$(Si(C_2H_5)_2)_2$ (ref 3, 4, and 23, respectively) all contain simple terminal hydrogens. The plausibility of the weak bridge system (II and V) remained as a result of our initial studies of another series of silyl derivatives, *viz.*, $LMHSiR_3$. These studies now include the complete structural determination of the compounds $(h^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$, $(h^5\text{-}C_5H_5)Mn(CO)_2HSiCl_2C_6H_5$, $Fe(CO)_4HSi(C_6H_5)_3$, and $(h^3\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$ (ref 24, 25, 26, and 27, respectively). The weak silicon–hydrogen bridge[24,25] appears to result from the particularly crowded environment of the manganese atoms in the first two structures and does not appear in the iron or rhenium compounds. Previous speculation[1,3] on the use of the infrared silence of the metal–hydrogen stretch in these systems would appear to be doubtful. Our current view is that the bridges arise only in sterically crowded situations, and the dinuclear rhenium species do not qualify in this respect. This point will be discussed in detail in future papers in this series.

Acknowledgment. We thank Professor W. A. G. Graham and Mr. J. K. Hoyano for supplying the samples used in this work, and the National Research Council of Canada for financial support.

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(23) M. J. Bennett and M. Cowie, manuscript in preparation.

(24) M. J. Bennett and W. L. Hutcheon, manuscript in preparation; see also *Chem. Eng. News*, **48**, 75 (June 8, 1970).

(25) M. J. Bennett and K. A. Simpson, manuscript in preparation.

(26) M. J. Bennett and K. A. Simpson, manuscript in preparation.

(27) M. J. Bennett and R. Smith, manuscript in preparation.

Kinetic and Equilibrium Studies on Azidochromium(III) Ion in Concentrated Perchloric Acid[1]

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Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received January 4, 1971*

Abstract: The spectrum of azidochromium(III) ion in perchloric acid shows a dependence upon acidity which is consistent with protonation; the derived acid dissociation constant $K_1 = [CrN_3^{2+}]h_0/[CrN_3H^{3+}]$ is equal to 2.7×10^3 at 30°. The rate of aquation of azidochromium(III) ion in concentrated perchloric acid (1–11 *M*) at 30° is correlated with the solution composition by the rate law $-\mathrm{d}\ln[CrN_3]_T/\mathrm{d}t = (k_2a_w + k_3)h_0/(K_1 + h_0)$, with $k_2 = 2.7 \times 10^{-3}\ \mathrm{sec}^{-1}$, $k_3 = 1.8 \times 10^{-4}\ \mathrm{sec}^{-1}$, and $K_1 = 2.70 \times 10^3$ (the value determined from spectra). This rate law indicates that aquation occurs by both SN2 and SN1 pathways. The Henry's law constant for hydrazoic acid was evaluated for perchloric acid solutions with a range of concentrations (0.1–11 *M*); in solutions of high acidity (>8 *M*), hydrazoic acid is protonated, thereby lowering the Henry's law constant.

The aquation reactions of coordination complexes containing relatively basic ligands are governed by rate laws with terms involving a positive dependence upon the concentration of hydrogen ion in addition to the generally observed inverse dependences. Swaddle and King[2] found that the rate law

$$-\frac{\mathrm{d}\ln[CrN_3^{2+}]}{\mathrm{d}t} = k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$$

correlates the rate of aquation of pentaaquoazidochromium(III) ion[3]

$$Cr(OH_2)_5N_3^{2+} + H_3O^+ = Cr(OH_2)_6^{3+} + HN_3$$

over the range of hydrogen ion concentration 10^{-3}–1 *M*. The present paper deals with studies at 30° which extend the acidity range to 11 *M* perchloric acid.

The purpose of extending the acidity range was to determine, if possible, the basicity of azidochromium(III) ion[4,5] and to investigate the appropriateness of using the Hammett acidity function in correlating the basicity of a basic coordination complex of charge 2+. In this study both spectrophotometric and kinetic data have been employed to seek these objectives. The protonation of hydrazoic acid in concentrated perchloric acid also has been studied at 30° by evaluation of the Henry's law constant for hydrogen azide in such solutions.

Experimental Methods

Equipment and Reagents. Spectrophotometric measurements were made with a Cary Model 15 spectrophotometer. In the study

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(1) Taken in part from the Ph.D. Thesis of J. C. T., University of Colorado, 1970. This work was supported by National Science Foundation Grant No. GP7185-X.

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

(3) In general, the complete coordination shell will not be specified; this species will be called simply azidochromium(III) ion.

(4) Appreciable protonation of other azide complexes has been observed.[5]

(5) (a) $Co(CN)_5N_3^{3-}$: A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1, 583 (1962); (b) *trans*-$Co(en)_2Cl(N_3)^+$: P. J. Staples, *J. Chem. Soc.*, 7320 (1965); (c) $Cr(NH_3)_5N_3^{2+}$, $Co(NH_3)_5N_3^{2+}$, and $Rh(NH_3)_5N_3^{2+}$: *ibid.*, *A*, 2731 (1968); (d) $Rh(NH_3)_5N_3^{2+}$: C. S. Davis and G. C. Lalor, *ibid.*, *A*, 445 (1970).

of kinetics of reactions with a half-time of less than 1.5 hr, a thermostated cell compartment was used. (For slower reactions, portions of the thermostated reaction mixture were withdrawn at various times for prompt measurement of light absorption.)

Reagent grade chemicals were used without further purification.

Solutions containing azidochromium(III) ion were prepared essentially as described earlier.[2] Analyses of the chromium(III) species eluted with 1.0 *M* perchloric acid (which followed elution with 0.10 *M* perchloric acid) gave azide to chromium(III) ratios of 1.00 ± 0.02. Solutions of separated azidochromium(III) ion prepared in this way were used promptly.

Analyses. Analyses for the total salt normality in solutions of lithium perchlorate, sodium perchlorate, or calcium perchlorate were performed by titration with standardized base after the salt solution was passed through a column of cation-exchange resin in the hydrogen ion form. Azide ion was analyzed by oxidation with excess cerium(IV) followed by titration of the excess with iron(II).[6] At the low amounts of azide ion being analyzed (0.040–0.13 mmol), the analysis was accurate to ±3%. Azide ion was analyzed also by spectrophotometric measurements at 260 and 271 nm; the molar absorptivity values (reported later in this paper for 260 nm) show a mild dependence upon the concentration of strong acid. Chromium(III) species were analyzed for chromium by conversion to chromate ion with peroxide in alkaline solution. Chromate ion then was determined spectrophotometrically at 372 nm.[7]

Analysis for the changing concentration of azidochromium(III) ion in the kinetic experiments was carried out by spectrophotometric measurements. Most measurements were made at 271 nm, but some were made at 250, 290, and 585 nm. Obedience of azidochromium(III) ion to Beer's law in solutions of 1 and 10 *M* perchloric acid was checked carefully at 271 and 585 nm.

Nitrogen Purging of Hydrogen Azide from Solution. Hydrogen azide was purged from solution with nitrogen using a gas washing bottle fitted with a fritted Pyrex membrane. The hydrogen azide then was trapped in a solution containing base. The rate of gas flow from the trap was measured using a soap bubble flowmeter.[8]

Experimental Results

The Spectrophotometric Study of the Protonation of Azidochromium(III) Ion. The spectra of solutions of azidochromium(III) ion in perchloric acid (1.00–10.50 *M*) were studied as a function of time. Extrapolation of the observed absorbance to the time of mixing of the acid and the complex allowed evaluation of the apparent molar absorptivity of azidochromium(III) ion with no complications due to aquation. Figure 1 shows the spectrum measured for solutions with different concentrations of perchloric acid. To demonstrate the reversibility of the spectral dependence upon acidity, two solutions of azidochromium(III) ion in 5.00 *M* perchloric acid were compared. In one, the concentration of acid was raised to 5.00 *M* from the value existing in the stock solution of complex; in the other, it was raised to 10.00 *M* followed by a twofold dilution. Over the entire spectral range (240–640 nm), these two solutions gave the same molar absorptivity within approximately 2%. A number of solutions with different acidities were measured at 585 and 271 nm. The data obtained at 585 nm, presented in Table I, were more amenable to treatment to obtain a value of K_1, the acid dissociation constant for hydrogenazidochromium(III) ion ($Cr(OH_2)_5N_3H^{3+}$). This wavelength (585 nm) is essentially a maximum in absorbance at all of the acidities studied. (The spectral changes at 271 nm[9] were qualitatively consistent with those at 585 nm, but quantitative treatment of these data was less successful. Although 271 nm is an absorption maximum for azidochromium(III) ion, it is not for hydrogenazidochromium(III) ion. Interactions of azidochromium(III) and/or hydrogenazidochromium(III) with perchlorate ion may have mild spectral manifestations in the ultraviolet region.)

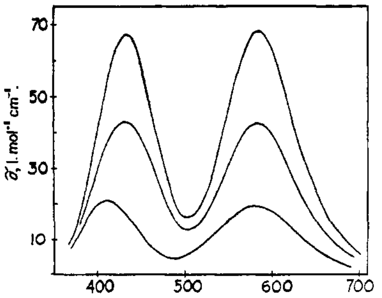

Figure 1. The visible spectra of azidochromium(III) ion in solutions of various concentrations of perchloric acid: top, 1.00 *M* $HClO_4$; middle, 6.8 *M* $HClO_4$; bottom, 10.0 *M* $HClO_4$. (These solutions contain approximately 0, 50, and 100% protonated azidochromium(III) ion.)

Table I. The Molar Absorptivity for Azidiochromium(III) Ion at 585 nm in Aqueous Perchloric Acid[a]

$[H^+]$, *M*	$\tilde{a}$, l. mol^{-1} cm^{-1} Obsd	$\tilde{a}$, l. mol^{-1} cm^{-1} Calcd[b]	$[H^+]$, *M*	$\tilde{a}$, l. mol^{-1} cm^{-1} Obsd	$\tilde{a}$, l. mol^{-1} cm^{-1} Calcd[b]
1.00	67.5	67.5	7.25	34.1	32.3
2.00	67.2	67.4	7.50	30.1	28.9
3.00	67.0	67.2	8.00	24.9	23.6
4.00	66.9	66.6	8.50	20.8	20.6
5.00	65.9	64.6	9.00	19.1	19.2
5.50	60.2	62.1	9.25	19.0	18.8
6.00	55.9	57.4	9.50	18.6	18.5
6.50	48.9	48.6	10.00	18.0	18.2
7.00	38.9	37.7	10.50	18.0	18.1

[a] Temperature = 30°. Molar absorptivity values obtained by extrapolation of observed values to zero time. [b] Calculated using the equation $\bar{a} = [67.5 + 6.65 \times 10^{-3}h_0]/[1 + 3.7 \times 10^{-4}h_0]$.

The Stoichiometry of the Decomposition Reaction. Because several decomposition reactions of azidochromium(III) ion are possible, it was necessary to establish the stoichiometry of the reaction. This was done by analysis for azide in a solution in which the extent of decomposition was greater than 99.9%. Azide ion can be analyzed spectrophotometrically at 260 and 271 nm (as already described) in the presence of hydroxylamine and hydrazine, possible products of side reactions, because these latter species are essentially transparent in this spectral region. The azide ion in solution after complete aquation was analyzed also by the nitrogen purging procedure already described. In a number of experiments at 2, 4, 6, 8, and 10 *M* perchloric acid, the azide recovered was

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(6) J. W. Arnold, *Ind. Eng. Chem., Anal. Ed.*, 17, 215 (1945).

(7) G. W. Haupt, *J. Res. Nat. Bur. Stand., U. S.*, 48, 414 (1952).

(8) A. I. M. Keulemans, "Gas Chromatography," 2nd ed, Reinhold, New York, N. Y., 1959, p 58.

(9) The values of $\tilde{a}$ obtained at 271 nm are [given as C_{HClO_4} (*M*), $\tilde{a}$ (l. mol^{-1} cm^{-1})]: 1.00, 3790; 2.00, 3785; 3.00, 3780; 4.00, 3760; 5.00, 3560; 5.50, 3340; 6.00, 2960; 6.50, 2340; 7.00, 1820; 7.25, 1390; 7.50, 1070; 8.00, 674; 8.50, 380; 9.00, 216; 9.25, 185; 9.50, 146; 10.00, 136; 10.50, 120; and 11.00, 119.

equal, within a few per cent, to the amount of azidochromium(III) ion present initially. (If hydroxylamine or hydrazine had been produced, they would not have escaped from the acidic solution, and their reducing capacity would not have been determined in the cerium(IV) titration.)

The Rate of Aquation of Azidochromium(III) Ion. Results of the kinetic studies carried out in perchloric acid solution are presented in Table II. Values of the first-order rate constant, k, presented in this table were determined in each experiment from the slopes of the nicely linear plots of log $(A_t - A_\infty)$ *vs.* time or log $(A_t - A_{t+\tau})$ *vs.* time. (The subscript to the absorbance A denotes the time; τ is the constant time interval ($>2t_{1/2}$) of the Guggenheim method[10] for treating first-order kinetic data.) Each value reported is the average of two independent experiments. The table includes values of k_{CrN_3H}, which is equal to $k(K_1 + h_0)/h_0$. This is the pseudo-first-order rate constant for the rate law written in terms of the concentration of protonated azidochromium(III): $-d[CrN_3]_T/dt = k_{CrN_3H} \cdot [CrN_3H^{3+}]$. The results of kinetic experiments carried out at constant ionic strength are presented in Table III.

Table II. The First-Order Rate Constant, k,[a] for Aquation of Azidochromium(III) Ion in Perchloric Acid Solution at 30°

$[H^+]$, M	10^6k, sec^{-1}	$10^4k_{CrN_3H}$, sec^{-1}	$[H^+]$, M	10^6k, sec^{-1}	$10^4k_{CrN_3H}$, sec^{-1}
1.00	1.63	24.6[b]	7.50	561	7.20
2.00	5.79	25.5[b]	8.00	576	6.49
3.00	16.6	26.6	8.50	518	5.46
4.00	44.2	23.1	9.00	452	4.63
5.00	120.0	20.3	9.25	433	4.40
5.50	190.0	17.4	9.50	402	4.06
6.00	280.0	13.7	10.00	354	3.55
6.50	401.0	10.6	10.50	316	3.16
7.00	501.0	8.33	11.00	279	2.79
7.25	540.0	7.61			

[a] $k = 2.303\Delta \log (A_t - A_\infty)/\Delta t = 2.303\Delta \log (A_t - A_{t+\tau})/\Delta t$. [b] In calculation of k_{CrN_3H} at the two lowest acidities studied, the value of k is corrected for the contribution from the pathway which is zero order in hydrogen ion ($k_0 = 1.15 \times 10^{-7}$ sec^{-1} [2]). The value of k_{CrN_3H} is obtained from the value of k by dividing by $h_0/(K_1 + h_0)$.

The Vapor Pressure of Hydrogen Azide over Aqueous Hydrazoic Acid. The equipment (already described) for purging volatile components from an aqueous solution was used to determine the vapor pressure of hydrogen azide over aqueous solutions of hydrazoic acid. These experiments, involving aqueous salt and aqueous perchloric acid solutions, were performed to evaluate the basicity of hydrazoic acid. Plots of log (C/C_0) *vs.* volume of purging gas passed were linear; the final observed values of C/C_0 ranged from 0.43 to 0.11. (The stoichiometric concentrations of azide at times 0 and t are represented by C_0 and C, respectively.) (In an experiment at 6 M perchloric acid and a flow rate of 3 l./hr of nitrogen, the observed values of C/C_0 and values calculated from the equation log $(C/C_0) = -0.0289$ $(V_t - 0.06$ l.) are (given as V_t, $(C/C_0)_{obsd}$, $(C/C_0)_{calcd}$): 3.0, 0.819, 0.822; 9.0, 0.550, 0.552; 15.0, 0.375, 0.370; 21.0, 0.252, 0.248; 27.0, 0.170, 0.167; and 33.0, 0.109, 0.112.) Empirical correlation of the data was made with the equation

$$-\log C_t/C_0 = m(V_t - V_0)$$

in which V_t is the volume of nitrogen gas passed through the solution at time t. The volume V_0 is incorporated in the equation to remove the constraint that the linear plots must pass through the origin. The slope of the line is related, by a simple derivation, to the Henry's law constant, κ' ($\kappa' = P_{HN_3}/C_{NH_3}$)

$$\kappa' = 2.3RTV_{soln}m$$

This relationship depends, of course, upon equilibrium being established between the two phases. Studies as a function of the flow rate of the nitrogen gas were carried out at several acidities. At 2.00 M perchloric acid, $\kappa' = 0.091$ and 0.090 l. atm mol^{-1} at 6 l. hr^{-1}, 0.095 and 0.088 at 3 l. hr^{-1}, and 0.094 at 1.5 l. hr^{-1}. It will be assumed that equilibrium is essentially established at a flow rate of 6.0 l. hr^{-1}, the rate for most experiments. Values of log κ' *vs.* perchlorate concentration are presented in Figure 2. The common intercept of the three linear plots is $\kappa' = 0.100$ l. atm mol^{-1}, the Henry's law constant for hydrazoic acid at 30°. This value is close to that for hyrogen cyanide ($\kappa' = 0.114$ l. atm mol^{-1} at 25°).[11]

Table III. The First-Order Rate Constant, k, for Aquation of Azidochromium(III) Ion in Perchloric Acid–Perchlorate Salt Solutions of Constant Ionic Strength[a]

	10^6k, sec^{-1}		
$[H^+]$, M	$I = 2.00$ M	$I = 4.00$ M	$I = 8.00$ M
1.00	2.55[b]	5.74[b]	32.0[b]
	3.06[c]	10.65[c]	
2.00	5.79	14.2[b]	80.2[b]
		21.8[c]	
3.00		25.6[b]	153[b]
		32.4[c]	
4.00		44.2	256[b]
8.00			576

[a] 30°. [b] Sodium perchlorate used to maintain ionic strength. [c] Lithium perchlorate used to maintain ionic strength.

Each electrolyte has a characteristic effect on the solubility of hydrogen azide, and the slopes of the lines in Figure 2 identify the Setschenow coefficients for each electrolyte: $\mathcal{S} = 0.0385, 0.0178$, and -0.0148 l. $equiv^{-1}$ for sodium perchlorate, calcium perchlorate, and perchloric acid, respectively. For perchloric acid, only the data at concentrations less than 6 M were included in this correlation. The data at perchloric acid concentrations greater than 8 M show the effect of protonation of hydrazoic acid.

The Spectrophotometric Study of Hydrazoic Acid in Concentrated Perchloric Acid. The light absorption of hydrazoic acid at 260 nm was measured at room tem-

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(10) E. A. Guggenheim, *Phil. Mag.*, [7] 2, 538 (1926).

(11) "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1933, p 255.

perature as a function of acidity. For perchloric acid solutions, values of $\tilde{a}$ as a function of concentration of perchloric acid are [given as molarity of acid, $\tilde{a}$ (l. mol^{-1} cm^{-1})]: 1.0, 43.5; 2.0, 42.8; 4.0, 42.4; 6.0, 41.6; 8.0, 40.8; and 10.0, 38.4. For sulfuric acid solutions, the values are: 0.76, 43.8; 1.68, 43.3; 3.53, 42.3; 5.96, 41.0; 8.85, 39.8; 11.3, 38.8; 12.5, 35.8; 14.3, 24.6; and 16.1, 9.5.

Interpretation of Results

Although each of the electrolytes studied (sodium perchlorate, calcium perchlorate, and perchloric acid) has an effect upon the Henry's law constant for hydrogen azide in its aqueous solutions, the effect of perchloric acid is unusual. Figure 2 shows the deviation of points from the linear plot at >8.0 *M* perchloric acid. If this deviation is ascribed to protonation of hydrazoic acid, the expected relationship is

$$\kappa/\kappa' - 1 = h_0/K_4$$

in which κ and κ' are the Henry's law constants defined by the equations $P_{HN_3} = \kappa[HN_3]$ and $P_{HN_3} = \kappa' C_{HN_3}$, respectively, h_0 is the acidity function defined by Hammett indicator bases, $h_0 = [H^+]\gamma_{H^+}\gamma_B/\gamma_{BH^+}$ [$h_0 = \log^{-1}(-H_0)$],[12] and K_4 is the acid dissociation constant for $H_2N_3^+$ ($K_4 = h_0[HN_3]/[H_2N_3^+]$). The values of κ for particular concentrations of perchloric acid were obtained from the extended linear plot in Figure 2; these are the values of the Henry's law constant expected in the absence of protonation. The data at 9.40, 10.0, and 11.0 *M* perchloric acid treated in this way yield calculated values of $10^{-6}K_{4'} = 1.2 \pm 0.7$, 1.8 ± 0.5, and 4.7 ± 0.7, respectively. The dashed line in Figure 2 is that calculated based upon $K_4 = 4 \times 10^6$. Bak and Praestgaard[13a] have studied the distribution of hydrazoic acid between concentrated sulfuric acid (77.96–84.56%) and chloroform; on the basis of the variation of the distribution constant with acidity of the aqueous phase, they evaluated this acid dissociation constant to be 1.6×10^6 at 25°. Because of the difference of acidity range studied (the highest h_0 studied in the present work was $\sim 4.1 \times 10^6$; the acidities studied in ref 13a range from $h_0 = \sim 3.6 \times 10^6$ to 3.5×10^7) and the nature of the anion (perchlorate in the present study and sulfate in ref 13a), the agreement between these two studies is considered adequate. As suggested by Bak,[13] the protonation of hydrazoic acid is relevant to the mechanism of the Schmidt reaction.[14]

The mild dependence upon concentration of strong acid of the light absorption at 260 nm by hydrazoic acid does not appear to be related simply to the protonation equilibrium. Accepting the interpretation of the vapor pressure study and the solvent distribution study, one must conclude that the molar absorptivity of hydrazoic acid and its conjugate acid are approximately the same at 260 nm, and that these quantities depend mildly upon the concentration of electrolyte.

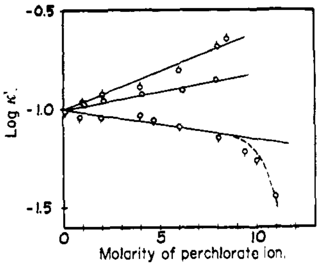

Figure 2. The Henry's law constant for hydrazoic acid in electrolyte solution (30°); $\kappa' = P_{HN_3}/C_{HN_3}$: ♁, sodium perchlorate; ○, calcium perchlorate; ♀, perchloric acid. The straight lines are the linear Setschenow plots, $\log \kappa'/\kappa_0' = \mathcal{S}[ClO_4^-]$. The dashed line was calculated for $K_4 = 4 \times 10^6$.

The dependence upon acid concentration of light absorption at 585 nm by azidochromium(III) ion is nicely consistent with the protonation equilibrium to form hydrogenazidochromium(III) ion. Although the acidity function h_0 is not strictly appropriate for correlation of the protonation of a base of charge 2+, it is being used in the absence of a more appropriate acidity function based upon the protonation of bases of the type in question (octahedral hydrated complexes of charge 2+). The spectral data presented in Table I are correlated nicely with

$$K_1 = [CrN_3^{2+}]h_0/[CrN_3H^{3+}] = 2.7 \times 10^3$$

and the molar absorptivities $a_2 = 67.5$ l. mol^{-1} cm^{-1} and $a_3 = 18.0$ l. mol^{-1} cm^{-1}, where the subscripts refer to the charge on the species. This equation has the expected form if $\gamma_{2+}\gamma_+[H^+]/\gamma_{3+} \cong h_0$, where the subscripts to γ refer to the charge on the species. Values of $\tilde{a}$ calculated using these parameters

$$\tilde{a} = (a_2 + a_3 h_0/K_1)/(1 + h_0/K_1)$$

are given in Table I. The average difference between observed and calculated values of $\tilde{a}$ is 1.8%. An acid dissociation constant of $K_1 = 2.7 \times 10^3$ corresponds to 50% protonation at $h_0 = 2.7 \times 10^3$ (or in $\sim$6.8 *M* perchloric acid). Figure 1 shows the spectrum of azidochromium(III) ion in a 6.8 *M* perchloric acid solution. If only the two species azidochromium(III) ion and hydrogenazidochromium(III) ion are present at appreciable concentrations in the acidity range correlated by this equilibrium constant, this spectrum should be the average of the spectrum of azidochromium(III) ion (determined at 1.0 *M* perchloric acid) and the spectrum of hydrogenazidochromium(III) ion (determined at 10.0 *M* perchloric acid). In the spectral regions where the best data were obtained (away from regions of minima), the values of $\tilde{a}$ calculated as the average of the values observed in 1.0 and 10.0 *M* perchloric acid differ from the values observed in 6.8 *M* perchloric acid by only 2.2%. (This is the average difference at 30 wavelengths in the regions 700–520, 440–370, and 270–250 nm.)

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[12] M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957). The values for H_0 for 25° tabulated in this review were used in interpretation of the present work despite the 5° difference in temperature. The H_0 function does not change rapidly with changing temperature: A. I. Gel'bschtein, G. C. Shcheglova, and M. I. Tempkin, *Russ. J. Inorg. Chem.*, 1, 282, 506 (1956).

[13] (a) T. A. Bak and E. L. Praestgaard, *Acta Chem. Scand.*, 11, 901 (1957); (b) T. A. Bak, *ibid.*, 8, 1733 (1954).

[14] H. Wolff, *Org. React.*, 3, 307 (1946).

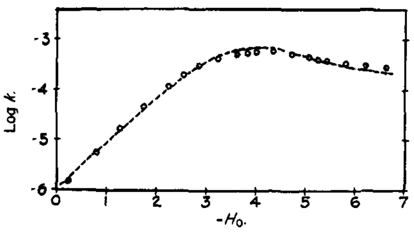

Figure 3. The dependence of rate upon acidity, $-\log k$ *vs.* $-H_0$. The dashed line was calculated using the parameters presented in the text.

Striking features of the kinetic data are: (1) the remarkable increase in the pseudo-first-order rate coefficient with an increase in acidity at the lower concentrations of acid (the value of k increases by a factor of 10.2 between 1 and 3 M, over which range h_0 increases by a factor of 10.3); (2) the decrease in the pseudo-first-order rate coefficient with increasing acidity at perchloric acid concentrations greater than $\sim$8.0 M. This feature is analogous to that observed by Deutsch and Taube[15] in their study of acetatochromium(III) ion in concentrated perchloric acid and by Yates and McClelland[16] in their study of the hydrolysis of esters in concentrated sulfuric acid. These authors attribute the decrease in rate coefficient at high acid concentrations to a proportionality between the rate and the activity of water.

Before attempting a quantitative correlation of the kinetic data with the activity of water, it is appropriate to take into account the protonation equilibrium. Since the rate is approximately proportional to h_0 at low acidities, it is convenient to express the rate law in terms of the concentrations of hydrogenazidochromium(III) ion

$$-\mathrm{d}[\mathrm{CrN_3}]_\mathrm{T}/\mathrm{d}t = k_{\mathrm{CrN_3H}}[\mathrm{CrN_3H^{3+}}]$$

Values[17] of $k_{\mathrm{CrN_3H}}$ (obtained from the empirical values of k: $k_{\mathrm{CrN_3H}} = k(K_1 + h_0)/h_0$) which are presented in Table II decrease with decreasing activity of water. The values, however, *do not approach zero as the activity of water approaches zero.* A plot of $k_{\mathrm{CrN_3H}}$ *vs.* a_w is approximately linear with an intercept (at $a_\mathrm{w} = 0$) of 1.8×10^{-4} sec^{-1} and a slope of 2.7×10^{-3} sec^{-1}. Figure 3 is a plot of log k *vs.* $-H_0$ showing experimental values of k and the theoretical line calculated from the rate law

$$k \equiv \frac{-\mathrm{d}\ln[\mathrm{CrN_3}]_\mathrm{T}}{\mathrm{d}t} = \left\{\frac{h_0}{K_1 + h_0}\right\}(k_2 a_\mathrm{w} + k_3)$$

with $K_1 = 2.70 \times 10^3$, $k_2 = 2.7 \times 10^{-3}$ sec^{-1}, and $k_3 = 1.8 \times 10^{-4}$ sec^{-1}. Values of k calculated using these parameters agree with the observed values with an average deviation of 11%. This deviation is larger than the expected experimental error. In addition, the pattern of deviations is not random. We attribute this to mild failure of the assumptions necessary to reduce the rate law derivable from the proposed mechanism (to be given) to this simpler form.

The decrease in the value of $k_{\mathrm{CrN_3H}}$ with increasing concentration of perchloric acid (decreasing activity of water) is qualitatively consistent with rate laws in addition to that given above. If the important species in solution were azidochromium(III) ion, hydrogenazidochromium(III) ion, and a perchlorate ion pair of the latter species, and the only important transition state had the composition $\{\mathrm{Cr(OH_2)_5N_3H^{3+}}\}^{\ddagger}$, the rate law would be

$$-\frac{\mathrm{d}\ln[\mathrm{CrN_3}]_\mathrm{T}}{\mathrm{d}t} = \frac{kh_0}{K_1 + h_0 + \beta a_{\mathrm{HClO_4}}}$$

in which $a_{\mathrm{HClO_4}}$ is the activity of perchloric acid.[18] (In deriving this rate law, it is assumed that $[\mathrm{CrN_3H^{3+}}\cdot\mathrm{ClO_4^-}] \propto [\mathrm{CrN_3^{2+}}]a_{\mathrm{HClO_4}}$.) This rate law is not consistent with the kinetic data if the value of K_1 is taken as 2.70×10^3, the value obtained spectrophotometrically. However, with $k = 5.9 \times 10^{-4}$ sec^{-1}, $K_1 = 630$, and $\beta = 1.37 \times 10^{-3}$, the fit is good, the average difference between observed values of the pseudo-first-order rate coefficient and the calculated values being 5.5%. This value of K_1 is quite inconsistent, however, with the spectrophotometric data. This value of K_1 implies 50% protonation at $h_0 = 630$, where the value of $\tilde{a}$ has changed only $\sim$20% of the way from the value characteristic of azidochromium(III) ion to that characteristic of the protonated form.[19]

The kinetic data obtained in solutions of constant ionic strength are consistent with the use of h_0 in correlation of the acidity dependence of the rate. A plot of k *vs.* [H$^+$] for the studies in perchloric acid–lithium perchlorate solutions of ionic strength 4.00 M is nicely linear; the corresponding plot for perchloric acid–sodium perchlorate solutions is curved. Plots of h_0 *vs.* [H$^+$] for perchloric acid–perchlorate salt solutions of ionic strength 6.0 M have analogous forms;[20] h_0 *vs.* [H$^+$] is linear for perchloric acid–lithium perchlorate solution but shows curvature for perchloric acid–sodium perchlorate solutions.

Discussion

Since azide ion is much more basic than water, it is assumed that azide ion, not water, is the site of proton-

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[15] E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

[16] K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, **89**, 2686 (1967).

[17] At 1.0 and 2.0 M perchloric acid, 7.1 and 2.0%, respectively, of the aquation occurs by a pathway with a transition state of the composition $\{\mathrm{Cr(OH_2)_5N_3^{2+}}\cdot n\mathrm{H_2O}\}^{\ddagger}$. These percentages, calculated using the data from ref 2, were subtracted from the experimental values of k before calculation of the value of $k_{\mathrm{CrN_3H}}$.

[18] Values of the activity of perchloric acid to a concentration of 16 m are given in R. Parsons, "Handbook of Electrochemical Constants," Butterworths, London, 1959, p 29. For higher concentrations, values were estimated using the Gibbs-Duhem equation and values of the activity of water in such concentrated solutions: H. Wai and K. Yates, *Can. J. Chem.*, 47, 2326 (1969).

[19] Another form of rate law which is qualitatively consistent with the observed decrease in the pseudo-first-order rate coefficient at high concentrations of perchloric acid is

$$-\frac{\mathrm{d}\ln[\mathrm{CrN_3}]_\mathrm{T}}{\mathrm{d}t} = \frac{kh_0}{K_1 + h_0 + \alpha h_0^2}$$

This rate law, which has approximately the form consistent with the predominant species $\mathrm{CrN_3^{2+}}$, $\mathrm{CrN_3H^{3+}}$, and $\mathrm{CrN_3H_2^{4+}}$ and a transition state $\mathrm{CrN_3H^{3+}}$ (water of solvation not shown), does not fit the data adequately, and it will not be considered further.

[20] J. S. Day and P. A. H. Wyatt, *J. Chem. Soc. B*, 343 (1966).

ation of azidochromium(III).[21] As expected, the acid strength of hydrazoic acid is increased upon coordination to chromium(III). There is a $\sim 10^8$-fold difference between the dissociation constants for hydrazoic acid[22] and the protonated chromium(III) azide species

$$HN_3 \rightleftharpoons H^+ + N_3^- \qquad K = 2.8 \times 10^{-5}$$

$$(H_2O)_5CrN_3H^{3+} \rightleftharpoons H^+ + (H_2O)_5CrN_3^{2+}$$
$$K = 2.7 \times 10^3 \quad (30°)$$

The corresponding factor for acetic acid and acetic acid coordinated to chromium(III) is $\sim 3 \times 10^6$.[15,23] The acid strengthening effect of the pentaaquochromium(III) moiety is much greater than that of the pentacyanocobalt(III) moiety (for $Co(CN)_5N_3H^{2-}$, $K_a = 0.21$ at 40°, $I = 1$ *M*);[5a] because of the difference of net charge, this is expected. The acid strengthening effect of the pentaamminecobalt(III) moiety with charge 3+ is comparable to that of pentaaquochromium(III); for $Co(NH_3)_5N_3H^{3+}$, $K_a \cong 6 \times 10^2$ [5c] (or $K_a \cong 1.5 \times 10^3$ if the activity of water is incorporated into the rate law). Although the rate law for the oxidation–reduction reaction of hydrazoic acid and manganese(III) ion has been interpreted[24] in terms of a manganese(III) azide complex being appreciably protonated at 2.5 *M* perchloric acid, the data, which shed light only on the transition state composition, do not justify this conclusion. Another comparison of acid strengths is that of hydrogenazidochromium(III) ion ($K_1 = 2.7 \times 10^3$) with dihydrogenazide cation, $H_2N_3^+$ ($K_4 \cong 4 \times 10^6$). It may seem surprising that hydrogen ion (of charge 1+) has an approximately 10^3-fold greater acid strengthening effect upon hydrazoic acid than does chromium(III) (of charge 3+), but this trend is shown by other examples: hydrogen ion has a greater acid strengthening effect on water ($K_{H_3O^+} = 55$) than does chromium(III) ($K_{Cr(OH_2)_6^{3+}} = 1.5 \times 10^{-4}$).[25]

The ratio of the equilibrium constants for the two stepwise acid dissociation reactions of dihydrogen azide cation is very large ($\sim 10^{11}$); a large value is observed also for hydronium ion, another cationic acid ($K_1 = 55$, $K_2 = 1 \times 10^{-14}$). On the other hand, lower values of the ratio of successive stepwise acid dissociation constants are observed for neutral acids; for hydrogen sulfide, the ratio is $\sim 10^5$.

The pattern of the Setschenow coefficients for the influence of sodium perchlorate, calcium perchlorate, and perchloric acid upon hydrazoic acid is the same as the influence shown by these electrolytes upon most nonelectrolytes, and not that associated with salt effects upon hydrocyanic acid.[26] Since the unusual pattern of salt effect observed for hydrogen cyanide is attributed to the fact that it raises the dielectric constant of an aqueous solution, it can be concluded that addition of hydrogen azide to aqueous solution lowers the dielectric constant of the solution.

The empirical rate law with which the data have been correlated is consistent with a mechanism involving two pathways (1 and 2) for aquation of hydrogenazidochromium(III) ion

$$Cr(OH_2)_5N_3H^{3+} + H_2O \xrightarrow{k_2} Cr(OH_2)_6^{3+} + HN_3 \qquad (1)$$

$$\begin{array}{l} Cr(OH_2)_5N_3H^{3+} \xrightarrow{k_3} Cr(OH_2)_5^{3+} + HN_3 \\ Cr(OH)_2)_5^{3+} + H_2O \longrightarrow Cr(OH_2)_6^{3+} \end{array} \qquad (2)$$

Since the reaction was nicely first order over the extent studied (over two half-times), there is no evidence for the reverse of the first step in pathway 2. (No experiments were performed, however, in which hydrazoic acid was added to the reaction mixtures.) The rate law derived from this mechanism is

$$\frac{-\mathrm{d}\ln[CrN_3]_T}{\mathrm{d}t} = \left(\frac{h_0}{K_1 + h_0}\right)\left(k_2^0 a_w \frac{\gamma_{3+}}{\gamma_{A\ddagger}} + k_3^0 \frac{\gamma_{3+}}{\gamma_{B\ddagger}}\right)$$

The quotient $h_0/(K_1 + h_0)$ is a simplification already justified on the basis of the spectrophotometric study of protonation. If the quotients of activity coefficients $\gamma_{3+}/\gamma_{A\ddagger}$ and $\gamma_{3+}/\gamma_{B\ddagger}$ are independent of medium, the empirical rate law results, with $k_2 = k_2^0\gamma_{3+}/\gamma_{A\ddagger}$ and $k_3 = k_3^0\gamma_{3+}/\gamma_{B\ddagger}$. Some variation of these activity coefficient ratios with reaction medium may be responsible for the imperfect correlation of the data with the rate law. Since correlation of the equilibrium data with h_0 is more successful than is the correlation of the kinetic data, it is reasonable to attribute the flaws in the latter correlation to the assumptions regarding medium independence of the quotients involving the activity coefficient of the transition states, $\gamma_{A\ddagger}$ and $\gamma_{B\ddagger}$. Mild interaction of either or both transition states with perchlorate ion may be responsible for this proposed medium dependence. It is known that use of the h_0 acidity scale for correlation of kinetic and equilibrium data where this acidity function is not strictly appropriate may be reconciled by incorporation of water molecules into the equations for the net activation process and the net reactions.[27] The discussion of mechanism which has been given ignores, of course, this uncertainty. Pathway 1 is the SN2 pathway and pathway 2 is the SN1 pathway. The relative contribution of the two pathways varies with the activity of water. In the most acidic solution studied ($a_w = 0.018$), the SN1 pathway accounts for ~77% of the aquation. In the hypothetical situation of hydrogenazidochromium(III) ion

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(21) There is evidence, however, for protonation of hexaaquochromium(III) ion to form a transition state in the work of T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, **5**, 1100 (1966). This proton magnetic resonance study in nitric acid solution ($[H^+] < 2$ *M*) does not, however, disclose appreciable protonation in this concentration range. A transition state of the composition $\{Cr(OH_2)_5N_3^{2+}\cdot H^+\}^\ddagger$ plays a role in the exchange of protons between solvent water and coordinated water protons: R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, **9**, 2639 (1970). This latter study, carried out to acidities as high as ~4 *m* perchloric acid, did not lead to a value for K_1.

(22) M. Quintin, *C. R. Acad. Sci.*, **210**, 625 (1940).

(23) In calculation of the above-cited figure, the concentration acid dissociation equilibrium quotient for hydrogenacetatochromium(III) ion reported by Deutsch and Taube,[15] $K \cong 4$ for ionic strength 4 *M*, was expressed in terms of h_0, under these circumstances $K \cong 53$.

(24) C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1622 (1968).

(25) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(26) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952); W. F. McDevit and F. A. Long, *J. Amer. Chem. Soc.*, **74**, 1773 (1952); G. Akerlof, *ibid.*, **57**, 1196 (1935).

(27) E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964); J. F. Bunnett and F. P. Olson, *Can. J. Chem.*, **44**, 1899 (1966); **44**, 1917 (1966).

aquating in a solution with $a_w = 1$, the SN1 pathway would account for ~6.4% of the aquation. Hydrogen azide is a good leaving group, and it is reasonable that an SN1 pathway would make a contribution to the aquation. Iodochromium(III) ion, which aquates more slowly[28] than hydrogenazidochromium(III) ion, does so predominantly by the SN1 mechanism.[29]

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

[29] S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, **92**, 1215 (1970).

Influence of Back Bonding on the Hydrate–Carbonyl Equilibrium for 4-Formylpyridine as Ligand

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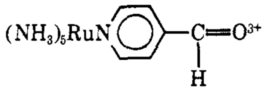
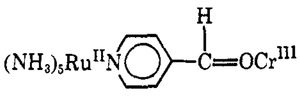
Abstract: Absorption spectra focusing on the πd–π* transition, infrared spectra, and nmr spectra agree in supporting the conclusion that at 25° the pentaammineruthenium(III) complex of 4-formylpyridine is largely (>90%) hydrated, while the corresponding Ru(II) complex is largely (>90%) in the carbonyl form. The effect on the extent of hydration of changing the oxidation state of the ruthenium is attributed to back bonding, which is greater for Ru(II) than for Ru(III) and greater when the ligand is in the carbonyl rather than in the hydrated form. Reduction of the Ru(III) complex by V^{2+} acting as an outer-sphere reducing agent produces the Ru(II) complex in the hydrated form (>95% at 6.5°). The dehydration of the complex was studied as a function of acidity, and Ru(II) is found to reduce the rate of dehydration, as compared to the free ligand, by a factor of 70. Ruthenium(III) increases the rate of dehydration of the Ru(II) complex, and its effect is attributed to electron-transfer catalysis.

The present study grew out of an interest in the reaction of *p*-formylbenzoatopentaamminecobalt(III) with Cr(II), in the course of which an intermediate product,[2] presumed to be the aldehyde complex of Cr(III), was encountered. We felt that by using the Ru(III) complex



as oxidant, we would have a ready means of following the decay of the intermediate aldehyde complex



which, by analogy with the other systems, was expected to form when Cr^{2+} was the reductant. It is known[3] that the πd–π* charge-transfer transitions for Ru(II)–pyridine complexes are very sensitive to substitution on the pyridine ring, and thus the release of Cr(III) from the aldehyde could easily be followed. Events showed that the Ru(II)-containing intermediate is a poor model for a simple aldehyde complex of a metal ion because Ru(II) exerts a profound and specific effect on the aldehyde function. Our interest then turned to exploring the effect of coordination to nitrogen on the behavior of the aldehyde in the para position. The results obtained from this study form the subject of this communication.

The major results deal with the degree of hydration of the ligand when it is coordinated to Ru(II), Ru(III), or H^+. Measurements of absorption spectra covering the visible region, infrared spectra, and nmr spectra have proved to be useful in estimating the equilibrium constant for the hydration reaction. Data on the rate of dehydration of the Ru(II) complex were obtained by using the reaction of $V(H_2O)_6^{2+}$ with the Ru(III) complex to generate the Ru(II) complex in an unstable state with respect to the aldehyde hydration equilibrium.

Related, but of secondary interest, are data on the rate of reduction of the Ru(III) complex. Those with Cr(II) as reductant show some special and unexplained features, undoubtedly related to the capacity of Cr(II) to reduce by "capturing" a ligand derived from the oxidant, but they also show features which correlate with the dehydration reaction observed for V(II) as reductant.

Experimental Section

Reagents. All common chemicals were of reagent grade and were used without further purification unless otherwise noted. Tap distilled water was redistilled from alkaline permanganate. Water-pumped, compressed nitrogen was deoxygenated by passing it through two gas-scrubbing bottles containing 0.1 *M* Cr(II) solutions in 4 *M* $HClO_4$ over zinc amalgam. Compressed hi-pure argon was similarly treated.

Lithium perchlorate was prepared by the reaction of lithium carbonate with perchloric acid, following Gaunder's procedure[4a]

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[1] Postdoctoral Fellow, Research School of Chemistry, Australian National University, Canberra.

[2] A. Zanella and H. Taube, unpublished results.

[3] P. C. Ford, D. F. P. Rudd, R. G. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).