metal atom is σ-bonded to the carbon atom in a position α to the "free" double bond. The metal atom, being very close to the free double bond, is attacked by it and a σ–π complex is formed. This complex may rearrange to a π-allylic complex. A π-allylic bonding is known to result in a downfield shift of the nmr chemical shift due to the proton on the central allylic carbon atom. Such a shift has not been observed in the nmr spectra of the intermediates isolated by us. It is thus more likely that the intermediate involves one π and one σ bond to the metal atom. The π bond to the metal weakens the metal–carbon σ bond and makes it susceptible to attack by hydrogen (or hydride ion) in a manner similar to the replacement of chloride ion in platinum hydride complex formation. Thus, a π metal–monoene–hydrido complex is obtained.

(v) Exchange of the coordinated monoene with "free" diene.

It should be pointed out that olefin exchange takes place at every stage of the over-all reaction. This is suggested by the fact that isomerized or partly hydrogenated olefins can be isolated at intermediate stages of the reactions. Thus, at one point during the hydrogenation of 1,5-cyclooctadiene, the reaction mixture consists of 1,5-, 1,4-, and 1,3-cyclooctadiene and cyclooctene.

Once the monoene is formed, it may undergo isomerization or double-bond migration to an equilibrium mixture of monoenes. Thus, the positions of the double bonds in the original polyolefins do not determine the position of the double bond in the monoene. 4-Vinylcyclohexene gave a mixture of two monoenes, the major component of which was ethylidenecyclohexane. 1,4,9-Decatriene gave a mixture of decenes. 1,7-Octadiene yielded a mixture of octenes of composition similar to the equilibrium mixture of octenes obtained from the isomerization of 1-octene and 4-octene under hydrogenation conditions.

That hydrogenation to the monoene occurs through coordination of the conjugated diene is reflected in the relative rates of hydrogenation of polyolefins of different steric arrangements. Thus, open-chain dienes such as 1,7-octadiene are hydrogenated much faster than cyclic dienes such as 1,5-cyclooctadiene. It is also reflected in the general observation that the rate of isomerization is much greater than the rate of hydrogenation. This is due to the fact that the isomerization reaction is less stereospecific than the hydrogenation reaction, mainly because a diene has to be conjugated before it can be hydrogenated by the catalyst.

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Activation Parameters for the Aquation of Acidopentaaquochromium(III) Complexes. The Nitratopentaaquochromium(III) Ion[1]

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Abstract: Reduction of aqueous acidic nitratopentaamminecobalt(III) by chromium(II) yields nitratopentaaquochromium(III), in addition to $(H_2O)_5CrNO^{2+}$ and other products; however, the nitratochromium(III) complex is best made by fusion of chromium(III) nitrate nonahydrate at 100°, followed by ion-exchange chromatography. The aquation of nitratopentaaquochromium(III) in aqueous perchloric acid–lithium perchlorate media of ionic strength 1.00 M has been studied. The rate law is of the form $-d[CrNO_3^{2+}]/dt = \{k_0 + k_{-1}[H^+]^{-1}\}[CrNO_3^{2+}]$ over the acidity range 0.08 to 1.0 M and a temperature range 0 to 43°. The corresponding activation parameters are: $\Delta H_0^* = 21.6 \pm 0.1$ kcal mole^{-1}, $\Delta S_0^* = -5.1 \pm 0.2$ eu, $\Delta H_{-1}^* = 24.9 \pm 1.5$ kcal mole^{-1}, $\Delta S_{-1}^* = -2.2 \pm 4.9$ eu. The contribution of the k_{-1} term was very small under the experimental conditions. The value of ΔS_0^* for the aquation of this and other species of the type $(H_2O)_5CrX^{2+}$, where X^- is nonbasic, can be linearly correlated with the entropy of the free aqueous ion X^- if this is corrected for entropy of rotation of X^-.

It has been suggested[2] that, in the aquation of the cations $(H_2O)_5CrX^{2+}$, the entropy ΔS_0^* of activation for the acid-independent reaction pathway may be linearly related to the entropies, $S°$, of the corresponding free aqueous ions X^-, at least when these anions are not basic (in the Brønsted sense) in water. This suggestion was not without precedent[3] and appears to be applicable to the halopentaaquochromium(III) series.[2]

Such a correlation, if generally valid, would be a double-edged sword. On the one hand, it would permit prediction of entropies of activation for reactions

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[1] This work was supported in part by the National Research Council, Ottawa, and by The University of Calgary General Research Fund.

[2] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

[3] A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 25 (1951).

of species which have yet to be studied, if a uniformity of reaction mechanism is assumed within a given series of chemical species. Conversely, it could be used as a criterion of reaction mechanism, since the marked failure of some particular member of a given series to correlate with the others in the light of the above hypothesis might well indicate that a member reacts *via* a mechanism different from that of its congeners. Thus, it was argued[2] that the acid-independent aquation of fluoropentaaquochromium(III) proceeds predominantly through a transition state in which molecular HF separates from an $(H_2O)_4CrOH^{2+}$ residue, whereas the acid-independent aquation of the other halopentaaquochromium(III) species probably involves the separation of halide ion from a $Cr(H_2O)_5{}^{3+}$ residue. Since the former mechanism involves much less electrostriction of solvent than does the latter, we can account for the fact that the observed entropy of activation for the fluoro complex exceeded that predicted by applying our postulated entropy correlation to its congeners by some 12 eu. This conclusion is reinforced by the observation that the fluoro complex also exhibits an aquation path with a positive dependence on hydrogen ion concentration, whereas no such pathway was observed for the other halo complex. This is not surprising, since fluoride ion is markedly basic in water, while the other halide ions are not.

The object of the present study was to attempt to strengthen this hypothesis by extending the correlation to include the analogous pentaaquochromium(III) complexes of nonbasic polyatomic ions. Comparatively few such anions exist which also give aquochromium(III) complexes. The thiocyanato complex has been studied[4] and it has been found that it can be made to fit the correlation excellently by correcting for the rotational entropy of the free thiocyanate ion. We therefore sought to substantiate this procedure by investigating the nitratopentaaquochromium(III) ion; this species has not been reported to date, although Taube[5] undoubtedly produced it by reduction of nitratopentaamminecobalt(III) with chromium(II), but apparently mistook it for hexaaquochromium(III), which it resembles visually. We have therefore repeated Taube's experiment and have also devised a more convenient procedure for making the nitratopentaaquochromium(III) ion.

Experimental Section

Distilled deionized water was used for all solutions. Baker Analyzed perchloric acid was used without further purification. Acids were standardized against analytical reagent grade mercuric oxide, freshly dissolved in excess aqueous potassium iodide. The chromium contents of the solutions were determined by oxidizing aliquots with alkaline hydrogen peroxide solution and measuring the absorbance of the resulting chromate ion at 372 mμ (ε 4842). All spectrophotometric measurements were made with a Cary Model 15 spectrophotometer.

Preparation of Nitratopentaaquochromium(III) Ion. Typically, a stoppered tube containing 8.11 g (20.12 mmoles) of chromium(III) nitrate nonahydrate (British Drug Houses) was immersed in boiling water (97.8°) for 15.0 min; the purple crystals melted[6] within 1 min to a green liquid. A rough estimation of the volume of the melt showed it to be, in effect, a 4.0 *F* solution of chromium(III) nitrate. The melt was dissolved quickly in ice-cold 0.01 *M* perchloric acid (1000 ml), and the solution was promptly passed through a 10-cm column of Dowex 50W-X8 cation-exchange resin (H^+ form, 50–100 mesh) contained in a tube of 2.5-cm internal diameter which was maintained at 0° by circulating ice water through a jacket. All the chromium was absorbed on the resin. Elution with 0.2 *M* perchloric acid (200 ml) yielded a nearly colorless solution containing only 5.88 × 10^{-4} mmole of chromium. Elution with 1.0 *M* perchloric acid yielded some 500 ml of a gray-blue solution containing 11.56 mmoles of nitratopentaaquochromium(III) ion. A center cut of this, for analytical, spectroscopic, and kinetic studies, was stored at 0° (at which $t_{1/2}$ for aquation is 81 hr). Excellent separation was obtained between this and the succeeding purple-blue band, which could be eluted freely only after increasing the eluent acid concentration to 3.0 *M;* the purple-blue species was identified spectroscopically as hexaaquochromium(III) ion (5.00 mmoles). A green band (hydrolytic polymers of chromium(III)[7]) remained on the column.

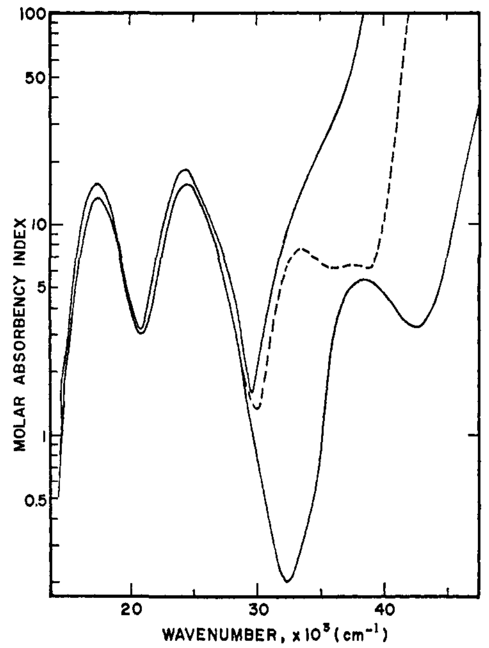

Figure 1. Visible–ultraviolet spectra of (upper solid line) nitratopentaaquochromium(III), (lower solid line) hexaaquochromium(III), and (broken line) aquation products of nitratopentaaquochromium (III).

The ultraviolet spectrum of the freshly prepared nitratopentaaquochromium(III) solution in 1.0 *M* perchloric acid showed clearly that it was *not* hexaaquochromium(III), despite the close similarity in the visible region (Figure 1). The molar absorbancy indices are given here in parentheses, following the wavelength of the corresponding maxima in mμ: 669 (shoulder, 2.71), 577 (15.84), 409 (18.57), 205 (10,600.).

Several such preparations were carried out, using a different brand of chromium nitrate (Baker and Adamson) and different fusion times (5 to 30 min); the spectra, analyses, and aquation kinetics of the nitratopentaaquochromium(III) product were always the same, and the yield was always 57.5 ± 1.0%.

An attempt to isolate a solid sulfate salt of nitratopentaaquochromium(III), by the manner of Moore and Basolo,[8] was unsuccessful.

Analysis of Nitratopentaaquochromium(III) Ion. The chromium content of aliquots was determined as above. The presence of one nitrato ligand per chromium atom was demonstrated using the small absorption maximum of aqueous nitrate ion at 300 mμ. Typically, a sample of $(H_2O)_5CrNO_3{}^{2+}$ in 1.0 *M* perchloric acid was held at 65° overnight to aquate it, and then its spectrum was

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(4) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

(5) H. Taube, *J. Am. Chem. Soc.*, 77, 4481 (1955).

(6) The melting point of the B.D.H. sample was 66.5–67.2°; a drier Baker and Adamson sample melted at 67.3–67.5°; compare 66–66.5° reported by J. R. Partington and S. K. Tweedy, *J. Chem. Soc.*, 1142 (1926).

(7) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

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

Table I. Spectrum of Aquated Nitratopentaaquochromium(III) near 300 mμ

Wavelength, mμ	320	315	310	305	300	295	290	285	280
ϵ of aquated sample (per Cr)	3.33	4.84	6.30	7.21	7.46	7.20	6.67	6.21	5.99
ϵ of $(H_2O)_6Cr^{3+}$ (1 M H^+)	0.30	0.23	0.18	0.21	0.27	0.47	0.79	1.42	2.29
Difference	3.03	4.61	6.12	7.00	7.19	6.73	5.88	4.79	3.70
ϵ of NO_3^-	3.06	4.67	6.08	6.96	7.12	6.66	5.80	4.75	3.74
NO_3^- per Cr^{3+}	0.990	0.987	1.006	1.006	1.010	1.010	1.014	1.008	0.989

recorded carefully (Figure 1, broken line), especially over the region 280–320 mμ. The observed molar absorbancy indices (ϵ) were in excellent agreement with those calculated for an equimolar mixture of hexaaquochromium(III) and nitrate ions in 1.0 M perchloric acid. The nitrate:chromium ratios in the example given in Table I give an average of 1.00_2, and hence the blue-gray species is $(H_2O)_n$-$CrNO_3^{2+}$.

The analysis was verified independently by treating aliquots of the solution with excess sodium hydroxide and Devarda's alloy, thereby reducing the nitrate to ammonia which was distilled into a small excess of sulfuric acid. The distillate was then made alkaline and the ammonia was redistilled into an aliquot of standard acid and estimated by back-titration with standard sodium hydroxide solution against methyl red indicator. The sample used in the above spectroscopic analysis gave nitrate:chromium ratios of 0.991 and 0.982 by this Devarda reduction method.

Nitratopentaamminecobalt(III) Perchlorate. Nitratopentaamminecobalt(III) nitrate was made by the method of Basolo and Murmann,[9] but attempts to convert this to the perchlorate salt according to Ephraim[10] gave an impure product. A good specimen was obtained by dissolving 2.0 g of the nitrate in 500 ml of water at room temperature, precipitating the crude perchlorate at once with an ice-cold mixture of 200 ml of 36% perchloric acid and 1000 ml of ethanol, filtering, and then reprecipitating the product from 200 ml of water with ice-cold 48% perchloric acid (150 ml) and ethanol (350 ml). The red precipitate was washed with ethanol and dry ether and dried under vacuum (yield 0.86 g). *Anal.*[11] Calcd for $CoN_6O_{11}H_{15}Cl_2$: N, 20.75; H, 3.71. Found: N, 20.65; H, 3.78.

Reaction of Nitratopentaamminecobalt(III) with Chromium(II). An aliquot (4.0 ml) of a solution of chromium(II) perchlorate (0.25 M) in perchloric acid (0.50 M), made according to Crabtree,[12] was added to a solution of nitratopentaamminecobalt(III) perchlorate (0.398 g, 0.982 mmole) in 0.1 M perchloric acid (100 ml) at 23°, under an atmosphere of carbon dioxide. The bright red color of the solution rapidly dulled; after 1 min, no further change was evident, and air was blown through the solution to remove any unreacted chromium(II) (no change was seen). The solution was ion-exchanged on a column of 10 ml of Dowex 50W-X8 (50–100 mesh) contained in a 50-ml buret fitted with a jacket through which ice water circulated. After washing the column with 0.1 M perchloric acid, a nonuniform olive-green fraction was eluted with 1.0 M acid; this was followed by a pale red fraction (cobalt(II)). Elution with 3.0 M perchloric acid revealed a small but distinct purple-blue fraction ($Cr(H_2O)_6^{3+}$), which was followed by an extensive rose-red band (unchanged $(NH_3)_5CoNO_3^{2+}$) and then a minor brick-red band (probably $(NH_3)_5CoOH_2^{3+}$); a strong green band of $(H_2O)_4Cr(OH)_2Cr(OH_2)_4^{4+}$ remained at the top of the resin.

The olive-green fraction was reabsorbed on a fresh column (as above, but with 13 ml of resin) and reeluted with 1.0 M perchloric acid to separate its components. A gray-blue species came off first, and this was shown to be nitratopentaaquochromium(III), firstly by its ultraviolet and visible spectrum, and secondly by its aquation to give equimolar amounts of nitrate and hexaaquochromium(III) ions (identified and estimated spectroscopically as described above). The yield of nitratopentaaquochromium(III) was 0.333 mmole, thus accounting for 33% of the chromium(II). The remaining rum-colored absorbate was evidently $(H_2O)_5CrNO^{2+}$ (see below) together with some cobalt(II); these could not usefully be separated further.

Reaction of Nitrate Ion with Chromium(II). A solution of dry sodium nitrate (0.219 g, 2.58 mmoles) in 175 ml of water was deoxygenated with carbon dioxide and treated, at 16° while stirring vigorously, with 5.0 ml of a solution 0.25 M in chromium(II) perchlorate and 0.50 M in perchloric acid. The mixture remained sky blue for some 3 sec before steadily becoming greenish brown. After 2 min, no further color change was apparent, and, after passing air through the solution to remove any surviving chromium(II), the reaction mixture was ion-exchanged as described in the preceding section. Elution with 1.0 M perchloric acid yielded a rum-colored species, identified by ultraviolet-visible spectrum[13] as $(H_2O)_5CrNO^{2+}$ (maxima at 562, 448, and 325 mμ, with molar absorbancy indices of 26.6, 108.5, and 83.1, respectively) in a yield of 0.234 mmole (18.7% of total chromium). Elution with 3.0 M perchloric acid yielded hexaaquochromium(III) (0.286 mmole, 22.8% of total chromium), and a green band of $(H_2O)_4Cr(OH)_2$-$Cr(OH_2)_4^{4+}$ remained on the resin (by difference, 58.5% of total chromium). Note that no nitratopentaaquochromium(III) ion was observed.

Reaction of Nitratopentaaquochromium(III) with Chromium(II). In this qualitative experiment, a freshly prepared solution of nitratopentaaquochromium(III) (0.012 M, 25 ml) in 1.0 M perchloric acid was treated, under 1 atm of carbon dioxide, with 1.2 ml of a solution of chromium(II) perchlorate (0.25 M) in perchloric acid (0.5 M). The solution turned green within about 1 sec of the time of mixing, and the reaction appeared to be complete within 1 min. Ion-exchange separation and spectroscopic examination of the reaction products showed that the solution contained $(H_2O)_5CrNO^{2+}$, $Cr(H_2O)_6^{3+}$, $(H_2O)_4Cr(OH)_2Cr(OH_2)_4^{4+}$, and some unchanged $(H_2O)_5CrNO_3^{2+}$.

Kinetics of Aquation of Nitratopentaaquochromium(III). Solutions of nitratopentaaquochromium(III) were prepared from chromium(III) nitrate as described above. Lithium perchlorate trihydrate was made from Baker Analyzed lithium carbonate and perchloric acid and was recrystallized from water until it contained no detectable free acid or base. The initial concentrations of the nitrato complex were determined spectrophotometrically as chromate; the free acid present was determined by washing aquated aliquots through a Dowex 50W-X8 (H^+ form) column, titrating the issuing acid with standard alkali, and correcting for the acid released on absorption of the chromium(III) ion. The solutions for kinetics were made up by diluting suitably chosen quantities of nitratochromium(III) solution, and standard perchloric acid and lithium perchlorate as necessary, such that the ionic strength was 1.00 M.

The progress of the reaction was followed by measuring the decrease with time of the light absorption at 260 mμ, at which wavelength the molar absorbancy index of nitratopentaaquochromium(III) is 100.2, as compared with 6.5 for the reaction products. The sampling procedure differed in detail at different reaction temperatures.

(a) For runs at 0°, suitable volumes of reaction mixture were sealed into Pyrex test tubes and immersed in ice–water in a large, well-insulated dewar vessel. The slurry was stirred occasionally, and periodically samples were removed and transferred to optical cells for immediate spectrophotometric analysis.

(b) For runs at 16.9°, the sample, in a spectrophotometer cell, was enclosed in a thin plastic bag which was then lowered into a thermostat bath maintained within 0.01° of the stated temperature. The cell was removed quickly for spectrophotometry as required.

(c) For the runs at 25° and above, the reaction was followed *in situ*, in the spectrophotometer cell compartment, with the cell in a

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(9) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 174 (1958).

(10) F. Ephraim, *Ber.*, **56**, 1530 (1923).

(11) The author thanks Mrs. S. J. Bagley for these microanalyses.

(12) J. M. Crabtree, *J. Chem. Soc.*, 4647 (1964). The author thanks Mr. D. McKerron and Union Carbide Canada Ltd. for a gift of high-purity chromium metal flake.

(13) M. Ardon and J. I. Herman, *J. Chem. Soc.*, 507 (1962).

jacket (Cary 1540750) which was thermostated with water from a Colora circulating bath. The temperature of the actual solution in the cell was measured with a modified Atkins Technical thermistor thermometer assembly; this (and the thermometers used in parts a and b) was calibrated against a platinum resistance thermometer, which in turn was standardized against a water triple-point cell.

In all cases, the samples were protected from light during the kinetic experiments.

Results

Calculation of Rate Constants and Activation Parameters. The reactions were found, by graphical analysis, to be strictly first order in nitratopentaaquochromium(III) within a given run, over the first 90% of reaction at least.

$$kt = \ln \{(A_0 - A_\infty)/(A_t - A_\infty)\}$$

where A_t is the optical absorbance measured at time t, and k is the first-order rate coefficient. Careful examination of the first 15% of reaction in a typical experiment showed that the over-all rate coefficient was completely representative of these initial stages, within the experimental error; accordingly, since the products of reaction after about 10 half-periods were demonstrably hexaaquochromium(III) and nitrate ions, the process observed must be a single-step aquation throughout. It therefore seems reasonable to assume that the species under examination was $(H_2O)_5CrNO_3^{2+}$, with a monodentate nitrato ligand, although the above observations are also consistent with the existence of a chelated species, $(H_2O)_4CrNO_3^{2+}$, for which the opening of the chelate ring is very rapid compared with the subsequent aquation of the monodentate nitrato ligand.

The rate coefficients were recalculated using a nonlinear least-squares program on an IBM 360 computer;[14] in cases in which sufficient (more than 12) data points were available, it became possible to treat the end-point reading (A_∞) as a free parameter to be calculated along with the rate coefficient k, and thus eliminate the dependence of the accuracy of the entire experiment upon the accuracy of the end-point reading. In general, however, the calculated value of A_∞ agreed excellently with the experimental value. In one experiment, the initial reading (A_0), being inaccurate, was also treated as a free parameter, with a resulting improvement in standard deviation. The data are summarized in Table II; an entry in the "parameters fixed" column indicates that the experimental value of that quantity was used in computation. The limits of error cited are standard deviations. The values of k recalculated from the derived activation parameters (see below) are listed under "10^6k, calcd."

Graphical analysis of the hydrogen-ion dependence of the rate coefficient indicated a relationship of the form

$$k = k_0 + k_{-1}[H^+]^{-1}$$

However, the contribution of the acid-dependent pathway characterized by k_{-1} was never more than 16%, in the conditions of these experiments, and usually much less; indeed, at 0°, the hydrogen ion dependence of k was almost negligible, owing to the relatively high enthalpy of activation associated with the k_{-1} path. Restrictions imposed by the experimental method prevented extension of the lower limit of the acidity beyond 0.08 M.

Table II. First-Order Rate Coefficients for the Aquation of Nitratopentaaquochromium(III) Ion at Ionic Strength 1.00 M

Temp, °C	$[H^+]$, M	[Cr species], mM	10^6k, sec^{-1}	Parameters fixed	10^6k, calcd, sec^{-1}
43.09	0.980	6.76	621 ± 2	A_0	627
34.60	0.172	9.86	270 ± 3	None	259
34.92	0.963	9.86	240 ± 1	A_0	245
34.79	0.086	4.93	284 ± 1	A_0, A_∞	293
34.33	0.370	9.86	238 ± 1	A_0, A_∞	236
34.35	0.568	9.86	232 ± 1	A_0, A_∞	232
25.02	0.935	27.1	72.6 ± 0.5	A_0	73.3
25.04	0.968	8.62	73.5 ± 0.2	A_0	73.5
25.03	0.178	8.62	79.3 ± 0.1	A_0	79.2
25.10	0.375	8.62	76.0 ± 0.2	A_0	76.1
25.10	0.089	4.31	84.8 ± 0.9	A_0	87.0
16.89	0.178	8.62	27.3 ± 0.1	A_0	27.3
16.89	0.089	4.31	28.8 ± 0.2	A_0	29.5
16.89	0.968	8.62	25.9 ± 0.1	A_0, A_∞	25.6
16.89	0.375	8.62	26.1 ± 0.1	A_0, A_∞	26.2
0.00	0.178	8.62	2.44 ± 0.01	A_0, A_∞	2.48
0.00	0.968	8.62	2.38 ± 0.02	A_0, A_∞	2.37
0.00	0.573	8.62	2.41 ± 0.01	A_0, A_∞	2.39
0.00	0.375	8.62	2.43 ± 0.01	A_0, A_∞	2.40

A numerical analysis of the rate coefficients in terms of activation parameters, using the Los Alamos least-squares computer program and weighting each data point as the reciprocal of the square of its standard deviation as given in Table II, gave excellent parameters (ΔH_0^*, ΔS_0^*) for the acid-independent path, but only very crude ones (ΔH_{-1}^*, ΔS_{-1}^*) for the path with inverse hydrogen ion concentration dependence. This is because the latter pathway makes only a very small contribution to the observed values of k in these experiments, and so the latter data are best regarded merely as "corrections" to be applied for the small dependence of k upon hydrogen ion concentration. The activation parameters are summarized in Table III; the probable limits of error ascribed by the computer are standard deviations. The rate coefficients are represented by these parameters to within 1.2%, on the average. The remarkably narrow standard deviation for ΔH_0^* indicates that the implicit assumption, that ΔC_p^* is negligible, is justified in this case.

Table III. Parameters Associated with the Rate Law $-d[CrNO_3^{2+}]/dt = \{k_0 + k_{-1}[H^+]^{-1}\}[CrNO_3^{2+}]$ at Ionic Strength 1.00 M

	k_0	k_{-1}
ΔH^*, kcal mole^{-1}	21.6 ± 0.1	24.9 ± 1.5
ΔS^*, cal deg^{-1} mole^{-1}	−5.1 ± 0.2	−2.2 ± 4.9

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[14] The author thanks Drs. R. H. Moore and T. W. Newton for helpful discussions and for supplying the program (described in Report LA-2367, Los Alamos Scientific Laboratory), and Mr. R. Nicol for adapting it for use with the IBM 360 system of The University of Calgary.

Discussion

The chemical analyses, the ease of elution from Dowex 50W-X8 resin with 1.0 *M* $HClO_4$, the spectrum of the aquated product, and the strict pseudo-first-order behavior of the rate of aquation over the entire reaction all indicate that the gray-blue species isolated from fused chromium(III) nitrate nonahydrate is nitratopentaaquochromium(III).[15] As can be seen from Figure 1, its spectrum in the visible region is closely similar to that of hexaaquochromium(III), which fact undoubtedly explains Taube's apparent failure[5] to observe the nitratochromium(III) complex among the products of reduction of aqueous acidic nitratopentaamminecobalt(III) by an equimolar amount of chromium(II).

On repeating Taube's experiment with approximately similar conditions, we find that some 33% of the chromium(II) does, in fact, reduce the cobalt(III) center to cobalt(II) through the nitrato ligand as a bridge, thus forming nitratopentaaquochromium(III).

$$(H_2O)_6Cr^{2+} + NO_3Co(NH_3)_5{}^{2+} \longrightarrow$$

$$\{(H_2O)_5Cr\cdots NO_3\cdots Co(NH_3)_5\}^{4+} + H_2O \xrightarrow{5H_3O^+}$$

$$(H_2O)_5CrNO_3{}^{2+} + Co(H_2O)_6{}^{2+} + 5NH_4{}^+$$

The remaining chromium(II) was found to have been oxidized to $(H_2O)_4Cr(OH)_2Cr(OH_2)_4{}^{4+}$, $(H_2O)_5CrNO^{2+}$, and $Cr(H_2O)_6{}^{3+}$, presumably through reaction with the nitrate group itself. In a separate experiment, the partial reduction of free nitrate ion in acidic solution by an equimolar amount of chromium(II) was shown to yield $(H_2O)_4Cr(OH)_2Cr(OH_2)_4{}^{4+}$, $Cr(H_2O)_6{}^{3+}$, and $(H_2O)_5CrNO^{2+}$ in the ratios 1.00 to 0.78 to 0.64; these data are consistent with the following stepwise scheme (compare Ardon and Herman[13]).

$$Cr^{2+} + NO_3^- + 2H^+ \longrightarrow Cr(IV) + NO_2^- + H_2O$$

$$Cr(IV) + Cr^{2+} \xrightarrow{H_2O} (H_2O)_4Cr(OH)_2Cr(OH_2)_4{}^{4+}$$

$$Cr^{2+} + NO_2^- + 2H^+ \xrightarrow{H_2O} Cr(H_2O)_6{}^{3+} + NO + H_2O$$

$$Cr^{2+} + NO \longrightarrow (H_2O)_5CrNO^{2+}$$

Thus, we may conclude that, in the reduction of nitratopentaamminecobalt(III) by chromium(II), the remaining 67% of the chromium(II) reduces a nitrato ligand instead of a cobalt(III) center. Since neither the cobalt(III) nor the chromium(III) nitrato complex aquates sufficiently in the short time required for the reduction reaction to go to completion, we must infer that it is a *bound* nitrato group that is reduced. It is not known whether the reduction of the nitrato ligands takes place while they are still bound to cobalt(III) or whether some or all are reduced while bound to chromium(III) following the reduction of cobalt(III) to cobalt(II) in the nitrato-bridged electron-transfer reaction described above. It was found that the nitrato ligand in a fresh preparation of nitratopentaaquochromium(III) was reduced by chromium(II) at least as rapidly as is free nitrate ion; however, it was not possible to determine whether bound nitrate is reduced more rapidly in nitratopentaamminecobalt(III) than in nitratopentaaquochromium(III). The results of Fraser[16] on the reduction of $(NH_3)_5CoNO_2{}^{2+}$ isomers by chromium(II) suggest that reduction of the nitrato ligand in nitratopentaamminecobalt(III) could well be preceded by reduction of the cobalt(III) center.

The rate of aquation of nitratopentaaquochromium(III) is only slightly affected by the hydrogen ion concentration over the acidity and temperature ranges studied; however, it is clear that, although there is a small contribution to the over-all reaction rate from the familiar "conjugate-base" mechanism involving the species $(H_2O)_4Cr(OH)NO_3{}^+$, there is no detectable contribution from pathways involving protonation of the nitrato complex in the transition state. This was anticipated since the nitrate ion is not basic in water. Thus, the aquation behavior of nitratopentaaquochromium(III) apparently resembles that of its chloro, bromo, iodo, and thiocyanato analogs, rather than the fluoro and azido congeners.[2,14,17]

It may therefore be expected that, if our postulated linear relationship between the entropy of activation for the acid-independent aquation path of $(H_2O)_5CrX^{2+}$ and the entropy of the free aqueous ion X^- is valid, the species for which X is NO_3 and NCS should obey the relationship defined by the halo complexes, if we can somehow correct for the rotational and vibrational entropies which the polyatomic anions possess in the free aqueous state, but which must be reduced or nullified in the ground-state complexes or in the transition states during aquation. It can readily be calculated[18] that the total vibrational entropy of the gaseous thiocyanate ion (for example) is of the order of a mere 1 eu, and that the difference in internal vibrational entropies between the free aqueous and the complexed thiocyanate ions will be insignificant (about 0.1 eu). The question of the vibrational entropy of a polyatomic ligand may therefore be ignored. However, the entropy of rotation (S_{rot}) of the free thiocyanate ion in the gaseous state at 25° will be found[18] to be quite large (15.8 eu, based on N–C and C–S bond lengths[19] of 1.25 and 1.59 A, respectively); the same is true of azide (12.81 eu, using N–N distances[20] of 1.15 A) and of nitrate (19.40 eu, based on N–O distances[21] of 1.22 A). It is not possible at present to determine the extent to which these rotational entropies will be decreased on transferring the gaseous ions to aqueous solution; however, in the absence of any strong specific interactions (such as hydrogen bonding) with the solvent or solutes, the complete randomness of orientation of the aqueous ions with respect to external points of reference would be retained in the condensed phase, and so it is not unreason-

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(15) It is a little surprising that, while the yield of $(H_2O)_5CrNO_3{}^{2+}$ was as much as 57.5%, no more than 0.003% of the chromium appeared as species of charge 1+, *i.e.*, as $(H_2O)_4Cr(NO_3)_2{}^+$. This is an indication of the thermodynamic instability of nitratochromium(III) complexes, even under the forcing conditions of these experiments.

(16) R. T. M. Fraser, *J. Chem. Soc.*, 3641 (1965).

(17) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 3, 234 (1964).

(18) G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, pp 424–437.

(19) Z. V. Zvonkova and G. S. Zhdanov, *Zh. Fiz. Khim.*, 23, 1495 (1949).

(20) L. K. Frevel, *J. Am. Chem. Soc.*, 58, 779 (1936).

(21) R. L. Sass, R. Vidale, and J. Donohue, *Acta Cryst.*, 19, 567 (1957).

Table IV. Activation and Other Parameters Relating to the Acid-Independent Aquation Path of Acidopentaaquochromium(III) Ions at Ionic Strength 1.00 M

X in $(H_2O)_5CrX^{2+}$	ΔS_0^*, eu	$S°$ of X^-(aq), eu[f]	S_{rot} of X^-, eu[e]	$S°_{oor}$, eu	ΔH_0^*, kcal mole^{-1}	E_I, cm^{-1}
F	-3.9 ± 1.8[a]	-3.6[g]	0	-3.6	28.7	16,810
Cl	-7.1 ± 0.5[a]	13.2	0	13.2	24.3	16,420
Br	-3.5 ± 0.9[b]	19.3	0	19.3	23.8	16,000
I	-0.2 ± 0.9[a]	26.1	0	26.1	23.0	15,390
NCS	-3.5[c]	36	15.8	20.2	27.5	17,390
N_3	$+16.2$[d]	25.4[h]	12.8	12.6	32.4	17,090
NO_3	-5.1 ± 0.2[e]	35.0	19.4	15.6	21.6	17,330

[a] Reference 2. [b] F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964). [c] Reference 4. [d] Reference 17. [e] This work. [f] Except as indicated from V. P. Vasil'ev, E. K. Zolotarev, A. F. Kapustinskii, K. P. Mishchenko, E. A. Podgornaya, and K. B. Yatsimirskii, *Zh. Fiz. Khim.*, **34**, 1763 (1960). [g] C. C. Stephenson, H. P. Hopkins, and C. A. Wulff, *J. Phys. Chem.*, **68**, 1427 (1964). [h] L. A. D'Orazio and R. H. Wood, *ibid.*, **67**, 1435 (1963).

able to equate approximately the rotational entropies of the free aqueous ions with those calculated for the gaseous state. The objection may quite fairly be raised that the hydrating water molecules should restrict the rotation of a polyatomic ion in solution; however, in accordance with Newtonian mechanics, these water molecules themselves would necessarily tend to follow the tumbling of the ion (although not freely, since some interaction between the hydrating molecules and the quasi-crystalline bulk solvent structure would persist). The resulting increase in the apparent moment of inertia (and therefore in the entropy of rotation) of the ion would probably compensate approximately for any loss of rotational entropy of the free ion due to hydrational restrictions.

It is equally reasonable to assume that little or no internal rotational freedom exists for the bound anions X in the complexes $(H_2O)_5CrX^{2+}$; thus, for X = NO_3, it is probable that the Cr–O–NO_2 bond angle is about 105° (by analogy with FNO_3 and CH_3NO_3[22]), and a scale drawing shows at once that there must be acute steric hindrance to rotation of the nitrato ligand about either the Cr–O or the O–N axes. If, however, the Cr–O–NO_2 angle is 180°, some rotation of the ligand about this axis is possible; this could contribute an entropy of internal rotation of up to 6.8 eu. In the case of bound thiocyanate or azide, the chromium center could be coaxial with the ligand, in which case there can be no significant internal rotation of the ligand; alternatively, if the Cr–N–CS and Cr–N–NN angles are less than 180°, steric hindrance would prevent free rotation.

We may therefore reasonably conclude that the entropies, $S°$, of the aqueous polyatomic anions NO_3^-, NCS^-, and N_3^- can be "corrected" for rotation by subtracting the entropies of rotation calculated for the gaseous phase, thus giving a quantity $S°_{cor}$ which can be used to treat polyatomic ligands along with monatomic ligands in our proposed correlation. The appropriate quantities are listed in Table IV.

A plot of the activation entropies ΔS_0^* against $S°_{cor}$ is shown in Figure 2. The straight line drawn is that defined by the chloro, bromo, and iodo complexes, since no assumptions concerning rotational entropies were necessary for these species. The line predicts values of ΔS_0^* (eu) of -3.1 for the thiocyanato, -5.6 for the nitrato, -16.0 for the fluoro, and -7.3 for the azido complex. The measured values of ΔS_0^* (eu) for the nitrato (-5.1) and thiocyanato (-3.5) complexes agree excellently with these predictions. The small discrepancy in the case of the nitrato complex is scarcely meaningful, but could be accounted for by invoking either a small amount of internal rotation or libration of the bound nitrato ligand, or else (more probably) some small restriction of the rotation of the aqueous, as compared to the gaseous, nitrate ion. It seems, then, that the proposed correlation is valid for $(H_2O)_5CrX^{2+}$ in which X is Cl, Br, I, NCS, and NO_3, none of which complexes shows any hydrogen ion catalysis of aquation, and which presumably aquate to liberate X^- and $Cr(H_2O)_5^{3+}$ initially. The existence of such a correlation suggests that separation of X^- from $Cr(H_2O)_5^{3+}$ is well advanced in the transition state, so that solvation of the departing ligand becomes a predominant influence. The slope of the

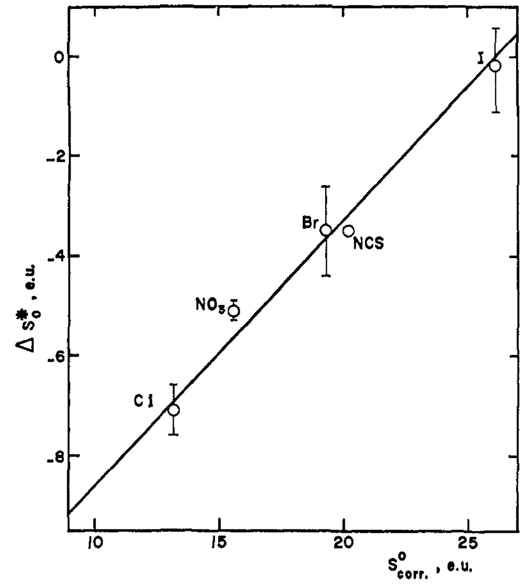

Figure 2. Entropy of activation for the acid-independent aquation of $(H_2O)_5CrX^{2+}$ *vs.* entropy of the aqueous ion X^- (corrected for rotation of X^-).

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(22) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).

representative straight line is 0.53, which suggests that solvation of the departing anion X^- is more than half complete in the transition state.

The failure of the azido ($\Delta S_0^* = +16.2$ eu)[17] and fluoro ($\Delta S_0^* = -3.9$ eu)[2] complexes to agree with the predictions is striking; the observed entropies of activation are too large by 25 and 12 eu, respectively. Since these complexes also exhibit major aquation paths involving protonated complexes $(H_2O)_5CrXH^{3+}$ from which HX presumably separates as such in the transition state, it can be reasonably inferred that the separating entities are HN_3 and HF even in the acid-independent aquation path, leaving $(H_2O)_4CrOH^{2+}$ behind. Thus, no formal charges would be generated in the transition states, and so electrostriction of solvent will be less (and ΔS_0^* correspondingly greater) than expected from comparison with the other acidopentaaquochromium(III) complexes studied, in which X^- evidently separates from $Cr(H_2O)_5{}^{3+}$ in the transition state with a marked increase in electrostriction of solvent.

Enthalpy of Activation. Basolo and Pearson[23] have suggested that enthalpies of activation for substitution reactions in octahedral complexes may be simply related to the loss of crystal field stabilization energy incurred in forming the transition state. Langford and Gray[24] have refined this concept in terms of molecular orbital theory but suggest that free energies of activation may be expected to follow trends of electronic effects more closely than do enthalpies of activation. Indeed, a good linear correlation was obtained[24] between the logarithms of the rate coefficients (measures of free energy of activation) for the aquation of acidopentaamminecobalt(III) complexes and the energies E_I of the first ligand-field spectral bands (measures of crystal field stabilization energy, or its equivalent in molecular orbital theory).

However, examination of the data for the aquation of acidopentaaquochromium(III) complexes (Table IV) will show that neither the free energies nor the enthalpies of activation can be simply related to E_I and hence to trends in internal electronic effects within the complexes. In particular, it will be noted that E_I is almost exactly the same for nitratopentaaquochromium(III) as for the thiocyanato complex, yet the enthalpies of activation differ by as much as 5.9 kcal mole^{-1} and the free energies of activation (25°) by 5.4 kcal mole^{-1}. It is probable that the enthalpy contributed by the hydration of the departing anion X^- must also be taken into consideration when attempting to rationalize the observed ΔH_0^* values. A relationship may exist of the type

$$\Delta H_0^* + \alpha(\Delta H_0) = \beta E_I + \gamma$$

where ΔH_0 is the standard enthalpy of the free aqueous ion X^-, and α, β, and γ are constants for a given reaction series, but clearly there are too many unknown parameters here to permit testing with the systems under consideration.

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[23] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reaction ," John Wiley and Sons, Inc., New York, N. Y., 1958, p 108 ff.

[24] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 60-65.