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Kinetics and Mechanism of Formation and Aquation of Hypophosphitochromium(III) Ion[1a]

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The 1:1 complex of chromium(III) and hypophosphite ions in acidic perchlorate solutions has been studied. The formula $CrH_2PO_2^{2+}$ was verified by analysis and ion-exchange behavior. The visible–ultraviolet spectrum of the complex places hypophosphite ion at the same position as fluoride ion in the spectrochemical series. Studies were carried out on the rates of formation and aquation of the complex at 45–65° and unit ionic strength, as a function of hydrogen ion concentration. The net rate of formation is given by the equation $d[CrH_2PO_2^{2+}]/dt = k_f[Cr^{3+}][H_3PO_2] - k_{aq}[CrH_2PO_2^{2+}][H^+]$. Values of the rate constants and the values of their thermodynamic activation parameters are presented and discussed, and comparisons are made with kinetic data for similar complexes.

Introduction

The net reaction for formation of the 1:1 complex between aquochromium(III) and hypophosphorous acid is

$$Cr(OH_2)_6^{3+} + H_3PO_2 = Cr(H_2O)_5H_2PO_2^{2+} + H_3O^+ \qquad (1)$$

We have carried out a kinetic study on the formation of this complex, and also on the reverse reaction for its aquation (decomposition). The mechanisms of some oxidation–reduction reactions of hypophosphorous acid have been studied,[2] but hypophosphite complexes of metal ions have received very little attention. Banerjee[3] reported complex formation between iron(III) and hypophosphite ions. The complexes with some metal ions appear reasonably stable; the equilibrium quotient for reaction 1 is ~25 at 45–65° and unit ionic strength. These kinetic results provide interesting comparisons of mechanism with analogous reactions involving ligands that have been previously studied.[4–7] Hypophosphorous acid is a weak, monobasic acid, with an ionization quotient of 0.074 M at 16° and ionic strength 1.13 M.[8] The hydrogen ion dependences of reaction rates for several other basic ligands, azide,[4] fluoride,[6] and cyanide[9] ions, reveal a reaction path for aquation with a first-order dependence upon hydrogen ion. This path is not observed with nonbasic anions, and the comparison can be extended to include hypophosphite ion. The spectral properties of hypophosphite complexes are also of interest, for the position of hypophosphite ion in the spectrochemical series has not previously been determined.

Experimental Section

Reagents.—Hypophosphorous acid was purified and freed of phosphorous acid by the recrystallization method of Jenkins and Jones.[10] The starting material was the reagent grade 50% acid. Hypophosphorous acid solutions were analyzed by oxidation–reduction procedures based on iodine[11] and on vanadium(V);[12] the two methods were in excellent agreement. A spectrophotometric metod was also used for analysis of lower concentrations of hypophosphite; hot concentrated perchloric acid oxidized hypophosphite to phosphate which was determined spectrophotometrically[13] as "molybdovanadophosphoric acid" at 4000 A, where its molar extinction coefficient is $2.83 \times 10^3\ M^{-1}\ cm^{-1}$. Hydrated chromium(III) perchlorate was prepared and analyzed as described previously.[5]

Solutions of monohypophosphitochromium(III) ion (the 1:1 complex of chromium(III) and hypophosphite ions, presumably hypophosphitopentaaquochromium(III), $[Cr(OH_2)_5(H_2PO_2)]^{2+}$), were prepared as follows. Chromium(III) perchlorate and hypophosphorous acid were mixed at relatively high concentrations, 0.5–2 M, with no additional hydrogen ion, and allowed to remain at ~45° for extended lengths of time. The desired complex was separated from the mixture of species $[Cr(OH_2)_{6-n}(H_2PO_2)]_n^{3-n}$ by cation exchange. A neutral species and species of apparent ionic charge +1 were removed from the resin column by elution with 0.3 F perchloric acid. A displacement procedure using 1 F barium perchlorate was used to isolate $CrH_2PO_2^{2+}$, in a procedure similar to that described by Finholt, *et al.*[14] The resin used was Dowex 50W-X8, 200–400 mesh, and a very low flow rate was essential for good separation. With this procedure we obtained *ca.* 0.3–0.8 M $CrH_2PO_2^{2+}$ at low acid concentration, containing essentially no other chromium species or free hypophosphorous acid.

The identity of the complex was established by analysis for the hypophosphite/chromium ratio, 1.04. In this analysis hypophosphite was determined by the spectrophotometric procedure described above, after volatilization of chromium as chromyl chloride. The net charge of +2 on the ionic species was indicated by its elution characteristics on cation-exchange resin, compared to chromium(III) species of known charge.

In the visible and ultraviolet spectral regions, hypophosphitochromium(III) ion has absorption maxima (A) and molar extinction coefficients (M^{-1} cm^{-1}) as follows: 5960 (15.6), 4200 (17.3), and 2660 (6.4). This spectrum is very similar to that of fluorochromium(III),[6] with values of 5950 (12.2), 4170 (11.9), and 2680 (4.34). These observations establish that hypophos-

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[1] (a) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 1866. (b) Based on the M.S. thesis of D. E. B., Iowa State University, 1966.

[2] (a) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, pp 192–197; (b) W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11**, 297 (1959).

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[6] T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

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[8] R. O. Griffith, A. McKeown, and R. P. Taylor, *Trans. Faraday Soc.*, **36**, 752 (1940).

[9] J. P. Birk and J. H. Espenson, unpublished experiments.

[10] W. A. Jenkins and R. T. Jones, *J. Am. Chem. Soc.*, **74**, 1353 (1952).

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[12] G. G. Rao and H. S. Gowda, *Z. Anal. Chem.*, **146**, 167 (1955).

[13] K. P. Quinlan and M. A. DeSesa, *Anal. Chem.*, **27**, 1626 (1955).

[14] J. E. Finholt, K. G. Careton, and W. J. Libbey, *Inorg. Chem.*, **3**, 1801 (1964).

phite ion falls very near fluoride ion in the spectrochemical series.[15] At wavelengths shorter than 2500 A the complex absorbs more intensely than does hexaaquochromium(III); at 2100 A, for example, the extinction coefficients are 522 and 33 M^{-1} cm^{-1}, respectively. The change in complex concentration in aquation and formation experiments was followed by measurements at 2100 A with a Cary Model 14 recording spectrophotometer. Wavelength positioning errors were shown not to be a source of appreciable uncertainty in absorbance readings, even though 2100 A lies on the side of a sharply rising band for $CrH_2PO_2^{2+}$, by repeated resetting of the wavelength scale and refilling of the silica cell with a particular solution of the complex.

Reagent grade lithium and sodium perchlorates were recrystallized three times from water. Reagent grade 72% perchloric acid was used without purification. Water used in all solutions was triply distilled from alkaline permanganate in a tin-lined Barnstead still.

Kinetics Experiments.—The rate of formation of $CrH_2PO_2^{2+}$ was followed by continuous absorbance measurements at 2100 A for reactions carried out directly in a thermostated silica spectrophotometer cell, which was stoppered tightly to prevent evaporation. The value of $d[CrH_2PO_2^{2+}]/dt$ was measured directly from the spectrophotometer chart record, using the synchronous motor of the spectrophotometer chart drive as the timer for the reaction. The recordings of absorbance *vs.* time were linear at the start of the runs, and a straight line was drawn through that absorbance change corresponding to a change of no more than 3% of the difference between initial and equilibrium concentrations of the limiting reagent. This was usually a change of 0.05–0.3 absorbance unit. (The formation runs generally were followed only a little beyond this point.) Operation of the spectrophotometer with the water-filled cell holder thermostated at these relatively high temperatures caused considerable noise in the instrument response, which was reduced to tolerable levels by placing desiccant in the cell compartment. (Presumably this prevented condensation of water vapor on the cooler glass windows in the optical light path.) The observed rate of absorbance increase was converted to a reaction rate by use of the known extinction coefficient of $CrH_2PO_2^{2+}$ at 2100 A, 522 M^{-1} cm^{-1}, assumed to be temperature independent.

Two methods were employed for the study of the kinetics of aquation of the complex. Most experiments involved measuring the disappearance of $CrH_2PO_2^{2+}$ at 2100 A. Solutions for these runs were made up in 250-ml volumetric flasks held at constant temperature; a small volume of concentrated complex was added at the start of a run. At regular intervals, *ca.* 10-ml samples were removed with a rapid draining pipet and were transferred to a dry test tube in an ethanol–Dry Ice bath. The quenched samples were stored at Dry Ice temperature for times from 1 day to 2 weeks without apparent change. The samples were melted quickly at 25°, and their absorbances were read at 2100 A at this temperature. This thawing and analysis procedure never took longer than *ca.* 40 min, and inappreciable reaction occurred at 25° in this interval. Experimental values for the equilibrium absorbance readings were obtained from samples taken after *ca.* 8–12 half-lives for aquation.

A number of aquation studies were also carried out by an alternative procedure in which samples were quenched, and free hypophosphorous acid was separated and analyzed. The cationic chromium complexes were retained by an ion-exchange resin column, and the free hypophosphorous acid was rinsed through for analysis by the spectrophotometric procedure described above.

Concentrations refer to room temperature; no correction was made for the error (based on the thermal expansion of pure water) of ~0.7–1.7% introduced at 45–65.°

Results

Formation of $CrH_2PO_2^{2+}$.—The kinetic study of formation of $CrH_2PO_2^{2+}$ was carried out under pseudo-zero-order conditions; changes in the concentration of complex were measured very early in a run, where the reactant chromium(III) and hypophosphorous acid concentrations remained effectively constant. This technique was used by Postmus and King[7] in their study of the formation of the chromium(III) thiocyanate complex. Studies were carried out at 45.0, 55.0, and 65.0° in solutions of 1.0 M ionic strength (perchloric acid–sodium perchlorate) covering hydrogen ion concentrations of 0.2–1.0 M. The initial aquochromium(III) concentration was varied from 0.001 to 0.01 M, and that of hypophosphorous acid from 0.01 to 0.15 M.

The rate of formation of complex is consistent with a one-term rate law

$$d[CrH_2PO_2^{2+}]/dt = k_f[Cr^{3+}][H_3PO_2] \qquad (2)$$

The value of k_f in each experiment was then calculated from the slope of the absorbance trace *vs.* time in the early portions of each experiment together with the known molar extinction coefficient of the complex and the known initial concentrations. Hypophosphorous acid is dissociated to a slight extent, ~4–18%, in this hydrogen ion concentration range. The acid ionization quotient Q_A at these temperatures was extrapolated from data[8] at 16 and 30° and 1.13 M ionic strength (KCl), assuming a linear dependence of log Q_A on $1/T$. The values of Q_A so calculated are 0.058, 0.050, and 0.044 M at 45, 55, and 65°. Acid ionization corrections are relatively small and do not depend critically on the values chosen for Q_A. The individual experiments and the average values of k_f are summarized in Table I.

TABLE I

OBSERVED SECOND-ORDER RATE CONSTANTS k_f (M^{-1} SEC^{-1} × 10^4) FOR FORMATION OF HYPOPHOSPHITOCHROMIUM(III) ION

(A) Experiments at 1.00 M H^+

$[Cr^{3+}]_0$, M	$[H_3PO_2]$, F	45.0°	55.0°	65.0°
0.001	0.074	2.84	7.26	19.9
0.002	0.0090	2.92	6.97	...
0.002	0.037	2.84	8.91	18.8
0.002	0.074	2.74	7.70	17.7
0.002	0.074	2.76	7.73	18.1
0.002	0.074	2.84	7.87	...
0.002	0.015	2.81	8.08	18.5
0.005	0.074	2.81	8.68	19.8
0.005	0.074	...	9.06	...
0.010	0.074	2.79	9.40	...
0.005	0.074	...	9.57	...

(B) Experiments at varying $[H^+]$[a]

$[H^+]$, M	45.0°	55.0°	65.0°
0.800	2.66	6.88	...
0.600	2.67	7.87	...
0.600	2.78	...	...
0.400	2.78	8.25	...
0.300	2.71	7.88	23.8
0.200	(3.43)[b]	9.41	...
Av k_f, M^{-1} sec^{-1} × 10^4[c]	2.78 ± 0.25	8.22 ± 0.86	19.5 ± 2.1

[a] Conditions: 0.002 M Cr^{3+}, 0.074 F H_3PO_2; 1.0 M ionic strength ($NaClO_4$). [b] This value excluded from the average. [c] Uncertainties are standard deviations.

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(15) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962.

Aquation of $CrH_2PO_2^{2+}$.—In all the experiments performed, the hydrogen ion concentration was much higher than that of the complex, and it remained effectively constant during a run. The net rate of aquation of hypophosphitochromium(III) ion at constant $[H^+]$ is given by the equation

$$-d[CrH_2PO_2^{2+}]/dt = k_1[CrH_2PO_2^{2+}] - k_f[Cr^{3+}][H_3PO_2] \qquad (3)$$

The spectrophotometric aquation experiments were performed with relatively low initial concentrations of $CrH_2PO_2^{2+}$ ($2\text{–}10 \times 10^{-4}\ M$), to ensure that the reactions ran near to completion. The solutions were maintained at 1.00 M ionic strength with lithium perchlorate–perchloric acid mixtures; variation of hydrogen ion concentration covered the range 0.08–1.0 M. The thermodynamic stability of the complex toward aquation at low $[H^+]$ set the lower limit of hydrogen ion concentration. The equilibrium per cent completion of the aquation runs lay in the range 82–99.8%, with the mean being 94%. In all the runs, the reverse reaction was taken into account.[16] A pseudo-first-order rate constant k_1 was calculated from the slope of a graphical treatment of the data, according to the relation[17]

$$k_1 = -\frac{f}{2-f}\frac{d}{dt}\ln\left\{\frac{[CrX]_0^2 - [CrX][CrX]_\infty}{[CrX]_0([CrX] - [CrX]_\infty)}\right\} \qquad (4)$$

where f represents the fraction of complex aquated at equilibrium, and the subscripts 0 and ∞ on complex concentrations refer to initial and equilibrium values. In the spectrophotometric experiments, absorbance values at 2100 A were used directly in eq 4 in place of concentrations.

The initial concentration of hypophosphite complex in the analytical aquation runs was 0.003–0.01 M. This was generally somewhat higher than in the direct spectrophotometric procedure to provide sufficient hypophosphorous acid for sensitive analysis. A limited number of these runs were performed, at only two hydrogen ion concentrations, 0.5 and 1.0 M, at a single temperature, 45.0°. Aquation was less complete under these conditions; the extent of aquation for these solutions ranged from 77 to 94%. The values of the equilibrium concentrations used in eq 4 in calculating the pseudo-first-order rate constants in the analytical runs were computed from initial concentrations and the equilibrium quotient for formation of the complex, evaluation of which will be presented subsequently.

TABLE II

CORRECTED[a] SECOND-ORDER RATE CONSTANTS (M^{-1} sec^{-1} $\times 10^5$) FOR AQUATION, k_{aq}

$[CrH_2PO_2^{2+}]_0$, $M \times 10^3$	$[H^+]$, M 0.081	0.149	0.300	0.538	0.600	1.00
	k_{aq} (45.0°)					
0.25	1.21	1.16	1.14		1.29	
0.25					1.35	
0.5	1.21	1.16	1.14		1.19	
0.5		1.19	1.14		1.20	
1					1.24	1.18, 1.26
1					1.25	1.27, 1.28
3^b						1.13, 1.20
5^b						1.27, 1.30
10^b				1.06		1.24, 1.25
10^b				1.12		1.27, 1.29
	k_{aq} (55.0°)					
0.5					3.01, 3.05	
0.5					3.11, 3.31	
1	3.06	3.07	3.03		2.95, 3.00	3.11, 3.16
1	3.06	3.18	3.03		3.02, 3.17	3.24, 3.31
	k_{aq} (65.0°)					
1	6.94	6.75	6.84		7.03	6.99
1	7.36	7.32	6.97		7.14	7.01

[a] Harned rule correction, with $\beta = 0.10\ M^{-1}$. The observed second-order rate constant k_2 can be calculated by dividing each entry here by $\exp(-\beta[H^+])$, with $\beta = 0.10\ M^{-1}$; for the six $[H^+]$ values shown here, values of $\exp(-\beta[H^+])$ are 0.992, 0.985, 0.970, 0.945, 0.942, and 0.905. [b] Analytical aquation experiments; all other values refer to spectrophotometric runs.

The pseudo-first-order rate constant for aquation of hypophosphitochromium(III) ion at constant hydrogen ion concentration, k_1, varies directly with $[H^+]$. Values of the second-order rate constant $k_2 = k_1/[H^+]$ are nearly constant; they do, however, show a small but regular increase with increasing hydrogen ion concentration. The assumption that replacing hydrogen ion by lithium ion at constant ionic strength ensures constant activity coefficients is not rigorously correct. Variations in rate constants on the order of ~10% on proceeding from 1 F $HClO_4$ to 1 F $LiClO_4$ are not unreasonable.[18,19] An empirical correction that can be made for this effect is in the form of Harned's rule

$$k_{aq} = k_2 \exp(-\beta[H^+]) \qquad (5)$$

where k_{aq} is a "true" second-order rate constant which incorporates an additional parameter β to account for changing activity coefficients. A value of $\beta = +0.10\ M^{-1}$ results in constant k_{aq} values (a meaningful temperature dependence of β was not observed). This value of β leads to a correction factor $\exp(-\beta[H^+]) = 0.992\text{–}0.905$ in the range of $0.081 < [H^+] < 1.00\ M$. In effect, a correction of this type amounts to referring all values of k_{aq} to the medium 1 F $LiClO_4$.

Values of k_{aq} for these experiments are summarized in Table II. At each of the three temperatures the average values of k_{aq} are 1.22 ± 0.01 (standard deviation), 3.03 ± 0.03, and 7.07 ± 0.07 (units M^{-1} sec^{-1} $\times 10^5$). These averages include only the spectrophotometric runs, since the equilibrium quotient used for calculating

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[16] Failure to account for the reverse of a reaction that runs 98% to completion will lead to an error of ~4% in the pseudo-first-order rate constant.

[17] This equation is valid only for experiments where $[Cr^{3+}]_0 = [H_3PO_2]_0 = 0$.

[18] (a) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963); (b) G. Gordon and P. H. Tewari, *ibid.*, **70**, 200 (1966); (c) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **4**, 1166 (1965).

[19] Our experiments on the rate of complex formation were done with sodium perchlorate as supporting electrolyte, whereas those on aquation were with lithium perchlorate. We have ignored any differences arising from this source, although in at least one study a sizable rate discrepancy was found [D. H. Huchital and H. Taube, *J. Am. Chem. Soc.*, **87**, 5371 (1965)]. In view of the relative insensitivity of the activity coefficient of HCl in HCl–MCl solutions of constant ionic strength when M is Li, compared to noticeable changes for M = Na [H. S. Harned, *ibid.*, **48**, 326 (1926)], lithium perchlorate appears to be the preferable choice for ensuring less variation in activity coefficient.

$[CrH_2PO_2^{2+}]_\infty$ in the analytical aquation experiments was derived from these kinetic data.

The term $\exp(-\beta[H^+])$ was used to resolve trends in the values of $k_{aq}/[H^+]$ as H^+ was traded for Li^+ over the range 0.08–1.0 M H^+ at constant unit ionic strength. The value of β, 0.10 M^{-1}, needed to resolve the discrepancy is not unreasonable, although it is near the upper limit one might care to invoke for the pair H^+, Li^+.[18] This seemed the most satisfactory of several alternatives. It would be possible to ignore the trend in k_2 with $[H^+]$. Another alternative is to ascribe this trend to an additional reaction pathway; *i.e.*, the rate equation for aquation

$$-d \ln [CrH_2PO_2^{2+}]/dt = k_{aq}'[H^+] + k_{aq}''[H^+]^2 \quad (6)$$

Although the added rate law term $k_{aq}'[H^+]^2$ apparently never gains sufficient importance to be studied accurately, a value of k_{aq}'could be obtained in this way. This explanation appears distinctly less desirable for the reason that the reaction path second order in hydrogen ion requires a transition state of composition $[CrH_2PO_2 \cdot 2H^{4+}]^*$. Such a formulation would be quite difficult to resolve on the basis of a reasonable reaction mechanism. Values of the main rate law term first order in hydrogen ion would be much the same on either basis. The additional rate law term, if it exists, never becomes sufficiently important to make a sizable contribution to the rate, and the preferable approach seems to be to admit that these data do not conclusively demonstrate its presence.

A number of similar aquation reactions of chromium(III) complexes (*e.g.*, halide, azide, thiocyanate ions), have been studied; in no previous instance has failure of the "constant ionic strength principle" been observed. This may be a consequence of the fact that, for each of these other complexes, terms that are inversely proportional to, and/or independent of, hydrogen ion concentration were also important. Any need for an activity coefficient correction of the sort made here could be hidden in the rate parameters of the multiterm rate equation.

Equilibrium Quotient.—The value of the equilibrium quotient Q for formation of hypophosphitochromium(III), eq 1, is related to the forward and reverse reaction rate constants. The net rate of formation of complex is given by the equation

$$d[CrH_2PO_2^{2+}]/dt = k_f[Cr^{3+}][H_3PO_2] - k_{aq}[CrH_2PO_2^{2+}][H^+] \quad (7)$$

and the equilibrium quotient $Q = k_f/k_{aq}$. The forward and reverse rate laws result in the correct form of the equilibrium quotient. In view of the fact that lithium perchlorate was the inert salt used in the aquation experiments, and sodium perchlorate in the formation experiments, a rate constant ratio would represent an equilibrium quotient with a slightly different activity coefficient reference for reactants than for products. This difference is not necessarily trivial, for several workers[18] have noted appreciable effects due to replacement of Li^+ by Na^+ in rather different types of reactions. To avoid such discrepancies the rate constants used in the equilibrium quotient computation were referred to the medium 1 F $HClO_4$ (*i.e.*, the values of k_{aq} without the Harned rule correction were used). On this basis, and considering each temperature separately, values of Q are 20.7 ± 3.2, 24.0 ± 3.7, and 25.0 ± 3.7 at 45.0, 55.0, and 65.0°.

In addition, the equilibrium quotient was studied in some direct experiments, with analysis for free hypophosphorous acid in equilibrated solutions prepared from initially pure complex. The results were not very precise nor the accuracy very high. Presumably the problem arises from two sources; the equilibrium concentration of complex was generally rather low, 6–23% of its starting value, and was calculated as the difference between total chromium and equilibrium hypophosphorous acid concentrations; errors in this difference may be substantial. This computation assumes initially pure complex. If as little as 1% Cr^{3+} were present in the original solution of complex prepared by ion-exchange procedure, the calculated value of Q in typical experiments under these conditions would be in error by ~8%. The equilibrium experiments were duplicated, in part, with several preparations of complex. Values of the equilibrium quotient in solutions prepared from the same sample of complex agreed considerably better than did one series compared to the other. For example, one preparation averaged $Q = 20.8 \pm 0.5$ (four runs), another 15 ± 1 (ten runs), and a third 14.7 (one run) at 45.0°. Although this procedure has not resulted in an accurate value for Q, the semiquantitative agreement with the value based on the kinetic comparisons lends some support to the correctness of the later calculation.

Interpretation and Discussion

The individual rate constants for formation of hypophosphitochromium ion were fit to the relation

$$k_f = \kappa(k_B T/h) \exp(\Delta S_f^*/R - \Delta H_f^*/RT) \quad (8)$$

considering simultaneously the 37 data points at the three temperatures. This computation of ΔH_f^* and ΔS_f^* ($\kappa = 1$) was carried out with the aid of a nonlinear least-squares computer program. An analogous relation was assumed to hold also for k_{aq}, and the activation parameters were evaluated in the same manner. These values can be used to calculate $\Delta H°$ and $\Delta S°$ for the equilibrium quotient Q. The results of these computations, with standard deviations also listed, are given in Table III. The values for the rate constants calculated from these activation parameters are in good agreement with the individual averages at the separate temperatures. The value of $\Delta S°$ associated with Q refers to the standard state 1 F $HClO_4$, as discussed above.

Labile outer-sphere association of Cr^{3+} and $H_2PO_2^-$

Table III

	ΔH, kcal mole^{-1}	ΔS, cal mole^{-1} deg^{-1}	Calcd at 45.0°
k_f, M^{-1} sec^{-1}	20.3 ± 0.4	−11.2 ± 1.3	2.82×10^{-4}
k_{aq}, M^{-1} sec^{-1}	18.1 ± 0.2	−24.1 ± 0.5	1.23×10^{-5}
Q	2.1 ± 0.6	12.7 ± 1.8	22.9

probably is not important under these conditions. No appreciable absorbance changes in the ultraviolet region were noted when the solutions were mixed, other than the very slow changes accompanying the inner-sphere complex formation. Outer-sphere interactions between ions of charge +3 and −1 have been shown to be extremely small, even in the case of $Co(NH_3)_6^{3+}$ plus halide ion, where very large ultraviolet spectral changes were noted.[20] Since the predominant form of the ligand in acidic solution is the neutral molecule, ion association appears rather unfavorable in these circumstances. At least, we find no spectral evidence for a stable or unstable outer-sphere complex and also no kinetic requirement for a stable one.

The rate law for aquation of hypophosphitochromium(III) ion consists of but a single term, directly proportional to $[H^+]$. This is a novel situation, for two or more rate law terms of the form $-d\ ln\ [CrX^{2+}]/dt = \Sigma k_n[H^+]^n$ have generally been noted in the aquation of similar complexes $Cr(OH_2)_5X^{2+}$, with values of n consisting of two or more adjacent members of the series −2, −1, 0, +1. Of all the ligands studied, and the list includes the halides,[5,6] azide,[4] thiocyanate,[7] and cyanide[9] complexes, for only the hypophosphite complex is the rate law term k_0 missing. Those ligands that are appreciably basic (cyanide, fluoride, azide, and hypophosphite) are the only ones for which the term $k_1 \cdot [H^+]$ was noted. It is most reasonable to attribute this k_1 term to a transition state with the immediate products HX and aquochromium(III),[4,6] since it is observed only for basic ligands, where HX is a favorable product. If the *presence* of this rate law term is attributed to HX being a weak acid, then one might hope to correlate the relative *magnitude* of such a term with the basicity of X^-. Such a correlation is, however, rather unsuccessful for the four anions for which data are available. The values of k_1/k_0 at 45° are >100 ($H_2PO_2^-$), 10.6 (F^-), 10.5 (CN^-), and 6.6 M^{-1} (N_3^-). The base strengths of the free ligands are in the order $CN^- \gg N_3^- > F^- > H_2PO_2^-$. That this correlation is as poor as it is may be due to the rather simple base strength parameter used; *e.g.*, the cyanide ion will form as preliminary product the less stable HNC, not HCN, and in the case of fluoride ion the proton is added rather near the positively charged chromium nucleus, whereas with hypophosphite ion the basic site is considerably further removed. The assumption made here in comparing k_1/k_0 ratios is that these reactions proceed by similar mechanisms. The inference has been made on the basis of arguments based on values of ΔS_0^* that for CrF^{2+} and CrN_3^{2+} the primary products of dissociation along the k_0 path are $CrOH^{2+}$ and HF (HN_3) rather than Cr^{3+} and F^- (N_3^-). This is not necessarily the case for $CrH_2PO_2^{2+}$, especially since the base strength of these ions increases in the order $H_2PO_2^- < CrOH^{2+} \sim F^- < N_3^-$. Perhaps the large k_1/k_0 ratio for $CrH_2PO_2^{2+}$ reflects a mechanism in which the k_0 term corresponds to initial production of Cr^{3+} and $H_2PO_2^-$.[21]

The partial molar entropy of an ion in aqueous solution is a function of its ionic charge and its radius. For a series of complexes $Cr(OH_2)_5X^{2+}$ one could expect that a large contribution to the differences in ΔS^* for the net activation processes

$$Cr(OH_2)_5X^{2+} + H^+ = [Cr(OH_2)_5X\cdots H^{3+}]^*$$

in the case of a series of CrX^{2+} complexes would be made by the entropy of solvation of the HX molecule.[22]

Values of $\Delta S°_{HX}$ (eu) are 48[23] (HN_3), 38 (H_3PO_2), 31 (HCN), and 26 (HF); the observed ΔS_1^* values are −8.3 (azide),[4] −11.1 (cyanide),[9] −12.4 (fluoride),[6] and −24 (hypophosphite). Three ligands follow the anticipated pattern, but the value of ΔS^* for the hypophosphitochromium(III) ion is considerably more negative (by *ca.* 15 eu) than predicted by this model; the net activation process for aquation of $CrH_2PO_2^{2+}$ creates more order than one predicts from the extent to which free hypophosphorous acid itself creates order in the solvent. This comparison has made the assumption that the ions $Cr(OH_2)_5X^{2+}$ have the same partial molar entropies, which appears quite reasonable. An additional assumption made here is that the four reactions have similar mechanisms. Failure of the attempted correlation suggests that there may be rather significant differences in the mechanisms. This entropy could be provided by involvement, in the net activation process for the hypophosphite complex, of one water molecule more than that in the analogous processes for the other complexes. Although this provides a mild suggestion that bond making to water, as well as bond breaking for the ligand, exerts more influence in the case of hypophosphite ion as a ligand, this does not constitute definitive proof of a displacement mechanism in this instance, compared to a dissociative mechanism in the other.

These results on hypophosphite complex formation are of interest in themselves, but a number of important related problems that merit attention should also be mentioned. The oxidation of hypophosphorous acid by chromium(VI) has been studied previously,[24,25] but the kinetic behavior was rather unusual and the two studies were not in agreement. The stoichiometry was not examined in detail and we have evidence that the Cr(III) product is not $Cr(OH_2)_6^{3+}$, but consists rather of hypophosphite and/or phosphite complexes of chromium(III). A study of the nature and extent of such complex formation should provide some important information on the mechanism. It may also explain some of the kinetic complexity noted in the earlier studies, for if reactant concentrations are diminished by complex formation,[26] this effect must be taken into

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[20] E. L. King, R. E. Visco, and J. H. Espenson, *J. Phys. Chem.*, **63**, 755 (1959).

[21] We are grateful to Prof. E. L. King for this suggestion.

[22] Such a correlation was shown to exist for the aquation of the halide complexes (ref 6).

[23] W. M. Latimer, "Oxidation Potentials," 2d ed, Prentice-Hall, Inc., New York, N. Y., 1952.

[24] A. D. Mitchell, *J. Chem. Soc.*, 564 (1924).

[25] K. Pan and S-H. Lin, *J. Chinese Chem. Soc.* (Taiwan), [II] **7**, 75 (1960).

[26] Several other instances have been noted where chromium(VI) captures ligands during its reduction to chromium(III) [M. T. Beck and I. Bardi, *Acta Chim. Acad. Sci. Hung.*, **29**, 283 (1961); M. T. Beck, I. Seres and I. Bárdi, *ibid.*, **41**, 231 (1964); G. P. Haight, Jr., E. Perchonock, F. Emmenegger, and G. Gordon, *J. Am. Chem. Soc.*, **87**, 3835 (1965)].

account in treating the kinetic data. Studies have not been made on hypophosphite ion as a "bridging" ligand in electron-transfer reactions; the rate of Cr(II)–Cr(III) exchange in $CrH_2PO_2^{2+}$ + $*Cr^{2+}$ should provide very useful information on this point. This reaction may be of especial interest, in view of the important role of phosphate ions in biochemical oxidation–reduction processes. Hypophosphorous acid is itself a reducing agent with some unusual kinetic properties, which have been previously summarized.[2]

The question of the mechanism of oxidation of coordinated hypophosphite ion merits attention. Preliminary experiments have shown that this ligand can be oxidized while remaining coordinated to chromium(III). For example, the net reaction with iodine solutions is

$$CrH_2PO_2^{2+} + I_3^- + H_2O = CrH_2PO_3^{2+} + 3I^- + 2H^+$$

The mechanism of this reaction has not yet been investigated in detail, but probably differs substantially from that for the free acid.

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Kinetics of *trans*-Dichlorobis(piperidine)platinum(II) in Different Solvents

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Rate data of monohalide displacements on *trans*-dichlorobis(piperidine)platinum(II) with several entering groups in five structurally different dipolar aprotic solvents are reported. The entering group reactivity order parallels the polarizability order in all the solvents and the reactivity does not vary strongly as the hydrogen-bonding capacity changes from protic to aprotic solvents. The kinetic data are discussed in terms of solvation of the reagent entering group.

Introduction

Rate data concerning the solvent effect in substitution reactions of some Pt(II) phosphine complexes have recently been reported.[1] The objectives of investigations on this subject are to offer, first, some evidence concerning the mechanism of nucleophilic displacement in the reactions of d^8 complexes and, second, to determine the factors which promote strong interactions between the reaction center and the entering group at the transition state.

This paper reports a kinetic study of *trans*-$[Pt(pip)_2Cl_2]$ (pip = piperidine) with several entering groups in a variety of structurally different dipolar aprotic solvents. The effect of the solvent on the rates of these reactions is investigated and a comparison between the rate data of the piperidine and of the analogous phosphine complex is presented.

Experimental Section

Materials.—Platinum(II) compounds were prepared following the methods reported in the literature.[2] All the compounds were characterized by analysis.

Acetone was dried with potassium carbonate and distilled, bp 56.5°; dimethyl sulfoxide was distilled under reduced pressure in nitrogen atmosphere; nitromethane was washed with aqueous sodium hydrogen carbonate, dried with calcium chloride, and fractionated, bp 101°; dimethylformamide was dried with calcium oxide and distilled, bp 153°; acetonitrile was dried with potassium carbonate and fractionated, bp 81°. Other materials used were reagent grade.

Kinetics.—The reactions of isotopic exchange were followed by the same procedure as previously reported.[1a]

Other reactions were followed by measuring changes in optical density of the reaction mixture in the ultraviolet region by means of 1-cm quartz cells in the thermostat-controlled cell compartment of a Beckman DK-2A, a Beckman DU, and an Optica CF-4 spectrophotometer. The reactions in nitromethane were carried out in 0.1-cm quartz cells. The reference cell in each case contained the reagent blank. In the case of relatively fast reactions, an Optica CF-4 was used and the chart drive on the attached recorder was started at the moment of mixing. The absorbance at a selected wavelength was recorded against time, starting a few seconds after mixing. The solution of entering group was added with a syringe. All solutions were kept at 25° prior to mixing. At the experimental temperature, 25 ± 0.1°, there was no evidence to suggest a *cis–trans* isomerization. In the range of the experimental concentrations, Beer's law was obeyed for both reactants and products in all the solvents examined.

The kinetics were performed with a 10–100-fold excess of the entering group in order to provide pseudo-first-order conditions and to force the reactions to go to completion. The complex concentration was changed in the range 10^{-4}–10^{-3} *M*. Tetrabutylammonium salts were used. Except in a few cases, at least four concentrations of entering group were examined, in the range 5×10^{-3} to 5×10^{-2} *M*. The ionic-strength effects were not important, as found for the reactions in methanol.[3] No attempt was made therefore to keep a constant electrolyte concentration.

The reactions proceed by a slow, rate-determining step, followed by a rapid second step

$$trans\text{-}[Pt(pip)_2Cl_2] + Y^- \xrightarrow{k_{obsd}} trans\text{-}[Pt(pip)_2YCl] + Cl^-$$

$$trans\text{-}[Pt(pip)_2YCl] + Y^- \xrightarrow{fast} trans\text{-}[Pt(pip)_2Y_2] + Cl^-$$

Except in acetone, good linearity was obtained for the plots of k_{obsd} *vs.* the initial reagent concentrations with nonzero intercepts in all the solvents.

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[1] (a) U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.*, **5**, 582 (1966); (b) U. Belluco, P. Rigo, M. Graziani, and R. Ettorre, *ibid.*, **5**, 1125 (1966).

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[3] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).