorption depends upon which of several possible courses is taken subsequent to the formation of the primary excited state.

The present investigation represents the initial effort of a program to develop a more quantitative understanding of the photochemistry of complex ions, and of its relationship to the thermal reactions of such ions and to the current interpretations of their spectra.

The general photosensitivity of Werner type complex ions is well known, of course, although only a scattering of quantitative observations appear in the literature. These include the reports of Linhard and of Schwartz and co-workers[1,2] on certain acido-amines of Co(III) and Cr(III), and on various hexacyano complexes. Recent investigations of the photochemical aquation of ferrocyanide ion have been made by Emschwiller.[3] Vranek[4] has studied the photo-decomposition of $Co(C_2O_4)_3^{-3}$, Taube[5] noted the photochemical exchange of Cl^- with $PtCl_6^{-2}$, and Plane and Hunt[6] recently found very low quantum yields for the photochemical exchange of H_2O^{18} with hexaaquochromic ion. Finally, fairly extensive studies have been made of the photochemical decomposition of the uranyl oxalate, ferric oxalate and mercuric oxalate complexes.[7,8]

Linhard, *et al.*,[1] observing that light of 366 mμ led to production of I_2 and of Na from the corresponding acidopentaminecobaltic complexes, concluded that the primary act involved an electron transfer from ligand to metal, in accord with the general interpretation of the near ultraviolet, high-intensity bands as being electron transfer in type. Williams[9] has similarly interpreted such bands in the case of Fe(II) and Fe(III) complexes.

On the other hand, the low intensity bands, usually in the visible, observed with most first row transition metal complexes are interpreted in terms of transitions between 3d levels whose degeneracy has been partially removed by the ligand field.[10,11] Thus, for an octahedral field, the d_{xy}, d_{xz} and d_{yz} orbitals, whose electron density is directed away from the ligand positions, are lowered in energy relative to the d_{x^2} and $d_{x^2-y^2}$ orbitals, whose electron density is directed toward ligand positions. The absorption of light in the ligand field band is thus thought to involve promotion of an electron from a T_{2g} to an E_{2g} 3d orbital, and might be expected to lead to a repulsion between the ligand and the metal ion.

Qualitatively, then, it might be expected that absorption in the region of an electron transfer band should lead to a oxidation–reduction process, and absorption in the region of a ligand field band, to a displacement of the ligand and hence to a sub-

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[7] A. C. Parker, *Proc. Roy. Soc. (London)*, **220**, 104 (1952).

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[10] J. Bjerrum, C. J. Balhousen and K. Jorgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

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stitution process. One of the purposes of the present investigation has been to test this conclusion.

Experimental

Preparation of Compounds.—$[Co(NH_3)_6](NO_3)_3$ was prepared according to "Inorganic Syntheses,"[12] $[Co(NH_3)_5Cl]Cl_2$, from the carbonato tetramine by the method of Walton,[13] the corresponding Cl^{36} labeled compound by heating $[Co(NH_3)_5H_2O]Cl_3$ according to the procedure of Linhard and Weigel,[1] and $[Co(NH_3)_5Cl^{36}]^{+2}$ in Cl^- free solution by removal of the free Cl^- with a stoichiometric amount of silver nitrate. $[Co(NH_3)_5I]Cl_2$ was prepared according to Linhard and Weigel, and $[Co(NH_3)_5SCN](ClO_4)_2$, as described previously[14]; Co^{60}-labeled complex was similarly obtained. The series $K_3[Co(CN)_5X]$, X = CN, Cl, Br, I, was prepared according to procedures previously described,[15,16] as was $K_4Mo(CN)_8$. $K_3CO(C_2O_4)_3$ was obtained according to "Inorganic Syntheses,"[17] and its resolution by strychnine precipitation as described by Johnson and Mead.[18]

$K_3Cr(C_2O_4)_3$ and $[Cr(NH_3)_5SCN](ClO_4)_2$ were obtained by the procedures in "Inorganic Syntheses,"[17] and as given by Adamson and Wilkins,[14] respectively. Potassium Reineckate, $K[Cr(NH_3)_2(SCN)_4]$, was of C.P. grade, further purified by recrystallizations from warm water. Finally, K_2PtBr_6 and K_2PtBr_4 were prepared according to Gutbier and Bauriedel[19] and Biilman and Anderson.[20] In this last case, the preparation involves reduction of $PtBr_6^{-2}$ by oxalate ion, and it might be noted that it is important to avoid adding excess oxalate even though reduction may not be complete; any unreacted bromoplatinate should be filtered out of the hot solution before letting it cool. In general purity was checked by comparison of spectra with those of analyzed compounds and was considered satisfactory in all cases, except for the $K_3Co(CN)_5Cl$, which probably contained some hexacyanide.

Apparatus.—The solutions to be studied were placed in 1 cm. spectrophotometer cells and exposed to light of wave length selected by the use either of Baird-atomic interference filters or of appropriate glass filters, or of combinations of the two such that only the desired "window" was present. The light source was an AH-6 General Electric high pressure, water cooled mercury lamp. Light intensities were measured by the use of the ferric oxalate actinometric solution[7] or by means of a bolometer. This last consisted of a 5-cm. copper disk, blackened on one side, and having a 10^5 ohm thermistor mounted on the back. The assembly was placed in a Dewar flask equipped with optically flat Pyrex windows, and the radiation intensity was determined from the rate of temperature rise of the disk, as followed by the change in resistance of the thermistor. A Wheatstone bridge circuit was employed, using a Honeywell vacuum tube null indicator. Intensities obtained by means of the bolometer were in excellent agreement with those using the actinometric solution. The intensity of absorbed light, needed for quantum yield estimates, was obtained from the difference in bolometer readings for the cell filled with water and with the solution in question. Values ranged from 10^{-6} to 10^{-7} einsteins per minute (in 10 cc. of solution).

Absorption spectra were obtained by means of a Cary recording spectrophotometer and radioactivity measurements were made by means of either a thin window G.M. counter or a scintillation counter, according to the type of radiation involved. Optical rotations were obtained using green light, and a J. and J. Frik polarimeter. Fluorescence, in the case of $Co(CN)_5Cl^{-3}$, was checked using dust free solutions and an adaptation of a BS Light Scattering Photometer (Phoenix Precision Instrument Co., Phil.).

Procedures.—The general procedure consisted of exposing a solution of known concentration to light of chosen wave length, determining the net light absorption, and, after suitable intervals, the type and amount of reaction. With the $Co(CN)_5X^{-3}$ series this was done by following the production of free cyanide ion by means of a Liebig[21] titration, and also by the change in absorption spectra with time. The decomposition of $Co(C_2O_4)_3^{-3}$ was followed both by this last means and by the amount of CoC_2O_4 formed, using labeled complex; racemization was determined from the loss of optical activity, corrected for decomposition. The aquation of $Co(NH_3)_5Cl^{+2}$ was followed by using labeled complex and precipitating $AgCl^{36}$ which was then counted; the production of free thiocyanate ion, in the case of the various thiocyanato complexes, was followed by means of a colorimetric test using ferric ion.[14] The amount of aquo complex and of Co(II) formed from $Co(NH_3)_5SCN^{+2}$ was determined by using Co^{60}-labeled complex, removing unreacted complex by a series of precipitations of its perchlorate salt (see ref. 14), and then precipitating the aquo complex as the ferricyanide salt and Co(II) as the hydroxide.

In those cases where I_2 was produced, standard thiosulfate was added before irradiation, and then back titrated; this procedure was followed to avoid the decrease in apparent quantum yield that would otherwise have resulted from light absorption by I_2. In general, where the light absorption by the products was much less than that of the initial species, the reactions were followed to near completion and good first-order rate plots were obtained. In other cases, as with the chloro and thiocyanato pentamines, it was necessary to use initial rates, based on the first few per cent. of reaction.

Where oxidation–reduction decompositions occurred, the irradiated solutions were kept slightly acid by means of acetic or hydrochloric acid; this was done to prevent clouding as a result of $Co(OH)_2$ precipitation rather than because of any obvious effect of *p*H on the photochemical reaction itself.

For the photo-exchange of Br^- with $PtBr_6^{-2}$, labeled complex was prepared by photochemical exchange, in concentrated solution, with Br^{80} ion, followed by precipitation as K_2PtBr_6. The radiobromide was obtained by means of a Szilard–Chalmers reaction on ethylene bromide, using a Ra–Be neutron source. In the photochemical exchange runs, separation was accomplished by precipitating out Cs_2PtBr_6 and then AgBr from the exchange solution, and counting these as solids, after allowing sufficient time for equilibration of the Br^{80} isomers.

Results

The results are summarized in Tables I and II, except for those on the decomposition of $Mo(CN)_8^{-4}$ and the $PtBr_6^{-2}$–Br^- exchange, discussed separately. For the convenience of the reader, the absorption maxima and corresponding extinction coefficients are given for each compound.

Where absorption by products did not interfere, good first-order rate plots generally were obtained. Thus Fig. 1 shows the progressive change in absorption spectrum of $Co(CN)_5I^{-3}$, terminating in that of $Co(CN)_5H_2O^{-2}$, and Fig. 2, the rate plots for the various members of the $Co(CN)_5X^{-3}$ series. In the case of $Mo(CN)_8^{-4}$, irradiation led to the production of free cyanide ion, presumably through aquation reactions. The quantum yield at 370 mμ was about unity after sufficient irradiation for one cyanide ion to be produced per molybdenum. A complicated reaction sequence was clearly involved, however, since the original yellow solution developed a red color on irradiation, which faded on removal of the solution from the light, and which, on further exposure, changed over to green, and, finally, to a light blue. The green stage cor-

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[12] W. C. Fernelius, Ed., "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 218.

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[18] C. H. Johnson and H. Mead, *Trans. Faraday Soc.*, **29**, 626 (1923).

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[20] E. Biilman and A. C. Anderson, *ibid.*, **36**, 1566 (1903).

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TABLE I

PHOTOCHEMICAL REACTIONS OF Co(III) COMPLEXES

No.	System	Abs. max. and extinct. coeff. (mμ/ε)		Nature of reaction on which φ based	φ
12	0.014 M $Co(NH_3)_6^{+3}$	475/55; 340/49	370	No reaction obsd.	(<0.01)
	Same, in 0.08 M KI	475/55; 340/98[a]	370	I_2 produced	0.77
			500	I_2 produced	.0015
7	0.01 M $Co(NH_3)_5Cl^{+2}$	530/48; 360/45	370	Aquation, trace Co^{++}	.052
			550	Aquation	.0066
11	Same, in 0.08 M KI, 0.0033 M S_2O_3	530/48; 360/80*	370	I_2 produced	.40
			550	I_2 produced	.009
1	0.0025 M $Co(NH_3)_5SCN^{+2}$	500/170; 330/1000	370	SCN^- produced (aquation/Co^{++} = 0.47)	.31
			550	SCN^- produced (aquation/Co^{++} = 4.1)	.0034
13	.01 M $Co(NH_3)_5I^{+2}$	585/75; 380/1880	370	I_2 produced	3.0
			550	I_2 produced (very little aquation)	0.47
8	.006 M $Co(CN)_6^{-3}$	310/190	370	Aquation	.89
5	.005 M $Co(CN)_5Cl^{-3}$	310/128; 380/94	370	Aquation	.25
10	.005 M $Co(CN)_5Br^{-3}$	395/170	370	Aquation	.69
6	.006 M $Co(CN)_5I^{-3}$	330/2630; 500/87	370	Aquation	.95
			550	Aquation	.67
4	.1 M $Co(C_2O_4)_3^{-3}$	420/220; 605/170	370	Co^{++}, CO_2 produced	1.0
			550	Co^{++}, CO_2 produced	0.0069
	(*levo*-complex)		550	No photoracemization	(<0.1)

[a] For comparison purposes; no maximum present.

responded to about one cyanide released per molybdenum.

The photochemical exchange between $PtBr_6^{-2}$ and Br^- clearly involved a chain reaction, since quantum yields up to 500 were found. While linear McKay plots were obtained, a rather high zero time exchange generally was observed, and it was difficult to achieve good reproducibility, especially at high quantum yields. This is illustrated in Fig. 3, showing the variation of ϕ with light intensity, at 450 mμ; the lines are drawn with a slope of one half. At high light intensities, reproducibility was better, and Fig. 4 shows the variation of quantum yield with complex concentration, under such conditions. The behavior at 360 mμ appeared to be the same as at 450 mμ and similar quantum yields were obtained. (The absorption spectrum of $PtBr_6^{-2}$ has a maximum at 310 mμ, with ε 1.6 × 10^4, a shoulder at 360 mμ, with ε 6500; at 450 mμ, ε 920). No detectable net decomposition occurred; specifically, the quantum yield for $PtBr_4^{-2}$ or Br_2 production was less than 0.1. The addition of scavengers such as allyl chloride and acetone did not affect the quantum yields for exchange. No specific test was made for possible effects of dissolved oxygen.

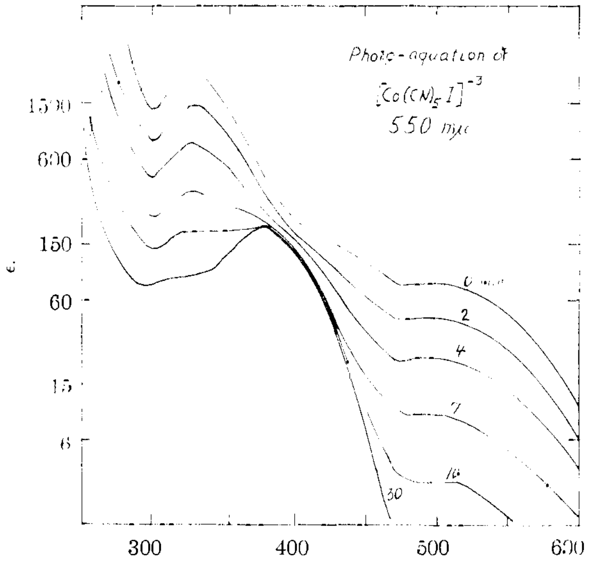

Fig. 1.—Photo-aquation of $[Co(CN)_5X]^{-3}$ at 550 mμ.

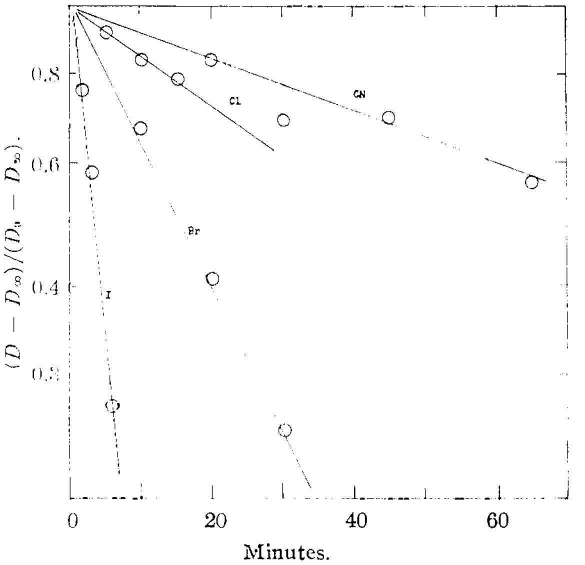

Fig. 2.—Photo-aquation of $[Co(CN)_5X]^{-3}$ at 370 mμ (X, wave length at which D was measured, intensity of absorbed light in einsteins/min. × 10^6): (CN, 380, 0.56), (Cl, 380, 3.6), (Br, 380, 2.9), (I, 500, 330, 6.5).

TABLE II

PHOTOCHEMICAL REACTIONS OF Cr(III) COMPLEXES

No.	System	Abs. max. and extinct. coeff. ($m\mu/\epsilon$)	Wave length, $m\mu$	Nature of reaction on which ϕ based	ϕ
2	0.0049 M $Cr(NH_3)_5SCN^{+2}$	300/6000; 500/80	550	Aquation	0.060
			370	Aquation	0.083
3	0.0078 M $Co(NH_3)_2(SCN)_4^-$	390/91; 520/103	370	Aquation	1.4
			550	Aquation	0.7
	Same, in methanol	(Same)	370	SCN^- formed	1.4
			550	SCN^- formed	0.5
	Same, in nitromethane	390/92; 520/118	370	SCN^- formed	0.47
9	0.01 M $Cr(C_2O_4)_3^{-3}$	420/97; 570/75	370	No reaction	<0.1
			550	No reaction	<0.01

Discussion

The $PtBr_6^{-2}$-Br^- Exchange System.—The data clearly indicate that a chain mechanism is operating, and the scheme (1)-(2) is proposed as a possibility

$$PtBr_6^{-2} \underset{k_2}{\overset{\phi_1}{\rightleftharpoons}} PtBr_5^{-2} + Br \qquad (1)$$

$$PtBr_5^{-2} + PtBr_6^{-2} \overset{k_3}{\rightleftharpoons} PtBr_6^{-2} + PtBr_5^{-2} \qquad (2)$$

The radicals $PtBr_5^{-2}$ and Br are supposed to exchange rapidly with Br^- ion. Reaction 2, the atom transfer process between $PtBr_6^{-2}$ and $PtBr_5^{-2}$ is proposed as the chain carrying reaction rather than one of the possibilities involving Br atoms because of the lack of effect of scavengers on the quantum yield. Also, the reverse of (1) is taken to be the termination step, rather than a disproportionation of $PtBr_5^{-2}$ into $PtBr_4^{-2}$ and $PtBr_6^{-2}$, such as was invoked by Taube[5] in the case of $PtCl_5^{-2}$, because of the absence of any appreciable net decomposition of the complex.

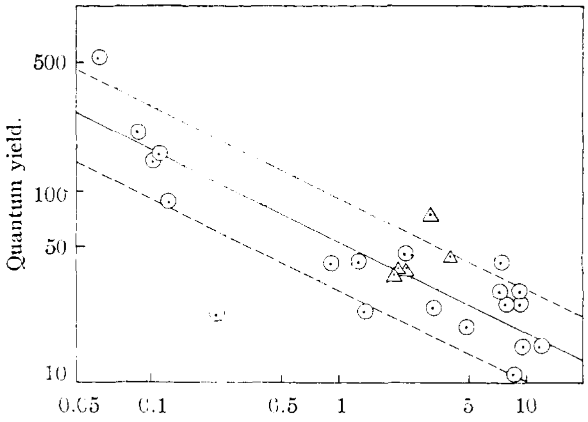

Fig. 3.—Quantum yield as a function of light intensity in the $PtBr_6^{-2}$-Br^- system.

The scheme leads to rate expression (3) for the quantum yield for exchange

$$\phi = \phi_1 + K(PtBr_6^{-2})/I^{1/2} \qquad (3)$$

Here, ϕ_1 denotes the quantum yield for exchange through the reverse of (1), and K is given by $k_3(\phi_1/k_2)^{1/2}$. Since ϕ_1 must be less than unity, equation (3) predicts that ϕ should vary approximately according to the second term, as was observed experimentally (see Figs. 3 and 4). On the other hand, other schemes lead to similar rate laws, so that the above is only illustrative and not proven. The inverse square root dependence of ϕ on light intensity does require, however, that the termination step be bimolecular in radical or chain carrying species.

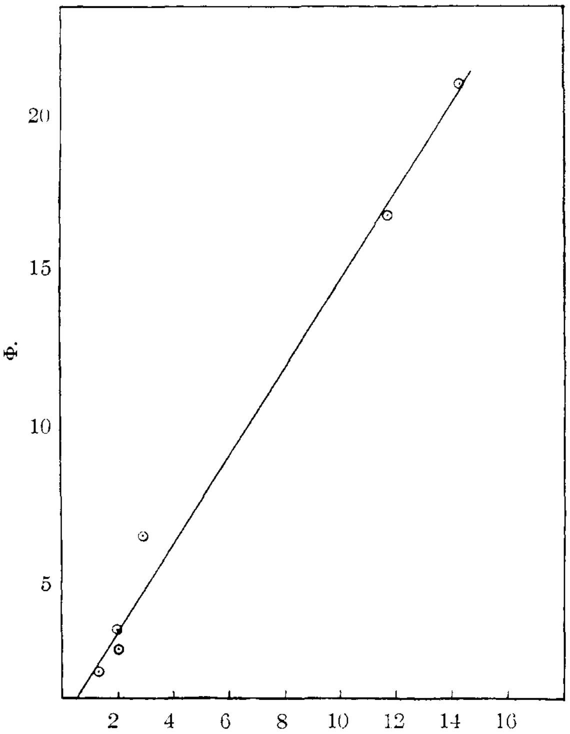

Fig. 4.—Quantum yield as a function of $PtBr_6^{-2}$ concentration.

Results with Co(III) and Cr(III) Species.—The first systems studied, as marked by the sequence numbers in the tables, tended to bear out the initial hypothesis, namely, that absorption in the region of an electron transfer band should lead to a homolytic breaking of the metal-ligand bond and hence to oxidation-reduction decompositions, while absorption in the region of a ligand field band should lead to an ionic splitting and hence to substitution reactions. Thus, in the photochemical decomposition of $Co(NH_3)_5SCN^{+2}$, if aquo-complex formation were attributed to ionic splitting and Co(II) formation to homolytic splitting, then the ratio of ionic to homolytic fission rose from 0.47 for light of 370 mμ to 4.1 for light of 350 mμ. Also, for the series $Co(CN)_5X^{-3}$ only the aquation product, *i.e.*, supposedly ionic splitting, resulted even though ultraviolet light was used, in accord with the ligand field character of the absorption band involved. Finally, the photochemical $PtBr_6^{-2}$–Br^- exchange clearly involved a homolytic splitting of a Pt–Br bond, in accord with the electron transfer character of the band.

With further work, however, serious questions developed. In the case of $Co(C_2O_4)_3^{-3}$, the intramolecular racemization reaction is considerably faster than the thermal decomposition[18]; the racemization apparently involves the sequential or simultaneous loosening of the ends of two oxalate groups... it is quite sensitive to the presence of di- and trivalent positive ions and would be expected to be readily induced by the type of ligand repulsion present in E_{2g} state. Our finding, however, was that light in the region of the crystal field band led to oxidation–reduction decomposition rather than to racemization.

In the case of the series $Co(CN)_5X^{-3}$, the quantum yields for aquation decreased in the order I, CN, Br, Cl, which is *not* the order of the spectrochemical series, as might be expected if the primary act were an ionic fission, but *is* the order of increasing difficulty of oxidation of the ligand. This suggests that the primary act is a homolytic fission, even though the final product is an aquocomplex and the absorption bands involved are of the ligand field type. Furthermore, the results of series 11, 12 and 13 made it clear that oxidation–reduction reactions could result from light absorption in the region of a ligand field band, if an easily oxidizable ion was attached to the metal ion. Thus yellow light led to a very efficient oxidation–reduction decomposition of $Co(NH_3)_5I^{+2}$, even though aquation is faster, thermally (in the absence of I^- ion, as was the case here.)[22] Also striking was the observation that yellow light, which caused aquation of $Co(NH_3)_5Cl^{+2}$ with a ϕ of 0.007, led to production of I_2 when KI was present, with a ϕ of 0.009, and that $Co(NH_3)_6^{+3}$, which was quite stable to yellow light by itself, was again able to sensitize iodide oxidation. The active species in both cases was probably the (complex)(I^-) ion pair, but the point is that the transition involved with light of 550 mμ was presumably still of the ligand field type since ion pairing affected neither the intensity nor the position of the band (from the data of Evans and Nancollas,[23] some 65% of the hexamine complex was present as the ion pair).

It thus appears that in the case of the Co(III) complexes, the presence or absence of photochemical oxidation–reduction reactions depends more on the oxidizability of the ligand than on the wave length used or on whether the band should be designated as electron transfer or ligand field in type. Also, aquation and racemization reactions, even though favored thermally, are not necessarily favored photochemically even though absorption is occurring in a ligand field band.

In the case of the Cr(III) complexes, no oxidation–reduction processes at all were observed, nor were there very large differences in quantum yields for aquation between 370 and 550 mμ. Some solvent effects were studied in the case of potassium reineckate. In water and methanol, the photochemical reaction appeared to follow exactly the same course as the thermal, namely, replacement of thiocyanate (up to two or more per chromium) by solvent; in the thermal reaction the loss of the first thiocyanate is followed by the more rapid loss of at least one more,[24] and the ϕ value of 1.4 in methanol indicates that a similar situation prevailed photochemically. Interestingly, however, there was an efficient reaction in nitromethane, leading to release of thiocyanate ion, although the complex is stable for weeks at 80° in this solvent, in the dark. Finally, the photochemical aquation of $Mo(CN)_8^{-4}$ is assumed to follow the same mechanism as $Co(CN)_6^{-3}$, discussed below.

A Proposed Mechanism for the Photochemical Reactions of the Complex Ions Studied.—It is possible to give a consistent explanation of all of the above results by supposing that the immediate chemical consequence of the absorption of a light quantum is the same in all cases and that the type and yield of final product is determined by competitive subsequent processes.

Specifically, it is supposed that the immediate consequence of light absorption is a homolytic fission.

First Stage Process:

$$M(III)A_5X + h\nu \longrightarrow \longrightarrow M(II)A_5{\cdot}X + \Delta \quad (4)$$

where Δ represents excess energy and is supposed to be dissipated rapidly by exchange of vibrational energy with the surrounding medium, concurrently with a more or less rapid recoil of the ligand from the complex. As suggested by the double arrow, there may be intervening states between the primary excited state and that in which bond fission has occurred. The essential assumption is that the species $M(II)A_5{\cdot}X$ is the common precursor to those formed subsequently.

The fate of $M(II)A_5{\cdot}X$ is now considered to depend upon the energy with which the oxidized ligand recoils from the complex, or, more generally, upon the size of Δ. If Δ is large, then process 6 below is favored, in which sufficient separation between complex and ligand develops for solvent to become interposed so that a net reaction is consummated, while if Δ is small, the opportunity for the return process 5 will be large. The over-all quantum yield is thus determined by that for (4) and by the competition between the second stage processes 5 and 6 and should therefore be lower the more difficultly oxidizable the ligand and the longer the wave length. This is in accord with the sequence for the $Co(CN)_5X^{-3}$ and $Co(NH_3)_5X$

Second Stage Processes:

$$\text{ligand return:} \quad M(II)A_5{\cdot}X \longrightarrow M(III)A_5X + \Delta' \quad \text{(favored if } \Delta \text{ small)} \quad (5)$$

$$\text{separMation:} \quad (II)A_5{\cdot}X \longrightarrow M(II)A_5H_2O){\cdot}X \quad \text{(favored if } \Delta \text{ large)} \quad (6)$$

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($X = I, Cl, NH_3$) series, and with Plane and Hunt's observation of a very low quantum yield for O^{18} exchange between solvent and the hexaaquochromic ion,[6] and with the lack of photodecomposition of $Cr(C_2O_4)_3^{-3}$ found here. Also, of course, the over-all quantum yields tended to decrease with increasing wave length.

The nature of any net reaction is now supposed to be determined by the fate of $M(II)A_5(H_2O)\cdot X$. If electron transfer is energetically favorable and can occur with high frequency, then process 7 may take place; this leads to *aquation* as the net reaction. Alternatively, continued separation of the homolytic fission products may occur, leading to the net oxidation–reduction reaction 8.

Third Stage Processes:

electron return:

$$M(II)A_5(H_2O)\cdot X \longrightarrow M(III)A_5H_2O + X^- \qquad (7)$$

net oxidation-reduction reaction:

$$M(II)A_5(H_2O)\cdot X \longrightarrow M(II) + 5A + X \qquad (8)$$

It is perhaps necessary to emphasize that the above scheme represents stages in a more or less continuous sequence and that the various species are not necessarily true intermediates in thermal equilibrium with the medium.

The significance of the scheme is that the sequence 4, 6, 8 is essentially that for the *thermal* oxidation–reduction decomposition so that it is reasonable to expect that if the thermal process occurs readily, the photochemical one should also. On the other hand, the sequence for photochemical aquation, (4), (6), (7) is undoubtedly *not* that for the thermal aquation or racemization. That is, the stage $M(II)A_5(H_2O)\cdot X$ is not traversed in the thermal process (see ref. 24, 25 for a discussion of the latter). In consequence, the ease of photochemical aquation is supposed to depend upon quite other factors, such as ligand oxidizability, than does the thermal process. One can thus see an explanation for the otherwise puzzling observation that the oxidation–reduction decompositions of $Co(C_2O_3)_4^{-3}$ and of $Co(NH_3)_5I^{+2}$ dominate photochemically, although the racemization and aquation reactions dominate thermally.

If ion pairing is present, oxidation of a Y^- ion can occur by electron transfer either as a second stage or as a third stage process, as shown by (9) and (10).

Second Stage Process:

$$[M(II)A_5\cdot X]Y^- \longrightarrow [M(II)A_5\cdot X^-]Y \longrightarrow M(II) + 5A + X^- + Y \qquad (9)$$

Third Stage Process:

$$[M(II)A_5(H_2O)\cdot X]Y^- \longrightarrow [M(II)A_5(H_2O)\cdot X^- \longrightarrow M(II) + 5A + X^- + Y \qquad (10)$$

If (9) competes favorably with (5), then photo-oxidation can occur even though the complex by itself is quite stable by itself. This explanation accounts for the observed photoöxidation of I^- in the presence of $Co(NH_3)_6^{+3}$ even though the absorption band involved is not one affected by ion pairing.

It is of interest to consider not only why the various reactions occurred, but also why they did not occur, *i.e.*, the cases of low over-all quantum yield. Plane and Hunt[6] observed that there was no fluorescence in the case of $Cr(H_2O)_6^{+3}$ ion, and concluded that energy degradation through a series of radiationless transitions to high vibrational levels occurred. It was qualitatively observed that the complexes studied here did not fluoresce, and in the case of $Co(CN)_5Cl^{-3}$, a quantitative test showed that the fluorescence of visible light, with 370 mμ incident light, was less than 1% of the absorbed intensity. In our systems too it must then have been possible for 50 to 80 kcal. of absorbed energy to be dissipated by the complexes without any net reaction occurring. The proposed scheme suggests that this energy dissipation takes place in steps (as Δ and Δ').

In summary, while the mechanism suggested is largely *ad hoc*, it serves to organize the results on a consistent basis and, moreover, has had predictive value. The study of systems 11 and 12 was undertaken with the expectation that if process 4 were indeed important then induced I^- oxidation should occur. Similarly, induced oxidation of Fe^{++} should occur in the presence of $Co(C_2O_4)^{-3}$; this has not yet been investigated. Even though the mechanism may well be incorrect in detail, our general findings indicate that photochemical reactions of complex ions (at least the ones studied) do not depend much in nature on the wave length of light involved and, in particular, do not depend upon whether the absorption band would be considered to be electron transfer or ligand field in type.

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