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Isomerization of *cis*- and *trans*-Tetraaquodichlorochromium(III) Ion in Acidic Aqueous Solution[1]

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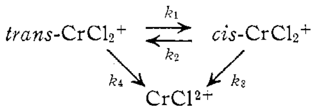
The aquation of tetraaquodichlorochromium(III) species has been studied by a number of investigators.[3] The earlier studies are incomplete, however, because either the existence of isomeric dichloro species was ignored or, if recognized, the possibility of direct isomerization was not taken into account. The study reported in the present paper gives data on this isomerization

$$trans\text{-}Cr(OH_2)_4Cl_2^+ = cis\text{-}Cr(OH_2)_4Cl_2^+$$

in acidic aqueous solution at 34.8°. The concentration of chloride ion has been kept low to eliminate pathways for isomerization involving pentaaquochlorochromium(III) ion as an intermediate. Isomerization *via* trichloro species, although possible, has been demonstrated to be absent by the lack of a dependence of isomerization rate upon concentration of added chloride ion.[4]

The results of the present study will be discussed, therefore, in terms of a reaction scheme



The spectra of isomeric dichlorochromium(III) species and monochlorochromium(III) ion are different,[5] but not different enough to allow accurate analysis of reaction mixtures by direct spectrophotometric measurement. In the present study, analysis of solutions containing only isomeric dichlorochromium(III) ions was made after separation of these species of charge 1+ from the product of aquation, monochlorochromium(III) ion, an ion of charge 2+, by an ion-exchange method.

Experimental Methods

Reagents.—Solutions containing only *trans*-dichlorochromium(III) ion were prepared using commercially available green chromium(III) chloride (which contains the *trans* isomer[5a,6]). Solutions containing essentially pure *cis*-dichlorochromium(III) ion were prepared starting with a solution of chromium(III) chloride in acetone–ether[7] which was extracted with aqueous perchloric acid prior to separation of chlorochromium(III) species by ion exchange. Such a starting solution containing trichlorochromium(III) species produces relatively large amounts of *cis*-dichlorochromium(III) upon aquation.[3a] Dowex-50W-X 8 (50–100 mesh) ion-exchange resin was used. Separation of the *cis* isomer in preparation of this species involved a 100-cm column (1-cm diameter) with elution at low temperature (~1°) by 0.2 M $HClO_4$. Analysis of the reaction mixtures involved use of 16-cm columns (1-cm diameter) with rinsing and elution at a low temperature by 0.2 M $HClO_4$.

Molar Absorbancy Indices.—The molar absorbancy indices of *trans*-dichlorochromium(III) ion were determined on solutions freshly prepared in the manner already described. For the *cis* isomer, published values were used.[5a] The wavelengths 450 and 640 mμ were employed in analysis. The molar absorbancy indices (based on decadic logarithms) of the *trans* isomer are $a_{450} = 21.7\ M^{-1}\ \text{cm}^{-1}$ and $a_{640} = 24.4\ M^{-1}\ \text{cm}^{-1}$, and those of the *cis* isomer are $a_{450} = 28.8\ M^{-1}\ \text{cm}^{-1}$ and $a_{640} = 19.6\ M^{-1}\ \text{cm}^{-1}$.

Kinetic Studies.—Conditions employed in the experiments were: *trans* experiments, $[H^+] = 0.203$, 0.054, and 0.011 M; *cis* experiment, $[H^+] = 0.203\ M$. In *trans* experiments, the initial concentration of *trans*-dichlorochromium(III) ion was ~0.094 M, and the initial concentration of the *cis* isomer was approximately zero. In the *cis* experiment, the initial concentration of *cis*-dichlorochromium(III) ion was 0.071 M, and the initial concentration of the *trans* isomer was approximately zero. In *trans* experiments, the initial concentration of chloride ion was the same as the initial concentration of chromium(III), and in the *cis* experiment it was approximately zero. All experiments were performed at 34.8°.

At various times portions of reaction mixture were removed and added to the column containing cation-exchange resin held at 1–2°. Rinsing and elution with cold 0.2 M perchloric acid separated the mixture of isomeric dichloro species from monochloro species, which is held in the resin phase more tightly. Measurements of light absorption at 450 and 640 mμ provided data from which the concentrations of *cis*- and *trans*-dichlorochromium(III) ion could be calculated.[8] (The total concentration of chromium in the dichloro fraction was checked by conversion of the dichloro species to chromate with alkaline peroxide, followed by spectrophotometric determination of chromium(VI).)

Figure 1 presents experimentally observed concentrations in the runs at 0.203 M H^+ as well as curves derived from the set of rate constants $k_1 = 7.8 \times 10^{-5}\ \text{sec}^{-1}$, $k_2 = 6.2 \times 10^{-5}\ \text{sec}^{-1}$, $k_3 = 8.3 \times 10^{-5}\ \text{sec}^{-1}$, and $k_4 = 1.8 \times 10^{-4}\ \text{sec}^{-1}$, obtained by trial and error fitting of the integrated rate equations[9] to the data. The agreement is good, the average percentage difference between observed and calculated concentrations being 2.7%.

At long times the ratio of concentrations $[cis\text{-}CrCl_2^+]/[trans\text{-}CrCl_2^+]$ should approach the value $(k_1 + k_4 + m)/k_2$ (where $m = {}^1/_2\{-(k_1 + k_2 + k_3 + k_4) + [(k_1 + k_2 + k_3 + k_4)^2 - 4(k_2k_4 + k_1k_3 + k_3k_4)]^{1/2}\}$). The value of this quantity corresponding to the set of rate constants just given is 2.36. Experimentally observed values of this ratio late in experiments starting with pure *trans* isomer are (given as time in minutes, $[cis]/[trans]$): 150, 1.05; 200, 1.55; 250, 1.80; 300, 2.04. For the run starting with pure *cis* isomer the corresponding values are: 150, 3.27; 200, 2.74. It is worth noting that the steady-state ratio [*cis*-

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[2] NSF Summer Research Participant, 1965.

[3] Two recent references are: (a) H. B. Johnson and W. L. Reynolds, *Inorg. Chem.*, **2**, 468 (1963); (b) C. W. Merideth, W. D. Mathews, and E. F. Orlemann, *ibid.*, **3**, 320 (1964). Earlier references are cited in these papers.

[4] This observation was made in a study, similar to the present study, by D. Freund at the University of Wisconsin in 1959. The highest concentration of chloride ion studied was ~0.5 M; this concentration was about threefold higher than the concentration in other comparable runs.

[5] (a) E. L. King, Sr. M. J. M. Woods, O.P., and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958); (b) J. E. Finholt, K. G. Caulton, and W. J. Libbey, *Inorg. Chem.*, **3**, 1801 (1964).

[6] (a) I. G. Dance and H. C. Freeman, *ibid.*, **4**, 1555 (1965); (b) B. Morosin, *Acta Cryst.*, **21**, 280 (1966).

[7] A. Recoura, *Compt. Rend.*, **194**, 229 (1932).

[8] An appendix giving the fractions of the chromium present as *cis*- and *trans*-dichlorochromium(III) ion as a function of time in each of the eight experiments has been deposited as Document No. 9152 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[9] R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957).

$CrCl_2^+]/[trans\text{-}CrCl_2^+] \cong 2.36$ is appreciably different from the equilibrium ratio $K = k_1/k_2 \cong 1.26$.

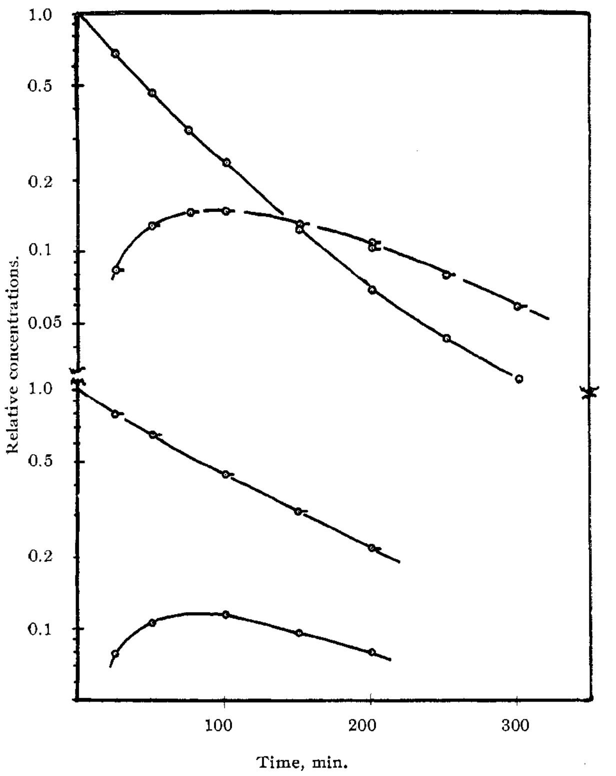

Figure 1.—Relative concentrations *vs.* time; [H$^+$] = 0.203 *M*; *t* = 34.8°: ⊙, [*trans*-$CrCl_2^+$]; ⊙-, [*cis*-$CrCl_2^+$]; upper part, experiment starting with pure *trans*; lower part, experiment starting with pure *cis*. (The points are experimental points. The lines are calculated using the derived rate constants.)

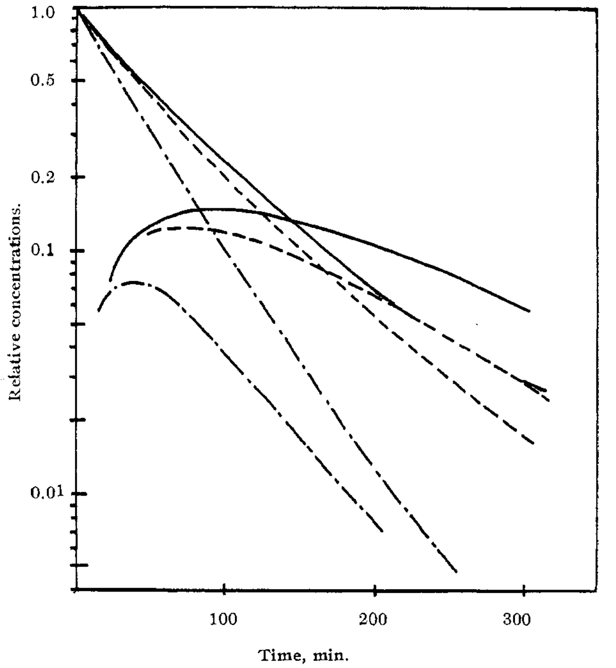

Figure 2.—Relative concentrations *vs.* time; *t* = 34.8°; all experiments staring with pure *trans*. Upper set of curves shows concentration of *trans*; lower set shows concentration of *cis*. [H$^+$] = 0.203 *M*, ———; 0.054 *M*, - - - -; 0.011 *M*, — - —. (The lines go through experimental points; except for [H$^+$] = 0.203 *M*, they are not calculated lines.)

Data from *trans* experiments at lower acidities given in Figure 2 indicate the rate of disappearance of reactant species is increased as the hydrogen ion concentration decreases. The data are not adequate, however, to allow evaluation of the dependence of each of the pseudo-first-order rate coefficients k_1, k_2, k_3, and k_4 upon the concentration of hydrogen ion. Consideration of the initial rate of disappearance of *trans*-$CrCl_2^+$ indicates that values of the rate constants k_1 and k_4 obtained for 0.203 *M* hydrogen ion correspond approximately to values for pathways independent of hydrogen ion concentration.

Discussion

The data presented in this paper are consistent with the reaction scheme already presented. This consistency does not prove, however, that unstable intermediates do not participate. In particular, the absence of an unstable pentacoordinated dichloro species as an intermediate in isomerization is not proved since differential equations for a more elaborate reaction scheme based upon the steady-state approximation applied to the intermediate have the same form as those used.

The value of the equilibrium quotient for the isomerization reaction *trans*-$CrCl_2^+$ = *cis*-$CrCl_2^+$ is $k_1/k_2 = 1.26$, a value appreciably lower than values obtained in the molten hydrated salt[5a] (1.8), equilibrated solutions of ionic strength ≅4 *M* (2.0 ± 0.6),[5a] or equilibrated solutions of ionic strength 7 *M* (2.1 ± 0.2).[3a] It seems reasonable that the less polar species would be more stable in solutions of lower electrolyte concentration.

A question naturally arises regarding consistency of our data and interpretation with that of a published study in which aquation of *cis*- and *trans*-dichlorochromium(III) ion was followed by spectrophotometric measurements directly on the reaction mixture and interpreted under the assumption that direct isomerization did not occur.[3a] To check this, concentration data from the *trans* runs pictured in Figure 1 were used to calculate the light absorption of the unprocessed reaction mixture as a function of time. (Such values were not, of course, observed directly in the present study since the monochloro species was separated from the reaction mixture before spectrophotometric analysis.) The absorbance values obtained were then used to calculate the apparent concentration of the *trans*-dichloro and mono species as a function of time under the assumption that no *cis* species was formed. Over the time period during which the apparent concentration of the *trans* species decreases by a factor of 20, the first-order plot log [*trans*-$CrCl_2^+$] *vs.* time is essentially linear, with a slope corresponding to an apparent first-order rate constant of 3.3×10^{-4} sec^{-1}. This value differs appreciably from both the correctly calculated value of the first-order rate constant for aquation of the *trans* isomer (1.8×10^{-4} sec^{-1}) and the sum of the first-order rate constants for both of the reactions open to the *trans* isomer (2.6×10^{-4} sec^{-1}). Clearly, the spectrophotometric method is not adequately sensitive to be applied directly to the unprocessed reaction mixture.