

ml. of glacial acetic acid for 15 hr. An ice bath was used for cooling. The reaction mixture was allowed to stand at room temperature overnight after having been treated with 30 cc. of 10% H_2O_2 . The mixture was concentrated on a steam-bath. The concentrate was treated with 20 cc. of 8% H_2O_2 , six times, being again concentrated after each addition. A yield of 36 mg. of the tetracarboxylic acid was brought to radiochemical purity by recrystallization from an ether-petroleum ether mixture, m.p. $> 350^\circ$, spec. activ. 1.50 $m\mu c./mg.C.$

Anal. Calcd. for $C_{10}H_{10}O_8$ 258.2: C, 46.51; H, 3.91. Found: C, 46.24; H, 4.42. Calcd. acid equiv.: 64.5. Found: 65.2.

Benzoic Acid.—Finely powdered potassium permanganate was added to a boiling solution of 1 g. of bitropyl (spec. act. 1.49; 1.463 $m\mu c./mg.C.$) in 10 ml. of acetone until the violet color of permanganate persisted. The acetone was removed *in vacuo*. The excess permanganate and the manganese dioxide was reduced with SO_2 . Benzoic acid was isolated by continuous extraction with *n*-pentane. The acid was brought to radiochemical purity by recrystallization from water and from petroleum ether, spec. act. 1.50 $m\mu c./mg.C.$

Degradation.—A degradation of benzoic acid by the Schmidt reaction²¹ gave carbon dioxide, spec. act. 1.50 $m\mu c./mg.C.$ Acetanilide obtained from the aniline sulfate had a spec. act. of 1.10 $m\mu c./mg.C.$ (not corrected for inactive carbon).

Diene Adduct of Cycloheptatriene.—The Diels-Alder adduct of cycloheptatriene- C_7^{14} and acetylene dicarboxylic acid methyl ester was prepared by the method of Alder and Jacobs.²² Cycloheptatriene, spec. act. 13.51, 13.41 $m\mu c./mg.C.$, gave a 65% yield of the dimethylester adduct; spec. act. 7.19 $m\mu c./mg.C.$ Saponification of the ester followed by treatment with HCl gave a dicarboxylic acid; spec. act. 8.44 $m\mu c./mg.C.$

Cyclopropanedicarboxylic Acid Anhydride.—This acid was made from the adduct acid by the method of Alder and Jacobs.²²

Cyclopropanedicarboxylic acid anhydride was obtained in 4.2% yield, spec. act., 18.63 $m\mu c./mg.C.$

(21) Cf. R. C. Anderson and A. P. Wolf, BNL 3222, a modification of the method of E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

(22) V. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH]

Complex Ions of Chromium. IX. Mechanism of Racemization and Isomerization, Reactions of Chelated Chromium(III) Ions¹

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The resolution of *cis*-potassium dioxalato diaquochromate(III) is reported. Studies of the rates of racemization give an activation energy (ΔH^\ddagger) of 13.4 kcal./mole. Theoretical calculations indicate that a likely mechanism for this reaction and also for the *trans-cis* isomerization is one involving dissociation of a water molecule to give an intermediate which is most like a trigonal bipyramid. Similar calculations on trisoxalatochromate(III) are in agreement with the recent experimental measurements on this compound.

In a previous paper² from this Laboratory the kinetics of the *trans-cis* isomerization of potassium dioxalato diaquochromate(III) were reported. A mechanism was suggested which involved the breaking of one bond to an oxalate and subsequent rearrangement to give the *cis* isomer. This suggested mechanism now appears less likely than one which starts with the dissociation of a water molecule.

A thorough search of the literature has shown no report of the successful resolution of *cis*-dioxalato diaquochromate(III). This resolution has been found to be possible using the proper experimental conditions. Because of this the kinetics of the racemization of this optically active compound have been studied.

The mechanisms for the isomerization and for the racemization reactions should be identical. Theoretical calculations on the simple possible mechanisms were undertaken, along with similar calculations on the racemization of tris-oxalatochromate(III).

Experimental

Reagents.—The *trans* and *cis*-potassium dioxalato diaquochromate were prepared by the method of Werner³ using reagent grade oxalic acid and potassium dichromate. The *cis* compound was resolved by dissolving a weighed quantity of potassium dioxalato diaquochromate(III) in a minimum

quantity of warm water and adding to it a warm saturated solution of strychnine sulfate of sufficient volume to have 3 moles of strychnine per mole of chromium. After mixing the solution was cooled rapidly in an ice bath. A crystalline precipitate was formed which had an almost metallic luster with a slight reddish tinge. It was compact and easily filterable. After air drying this precipitate was readily soluble in water. Solutions of this precipitate gave a higher optical activity than the amorphous precipitates which were obtained on slower crystallization from the solution.

The crystalline diastereoisomer was analyzed for chromium and for oxalate by methods previously used,² with application of a modification following the method of Johnson and Mead⁴ to avoid the interference of strychnine. Approximately 5 ml. of concentrated ammonium hydroxide was added to 50 ml. of the aqueous solution containing the weighed sample of the diastereoisomer, the solution was placed in a separatory funnel, an equal volume of chloroform was added and the mixture was shaken. The aqueous phase was separated and heated to remove dissolved chloroform, and the analysis for chromium and oxalate were then performed. An alternate method in which the precipitated strychnine was removed by filtration gave comparable results. Analyses of the diastereoisomer gave the following results. Found: 3.89% Cr, 18.57% C_2O_4 . Calcd. for $(C_{21}H_{22}N_2O_2)_3 \cdot H[Cr(C_2O_4)_2(H_2O)_2]$, 3.89% Cr, 18.23% C_2O_4 .

Polarimeter.—The polarimeter used was a Rudolph Model 80 High Precision Polarimeter, equipped with a Rudolph Model 95 Spectroscopic Monochromator.

Polarimetric Rate Determinations.—For determination of the rates of racemization, a weighed sample (65–75 mg.) of the diastereoisomer was metathesized with a measured volume of thermostated 0.10 *M* potassium iodide solution, the ratio of strychnine to iodide being 1:1. The potassium salt of the complex went into solution, and the strychnine iodide remained as a white precipitate. This solution was

(1) Presented at the Northwest Regional Meeting of the American Chemical Society, Richland, Washington, June 16–17, 1960.

(2) R. E. Hamm, *THIS JOURNAL*, **75**, 609 (1953).

(3) A. Werner, *Ann.*, **406**, 216 (1914).

(4) C. H. Johnson and A. Mead, *Trans. Faraday Soc.*, **29**, 626 (1933).

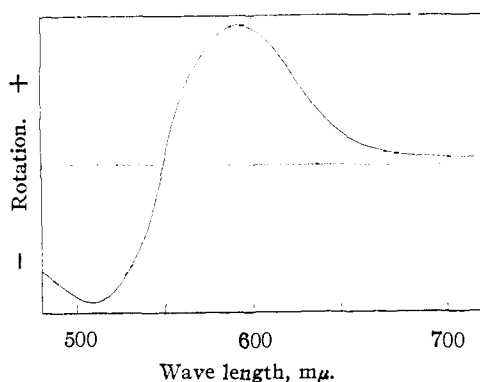


Fig. 1.—Rotary dispersion of *cis*-dioxalatodiaquo chromate (III).

rapidly filtered through a sintered glass filter and was diluted to volume in a 25 ml. volumetric flask. The final solution was placed in a jacketed 2 decimeter polarimeter tube which had thermostated water ($\pm 0.05^\circ$) pumped through the jacket. The optical activity of this solution was measured at 510 $m\mu$ as a function of time.

Rotary Dispersion.—At 0° the optical activity of a solution of the resolved potassium *cis*-dioxalatodiaquo chromate was determined as a function of wave length. The results of this run are shown in Fig. 1. This curve is seen to be a positive Cotton effect. Because of these results 510 $m\mu$ was chosen for rate measurements as a compromise of high angle of rotation and maximum precision of measurements.

Experimental Results

Using light of wave length 510 $m\mu$ the racemization was found to be first order with respect to complex concentration. Over a range of *pH* from 2.5 to 7.0 the rates were found to be independent of hydrogen ion concentration. Rate determinations were made over a temperature range of 0.3 to 43°. The results are shown in Table I. These data when plotted with $\log k_r h/kT$ vs. $1/T$ gave a straight line. The slope and intercept were determined by the method of least squares, finally yielding an activation energy, $\Delta H^\ddagger = 13.4$ kcal. per mole with a standard deviation of 0.3 kcal. and an entropy of activation, $\Delta S^\ddagger = -28$ cal./mole deg.

TABLE I
RACEMIZATION RATES FOR *cis*-DIOXALATODIAQUOCHROMATE(III)

Temp., °C.	No. runs	k_r , sec. ⁻¹ × 10 ⁴
0.3	2	0.36
26.4	13 ^a	3.68
29.9	1	4.70
33.9	2	5.78
34.5	1	7.0
37.3	1	8.4
41.4	1	12.3

^a *pH* varied from 2.5 to 7.0 for these 13 runs, the standard deviation of the 13 runs was 0.13×10^{-4} sec.⁻¹.

Theoretical Calculations and Discussion

Several possible simple reaction paths for either the isomerization reaction or for the racemization reaction $\text{CrOX}_2(\text{H}_2\text{O})_2$ are possible. The following mechanisms shall be considered: 1. intramolecular rearrangement without breaking any bonds, as suggested by Bailar,⁵ where the intermediate was as-

(5) J. C. Bailar, Jr., Chapter in "Chemistry of the Coordination Compounds, A Symposium," Pergamon Press, London, 1959, p. 165.

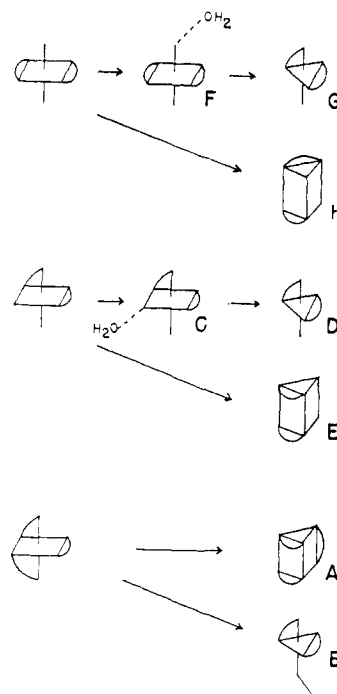


Fig. 2.

sumed to be a trigonal prism; 2, the separation of a water molecule to form a 5-coördinate intermediate, followed by rearrangement to form the lowest possible energy intermediate (trigonal bipyramid); 3, the breaking of a single oxalate-chromium bond.

The possibility of an oxalate ion completely separating from the chromium ion has not been considered as a possible reaction path because of the demonstrated lack of exchange with oxalate in the solution.⁶

Figure 2 shows schematically the simple reaction paths referred to, along with the different intramolecular mechanisms available for the racemization of *tris*-oxalatochromate(III). These mechanisms entirely correspond to the mechanisms enumerated above.

Calculations have been made for the energies of each of the forms shown in Fig. 2 by using the electrostatic theory of Magnus,⁷ modified by Garrick⁸ and simplified by Basolo and Pearson.⁹

The equation giving the potential energy of an octahedral complex where the ligands are uncharged as given by Basolo and Pearson⁹ is

$$E = -\frac{6q\mu}{r^2} + \frac{6(1.19)\mu^2}{r^3} + \frac{6\mu_1^2}{2\alpha} + \frac{6B}{r^9}$$

If the ligands are charged the equation must be modified as

$$E = -\frac{6qe^2}{r} - \frac{6q\mu}{r^2} + \frac{6(1.667)e^2}{r} + \frac{6(1.19)\mu^2}{r^3} + \frac{6\mu_1^2}{2\alpha} + \frac{6B}{r^9} + \frac{6(1.667)\mu e}{r^2}$$

(6) (a) F. A. Long, *THIS JOURNAL*, **61**, 570 (1939). (b) K. V. Krishnamurthy and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

(7) A. Magnus, *Z. anorg. Chem.*, **124**, 288 (1922).

(8) F. J. Garrick, *Phil. Mag.*, **9**, 131 (1930); **10**, 71, 76 (1930); **11**, 741 (1931); **14**, 914 (1932).

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 46-51.

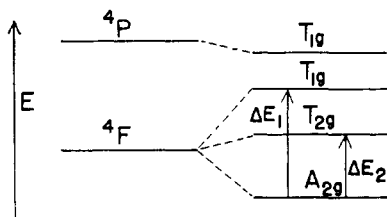


Fig. 3.

Where q is the number of charges on the central ion, r is the distance from the central ion to the ligand, μ is the entire dipole moment of the ligand, μ_i is the induced dipole moment of the ligand, α is the polarizability of the ligand, B is a constant which may be eliminated by differentiating the expression with respect to r and setting the differential equal to zero and e is the charge of an electron. The terms in the final equation have the following significance: 1. term: central ion–ligand charge attraction, 2. central ion–ligand dipole attraction, 3. ligand charge–ligand charge repulsion, 4. ligand dipole–ligand dipole repulsion, 5. energy required to induce dipoles, 6. Van der Waal's repulsion, and 7. ligand charge–ligand dipole repulsion.

The two halves of the oxalato-ion were each assumed to be equivalent to single monovalent negative ions and the C–C covalent bond between the two was assumed to be negligible for calculational purposes.

In order to make these calculations it was necessary to obtain values for the Cr–C₂O₄/2 and Cr–H₂O distances. This was done by calculating the electron energy level system for the absorption spectra of the complex ions Cr(C₂O₄)₃³⁻ and Cr(H₂O)₆³⁺, by the application of ligand field theory. The calculated energy level system was compared with the experimental spectra in order to obtain the distances between the central ion and the ligands.

The Cr³⁺ ion has 3 outer electrons (3d³), which are the only ones considered here. The ground term of a free Cr³⁺ ion is a ⁴F term. The 3d³ electron system was calculated by Hartmann and Kruse.¹⁰ They did not concern themselves with the signs of the terms of the eigenfunctions. These signs are important for calculations of the configurational interactions or second order perturbations. This treatment is similar to that of Hartmann and Kruse with the exception that the following operator rules are used to take account of the signs of the eigenfunction terms.

$$\begin{aligned} \mathcal{L}\psi(S L M_S M_L) &= \sqrt{(L + M_L)(L - M_L + 1)} \psi(S L M_S M_L - 1) \\ \mathcal{L}\phi(m_1^1, m_1^2, \dots) &= \pm \sqrt{(l^1 + m_1^1)(l^1 - m_1^1 + 1)} \phi(m_1^1 - 1, m_1^2, \dots) \\ &\pm \sqrt{(l^2 + m_1^2)(l^2 - m_1^2 + 1)} \phi(m_1^1, m_1^2 - 1, \dots) \\ &\pm \dots \\ &+ \text{for } m_1 \leq 0 \\ &- \text{for } m_1 > 0 \end{aligned}$$

Using these rules the given atomic eigenfunctions $\psi(S L M_S M_L)$ are replaced by sums of antisym-

(10) H. Hartmann and H. H. Kruse, *Z. phys. Chem.*, **5**, 9 (1955). The symbols used in this part are taken from this paper.

metrized products of one-electron eigenfunctions, $\phi(m_1^1, m_1^2, \dots)$. Finally there are obtained the following eigenfunctions corresponding to the proper irreducible representation¹¹

$$\begin{aligned} A_{2g} \quad \alpha &= \frac{1}{i} \sqrt{1/2} [\phi(2 1 -1) - \phi(1 -1 -2)] \\ T_{1g} \quad \beta_1 &= \sqrt{1/5} (1 0 -1) - \sqrt{4/5} \phi(2 0 -2) \\ \beta_2 &= \sqrt{5/16} [-\phi(2 1 0) + \phi(0 -1 -2)] - \\ &\sqrt{3/16} [-\sqrt{3/5} \phi(2 0 -1) + \sqrt{2/5} \phi(2 1 -2) + \\ &\sqrt{3/5} \phi(1 0 -2) - \sqrt{2/5} \phi(2 -1 -2)] \\ \beta_3 &= \frac{1}{i} \sqrt{5/16} [-\phi(2 1 0) - \phi(0 -1 -2)] + \\ &\frac{1}{i} \sqrt{3/16} [-\sqrt{3/5} \phi(2 0 -1) + \sqrt{2/5} \phi(2 1 -2) - \\ &\sqrt{3/5} \phi(1 0 -2) + \sqrt{2/5} \phi(2 -1 -2)] \\ T_{2g} \quad \gamma_1 &= \sqrt{1/2} [\phi(2 1 -1) + \phi(1 -1 -2)] \\ \gamma_2 &= \sqrt{3/16} [-\phi(2 1 0) + \phi(0 -1 -2)] + \\ &\sqrt{5/16} [-\sqrt{3/5} \phi(2 0 -1) + \sqrt{2/5} \phi(2 1 -2) + \\ &\sqrt{3/5} \phi(1 0 -2) - \sqrt{2/5} \phi(2 -1 -2)] \\ \gamma_3 &= \frac{1}{i} \sqrt{3/16} [-\phi(2 1 0) - \phi(0 -1 -2)] - \\ &\frac{1}{i} \sqrt{5/16} [-\sqrt{3/5} \phi(2 0 -1) + \sqrt{2/5} \phi(2 1 -2) - \\ &\sqrt{3/5} \phi(1 0 -2) + \sqrt{2/5} \phi(2 -1 -2)] \end{aligned}$$

The resulting energy expressions belonging to this irreducible representation are¹²

$$\begin{aligned} A_{2g}: E' &= 3E_2 \\ T_{1g}: E' &= 9/5 E_1 + 6/5 E_2 \\ T_{2g}: E' &= E_1 + 2E_2 \end{aligned}$$

where E' is the energy difference between the unsplit ⁴F level and the single split term as shown in Fig. 3.

The maxima of the absorption spectra are represented by the energy differences ΔE_1 and ΔE_2 . A higher ⁴P term gives in the ligand-field a T_{1g} split term. The configurational interaction between the two T_{1g} levels were calculated. The results are not given here because of their inaccuracy. The calculations made here used only the longer wave absorption peak, ΔE_2 . It may be represented by $\Delta E_2 = E_1 - E_2$.

Using Hartmann's formalism^{10,12} the integrals can be solved giving for the octahedral ion–ligand complex

$$\Delta E_2 = 23.806/r_1^5 + 119.03/r_1^6$$

and for the octahedral dipole–ligand complex

$$\Delta E_2 = 119.03/r_2^6$$

where r_1 is the distance from the central ion to the ion–ligand, r_2 is the distance from the central ion to the dipole–ligand, and is the total dipole moment of the ligand.

The total dipole moment is given by the sum of the permanent and the induced dipole moment, using the values given by Landolt–Börnstein.¹³

(11) The m_s values have been dropped from all of the one electron eigenfunctions since all of the m_s values are $+1/2$.

(12) H. Hartmann and F. E. Ilse, *Z. phys. Chem.*, **197**, 239 (1951), H. Hartmann, "Theorie der chemische Bindung," Springer, Berlin, 1954.

(13) Landolt–Börnstein, *Physikalisch-chemische Tabellen*, 5th Ed., Berlin, 1923–1936.

The permanent dipole moment of H_2O is reported as 0.72 Å. and the induced dipole moment was calculated to be 0.38 Å. The induced dipole moment of one-half of an oxalate ion was calculated to be about 1.2 Å. by using the method of Wang and Denbigh as given in Landolt-Börnstein.¹³ The errors in the dipole moments were found to be not very important in the determination of the final distance parameters.

It is a simple matter to calculate the distance parameters from the experimental absorption spectra by the use of the equations given above. The maxima are: at 565 $m\mu$, *i.e.*, $\Delta E_2 = 0.08064$ Å. (atomic units), for $Cr(C_2O_4)_3^{--}$, and at 576 $m\mu$, *i.e.*, $\Delta E_2 = 0.07911$ aU. for $Cr(H_2O)_3^{+++}$, then the distances calculated were: $r_1 = 3.8$ aU. for $Cr-C_2O_4/2$ and $r_2 = 3.5$ aU. for $Cr-H_2O$. These distances were used for all $Cr-C_2O_4/2$ and $Cr-H_2O$ bonds considered. The reason that such a complicated method was used to calculate the distances instead of using the well known ionic radii was that the ligand field theory and these other electrostatic calculations are based on the identical electrostatic model. Under these conditions even if the distance parameters obtained are wrong, a compensation of errors can be expected and the energy differences obtained will be more representative of the true facts, than would be the case if different models had been chosen for the two calculations.

The results of the calculations of the energies (in Å.) of the basic compounds are:

tris-Oxalatochromate(III)	-2.0315
<i>trans</i> -Dioxalatodiaquochromate(III)	-2.3814
<i>cis</i> -Dioxalatodiaquochromate(III)	-2.3219

The absolute values of these energies must not be taken literally because of the approximations made in the calculations. Contrary to these values experiment has shown² that the *cis* compound is the more stable one by 2 to 3 kcal. This disagreement is caused by the simplicity of the model which does not consider the distortions of the structures (*i.e.*, the changes in the $Cr-C_2O_4/2$ distances). Where the oxalates are parallel to each other, in the *trans* compound, there is a stronger interaction than in the *cis* form. The energies calculated for all structures having no oxalate ions lying parallel should be in correct relationship to one another.

The results of the calculations of energies required to form the various intermediates are shown in Table II.

The capital letters indicate the intermediates shown in Fig. 2. The value listed for the trigonal bipyramid, G, resulting from *trans*-dioxalato-

TABLE II
CALCULATED ENERGIES (IN KCAL.) REQUIRED TO FORM
POSSIBLE INTERMEDIATES

	Tri- gonal prism	Tetra- gonal pyramid (-H ₂ O)	Trigonal bipyramid	Exptl. ΔH^*
Racemization of tris-oxalatochromate(III)	140 A	>100	13.5 B	14.9 ¹³
Isomerization of <i>trans</i> -dioxalatodiaquochromate(III)	125 H	43 F	(10) G	17.5 ¹
Racemization of <i>cis</i> -dioxalatodiaquochromate(III)	125 E	45 C	12.3 D	13.4

diaquochromate(III) is estimated from the experimental fact that in solution the *trans* form is 2 to 3 kcal. less stable than the *cis* form.

The experimentally determined activation energies were in all three cases just slightly greater than the energies required to form the trigonal bipyramid-intermediates, (B, D, G) but considerably less than the energies of formation of the tetragonal pyramid-intermediates, (C, F), and very much less than the energies to form the trigonal prism-intermediates.

The conclusion from these results is that the mechanism presented by Bailar can be eliminated and that a mechanism through the formation of a five-coördinate intermediate is the most likely one. Such a mechanism for the racemization of optically active $Cr(C_2O_4)_3^{--}$ was originally suggested by Werner.¹⁴ It is in agreement with the recent experiments on oxygen-18 exchange reported for this compound by Llewellyn and Odell,¹⁵ who have reported that all 12 of the oxygen atoms exchange with oxalate ions in the solution at a rate considerably faster than any radioactive carbon exchange.

For the reactions of dioxalatodiaquochromate(III) it was assumed that during the period when one coördinate bond is stretching and eventually breaking the complex ion is simultaneously rearranging towards the trigonal bipyramid-intermediate. This rearrangement requires more energy in the case of the isomerization reaction than in the case of the racemization, because of the stronger interaction of the two parallel lying oxalate ions in the *trans*- $Cr(C_2O_4)_2(H_2O)_2^-$ ion. This is shown by the greater activation energy for this process.

Acknowledgment.—The authors gratefully acknowledge support of this research from a grant given by the National Science Foundation.

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

(14) A. Werner, *Ber.*, **45**, 3061 (1912).

(15) D. R. Llewellyn and L. Odell, *Proc. Aust. At. Energy Symposium*, 623 (1958).