tension of this study to aquation of this complex in perchloric acid solution, with the purpose of determining whether the weakly basic nitrate anion affects the products or kinetics of the aquation. It is known that the presence of nitrate ion may affect aquation reactions of chromium(III) complexes of this type from an investigation[5] of the aquation of *cis*-difluorobis-(ethylenediamine)-chromium(III) cation, for which the rate constant at 40.5° is twice as great in nitric acid as in perchloric acid of the same pH (1.04) under the same concentration conditions.

Experimental

trans-$[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ was prepared as described earlier[2] and dried at 105° for several hours. Fifty g. was dissolved in 250 ml. of 0.1 F $HClO_4$ (reagent grade) and 50 g. of recrystallized $NaClO_4$ was added; the mixture was stirred for 2–3 m.n. and filtered. The gray-green solid was washed with ethanol, then with diethyl ether, and dried at 105°; yield, 90%. Its visible absorption spectrum in water was essentially identical with the spectrum of *trans*-$[Cr(en)_2Cl_2]NO_3$ observed[3,4] in 0.1 F HNO_3. *Anal.* Calcd. for *trans*-$[Cr(en)_2ClCl_2]O_4$: Cr, 15.2; Cl (ligand), 20.7; C, 14.03; N, 16.36; H, 4.71. Found: Cr, 15.2; Cl (ligand), 20.7; C, 13.86; N, 16.41; H, 4.74.

The *trans* nitrate salt was precipitated from a 0.1 F HNO_3 solution of the chloride salt by addition of a tenfold excess of $NaNO_3$, and the solid was washed with ethanol and then with diethyl ether. The visible absorption spectrum in 0.1 F HNO_3 was the same as observed with earlier preparations.[3,4] *Anal.* Calcd. for *trans*-$[Cr(en)_2Cl_2]NO_3$: Cr, 17.0; Cl, 23.2; C, 15.75; N, 22.95; H, 5.29. Found: Cr, 16.6; Cl, 23.1; C, 15.59; N, 23.07; H, 5.16.

Two kinetic runs were made in 0.125 F $HClO_4$ with the perchlorate salt (initially 4.4 mF) and one, for comparison purposes, in 0.1 F HNO_3 with the nitrate salt (initially 8.8 mF), all in the dark at 35.00 ± 0.05° with the chromatographic separation technique developed earlier.[3,4] The Dowex AG50W-X8 (H^+ form, 100–200 mesh) cation-exchange column was operated at 5°, using $HClO_4$ eluting agents in the perchlorate runs and HNO_3 eluting agents in the nitrate run. Each chromatographic fraction was analyzed for Cr spectrophotometrically[4] and also titrimetrically[6]; the former method usually gave results 1–2% low relative to the EDTA titrimetric method.

Results and Discussion

Rate plots of ln c *vs.* t, where c is the molar concentration of unreacted *trans*-$[Cr(en)_2Cl_2]^+$ at time t determined from the *trans*-dichloro elution fraction, were linear over 3–4 half-times. Table I gives the first-order rate constants,[7] together with the value found earlier[3,4] in 0.1 F HNO_3. Within experimental error, the rates in $HClO_4$ and HNO_3 are the same; the rate constant found in the single HNO_3 run made in this investigation is 8% greater than the average value obtained earlier[3,4] in several runs with a different preparation of *trans*-$[Cr(en)_2Cl_2]NO_3$.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF *trans*-$[Cr(en)_2Cl_2]^+$ AT 35.00°

Medium	10^5k, sec.$^{-1}$
0.125 F $HClO_4$	9.7 ± 0.5[a]
	9.0 ± 0.4[a]
0.10 F HNO_3	9.5 ± 0.1[a,b]
	8.75 ± 0.05[c]

[a] This research. [b] Standard deviation of the four experimental points from linearity was only ±0.02; error given is an estimate of the over-all error. [c] MacDonald and Garner, ref. 3 and 4.

The same reaction products, namely, *trans*-$[Cr(en)_2(OH_2)Cl]^+$, *cis*-$[Cr(en)_2(OH_2)Cl]^+$, and the species tentatively characterized[3,4] as *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$, were found chromatographically in the $HClO_4$ and HNO_3 runs. The percentages of each of these products formed at 1, 2, 3, 4, 6, 8, and 12 hr. were essentially the same in $HClO_4$ as in HNO_3 and as in the previous investigations[3,4] in HNO_3.

Thus, within experimental error the kinetics and products of aquation of *trans*-$[Cr(en)_2Cl_2]^+$ are not affected by the substitution of a nitrate medium for a perchlorate medium, despite the fact that nitrate ion can affect the rates and presumably the products of certain related reactions. The greater rate of aquation of *cis*-$[Cr(en)_2F_2]^+$ in 0.1 F HNO_3 than in 0.1 F $HClO_4$ over the range 10–40° is associated with a decrease in Arrhenius activation energy from 23 ± 1 in $HClO_4$ to 14 ± 2 kcal. mole^{-1} in HNO_3.[5] The source of this difference in E_a is not definitely known, but since the aquation of the dichloro complex is not acid-catalyzed, the nitrate effect in the former may be due to a more ready reaction of nitrate ion with the presumed reactive protonated intermediate, *cis*-$[Cr(en)_2F_2H]^{+2}$.

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(6) J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, **44**, 33 (1955); method modified by omission of the ascorbic acid.

(7) Equivalent to $k_{12} + k_{13} + k_{14} + k_{12}'$ in the notation of ref. 3 and 4.

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The *cis–trans* Isomerization of Dihydroxobis-(ethylenediamine)-chromium(III) Cations[1]

BY DONALD C. OLSON AND CLIFFORD S. GARNER

Received September 17, 1962

In connection with a study of the hydrolysis of *cis*- and *trans*-$Cr(en)_2Cl_2^+$ ions in basic solution presently underway in this Laboratory a need arose to investigate the kinetics of *cis–trans* isomerization of $Cr(en)_2(OH)_2^+$. Woldbye[2] has made a thorough investigation of acid–base and *cis–trans* equilibria of the diaquo, hydroxoaquo, and dihydroxo complexes, but he reports only two semiquantitative data from which the approximate rate of isomerization of the dihydroxo ions might be deduced.

We report here a kinetic study of this isomerization, together with further observations on the *cis–trans* equilibrium.

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[1] Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California.

[2] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

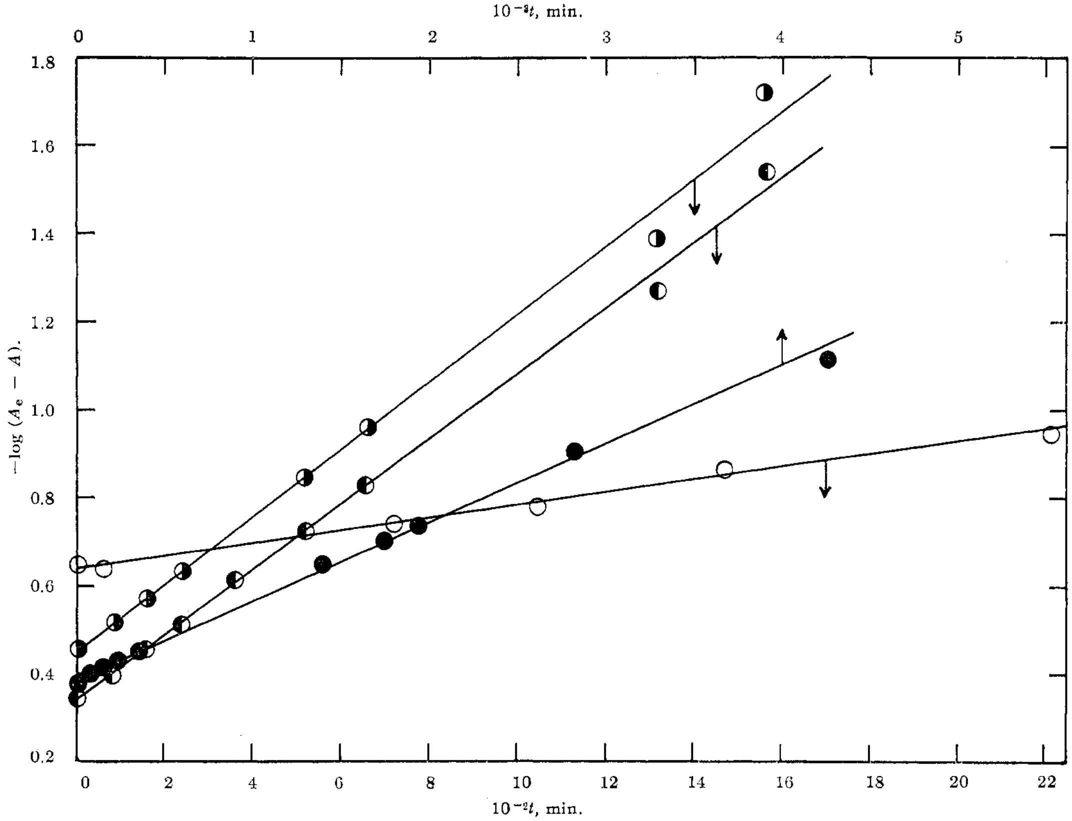

Fig. 1.—Rates of isomerization of $Cr(en)_2(OH)_2^+$ in 0.10 F ethylenediamine, 0.10 F $LiClO_4$: ○ pH 11.39, 25° (506 mμ); ● pH 10.90, 25° (530 mμ); ◐ pH 10.60, 35° (378 mμ); ◑ pH 10.60, 35° (530 mμ).

Experimental

***cis*- and *trans*-Diaquobis-(ethylenediamine)-chromium(III) Bromide Hydrates.**—These compounds were synthesized by the method of Woldbye.[2] The visible absorption spectra of fresh solutions of each salt in 4 F HNO_3 (*cis*) or in 0.1 F $HClO_4$ (*trans*) agreed well with the spectra reported[2] for the corresponding diaquo complex in 1 F $NaNO_3$. The spectrum of each compound in ethylenediamine buffer at pH 10.9 (in which diaquo is *ca.* 100% converted to dihydroxo) corresponded closely with the spectrum reported[2] for the corresponding dihydroxo complex. Analyses for Cr, Br, C, H, and N on the *trans* compound indicated the composition was intermediate between the 1-hydrate and the 2-hydrate. *Anal.* Calcd. for *cis*-$[Cr(en)_2(OH_2)_2]Br_3 \cdot 2H_2O$: Cr, 10.7. Found: Cr, 10.7.

Lithium Perchlorate and Ethylenediamine.—A stock solution of $LiClO_4$ was prepared by addition of a stoichiometric amount of concentrated $HClO_4$ (J. T. Baker Analyzed Reagent) to reagent grade Li_2CO_3 and dilution to 0.10 F. Eastman White Label ethylenediamine was distilled over NaOH and standardized by potentiometric titration with standard $HClO_4$. Other chemicals were C.P. or reagent grade.

Equilibrium Constants.—Molar absorbancy indices[3] of the dihydroxo complexes were determined at 25.0 and 35.0° at the *cis* absorption maxima (378 and 530 mμ) on fresh solutions of the corresponding diaquo complex in 0.10 F ethylenediamine buffer (0.10 F in $LiClO_4$), using a Beckman DU spectrophotometer. The 25° values obtained were in excellent agreement with those reported by Woldbye[2] at 25° in 1 F $NaNO_3$. These solutions were allowed to come to equilibrium in the dark at 25.0 and 35.0°. From final measurements taken at 8.3 days (25°) or 3.8 days (35°) the equilibrium constants K were calculated from the relation

$$K = (cis)/(trans) = \frac{c_T a_t - (A_e/d)}{(A_e/d) - c_T a_c} \qquad (1)$$

were c_T is the total molar concentration of both isomers, A_e is the observed equilibrium absorbancy, and a_t and a_c are the molar absorbancy indices of *trans*- and *cis*-$Cr(en)_2(OH)_2^+$, respectively.

Kinetic Runs.—Starting with *ca.* 1 mF solutions of *trans*-$Cr(en)_2(OH)_2^+$, formed *in situ* from the *trans*-diaquo salt dissolved in 0.10 F ethylenediamine buffer 0.10 F in $LiClO_4$ at 25.0 and 35.0°, the rates of isomerization were followed spectrophotometrically by quickly transferring reaction mixture at known times t from a thermostated bath to a 10.00-cm. quartz cell and back again after a reading on a Beckman DU spectrophotometer. The sum of the first-order rate constants ($k_t + k_c$) was obtained from 2.303 times the slopes of plots of $-\log(A_e - A)$ *vs.* t.

Results and Discussion

***cis–trans* Equilibrium Constant.**—The isomerization equilibrium constant, $K = (cis\text{-}Cr(en)_2(OH)_2^+)/(trans\text{-}Cr(en)_2(OH)_2^+)$, in 0.10 F ethylenediamine buffer 0.10 F in $LiClO_4$, was found to be 4.1 ± 0.1 at 35.0° and 5.1 ● 1.3 at 25.0°. The latter value agrees with the value 5.1 ± 0.8 obtained by Woldbye[2] in 0.1 F ethylenediamine buffer 1 F in $NaNO_3$ at 25° as an average of all values at pH 9.90, 9.95, and 10.30. Examination of Woldbye's data reveals that K has average values of 4.1 ± 0.7, 4.4 ± 0.3, and 5.9 ± 0.2 at these respective pH values. Inasmuch as $K = (cis\text{-}Cr(en)_2(OH_2)OH^{+2})/(trans\text{-}Cr(en)_2(OH_2)OH^{+2}) = 2.44^2$ at 25°, this trend may partially reflect the effect of the decreasing small fraction of hydroaquo species present at the higher pH values. Our K values for the dihydroxo isomerization at 25° were determined

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[3] The molar absorbancy index a, often called the extinction coefficient ϵ, is related to the absorbancy A by $A = \log(I_0/I) = acd$ at a given wave length, where c is the molar concentration of the absorbing species and d is the optical path length in cm.

at higher pH (10.90 and 11.39) and show no trend, although the errors are greater. We have taken $K = 5.1 \pm 0.8$ for calculation of the forward and reverse isomerization rate constants at 25° below.

In the absence of excess ethylenediamine the spectra of *cis–trans* mixtures of $Cr(en)_2(OH)_2^+$ continue to change slowly without attainment of the dihydroxo equilibrium, as noted by Woldbye. Further hydrolysis, probably with oxo-bridge formation, may be responsible; these changes were not investigated further.

Isomerization Rate.—First-order rate plots for the isomerization are shown in Fig. 1. Rate constants for the reactions

$$trans\text{-}Cr(en)_2(OH)_2^+ \underset{k_c}{\overset{k_t}{\rightleftharpoons}} cis\text{-}Cr(en)_2(OH)_2^+ \qquad (2)$$

are given in Table I. The 25° constants appear to have a small pH dependence.

TABLE I

RATE CONSTANTS FOR ISOMERIZATION OF $Cr(en)_2(OH)_2^+$ (0.10 *F* ethylenediamine, 0.10 *F* $LiClO_4$)

Temp., °C.	pH	$10^6(k_t + k_c)$, sec.$^{-1}$	10^6k_t, sec.$^{-1}$	10^6k_c, sec.$^{-1}$
25	9.95	$\sim 11^a$	$\sim 9^a$	$\sim 2^a$
	10.30	$\sim 8^a$	$\sim 7^a$	$\sim 1^a$
25.0	10.90	6.80 ± 0.14	5.7 ± 0.2	1.1 ± 0.2
	11.39	5.53 ± 0.11	4.6 ± 0.2	0.91 ± 0.13
35.0	10.60	28.9 ± 0.3	23 ± 1	5.7 ± 0.2

[a] Calculated by us from Woldbye's observation[2] that 46.1 and 44.6% isomerization occurs (starting with *trans*-isomer) in 21 hr. at pH 9.95 and in 27 hr. at pH 10.30, respectively, in 1 *F* $NaNO_3$.

The first and second acid dissociation constants of *cis*- and *trans*-$Cr(en)_2(OH)_2^+$ have values[2] such that less than 1% of the chromium should be present as hydroxoaquo complexes even at the lowest pH. However, the probably much greater lability of the hydroxoaquo species presumably is responsible for the small increase in observed rate constants with decreasing pH. The accuracy of the constants and the difficulty of making possible corrections for the difference in ionic strengths are such as not to warrant an attempt to deduce a quantitative rate law with a (H^+)-dependent term. Ignoring the small pH-dependence of k_t and k_c, and taking average values $10^6k_t = 5.2$ (25°), 23 (35°), $10^6k_c = 1.0$ (25°), 5.7 sec.$^{-1}$ (35°), we find $E_a \sim 27$ and ~ 32 kcal. mole^{-1} for the *trans*-to-*cis* and *cis*-to-*trans* isomerizations, respectively.

Comparison with Co Complexes.—Within 20%, $(k_t + k_c)$ found above for $Cr(en)_2(OH)_2^+$ isomerization in 0.1 *F* $LiClO_4$ (pH 10.9–11.4) at 25° is the same as observed[4,5] for isomerization of the cobalt(III) analog in 0.5–1 *F* NaOH at 25°. At 35°, $(k_t + k_c)$ is 1.5-fold smaller than the value reported[6] for the cobalt analog in 0.01–1 *F* NaOH ($\mu = 1$, $NaClO_4$). At 25°, *K* for $Cr(en)_2(OH)_2^+$ isomerization is ~6 times greater than was found[4,5] for the cobalt system.

This close similarity in isomerization behavior suggests that the isomerization mechanisms are the same for these complexes. Kruse and Taube[5] have discussed the mechanism for the cobalt case in terms of two different paths, based partly on their finding that although water exchange occurs on isomerization, the exchange corresponds to less than one molecule of water exchanged on the average per act of isomerization. They propose the possibility that one path may correspond to a $Co–OH^-$ bond scission and the other to a $Co–NH_2$ bond scission in the activated complex. Water-exchange experiments would be required for the chromium system to see if such an interpretation is permitted for that system.

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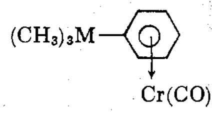
Trimethylsilyl-, Trimethylgermyl-, and Trimethylstannylbenzene Chromium Tricarbonyl

BY DIETMAR SEYFERTH[1a] AND DAVID L. ALLESTON[1b]

Received August 16, 1962

In connection with our study of germanium-containing transition metal organic compounds[2] we have prepared the trimethylsilyl-, trimethylgermyl-, and trimethylstannylbenzene tricarbonyl derivatives of chromium (I, II, and III) by the reaction of the



I, M = Si
II, M = Ge
III, M = Sn

trimethylphenyl compounds of silicon, germanium, and tin with chromium hexacarbonyl. This general procedure has been reported previously by several research groups.[3–5] The infrared spectrum of I has been reported,[6] but details concerning its preparation and physical properties were not given.

We investigated briefly the possibility of carrying out a transmetalation reaction between III and phenyllithium in ether at low temperature, since selective attack by the lithium reagent at the tin–phenyl linkage could give a chromium carbonyl complex of phenyllithium. Carbonation of the reaction mixture, however, gave no benzoic acid chromium tricarbonyl, and it is thus likely that attack by phenyllithium occurred

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(1) (a) Alfred P. Sloan Research Fellow; (b) Fellow of the M.I.T. School for Advanced Study, 1961–1962.

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