tion of solvent will have marked effects on ΔH^* and ΔS^*. Conversely, the fact that $Co(NH_3)_5N_3^{2+}$ and $Cr(H_2O)_5F^{2+}$ correlate in their respective LFER's for aquation, despite anomalously large ΔH^* and ΔS^* values,[6] lends further support to the argument[21] that ΔF^* can be expected to reflect electronic trends more closely than does ΔH^*.

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Photolysis of Oxalatoammine Complexes of Cobalt(III) in Aqueous Solution[1]

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Three mixed oxalatoamminecobalt(III) complexes, $[Co(NH_3)_5C_2O_4H]Cl_2$, $[Co(NH_3)_4C_2O_4]Cl$, and $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$, have been found to undergo photoredox decomposition when irradiated in the near-ultraviolet spectrum or part of the visible spectrum. The photolysis products were Co(II), NH_3, CO_2, and $C_2O_4^{2-}$. The photochemical quantum yield was wavelength dependent and varied gradually with the number of oxalate groups and O–Co coordinative sites. The over-all mechanism is discussed.

Hexamine complexes of Co(III) are known to be unreactive when irradiated in aqueous solution at wavelengths corresponding to $^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. Photochemical quantum yields of less than 10^{-3} have been reported for $Co(NH_3)_6^{3+}$ and $Co[H_2N(CH_2)_{2-4}NH_2]_3^{3+}$ under irradiation in visible and near-ultraviolet spectra around λ_{max} of the d–d absorption bands.[3-8] The photosensitivity of the ammine complexes is enhanced by the replacement of an NH_3 group by a halide, N_3^-, NO_2^-, $RCOO^-$, or SCN^- group.[3,9] The oxalato complexes of many transition metals are among the most light-sensitive complexes known. Tris(oxalato)cobalt(III) has been reported to undergo photoredox decompostion efficiently in aqueous solutions.[10-12] Quantum yields between 0.12 and 0.73 were published for $Co(C_2O_4)_3^{3-}$ on irradiation with light between 313 and 435 mμ.[13,14] Presently we want to report on the photochemical reactions of oxalatoamminecobalt(III) complexes in which the ratio of $C_2O_4^{2-}$ and NH_3 ligands is progressively changed. The following complexes have been photolyzed in aqueous solutions: $[Co(NH_3)_5C_2O_4H]Cl_2$, $[Co(NH_3)_4C_2O_4]Cl$, and $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$. The photochemical quantum yield was determined actinometrically at three different excitation wavelengths in the visible and near-ultraviolet regions of the spectrum. The chemical conversion was followed spectrophotometrically and the influence of the pH on the over-all reaction was considered.

Experimental Section

Synthesis of Complexes.—The three complexes were prepared by procedures previously described in the literature.[15,16] Only the violet isomer of potassium bis(oxalato)diamminecobaltate(III) monohydrate has been used in the present work, rather than the blue isomer which is relatively unstable in aqueous solution. The complexes were repeatedly recrystallized and characterized by comparison with reported spectroscopic properties.

Apparatus and Procedures.—Either a water-cooled 1000-W AH-6 mercury-arc lamp (high pressure) or a Hanovia 450-W arc source was used for irradiation except for quantum yield measurements in which a 125-W medium-pressure Hg-arc lamp (PEK Laboratories) was coupled with a high-intensity Bausch and Lomb monochromator. The irradiation wavelengths were selected by interposing appropriate glass and liquid filters between light source and sample cells or by the monochromator in actinometric measurements. Silica cells (1-cm) were used and absorption spectra were recorded on a Cary Model 15 spectrophotometer.

For preparative scale and product isolation experiments, the 450-W Hanovia arc source was used in conjunction with the immersion-well photochemical reactor in which approximately 225 ml of solution surrounded the water-cooled light source.

The ferric oxalate actinometer of Hatchard and Parker[17] was used to measure light intensities and photochemical quantum yields.

To follow the chemical conversion and to detect eventual dark reactions, 1-cm-path cells containing solutions of appropriate concentration were irradiated for different periods and the changes

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in the uv–visible absorption spectra were monitored at different intervals.

Product Analysis.—Co(II) was identified by its characteristic absorption as $CoCl_4^{2-}$ at 686, 660, and 622 mμ in concentrated HCl solution. The presence of carbon dioxide, ammonia, and oxalate ion was detected by conventional known analytical methods.

Results

The wavelengths corresponding to maximum absorption and the molar decadic extinction coefficients in l. mol^{-1} cm^{-1} as determined from absorption spectra of fresh solutions of known concentration in each complex are: $[Co(NH_3)_5C_2O_4]Cl_2$, 500 mμ (ε 92.5), 348 mμ (sh) (ε 130), and 265 mμ (ε 1.3 × 10^4); $[Co(NH_3)_4C_2O_4]Cl$, 508 mμ (ε 72.8), 350 mμ (ε 80.4), and 265 mμ (ε 1.0 × 10^4); violet $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$, 558 mμ (ε 120.4), 355 mμ (ε 230.5), and 260 mμ (ε 1.5 × 10^4).

The progressive decrease in the characteristic absorption peaks of Co(III) complex on consecutive irradiations and the absence of significant changes in the absorption spectra in the following dark period indicated that the thermal (dark) reactions were negligible. For all three oxalatoammine complexes, the identified photoproducts were Co(II), ammonia, and carbon dioxide. Small amounts of free oxalate ion were also detected. No fully or partly aquated Co(III) complexes were formed. Photodecomposition could easily be made quantitative in each case by irradiating to complete disappearance of the first ligand field absorption band. The primary photoproducts were essentially the same in neutral aqueous solution as in hydrochloric acid.

Figure 1 illustrates the changes in the uv–visible absorption spectrum of $[Co(NH_3)_4C_2O_4]Cl$ in concentrated HCl at different intervals of irradiation. One can easily observe the progressive decrease in intensity of the absorption bands at 350 and 508 mμ with parallel appearance and increase in a structured band in the 600–750 mμ region. The bands at 508 and 350 mμ correspond to the first and the second ligand field transitions of the original complex whereas the 600–750-mμ absorption proves the formation of the blue divalent $CoCl_4^{2-}$ ion. The existence of an isosbestic point at 570 mμ tends to confirm the absence of secondary thermal or photochemical reactions since it shows the presence of only unchanged Co(III) and its photoproduct $CoCl_4^{2-}$.

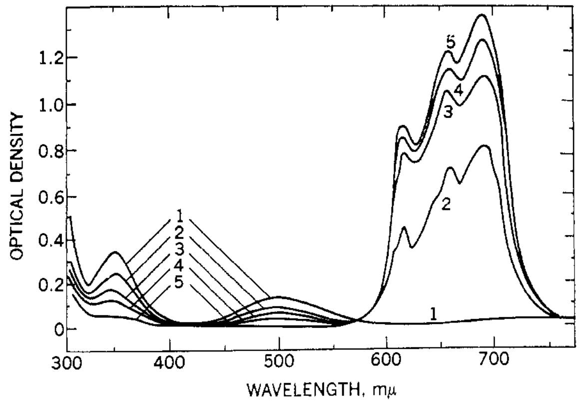

Figure 1.—Changes in the absorption spectrum of a 10^{-3} *M* solution of $[Co(NH_3)_4C_2O_4]Cl$ in concentrated hydrochloric acid: 1, before irradiation; 2, 3, 4, and 5, after 10, 20, 40, and 60 min of photolysis, respectively.

The pH of the aqueous solutions of $[Co(NH_3)_5C_2O_4H]Cl_2$ and $[Co(NH_3)_4C_2O_4]Cl$ changed upon irradiation from 2.8 to 6.6 and to 9, respectively, in agreement with the detection of free ammonia among the photoproducts. Unlike in concentrated HCl solution, in neutral aqueous solution all three oxalatoammine complexes yielded on photolysis an olive green precipitate of CoO and $Co(OH)_2$.

The quantum yields of the three oxalatoammine complexes examined are listed in Table I. The values were obtained actinometrically in thermostated cells at 25° and at three different excitation wavelengths corresponding approximately to the first two d–d absorption bands and to the charge-transfer absorption band. Included in Table I also are the values obtained for $[Co(NH_3)_4C_2O_4]Cl$ in concentrated HCl solution.

Discussion

The following mechanism seems to be consistent with the observed photoproducts and with the spectroscopic changes detected during the irradiation of $[Co(NH_3)_4C_2O_4]Cl$

$$Co^{III}(NH_3)_4C_2O_4^{+} + h\nu \longrightarrow Co^{III}(NH_3)_4C_2O_4^{+*} \quad (1)$$

$$Co^{III}(NH_3)_4C_2O_4^{+*} \longrightarrow Co^{III}(NH_3)_4C_2O_4^{+} + \text{heat} \quad (2)$$

$$Co^{III}(NH_3)_4C_2O_4^{+*} \longrightarrow Co^{II}(NH_3)_4\cdot C_2O_4^{+} \quad (3)$$

$$Co^{II}(NH_3)_4\cdot C_2O_4^{+} \longrightarrow Co^{III}(NH_3)_4C_2O_4^{+} \quad (4)$$

$$Co^{III}(NH_3)_4\cdot C_2O_4^{+} \longrightarrow Co^{2+} + 4NH_3 + C_2O_4\cdot^{-} \quad (5)$$

$$C_2O_4\cdot^{-} + Co^{III}(NH_3)_4C_2O_4^{+} \longrightarrow Co^{2+} + 2CO_2 + C_2O_4^{2-} \quad (6)$$

$$2C_2O_4\cdot^{-} \longrightarrow 2CO_2 + C_2O_4^{2-} \quad (7)$$

The asterisk indicates the excited state. The mechanism for the other two oxalatoammine complexes can be formulated in an analogous fashion.

The quantum yield value in Table I shows that the photoredox decomposition is inefficient for excitation in the first ligand field band and it becomes significant in the second ligand field and the charge-transfer bands. A reasonable explanation for the negligible quantum yield of the photoreaction at about 500 mμ is that the corresponding lowest excited singlet state is below the activation energy required for a chemical reaction. The only available path of deactivation, therefore, is step 2. On the other hand, near-uv excitation leads to an excited state having charge-transfer character as shown in step 3. The electron transfer originates probably on the oxygen atom of the oxalate ligand which is more easily oxidizable than the ammine group. This agrees with the esr-detected[18] radicals during the photolysis of $Co(C_2O_4)_3^{3-}$. Competing with the chemical reaction step 5 is the electron-return step 4 which tends to decrease the over-all quantum yield. Unlike cobalt(II) oxalate which is the stable product from the photolysis of $Co(C_2O_4)_3^{3-}$, the Co(II) photoproduct of the oxalatoammine complexes loses all

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TABLE I

QUANTUM YIELDS FOR OXALATOAMMINECOBALT(III) COMPLEXES IN AQUEOUS SOLUTIONS AT 25°

Compound	Concn × 10^3, M	Excitation wavelength, mμ	Light quanta absorbed, einstein	Moles reacted	Quantum yield
$Co(NH_3)_5C_2O_4H^{2+}$	10.0	500	7.8×10^{-5}	0.21×10^{-6}	$\sim 0.8 \times 10^{-3}$
	10.0	313	2.1×10^{-6}	0.43×10^{-6}	0.21
	10.0	254	1.6×10^{-6}	0.60×10^{-6}	0.38
$Co(NH_3)_4C_2O_4^+$	9.1	508	9.9×10^{-5}	0.45×10^{-6}	$\sim 5 \times 10^{-3}$
	9.1	350	1.6×10^{-6}	0.60×10^{-6}	0.37
	9.1	254	1.8×10^{-6}	1.00×10^{-6}	0.56
$KCo(NH_3)_2(C_2O_4)_2$	3.6	558	1.5×10^{-4}	0.30×10^{-6}	$\sim 2 \times 10^{-3}$
	3.6	355	1.7×10^{-6}	0.88×10^{-6}	0.52
	3.6	254	1.9×10^{-6}	1.22×10^{-6}	0.64
$Co(NH_3)_4C_2O_4^+$	7.1	508	1.01×10^{-4}	0.24×10^{-6}	$\sim 2 \times 10^{-3}$
(in concentrated HCl)	7.1	355	1.44×10^{-6}	0.37×10^{-6}	0.25
	7.1	254	1.65×10^{-6}	0.62×10^{-6}	0.38

original ligands with formation of either cobalt(II) oxide–hydroxide precipitate or $CoCl_4^{2-}$ in concentrated HCl. Apparently, the oxalate group leaves as an anion radical (step 5) which in turn attacks another complex molecule setting the limiting quantum yield to 2 (step 6). An alternate competing possibility is the disproportionation of the $C_2O_4\cdot^-$ particle to CO_2 and $C_2O_4^{2-}$ (step 7).

As the number of sites coordinated by oxalate groups increases from 1 in $Co(NH_3)_5C_2O_4H^{2+}$ to 4 in $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$, the quantum yield obtained on uv excitation increases markedly (see Table I). This is apparently due to the lowering of the electron-transfer energy as well as an increase in the number of sites available for attack to the reactive $C_2O_4\cdot^-$ anion radical. The proposed mechanism takes into account the lower photosensitivity of $Co(NH_3)_5C_2O_4H^{2+}$ which has a monocoordinated acid oxalate group compared to $Co(NH_3)_4C_2O_4^+$ which has a doubly coordinated oxalate dianion. Thus, the easily ionizable proton in $Co(NH_3)_5C_2O_4H^{2+}$ (pH 2.5) undoubtedly acts as a scavenger for the $C_2O_4\cdot^-$ radical ion decreasing the quantum yield to about the same value as for $Co(NH_3)_4C_2O_4^+$ in concentrated HCl (Table I). No photoaquation reaction has been observed with any of the three complexes at any excitation wavelengths studied; the only reaction detected was photoredox decomposition.

In general, we found that all mixed oxalatoamminecobalt(III) complexes behave photochemically more like tris(oxalato)cobalt(III) than like ammine complexes of cobalt(III) in spite of the large number of NH_3 ligands present. However, the photoreactivity varies with the number of oxalate groups and coordination sites in a gradual manner.

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Cyclic Amine Complexes of Nickel(I), -(II), and -(III). Electrochemistry, Preparation, and Properties[1]

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The electrochemistry, preparation, and properties of square-planar cyclic amine complexes of Ni(I), Ni(II), and Ni(III) are reported. The unipositive and tripositive oxidation states are unusual for nickel and have been described in only a few isolated cases in the literature. The polarographic behavior of square-planar complexes of two noncyclic amine ligands is included for comparison with the cyclic complexes.

Introduction

The synthesis and properties of square-planar transition metal complexes of some tetradentate macrocyclic amine ligands have been described previously. An extensive review of the subject has been published by Curtis.[2] These complexes are prepared by the condensation of aliphatic amines with ketones in the presence of certain transition metal salts. They are remarkably inert to dissociation which suggested that it might be possible to trap some of the more uncommon oxidation states of the transition metals by reduction or oxidation of the complexes containing the metals in their normal oxidation states. An investigation of the polarographic behavior of some of these complexes indicated that this was the case. This report deals with the electrochemistry, preparation, and properties of complexes containing nickel in the +1, +2, and +3 oxidation

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