expected from the 1.00:1.23:1.28 relative increase in ion size predicted by models. The total substitution of the N protons leads us again into the region of weak ion association where our results are not compatible with this treatment. All these effects are also emphasized in the results for the complex salt $[CrCl_2(DMSO)_4]^+$-ClO_4^- in DMF.

It is tempting to speculate on the order found for the dependence of K_{IP} on the metal, namely, $K_{IP}(Co(III))$ > $K_{IP}(Cr(III))$ > $K_{IP}(Rh(III))$. Because of the overall size of the solvated cations which must be taken, at least at first, as invariant and because of the identity of the charge type, one might have expected a dependence either on the dipole moment of the complexes, which would be dependent on the polarizability of the metal (Cr > Co > Rh), or on the acidity of the nitrogen protons (probably Rh > Cr > Co).[33] The present results suggest that neither of these two effects predominates. It may be significant that the order of rates of base hydrolysis is Co(III) ≫ Cr(III) > Rh(III).

In DMSO and DMF a temperature-dependent study was attempted for the *cis*-$[CrCl_2(en)_2]^+Cl^-$ ion pair. The variation of K_{IP} in DMSO for a 10° range in temperature was just beyond the limit of standard deviation in K_{IP} and gave $\Delta H°$ and $\Delta S°$ for ion association of -2.1 ± 0.4 kcal mol^{-1} and 4.4 cal deg^{-1} mol^{-1} as previ-

ously published. These results closely resemble the thermodynamic data derived from spectrophotometric techniques by Millen and Watts[34] for the association of *cis*-$[CoCl_2(en)_2]Cl$ in DMSO. However, the results in DMF show that the variation in K_{IP} over a 10° range in temperature is not beyond the standard deviation and casts doubt on the value for DMSO. An improvement in the precision of determination or the use of solvolysis-resistant complexes allowing the use of a greater temperature range appears essential to develop this aspect further.

The limiting molar ionic conductances of these chromium and rhodium complex cations are for the most part experimentally indistinguishable from the values previously obtained for the analogous Co(III) complexes. This can only serve to emphasize that the solvation of the analogous complexes is closely similar and lends support to our tendency to ascribe changes in ion association constants to predominant effects in the anion–cation interaction. It is notable that the new complexes involving larger more polarizable anionic ligands, such SCN$^-$, show significantly smaller values of λ_0^+, correlating with increased solvation.

(33) Reference 32, pp 188–189.

(34) W. A. Millen and D. W. Watts, *Aust. J. Chem.*, **19**, 43 (1966).

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Kinetics of the First-Stage Aquation of *trans*-Dichlorobis(propylenediamine)chromium(III) Cation

BY ROSITA R. BARONA AND JOHN A. McLEAN, JR.[*1]

The first-order rate constant for the disappearance of *trans*-Cr(pn)$_2$Cl$_2^+$ in 0.10 F HNO$_3$ at 35.04 $\pm$ 0.04° in the absence of light was found to be $(12.62 \pm 0.03) \times 10^{-5}$ sec^{-1}. The first-stage aquation of this complex gave three products—*trans*-Cr(pn)$_2$(OH$_2$)Cl^{2+}, pink Cr(pn)(OH$_2$)$_2$Cl$_2^+$, and *cis*-Cr(pn)$_2$(OH$_2$)Cl^{2+} with first-order rate constants of formation of $(8.14 \pm 0.18) \times 10^{-5}$, $(1.01 \pm 0.01) \times 10^{-5}$, and $(3.42 \pm 0.38) \times 10^{-5}$ sec^{-1}, respectively. The two former products are previously unreported and were isolated in solution and their visible absorption spectra were determined. The chloride release rate constant for *trans*-Cr(pn)$_2$Cl$_2^+$ was studied under the same conditions as the rate of disappearance of the complex and found to be $(11.62 \pm 0.07) \times 10^{-5}$ sec^{-1}.

Following the successful synthesis of *trans*-dichlorobis(propylenediamine)chromium(III) chloride,[2] the kinetics of the aquation of this complex has been investigated. The present study provides a means of (a) checking some of the possible reaction paths postulated for the acid hydrolysis of *cis*-dichlorobis(propylenedi-amine)chromium(III) cation,[3] (b) comparing this bis-

(propylenediamine)chromium(III)[4] complex with its ethylenediamine analog,[5] and (c) determining whether Cr–N bond breakage competes significantly with Cr–Cl bond breaking as has been reported for some similar systems.[5,6] A combination of techniques including ion-exchange chromatography, spectrophotometric identification of eluted fractions, and chloride release

(1) To whom correspondence should be addressed.

(2) J. A. McLean, Jr., and R. R. Barona, *Inorg. Nucl. Chem. Lett.*, **5**, 385 (1969).

(3) M. Esparza and C. S. Garner, *J. Inorg. Nucl. Chem.*, **29**, 2377 (1967).

(4) Abbreviations used: en = ethylenediamine, H$_2$NCH$_2$CH$_2$NH$_2$; pn = propylenediamine = 1,2-diaminopropane, H$_2$NCH(CH$_3$)CH$_2$NH$_2$.

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

(6) D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

rate data was used to realize the aforementioned objectives.

Experimental Section

trans-Dichlorobis(propylenediamine)chromium(III) Chloride.—This complex was prepared by a slight modification of the procedure we have previously reported.[2] This method involves chlorination of *trans*-[Cr(pn)₂(SCN)₂]SCN with Cl₂ gas. The crude product was filtered, dissolved in water, and placed in an HCl-exchange desiccator along with the original filtrate. After 2 days both samples were filtered, and the residues were combined and washed with concentrated HCl until washings became clear. The product was recrystallized from methanol and ether as before and dried under vacuum over KOH. When compared with the original procedure this modification gave a threefold increase in the yield of pure product.

Cation-Exchange Chromatographic Procedure.—The procedure used was essentially the same as that of MacDonald and Garner[6] with slight modifications. Appropriate reaction solutions were adsorbed on 40-mm × 9-mm diameter jacketed columns of Dowex AG50W-X8 cation-exchange resin (100–200 mesh in the H⁺ form) at the rate of 10 ml/min with the aid of compressed nitrogen. The columns were kept at 0° and protected from light with Al foil throughout the entire procedure except when opened quickly to check the progress of elution. These precautions were taken because complexes of this type have been shown to be light sensitive.[7] The various complex cations were selectively displaced from the resin by gradient elution with increasing acid concentrations and the progress of each colored band was followed visually. Preliminary experiments indicated that some bands tend to overlap during elution. In these cases we were able cleanly to separate the various species by using a large amount of dilute acid to move a particular band to the bottom of the column and a smaller amount of more concentrated acid to effect its elution. The following elution scheme was found to be most effective. Approximately 75 ml of 0.3 *F* HNO₃ was required to move the first band (*trans*-Cr(pn)₂Cl₂⁺) near the bottom of the column and an additional 100 ml of 0.3 *F* HNO₃ followed by 100 ml of 0.6 *F* HNO₃ completely eluted the first band. An additional 150 ml of 0.6 *F* HNO₃ was used to bring the second band (pink Cr(pn)(OH₂)₂Cl₂⁺) near the bottom of the column and elution was achieved with 100 ml of 0.6 *F* HNO₃ followed by 100 ml of 1.4 *F* HNO₃. After this treatment *ca.* 150 ml of 1.4 *F* HNO₃ was needed to separate the third and fourth bands (*trans*-Cr(pn)₂-(OH₂)Cl²⁺ and *cis*-Cr(pn)₂(OH₂)Cl²⁺, respectively); *ca.* 350 ml of 1.4 *F* HNO₃ was used to elute the third band and 200 ml of 3 *F* HNO₃ was required to elute the fourth band.

Preparation of Pink Dichlorodiaquopropylenediaminechromium(III) Cation.—This complex, which is one of six possible geometrical isomers of formula Cr(pn)(OH₂)₂Cl₂⁺, was synthesized in solution by allowing *trans*-Cr(pn)₂Cl₂⁺ (*ca.* 300 mg in 150 ml of 0.1 *F* HNO₃) to aquate in the dark at 35° for 90 min. The complex was isolated by adsorbing the reaction solution on the cation-exchange columns described above, at 0°. The unreacted *trans*-Cr(pn)₂Cl₂⁺ was moved to the bottom of the column with 0.3 *F* HNO₃ and eluted with 0.6 *F* HNO₃. The second band was moved to the bottom of the column with 0.6 *F* HNO₃ and the resin containing the upper bands was removed by pipet and discarded. The desired species was then eluted with 2 *F* HNO₃.

Preparation of *trans*-Chloroaquobis(propylenediamine)chromium(III) Cation.—*trans*-Cr(pn)₂Cl₂⁺ (*ca.* 50 mg[8] in 50 ml of 0.1 *F* HNO₃) was allowed to aquate in the dark at 35° for 90 min. The reaction solution was then adsorbed on the cation-exchange column, as above. Since the *trans*-chloroaquo is the third band in the separation scheme above, 300 ml of 1.4 *F* HNO₃ was used to elute the first and second bands and to move this third band to the bottom of the column. Solutions sufficiently concen-

trated for spectral analysis were obtained by using a pipet to remove carefully and discard the resin containing the fourth band and eluting the desired species with 3 *F* HNO₃.

Kinetic Measurements.—Originally we intended to employ three methods, spectrophotometric, chromatographic, and potentiometric, in our kinetic studies. However, spectral scans of reaction solutions proved to be unsuitable for following the kinetics. These measurements were complicated by the fact that changes in absorbance at the early stages of the reaction were quite small and secondary aquation of the products becomes important after 10% reaction.

In determining rate constants by the chromatographic method, an actinic flask containing a weighed amount of dry complex (*ca.* 200 mg) and a flask containing 0.10 *F* HNO₃ were first allowed to reach the bath temperature (35.04 ± 0.04°). One hundred milliliters of the acid was then added by pipet to the flask containing the complex and the start of the reaction was recorded as the time when the pipet was half empty. The reaction flask was shaken for *ca.* 40 sec to ensure complete dissolution of the complex. Aliquots (10 ml) of the reaction solution were removed at appropriate time intervals, quenched with 15 ml of ice-cold water, adsorbed on the cation-exchange columns, and separated as above. The composition of each aliquot was determined by chromium analysis of each eluted species. The first-order rate constant for the disappearance of *trans*-Cr(pn)₂-Cl₂⁺ was obtained from a linear plot of ln (C_0/C_t) *vs.* *t*, where C_0 and C_t are the complex concentrations at zero time and time *t*, respectively. The first-order plots obtained were linear for more than 3 half-lives.

The first-order rate constants for the formation of the products were determined from the initial slopes obtained by plotting mole fraction of product, x_p, at time *t*, *vs.* *t*. This is in accord with the relations

$$C \xrightarrow{k} P$$

$$\frac{d[P]}{dt} = k[C]$$

$$\frac{d\frac{[P]}{[C]_0}}{dt} = k\frac{[C]}{[C]_0} = \frac{dx_p}{dt} = kx_c$$

as $t \to 0$, $x_c \to 1$; therefore

$$\lim_{t \to 0} \frac{dx_p}{dt} = k$$

A plot of x_p *vs.* *t* thus has an initial slope equal to k, the specific rate constant for formation of product P.

The rate of chloride release was followed by potentiometric titration.[9] The reaction was begun in the same manner as used in the chromatographic studies except that reactant solutions were more dilute (*ca.* 3.0 × 10⁻³ *M*). Aliquots (5 ml) were removed at appropriate times and quenched in an ice-cold mixture of 50 ml of acetone, 45 ml of 0.01 *F* HNO₃, and 20 drops of a nonionic detergent. The quenched reaction mixture was titrated immediately while stirring with 0.005 *F* AgNO₃ to a potentiometric end point, using silver-saturated calomel electrodes and a Sargent Model DR pH meter as a potentiometer. All titrations were performed in an ice bath.

Analytical Methods.—Chloride and chromium were determined by the methods reported previously[2] except that solutions obtained by chromatographic separation were slowly evaporated to dryness on a hot plate prior to chromium analysis. When nitrogen analysis was desired, H₂SO₄ was substituted for HNO₃ in the chromatographic procedure, taking into account the differing pK_a values. Pyrex ampoules containing appropriate aliquots of samples were dried *in vacuo* for 24 hr, sealed, and heated for 30 min at 460–480° in a muffle furnace. Nitrogen was determined as ammonia by the indanetrione hydrate method.[10] Visible absorption spectra were determined with a

(7) D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

(8) Different amounts of starting materials are required in the two preparations above because of large differences in final yield of products.

(9) V. J. Shiner, Jr., and M. L. Smith, *Anal. Chem.*, **28**, 1043 (1956).

(10) S. Jacobs, "Analytical Chemistry 1962—The Proceedings of the International Feigl Anniversary Symposium," P. W. West, A. M. G. MacDonald, and T. S. West, Ed., American Elsevier, New York, N. Y., 1963, p 200.

TABLE I

VISIBLE ABSORPTION MAXIMA AND MINIMA OF RELATED pn– AND en–Cr^{III}
COMPLEXES IN ACIDIC AQUEOUS SOLUTIONS AT 15–25°^{a}

Complex	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ	λ_{min}, mμ	λ_{max}, mμ
cis-Cr(pn)$_2$Cl$_2^{+\ b}$	400 (77.0)	455 (23.0)	530 (80.6)		
cis-Cr(en)$_2$Cl$_2^{+\ b}$	402 (68.5)	456 (20.7)	528 (70.6)		
trans-Cr(pn)$_2$Cl$_2^{+\ b}$	395 (38.4)	438 (26.5)	450 (27.3)	515 (10.8)	577 (27.9)
trans-Cr(en)$_2$Cl$_2^{+\ b}$	395 (34.0)	439 (22.3)	453 (22.8)	514 (8.1)	578 (24.5)
cis-Cr(pn)$_2$(OH$_2$)Cl$^{2+\ b}$	387 (59.1)	440 (20.4)	511 (74.7)		
cis-Cr(en)$_2$(OH$_2$)Cl$^{2+\ b}$	385 (55.7)	438 (20.3)	510 (71.4)		
trans-Cr(pn)$_2$(OH$_2$)Cl$^{2+\ c}$	380 (47.2)	427 (22.9)	453 (25.0)	500 (16.0)	546 (20.9)
trans-Cr(en)$_2$(OH)$_2$Cl$^{2+\ b}$	380 (45.4)	428 (23.7)	448 (24.4)	500 (15.4)	546 (20.5)
Pink Cr(en)(OH$_2$)$_2$Cl$_2^{+\ d}$	410 (31.6)	463 (17.0)	529 (36.9)		
Blue Cr(en)(OH$_2$)$_2$Cl$_2^{+\ e}$	420 (22.7)	475 (16.3)	550 sh (37.6)		580 (39.1)
Green Cr(en)(OH$_2$)$_2$Cl$_2^{+\ f}$	440 (46)	502 (21)	590 (67)		
Purple Cr(pn)(OH$_2$)$_2$Cl$_2^{+\ g}$	420 (29.5)	480 (15.8)	555 sh (38)		580 (39.6)
Pink Cr(pn)(OH$_2$)$_2$Cl$_2^{+\ c}$	420 (41.3)	465 (25.9)	515 (41.3)		580 sh (26.6)
Magenta Cr(en)(OH$_2$)$_3$Cl$^{2+\ f,g}$	402 (30.5)	458 (14.1)	535 (38.9)		
Purple Cr(en)(OH$_2$)$_3$Cl$^{2+\ f,g}$	420 (46)	480 (19)	567 (72)		
Magenta Cr(pn)(OH$_2$)$_3$Cl$^{2+\ g}$	405 (23.4)	450 (10.7)	540 (31.8)		
Magenta Cr(pn)(OH$_2$)$_3$Cl$^{2+\ c}$	403 (35.4)	458 (15.5)	535 (39.3)		
Cr(en)(OH$_2$)$_4^{3+\ e}$	387 (22.0)	428 (10.7)	517 (32.0)		
Cr(pn)(OH$_2$)$_4^{3+\ f}$	383 (24.4)	438 (11.6)	515 (36.0)		

^{a} Values inside parentheses are the molar absorbancy indices a_M defined by $A = \log (I_0/I) = a_M c d$ in M^{-1} cm^{-1}. ^{b} Reference 3. ^{c} This work. ^{d} Reference 5. ^{e} D. A. House and C. S. Garner, *Inorg. Chem.*, 5, 840 (1966). ^{f} Reference 12. ^{g} Reference 11.

Cary Model 14 recording spectrophotometer, using matched quartz cells.

Results and Discussion

Characterization of Products.—Preliminary spectrophotometric studies of the aquation of *trans*-Cr(pn)$_2$-Cl$_2^+$ in 0.10 *F* HNO$_3$ at 35° indicated that the *trans*-chloroaquo species is not the sole initial product of the reaction. As a result, the behavior of the system on a cation-exchange resin was investigated in order to separate and identify the products. The chromatographic work showed clearly that the aquation of *trans*-Cr(pn)$_2$Cl$_2^+$ is similar to the aquation of its ethylenediamine analog.[5] The characterization of the three products obtained is discussed in the order of their elution from the column.

The reaction product eluted with 0.6 *F* HNO$_3$ has been characterized as the dichlorodiaquopropylenediaminechromium(III) cation on the basis of Cl:Cr and N:Cr atom ratios of 1.98:1 and 2.11:1, respectively. The isolation and identification of this reaction product demonstrate that Cr–N bond breakage contributes significantly to the first-stage aquation of *trans*-Cr(pn)$_2$-Cl$_2^+$, as has been shown for several bis(ethylenediamine)chromium(III) complexes.[3] The elution behavior of this pink complex, as well as its visible absorption spectrum, differs from that of the purple complex with the same stoichiometry which has been isolated in solution by Garner, *et al.*,[11] as one of the products formed when diperoxoaquopropylenediaminechromium(IV) dihydrate is decomposed by 12 *F* HCl. We believe that this pink complex is another one of the six theoretically possible geometric isomers of Cr(pn)(OH$_2$)$_2$Cl$_2^+$. Although the elution behavior of this complex is essentially the same as that of the pink isomer of Cr(en)-(OH$_2$)$_2$Cl$_2^+$ obtained as one of the products of acid hy-

drolysis of *trans*-Cr(en)$_2$Cl$_2^+$ at 35°,[5] the visible absorption spectra (Table I) and reactivities are quite different. The pink isomer of Cr(en)(OH$_2$)$_2$Cl$_2^+$ was reported to be essentially inert,[5] whereas the pink isomer of Cr(pn)(OH$_2$)$_2$Cl$_2^+$ reacts to give the tetraaquo[12] species in 2 *F* HNO$_3$ at 35°. Data from spectral scans were used to estimate a first-order rate constant of ~0.6 × 10^{-5} sec^{-1} for this reaction. Since this species was only available to us in relatively high acid concentrations, the effect of the acid concentration on the rate of the reaction could not be determined.

Original attempts to isolate this particular dichlorodiaquopropylenediaminechromium(III) cation by chromatographic separation of the solution resulting from 9 hr of aquation at 35° resulted in the isolation of a magenta species with Cr:Cl and Cr:N atom ratios of 1:1 and 1:2, respectively, but differing in its extinction coefficients from those previously reported for the magenta isomer of the chlorotriaquopropylenediaminechromium(III) cation.[11] The magenta species found in the present study appears to arise from the aquation of the pink Cr(pn)(OH$_2$)$_2$Cl$_2^+$, although a possible contribution to its formation from the aquation of the *trans*-chloroaquo species cannot be ignored.[6] This magenta species appears to be another one of the four theoretically possible geometric isomers of the chlorotriaquopropylenediaminechromium(III) cation. Spectrophotometric studies of this species showed that in 2.5 *F* HNO$_3$ at 35° it undergoes conversion to the tetraaquo species with a first-order rate constant of ~1 × 10^{-5} sec^{-1}. Again, we were not able to study the effect of the acid concentration on the reaction rate of this species.

The product which was eluted with 1.4 *F* HNO$_3$ has been characterized as *trans*-Cr(pn)$_2$(OH$_2$)Cl^{2+} on the

(11) D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 6, 1077 (1967).

(12) The product was identified as the tetraaquo species because the equilibrium spectrum agreed very well with that reported by R. G. Hughes and C. S. Garner, *ibid.*, 6, 1519 (1967).
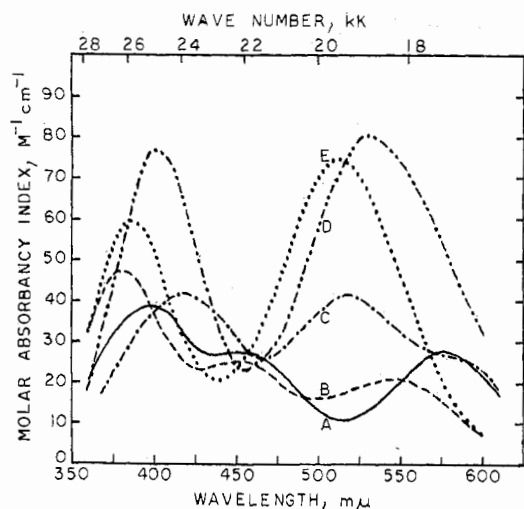
Figure 1.—Visible absorption spectra at 15–25° of (A) *trans*-Cr(pn)$_2$Cl$_2$$^+$, in 0.1 F HClO$_4$,[2] (B) *trans*-Cr(pn)$_2$(OH$_2$)Cl^{2+}, in 3 F HNO$_3$, (C) Cr(pn)(OH$_2$)$_2Cl_2$$^+$, in 2 F HNO$_3$, (D) *cis*-Cr(pn)$_2Cl_2$$^+$, in 0.1 F HClO$_4$,[3] and (E) *cis*-Cr(pn)$_2$(OH$_2$)Cl^{2+}, in 2 F HClO$_4$.[3]

basis of a Cl:Cr atom ratio of 0.98:1, its elution behavior, and a three-peak visible absorption spectrum as shown in Figure 1 (curve B).

The reaction product eluted with 2 F HNO$_3$ gave a visible absorption spectrum which agrees very well with that reported for the *cis*-Cr(pn)$_2$(OH$_2$)Cl^{2+} cation.[3] Table I summarizes the absorption maxima and minima of the various related propylenediamine and ethylenediamine complexes.

Kinetics.—The first-order rate constant for the disappearance of *trans*-Cr(pn)$_2$Cl$_2$$^+$ in 0.10 F HNO$_3$ at 35.0° in the dark was found from chromatographic separations to be (12.62 ± 0.03) × 10^{-5} sec^{-1}. Figure 2 shows the rate of growth and decay of the
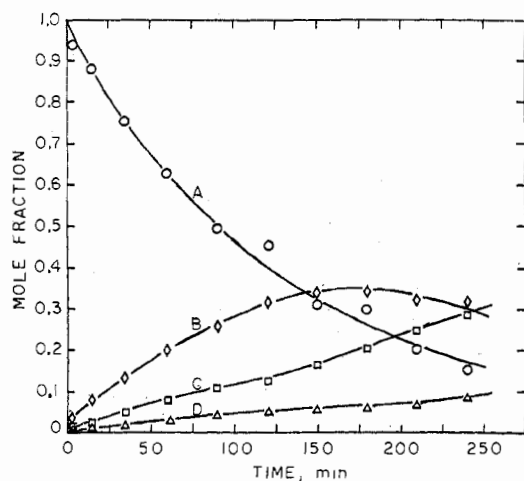

Figure 2.—Concentration–time curves for the aquation of *trans*-Cr(pn)$_2$Cl$_2$$^+$ at 35.0°: (A) *trans*-Cr(pn)$_2$Cl$_2$$^+$, (B) *trans*-Cr(pn)$_2$(OH$_2$)Cl^{2+}, (C) *cis*-Cr(pn)$_2$(OH$_2$)Cl^{2+}, (D) Cr(pn)(OH$_2$)$_2$Cl$_2$$^+$.

various chromium species formed during the first stage of the aquation. The first-order rate constants of formation of the products and the total rate of disappearance of *trans*-Cr(pn)$_2$Cl$_2$$^+$ in 0.10 F HNO$_3$ at 35.0°

are compared with those of ethylenediamine analogs in Table II. The rate of disappearance of *trans*-Cr(pn)$_2$-Cl$_2$$^+$ is 1.4 times faster than that of *trans*-Cr(en)$_2$Cl$_2$$^+$.

TABLE II
AQUATION RATE CONSTANTS OF *trans*-Cr(AA)$_2$Cl$_2$$^+$
IN 0.1 F HNO$_3$ AT 35.0° IN THE DARK

trans-Cr(AA)$_2$(OH)$_2$Cl^{2+}

k_1 ↗

trans-Cr(AA)$_2$Cl$_2$$^+$ + H$_2$O $\xrightarrow{k_2}$ *cis*-Cr(AA)$_2$(OH$_2$)Cl^{2+}

k_3 ↘

Cr(AA)(OH)$_2$Cl$_2$$^+$ [a]

Reaction	Method	——10^5k, sec^{-1}——	
		AA = en[b]	AA = pn[c]
k_1 + k_2 + k_3	Chromat sepn[d]	8.75 ± 0.05	12.62 ± 0.03
k_1 + k_2	Cl$^-$ titrn	8.02 ± 0.07	11.62 ± 0.07
k_1	Chromat sepn	7.2 ± 0.6	8.14 ± 0.18
k_1	Diff	6.90 ± 0.41	8.18 ± 0.30
k_2	Chromat sepn	1.12 ± 0.40	3.42 ± 0.38
k_3	Chromat sepn	0.78 ± 0.05	1.01 ± 0.01
k_3	Diff	0.73 ± 0.09	1.02 ± 0.07

[a] Configuration unknown. [b] Reference 5. [c] This work. [d] Chromat sepn refers to chromatographic separations.

This would be expected in a dissociation type of mechanism in which the bulkier pn ligands may enhance the rate of aquation. This effect is readily observed in the corresponding Co(III) analogs.[13–15]

Chloride-release rate studies gave a first-order rate constant of (11.62 ± 0.07) × 10^{-5} sec^{-1} at 35° in 0.10 F HNO$_3$. This value is in agreement with the sum of the first-order rate constants of formation of the *cis*- and *trans*-Cr(pn)$_2$(OH$_2$)Cl^{2+} cations.

The isolation of *trans*-chloroaquo as the major reaction product supports the postulation of Esparza and Garner[3] that at pH 1 *cis*-chloroaquobis(propylenediamine)chromium(III) cation is formed directly from *cis*-dichlorobis(propylenediamine)chromium(III) cation. Therefore, the results of the present study eliminate two other possible mechanisms proposed by these authors. These mechanisms were (1) a path whereby *cis*-Cr(pn)$_2$Cl$_2$$^+$ aquates in a rate-determining step to *trans*-Cr(pn)$_2$(OH$_2$)Cl^{2+}, followed by a rapid isomerization of the *trans*-chloroaquo ion to the cis form, and (2) the less likely path whereby *cis*-Cr(pn)$_2$Cl$_2$$^+$ slowly isomerizes to the trans isomer which then aquates rapidly to give the *cis*-chloroaquo product. The first path is ruled out because a fast trans → cis isomerization of the chloroaquo species could not give trans as the major product of our reaction. Our results also eliminate the second path because aquation of the trans isomer is not stereospecific.

The scheme shown in Figure 3 summarizes the possible paths involved in the first-stage aquation of *trans*-Cr(pn)$_2$Cl$_2$$^+$ in 0.10 F HNO$_3$ in the dark at 35.0.° The results obtained in the present study are consistent with a reaction path which produces the three products di-

(13) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 3089 (1953).
(14) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).
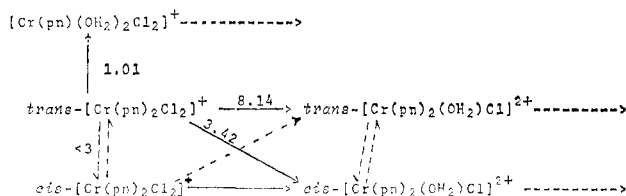(15) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 2673 (1956).

Figure 3.—First-order rate constants (10^5k, sec^{-1}) for aquation and isomerization reactions in 0.10 F HNO$_3$ at 35.0° in the absence of light.

rectly by three parallel first-order reactions. Alternative paths in which the *cis*-chloroaquo species is produced by isomerization of the *trans*-chloroaquo isomer

or by isomerization of the *trans*-dichloro species followed by aquation cannot be ruled out. Garner and Esparza[3] did not observe cis → trans isomerization in the aquation of *cis*-Cr(pn)$_2$Cl$_2$$^+$. Spectrophotometric detection of trans → cis isomerization in the present study was precluded because of the reactivity of the primary products of aquation. It is also possible that cis isomerization products do not reach detectable concentrations since cis complexes generally aquate much faster than the trans. Mechanistic choices must await more complete characterization of the kinetics of aquation of the chloroaquo species of the bis(propylenediamine)chromium(III) system.
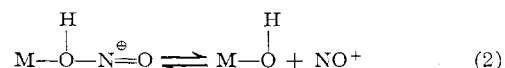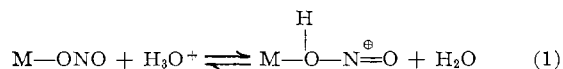
Hydrolysis of Chromium(III)–Nitrito Complexes[1a]

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The acid- and nonacid-catalyzed hydrolysis reactions of *cis*- and *trans*-Cr(en)$_2$(ONO)X^{n+} (cn = ethylenediamine; X = ONO$^-$, OH$_2$, OH$^-$, F$^-$, Cl$^-$, Br$^-$, *N,N*-dimethylformamide (DMF), or dimethyl sulfoxide (DMSO)) have been examined. Rate and activation parameters have been evaluated for the first-order H$^+$-catalyzed and for some spontaneous ONO$^-$-loss pathways. The acid-catalyzed reactions proceed with ~100% retention of geometrical configuration. Hydrolysis at pH 10.0–11.5 shows the following stereochemistries: *cis*-Cr(en)$_2$(ONO)$_2$$^+$ → 100% *cis*-Cr(en)$_2$(ONO)OH$^+$; *trans*-Cr(en)$_2$-(ONO)$_2$$^+$ → 90–100% *trans*-Cr(en)$_2$(ONO)OH$^+$; *cis*-Cr(en)$_2$(ONO)OH$^+$ → 75% *cis*- + 25% *trans*-Cr(en)$_2$(OH)$_2$$^+$ (complicated by reactant isomerization); *trans*-Cr(en)$_2$(ONO)OH$^+$ → a pH-dependent distribution of 78% *trans*- (pH 10.0) to 95% *trans*-Cr(en)$_2$(OH)$_2$$^+$ (pH 11.5). Use of ^{18}O has revealed that hydrolysis of *cis*- and *trans*-Cr(en)$_2$(ONO)$_2$$^+$ in 0.1 F NaOH proceeds with Cr–O bond cleavage. Rate constants were also obtained for the cis ↔ trans isomerizations of Cr(en)$_2$-(ONO)OH$^+$.

Introduction

By analogy with the behavior of cobalt(III)–carbonato complexes and the formation of the nitritopentaamminecobalt(III) ion in aqueous acidic solutions, Basolo and Pearson[2] predicted that acid hydrolysis of metal–nitrito (O-bonded nitrite) complexes should proceed *via* protonation, followed by "denitrosation" without the cleavage of the M–O bond, as represented by

$$\text{M—ONO} + \text{H}_3\text{O}^+ \rightleftharpoons \text{M—}\overset{\overset{\text{H}}{|}}{\text{O}}\text{—N}\overset{\oplus}{=}\text{O} + \text{H}_2\text{O} \quad (1)$$

$$\text{M—}\overset{\overset{\text{H}}{|}}{\text{O}}\text{—N}\overset{\oplus}{=}\text{O} \rightleftharpoons \text{M—}\overset{\overset{\text{H}}{|}}{\text{O}} + \text{NO}^+ \quad (2)$$

In a careful study of the acid hydrolysis of Cr(NH$_3$)$_5$-

ONO^{2+}, Matts and Moore[3] confirmed this prediction by finding a first-order dependence of the rate on [H$^+$] at [H$^+$] ≤ 0.1 M. The rate enhancement in acid solution was so great when compared to the H$^+$ catalysis for species such as Cr(OH$_2$)$_5$F^{2+},[4] which necessarily aquates with Cr–F bond fission, that CrO–N fission seemed more likely. However, side reactions involving ammonia loss prevented an accurate measurement of the uncatalyzed (spontaneous) hydrolysis rate and precluded a direct determination of bond-cleavage position in the acid-catalyzed reaction.

While the tendency toward amine loss is not entirely eliminated in Cr(en)$_2$XY^{n+} hydrolysis,[5] it is vastly di-

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