determined by the gas saturation method,[10] is 0.09 mm. The chemical analysis of sublimed material is approximately the same as before sublimation. The solubility in CS_2 is about 0.05 g./100 ml., and in benzene about 0.2 g./100 ml. The material tends to decompose slowly in both solvents. X-Ray diffraction patterns of $I_3B:PI_3$, PI_3, and BI_3 were obtained with a Debye–Scherrer powder camera (Table I). The results shown in this table indicate the pattern of the compound does not correspond to the patterns of the reagents used.

Hydrogen iodide is evolved when the material hydrolyzes at room temperature in water or with moisture in air. In dry air it reacts slowly with the evolution of iodine. Nitric acid reacts rapidly with the material with the evolution of iodine. Vapor phase decomposition of the material at 900° in an inert atmosphere produces a gray coating on the reactor wall. X-Ray patterns of this material correspond to the published pattern for cubic boron phosphide.[11]

(10) S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Company, New York, N. Y., 1954, p. 448.

(11) J. Perri, ASTM Card Index No. 11-119.

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The Kinetics of Aquation of Bromopentaaquochromium(III) Ion in Acidic Solution[1]

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The aquation of inner-sphere complexes of chromium(III) ion in acidic solution generally proceeds *via* several pathways with which are associated transition states containing different numbers of protons. The relative importance of the several pathways is of interest, as are the associated activation parameters. The present study deals with aquation of bromopentaaquochromium(III) ion

$$Cr(OH_2)_5Br^{2+} + H_2O = Cr(OH_2)_6^{3+} + Br^-$$

in acidic solution ($[H^+] = 0.06\text{–}1.0\ M$) of constant ionic strength ($I = 1.0\ M$). In solutions with this range of acidity, the rate law established by this study is

$$-\frac{d \ln [CrBr^{2+}]}{dt} = k_0 + k_{-1}[H^+]^{-1}$$

A term first order in hydrogen ion, observed for aquation of analogous species with relatively basic ligands (*e.g.*, azide ion[3a] and fluoride ion[3b]), is not observed for this species with a less basic ligand. Measurements were made at 30, 45, and 60°.

Experimental Details and Results

Acidic solutions containing bromopentaaquochromium(III) ion, hereafter called bromochromium(III) ion, as the only species containing either bromide ion or chromium(III) ion were prepared in the following way. Chromium(III) perchlorate solution was prepared by reduction of potassium dichromate with hydrogen peroxide in perchloric acid solution. After excess hydrogen peroxide was decomposed by heating the solution, oxygen was removed by aeration with carbon dioxide; then chromium(III) ion was reduced to chromium(II) ion with lightly amalgamated zinc. Bromochromium(III) ion was prepared by reaction of chromium(II) ion with bromine,[4] the excess of which was removed by extraction with carbon tetrachloride. After absorption of bromochromium(III) ion onto Dowex 50-W, X-8 resin (100–200 mesh), bromide ion was rinsed from the column with chilled 0.1 *M* perchloric acid, followed by elution of cationic bromochromium(III) ion with 0.8–1.0 *M* perchloric acid. Solutions prepared in this way contained zinc ion. These stock solutions were stored at ~0° for use in kinetic experiments.

The bromide and chromium contents of solutions prepared in this manner were determined by applying standard procedures to portions of completely aquated complex (bromide by the Volhard method and chromium by spectrophotometry after conversion to chromate by alkaline peroxide). The ratio of concentrations of these elements was found to be 1.000 ± 0.003.

Lithium perchlorate solutions containing perchloric acid were prepared by reaction of reagent grade lithium carbonate with a slight excess of perchloric acid.

Reaction solutions were prepared by mixing stock solutions of perchloric acid, lithium perchlorate, and bromochromium(III) ion in perchloric acid. Aliquots, withdrawn at 7–9 different times during each kinetic experiment, were quenched with an approximately equal amount of ice. The resulting solution was analyzed for free bromide ion and, in some experiments, for unreacted bromochromium(III) ion also by an ion-exchange procedure coupled with the Volhard analysis for bromide ion. Uncomplexed bromide ion present in a quenched aliquot was washed from the column of cation-exchange resin with a limited volume of chilled 0.1 *M* perchloric acid. Then unreacted bromochromium(III) ion was eluted with chilled 0.8 *M* perchloric acid. This eluent was analyzed for bromide ion after allowing it to aquate completely, or for chromium by the spectrophotometric method already mentioned. Extents of reaction determined in the two ways, analysis for bromide ion produced or for unreacted bromochromium ion, agreed reasonably well. (The average difference of the concentrations of bromochromium(III) ion in twenty aliquots determined both ways was 4%.)

In each experiment, aquation conformed to a first-order rate equation

$$\frac{\Delta \ln [CrBr^{2+}]}{\Delta t} = k$$

to >95% reaction. The absence of retardation due to the reverse reaction is consistent with the known equilibrium quotient for the aquation reaction, which is ~270 at 45° and $I = 2.00$ *M*.[5] For the initial concentration of bromochromium(III) ion employed (~0.01 *M*), the equilibrium extent of aquation of bromochromium(III) ion is ~99.5%. Values of the first-order rate coefficient *k* are presented in Table I. Treatment of these empirical rate coefficients to obtain rate parameters for each of the two pathways yielded the enthalpies and entropies of activation given in Table II[6]; values of k_0 and k_{-1} for 45°

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[2] N.S.F. Summer Research Participant from Rose Polytechnic Institute, Terre Haute, Ind.

[3] (a) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964); (b) T. W. Swaddle and E. L. King, forthcoming publication.

[4] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[5] J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

[6] These values were obtained by T. W. Newton of the Los Alamos Scientific Laboratory using a least-square program written by R. H. Moore to obtain values of ΔH^* and ΔS^* for each term of a multi-term rate law using the original data at all temperatures.

derived from these parameters also are presented. The root-mean-square deviation between the observed rate coefficients and those calculated using the "best" values of enthalpy and entropy of activation is ~2.0%.

TABLE I

FIRST-ORDER RATE COEFFICIENT

$$k = -\frac{\Delta \ln [\mathrm{CrBr}^{2+}]}{\Delta t}$$

FOR AQUATION OF BROMOCHROMIUM(III) ION[a]

$I = 1.00\ M$

$[H^+]$, M	$10^5 k \times$ sec. 30°	45°	60°
0.056	4.40		
0.060		34.0	
0.070	3.77		216.
0.080		27.8	
0.100	2.32[b]	22.6	161.
0.160	2.15	16.7	113.
0.300	1.59	11.4	74.5
1.00	1.01	7.40	44.9

[a] The initial concentration of bromochromium(III) ion ranged from 0.0085 to 0.014 M. The solutions contained zinc ion at a concentration less than half the initial concentration of bromochromium(III) ion. [b] Omitted for correlations to obtain ΔH^* and ΔS^*.

TABLE II

PARAMETERS ASSOCIATED WITH THE RATE LAW

$$-\frac{\mathrm{d} \ln [\mathrm{CrBr}^{2+}]}{\mathrm{d}t} = k_0 + k_{-1}[\mathrm{H}^+]^{-1}$$

$I = 1.00\ M$

	k_0	k_{-1}
$\Delta H^* \times$ mole kcal.$^{-1}$	23.8 ± 0.3	27.1 ± 0.2
$\Delta S^* \times$ mole deg. cal.$^{-1}$	-3.5 ± 0.9	4.7 ± 0.7
k (at 45°)	5.7×10^{-5} sec.$^{-1}$	1.77×10^{-5} mole l.$^{-1}$ sec.$^{-1}$

Discussion

The contrast in relative importance of transition states of charge 2+ and 1+ for aquation of bromopentaamminechromium(III) ion[7] and bromopentaaquochromium(III) ion is striking. Reaction goes to an equal extent by each of the two transition states $\{\mathrm{CrA_5Br^{2+}}\}^*$ and $\{\mathrm{CrA_4BBr^{+}}\}^*$, where A is ammonia or water and B is amide ion or hydroxide ion,[8] at a hydrogen ion concentration of $\sim 7 \times 10^{-12}\ M$ for the ammine species (at 25.3°) and 0.31 M for the aquo species (at 45°). This difference arises largely from the greater enthalpy of activation for the transition state of charge 1+ for the ammine species. For bromopentaamminechromium(III) ion $(\Delta H_{-1}^* - \Delta H_0^*)$[9] $= 18.2$ kcal. mole^{-1} in contrast to $(\Delta H_{-1}^* - \Delta H_0^*)$[9] $= 3.3$ kcal. mole^{-1} for bromopentaaquochromium(III) ion. On the other hand, values of the entropy of activation for aquation of bromopentaamminechromium(III) *via* the two pathways, $\Delta S_0^* = -6.7$ cal. mole^{-1} deg.$^{-1}$ and $\Delta S_{-1}^* = +3.0$ cal. mole^{-1} deg.$^{-1}$, are very similar to the corresponding values given in Table II for the aquo species.

There are two possible transition states of charge 1+, a conjugate base of the reactant species[10] and a combination of hydroxide ion with the reactant species. If the only important transition state of charge 1+ involved combination of hydroxide ion with the reactant species, it would be difficult to rationalize the contrasting properties of the bromoammine species and bromoaquo species just discussed. If, however, these transition states were conjugate bases of the reactants, the much greater acidity of water relative to ammonia[11] would provide a reasonable explanation for the much greater relative importance of the transition state of charge 1+ in reaction of the bromoaquo species.[12] Only for bromopentaaquochromium(III) ion does this argument demand a transition state which is a conjugate base of the reactant; for bromopentaamminechromium(III) ion the transition state could be made up of hydroxide ion and the complex ion and the argument would still be valid.[13] The similarity of values of ΔS^* for corresponding pathways for reactions of bromopentaaquochromium(III) ion and bromopentaamminechromium(III) ion suggests mildly that the transition states for analogous pathways are similar. The present data leave unanswered, however, the question of whether or not a water molecule is incorporated into these transition states.

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[7] M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).

[8] The specific participation of water in these transition states is not shown, but this formulation is not intended to exclude this possibility.

[9] The subscripts to ΔH^* use the notation used for rate coefficients of our rate law. For reaction of the ammine species, values of k_{-1} and ΔH_{-1}^* were obtained from values associated with the rate law term $k_\mathrm{b}[\mathrm{Cr(NH_3)_5Br^{2+}}][\mathrm{OH^-}]$ by appropriate correction using the equilibrium constant and other parameters for dissociation of water: $k_{-1} = k_\mathrm{b} K_\mathrm{w}$ and $\Delta H_{-1}^* = \Delta H_\mathrm{b}^* + \Delta H_\mathrm{w}$.

[10] F. J. Garrick, *Nature*, **139**, 507 (1937).

[11] The acidity of ammonia is discussed by R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp. 87–88.

[12] Y. P. Nazarenko and Y. I. Bratushko [*Ukr. Khim. Zh.*, **28**, 17 (1962); *Chem. Abstr.*, **57**, 4083g (1962)] have observed the rates of aquation of $\mathrm{Cr(NH_3)_5Cl^{2+}}$ and $\mathrm{Cr(OH_2)(NH_3)_4Cl^{2+}}$. The former rate does not increase appreciably in going from a solution with $10^{-3}\ M$ hydrogen ion to one with no added acid, but the latter rate increases by a factor of ~3 with this ill-defined change of acidity. This indicates that a rate law term $k_{-1}[\mathrm{Cr(OH_2)(NH_3)_4Cl^{2+}}][\mathrm{H^+}]^{-1}$ is neither dominant nor trivial in slightly acidic solution.

[13] Whether base hydrolysis of amminecobalt(III) species occurs by S_N2 or S_N1CB mechanisms is an unsettled question. [C. K. Ingold, "Substitution at Elements Other than Carbon," Weizmann Science Press, Jerusalem, 1959, Chapter 1; M. L. Tobe, *Sci. Progr.*, **48**, No. 191, 483 (1960); F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 25 (1961).]

Photochemical Reactions of the Difluoramino Radical with Some Inorganic Substrates

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Photolytic decomposition of the difluoramino free radical ($\mathrm{NF_2}$), present as a result of the equilibrium[1]

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[1] C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960); F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).