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Photochemistry of Complex Ions. II. Photoracemization[1,2]

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Studies have been made of the photochemistry of the following optically active compounds: $[Cr(C_2O_4)_3]^{3-}$, $[Co(C_2O_4)_3]^{3-}$, $[Rh(C_2O_4)_3]^{3-}$, $[Co(EDTA)]^{1-}$, $[Co(en)_2Cl_2]^{1+}$, $[Co(en)_2C_2O_4]^{1+}$, $[Co(en)_2(NO_2)_2]^{1+}$, and $[Co(en)_3]^{3+}$. Quantum yields are reported for oxidation–reduction decompositions, aquation, and racemization processes, and, in the case of $[Cr(C_2O_4)_3]^{3-}$, a detailed investigation of the wave length, temperature, and solvent dependence of the photoracemization quantum yield was carried out. These findings plus data on both the thermal and photoexchange of O^{18} between $[Cr(C_2O_4)_3]^{3-}$ and water are discussed in terms of possible mechanisms.

Previous publications have described various photoaquation and other substitution reactions with Cr(III) complexes,[3] and photoaquation and photo-oxidation–reduction processes with Co(III) species.[1,4]

The present paper is largely concerned with photoracemization, which was first described for complex ions such as $[Cr(C_2O_4)_3]^{3-}$ in our preliminary report of 1959.[5] More recently, Dwyer and his colleagues[6,7] have reported that photoracemization occurs with two complexes of Rh(III) and one of Co(III).

The mechanism of photoracemization reactions may, or may not, be similar to photosubstitution reactions and one purpose of this study has been to find evidence that pertains to this question.

Experimental

Preparation of Compounds.—The complexes listed were prepared by procedures given in "Inorganic Syntheses" and resolved by the indicated literature methods: $K_3[Cr(C_2O_4)_3]$,[8,9] $K_3[Co(C_2O_4)_3]$,[8,9] $[Co(en)_3]Cl_3$,[10–12] *cis*-$[Co(en)_2Cl_2]Cl$,[13] *cis*-$[Co(en)_2(NO_2)_2]Br$.[14] $[Co(en)_2(C_2O_4)]Cl$ was prepared according to the procedure of Werner[15] and the optically active complex was made directly from *l*-*cis*-$[Co(en)_2Cl_2]Cl$ by triturating with ammonium oxalate. $K_3[Rh(C_2O_4)_3]$ also was prepared and resolved according to the procedure of Werner.[16] The $K_3[Cr(C_2O_4)_3]$ containing O^{18} was prepared as described by Palmer,[17] except that 20 ml. of enriched water (1.575% O^{18})[18] was used in place of normal water. All racemic complexes were recrystallized and checked for purity by means of their spectra.

Apparatus.—A Beckman DU spectrophotometer and a Cary Model 14 PM recording spectrophotometer were used to measure optical densities. Optical activities were measured with a Bellingham-Stanley Model A polarimeter, No. 507005. The light source was either a sodium lamp or a 1000-watt tungsten projection lamp with filters to select appropriate wave lengths.

The photochemical runs were carried out using the same general equipment as described previously[1,3] and the same method for determining the intensity of absorbed light. The cell, of about 2 cm. path, was thermostated to ±0.2°. Absolute quantum yields were obtained by calibration with standard actinometric solutions.[19,20]

The gradient density tube[21] used in the determination of O^{18} concentrations consisted of two bulbs connected by a straight stem. The lower and upper bulbs had diameters of 7 and 6 cm., respectively. The stem was 20 cm. long and 2.5 cm. in diameter and contained a steady-state diffusion column of kerosene–bromobenzene. The tube was kept in a constant temperature bath maintained at 24.98 ± 0.01°. The equilibrium positions of the water drops were measured with a traveling microscope which could be read to 0.01 mm.

Procedure.—For $K_3[Cr(C_2O_4)_3]$ there is no net photochemical reaction other than photoracemization. Therefore, a solution of known concentration was irradiated with light of suitable wave length and the constant net

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[1] See *J. Am. Chem. Soc.*, **80**, 3865 (1958) for the preceding paper.

[2] This paper is taken from the Ph.D. dissertation of S. T. Spees, presented to the University of Southern California in August, 1961.

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

[4] A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960).

[5] A. W. Adamson and S. T. Spees, Abstracts of Papers, International Conference on Coördination Chemistry, 1959, Special Publication No. 13, The Chemical Society, London, 1959, p. 165.

[6] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **82**, 4823 (1960); **83**, 2610 (1961).

[7] F. P. Dwyer, I. K. Reid, and F. L. Garvan, *ibid.*, **83**, 1285 (1961).

[8] H. S. Booth, ed., "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., New York, N. Y., 1939, p. 37.

[9] C. H. Johnson and A. Mead, *Trans. Faraday Soc.*, **29**, 628 (1933).

[10] W. C. Fernelius, ed., "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., New York, N. Y., 1946, p. 221.

[11] A. Werner, *Ber.*, **45**, 121 (1912).

[12] D. H. Busch, *J. Am. Chem. Soc.*, **77**, 2747 (1955).

[13] Reference 10, p. 222.

[14] E. Rochow, ed., "Inorganic Syntheses," Vol. 6, McGraw-Hill Book Co., New York, N. Y., 1960, p. 196.

[15] A. Werner, *Ber.*, **47**, 2174 (1914).

[16] A. Werner, *ibid.*, **47**, 1954 (1914).

[17] W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1954, p. 386.

[18] The O^{18} labeled water was obtained from Bio-Rad Laboratories, Richmond, California.

[19] C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953).

[20] F. P. Brackett and G. S. Forbes, *J. Am. Chem. Soc.*, **55**, 4459 (1933).

[21] A. Hvidt, G. Johansen, K. Linderstrom-Lang, and F. Vaslow, *Compt. rend. Lab. Carlsberg, Ser. chim.*, **29**, 129 (1954).

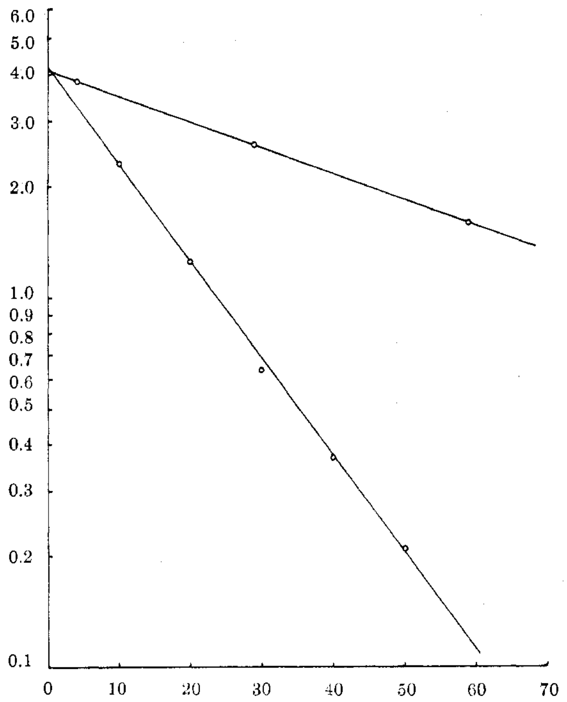

Fig. 1.—Thermal and photochemical racemization of $Cr(C_2O_4)_3^{-3}$: 0.01 *M* complex, 420 mμ, 14.5°; lower line, photochemical (plus thermal); upper line, thermal only; ordinate, optical rotation (degrees); abscissa, time (minutes).

light absorption was determined from the bolometer readings. After suitable intervals of about 10 min., the optical actvity was measured and these data gave good first-order plots for both the light and dark reactions. The loss of optical activity was followed for at least one half-life and usually for two or three half-lives. The quantum yields were calculated by dividing the rate of racemization, corrected for the thermal reaction, by the rate of light absorption.

In the case of $K_3[Co(C_2O_4)_3]$ the decomposition was followed by measuring the optical density at 605 mμ. The decomposition of *cis*-$[Co(en)_2Cl_2]Cl$ was followed by measuring the Co^{2+} formed. The cobaltous ion was precipitated with 6 *N* NaOH; after standing a few minutes, the solution was centrifuged and the supernatant liquid discarded. Concentrated HCl was added to the precipitate and the optical density of the complex formed was measured at 660 mμ, where the molar extinction coefficient of $CoCl_4^{2-}$ is 475. The aquation of *cis*-$[Co(en)_2Cl_2]^+$ was measured by conductimetric $AgNO_3$ titration of the chloride released at 0°, and also from the change in optical density of the irradiated solution.

The analysis for O^{18} was carried out as follows: The complex, $K_3[Cr(C_2O_4)_3]$, was precipitated from aqueous solution by the addition of two volumes of ethanol and filtered with suction. The precipitate was dried in an oven at 110° for 1 hr. and then reduced with hydrogen at 900°. A porcelain boat containing the complex was placed in a Vycor tube which extended through an electric furnace. Hydrogen was passed through a trap of Dry Ice in acetone, through the Vycor tubing, and finally through a second trap of Dry Ice in acetone. The system was flushed for about 5 min. and then the complex was moved into the heated region of the tube. The water produced by the reduction of the complex was collected in the second trap. After passing hydrogen for 30–40 min. enough was collected to analyze the O^{18} content according to the gradient density tube method.[21] At least a 400–500-mg. sample of the complex was necessary in order to collect enough water to measure. The equilibrium positions of small drops ($\sim$5 λ) of the collected water were compared to standards of known O^{18} content. The methods used to prepare the gradient and to make the actual measurements were the same as described in the reference.

Thermal and Photoracemization of $[Cr(C_2O_4)_3]^{3-}$

Temperature Dependence.—Data for a typical run are displayed in Fig. 1, in which is shown the decay of the optical activity of 0.01 *M* $K_3[Cr(C_2O_4)_3]$ under irradiation, along with the decay of a portion of the same solution which was kept in the dark and at the same temperature. It was always necessary to run a thermal racemization parallel to the photochemical one since the correction was generally quite large, and a considerable body of thermal rate data therefore was accumulated.

Average data from some 27 runs, together with those of Schweitzer and Rose[22] and of Bushra and Johnson,[23] are summarized in Fig. 2. Our results alone indicate an activation energy of 14.6 kcal./mole, but the best line through all points shown gives an activation energy of 15.0 kcal./mole as given by

$$k_{\text{rac}} = 1.63 \times 10^7 \exp(-15{,}000/RT) \text{ sec.}^{-1} \quad (1)$$

As will be seen below, photoracemization quantum yields were almost independent of wave length so that the data of Table I summarizing the temperature dependence for light of 420 mμ probably are representative of other wave lengths in the visible region. Experimental scatter makes the slope of the activation energy plot relatively uncertain, but a least squares analysis gives

$$\phi = 3.67 \exp(-2{,}100/RT) \quad (2)$$

where the quantum yield (ϕ) is the moles of complex racemized per minute per einstein of light absorbed per minute. The rate of photoracemization has been corrected for the rate of thermal racemization.

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(22) G. K. Schweitzer and J. L. Rose, *J. Phys. Chem.*, **56**, 428 (1952).

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

TABLE I

TEMPERATURE DEPENDENCE OF THE PHOTORACEMIZATION OF $K_3[Cr(C_2O_4)_3]$

0.01 *M* Complex λ = 420 mμ

Temp., °C.	$I \times 10^6$, einsteins/sec.	$R \times 10^7$, *M*/sec.	ϕ
−2.0	1.68	1.20	0.071
1.0	1.85	1.50	.081
4.0	2.13	1.59	.074
8.0	1.81	1.77	.098
8.0	1.53	1.64	.106
15.0	1.98	1.85	.093
15.0	2.02	1.77	.087

Effect of Solvent Medium.—Schweitzer and Rose[22] reported on extensive investigations on the reduction in the thermal racemization rate at 25 and 35° with increasing organic solvent content of the medium. Our data, included in Table II, in general agree with theirs at 25°, but in 30 mole % ethanol, for which we have the temperature dependence, we find

$$k_{\text{rac}} = 6.23 \times 10^8 \exp(-17{,}600/RT) \text{ sec.}^{-1} \quad (3)$$

In contrast, Schweitzer and Rose report data corresponding to an activation energy of 42.5 kcal./mole; the discrepancy is at 35°, where we reproducibly find a half-life of 56 min. rather than the 18-min. value reported by them.

The solvent dependence of the quantum yields for photoracemization at 420 mμ is much smaller than that of the thermal process, as shown by the data of Table II. Thus, in 30 mole % ethanol at 15°, k_{rac} is reduced tenfold over that in water, while ϕ at 420 mμ is reduced only threefold.

The activation plot for 30 mole % ethanol gives, subject to considerable uncertainty because of the scatter of the points

$$\phi = 25.8 \exp(-3{,}200/RT) \quad (4)$$

It thus appears that both the reduction in k_{rac} and in ϕ on going to 30 mole % ethanol as a medium are due to an increase in the apparent activation rather than to a decrease in frequency factor.

The thermal aquation rate, which may involve a mechanism related to that for racemization (see below) is known to be acid catalyzed,[24] and the same might be true for racemization. Thus at 0°, we find the values of k_{rac} to be 6.67×10^{-5}, 2.25×10^{-4}, and 3.93×10^{-4} sec.$^{-1}$ in water, 0.12 *N*, and 0.24 *N* perchloric acid, respectively. The corresponding quantum yields at 420 mμ, however, were 0.078, 0.073, and 0.065, and we conclude that there is no detectable dependence on acidity.

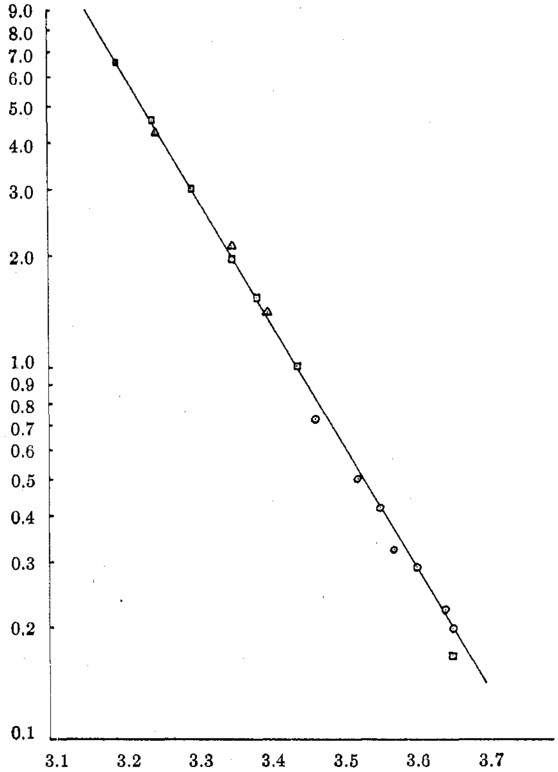

Fig. 2.—Thermal racemization of $Cr(C_2O_4)_3^{-3}$: O, our data (0.01 *M* complex); Δ, Schweitzer and Rose[25]; □, Bushra and Johnson[26]; ordinate, k_{rac} (10^2 min.$^{-1}$); abscissa, $10^3/T$.

As an additional medium effect, it was found that the thermal racemization rate (in non-acidified aqueous media) is reduced in D_2O

$$k_{H_2O}/k_{D_2O} = 1.26 \pm 0.10$$

In contrast to other solvent effects, exactly the same reduction was found for the quantum yields at 420 mμ

$$\phi_{H_2O}/\phi_{D_2O} = 1.24$$

Wave Length Dependence.—As previously noted,[5] there is no detectable change in quantum yield between about 600 and 360 mμ, but in view of the suggestion[25] that the doublet band is the photochemically active one for Cr(III) complexes, it was thought worthwhile to determine the quantum yield on direct irradiation of this band (697 mμ in this case). In aqueous solution, the results did suggest some increase in ϕ at this wave length. Even though a special 15-cm. path length cell was used, the results were subject to consider-

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[24] F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959); K. V. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960); *Chem. Rev.*, **61**, 213 (1961).

[25] H. L. Schlafer, *Z. physik. Chem.*, **11**, 65 (1956).

Table II

Photoracemization at 420 mμ of $K_3[Cr(C_2O_4)_3]$ in Mixed Solvent Media

Solvent	Temp., °C.	$C \times 10^3$, M	k_{thermal}, sec.$^{-1}$ $\times 10^5$	$I \times 10^6$, einstein/sec.	$R \times 10^8$, M/sec.	ϕ
30% acetone	15	12.0	0.42	2.80	2.88	0.010
57% methanol	10	4.27	0.77	1.50	2.73	.018
30% ethanol	25	4.27	8.54	1.47	5.02	.034
30% ethanol	15	3.84	2.88	1.09	3.65	.034
30% ethanol	20	3.84	4.02	2.40	4.66	.019
30% ethanol	30	2.98	12.48	1.57	4.91	.031
30% ethanol	10	2.76	1.73	1.64	3.40	.021
30% ethanol	25	2.98	6.22	1.14	3.27	.029
30% ethanol	15	2.98	2.23	1.09	2.93	.027
30% ethanol	17	2.14	2.58	1.30	2.65	.020
30% ethanol	17	4.13	2.68	1.83	3.38	.018
30% ethanol	17	3.20	2.54	1.19	2.52	.021
30% ethanol	17	3.20	2.54	0.97	2.23	.023
30% ethanol	17	2.14	2.58	1.44	3.56	.025
30% ethanol	25	3.03	6.78	2.10	4.48	.021
30% ethanol	35	2.98	20.65			
30% ethanol	0	3.41	0.60			

able error since so little light absorption occurs at this wave length that the correction for the background rate of thermal racemization was quite large. The study therefore was repeated in 30 mole % ethanol medium where, as noted above, the thermal racemization rate is decreased more than is the photochemical rate, allowing a more precise determination of the latter. These results, as shown in Table III, should be much more reliable and show a slight decrease, and certainly no increase in ϕ occurs when the region of the doublet band is irradiated. These are not absolute quantum yields, since this cell was not calibrated directly with actinometric solutions.

Table III

Wave Length Dependence of the Photoracemization of $K_3[Cr(C_2O_4)_3]$

(0.004 M complex in 30 mole % ethanol, temperature 4°, cell path length 15 cm.)

λ, mμ	I, einsteins/sec. $\times 10^7$	R, M/sec. $\times 10^8$	ϕ
420	0.39	0.35	0.089
570	3.17	2.58	.082
697	0.27	0.18	.068

O^{18} Exchange.—The exchange of solvent oxygen with oxalate has been reported[26] to be measurable for $[Cr(C_2O_4)_3]^{3-}$ (although no exchange occurs with free oxalate ion), and it was thought to be of interest to confirm this as well as to determine whether any photochemical exchange took place. We find the thermal exchange rate to be somewhat slower than that for racemization, the first order rate constants being 2.51×10^{-5} and 6.63×10^{-5} sec.$^{-1}$, respectively, at 0°. The ratio of rate constants (taking that for exchange as involving all oxalate oxygens) is 2.6. Likewise, the quantum yield for O^{18} exchange is somewhat lower than that for photoracemization, being 0.034 compared to 0.078 at 0°. As with the D_2O effect, the behavior roughly parallels that of the corresponding thermal processes; thus we find $\phi_{\text{rac}}/\phi_{\text{exch}} = 2.3$.

Discussion of Results with $[Cr(C_2O_4)_3]^{3-}$.—Harris and co-workers[24] have proposed the reaction steps shown below as part of their mechanism for aquation and oxalate exchange: *Rapid pre-equilibria* (detachment of one oxalate end)

$$[Cr(C_2O_4)_3]^{3-} + H_2O \rightleftharpoons [Cr(C_2O_4)_2(O\text{–}COCO_2)(H_2O)]^{3-} \quad (5)$$

and

$$[Cr(C_2O_4)_3]^{3-} + H_3O^+ \rightleftharpoons [Cr(C_2O_4)_2(O\text{–}COCO_2)(H_3O)]^{2-} \quad (6)$$

rate determining step for aquation

$$[Cr(C_2O_4)_2(O\text{–}COCO_2)(H_2O)]^{3-} + H_2O \rightleftharpoons [Cr(C_2O_4)_2(H_2O)_2]^- + (C_2O_4)^{2-} \quad (7)$$

$$[Cr(C_2O_4)_2(O\text{–}COCO_2)(H_3O)]^{2-} + H_2O \rightleftharpoons [Cr(C_2O_4)_2(H_2O)_2]^- + (HC_2O_4)^- \quad (8)$$

Thermal racemization, while not directly geared to aquation and hence presumably not involving reactions 7 or 8, may well have the pre-equilibria (5) and (6) in common. Thus, as with aquation, there is an acid-catalyzed path. On this basis,

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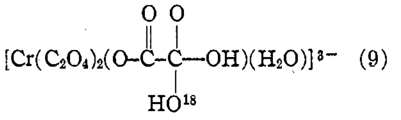
(26) D. R. Llewellyn and A. L. Odell, *Proc. Australian Atomic Energy Symp.*, **5**, 623 (1958).

it then is tempting to suppose that O^{18} exchange occurs through hydration of the monodentate intermediate, *i.e.*

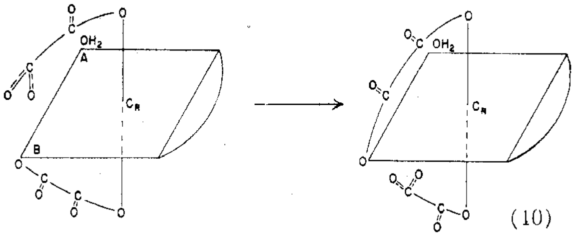
$$[Cr(C_2O_4)_2(O\text{-}COCO_2)(H_2O)]^{3-} + H_2O^{18} \rightleftarrows$$



$$[Cr(C_2O_4)_2(O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{HO^{18}}{\overset{\overset{O}{|}}{C}}\text{—}OH)(H_2O)]^{3-} \quad (9)$$

This reaction presumably does not occur with free oxalate ion, in view of the absence of exchange with solvent oxygen, and it seems reasonable to suppose that even under the stimulation of monodentate coördination, process 9 does not always occur.

The fact that thermal racemization does take place at a rate comparable to that of the O^{18} exchange suggests that the monodentate species of (5) and (6) are involved, and that racemization does not go through some entirely different sequence such as an intramolecular twisting of opposing triangular faces of the octahedron. As will be seen below, this conclusion is further supported by our interpretation of the data for mixed solvent media. We propose, then, that thermal racemization occurs through (5) and (6) followed by an intramolecular oxalate–oxalate displacement, as shown schematically below.



Thus the free end of the monodentate oxalate may carry out an internal displacement at position A, thus effecting the reverse of process 5 through which the monodentate intermediate was formed. If instead, however, the displacement occurs on position B and the new monodentate oxalate ligand produced in turn now displaces water at A, the reverse of (5) again occurs, but with inversion of configuration. As with the aquation of Reinecke's salt,[27] the negative D_2O effect found for thermal racemization in neutral media then would be interpreted as a consequence of solvent hydrogen bonding participation either in the rate determining oxalate–oxlate displacement, or in (5).

The acid-catalyzed racemization could be either faster or slower in D_2O, depending on the balance between the positive isotope effect on the acid–base type pre-equilibrium (6) (as deduced by Harris, *et al.*, from aquation studies) and the probably negative isotope effect on the subsequent oxalate–oxalate displacement step (10). This has not been tested, however.

Turning to the behavior in mixed solvents, one might expect dilution of the water by an organic species to affect (5) to the extent that the organic component was unable to substitute for water as a ligand, and further, to the extent that the local solvent environment encouraged the charge separation involved in forming a monodentate oxalate ligand. The effect of solvent medium on process 10 might well be much less since water is neither directly involved nor is there a change in charge separation.

Reactions such as (5) where a component of the solvent enters the first coördination sphere, *i.e.*, coördinative solvation, probably are best viewed as solvent cage reactions. That is, upon obtaining the necessary energy of activation the complex undergoes substitution, with a probability determined by the chance of finding the appropriate entering ligand in the immediate vicinity. In mixed solvents, then, the composition of the solvent cage, which is not necessarily the same as the average solvent composition, becomes the important quantity. In the absence of some independent means of determining this solvent cage composition, it is difficult to make any detailed treatment of either our data or that of Schweitzer and Rose[22] on the racemization rates in mixed solvent systems.

Turning to the photochemical findings, we would suppose that process 5 is driven photochemically, followed by (9) or (10) as subsequent steps. This accounts for the small solvent medium effect on the quantum yield and the absence of any acid catalysis, on the one hand. On the other hand, it likewise accounts for the observation that $\phi_{exch}/\phi_{rac} = k_{exch}/k_{rac}$ and $\phi_{H_2O}/\phi_{D_2O} = k_{H_2O}/k_{D_2O}$, since these effects involve (9) and (10) and hence would be common to both the photochemical and the thermal processes. There is much *ad hoc* reasoning in the above, of course, and perhaps at best it should only be said that it is possible to hang all of the present thermal and photochemical data on the proposed general framework.

Thermal and Photochemistry of $[Co(C_2O_4)_3]^{3-}$.—

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[27] A. W. Adamson, *J. Am. Chem. Soc.*, **80**, 3183 (1958).

TABLE IV

THE PHOTOLYSIS OF $K_3[Co(C_2O_4)_3]$

Concn.,[a] $M \times 10^3$	$I \times 10^6$, einsteins/ min.	a, M^{-1}	T, °C.	λ, mμ	ϕ	ϕ_{OA}/ϕ_{OD}
4.51	21.0	195	10.0	>530	7.94×10^{-4}	1.16
4.67	22.6	206	25.0	>530	1.59×10^{-3}	
4.69*	14.2	195	25.0	>530	1.70×10^{-3}	
41.1	3.80	43	10.0	>530	1.66×10^{-3}	
5.43	5.36	175	0.5	>530	6.43×10^{-4}	1.22
10.10	0.661	231	12.9	450	1.41×10^{-1}	
5.09*	.509	350	12.9	450	1.46×10^{-1}	1.00
10.18	.515	173	14.5	450	1.24×10^{-1}	1.27
5.00	.493	384	14.0	450	1.28×10^{-1}	1.09
5.03	.476	293	0.4	450	8.90×10^{-2}	1.16
4.54	.460	303	29.9	450	9.25×10^{-2}	
4.74	.536	378	19.9	410	2.43×10^{-1}	
4.70	.380	468	0.5	410	2.22×10^{-1}	
4.67	.430	355	9.9	410	2.60×10^{-1}	
4.71	1.47	120	9.9	355–385	5.13×10^{-1}	
4.62	1.27	150	0.4	355–385	4.07×10^{-1}	
4.60	1.21	186	19.9	355–385	4.12×10^{-1}	
4.65	1.19	192	29.9	355–285	3.98×10^{-1}	

[a] All runs 0.1 M in $K_2C_2O_4$ except those starred.

It has been known for some time that the principal thermal and photochemical reaction undergone by $[Co(C_2O_4)_3]^{3-}$ is one of oxidation–reduction decomposition to Co(II) and carbon dioxide.[28] Our interest, however, lay in the possibility that some photoracemization occurred as well as photodecomposition. Neither thermal process was sufficiently important at room temperature to require correction of the photochemical runs,[28] and in the presence of some added free oxalate to prevent precipitation of Co(II) as the oxalate during any extensive photolysis, it became merely a matter of comparing the rate of loss of optical activity (measured at 500 mμ) on irradiating a solution of optically active complex with the rate of disappearance of complex, as determined by the decrease in optical density at the 605-mμ peak. Absorption at this wave length due to products is negligible.

Unlike the situation with $[Cr(C_2O_4)_3]^{3-}$, the intensity of the absorbed light decreases during irradiation, as decomposition occurs, and this must be recognized in order to obtain a linear form for plotting. Since the complex is the principal absorbing species, the absorbed light is, to a good approximation, given by

$$\Delta I = I_0(1 - e^{-aC}) \qquad (11)$$

where I is light intensity in einsteins per minute and the absorption coefficient a is determined from measurements on the cell when filled with solution of initial concentration C_0. Integration of the rate equation

$$dC/dt = -(\phi \Delta I/V) \qquad (12)$$

where V denotes the volume of solution irradiated, then gives

$$a(C_0 - C) - \ln \frac{1 - e^{-aC}}{1 - e^{-aC_0}} = (\phi I_0 a/V)t \qquad (13)$$

Equation 13 served well to represent our experimental results, as illustrated by a representative run shown in Fig. 3.

Data for runs under various conditions are summarized in Table IV and indicate that there is little if any dependence of quantum yield on light intensity (in the region of 10^{-5} to 10^{-} einstein/sec.), complex concentration (in the range 0.001 to 0.01 M), or concentration of added oxalate (up to 0.1 M). There is a strong wave length dependence, however, and a summary of runs bearing on this point is given in Table V, showing the rapid decrease in ϕ with increasing wave length that is typical of Co(III) complexes.[5] Our values agree well with those of Copestake and Uri,[29] included in the table for purposes of comparison.

We find, in addition, only a slight temperature dependence for ϕ, except that at 605 mμ the apparent activation energy rises to about 6 kcal./mole.

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[28] See A. W. Adamson, H. Ogata, J. Grossman, and R. Newburg, *J. Inorg. Nucl. Chem.*, **6**, 319 (1958).

[29] T. B. Copestake and N. Uri, *Proc. Roy. Soc.* (London), **A288**, 252 (1955).

TABLE V

WAVE LENGTH DEPENDENCE OF THE PHOTODECOMPOSITION OF $K_3[CO(C_2O_4)_3]$ AT 25°

Wave length, mμ	Quantum yield Ref. 32	Quantum yield This work
313	0.73	
365	.69	
355–385		0.44
405	.17	
410		.24
435	.12	
450		.12
530		.0017

Turning to the matter of possible photoracemization, it will be noticed that in Fig. 3 the rate of disappearance of complex as deduced from the rate of loss of optical activity is noticeably larger than that obtained from the decrease in concentration as measured directly by following the optical density decrease. The ratio ϕ_{OA}/ϕ_{OD} (OA = optical activity, OD = optical density) was obtained for several runs and these values are included in Table IV. It is seen that except for the run with no added free oxalate, ϕ_{OA} was always somewhat larger than ϕ_{OD}, and we conclude that the effect is sufficiently systematic to mean that about 15% of the time loss of optical activity occurs through racemization. At 450 mμ, ϕ_{rac} is thus about 0.018 *vs.* 0.12 for ϕ_{decomp}. The precision of the results was unfortunately not sufficient to allow any accurate conclusions as to how ϕ_{rac} varies with wave length, concentration, or other variables. Such dependencies cannot be very great, however.

There is no reason, of course, why Co(III) complexes should not undergo photoracemization, and, indeed, Dwyer and co-workers recently have reported qualitatively on such an effect with $[Co(en)(C_2O_4)_2]^{-1}$.[7] In the present case the racemization could be occurring through some mechanism which is entirely independent of that for the oxidation–reduction decomposition, but it seems more plausible to assume that the two processes have similar quantum yields, even under various conditions, because of a common initial step. The initial step for the thermal reaction is probably[28, 29]

$$[Co(C_2O_4)_3]^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(C_2O_4)_2]^{2-} + (C_2O_4)^- \quad (14)$$

and the over-all first step for the photolysis is probably the same. Equation 15 of reference 28 gives the maximum rate of racemization expected *associated with* thermal decomposition, and if it is supposed that the only difference in the photochemical process is that k_1 above is replaced by the specific rate of photoactivation, then our values for ϕ_{rac}/ϕ_{decomp} are quite reasonable. In fact, on this interpretation, the apparently anomalous finding of a low value for the ratio ϕ_{OA}/ϕ_{OD} where no added oxalate was present might actually be a consequence of the fact that in the absence of added oxalate, the $Co(C_2O_4)_2{}^{2-}$ formed would be extensively dissociated, thus reducing the rate of the reverse step and hence the amount of racemization. Thus from the data of Barney, Argersinger, and Reynolds,[30] in 0.001 *M* $C_2O_4{}^{2-}$ only about 50% of Co(II) should be present as the dioxalate.

In summary, the present results seem to be no exception to what appears to be a general characteristic of Co(III) complexes, *i.e.*, that all photolytic processes occurring in appreciable yield appear to represent one or another secondary process following a common primary step involving a homolytic fissioning of a cobalt–ligand bond.[5]

Other Complexes.—Some evidence was found for photoracemization of $[Rh(C_2O_4)_3]^{3-}$ at 24° and with light of 546 mμ. On irradiation, both the optical density and activity decreased nearly lin-

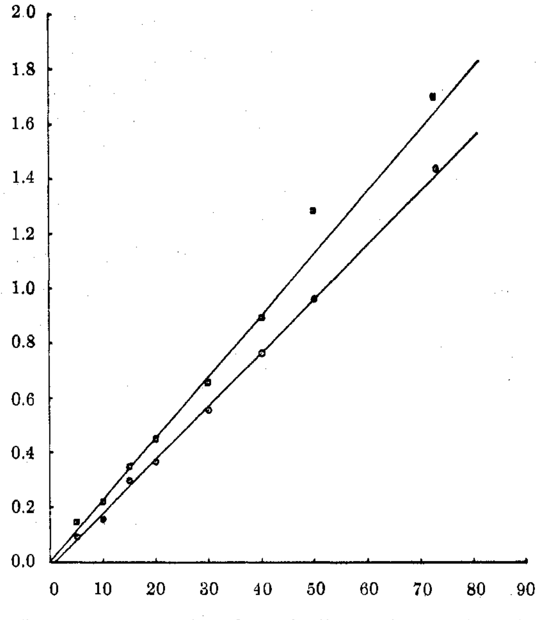

Fig. 3.—Photolysis of optically active $Co(C_2O_4)_3{}^{-3}$: 0.005 *M* complex, 0.4°, 410 mμ. The function given by the left hand terms of eq. 14 is plotted as ordinate. Upper line, *C* based on loss in optical activity; lower line, *C* based on loss in optical density at 605 mμ; abscissa, time (minutes).

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[30] J. E. Barney, W. J. Argersinger, and C. S. Reynolds, *J. Am. Chem. Soc.*, **73**, 3788 (1951).

TABLE VI

SUMMARY OF RUNS WITH *cis*-$[Co(en)_2Cl_2]^+$ AT 1°

Concn., *M*	Wave length, mμ	$\Delta I \times 10^6$, einsteins/sec.	% photo-aquation	Process and quantum yield,[a] $\phi \times 10^3$	% Retention of configuration
0.0101	340–375	0.21		Redox. 0.31	
.010	550–650	3.90		Aquat. 3.3	
.0081	550–650	3.52	34	Aquat. 2.8	62
.0081	550–650	3.43	55	Aquat. 3.5	47
.0075	550–650	2.30	27	Aquat. 3.3	
				Redox. 0.069	35
.010[b]	550–650	2.20		Racem. 3.5	

[a] These are partial quantum yields, *i.e.*, based on the named process per einstein absorbed. [b] This run made with 1-*cis*-$[Co(en)_2(H_2O)Cl]^{2+}$.

early on a semilogarithmic plot *vs.* time, at least at first. Assuming the former decrease to be due to decomposition, and correcting the latter for it, the two quantum yields would be: $\phi_{\text{decomp}} = 7.6 \times 10^{-4}$ and $\phi_{\text{rac}} = 4.3 \times 10^{-3}$. Since the decomposition products were not identified, the interpretation of the data may not be entirely correct, but there is no doubt that relative to other processes the Rh(III) complex photoracemizes more easily than does the corresponding Co(III) one. Interestingly, Dwyer and Garvan[7] have noted photoracemization to occur fairly readily with $[Rh(EDTA)(H_2O)]^-$.

Turning to ammine type Co(III) species, we find no evidence for any photoracemization of $[Co(en)_3]^{3+}$, the upper limit for ϕ_{rac} being about 5% of the value of 3×10^{-4} (white light) for photodecomposition. Similarly with $[Co(en)_2(C_2O_4)]^+$ and *cis*-$[Co(en)_2(NO_2)_2]^+$. For both, the quantum yield (with yellow light) for either decomposition or racemization was less than 5×10^{-5}. Under white light irradiation, slight decomposition eventually occurs but no effort was made to detect some minor amount of racemization.

It is interesting to consider the series

$[Co(en)_3]^{3+}$	Stable toward both photodecomposition and photoracemization
$[Co(en)_2(C_2O_4)]^+$	Same
$[Co(en)(C_2O_4)_2]^-$	Photoracemizes (with photodecomposition?)[7]
$[Co(C_2O_4)_3]^{3-}$	Photodecomposes with some photoracemization

Evidently, increasing substitution of ethylenediamine by oxalate labilizes the complex toward photo (and thermal) oxidation–reduction decomposition, and, at the same time, toward photo (and thermal) racemization. Further studies are needed, especially on the bisoxalate complex, to determine how uniform the progression in these reactivities is, but, qualitatively, at least, the behavior of the series broadens our earlier observation[4] in that the photo-lability of Co(III) complexes toward racemization, as well as toward aquation, appears to be closely geared to the ease of oxidizability of the acido group and thus to the ease of photo-oxidation–reduction decomposition.

Except for its multidentate character, $[Co(EDTA)]^-$ might be thought somewhat to resemble the bisoxalate complex above. We find, however, that optically active $[Co(EDTA)]^-$ (kindly supplied by Dr. S. Kirschner, Wayne State University) is extremely stable toward photoracemization. Only under intense white light irradiation did some loss in optical activity occur, and this was evidently due to a small amount of photodecomposition. On the other hand, $[Co(EDTA)(Br)]^{2-}$ has been found from preliminary studies[31] to undergo both photoaquation and photo-oxidation–reduction decomposition. Here again, the presence of an easily oxidizable acido group exerts a photo-labilizing effect.

Finally, a brief investigation of *cis*-$[Co(en)_2Cl_2]^+$ provided an example of a different type of stereophotochemistry. This complex is known to undergo a stereospecific aquation to the monochloro species[32]; on standing, the optical activity of an aqueous solution (measured at 450 mμ) first increases, then, more slowly, goes to zero. By analogy with $[Co(NH_3)_5Cl]^{2+}$[7] and *cis*- and *trans*-$[Co(en)_2Br_2]^+$[31] irradiation of *cis*-$[Co(en)_2Cl_2]^+$ should lead to both some oxidation–reduction decomposition and some aquation. Our interest was in whether the photoaquation would be stereospecific.

The results are summarized in Table VI. First,

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(31) Unpublished work from this Laboratory by A. W. Adamson and M. A. Bennett.

(32) J. P. Mathiew, *Bull. soc. chim. France*, **4**, 687 (1937).

the oxidation–reduction quantum yield shows the decrease with increasing wave length of irradiating light that seems characteristic of Co(III) complexes,[5] and to minimize complications from this process the retention of configuration studies were confined to the longer wave length region, where aquation was dominant. To exemplify the type of effect found, in the case of the run given by the third line of Table VI, the 34% photoaquation that occurred should have been accompanied by an increase of 0.09° in optical rotation, if entirely stereospecific, and by a decrease of 0.17°, if entirely non-stereospecific. We observe a decrease of 0.01°, corresponding to 62% retention of configuration.

It was not possible entirely to disentangle the above interpretation from the alternative ones that (a) some direct photoracemization occurs in the parent complex, that (b) the product $[Co(en)_2(H_2O)Cl]^{2+}$ is easily photoracemized or isomerized, or that (c) it photoaquates readily.

As noted in Table VI, however, a separate run with 1-*cis*-$[Co(en)_2(H_2O)Cl]^{2+}$ did give a fairly high quantum yield for loss of activity, although it was not ascertained whether this was due to process (b) or (c). We conclude, therefore, that the photoaquation of *cis*-$[Co(en)_2Cl_2]^+$ may be entirely stereospecific, and is at least partially so. It would be of interest to pursue this or related systems somewhat further, particularly to the point of determining whether the stereospecificity of photoaquation processes is at all wave length dependent. We suspect that it will be.

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The Application of Zone Melting Techniques to the Resolution of Two-Component Inorganic Salt Systems and Racemic Mixtures of Optically Active Compounds and their Diastereoisomers

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Evidence is presented that zone melting techniques are applicable to the partial resolution of two-component inorganic salt systems in aqueous solution as well as of diastereoisomeric mixtures of optically active compounds and racemic mixtures of asymmetric complexes. Resolution is achieved when one of the components is more soluble than the other and/or when the rates of dissolution at the solid–liquid interface of the two components are unequal. Unsaturated aqueous solutions containing two components which differ in solubility were subjected to the zone melting process, and the degree of resolution with respect to solubility differences was determined. In addition, partial resolution of diastereoisomeric mixtures of optically active compounds as well as enantiomeric mixtures of an inner complex in an asymmetric environment were achieved.

Discussion

Since the first papers on zone melting by Pfann[1] were published, several others have appeared which deal with various aspects of the subject, most being concerned with metals and alloys and the purification of these and other substances.[2] Pepinsky[3] suggested the use of zone melting for the separation of solutes which differ in solubility (especially diastereoisomers) from solutions which are liquid at room temperature. Essentially, the method described here consists of freezing a solution which contains two components and then causing a molten zone to traverse the frozen charge *via* the techniques presented.

It was considered of interest to study the factors responsible for the resolution of these systems since they are somewhat different from the usual zone melting situations in that rather than separating small quantities of impurities from a solvent, this method attempts to separate two components present in relatively large and ap-

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[1] W. G. Pfann, *Trans. AIME*, **194**, 747 (1952).

[2] N. L. Parr, "Zone Refining and Allied Techniques," G. Newnes, Ltd., London, 1960.

[3] R. Pepinsky, private communication, Pennsylvania State University, University Park, Pennsylvania.