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Trans Effect in Water-Exchange Reactions of Chromium(III) Complexes[1]

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Rates of water exchange of chloro-, bromo-, and, isothiocyanatopentaaquochromium(III) ions have been measured over the course of approximately 80% of complete exchange of the five waters. Fitting of the data to a derived curve allows calculation of the exchange rate constants of the single trans water and the four cis waters. Relative rates of trans water exchange reveal the trans-labilizing effect of the ligands to be in the sequence $I^- > Br^- > Cl^- > NCS^- > H_2O$. Relative cis rates are uniform and independent of the ligand.

Introduction

There is comparatively little experimental evidence to suggest that ligands exert a trans-labilizing influence in substitution reactions of octahedral complexes. Basolo and Pearson[3] have suggested that kinetic complexities make assignment of a trans effect difficult, if not impossible, in reactions of cobalt(III) and platinum(IV); isomerism, dependent on the trans ligand and the leaving group, complicates reactions of cobalt(III), and catalysis by platinum(II) leads to ambiguities in reactions of platinum(IV). However, for certain cobalt(III) complexes, Halpern, *et al.*,[4] have shown that the S-bonded sulfito ligand appears to have a marked trans-labilizing influence. Confirmation of this behavior is provided by the observation that only one of the five ammonia ligands in $Co(NH_3)_5SO_3^+$ exchanges with excess $^{15}NH_3$.

Reactions of rhodium(III) complexes occur without stereochemical rearrangement and catalytic effects, and the manifestation of the trans effect is well documented in this system. Poe, *et al.*,[5-8] have examined the aqueous solution kinetics of substitution of X in complexes of the type *trans*-RhA_4LX^{z+} ($X = Cl^-, Br^-, I^-$, or H_2O; $L = Cl^-, Br^-, I^-, OH^-, NH_3$, or H_2O; $A = (en)_{1/2}$ or NH_3; $z = 1, 2$, or 3), and presented rate constants and activation enthalpies for the various reactions. Their data permit sequencing L in order of decreasing trans-labilizing influence on X: $I^- > Br^- > OH^- \approx NH_3 \approx Cl^- > H_2O$. Corroboration of the trans influence of ligand chloride in rhodium complexes has been provided by Pavelich and Harris.[9]

Moore, Basolo, and Pearson[10] ascribed the rapid water exchange they observed in iodopentaaquochromium(III) ion to a trans-labilizing influence of iodide, but their measurements did not permit comparison with the rate of cis water exchanges.

In the present study, chloro-, bromo-, and isothiocyanatopentaaquochromium(III) ions were chosen for investigation because aquation rates for the acido complexes are known[11-13] and are moderately slow compared with that of iodopentaaquochromium(III) ions.

Experimental Section

Preparation of Complexes. Chloropentaaquochromium(III) Perchlorate. A solution containing chlorochromium(III) ion was prepared by the procedure described by Finholt, *et al.*[14] Forty-five grams of $CrCl_3 \cdot 6H_2O$ was dissolved in 900 ml of water and permitted to remain at room temperature for 2 hr; then 15 ml of concentrated perchloric acid was added. The resulting mixture of isomers was absorbed on a column of cation-exchange resin (hydrogen form of Dowex 50W-X8, 200–400 mesh) 50 cm in length and 4 cm in diameter. Individual isomers were consecutively removed from the column by displacement ion exchange, using 0.2 *M* $Ba(ClO_4)_2$ in 0.1 *M* $HClO_4$ as eluent. The middle one of three sharply defined bands contained the $CrCl^{2+}$ species, as determined by spectral and elemental analyses. The dilute effluent containing the complex sought was concentrated about 20-fold at room temperature by using a rotary flash evaporator, and the viscous concentrate yielded crystals through evaporation on a high-vacuum line. The hygroscopic crystals were stored, tightly stoppered, below 0° until use.

Bromopentaaquochromium(III) Perchlorate. Using Recoura's method[15] with minor modifications, a mixture of chromium(III) bromide isomers was obtained. To 10 g of solid chromic oxide was slowly added 140 ml of cold, fuming hydrobromic acid. The by-product, bromine, was removed by repeated extractions with carbon tetrachloride. Ion-exchange separation was effected at 3°, and effluent concentration, evaporation to yield crystals, and storage were carried out in the same manner as described for the chlorochromium(III) complex.

Isothiocyanatopentaaquochromium(III) Perchlorate. The method of King and Dismukes[16] was used for the preparation of this complex. Seven grams of potassium thiocyanate and 50 g of chromium perchlorate hexahydrate were dissolved in 400 ml of 0.1 *M* $HClO_4$, maintained at the boiling point for 3 hr, and then cooled to 0° to precipitate potassium perchlorate. The mixture of isomers in the filtrate was separated by the ion-exchange procedure described above, and flash evaporation of the appropriate fraction of effluent yielded crystals of the complex. Following filtration, the crystals were stored over anhydrous magnesium perchlorate.

Analytical Procedures. Spectra for all complexes studied were measured with a recording spectrophotometer (Cary Model 14) over the range 200–700 nm. Samples of effluent taken directly from the ion-exchange column and diluted aliquots of all solutions used in kinetic runs were examined. Chromium was assayed (as chromate) spectrophotometrically. Halides and isothiocyanate were determined (as silver salts) by gravimetric procedures. Perchloric acid was analyzed by difference by acid–base titration of the effluent from the acid form of a cation-exchange column which absorbed the complex from an aliquot of solution.

Measurement of Exchange Rates. To a weighed sample of the hydrated complex in a 50-ml round-bottomed flask, cooled in an ice bath, was added 10 ml of cold 1.0 *M* $HClO_4$ prepared using enriched

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(1) (a) Based in part on Ph.D. thesis of D. E. Bracken, Sept 1967, University of Western Ontario. (b) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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(3) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 4, 381 (1962).

(4) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, 88, 2877 (1966).

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Table I. Analytical Data on Prepared Complexes

Complex	X:Cr	Spectral data[a]				
		This work	Ref 11	Ref 16	Ref 17	Ref 18
$[CrCl(H_2O)_5]^{2+}$	1.00	428 (21.7)	428 (20.8)		428 (21.9)	
		608 (17.4)	609 (16.4)		608 (17.4)	
		675 sh[b] (7.9)	675 (6.7)		674 (7.5)	
$[CrBr(H_2O)_5]^{2+}$	0.97	433 (22.4)			432 (23.7)	432 (22.4)
		470 sh (15)			470 (15)	
		622 (20.2)			622 (21.3)	622 (19.9)
		675 sh (12)			675 (12)	675 (11.3)
$[CrNCS(H_2O)_5]^{2+}$	0.98	411 (33.8)		410 (33.6)		
		570 (31.7)		570 (31.5)		

[a] Reported as λ (ε), where λ is the wavelength of maximum absorption in nm and ε is the molar absorptivity at the particular λ in M^{-1} cm^{-1}. [b] sh = shoulder.

water. (The resulting solution was approximately five-fold enriched in oxygen-18.)

Immediately on dissolution, a 0.5-ml aliquot was transferred to a sampling flask. This was placed on a vacuum line, partially evacuated, and then immersed in liquid nitrogen. The time of immersion was recorded as "zero time." After evacuation of the sampling flask (pressure $<10^{-3}$ Torr) the sample was melted and a portion of solvent water taken by distillation. After recording the weight of the water sample thus gathered and transferred to an evacuated sample tube, a known amount of CO_2 of known isotopic composition was added and left at room temperature for 3 days for isotopic equilibration.

At the time the "zero-time" sample was taken, the flask containing the solution for the run was thermostated. Additional samples were taken at scheduled times over a period estimated to cover 2-3 half-lives on the approach to isotopic equilibrium in the same manner as described for the "zero-time" sample. The "infinite-time" sample was similarly taken after approximately 10 half-lives for exchange.

Isotopic Analysis. Carbon dioxide, after equilibration with water samples, was analyzed relative to the standard carbon dioxide used in the equilibration procedure by means of a double-collector type isotope ratio mass spectrometer.

Results and Discussion

Identification of Prepared Species. Confirmation of the identity of the complexes prepared for this study was made by means of elemental and spectral analyses. Table I presents the data obtained along with comparable spectral data from the literature.[16-18] The ratios reported for X:Cr, based on elemental analyses, have a precision limit of *ca* ±5%. Comparisons of the spectrophotometric data show good agreement between values obtained and those reported in the literature for these complexes.

Initial Treatment of Exchange Data. Mass analysis was performed on carbon dioxide, and the oxygen isotopic composition of solvent water at time "*t*" (N_t) was calculated by the Dostrovsky and Klein equation,[19] which takes into account the equilibrium distribution of oxygen-18 between water and carbon dioxide[20] as well as dilution of the sample by the oxygen atoms of carbon dioxide.

In order to plot the data on the basis of the McKay equation,[21] calculations were made of

$$1 - F = \frac{N_t - N_\infty}{N_0 - N_\infty}$$

where F is the fraction exchange at time "t," and N_0 and N_∞ are the isotopic compositions of solvent water at "zero" time and "infinite" time. A McKay plot ($-\log(1 - F)$ *vs.* t) for run Cl-3 is shown in Figure 1. The curve displays features common to all the water-exchange reactions of the acidopentaaquochromium(III) complexes studied: the curve is nonlinear, and extrapolation of the linear limiting portion to zero time intersects the ordinate at a value of $(1 - F) \approx 0.8$.

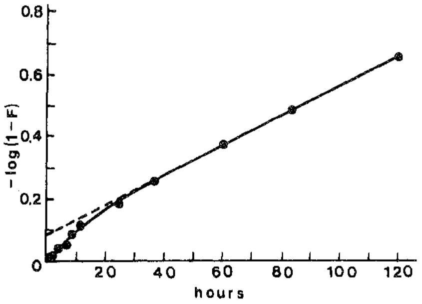

Figure 1. McKay plot of $H_2{}^{18}O$ exchange between $CrCl(H_2O)_5{}^{2+}$ and solvent. The solid line is the computer-generated "best fit" curve based on eq 6; ●, experimental values for run Cl-3..

Implicit in the development of the McKay equation for "simple isotopic exchange" are the following assumptions. The composition of the reacting mixture remains chemically unchanged throughout the approach to isotopic equilibrium, and if more than one atom of the same element in the compound undergoes exchange, these atoms are in equivalent structural positions. Although decomposition by aquation does occur, it is slow compared to exchange; thus the first assumption may be assumed valid. That the second assumption does not apply to these complexes is apparent, and the value of the intercept of the extrapolated linear portion of the curve suggests that the unique (trans) water molecule exchanges at a more rapid rate than the other four.

Attempts to derive an expression analogous to the McKay equation for the case of two simultaneous first-order exchange processes

$$[CrX(\textit{cis}\text{-}H_2O)_4(\textit{trans}\text{-}H_2O)]^{2+} + H_2O^* \overset{k_{trans}}{\rightleftharpoons} [CrX(\textit{cis}\text{-}H_2O)_4(\textit{trans}\text{-}H_2O^*)]^{2+} + H_2O$$

$$[CrX(\textit{cis}\text{-}H_2O)_4(\textit{trans}\text{-}H_2O)]^{2+} + 4H_2O^* \overset{k_{cis}}{\rightleftharpoons} [CrX(\textit{cis}\text{-}H_2O^*)_4(\textit{trans}\text{-}H_2O)]^{2+} + 4H_2O$$

lead to two simultaneous differential equations for which the solution is complex

$$dy/dt = (R_{cis}/ab)(bx - ay) \qquad (1)$$

$$dz/dt = (R_{trans}/ac)(cx - az) \qquad (2)$$

where a = [O] + [O*] in solvent water, b = [O] + [O*] in cis positions of complex ion, c = [O] + [O*] in the trans position of complex ion, x = [O*] in solvent water, y = [O*] in cis positions of complex ion, and z = [O*] in the trans position of complex ion. (It is assumed that isotopic

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(17) P. Moore and F. Basolo, *Inorg. Chem.*, **4**, 1670 (1965).

(18) H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

(19) I. Dostrovsky and F. S. Klein, *Anal. Chem.*, **24**, 414 (1952).

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Table II. Acidopentaaquochromium(III) Ion–Solvent Water Exchange Rate Constants at 25°

Run	$[CrX^{2+}]$,[a] M	$[HClO_4]$, M	I,[b] M	$[ClO_4^-]$, M	$10^6 k_{trans}$, sec^{-1}	$10^6 k_{cis}$, sec^{-1}	k_{trans}/k_{cis}
NCS-1	1.04	1.17	4.29	3.25	16 ± 2	3.0 ± 0.2	5.2 ± 0.8
NCS-2	1.12	1.04	4.39	3.27	15 ± 2	3.0 ± 0.1	5.1 ± 0.8
NCS-3	1.32	0.98	4.94	3.62	19 ± 2	3.1 ± 0.1	6.1 ± 0.6
Cl-1	0.73	1.02	3.19	2.47	15 ± 6	2.0 ± 0.2	7.7 ± 3.0
Cl-2	0.99	1.31	4.28	3.29	39 ± 11	2.4 ± 0.1	16 ± 5
Cl-3	1.25	1.01	4.75	3.50	24 ± 4	2.9 ± 0.2	9.8 ± 1.3
Cl-4	1.42	1.45	5.70	4.28	33 ± 4	3.2 ± 0.2	10.4 ± 1.2
Cl-5	1.53	1.18	5.77	4.24	55 ± 8	3.4 ± 0.2	16 ± 2.4
Br-1	0.75	1.22	3.47	2.72		2.9 ± 0.1	
Br-2	0.97	1.62	4.52	3.56		3.0 ± 0.6	
I[c]	0.40	1.00	2.6	1.00[d]	270		
					(260	3.1	84)[e]

[a] $CrX^{2+} = CrX(H_2O)_5{}^{2+}$; X = Cl, Br, NCS, or I. [b] I = ionic strength. [c] Reference 10. [d] $[SO_4{}^{2-}] = 0.4\ M$. [e] Calculated using data from ref 10.

discrimination and, for the level of enrichment (~5-fold) employed, double labeling are negligible.)

R_{cis} and R_{trans} are the rates of exchange of oxygen in cis positions and the trans position with oxygen in solvent water. The experimental conditions (concentrations) permit approximations which allow independent solutions of eq 1 and 2. Since the concentration of water is very much greater than that of the dissolved complex, it can be calculated that during the course of complete exchange, x is altered by *ca.* 10% whereas y and z undergo changes of *ca.* 400%. The approximations made are that for the process of cis exchange, the depletion of x by trans exchange is ignored, and for trans exchange, the depletion of x by cis exchange is ignored. Applying these approximations permits the solutions

$$F_{cis} = 1 - \exp[-k_{cis}((a + b)/a)t] \tag{3}$$

$$F_{trans} = 1 - \exp[-k_{trans}((a + c)/a)t] \tag{4}$$

where $R_{cis} = k_{cis}b$ and $R_{trans} = k_{trans}c$. The relative contributions of cis and trans exchange to the total fraction exchange, F, is 4:1, *i.e.*, the ratio of sites available for exchange. Thus

$$F = {}^1/_5(4F_{cis} + F_{trans}) \tag{5}$$

where $^1/_5$ is the normalizing factor. Substituting $4c$ for b and eq 3 and 4 in eq 5 gives upon rearrangement

$$1 - F = 0.8 \exp[-k_{cis}((a + 4c)/a)t] + 0.2 \exp[-k_{trans}((a + c)/a)t] \tag{6}$$

Computation of Rate Constants. The two first-order rate constants, k_{trans} and k_{cis}, were calculated by substituting experimental data in the rate expression 6. A nonlinear weighted least-squares computer program facilitated computation of the two parameters which gave the best fit of experimental data to the derived equation. Since the program required trial values for the parameters, an approximate value for k_{cis} was determined graphically from the limiting linear portion of the McKay plot, and k_{trans} was estimated to be 10 times k_{cis}.

The program also generates a curve based on the "best fit" values of k_{cis} and k_{trans} for a given run. The solid line in Figure 1 represents such a generated curve, whereas the circles denote experimental points.

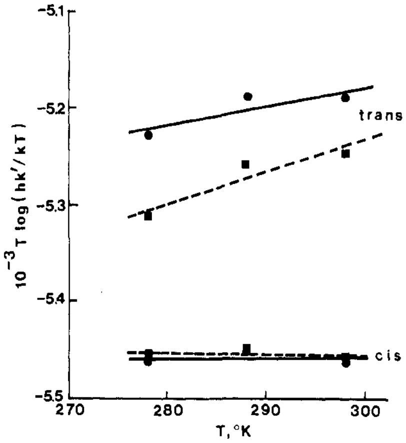

Figure 2. Plot of temperature dependence of rate constant to obtain entropy of activation. k' is k_{trans} or k_{cis}; ●, $CrCl(H_2O)_5{}^{2+}$; ■, $Cr\text{-}NCS(H_2O)_5{}^{2+}$.

Rate constants for all runs conducted at 25° along with errors estimated by standard error analysis are given in Table II; also given is the datum previously reported for CrI^{2+}, along with a recalculated value assuming contribution to exchange by cis waters to be the same as in the cases reported here. Table III provides similar data for runs at 25, 15, and 5°, conducted with comparable concentrations. The temperature-dependence data enabled calculation of enthalpies and entropies of activation for exchange of cis and trans waters with solvent from the relation

$$\log [(k'/T)(h/k)] = (\Delta S^*/2.303R) - (\Delta H^*/2.303R)(1/T)$$

where k' is the rate constant. Figure 2 displays the data from Table III plotted appropriately for the calculation of ΔS^*. The slopes were obtained from the best straight lines for each of three points. Values of the activation parameters and estimated errors[22] are summarized in Table IV.

Effect of Systematic Errors. "Zero-Time" Exchange. The length of time elapsed between dissolution of complex and collecting the first (zero time) sample can be calculated to correspond to exchange of less than one-tenth of a water molecule for the chloro and isothiocyanato complexes and may be responsible in part for inconsistencies and low precision of the k_{trans} values. A similar time for the bromo complex yielded rather discrepant experimental data; if k_{trans} in this case is assumed to be 10^{-4} sec^{-1}, the delay would correspond to the time required for exchange of nearly 50% of a water molecule. A dependable value of k_{trans} for the bromo ion cannot be obtained from the data.

Control of Concentration of Solutions. The complexes (as perchlorates) were not prepared in forms which contained predictable and/or reproducible amounts of water and perchloric acid, and this precluded the preparation of solutions

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(22) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, pp 91-94.

Table III. Chloro- and Isothiocyanatochromium(III) Ions–Solvent Water Exchange Rate Constants at 25, 15, and 5°

Run	Temp, °C	$[CrX^{2+}]$,[a] M	$[HClO_4]$, M	I,[b] M	$[ClO_4^-]$, M	$10^6 k_{trans}$, sec^{-1}	$10^6 k_{cis}$, sec^{-1}
Cl-3	24.78	1.25	1.01	4.75	3.50	24 ± 4	2.9 ± 0.2
Cl-6	14.86	1.25	1.19	4.93	3.69	5.8 ± 1.2	0.72 ± 0.01
Cl-7	4.99	1.29	1.20	5.07	3.98	0.93 ± 0.20	0.133 ± 0.005
NCS-2	24.78	1.12	1.04	4.39	3.27	15 ± 2	3.0 ± 0.1
NCS-4	14.86	1.02	0.74	3.80	2.78	3.3 ± 1.3	0.73 ± 0.06
NCS-5	4.99	1.13	1.01	4.39	3.26	0.46 ± 0.09	0.140 ± 0.002

[a] See footnote *a*, Table II. [b] See footnote *b*, Table II.

Table IV. Activation Parameters for Trans and Cis Water Exchange

	ΔH^*, kcal/mol		ΔS^*, eu	
Complex	Trans	Cis	Trans	Cis
$CrNCS^{2+}$	29 ± 4	24.9 ± 1.0	15 ± 6	−0.3 ± 2.4
$CrCl^{2+}$	26 ± 4	25.1 ± 0.7	9 ± 5	0.2 ± 3.5

Table V. Cis Water Exchange and Aquation Rates for CrX^{2+} at 25°

Complex	$10^6 k_{cis}$, sec^{-1}	$10^6 k_{aq}$,[a] sec^{-1}
$CrNCS^{2+}$	3.0	0.0090[b]
$CrCl^{2+}$	2.9	0.31[c]
$CrBr^{2+}$	3.0	5.0[d]

[a] k_{aq} is the aquation rate constant. [b] Reference 13. [c] Reference 11. [d] Extrapolated from the data of reference 12.

of exactly predetermined complex concentration and acid strength. The influence of these factors on the rate constants can be roughly inferred from scrutiny of the data of Table II. Increases in concentration of complex ion and perchlorate ion, as well as total ionic strength, parallel increases in both k_{trans} and k_{cis} (excepting the apparently anomalous result for k_{trans} for run Cl-2), although the influence on the thiocyanato complex is somewhat less than on the chloro complex. Since the ionic strength and perchlorate ion concentration were not varied independently of the complex ion concentration, the dependence of the rates on any particular factor cannot be resolved on the basis of the present data.

At high concentrations of complex, an apparent rate dependence on anion concentration and ionic strength is found for solvent water exchange with hexaaquochromium(III) ion.[23] The same factors may account for the rate variation found here, although k_{trans} for the chloro complex appears markedly dependent.

Aquation. The importance of aquation can be estimated from the rates calculated for cis exchange compared with aquation rates, available in the literature; such data are summarized in Table V. In the exchange experiments at 25° with the chloro and isothiocyanato complexes, the penultimate sample was removed about 120 hr after "zero time;" the hydrolytic decomposition of these complexes to the aquo ion amounts to *ca.* 13 and 0.4%, respectively, for this time interval. That the influence of this decomposition is unimportant is borne out by the McKay plots, the latter portions of which exhibit excellent linearity. The effect of aquation in experiments on the bromo complex is more important; approximately 66% decomposition had resulted at the time the penultimate samples were taken (60 hr). The earlier points, for which aquation is less, were favored by weighting in the best-fit computer program. Nevertheless the values reported for k_{cis} are to be taken as representing lower limits, although they are judged valid to ±20%.

The criterion chosen for demonstrating a trans effect in the complexes studied is the ratio of exchange rate constants, $k_{trans}:k_{cis}$. The advantage of this measure is that both rates were determined simultaneously in the same environment, and therefore within the limits of the systematic errors discussed, the ratio for a particular run is independent of variations in concentration of complex and anion and ionic strength.

For run Cl-1, the ratio $k_{trans}:k_{cis}$ is *ca.* 8; *i.e.*, the water in the trans position exchanges with solvent water 8 times as rapidly as a water molecule in a cis position, under the particular conditions of that experiment. Chloride in the first coordination sphere of chromium(III) exerts a significant labilizing influence on the water molecule trans to itself, relative to water molecules in cis positions.

Despite variations, an estimate of the trans effect for these experiments can be obtained by averaging the ratios. The average $k_{trans}:k_{cis}$ value for chlorochromium(III) ion is 12. For purposes of discussion, this value is considered the trans-labilizing factor for chloride ligand on water exchange at 25°.

Application of the same approach yields a trans-labilizing factor of 5.5 for isothiocyanate ligand at 25°.

The absence of curvature in McKay plots of the data from experiments on the bromo complex can be interpreted to imply a trans-labilizing factor of unity for the bromide ion (*i.e.*, no trans effect); alternately it must be assumed that the rate of exchange of the trans water is sufficiently rapid that exchange is essentially complete within the time of first sampling. The latter interpretation leads to a minimum trans-labilizing factor for bromide ligand of *ca.* 25.

To derive the trans-labilizing influence of iodide in iodopentaaquochromium(III) ion, the data of Moore, Basolo, and Pearson[10] were reevaluated. The recalculation, based on the assumption that cis water exchange occurs at the same rate observed for the complexes reported in this study, gave the value cited in Table II. From this the trans effect factor is found to be 84. (The alternate limiting assumption, that there is *no* trans effect for iodide, is held to be untenable; this would lead to a rate constant for water exchange of $^1/_5 \times 2.7 \times 10^{-4}$ sec^{-1}, a value comparable to that for the trans rate for the chloro complex.)

The relative values of the trans-labilizing factors determined for isothiocyanate and chloride ligand and tentatively given for bromide and iodide ligands in the acidopentaaquochromium(III) complexes provided no new insights as to the basis of trans effects *per se*. The relative values of the activation parameters for trans and cis exchange do permit some discussion of the reasons for the differences in the rates and may lead to a model for these exchange processes.

The difference in enthalpies of activation does not cause k_{trans} to be greater than k_{cis}; the relative values of ΔH^* indicate the opposite order of exchange rates is expected for both chloro and isothiocyanato complexes. A large, positive entropy of activation for the trans process, in contrast to a zero entropy of activation for the cis process, counteracts the enthalpy effect.

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(23) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

If the value of the activation entropy can be used as an indication of mechanism, as in an analogous system reported by Hunt and Taube,[24] trans exchange would be inferred to be a dissociative interchange, whereas cis exchange would be characterized as an interchange in which bond formation is comparable in importance to bond breaking. Relative values of ΔH^* are consistent with such a conclusion.

In the second coordination sphere of the polar acidopentaaquochromium(III) ion, it appears reasonable to assume a lesser degree of ordering of water molecules in the region surrounding the acido ligand and that water molecules would be unsuitably oriented to provide concerted assistance to the displacement of a cis-bound water from that direction. If that is the case, a statistical factor would favor the exchange of the water molecule in the trans position compared to a molecule in a cis position.

Registry No. Chloropentaaquochromium(III) perchlorate, 51052-36-9; bromopentaaquochromium(III) perchlorate, 51052-37-0; isothiocyanatopentaaquochromium(III) perchlorate, 27295-40-5.

(24) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 76, 5960 (1954).

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Kinetics of the Spontaneous Ring-Closing and Aquation Reactions of Malonatopentaaquochromium(III)

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The spontaneous dynamic behavior of malonatopentaaquochromium(III), a complex containing monodentate malonate, was investigated in the acidity range $0.1 \leqslant (H^+) \leqslant 1.0\ M$ at 25°. Experiments were carried out in which the concentrations of the monodentate species, the chelate complex malonatotetraaquochromium(III), and hexaaquochromium(III) were monitored chromatographically. The data were quantitatively consistent with a kinetic scheme in which the monodentate complex simultaneously undergoes irreversible aquation and reversible ring closing. The latter process, which is the faster of the two, approaches a steady state in which the monodentate and chelate complexes are very nearly at equilibrium; the acid-independent half-life for this transient phase of the reaction is 7 hr. Subsequent aquation of the steady-state mixture, in which the chelate predominates, is very slow. Substantial discrepancies between our results and those of earlier investigations are discussed.

Introduction

The kinetic inertness of chromium(III) complexes has made it possible to isolate and study many unusual, thermodynamically unstable species. We have investigated one such complex in detail, malonatopentaaquochromium(III). This complex, which contains a monodentate malonate ligand, was first reported by Huchital and Taube.[1]

Our involvement arose from an interest in its properties as an oxidizing agent; once we had prepared the complex, however, it became evident that the spontaneous dynamic behavior of our samples differed significantly from that described previously.[1-3] To resolve this discrepancy, we undertook a thorough kinetic study, the results of which are reported herein.

Experimental Section

Malonatotetraaquochromium(III). A 25-ml solution was prepared containing 1.0 *M* malonic acid, 0.25 *M* perchloric acid, and 0.25 *M* hexaaquochromium(III). It was thermostated at 40° for 5 days, diluted to 100 ml with water, and then charged onto an ion-exchange column with a bed volume of 50 ml (22-mm i.d.). The ion-exchange resin in this procedure, as well as all others described in this section, was specially cleaned[4] Bio-Rad AG50W-X2, 200–400 mesh resin in the hydrogen form. After charging was complete, the column was rinsed with 150 ml of 0.05 *M* perchloric acid to remove free malonic acid and anionic complexes. The main band of malonatotetraaquochromium(III) was then eluted with 0.50 *M* perchloric acid. A typical preparation yielded 30 ml of $5 \times 10^{-2}\ M$ solution, collected from the central region of the 1+ band. The stock solution was stored at 0°.

Malonatopentaaquochromium(III). Three different preparations were used.

Method A. This procedure was a modified version of one described by Huchital and Taube.[1] It proved to be the simplest method of synthesizing substantial quantities of the complex. A 60-ml solution was prepared containing 0.10 *M* hexaaquoiron(III) (a stock solution of which had been made by dissolving iron wire in perchloric acid and oxidizing with hydrogen peroxide), 0.50 *M* malonic acid, and 0.06 *M* perchloric acid. It was then deaerated with argon and 30 ml of a solution containing 0.20 *M* chromium(II) (prepared by the zinc reduction of hexaaquochromium(III)) and 0.18 *M* perchloric acid was injected. The chromium(II)–iron(III) reaction occurred on mixing, after which the solution could be opened to the air. At this stage, 20 ml of 0.05 *M* sodium dichromate was added to oxidize the iron(II) to iron(III); if this step was omitted, the desired malonatopentaaquochromium(III) (2+ charge) was not easily separated from the large amounts of hexaaquoiron(II) present. The reaction mixture was then charged onto an ion-exchange column identical with that described above. After charging was complete, the column was rinsed with 200 ml of 0.10 *M* perchloric acid and then the malonatopentaaquochromium(III) was eluted with 0.50 *M* perchloric acid. Typically, 80 ml of the acid moved the 2+ band to the bottom of the column and its central portion could be collected in the next 25 ml. The resulting solution generally had a concentration of about $3.5 \times 10^{-2}\ M$.

Method B. A 20-ml 0.05 *M* malonatotriethylenetetraminecobalt(III) perchlorate solution (see below) was deaerated with argon and then 10 ml of a solution that was 0.10 *M* in chromium(II) and 0.60 *M* in perchloric acid was injected. The chromium(II)–cobalt(III) reaction appeared to be complete in about 1 min; after a few additional minutes, the reaction mixture was opened to the air. The chromatographic work-up, which followed the procedure described in method A (on a suitably reduced scale), typically produced 7 ml of 0.10 *M* product.

Method C. Malonatopentaaquochromium(III) could be recovered in small yield from the standard preparation of malonatotetraaquochromium(III), the recipe for which was described above. Elution was simply continued after the 1+ band had been collected with the perchloric acid concentration raised to 1.0 *M*; a small, but easily

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(4) E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).