in the InAs end of the diagram. Attempts to determine the extent of this field were not very successful due to the inability to attain equilibrium in the solid alloys, even after heating for three months. The alloys were too brittle to permit acceleration of homogenization by working before heat treatment. Extrapolation of the solidus in this area gives an approximate value of 2% InSb as the maximum extent of the one-phase region.

Thus, all alloys in the system form a solid solution as the primary phase upon freezing, and practically all alloys complete freezing at 525° with the formation of InSb.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Complex Ions of Chromium. II. *trans–cis* Isomerization of Potassium Dioxalatodiaquochromate(III)[1]

BY RANDALL E. HAMM

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The absorption spectra of *trans*- and *cis*-potassium dioxalatodiaquochromate(III) were determined, the *cis* form absorbing considerably more at peaks slightly shifted toward the red. Using this difference in absorption at a wave length of 415 mμ, the rate of the *trans–cis* isomerization was followed spectrophotometrically. The rate was found to be first order with respect to the chromium salt and independent of added hydrogen ion. The rate varied only slightly with ionic strength. Rates determined at different temperatures enabled calculation of heat and entropy of activation for the isomerization.

Methods of preparation of the solid salts of dioxalatodiaquochromate(III) were reported by Croft,[2] Rosenheim and Cohn,[3] and E. A. Werner[4] but it was A. Werner[5] who first recognized that both *trans* and *cis* isomers should exist and that all previous workers had prepared only the *trans* isomer because of the very much smaller solubility of that isomer. Werner described a procedure for preparing the *cis* isomer.

In a solution of dioxalatodiaquochromate(III), the equilibrium between the isomers is such that the *cis* isomer is the main species present; however, the solubility of the *trans* isomer is so small that it crystallizes out first when a solution is allowed to evaporate slowly. Since there have been no reports on the exact relationships existing between these isomers in solution, it was the purpose of this investigation to study the kinetics of the *trans–cis* isomerization of potassium dioxalatodiaquochromate(III). This was possible by spectrophotometric methods since in solution the *cis* isomer absorbs much more strongly than the *trans* isomer. This was first recognized by observation of the color of the fresh *cis* and *trans* solutions at equivalent concentrations. Under these conditions the solution of the *trans* isomer is much less intensely colored.

Experimental

Reagents.—The *trans*- and *cis*-potassium dioxalatodiaquochromate(III) were prepared by the methods of Werner[5] using reagent grade oxalic acid and potassium dichromate. The ionic strength was controlled by adding reagent grade sodium nitrate, and the acidity was controlled by addition of reagent grade perchloric acid.

Procedure.—The salts used were analyzed for both oxalate and chromium. The reference standard for both analyses was a cerium(IV) sulfate solution prepared from Certified Ceric Ammonium Nitrate from the G. Frederick Smith Chemical Company. This ensured that the salts used had two moles of oxalate for each mole of chromium.

To analyze for oxalate a weighed sample was boiled with excess potassium hydroxide to precipitate the chromium(III) hydroxide, the solution was acidified, treated with excess standard cerium(IV) solution, boiled, cooled, and the excess cerium back-titrated with standard ferrous solution. To analyze for chromium a weighed sample was acidified, boiled with excess ammonium persulfate for 15 minutes in the presence of silver nitrate as catalyst. The chromate produced was titrated with standard ferrous solution.

The absorption spectra and rates were determined by use of a Model DU Beckman spectrophotometer, using 2-cm. cells. The solutions were suspended in a constant temperature bath except while making the measurements. The rate measurements were made by the method of Guggenheim[6] as modified by King.[7] Two identical samples were weighed out. The first was dissolved, diluted to volume and allowed to stand in the constant temperature bath for several times the half-life of the reaction. The second weighed sample was dissolved, diluted and the absorbancy[8] of the first sample measured as a function of time after putting the second sample into solution, using the second solution in the reference cell.

The reaction was considered to be

$$\textit{trans} \xrightarrow{k_1} \textit{cis}$$

and the equation that was applied to treat the data was

$$A_s' = (A_s)_{t+\gamma} - (A_s)_t = b(T)_0(1 - e^{-k_1\gamma})[(a_M)_C - (a_M)_T]e^{-k_1t}$$

where A_s' was the measured absorbancy of the first, more strongly absorbing solution with reference to the second solution, b was the cell thickness, $(T)_0$ was the molar concentration of the starting *trans* compound, $(a_M)_T$ and $(a_M)_C$ were the molar absorbancy indexes of the *trans* and *cis* species, γ was the time between mixing the first and second solutions, and t was the time since mixing the second solution. By plotting $\log A_s'$ against t the slope of the straight line obtained was $-k_1/2.303$, where k_1 was the specific reaction rate constant. By plotting in this manner

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[1] The work on this investigation was supported by National Science Foundation Research Grant NSF-G62. The first paper of this series is considered to be THIS JOURNAL, **73**, 1240 (1951).

[2] H. Croft, *Phil. Mag.*, **21**, 197 (1842).

[3] A. Rosenheim and R. Cohn, *Z. anorg. Chem.*, **28**, 337 (1901).

[4] E. A. Werner, *J. Chem. Soc.*, **53**, 404 (1888).

[5] A. Werner, *Ann.*, **406**, 261 (1914).

[6] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

[7] E. L. King, THIS JOURNAL, **74**, 563 (1952).

[8] The terms used for spectrophotometric data are those recommended by the National Bureau of Standards, Letter Circular, LC-857 (1947).

it is not necessary to know the molar absorbancy indexes, the original concentration or the value of γ.

In order to obtain the absorption spectra of the *trans* isomer, before appreciable isomerization had occurred, solutions were prepared at 15° and the spectra run as rapidly as possible. At this temperature no points which were measured more than 10 minutes after preparing the solution were considered for plotting.

Results and Discussion

The absorption spectra of the *cis* and *trans* isomers of potassium dioxalatodiaquochromate (III) are shown in Fig. 1. It may be seen that the *cis* isomer had absorption peaks that were much higher than the comparable peaks for the *trans* isomer, and also that these peaks are only very slightly shifted toward the red. The absorption curve obtained for the *trans* compound that had aged long enough for the isomerization to be complete was identical with the curve for the pure *cis* isomer.

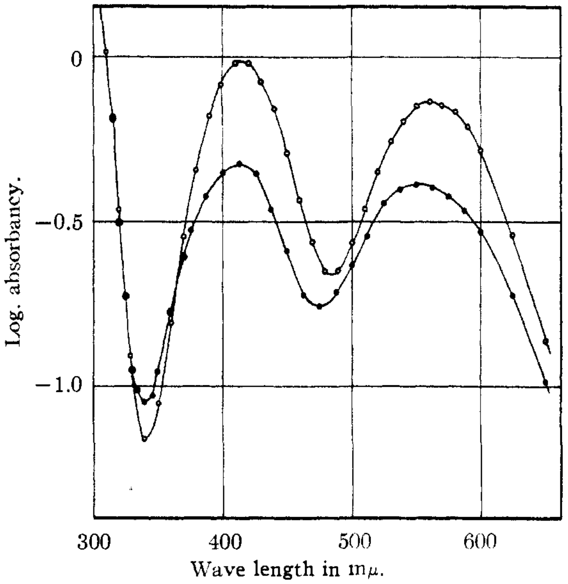

Fig. 1.—Absorption spectra of potassium dioxalatodiaquochromate(III): ○, *cis*; ●, *trans*; 8.25×10^{-3} molar solutions in 2.003 cm. cell; Beckman DU spectrophotometer used at 25° for the *cis* and 15° for the *trans*; no temperature effect was noted upon running the *cis* at temperatures lower than 25°; the spectrophotometer was operated to use minimum slit widths possible at each wave length.

By using 415 mμ as a wave length it was possible to determine the rate of isomerization by following the increase in absorbancy as indicated under procedure. Values of $\Delta \log A_{s'}$ plotted against time gave straight line plots at all temperatures investigated.

In Table I are given the rates determined for various values of temperature, ionic strength and hydrogen ion concentration. The results listed show that varying the *p*H over a range from 1.85 to 4.28 gave the same rate within experimental error. Observation of the results of rates determined at 29.3° where ionic strength was varied from 0.00825 to 0.352 indicate that the rate does increase slightly with ionic strength, but in a manner that would be predicted if we imagine the reaction to take place by a collision between the singly negative charged complex ion and an uncharged water molecule. These data were fitted approximately by an equation that is linear in ionic strength

$$k_1 = 6.41 \times 10^{-4} + 4.31 \times 10^{-4} \mu$$

TABLE I

Temp., °C.	Ionic strength	*p*H	$k_1 \times 10^4$ per second
17.3	0.00825	4.45	1.83
25.0	.0182	1.85	4.19
	.0102	2.63	4.20
	.00925	2.96	4.17
	.00825	4.38	4.23
25.4	.00825	4.48	4.30
29.3	.00825	4.48	6.43
	.0132		6.48
	.117		6.77
	.235		7.50
	.352		7.94
36.2	.00825	4.47	12.4
	.00825		12.6

According to the absolute theory of reaction rates[9]

$$k_1 = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

where k is the Boltzman constant, h is the Planck constant, T is the temperature in degrees Kelvin, $\Delta S^{\ddagger}$ is the entropy of activation, and $\Delta H^{\ddagger}$ is the heat of activation. In Fig. 2 there is shown the log k_1h/kT *vs.* $1/T$ plot from which the heat and entropy of activation were calculated. These values were also calculated for the exchange of a water molecule for one of the chlorides of dichlorotetraaquochromium(III) ion, rates for which were reported in the first paper of this series,[1] and from

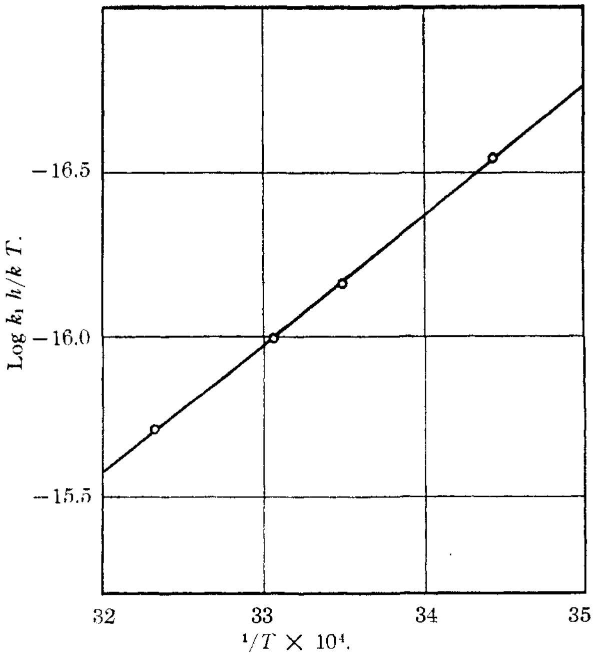

Fig. 2.—Heat and entropy of activation plot for the *trans-cis* isomerization of potassium dioxalatodiaquochromate (III).

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[9] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., p. 99.

the results on racemization of trioxalatochromate (III) reported by Bushra and Johnson.[10] Table II gives the values calculated for these reactions.

TABLE II

	$\Delta S^{\ddagger}$, cal./deg.	$\Delta H^{\ddagger}$, kcal.	$\Delta F^{\ddagger}_{298}$, kcal.
trans–cis Isomerization dioxalatodiaquochromate(III)	−15.3	17.5	22.1
Exchange of H_2O for Cl in dichlorotetraaquochromium(III)	−16.3	14.4	19.3
Racemization of trioxalatochromate-(III)	−24.5	14.9	22.3

Long[11] has conclusively demonstrated that the racemization of trioxalatochromate(III) does not involve the separation of oxalate ions from the complex. It is likely that this separation of oxalate ions does not occur in the isomerization of the dioxalatochromate(III). It may be postulated that the reaction could occur upon collision of the *trans* complex ion with a properly oriented water molecule. A reaction intermediate would be formed in which the incoming water molecule would occupy a position in the chromium octahedron. The end of the oxalate thus released could be held loosely by the three water molecules, possibly through hydrogen bonding. If the central water were released the *trans* isomer would be recovered, but if either of the other water molecules were released by rebonding the oxalate, the *cis* isomer would be the product. This reaction may be represented by

$$\textit{trans} + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{intermediate} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \textit{cis} + H_2O$$

In order to explain the results obtained, both k_2 and k_3 would have to be very large with respect to k_1, and to explain the final equilibrium being shifted very far in the direction of the *cis* isomer k_1 must be very large with respect to k_4. If the slow steps are those forming the intermediate there will be no appreciable amount of the intermediate present at any time as it will be reacting very rapidly to form the end-products. The negative entropy of activation obtained is in agreement with this postulate, since in addition to requiring a properly oriented water molecule, which will require the water molecule to lose its rotational freedom, there is the formation of the additional bond in the intermediate.

The exchange of a water molecule for a chloride in the dichlorotetraaquochromium(III) has essentially the same entropy of activation and therefore can be assumed to involve the same type process. The greater part of the negative entropy of activation in both cases can be explained by the loss of freedom of rotation of a water molecule. In the case of the racemization of the trioxalatochromate (III) the large negative entropy of activation may involve either the requirement of two properly oriented water molecules or a transmission coefficient which is considerably less than unity.

The lower heat of activation in the case of the racemization of the trioxalatochromate may be explained by the fact that this is a triply negative charged ion instead of a singly negative charged ion as in the case of the dioxalatochromate. This larger negative charge would make it easier to separate the bonds to give the reaction intermediate despite the fact that there are two bonds to be separated.

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

[11] F. A. Long, THIS JOURNAL, **61**, 570 (1939).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY]

Spectrophotometric Investigation of the Complexes Formed between Copper and Pyrophosphate Ions in Aqueous Solution

BY JAMES I. WATTERS AND ARNOLD AARON

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A series of complex species, $[Cu(P_2O_7)_2]^{6-}$, $[CuP_2O_7]^{2-}$, $[Cu_2P_2O_7]^0$ and $[Cu_4P_2O_7]^{4+}$ exist in solutions containing the corresponding ratios of copper to pyrophosphate ions. The last two, which have not been reported before, were detected only in very dilute solutions due to the low solubility of precipitates such as $Na_2Cu_3(P_2O_7)_2 \cdot Aq$. Dipyrophosphatocuprate(II) ion is the predominant complex of copper(II) in solutions containing a moderate excess of pyrophosphate ion, in the *p*H range of about 10 to 7. If the pyrophosphate ion concentration is decreased or if the solution is made weakly acidic, the equilibrium shifts to form an increasing proportion of monopyrophosphatocuprate(II) complex. With sufficient acid added to yield a *p*H in the range of 5.5 to 2, a precipitate such as $Na_2Cu_3(P_2O_7)_2 \cdot Aq$ may form. In more acidic solutions no precipitate forms and acidic complexes containing hydrogen ion are obtained. At an ionic strength of unity, the first and second instability constants for the stepwise dissociation of dipyrophosphatocuprate(II) are 2×10^{-4} and 2×10^{-9}.

It has long been evident that copper and pyrophosphate ions form complexes in aqueous solution since the blue color of the mixture is considerably more intense than that due to the hydrated copper ion alone. Bassett, Bedwell and Hutchinson[1] observed that the intensely blue color of the copper complex in solutions persisted in only one crystal, namely, the moderately soluble crystalline $Na_6Cu(P_2O_7)_2 \cdot 16H_2O$. On the basis of this observation they concluded that a dipyrophosphatocuprate(II) complex was present in this particular crystalline phase but that the copper ions were hydrated with variable amounts of water in other crystals containing copper and pyrophosphate ions. Rogers and Reynolds,[2] in an investigation of the complexes of copper and other metals with alkali pyrophosphates by potentiometric, conductometric and amperometric titrations, found that the equivalence

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[1] H. Bassett, W. L. Bedwell and J. B. Hutchinson, *J. Chem. Soc.*, 1412 (1936).

[2] L. B. Rogers and C. A. Reynolds, THIS JOURNAL, **71**, 2081 (1949).