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The Rate of Aquation of Azidopentaaquochromium(III) Ion in Acidic Solution[1]

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The rate of aquation of azidopentaaquochromium(III) ion in acidic solution, $Cr(OH_2)_5N_3^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HN_3$, is governed by the rate law $-d \ln [Cr(OH_2)_5N_3^{2+}]/dt = k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$. At 50° in perchloric acid–sodium perchlorate solutions of ionic strength 1.00 M the rate coefficients are: $k_1 = 1.72 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$, $k_0 = 3.1 \times 10^{-6}$ sec.$^{-1}$, $k_{-1} = 2.9 \times 10^{-9}$ mole l.$^{-1}$ sec.$^{-1}$, and $k_{-2} = 1.2 \times 10^{-12}$ mole^2 l.$^{-2}$ sec.$^{-1}$. Studies also were made at 30 and 70°, and the temperature dependence of the rate coefficients corresponds to the following activation parameters: k_1, $\Delta H^* = 23.2$ kcal. mole^{-1}, $\Delta S^* = -8.3$ e.u.; k_0, $\Delta H^* = 32.4$ kcal. mole^{-1}, $\Delta S^* = +16.2$ e.u.; and k_{-1}, $\Delta H^* = 37.2$ kcal. mole^{-1}, $\Delta S^* = +17.3$ e.u.

The aquation of azidopentaaquochromium(III) ion[3] in acidic solution

$$Cr(OH_2)_5N_3^{2+} + H^+ + H_2O = Cr(OH_2)_6^{3+} + HN_3$$

proceeds at a measurable rate in the temperature range 30–70°. This paper reports a kinetic study of this reaction in solutions with hydrogen ion concentration from 10^{-3} to 1 M. The reaction proceeds by several pathways, including one with a protonated transition state $\{Cr(OH_2)_5N_3H^{3+}\}^*$; the other transition states of importance in this acidity range have net charges of 2+, 1+, and 0. The rate of aquation of most aquochromium(III) complexes is inversely dependent upon acidity, but a positive dependence is less common, being restricted to complexes with ligands of appreciable basicity. Among the pathways for aquation of azidopentaamminecobalt(III) ion,[4] azidoiron(III) ion,[5] and fluoroiron(III) ion[6] are ones involving a protonated transition state.

Experimental Details and Results

Reagents.—All solutions were prepared with doubly-distilled water, the second distillation being from alkaline permanganate solution using a Barnstead still. Reagent grade perchloric acid (Mallinckrodt), sodium hydroxide (Mallinckrodt), and sodium perchlorate (G. F. Smith) were used without further purification. Lithium perchlorate was prepared from reagent grade lithium carbonate (Mallinckrodt) and excess perchloric acid; hydrated lithium perchlorate ($LiClO_4 \cdot 3H_2O$) crystallized from the partially evaporated solution. Sodium formate (Mallinckrodt) was recrystallized before use.

Azidopentaaquochromium(III) ion was prepared by the direct reaction of chromium(III) ion and azide ion in solutions buffered with hydrazoic acid to pH values not greater than ~4.5. In one preparative experiment designed primarily to produce diazidochromium(III) ion, a solution with the stoichiometric composition 0.3 M chromium(III) perchlorate, 0.6 M sodium azide, 0.9 M hydrazoic acid was allowed to stand at room temperature for 4.5 days,[7] at the end of which the pH was ~2. The solution was acidified further, excess azide was removed as hydrazoic acid by successive extraction into ether followed by aeration with nitrogen (which also removed the traces of ether), and ion-exchange procedures were used to separate species of charge ≤1+, 2+, and 3+.[8] Direct analysis of eluent portions was made for chromium by spectrophotometry after conversion to chromate with alkaline peroxide and for azide by oxidation with excess cerium(IV) in sulfuric acid followed by back titration with standardized iron(II) solution. The material which came directly through the cation-exchange column combined with the 0.2 M perchloric acid eluent contained ~45% of the chromium and had an azide:chromium ratio of 2.12, suggesting the presence of triazidotriaquochromium(III). This solution was treated with chromium(II) ion to aquate triazidochromium(III) and *trans*-diazidochromium(III) ion according to the procedure of Snellgrove and King.[9] Further ion-exchange separation of species in this solution yielded a fraction which contained *cis*-diazidochromium(III) ion[9]; the azide: chromium ratio was 2.00 The positions and molar absorbancy indices of spectral peaks for *cis*-diazidochromium(III) ion are 603 mμ, 87.5 cm.$^{-1}$ mole^{-1} l.; 443 mμ, 87.2 cm.$^{-1}$ mole^{-1} l.; 277 mμ, 5450 cm.$^{-1}$ mole^{-1} l.; and 222 mμ, 9440 cm.$^{-1}$ mole^{-1} l. The 1.0 M perchloric acid eluent contained ~34% of the chromium in the form of a species with azide:chromium ratio of 1.00. The positions and molar absorbancy indices of spectral peaks for azidochromium(III) ion are: 585 mμ, 67.5 cm.$^{-1}$ mole^{-1} l.; 434 mμ, 66.4 cm.$^{-1}$ mole^{-1} l.; 271 mμ, 3740 cm.$^{-1}$ mole^{-1} l.; and 222.5 mμ, 6850 cm.$^{-1}$ mole^{-1} l. This spectrum was independent of the hydrogen ion concentration in the range 0.024 to 0.94 M, suggesting that inappreciable protonation of azidochromium(III) ion occurs at 1.0 M hydrogen ion.

Direct formation of chromium(III) azide complexes is possible as suggested by Sherif and Oraby,[10] although the objections stated by Ardon[11] to their interpretation seem justified, since these authors studied the spectra of their reaction solutions without acidification.

Kinetic Studies.—The rate measurements were made at 70.00, 50.00, and 30.05°. The reaction solutions contained perchloric acid and either sodium perchlorate or lithium perchlorate in addition to the reaction participants; the ionic strength was maintained at 1.00 M. The initial concentration of azidochromium(III) ion was low in all experiments, being in the range 10^{-3} to 10^{-4} M. In experiments at low acidity, part of the hydrogen ion coming from the stock solution of azidochromium(III) ion was neutralized with sodium hydroxide. Because of localized high concentrations of base during this process some aquation of complex occurred, and such kinetic runs were carried out, therefore, with an appreciable amount of reaction products present at zero time.

Aliquots of reaction mixture were analyzed for extent of reaction by measurement of absorbancy at 271 mμ, where azidochro-

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[3] In general this species will be called azidochromium(III) ion.

[4] G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963).

[5] D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

[6] D. Pouli and W. MacF. Smith, *Can. J. Chem.*, **38**, 567 (1960).

[7] It has not been proved that this time is required.

[8] E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).

[9] R. Snellgrove and E. L. King, *ibid.*, **84**, 4608 (1962).

[10] F. G. Sherif and W. M. Oraby, *J. Inorg. Nucl. Chem.*, **17**, 152 (1961).

[11] M. Ardon, *ibid.*, **20**, 173 (1961).

TABLE I

FIRST-ORDER RATE COEFFICIENTS FOR AQUATION OF $Cr(OH_2)_5N_3^{2+}$ AT $I = 1.0\ M$

HClO₄–LiClO₄ solutions		HClO₄–NaClO₄ solutions	
$10^2[H^+]$	$10^6k \times$ sec.	$10^2[H^+]$	$10^6k \times$ sec.
70.00°		70.00°	
94.3	213.	40.3	125.
75.6	185.	26.9	104.5
38.3	127.	10.5	79.7
19.7	97.2	3.09	70.8
8.51	79.7	0.885	74.0
		0.387	87.3
50.00°		0.242	104.
94.3	19.55	0.176	122.
38.3	10.0	0.127	146.
19.7	6.84	0.101	166.
8.51	4.89	0.084	199.
4.78	4.25	0.065	245.
2.64	3.89		
1.05	3.71	50.00°	
		0.408	3.93
30.05°		0.311	4.20
94.3	1.56	0.273	4.27
75.6	1.27	0.215	4.59
38.3	0.706	0.164	5.35
19.7	0.419	0.117	6.40
		0.095	7.52
		0.071	9.13

mium(III) ion has an absorption maximum. Light absorption by the reaction products in all experiments except those at the lowest acidities was negligible. The slowness of reaction allowed the light absorption of reaction solutions to be measured at room temperature regardless of the reaction temperature. In general 5 to 12 portions of reaction solution were removed during a run. Plots of log $(A - A_\infty)$ *vs.* time were linear over ~85% reaction at higher acidities and ~50% reaction at the lowest acidities. First-order rate coefficients were calculated from the slopes of these linear plots, $k = 2.303\ \Delta \log (A - A_\infty)/\Delta t$. A summary of experimental results is given in Table I.

Discussion

The experimentally observed dependence of the first-order rate coefficient upon hydrogen ion concentration can be expressed in the equation

$$k = k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$$

Values of these individual rate coefficients are summarized in Table II. The adequacy of these parameters can be judged by the differences between observed and calculated values of k which are given. Under some experimental conditions studied, each rate law term except that with coefficient k_{-2} contributes over 50% to the total reaction rate. Therefore, it is unlikely that any of the three important terms is simply a medium effect disguised as a new reaction pathway.[12]

The details of reaction mechanism for aquation *via* each pathway are not given by the form of the rate law terms. Only the net charge and composition of the transition states exclusive of specific solvation are given; these are $\{Cr(OH_2)_{5+x}N_3H^{3+}\}$, $\{Cr(OH_2)_{5+x}N_3^{2+}\}^*$, $\{Cr(OH_2)_{4+x}(OH)N_3^+\}^*$, and $\{Cr(OH_2)_{3+x}(OH)_2N_3\}^*$. Remaining points of interest are whether or not there are intermediates along the reaction pathways and the distribution of protons in the transition states of charge 2+ or lower.

TABLE II

VALUES OF RATE COEFFICIENTS IN THE RATE LAW

$$-\frac{d \ln [Cr(OH_2)_5N_3^{2+}]}{dt} = k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_2[H^+]^{-2}$$

	30.05°	50.00°	70.00°
HClO₄–LiClO₄ solutions			
$10^6k_1 \times$ mole l.$^{-1}$ sec.	1.53	17.2	156.
$10^7k_0 \times$ sec.	1.15	34.4	670.
Av. % difference[b]	0.5%	0.6%	0.4%
HClO₄–NaClO₄ solutions			
$10^6k_1 \times$ mole l.$^{-1}$ sec.		(17.2)[a]	153.
$10^7k_0 \times$ sec.		31.	640.
$10^9k_{-1} \times$ l. mole^{-1} sec.		2.9	90.
$10^{12}k_{-2} \times$ l.^{2} mole^{-2} sec.		1.2	20.
Av. % difference[b]		1.6%	1.5%

[a] This value taken from studies in perchloric acid–lithium perchlorate solutions. [b] This is the average of the differences between experimental values of k and values calculated using these parameters.

The first of these points is the question of whether the mechanism approaches the limiting SN1 mechanism with a pentaaquochromium(III) ion intermediate (with $x = 0$) or the limiting SN2 mechanism (with $x = 1$). That a species with coordination number five is an intermediate in aquation of azido- and thiocyanatopentacyanocobalt(III) ion[13] does not prove an analogous pathway for the present reaction; the π-bonding ligand cyanide ion may stabilize the species with coordination number five relative to the stabilization of an analogous species with five water molecules as ligands.

The distribution of protons in the transition state of charge 3+ is undoubtedly that implied by the formulation $\{Cr(OH_2)_{5+x}N_3H^{3+}\}^*$; there would be little reason for this transition state of charge 3+ to have a structure containing hydronium ion and azide ion bound to chromium(III).

The transition state of composition $\{Cr(OH_2)_{5+x}N_3^{2+}\}^*$ may have a different geometry from that of the reactant with which it is "isomeric." Since both protonated and deprotonated transition states are more important than the "isomeric" species, the transition state of charge 2+ probably involves the distribution of protons corresponding to one hydroxide ion and hydrazoic acid, not azide ion. Seewald and Sutin[5] suggest this geometry for the analogous pathway for formation of azidoiron(III) ion. Closely related to this structure would be one involving internal hydrogen bonding between bound water and azide ion which would allow direct production of hydrazoic acid.

Whether the transition state of charge 1+ contains azide ion and one hydroxide ion or hydrazoic acid and two hydroxide ions or is a mixture is not known. At 50° the transition states of charge 2+ and 1+ are equally important at ~10^{-3} M hydrogen ion, at which acidity hydrazoic acid is largely undissociated.

Temperature dependences of the individual rate coefficients except k_{-2} were correlated using log (k/T)

(12) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

(13) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573, 583 (1962).

vs. $(1/T)$ plots to obtain values of entropy and enthalpy of activation. The values so obtained, with ΔC_p^* assumed to be zero, are: k_1, $\Delta H^* = 23.2$ kcal. mole^{-1} and $\Delta S^* = -8.3$ cal. mole^{-1} deg.$^{-1}$; k_0, $\Delta H^* = 32.4$ kcal. mole^{-1} and $\Delta S^* = +16.2$ cal. mole^{-1} deg.$^{-1}$; and k_{-1}, $\Delta H^* = 37.2$ kcal. mole^{-1} and $\Delta S^* = +17.3$ cal. mole^{-1} deg.$^{-1}$.[14] Table III summarizes these parameters and those for other similar systems.

Particularly striking are comparisons of entropies of activation for reaction of cationic azide complexes and analogous thiocyanate complexes, $(\Delta S^*_{\mathrm{MN_3}} - \Delta S^*_{\mathrm{MNCS}}) = 19.7$ and 22.9 e.u. for $\{\mathrm{Cr(OH_2)_{5+\mathit{x}}X^{2+}}\}^*$ and $\{\mathrm{Co(NH_3)_5X^{2+}}\}^*$, respectively. These large differences support the geometry already suggested for the transition state of charge 2+, *i.e.*, one in the act of producing hydrazoic acid, not azide ion. A more positive entropy of activation is expected for conversion of a reactant of charge 2+ to a transition state which yields a neutral molecule ($\mathrm{HN_3}$) and an ion of charge 2+ ($\mathrm{Cr(OH_2)_{4+\mathit{x}}(OH)^{2+}}$) than for conversion to one which yields an anion ($\mathrm{SCN^-}$) and an ion of charge 3+ ($\mathrm{Cr(OH_2)_{5+\mathit{x}}^{3+}}$). The similarity of the difference $(\Delta S^*_{\mathrm{MN_3}} - \Delta S^*_{\mathrm{MNCS}})$ for $\{\mathrm{Cr(OH_2)_{5+\mathit{x}}X^{2+}}\}^*$ and $\{\mathrm{Co(NH_3)_5X^{2+}}\}^*$ suggests, therefore, that this transition state for aquation of azidopentaamminecobalt(III) ion yields hydrazoic acid and a cobalt(III) species of charge 2+. The lower acidity of ammonia relative to water may make production of an amido species unlikely; perhaps involvement of water *via* hydrogen bonding may lead to hydroxopentaamminecobalt(III) ion as the other product of decomposition of this transition state.

The enthalpy and entropy of activation for aquation of azido- and thiocyanatopentacyanocobalt(III) ion are given in Table III. The difference in entropies of activation for these two anionic species is large and has the opposite sign $(\Delta S^*_{\mathrm{MN_3}} - \Delta S^*_{\mathrm{MNCS}}) = -12.1$ e.u., relative to the comparisons already discussed. That first-order aquation of the anionic thiocyanate species $\mathrm{Co(CN)_5NCS^{3-}}$ should have a more positive entropy of activation than that for the cationic species $\mathrm{Cr(OH_2)_5NCS^{2+}}$ is reasonable. Extra charge to immobilize solvent is being developed in the latter reaction, but charge is being dissipated in the former. Since first-order aquation of the azidocyano complex probably produces azide ion, not hydrazoic acid, it is surprising that values of the entropies of activation for these anionic azido and thiocyanato complexes are not similar. The comparison of these values and those for aquation at the cationic species does, however, strengthen arguments that the transition states for aquation of cationic azido complexes in acidic solution yield hydrazoic acid directly.

TABLE III

VALUES OF ΔH^* AND ΔS^* ASSOCIATED WITH RATE LAW TERMS

$$-\frac{\mathrm{d}\ln[\mathrm{MX_5Y}]}{\mathrm{d}t} = k_n[\mathrm{H^+}]^n$$

$\mathrm{MX_5Y}$	ΔH^* × kcal.$^{-1}$ mole	ΔS^* × cal.$^{-1}$ mole deg.	Ref.
	$n = 1$		
$\mathrm{Cr(OH_2)_5N_3^{2+}}$	23.2	−8.3	*a*
$\mathrm{Co(NH_3)_5N_3^{2+}}$	25.9[f]	−8.0[f]	*b*
	$n = 0$		
$\mathrm{Cr(OH_2)_5N_3^{2+}}$	32.4	+16.2	*a*
$\mathrm{Co(NH_3)_5N_3^{2+}}$	33.4[f]	+13.5[f]	*b*
$\mathrm{Cr(OH_2)_5NCS^{2+}}$	27.5	−3.5	*c*
$\mathrm{Co(NH_3)_5NCS^{2+}}$	26.2	−9.4	*d*
$\mathrm{Co(CN)_5N_3^{3-}}$	27.3	−0.6	*e*
$\mathrm{Co(CN)_5NCS^{3-}}$	31.1	+11.5	*e*

[a] This work. [b] Reference 4. [c] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955). [d] A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954). [e] Reference 13. [f] Lalor and Moelwyn-Hughes (ref. 4) summarized their measurements on aquation of azidopentaamminecobalt(III) ion in acidic solution (~0.015–0.20 *M* perchloric acid) of varying ionic strength (no inert salts were present) in terms of the empirical equation $k_2 = k_0 + b[\mathrm{H^+}] + c[\mathrm{H^+}]^2$. Although k was demonstrated to be relatively insensitive to ionic strength at low acidity ($[\mathrm{H^+}] = 0.014$ *M*) where k_0 is the dominant term of the sum, the assumption that this lack of dependence on ionic strength persists at acidities where the term $b[\mathrm{H^+}]$ is important is incorrect. It seems reasonable to interpret the $c[\mathrm{H^+}]^2$ term simply as a means of accounting for the ionic strength dependence of b (*i.e.*, k_1 of our rate law). A preferable equation for k in solutions of varying acidity and ionic strength is

$$k = k_0 + k_1[\mathrm{H^+}]10^{4A\sqrt{I}/(1+\sqrt{I})}$$

where A is the Debye–Hückel slope for the temperature in question. The data are fit adequately by this equation; for 69.6°: $k_0 = 3.54 \times 10^{-6}$ sec.$^{-1}$, $k_1 = 3.8 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$; 79.6°: $k_0 = 1.45 \times 10^{-5}$ sec.$^{-1}$, $k_1 = 1.1 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$; and 89.6°: $k_0 = 5.7 \times 10^{-5}$ sec.$^{-1}$, $k_1 = 3.3 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ The values of k_0 are very similar to those presented by Lalor and Moelwyn-Hughes, but the values of k_1 differ greatly from the values of b, which they did not interpret as a bona fide rate constant.

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(14) These parameters have also been evaluated 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 multiterm rate law using the original data at all temperatures (not the derived rate coefficients). The best values so obtained are: k_1, $\Delta H^* = 23.4 \pm 0.2$ kcal. mole^{-1} and $\Delta S^* = -7.9 \pm 0.6$ cal. mole^{-1} deg.$^{-1}$; k_0, $\Delta H^* = 31.4 \pm 0.3$ kcal. mole^{-1} and $\Delta S^* = 13.5 \pm 0.8$ cal. mole^{-1} deg.$^{-1}$; k_{-1}, $\Delta H^* = 43.7 \pm 2.5$ kcal. mole^{-1} and $\Delta S^* = +36.3 \pm 7.3$ cal. mole^{-1} deg. (The k_{-2} term was included in the calculation.) With the exception of the k_{-1} term the agreement with the parameters determined originally is reasonable. The large discrepancy for parameters associated with the k_{-1} term may arise from the computer paying too much attention to the barely detectable k_{-2} term, thereby giving distorted values for parameters associated with the adjacent k_{-1} term. Comparison of the parameters obtained in the two ways indicates, however, the inevitable flexibility in fitting data of moderate quality to a power series.