reactor, 0.3628 g, corresponded to a composition of $1.94XeF_6 \cdot PF_5$. The substance in the reactor was then removed by pumping at 0°. The complex could be pumped away at that temperature at a rate of about 10 mg/min in the system employed. Analysis of the sublimate for Xe at two random intervals indicated that XeF_6 and PF_5 were being lost close to a 2:1 molar ratio (calcd: Xe, 42.7; found: Xe, 43.0, 41.0).

In a typical experiment involving excess XeF_6, 0.3255 g (1.32 mmoles) of XeF_6 was contacted with 0.0653 g (0.518 mmole) of PF_5 (molar ratio, 2.54:1) for 24 hr at 22° and 3 hr at 0°. The mixture was then pumped at 0°. Pumping for 0.5 min produced a weight loss of 57.4 mg. The analysis for Xe (found: 49.4) corresponded to a loss of 53.0 mg of XeF_6 and 4.4 mg of PF_5. Pumping for another minute resulted in a further weight loss of 40.4 mg. The analysis for Xe (found: 48.8) corresponded to a loss of 36.8 mg of XeF_6 and 3.6 mg of PF_5. The XeF_6 to PF_5 molar ratio of the material remaining in the reactor at this point was 2.08:1. The pumping was then continued, but additional weight was lost at a slower average rate (about 11 mg/min). Analysis of the sublimate for Xe at three random intervals indicated that the rest of the material was pumped away with a molar ratio of XeF_6 to PF_5 close to 2.0 (found: Xe, 43.9, 43.3, 42.0).

Properties of $2XeF_6 \cdot PF_5$.—The dissociation pressure of the complex was measured using an apparatus which consisted of a glass manifold and a prefluorinated copper manifold, each having a volume of about 30 cm³. The two manifolds were connected and could be closed off from each other by means of a metal valve. The glass manifold was equipped with a mercury manometer.

With the valve separating the two manifolds open, the reaction vessel containing the complex was attached to the metal manifold and both manifolds were evacuated. The valve connecting the two manifolds was then closed and the valve of the reaction vessel was opened. The glass manifold was filled with dry nitrogen to a pressure estimated to be equal to the dissociation pressure of $2XeF_6 \cdot PF_5$ at the temperature in question. After equilibrium in the metal portion of the system had been reached, the valve of the reactor was closed, the valve separating the manifolds was opened, and the change in pressure was noted. The gases were then pumped out, and the process was repeated (using a more suitable nitrogen pressure) until the manometer indicated no change in pressure upon opening the valve between the two manifolds. Measurements yielded the data: 8.9 mm, 23.1°; 4.8 mm, 17.7°; 2.9 mm, 12.9°; and 1.3 mm, 9.0°.

The white solid reacted violently when flooded with water, and a little O_2 (0.4 equiv/mole of $2XeF_6 \cdot PF_5$) was observed as a product of reaction. The solution remaining contained an oxidizing agent capable of liberating iodine in the proportion 11.4 equiv/mole of $2XeF_6 \cdot PF_5$ consumed (total oxidizing equivalents found: 11.4 + 0.4 = 11.8; theoretical: 12.0).

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The Formation Constant and Aquation Rate of the Nitratopentaaquochromium(III) Ion[1]

BY MICHAEL ARDON[2] AND NORMAN SUTIN

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We wish to report the results of an investigation of the formation constant and aquation rate of the nitratopentaaquochromium(III) ion. The aquation of this ion also formed the subject of a paper which appeared after this work had been completed.[3] Our kinetic data are in good agreement with the results obtained in the earlier work. We obtained, in addition, equilibrium data pertaining to the stability of the nitrato complex.

Experimental Section

Preparation of the Nitratopentaaquochromium(III) Ion.—A saturated solution of $Cr(NO_3)_3 \cdot 9H_2O$, acidified by a few drops of concentrated nitric acid, was boiled for about 20 min and then diluted tenfold with cold water. The resulting solution was passed through a cooled Dowex 50W-X8 cation-exchange resin in the H^+ form and the nitratopentaaquochromium(III) ion was eluted with 1 *M* perchloric acid. In common with Swaddle, we find that $(H_2O)_5CrNO_3^{2+}$ is also produced in good yield in the reaction of nitratopentaamminecobalt(III) with chromium(II). The nitratopentaaquochromium(III) complex has two maxima in the visible region of the spectrum, at 412 mμ (18.9) and at 581 mμ (16.1).[4] The molar absorptivities reported by Swaddle are slightly lower and the maxima are shifted toward shorter wavelengths [409 mμ (18.57) and 577 mμ (15.84)].

Equilibrium Measurements.—Solutions for the equilibrium measurements were prepared from mixtures of $Cr(NO_3)_3 \cdot 9H_2O$, perchloric acid, and nitric acid so that the final ionic strength was 1.0 *M* and the hydrogen ion concentration was 0.40 *M*. After warming the solutions for several hours at 45° they were kept for 8 half-lives of the aquation reaction at each temperature. Aliquots were then diluted tenfold with cold water and passed through a cooled Dowex 50W-X8 cation-exchange resin in the H^+ form. The nitrato complex was eluted with 1 *M* perchloric acid and hexaaquochromium(III) was eluted with 4 *M* perchloric acid. The chromium content of the fractions was determined at 327 mμ after oxidation to chromate with alkaline hydrogen peroxide. At least two samples were taken from each solution and the agreement was always better than 1%.

Kinetic Measurements.—For the kinetic measurements solutions containing the nitrato complex were passed through the Dowex resin in the Li^+ form and the complex was eluted with 1 *M* lithium perchlorate. The progress of the reaction was followed at 260 mμ on a Cary 14 spectrophotometer equipped with 10-cm cells. Plots of $\log (A_t - A_\infty)$ against t, where A_t is the absorbance of the solution at time t, gave straight lines from which the rate constants were calculated.

Results and Discussion

Equilibrium Measurements.—Values of the equilibrium constant $K = (CrNO_3^{2+})/(Cr^{3+})(NO_3^-)$ are presented in Table I. These values were calculated on the assumption that ion-pairing effects are negligible. It is apparent from Table I that there is a definite decrease in the values of the equilibrium constants with increasing nitrate concentration. This decrease in the equilibrium constant could be due either to a medium effect or to ion pairing or to both. If it is attributed solely to ion pairing (with a resulting decrease in free chromic and nitrate concentrations) and a formation constant of 0.3 M^{-1} is assumed for the ion pair, then the values become independent of the nitrate concentration at each temperature. The corrected values of K are 1.23×10^{-2}, 0.97×10^{-2}, and 0.67×10^{-2} M^{-1} at 34.9, 25.1, and 10.2°, respectively. The enthalpy and entropy change calculated from the corrected values are

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Visiting chemist from the Hebrew University, Jerusalem.

[3] T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).

[4] The numbers in parentheses are the values of the molar absorptivities at the absorption maxima.

TABLE I

EQUILIBRIUM CONSTANT FOR THE FORMATION OF THE NITRATOPENTAAQUOCHROMIUM(III) COMPLEX AT IONIC STRENGTH 1.0 M^a

Temp, °C	$(NO_3^-)_0$, M	$10^3(CrNO_3^{2+})_{eq}$, M	10^2K, M^{-1}
34.9	0.70	6.95	0.99
34.9	0.50	5.16	1.03
34.9	0.30	3.29	1.09
25.1	0.70	5.48	0.78
25.1	0.50	4.19	0.84
25.1	0.30	2.57	0.85
10.2	0.70	3.85	0.55
10.2	0.50	2.82	0.56
10.2	0.30	1.76	0.59

[a] $(H^+) = 0.40$ M and $[Cr(III)] = 0.10$ M. Ionic strength maintained with $HClO_4$.

$\Delta H° = 4.5 \pm 0.2$ kcal mole^{-1} and $\Delta S° = 5.9 \pm 0.6$ cal mole^{-1} deg^{-1} at 25.0°. If no correction is applied and ΔH is calculated at each nitrate concentration, then the mean values are $\Delta H_m° = 4.2 \pm 0.2$ kcal mole^{-1} and $\Delta S_m° = 4.6 \pm 0.6$ cal mole^{-1} deg^{-1} at 25.0°.

The entropies of formation of various chromium(III) complexes are compared in Table II. The entropies of the anions presented in this table have been corrected for the loss of rotational entropy upon complex formation.[3,5] It will be seen that there is a good correlation between $\Delta S°$ and the corrected entropies of the anions. The slope of the plot of $\Delta S°$ against $S°_{X^-}$ is close to the theoretical value of -1.[5,6] The fact that the nitrato complex satisfies this relation between $\Delta S°$ and $S°_{X^-}$ indicates that, in common with the other chromium(III) complexes, only one water molecule is lost upon formation of the nitrato complex and thus that the nitrato ligand is not chelated.[7]

TABLE II

ENTROPIES OF FORMATION OF CHROMIUM(III) COMPLEXES

$$Cr^{3+} + X^- \rightleftharpoons CrX^{2+}$$

X^-	Ionic strength, M	$\Delta S°$, eu	$S°_{X^-}$, eu[a]	Ref
F^-	0.5	28.2	−3.6	*b*
Cl^-	1.0	15.7	13.2	*c*
Br^-	2.0	4.9	19.3	*d*
NCS^-	0.5	~2	20.2	*e*
NO_3^-	1.0	5.9	15.6	*f*

[a] The entropies of the polyatomic anions have been corrected for the loss of rotational entropy upon complex formation. For purposes of comparison with the earlier work the corrected entropies are those reported in ref 3. [b] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965). [c] C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967). [d] Reference 9. [e] C. Postmus and E. L. King, *ibid.*, **59**, 1208, 1216 (1955). [f] This work.

The Aquation Reaction.—The first-order rate constants for the aquation of the nitrato complex are presented in Table III. In the range $(H^+) = 0.076$–0.99 M the observed rate constant is given by

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF THE NITRATOPENTAAQUOCHROMIUM(III) ION AT IONIC STRENGTH 1.0 M^a

Temp, °C	(H^+), M	10^5k, sec^{-1}
34.9	0.990	23.3
34.9	0.401	24.8
34.9	0.201	26.3
34.9	0.081	29.9
25.1	0.990	7.19
25.1	0.201	7.94
25.1	0.081	9.14
15.6	0.990	2.17
15.6	0.201	2.58
15.6	0.076	2.72

[a] Ionic strength maintained with $LiClO_4$.

$$k = k_0 + k_{-1}/(H^+)$$

where $k_0 = (7.2 \pm 0.2) \times 10^{-5}$ sec^{-1} and $k_{-1} = (1.4 \pm 0.7) \times 10^{-7}$ M sec^{-1} at 25°. The enthalpy and entropy of activation for the acid-independent path are $\Delta H_d^{\ddagger} = 21.4 \pm 0.2$ kcal mole^{-1} and $\Delta S_d^{\ddagger} = -5.7 \pm 0.6$ cal mole^{-1} deg^{-1}. These values are in very good agreement with those obtained by Swaddle.[3] The contribution of the acid-dependent path is small and accurate activation parameters for this reaction were not obtained. The rate constant for the acid-independent formation reaction, calculated from the equilibrium constant and the aquation rate, is approximately 7×10^{-7} M^{-1} sec^{-1} at 25.0°. $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ are calculated to be about 28.8 kcal mole^{-1} and 0.2 cal mole^{-1} deg^{-1}, respectively. The values of the various activation parameters are similar to those calculated for the corresponding reactions of the bromopentaaquochromium(III) ion[8,9] and are consistent with the view that the nitrato ligand is monodentate in the nitrato chromium(III) complex.

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(7) If the nitrato group were chelated in the chromium(III) complex, then 16.7 cal mole^{-1} deg^{-1}, the entropy of a water molecule, would have to be subtracted from $\Delta S°$ for the nitrato complex in order to make the value of $\Delta S°$ for the nitrato complex comparable with those for the other chromium(III) complexes. This corrected value of $\Delta S°$ does not lie on the plot of $\Delta S°$ against $S°_{X^-}$.

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Absorption Spectra of Square-Planar Complexes of Ethylenebisbiguanide with Nickel(II) and Palladium(II)

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It has been proposed by Gray[1] and by Gray and Ballhausen[2] that the energy levels of the antibonding molecular orbitals derived from atomic d orbitals in square-planar transition metal complexes most often occur in the order $x^2 - y^2 \gg xy > z^2 > xz, yz$. More recently, elegant use of molecular orbital theory has led to simi-

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