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Photolysis of Transition Metal Oxalato Complex Ions

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The photochemical decomposition of solutions containing the complex ions $Co(C_2O_4)_3^{3-}$, $Mn(C_2O_4)_3^{3-}$ and $Cr(C_2O_4)_3^{3-}$ has been studied at a number of different wave lengths and compared with that of $Fe(C_2O_4)_3^{3-}$. Except for the Cr(III) complex, which is inactive photochemically, the quantum yields for decomposition into CO_2 and the divalent ion are very nearly constant in the short wave length charge-transfer region of the spectrum, but then decrease with increasing wave length. To account for this behavior, it is proposed that at short wave lengths dissociation competes with a degradative internal conversion. At long wave lengths, the decrease in the primary quantum yield indicates that dissociation may be limited by competition with collisional degradation or by primary recombination.

Introduction

The trisoxalato complexes of the trivalent ions chromium, manganese, iron and cobalt, provide a wide spectrum of kinetic and photochemical activity. The latter three complexes are decomposed by visible as well as ultraviolet light to form carbon dioxide and the divalent ion. Of the series, the iron(III) complex has been studied in detail by Parker,[1] who has thereby provided photochemists with an accurate and convenient actinometer. It has been used as such in this work. The cobalt complex has had a long and varied history; the most complete modern work on the subject of its photochemistry and thermal decomposition is that of Copestake and Uri.[2] Adamson and Sporer[3] made quantum yield measurements at several wave lengths which disagree with Copestake and Uri's data where they overlap. A number of references note the fact that the trisoxalatochromate(III) ion is not affected by light.[1,3] In the directions for the preparation of the Mn complex, Cartledge and Ericks[4] caution that recrystallizations of the potassium salt should be done in dim light, but there are no quantitative data in the literature on its photodecomposition, probably because it decomposes thermally in solution even at 0°.[4]

In order to make a comparison of the photochemical activity of these four complex ions and thus investigate the effect of changing the metal ion in the complex, the Co complex has been restudied to confirm Copestake and Uri's results, the Mn complex has been examined quantitatively and the question of the inactivity of the Cr complex confirmed.

Experimental

Materials.—The salt $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ and its solutions were prepared from reagent grade chemicals as recommended by Parker.[1] Oxidation of a solution of cobaltous carbonate in potassium oxalate by lead dioxide, followed by addition of alcohol precipitated $K_3Co(C_2O_4)_3 \cdot 3^1/_2H_2O$ by the method of Sørensen.[5] The compound $K_3Mn(C_2O_4)_3 \cdot 3H_2O$ was made by the reduction of recrystallized potassium permanganate following the directions of Cartledge and Ericks.[4] To prepare the salt $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ the stoichiometric amounts of potassium oxalate and oxalic acid were oxidized with a hot solution of potassium dichromate. The product was precipitated from solution by addition of alcohol. Solutions of these compounds were prepared as required under a Wratten series 1A safe light.

Optical Equipment.—The photolyses were carried out in a split beam apparatus, allowing simultaneous actinometry of the incident and transmitted intensities. Stoppered quartz cells 1 cm. long were immersed in ice-water during photolyses to maintain a fixed temperature and to prevent, or at least reduce, thermal decomposition of the solutions.

The radiation from a BTH 250 watt medium pressure mercury arc lamp was either collimated and passed through the filters listed in Table I or focused on the entrance slit of a wide aperture grating monochromator. An RCA 935 phototube connected to a Leeds and Northrup DC amplifier was used in some of the experiments to monitor the output of the lamp.

TABLE I

ISOLATION OF MERCURY ARC LINES

Wave length, Å.		
2804		Monochromator
3020		Monochromator
3130		Jena interference filter
	or	1 cm. 0.132 *M* $KHC_8H_4O_4$
		1 cm. 0.0228 *M* K_2CrO_4
		Corning filter 9863
3340		Jena interference filter
3660		Jena interference filter
	or	Corning filters 7380 and 5860
4046		Corning filters 3060, 4308 and 5970
4358		Corning filters 3389 and 5113
5470		Monochromator
5780		Monochromator
	or	Corning filters 3480 and 4303

Optical densities of photolyzed solutions and of developed actinometer solutions were measured on a Unicam 600 spectrophotometer. Spectra were recorded with a Cary 11 spectrophotometer.

Procedures.—Solutions of $Co(C_2O_4)_3^{3-}$ were photolyzed to less than 1% completion to avoid the difficulty of a changing absorbance during an experiment. This could be done in this specific case because a sensitive analytical method provided the means of determining the resulting small amounts of Co(II) colorimetrically.[6] After photolysis in a dilute acetate buffer solution, the solution was mixed with appropriate quantities of dilute ferric chloride and *o*-phenanthroline, then diluted to volume in a low actinic glass volumetric flask. The Co(II) formed in the photolysis was oxidized quantitatively and formed an equivalent amount of ferrous-phenanthroline complex ion. The optical density of the latter, which is the same product as that formed in the Parker actinometer,[1] was compared with that of a blank solution. The method was found to be quantitative for concentrations over the range of those produced by photolysis. Corrections were made for the fraction of the radiation absorbed by the solutions of the complex and of the actinometers as well as for the losses in reflection and absorption of the cell windows.

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(1) C. A. Parker, *Proc. Roy. Soc.* (*London*), **A220**, 104 (1953); *Trans. Faraday Soc.*, **50**, 1213 (1954); C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (*London*), **A235**, 518 (1956); C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959).

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

(3) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958); *J. Inorg. Nucl. Chem.*, **8**, 209 (1958).

(4) G. H. Cartledge and W. P. Ericks, *J. Am. Chem. Soc.*, **58**, 2061 (1936).

(5) S. P. L. Sørensen, *Z. anorg. Chem.*, **11**, 1 (1896).

(6) F. Vydra and R. Pribil, *Talanta*, **5**, 44 (1960).

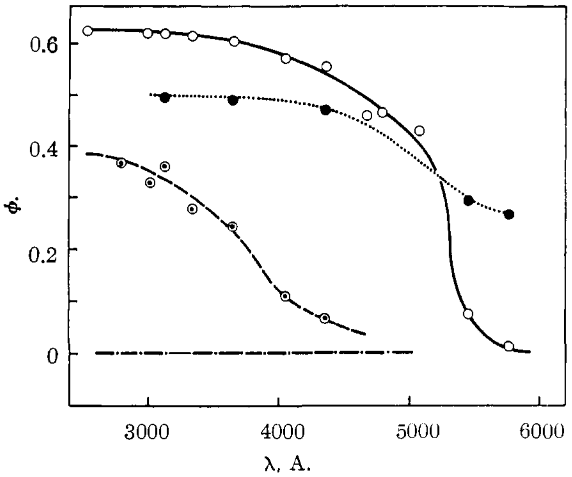

Fig. 1.—Primary quantum yield action spectra: ———, $Fe(C_2O_4)_3^{3-}$; ......, $Mn(C_2O_4)_3^{3-}$; – – – –, $Co(C_2O_4)_3^{3-}$; – · – · –, $Cr(C_2O_4)_3^{3-}$.

There is no convenient analytical method available for the determination of Mn(II) in solutions containing the trivalent complex; hence the photolysis was followed by the decrease in absorbance of the solution. Fortunately the products of the reaction, Mn(II) and CO_2, do not absorb at 5000 Å., at which the optical density was followed. Correction for the concurrent thermal decomposition of the manganese complex required careful blank experiments which, except for exposure to light, were treated in the same way as the photolyzed solutions.

A solution of the chromium complex was outgassed and exposed to the collimated beam from the mercury lamp without filters. The optical density was measured at 4200 and 5800 Å. before and after the experiment.

Results

The results are summarized in Fig. 1, which shows the primary quantum yields plotted against the wave length of the radiation absorbed. Parker's[1] results on the Fe(III) complex are included for comparison with the other data. In each case, the quantum yields were independent of the intensity, the extent of decomposition and the concentration of the complexion.

Since the decomposition of $Co(C_2O_4)_3^{3-}$ was limited in extent, the absorbance was essentially constant during any one experiment. Thermal decomposition required only a relatively minor correction; therefore the calculation of the quantum yield was straightforward.

The analysis of the data for the $Mn(C_2O_4)_3^{3-}$ ion posed more of a problem. Thermal decomposition would probably have been negligible if the solutions could have been maintained at 0°, but during the measurement of their absorbance, the solutions warmed up slightly. At 25° the thermal decomposition is rapid, *i.e.*, it has a half-life of about 13 minutes; thus it was essential to make optical density measurements rapidly and to treat blank solutions in the same way. At 3130 Å., the solution of the Mn(III) complex used was totally absorbing. Therefore the rate equation

$$-dC/dt = \Phi I_0 + kC \qquad (1)$$

with C the molar concentration of the complex ion, k the specific rate constant, Φ the quantum yield of Mn(II), could be integrated directly. On rearrangement, there results

$$\Phi = \frac{k}{I_0}\left[\frac{C_0 - Ce^{kt}}{1 - e^{kt}}\right] \qquad (2)$$

The rate constant k was found to be 2.9×10^{-5} sec.$^{-1}$ under the conditions of these experiments.

At longer wave lengths the absorption of solutions containing $Mn(C_2O_4)_3^{3-}$ was not complete and also decreased during photolysis. The appropriate rate equation

$$-dC/dt = \Phi I_0(1 - 10^{-\epsilon l C_0}) + kC \qquad (3)$$

in which ϵ is the decadic molar extinction coefficient and l the length of the optical cell, could not be integrated explicitly. The assumption was therefore made that the term involving the thermal decomposition, kC, was constant between two consecutive optical density measurements. On this basis, eq. 3 can be integrated to give

$$\Phi = \frac{1}{\epsilon l I_0 K}\log\left[\frac{K\,10^{-\epsilon l C_0} - 1}{K\,10^{-\epsilon l C} - 1}\right] \qquad (4)$$

with the quantity K defined as

$$K = 1 + (kC)/\Phi I_0$$

The iteration required in the solution of eq. 4 converges rapidly.

The inactivity of $Cr(C_2O_4)_3^{3-}$ to light was confirmed by a 15-hour, full-arc photolysis, during which no change in the absorption spectrum of the solution could be detected. From the estimated total absorbed intensity and the precision with which the optical densities could be determined, the quantum consumption of Cr(III) must be less than about 10^{-4}.

Discussion

The mechanism postulated for the photochemical decomposition of the Fe(III)[1] and Co(III)[2] complexes in the ultraviolet and visible regions of the spectrum is

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

$$C_2O_4^- + M(C_2O_4)_3^{3-} \longrightarrow 2CO_2 + M(C_2O_4)_2^{2-} + C_2O_4^{2-}$$

or some variation of this. The important point is that the primary quantum yield is one-half the quantum yield of the divalent ion. A similar mechanism is assumed to hold for the decomposition of the Mn(III) complex ion.

There are two features common to each of the three photochemical action spectra in Fig. 1. The first is a region of the spectra at short wave lengths in which the primary quantum yield is less than unity and essentially independent of wave length. The second is that the quantum yield at longer wave lengths decreases more or less uniformly toward zero. These can be compared with the absorption spectra in Fig. 2. These spectra are characterized by an intense charge-transfer band at short wave lengths, in which an electron is promoted from an occupied π-orbital of a ligand to an empty e_g-antibonding orbital essentially localized on the metal atom. This is followed at longer wave lengths by ligand field bands of low intensity which involve promotion of an electron from a non-bonding t_{2g}-orbital to an antibonding e_g-orbital. In the Fe(III) spectrum there is a peak at about 6800 Å. of very low intensity which is spin as well as Laporte forbidden. In a qualitative sense, the constant quantum yield regions of the spectra correspond to the charge-transfer bands, while in the region of the ligand field bands the quantum yield decreases with increasing wave length.

Region of Constant Quantum Yield.—The primary act leading to net decomposition in the photolysis must be the dissociation of a radical ion ligand from the then-reduced metal complex ion. Since the reduced product has no effect on the quantum yield, secondary recombination cannot be responsible for a primary quantum yield less than unity. Nor can the cage effect (primary recombination) be cited as a cause of the low quantum yield, for then it would almost certainly vary with wave length. Thus there can only be a degradative reaction, *i.e.*, an internal conversion process, which competes directly with the dissociation reaction and the ratio of their rates cannot depend on wave length of the light absorbed. These processes must have (first order) rate constants greater than about 10^{10} sec.$^{-1}$ on the basis that the radiative transition probability for the charge transfer band will be about 10^8 sec.$^{-1}$, coupled with the fact that these solutions show no fluorescence.

The limiting value of the primary quantum yield bears a direct relation to the position of the charge-transfer band, or to the ease of reducibility of the metal atom, an effect noted in the work of Adamson[8] in which a series of ligands was studied. The order of increasing quantum yield and of decreasing energy of the charge transfer state is Cr, Co, Mn, Fe. On the other hand, they do not correlate in the same way with increasing thermal reactivities: Cr, Fe, Co, Mn.

Region of Decreasing Quantum Yield.—The wave length at which the quantum yield starts to decrease matches the minimum between the charge-transfer band and the first ligand field band. Yet it is quite obvious in the case of the manganese and cobalt complexes that the decrease in the quantum yield does not follow the decreasing relative intensity of the charge-transfer band; that is, absorption in the first ligand field band still leads to photochemical oxidation and reduction. At wave lengths longer than 4000 Å. for the cobalt complex and 5000 Å. for the manganese complex, certainly far less than 1% of the light can be considered as being absorbed in the charge transfer band. Yet at these wave lengths the quantum yield has decreased to only 20% and 75%, respectively, of the maximum values.

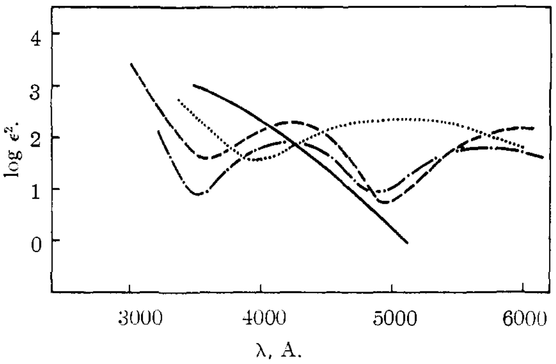

Fig. 2.—Absorption spectra: ———, $Fe(C_2O_4)_3{}^{3-}$; ......, $Mn(C_2O_4)_3{}^{3-}$; ----, $Co(C_2O_4)_3{}^{3-}$; -·-·-, $Cr(C_2O_4)_3{}^{3-}$.

In solution, it is well known that extremely rapid internal conversion processes occur which degrade excited electronic states to the lowest excited state of the same multiplicity. If this type of internal conversion were to occur, then any subsequent reactions, such as dissociation, would have quantum yields independent of wave length and of the electronic state reached in absorption. Since that is not so here, the dissociation reaction must compete with or precede internal conversion. Further, since the oxidation and reduction process must be initiated by dissociation of an oxidized oxalate radical ion from a reduced metal complex, the charge-transfer state must be an intermediate in the process even when absorption is predominantly into a ligand field band. Thus we envision that the charge-transfer state extends down in energy through the visible region of the spectrum, although it must have a very low extinction coefficient there because of Franck–Condon restrictions. There must then be mixing of the ligand field state with the charge-transfer state which allows rapid radiationless conversion from the former to the latter. This seems reasonable in view of the fact that the orbitals from which the electron is promoted in these transitions have the same symmetry. The decrease in the primary quantum yield with wave length would then arise from either or both of competition between interconversion of the two states and collisional internal conversion or of a cage effect primary recombination of fragments with reduced kinetic energy. The latter would be required to account for the photochemistry of the Fe(III) complex.

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(8) A. W. Adamson, *Disc. Faraday Soc.*, **29**, 163 (1960).