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Kinetics of Aquation and Chloride Anation of Chloroaquobis(ethylenediamine)chromium(III) Cations[1a,b]

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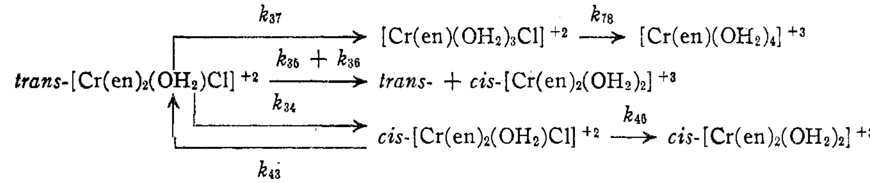
The first-order rate constants for production of ionic chloride from *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 0.10 and 1.3 F HNO_3 at 35.0° were found by chloride titrations to be $k_{46} = (9.23 \pm 0.02) \times 10^{-5}$ sec.$^{-1}$ and $(22.8 \pm 0.3) \times 10^{-5}$ sec.$^{-1}$, respectively. The stereochemical result of the aquation is ~100% *cis*-$[Cr(en)_2(OH_2)_2]^{+3}$. Aquation of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 0.10 F HNO_3 at 35.0° was found from chloride titrations, spectrophotometry, and chromatography to be complex; a reaction scheme which accounts satisfactorily for the observations is



with first-order rate constants (10^5k, sec.$^{-1}$): $k_{35} + k_{36} = 0.28 \pm 0.14$, $k_{37} = 4.2 \pm 1.4$, $k_{78} = 2.8 \pm 0.6$, $k_{34} < 0.6$, $k_{43} < 2$, $k_{46} = 9.23 \pm 0.02$. Pseudo first-order rate constants obtained spectrophotometrically at 35.0° for chloride anation of *trans*- and *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ are (10^5k, sec.$^{-1}$): $k_{31}(trans) = 17 \pm 5$ in 10.2 F HCl, $k_{42}(cis) = 140 \pm 10$ in 10.9 F HCl and 27 ± 4 in 5.69 F HCl. The *trans* isomer produces only *trans*-$[Cr(en)_2Cl_2]^+$ and the *cis* isomer only *cis*-$[Cr(en)_2Cl_2]^+$ up to the attainment of a quasi-equilibrium, which lies at the following % dichloro complex: ~35 (*trans* in 10.2 F HCl); ~84 and ~46 (*cis* in 10.9 and 5.69 F HCl, respectively). All reactions were studied in the absence of light, with initial complex concentrations ~1–40 mF.

In an earlier paper[2] we described the determination of nine rate constants involved in the primary aquation of *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ and the rearrangements of these two cations and their first-stage aquation products at 35°. We report here kinetic data for the aquation and chloride anation[1a] of *cis*- and *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ at 35°, together with information on the products and steric courses of the reactions and certain related considerations.

Experimental

***trans*-Chloroaquobis(ethylenediamine)chromium(III) Cation.**—This substance was isolated in solution from mixtures produced by aquation of 200–400 mg. of *trans*-$[Cr(en)_2Cl_2]NO_3$, the preparation and characterization of which is described elsewhere,[3] in 100–150 ml. of 0.1 F HNO_3 for ~3 hr. at 35° in the dark. The reaction mixture was absorbed on a 70-mm. × 9-mm. diameter column of Dowex AG50W-X8 cation-exchange resin (100–200 mesh, in H^+ form). After elution with ~150 ml. of 0.6 F HNO_3 (to remove dichloro species) and rejection of that eluate, elution with 100 ml. of 1.4 F HNO_3 gave an eluate containing the desired *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 2-5 mF concentration, essentially free of other chromium species, as shown in earlier work.[2] In order that the HNO_3 concentration be decreased from 1.4 F to 0.1 F so that the aquation could be investigated under the conditions used in the aquation study[2] of *trans*-$[Cr(en)_2Cl_2]^+$, the eluate containing the *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ was "titrated" by successive additions of beads of Dowex AG2-X8 anion-exchange resin (100–200 mesh) in the OH^- form[4] to a final pH of 1.10 (corresponding to 0.10 F HNO_3), determined with a Beckman pH meter. The resin then was removed promptly by filtration. This procedure lowers the HNO_3 concentration to the desired level, since the OH^- ions displaced from the resin by the NO_3^- ions react with the H^+ ions in the solution of the complex to form only water. Spectrophotometric analyses showed that the complex was not altered by the resin treatment.

***cis*-Chloroaquobis(ethylenediamine)chromium(III) Cation.**—Solutions of this species were prepared by cation-exchange chromatography of mixtures formed by aquation in the dark of ~40 mg. of *cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$, prepared and characterized as described earlier,[2] in ~50 ml. of 0.1 F HCl at 35° for 1 hr. A reaction mixture was ad-

(1) (a) Anation is the replacement of ligand water in an aquo complex by an anion; (b) work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University; (c) California Research Corp., Richmond, California.

(2) D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

(3) D. J. MacDonald and C. S. Garner, *J. Inorg. & Nuclear Chem.*, **18**, 219 (1961).

(4) Chloride resin was converted to the nitrate form with NH_4NO_3 solution, followed by conversion from nitrate to hydroxide form with NH_4OH; fresh hydroxide resin was prepared just before each use inasmuch as the resin was not stable in this form.

sorbed on a Dowex AG50W-X8 column like those described above, then the column was subjected to elution with ~200 ml. of 0.6 *F* HCl to remove dichloro species (eluate discarded). Upon elution with ~100 ml. of 2.5 *F* HCl, an eluate was produced containing the desired *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ free of other chromium complexes.[3]

In order to obtain *cis*- or *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ at a sufficient concentration in 6–11 *F* HCl for chloride anation studies, we used a small volume of the appropriate eluent to bring the desired band of chloroaquo complex, adsorbed on a Dowex AG50W-X8 resin column, close to the bottom of the column, after which the resin containing the band remaining near the top of the column was removed with a dropper and discarded. Elution of the desired complex then was achieved with a small volume of 6 or 12 *F* HCl.

Aquation Rate Procedure.—Solutions were prepared ~0.04 *F* in complex by dissolving *cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ in 0.10 *F* HNO_3 and held at 35.00 ± 0.05° in sealed, light-tight Pyrex containers. Since it was discovered earlier[3] that *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ is the only product of the primary aquation of *cis*-$[Cr(en)_2Cl_2]^+$ and that the secondary aquation is ~1/10 as fast as the primary aquation at 35°, the above solutions were allowed to react for 12 half-times for aquation of *cis*-$[Cr(en)_2Cl_2]^+$ to give the *cis*-chloroaquo cation in higher concentration than is readily obtained by chromatographic separation. Solutions ~2 m*F* in *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ and 0.10 *F* in HNO_3 were prepared by the chromatographic separation procedure described above and immediately thermostated at 35.00 ± 0.05° in the dark. Total chromium in aliquots of the solutions was determined by spectrophotometric analysis of chromate at 372 mμ after decomposition and oxidation with hot alkaline peroxide. Aliquots of the reaction mixtures were taken at known time intervals and titrated with standard $AgNO_3$ to a potentiometric end-point, as described earlier,[3] to determine the rate of production of ionic chloride during aquation. At varying time intervals other reaction mixtures were examined spectrophotometrically and subjected to chromatographic separations. The latter were achieved as described earlier,[3] except that an extra fraction consisting of chloride-free complexes (presumably *cis*- and *trans*-$[Cr(en)_2(OH_2)_2]^{+3}$ and $[Cr(en)(OH_2)_4]^{+3}$) was obtained by elution with 50 ml. of 10 *F* HNO_3 or HCl.

Anation Rate Procedure.—Solutions ~2–7 m*F* in *cis*- or *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ and ~6 or ~11 *F* in HCl were prepared by the chromatographic procedure outlined earlier, and the HCl formality determined by titration of weighed samples of Na_2CO_3, using methyl orange indicator. Each such reaction solution immediately was placed in a 10-cm. Cary-type g.s. quartz absorption cell, prewarmed quickly to 35°, then transferred into the cell holder (thermostated at 35.00 ± 0.05°) of a Cary Model 11 recording spectrophotometer, and the absorption spectrum repeatedly recorded between 360 and 580 mμ at known time intervals. In subsequent runs the spectrophotometer was left set at 400 mμ for *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ and at 520 mμ for the *trans* isomer, these having been found to be the wave lengths of greatest change in absorbancy, and the chart drive run steadily to produce a chart of absorbancy *vs.* time *t*, thus eliminating random errors in setting the wave lengths. Freshly prepared solutions of *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ were made by dissolution of *cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ and *trans*-$[Cr(en)_2Cl_2]NO_3$, respectively, in HCl of approximately the same concentration as used in the anation studies and the spectrum of each solution was determined immediately for use in interpreting the spectral changes. All solutions were exposed to light (that of the spectrophotometer) only during the scanning. The spectral data were analyzed by use of the relation $\ln[(A_\infty - A_0)/(A_\infty - A)] = (k_1 + k_{-1})t$, where A_0, A, and A_∞ are the absorbancies at the given wave length at time zero, t, and at equilibrium, respectively, and k_1 and k_{-1} are the pseudo first-order rate constants for the anation and its reverse, respectively. Plots of $\ln[(A_\infty - A_0)/(A_\infty - A)]$ *vs.* t were curved convex upward if A_∞ was taken as A corresponding to 100% dichloro product (*cis* for *cis* anation, *trans* for *trans* anation); the anation rate constant k_1 was taken as the extrapolated zero-time slope of each such plot. If the experimentally observed A at equilibrium was taken as A_∞, the resulting plot was reasonably linear, showing that the anation is essentially a pseudo first-order reversible reaction, as expected in the presence of the large excess of chloride ion reactant; the slope of this plot gives $(k_1 + k_{-1})$, which then permits calculation of k_{-1} under these conditions of high chloride ion concentration.

Results and Discussion

Aquation of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$.—This species in 0.10 *F* HNO_3 at 35.0° in the absence of light produced ionic chloride according to a first-order rate law (log concentration of unreacted complex *vs.* *t* linear over 50% reaction) with a rate constant of $(9.23 \pm 0.02) \times 10^{-5}$ sec.$^{-1}$. The aquation also was examined by cation-exchange chromatographic separation of the unreacted *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ from its reaction products, which data gave an aquation rate constant of $(9.7 \pm 1.1) \times 10^{-5}$ sec.$^{-1}$, in reasonable agreement with the chloride titration value. Selbin and Bailar[5] have used a method of successive approximations of *cis*-$[Cr(en)_2Cl_2]^+$ chloride-release data to estimate the aquation rate constant of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 0.10 *F* HNO_3 at 20.0° and 25.0°; their values lead to an estimated Arrhenius activation energy of ~36 kcal., with which their 25° constant may be extrapolated to give $\sim 20 \times 10^{-5}$ sec.$^{-1}$ at 35°. The agreement is satisfactory considering the approximations involved. Thus the aquation of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 0.1 *F* HNO_3 at 35° is ~1/10 as fast as the aquation[2,5] of *cis*-$[Cr(en)_2Cl_2]^+$ under these same conditions.

The aquation also was followed spectrophotometrically in 1.3 *F* HNO_3. The spectrum changed with time in accord with the sequence *cis*-chloro-

(5) J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957).

aquo → *cis*-diaquo → tetraaquomono(en), without evidence that *trans*-chloroaquo or *trans*-diaquo species were forming. This fact allows placing a very conservative upper limit of $< 1 \times 10^{-5}$ sec.$^{-1}$ on the rate constant at 35° for aquation of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ directly to *trans*-$[Cr(en)_2(OH_2)_2]^{+3}$ and $< 2 \times 10^{-5}$ sec.$^{-1}$ for *cis*-to-*trans* isomerization of the former; the latter upper limit can be set lower by taking into consideration data on aquation of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ (*vide infra*). Isomerization has been observed[6] between the *cis* and *trans* diaquo cations in solutions 0.02 *F* in HNO_3 and 2 *F* in $NaNO_3$ at 25°; from the data of Woldbye[6] and Schläfer and Kollrack[7] we estimate first-order rate constants of $< 1 \times 10^{-6}$ and $< 1 \times 10^{-5}$ sec.$^{-1}$, respectively, for the *cis*-to-*trans* and *trans*-to-*cis* isomerization at 35°.

Since *cis-trans* rearrangements of $[Cr(en)_2(OH_2)Cl]^{+2}$ and $[Cr(en)_2(OH_2)_2]^{+3}$ cations are thus too slow at 35° to play a significant role in affecting the configuration of the diaquo product, the spectral changes show that the stereochemical result of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ aquation is ~100% *cis*-$[Cr(en)_2(OH_2)_2]^{+3}$. Ingold[8] and Ingold, Nyholm, and Tobe[9] have observed that aquation of all *cis*-cobalt(III) octahedral complexes examined appears to give complete retention of configuration. This stereokinetic rule may well be valid for *cis*-chromium(III) complexes also, and our results on aquation of *cis*-$[Cr(en)_2Cl_2]^+$ and *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ are in accord with this rule.

Our spectral data (based on measurements at 385, 510, and 520 mμ, and assuming *cis*-diaquo as the only initial aquation product) lead to a value of $(22 \pm 2) \times 10^{-5}$ sec.$^{-1}$ for the aquation rate constant in 1.3 *F* HNO_3 at 35.0°. This value is in agreement with our more accurate value $(22.8 \pm 0.3) \times 10^{-5}$ sec.$^{-1}$ determined in 1.3 *F* HNO_3 by chloride titration. The fact that the rate constant in 1.3 *F* HNO_3 is approximately twice that in 0.1 *F* HNO_3 may arise from increased ion-pair effects in the more concentrated acid.

Aquation of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$.—The chloride titration data from aquation of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 0.10 *F* HNO_3 at 35.0°, when treated on a first-order basis, gave values of the rate constant which increased with reaction time, indicating that the aquation is not a simple one-step reaction. Qualitatively, the behavior can be explained by assuming that *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ not only aquates with loss of its chloro ligand but also reacts to produce one or more species with a Cl/Cr atom ratio of one, which species then aquate to produce ionic chloride. One possibility is the reaction scheme (scheme I)

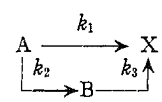
$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + H_2O \xrightarrow{k_1} [Cr(en)_2(OH_2)_2]^{+3} + Cl^- \quad (1)$$

$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + 2H_2O \xrightarrow{k_2} [Cr(en)(OH_2)_3Cl]^{+2} + en \quad (2)$$

$$[Cr(en)(OH_2)_3Cl]^{+2} + H_2O \xrightarrow{k_3} [Cr(en)(OH_2)_4]^{+3} + Cl^- \quad (3)$$

in which reaction 2 is analogous to the path in the aquation of *trans*-$[Cr(en)_2Cl_2]^+$ by which *trans*-$[Cr(en)(OH_2)_2Cl_2]^+$ appears to be formed.[2] Preliminary attempts to isolate with cation-exchange chromatography a species such as $[Cr(en)(OH_2)_3Cl]^{+2}$ from the reaction mixtures were not successful. Moreover, the initial concentration of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ was unavoidably so low (0.0017 *F*) and the acid concentration used to prevent base hydrolysis so high (0.1 *F*) that the release of ethylenediamine postulated by reaction 2 could not be detected.

It is of interest to know if the above reaction scheme can account quantitatively for the observed rate of production of ionic chloride. This scheme can be formulated as a three-component first-order scheme



where A here represents *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, B a reaction product having a Cl/Cr atom ratio of one, and X either $[Cr(en)_2(OH_2)_2]^{+3}$ (*cis* and/or *trans*) or $[Cr(en)(OH_2)_4]^{+3}$, one ionic chloride being produced per X formed. Integration of the differential rate equations for this scheme gives

$$X/A_0 = [1 - (k_2/k)][1 - e^{-(k_1+k_2)t}] + (k_2/k)[1 - e^{-k_3t}] \quad (4)$$

where $k = k_1 + k_2 - k_3$ and initial concentra-

(6) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

(7) H. L. Schläfer and R. Kollrack, *Z. physik. Chem.* (Frankfurt), **18**, 22 (1958).

(8) C. K. Ingold, "Theoretical Organic Chemistry," Butterworths Scientific Publications, London, 1959, p. 84–102.

(9) C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

tions are A_0 and $B_0 = X_0 = 0$.[10] With the help of the IBM-709 electronic computer of the Western Data Processing Center at U.C.L.A., we used equation 4 to find that set of values for k_1, k_2, and k_3 which gave values of X/A_0 most nearly equal to the experimental values. The results were checked and slightly refined by manual computations, giving $k_1 = (2.8 \pm 1.4) \times 10^{-6}$ sec.$^{-1}$, $k_2 = (4.2 \pm 1.4) \times 10^{-5}$ sec.$^{-1}$, and $k_3 = (2.8 \pm 0.6) \times 10^{-5}$ sec.$^{-1}$ in 0.1 F HNO_3 at 35.0° in the absence of light; this set of three rate constants gave X/A_0 values agreeing with the experimental X/A_0 values, determined at 15 well-spaced intervals from 1 to 45 hr., within the titration accuracy (usually 1–5%). The standard errors given allow for the fact that certain other combinations of k_1, k_2, and k_3 values taken within the indicated limits gave poorer but approximate fits with the data. Although not subjected to a detailed analysis of the data, a run made in 0.27 F HNO_3 seemed to give about the same results.

An alternative scheme (scheme II) may appear to be

$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + H_2O \xrightarrow{k_1} [Cr(en)_2(OH_2)_2]^{+3} + Cl^- \quad (1)$$

$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} \xrightarrow{k_{34}} cis\text{-}[Cr(en)_2(OH_2)Cl]^{+2} \quad (5)$$

$$cis\text{-}[Cr(en)_2(OH_2)Cl]^{+2} \xrightarrow{k_{46}} cis\text{-}[Cr(en)_2(OH_2)_2]^{+3} + Cl^- \quad (6)$$

which has an expression for X/A_0 analogous to equation 4 except that k_{34} and k_{46} replace k_2 and k_3, respectively. That this scheme alone cannot be correct is shown by the fact that k_{46} is known to be $(9.23 \pm 0.02) \times 10^{-5}$ sec.$^{-1}$ (*vide ante*), whereas fitting the experimental X/A_0 data by this scheme would require k_{46} to be $(2.8 \pm 0.6) \times 10^{-5}$ sec.$^{-1}$. Not only is k_{46} too small to account for the results, but also one can show that k_{34} is too small to allow scheme II to compete seriously with scheme I for production of ionic chloride, assuming both schemes can participate. We calculate that $k_{34} < 6 \times 10^{-6}$ sec.$^{-1}$, even if we double the value 2.8×10^{-6} sec.$^{-1}$ found above for k_1 (reaction 1 is common to both schemes) and then compute what value k_{34} must have to generate Cl^- at that rate assuming *all* Cl^- were produced by reactions 5 and 6. With competing reactions allowed (such as reactions 1, 2, 3, and the reverse of reaction 5), k_{34} would be much smaller[11]; accordingly, we take $k_{34} < 6 \times 10^{-6}$ sec.$^{-1}$ as a very conservative upper limit. The ratio k_2/k_{34} then is at least 5, and probably very much greater, so that the scheme II reaction sequence perturbs only slightly, if at all, the values found above for k_2 and k_3, which we now can identify as k_{37} and k_{78}, respectively, of the general scheme given in Fig. 1.[12] An additional rough check on this over-all scheme of aquation of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ is given by the fact that chromatographic separation data on *trans*-$[Cr(en)_2Cl_2]^+$ reaction mixtures at long reaction times can be used to give an approximate value for the total rate constant $(k_{34} + k_{35} + k_{36} + k_{37})$ with which *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ disappears by all paths, and the value $\sim 5 \times 10^{-5}$ sec.$^{-1}$ so obtained agrees with the sum of the individually determined k values within experimental error.

Since component 7 of Fig. 1, postulated to account for the chloride ion release data, has not been isolated or otherwise characterized, we must regard its composition as hypothetical. In this connection, some slight additional support for some such component may be adduced from spectrophotometric observations on *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ reaction mixtures 1.2 F in $HClO_4$ and partial chromatographic separations of reaction mixtures 0.25 F in HNO_3, both at 35°; these appeared to suggest the presence of a chromium species in addition to the expected *cis*- and *trans*-$[Cr(en)_2(OH_2)_2]^{+3}$, the subsequently produced $[Cr(en)(OH_2)_4]^{+3}$, and the conceivably formed *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$.

Whether the diaquo product of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ aquation is *cis* or *trans* or a mixture of both isomers is unknown since we have not succeeded so far in separating these two isomers chromatographically and the mixture appears to be too complex to analyze spectrophotometrically. The experiments are further complicated by aquation of both *trans*- and *cis*-$[Cr(en)_2(OH_2)_2]^{+3}$ to $[Cr(en)(OH_2)_4]^{+3}$. The *cis* aquation has been investigated in 0.1 F $HClO_4$ by Schläfer and Kollrack.[7] From their 30° k and their E_a we calculate $k_{68} = 4.51 \times 10^{-6}$ sec.$^{-1}$ for this aquation at

(10) Subsequently we found that an integrated equation equivalent to ours had been obtained for this type of scheme by R. J. A. M. Van der Borg, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **62B**, 299 (1959); his expressions for ratios of the rate constants are not applicable to our data since we have no experimental measurements of (B) as a function of time.

(11) Although the differential equation for dX/dt can be integrated for the combination of schemes I and II, the computational effort required to evaluate k_{34} thereby is unwarranted.

(12) Rate constant k_{37} is that for the direct production of component 7 from component 3 of Fig. 1; this notation system is used for all other k values given.

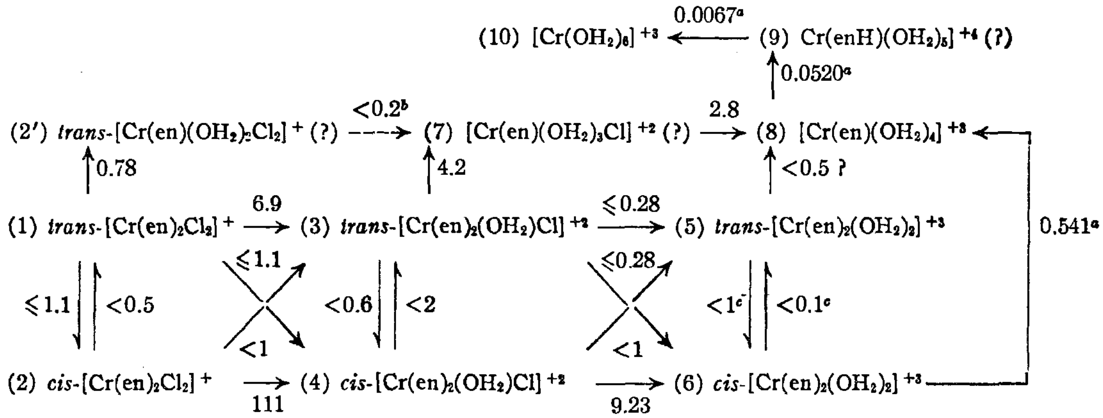


Fig. 1.—First-order rate constants (10^5k, sec.$^{-1}$) for aquation and isomerization reactions in 0.1 F HNO_3 at 35.0° in the absence of light. [a] In 0.1 F $HClO_4$, ref. 7. [b] In 2 F $HClO_4$. [c] In 0.02 F HNO_3, 2 F $NaNO_3$.

35°, which value would probably not be much different in 0.1 F HNO_3. Since aquation of a *trans* complex normally is slower at room temperature than aquation of the *cis* isomer, $k_{58} < 5 \times 10^{-6}$ sec.$^{-1}$ may reasonably be taken for the aquation of *trans*-$[Cr(en)_2(OH_2)_2]^{+3}$ to $[Cr(en)(OH_2)_4]^{+3}$ at 35°. Thus, aquation of *cis*-diaquo ion, and perhaps of *trans*-diaquo ion, is fast enough to form appreciable amounts of $[Cr(en)(OH_2)_4]^{+3}$ during the experiments. Subsequent aquation of $[Cr(en)(OH_2)_4]^{+3}$ to $[Cr(OH_2)_6]^{+3}$ through an intermediate,[13] which is probably $[Cr(enH)(OH_2)_5]^{+4}$, has been studied in 0.1 F $HClO_4$ by Schläfer and Kollrack[7]; at 35° the first-order rate constants (calculated from 30° k values with E_a values) are $k_{89} = 5.20 \times 10^{-7}$ and $k_{910} = 6.7 \times 10^{-8}$ sec.$^{-1}$, respectively, for the aquation of the tetraquomono(en) cation and pentaquo intermediate. The former aquation may well be comparable in rate with that of *trans*-$[Cr(en)_2(OH_2)_2]^{+3}$ aquation (rate known only as an upper limit), which could further complicate investigation of the stereochemical outcome of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ aquation.

Chloride Anation of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$.—The visible absorption spectra of two solutions of *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$, one 2.1 mF in complex and 10.9 F in HCl and the other 4.0 mF in complex and 5.69 F in HCl, slowly changed at 35.0° to that of a mixture of this complex and *cis*-$[Cr(en)_2Cl_2]^{+}$. Isosbestic points near 383, 445, and 510 mμ showed that only these two complexes were present in measurable concentrations during the first 3–4 hr. A quasi-equilibrium, corresponding to ~84% *cis*-$[Cr(en)_2Cl_2]^{+}$, ~16% *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 10.9 F HCl and ~46% *cis*-$[Cr(en)_2Cl_2]^{+}$, ~54% *cis*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in 5.69 F HCl, was attained with no spectral change during the interval 1.9–3.6 hr.

Analysis of the spectral changes (see Experimental) gave the following pseudo first-order rate constants at 35.0° for the reversible reactions

$$cis\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + Cl^- \underset{k_{24}}{\overset{k_{42}}{\rightleftharpoons}} cis\text{-}[Cr(en)_2Cl_2]^{+} + H_2O \quad (7)$$

in 10.9 F HCl: $k_{24} + k_{42} = (1.8 \pm 0.2) \times 10^{-3}$ sec.$^{-1}$, $k_{42} = (1.4 \pm 0.1) \times 10^{-3}$ sec.$^{-1}$, and (by difference) $k_{24} = (4 \pm 2) \times 10^{-4}$ sec.$^{-1}$; and in 5.69 F HCl, $k_{24} + k_{42} = (6.4 \pm 0.8) \times 10^{-4}$ sec.$^{-1}$, $k_{42} = (2.7 \pm 0.4) \times 10^{-4}$ sec.$^{-1}$, and (by difference) $k_{24} = (3.7 \pm 0.9) \times 10^{-4}$ sec.$^{-1}$. The k_{42} values are given as pseudo first-order constants inasmuch as the Cl^- concentration was constant in each run and the dependence of the rate on Cl^- concentration cannot be deduced from the data at such high HCl formalities.

The rate constants for aquation of *cis*-$[Cr(en)_2Cl_2]^{+}$ in 10.9 and 5.69 F HCl appear to be approximately the same and about one-third of that[2] in 0.10 F HCl at 35.0°.

Chloride Anation of *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$.—A solution 7.45 mF in *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ and 10.2 F in HCl exhibited slow changes in its visible absorption spectrum at 35.0°. Isosbestic points near 470 and 550 mμ indicated that the only complexes present in significant concentrations during the first ~3 hr. were *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ and *trans*-$[(Cr(en)_2Cl_2]^{+}$. A steady-

(13) The intermediate, shown as component 9 in Fig. 1, has been postulated (ref. 7) to be $[Cr(en—)(OH_2)_5]^{+3}$, with one end of the en ligand bound and the other end free. By analogy with $[Cr(en)_2(enH)(OH_2)]^{+4}$, postulated by E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **13**, 2075 (1959), to explain certain data in ref. 7, we prefer to consider component 9 as $[Cr(enH)(OH_2)_5]^{+4}$, with the free end of the en ligand stabilized by uptake of a proton.

state spectrum, corresponding to ~35% *trans*-$[Cr(en)_2Cl_2]^+$, ~65% *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$, was observed during the period ~2.2–3 hr.

At 35.0° pseudo first-order rate constants for the reversible reactions

$$trans\text{-}[Cr(en)_2(OH_2)Cl]^{+2} + Cl^- \underset{k_{13}}{\overset{k_{31}}{\rightleftharpoons}} trans\text{-}[Cr(en)_2Cl_2]^+ + H_2O \quad (8)$$

in 10.2 *F* HCl are: $k_{13} + k_{31} = (6.0 \pm 3.0) \times 10^{-4}$ sec.$^{-1}$, $k_{31} = (1.7 \pm 0.5) \times 10^{-4}$ sec.$^{-1}$, and by (difference) $k_{13} = (4.3 \pm 3.0) \times 10^{-4}$ sec.$^{-1}$. The uncertainty in the latter is so great that one can say only that aquation of *trans*-$[Cr(en)_2Cl_2]^+$ is not more than one order of magnitude, if at all, faster in 10.2 *F* HCl than in 0.10 *F* HCl at 35.0°.

The *trans* isomer of the above complexes reacts more slowly at 35° than the *cis* isomer in chloride anation. This relation also holds for aquation in 0.1 *F* HCl, but in 10–11 *F* HCl the experimental errors were large enough to obscure the comparison.

Spectra.—The visible absorption spectra of nearly all the complexes involved in this investigation have been described previously.[2,7] Determination of the spectra of *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ and of *cis*- and *trans*-$[Cr(en)_2(OH_2)Cl]^{+2}$ in ~6 and ~11 *F* HCl showed that the wave lengths of the absorption maxima and minima for a given complex are the same within a 6-mμ range as in 0.1–0.2 *F* HNO_3 (1.3 *F* HNO_3 and 2 *F* HCl for *cis*-chloroaquo) at ~25°. However, the molar absorbancy indices at the absorption maxima and minima of a given complex were found to change up to 35% and their ratio for the two main peaks up to 17% in going from the above dilute acid to the concentrated acid solutions. Thus, use of spectra for quantitative determinations of concentrations of these complexes may require determination of the molar absorbancy indices in the particular medium of interest.

Comparison of Reaction Rates for Cr and Co Complexes.—Fig. 1 summarizes the rate constants at 35.0° for the system of aquation and isomerization reactions which appear to occur when *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ are dissolved in 0.1 *F* HNO_3 in the dark. Chloride anation rates are not included since they have been determined under greatly different concentration conditions. From a summary[14] of the limited comparative data available for the cobalt(III) analogs, there appear to be no striking rate differences between these Cr complexes and their Co analogs despite the prediction of crystal-field theory (ignoring the influence of solvent water) that lower activation energies would be expected for aquation and similar reactions of the d^3 chromium(III) complexes than for the d^6 cobalt(III) complexes. A more detailed comparison, as well as an understanding of the mechanisms of these reactions, must await further research, including resolution of the over-all rate constants into rate constants of individual characterized reactions for the cobalt complexes and determinations of E_a and ΔS^{0*} for both the chromium and cobalt systems.

(14) C. S. Garner and D. J. MacDonald, in S. Kirschner (ed.), "Advances in the Chemistry of the Coördination Compounds," Macmillan Co., New York, N.Y. 1961, p. 266–275. More recent values of k_{56} for isomerization of *trans*-$[Co(en)_2(OH_2)_2]^{+3}$ to the *cis* isomer have been obtained by W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961), namely 4.0×10^{-5} sec.$^{-1}$ in 1 *F* $HClO_4$ at 37.5°, and by J. Y. Tong, private communication, namely 3.4×10^{-5} sec.$^{-1}$ in 0.004–1.0 *F* $HClO_4$ at 35° ($k_{56} \dotplus k_{65}$) from which $k_{65} < 0.1 \times 10^{-5}$ sec.$^{-1}$, redetermined by Kruse and Taube, has been subtracted).

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The Infrared Spectra of Substituted Metal Carbonyls

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The assignment of the CO stretching frequencies in substituted carbonyls of the type $[L_nM(CO)_{6-n}]$ is attempted.

Introduction

The C–O stretching frequencies of metal carbonyls decrease as the extent of π-electron donation from the metal to the carbonyl group increases. The steady fall of the carbonyl frequency along the series $Ni(CO)_4$, $[Co(CO)_4]^-$,