# Kinetics and Mechanism of the Inner-Sphere Electron-Exchange Reaction of Hypophosphitochromium(III) and Chromium(II) Ions in Acidic Solution[1a]

**Kermit A. Schroeder[1b] and James H. Espenson**

*Contribution from the Institute for Atomic Research and the Department of Chemistry, Iowa State University, Ames, Iowa 50010.* *Received November 12, 1966*

**Abstract:** The kinetics of electron exchange between $Cr(OH_2)_5(H_2PO_2)^{2+}$ and $Cr^{2+}$ has been studied in aqueous acid solution. Over the range of acid concentration studied, 0.03–1.0 *M*, the rate equation has the form $k[CrH_2PO_2^{2+}]\cdot[Cr^{2+}]/[H^+]$, with $k = 6.11 \times 10^{-4}$ sec$^{-1}$ at 25.0° and unit ionic strength. Values of the activation parameters associated with this rate constant are $\Delta H^{\ddagger} = 19.7 \pm 1.0$ kcal mole$^{-1}$, and $\Delta S^{\ddagger} = -7.2 \pm 3.3$ eu. Ion-exchange equilibration experiments were used to confirm the net charge on the complex as +2. The reaction mechanism involves a hypophosphite bridged transition state. The probable structure of the transition state, suggested by the inverse dependence of exchange rate upon $[H^+]$, involves double bridging by hypophosphite and hydroxide ions. Alternative formulations are also presented.

In an acidic solution electron exchange occurs between chromium(II) and a monosubstituted chromium(III) complex $(H_2O)_5CrX^{2+}$ (eq 1). This process establishes Cr(II)–Cr(III) isotopic equilibrium, although net chemical change does not occur (at least until much longer times have elapsed).

$$(H_2O)_5CrX^{2+} + (H_2O)_6{}^*Cr^{2+} = (H_2O)_6Cr^{2+} + (H_2O)_5{}^*CrX^{2+} \quad (1)$$

Each reaction transfers $X^-$ from Cr(III) to Cr(II) during electron exchange and the mechanism is most simply formulated as involving a transition state in which ligand X has penetrated the inner coordination sphere of both metal ions.[2]

The rates and mechanisms of a number of such inner-sphere Cr(II)–Cr(III) exchange reactions have been studied, including Cr(III) complexes containing fluoride,[3] chloride,[4] bromide,[4] thiocyanate,[4] and azide[4,5] ions. Cr(II)–Cr(III) electron exchange has been studied also in the case of two tripositive Cr(III) species, $(H_2O)_6Cr^{3+}$ [6] and $(H_2O)_5CrNH_3^{3+}$.[7] These reactions likewise have been interpreted[7] in terms of an inner-sphere mechanism involving the ligand $OH^-$, although here only indirect evidence is available. The exchange rate law obeyed by each of these reactions takes the form $k[(H_2O)_5CrX^{n+2}][(H_2O)_6Cr^{2+}]/[H^+]^n$, with $n$ = 0 and 1. The transition states for electron exchange have a 4+ ionic charge in each case.

We report here on a study of electron exchange between chromium(II) and monohypophosphitochromium(III) ions. In earlier work,[10] we reported the preparation and characterization of the complex $(H_2O)_5CrH_2PO_2^{2+}$ and studied the kinetics and thermodynamics of its formation and decomposition (eq 2).

$$(H_2O)_6Cr^{3+} + H_3PO_2 = (H_2O)_5CrH_2PO_2^{2+} + H^+ \quad (2)$$

This study of electron-exchange rates was undertaken with the expectation that the exchange-rate law and mechanism would parallel the previous studies on related complexes. In addition, since phosphorus oxyanions had not been studied previously as bridging groups for Cr(II)–Cr(III) electron transfer, the hypophosphite complex appeared interesting in this respect. The role of phosphorus oxyacids in biological oxidation–reduction reactions added interest to this subject. Although we confirmed that Cr(II)–Cr(III) exchange occurs with transfer of the ligand and without observable net reaction, it soon becomes apparent to us that the reaction mechanism differed appreciably from earlier exchange systems. The observed dependence of exchange rate on $[H^+]^{-1}$, corresponding to a transition state of 3+ charge, constitutes a novel situation for exchange, and one that provides some information on the structure of the transition state that can be interpreted in terms of an isomeric $HP(O)(OH)^-$ ligand, or in terms of a double-bridged electron-transfer mechanism.

## Experimental Section

**Reagents.** Solutions of the monohypophosphitochromium(III) complex were prepared from chromium(III) perchlorate and hypophosphorous acid as described previously.[10] The complex was isolated from the starting materials and from other chromium species by ion exchange. The resin column was first rinsed with 0.3 *F* perchloric acid to remove the free acid and any complexes of charge lower than 2+. The complex of interest was eluted with 1 *F* lithium perchlorate or perchloric acid. The visible and ultraviolet spectra of the complex have been reported earlier,[10] and spectra of all samples obtained here were in quantitative agreement with the published values. Solutions of the separated complex generally

---

(1) (a) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1992. (b) Visiting summer faculty research participant; Department of Chemistry, State University College, Brockport, N. Y.

(2) (a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); (b) J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 7 (1960); (c) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(3) Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

(4) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(5) E. L. King and R. Snellgrove, *Inorg. Chem.*, **3**, 288 (1964).

(6) M. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(7) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966). The reaction of $Cr(OH_2)_5NH_3^{3+}$ and $Cr(OH_2)_6^{2+}$ is not strictly an exchange reaction, since $NH_3$ is released as an accompanying feature of the electron transfer. It is closely related to the other reactions, however, in which all but one of the ligands originally on Cr(III) are labilized upon its reduction to Cr(II). In the other instances these ligands are $H_2O$, however, and this change is not reflected in observable net chemical reaction. Recent experiments[8,9] have shown that halide complexes of chromium(III) undergo a chromium(II)-catalyzed aquation with a rate equation of the form $k[Cr^{2+}][(H_2O)_5CrX^{2}]/[H^+]$. This path presumably is a hydroxo-bridged process that releases the nonbridging $X^-$ and is quite analogous to the reaction of $(H_2O)_5CrNH_3^{3+}$.

(8) D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, **88**, 3450 (1966).

(9) A. Adin and A. G. Sykes, *J. Chem. Soc., Sect. A*, 518 (1966).

(10) J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **5**, 1365 (1966).

were stored 12–24 hr at −78°, which apparently preserved the complex unchanged since the spectrum remained unaltered.

In all experiments chromium(II) was labeled with chromium-51 radiotracer, obtained as a solution of chromium(III) chloride in 0.5 *F* hydrochloric acid. Labeled chromium(III) perchlorate stock solutions were prepared from *ca.* 0.1 *F* chromium(III) perchlorate solution to which had been added *ca.* 0.5 mcurie of $^{51}Cr$ per 100 ml of solution. Chromium(III) was reduced electrolytically at a mercury cathode under purified nitrogen. The concentration of chloride ion introduced from the tracer solution by this technique was negligibly low (*ca.* 0.005 *M*).

Lithium perchlorate, used to adjust ionic strength, was prepared from lithium carbonate and perchloric acid and recrystallized three times. Reagent grade perchloric acid was used without purification. Conductivity water, a double redistillation of laboratory distilled water from alkaline permanganate in a Barnstead still, was used in all solutions.

Dowex 50 W-X8 (50–100 mesh, Baker reagent grade) cation-exchange resin was washed with 4 *F* hydrochloric acid until free of iron(III) (negative test with thiocyanate) and then allowed to stand overnight in the presence of excess sodium hydroxide and hydrogen peroxide. The resin was reconverted to the hydrogen ion form by repeated washing with 4 *F* hydrochloric acid. A finer particle size resin (200–400 mesh) was employed in the experiments used to determine the net charge on the chromium complex.

**Exchange Kinetics.** The procedures employed in the kinetic runs and separations are as follows. All reagents except chromium(II) were added to a 150-ml milk dilution bottle equipped with a self-sealing rubber cap which served as the reaction vessel. The solution was flushed with oxygen-free nitrogen for at least 30 min; then chromium(II) was introduced by syringe. Samples were withdrawn by syringe at appropriate intervals and quenched in a stream of air which oxidized chromium(II) to $Cr_2(OH)_2^{4+}$, a dimeric form of chromium(III).[11] (Sample volumes generally were 1–3 ml but were not measured or controlled accurately since the *specific* activity was the quantity being measured.)

An ion-exchange separation of $CrH_2PO_2^{2+}$ from $Cr_2(OH)_2^{4+}$ was employed. In 16 experiments only $Cr^{2+}$ activity was followed, in four experiments only $CrH_2PO_2^{2+}$. In an additional five experiments both activities were followed. Thus a total of 30 rate constants were measured. The air-quenched sample was transferred to a 12 mm × 8 cm column of resin in the hydrogen ion form, contained in a short length of Tygon tubing, and eluted with 2 *F* perchloric acid. The first 7–8 ml of solution contained most of the hypophosphite complex, the specific activity of which was determined by counting a standard volume of the sample in a well-type scintillation counter and spectrophotometrically analyzing for chromium as chromate ion in alkaline solution after oxidation with hydrogen peroxide. In experiments where the chromium(II) fraction was followed with time, the column was first rinsed with *ca.* 200 ml of 2 *F* perchloric acid to remove all chromium species but $Cr_2(OH)_2^{4+}$, which then was removed from the resin by treatment with sodium hydroxide and hydrogen peroxide. The specific activity of chromium in the resulting solution was determined as before.

Chromium(II) in each reaction solution was analyzed directly by spectrophotometric determination of the cobalt(II) produced by reaction with a small excess of pentaamminechlorocobalt(III) ion.[12] Usually two to four samples were withdrawn for analysis during the course of a run.

## Results

**Net Ionic Charge.** The unexpected results found for the effect of hydrogen ion on the electron-exchange rate (see below) led us to reconsider the composition of the hypophosphite complex, previously formulated as $CrH_2PO_2^{2+}$. Earlier work[10] had established a 1:1 mole ratio of phosphorus and chromium in the complex, and the qualitative behavior of this species on elution from cation-exchange resin indicated the species had net charge 2+ in 1 *F* solutions of either perchloric acid or lithium perchlorate.

Ion-exchange equilibration experiments of the type developed by Cady and Connick[13] were carried out to determine unambiguously the ionic charge on the hypophosphite complex. A low concentration of the species of interest was equilibrated with cation-exchange resin at two known hydrogen ion concentrations, 1 and 0.5 *M*. The presumed constancy of the equilibrium quotient for reaction 3 (overline = resin phase) on changing from 1 to 0.5 *M* $H^+$ allows computation of *b* from equilibrations with the same resin at two $[H^+]$

$$MX^{b+} + b\overline{HR} = \overline{MXR_b} + bH^+ \qquad (3)$$

values. Precision of the method is limited by variation of the charge *b* from integral values, which may be caused by a change in the value of the equilibrium quotient for reaction 3 in 1 *F* compared to 0.5 *F* perchloric acid solution. A changing degree of protonation of the complex over this range of $[H^+]$ also would give nonintegral values. Hexaaquochromium(III) was carried through some experiments as a check on the procedure. The results for this ion and for hypophosphitochromium(III) are presented in Table I. The charge value found (2.94) for hexaaquochromium(III) is close to the value found by Cady and Connick (2.89).[13] The value (average 2.11) determined for hypophosphitochromium(III) is slightly larger than the integral +2 value presumed for $CrH_2PO_2^{2+}$. Although the value is not an integer, this does not seem to constitute compelling evidence that the true charge on the hypophosphite complex is not +2. Since the kinetic evidence presented later indicates that almost certainly only a *single* species predominates over the range 0.026–1 *M* $H^+$, the conclusion seems justified that this species is the dipositive ion $CrH_2PO_2^{2+}$, as in the original formulation.[10]

**Table I.** Net Ionic Charge on Chromium(III) Species

| Total Cr(III), mmoles[a,b] | $[H^+]$, *M* | Vol, ml | [Cr(III)], *M* × $10^3$ | Charge |
|---|---|---|---|---|
| A. Hexaaquochromium(III) Ion | | | | |
| 0.432 | 0.980 | 120 | 0.935 | 2.94 |
| 0.413 | 0.490 | 200 | 0.1528 | |
| 0.432 | 1.012 | 60 | 1.271 | 2.95 |
| 0.419 | 0.506 | 100 | 0.1920 | |
| B. Hypophosphitochromium(III) Ion | | | | |
| 0.437 | 1.017 | 120 | 2.43 | 2.08 |
| 0.388 | 0.508 | 200 | 0.868 | |
| 0.437 | 1.017 | 120 | 2.42 | 2.08 |
| 0.389 | 0.508 | 200 | 0.862 | |
| 0.437 | 1.050 | 60 | 4.054 | 2.14 |
| 0.396 | 0.525 | 100 | 1.300 | |
| 0.437 | 1.050 | 60 | 4.046 | 2.15 |
| 0.397 | 0.525 | 100 | 1.294 | |

[a] The difference in the amount of total chromium between the first and second parts of an experiment reflects the amount removed for analysis of the first concentration. This removal of solution also accounts for the relation of $[H^+]$ and volume. [b] In the various experiments, between 3.45 and 3.57 g of resin, with a capacity of 3.55 mmoles of $H^+$ per gram, was used.

**Exchange Rate Law.** Where chromium(II) specific activity was followed with time, the McKay equa-

---

(11) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(12) This reduction technique for chromium(II) analysis was employed by B. Zabin and H. Taube, *Inorg. Chem.*, **3**, 968 (1964). The spectrophotometric analysis of cobalt(II) has been described previously: J. H. Espenson, *ibid.*, **4**, 1025 (1965).

(13) H. H. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958).

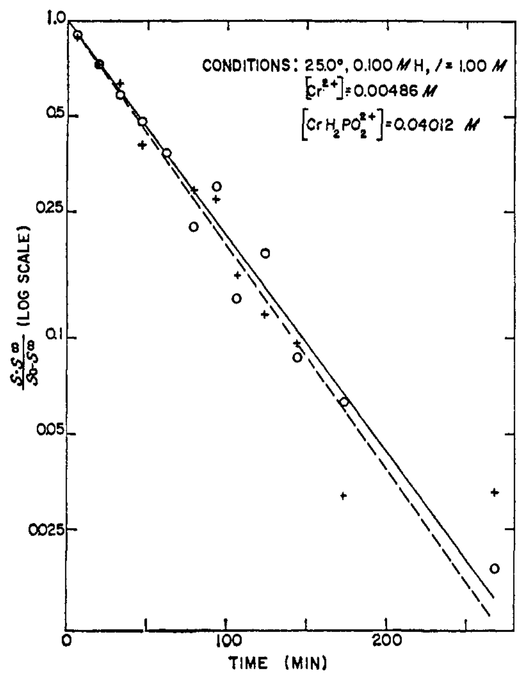


Figure 1. Illustrating McKay plots (eq 4) in a typical exchange experiment with the concentrations shown. The points represent $Cr^{2+}$ sampling (+) and $CrH_2PO_2^{2+}$ sampling (O). The straight lines have slopes given by the computer calculated rate constants and correspond to half-times of 42.5 (+) and 44.3 min (O). The rate constants are $10^3k_2 = 5.80 \pm 0.59$ $M^{-1}$ sec$^{-1}$ (+) and $6.04 \pm 0.60$ $M^{-1}$ sec$^{-1}$ (O), where the uncertainties represent the standard deviation of $k_2$.

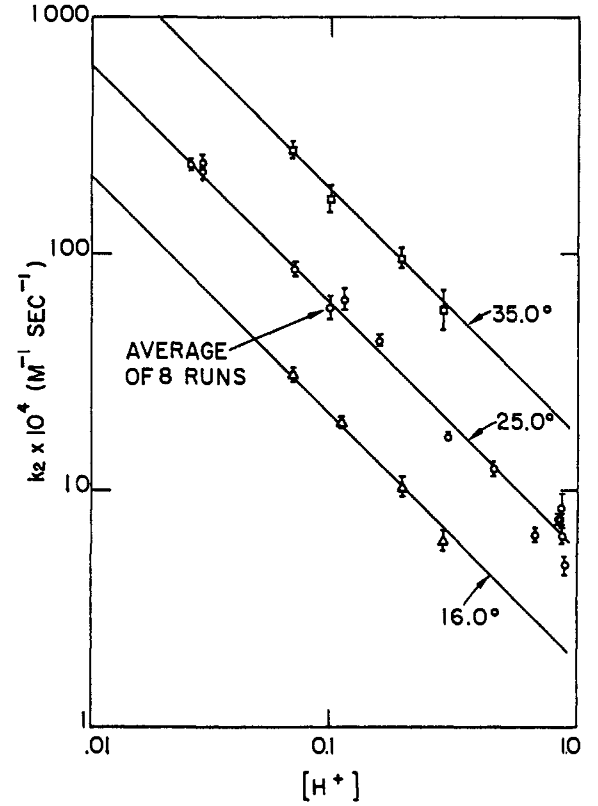


Figure 2. Illustrating the relation of $k_2$ and [H$^+$] in a log–log plot. The lines drawn through the points have a slope of −1.

tion[14] takes the form given in eq 4 in which $S$ stands

$$d \ln \frac{S_t - S_\infty}{S_0 - S_\infty} = -R\frac{[Cr^{2+}] + [CrH_2PO_2^{2+}]}{[Cr^{2+}][CrH_2PO_2^{2+}]}dt \qquad (4)$$

for specific activity of chromium(II), counts per minute per millimole, and $R$ represents the rate law for exchange. An analogous equation with $S_0 = 0$ holds for runs where the activity of $CrH_2PO_2^{2+}$ was measured. As a working hypothesis we assumed that, at constant [H$^+$], the rate of electron exchange is first order in each chromium species according to

$$R = k_2[Cr^{2+}][CrH_2PO_2^{2+}] \qquad (5)$$

A nonlinear, least-squares computer program[15] was used to fit the exchange data in each run to eq 4 and 5. This program calculated $R$ or $k_2$, and also the "best" values of $S_0$ and $S_\infty$. This fit for $S_\infty$ is preferable to the experimental value, since secondary reactions set in at long times.[16,17] Data from a typical run in which both chromium(II) and the hypophosphitochromium(III) complex were followed are shown in Figure 1. For the run shown here, the two sampling techniques gave rate constants that agreed to within an average deviation of 2%. In the four other such pairs of determinations, average deviations were 0.1, 0.3, 4.3, and 12%, and no systematic bias of the direction of the deviation and the oxidation state sampled was noted.

Exchange experiments at 25.0° covered these concentrations: $Cr^{2+}$, 0.18–2.5 × $10^{-2}$ $M$; $CrH_2PO_2^{2+}$, 0.37–4.0 × $10^{-2}$ $M$. Every experiment fit the McKay equation, and constancy of the calculated $k_2$ at a particular [H$^+$] confirmed the second-order exchange rate law shown in eq 5. The average of the standard deviations in 22 runs at 25.0° was 8.5%. When eight additional values at other temperatures were included as well, it was 8.9%.

**Effect of Hydrogen Ion.** Exchange experiments were carried out at several hydrogen ion concentrations in the range 0.026–1.0 $M$. Hydrogen ion exerted a strong inverse effect on the reaction rate. Figure 2 shows the variation of $k_2$, the pseudo-second-order rate constant, plotted *vs.* [H$^+$] on a log–log scale.

---

(14) H. A. C. McKay, *Nature*, **142**, 997 (1938).

(15) This program is based on a report from Los Alamos Scientific Laboratory, LA2367 + Addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for supplying us with the computer programs and to Mr. J. P. Birk for adapting them to the IBM 360 computing facilities.

(16) Spontaneous aquation of the metastable hypophosphite complex must be considered. This reaction becomes an important factor in exchange runs only at high [H$^+$], however, since its rate varies as [H$^+$], whereas the exchange rate varies as [H$^+$]$^{-1}$. Any interference from appreciable spontaneous aquation during an exchange run would result in a higher value of the calculated exchange rate constant. Of course, aquation, after exchange is substantially complete, has no effect. The $Cr^{3+}$ that is the product of aquation would be collected with neither of the separated exchanging species. In one experiment with relatively low [$Cr^{2+}$], 1.8 × $10^{-3}$ $M$, and 0.95 $M$ H$^+$, the rates of aquation and exchange were comparable, and in another run exchange was only twice as fast as aquation. In all other experiments the effect of aquation was smaller, generally a good deal smaller.

(17) In eight runs at low [H$^+$], <0.16 $M$, samples were taken at sufficiently long times to enable comparison of observed values of $S_\infty$ with those calculated by the computer fit of the data. The average deviation of observed and fitted $S_\infty$ values was 1.9% in these eight runs, justifying the procedure used. In principle $S_0$ and $S_\infty$ are given by the solution composition. Loss of small amounts of chromium(II) by air oxidation prior to exchange, however, causes this to be a distinctly less attractive procedure. The extent of such loss of *Cr to exchange could be estimated roughly from the chromium(II) analyses. These corrections were extremely imprecise; they did show, however, that the observed $S_0$ and $S_\infty$ values were in reasonable agreement with those calculated from the composition and the amount of chromium(II) converted to the nonexchanging dimer.

These data are consistent with a rate equation containing a single term[18] inversely proportional to $[H^+]$, eq 6. The unweighted average value of $10^4k$ (sec$^{-1}$)

$$\text{exchange rate} = k[Cr^{2+}][CrH_2PO_2^{2+}]/[H^+] \qquad (6)$$

at 25.0° is 6.26 (±0.87 std dev). A weighted average rate constant expresses the results more meaningfully. Each value is weighted by the computer-calculated standard deviation of $k$ between observed and calculated values of specific activities fit to the McKay equation. With this weighting, the average value of $10^4k$ (sec$^{-1}$) is 6.11 (±0.84 std dev). The effect of this weighting procedure is to count most heavily those runs where the scatter in the data was lowest, and where the greatest precision was obtained.

**Temperature Dependence.** The exchange rate was also studied at two other temperatures, 16.0 and 35.0°. The values[19] of $10^4k$ (eq 6) are as follows: 35.0°, $CrH_2PO_2^{2+}$ sampling only, 18.3 sec$^{-1}$ (±1.1 std dev, four runs), and 16.0°, $Cr^{2+}$ sampling only, 2.08 sec$^{-1}$ (±0.14 std dev, four runs). When these values are weighted as at 25.0°, $10^4k$ (sec$^{-1}$) = 18.5 ± 1.0 and 2.10 ± 0.12.

Values of the enthalpy and entropy of activation were computed from the 30 individual rate constants according to the absolute rate theory expression with $\kappa = 1$. The customary weighting procedure in the least-squares fit of the rate constants would be a weight of $1/k^2$, since the per cent accuracy is presumed to be the same at each temperature. We have chosen a weighting scheme where the precision of each run is taken into account; here each value is weighted as $1/k\sigma_k$ where $\sigma_k$ represents the standard deviation in $k$, as generated by the fit of the data in that particular run. On this basis the activation parameters and their standard deviations are $\Delta H^{\ddagger} = 19.7 \pm 1.0$ kcal mole$^{-1}$ and $\Delta S^{\ddagger} = -7.2 \pm 3.3$ eu. Rate constants ($10^4k$, sec$^{-1}$) recalculated from these parameters at 16.0, 25.0, and 35.0° are 2.073, 6.016, and 18.29, compared to the individual averages at these temperatures of 2.10, 6.11, and 18.5.

## Discussion

**Structure of Hypophosphitochromium(III) Ion.** The ionic charge on $(H_2O)_5CrH_2PO_2^{2+}$ was determined above. The question remains of the structure of the coordinated anion in this complex. Consider the two formulas $(H_2O)_5Cr(OPH_2O)^{2+}$ and $(H_2O)_5Cr(OPHOH)^{2+}$. Hypophosphorous acid is a monobasic acid in which coordination number four for phosphorus is preserved; its formula is $HOPH_2O$. Considerable kinetic evidence has been noted for a second and more reactive form of the acid which plays an important role in a number of oxidation reactions[20] of hypophosphorous acid and also in the exchange reaction[21] of the nonacidic protons. The rate-limiting step in these reactions involves only hypophosphorous acid (and an acid catalyst), in which a structural rearrangement is presumed (eq 7). The latter structure is by far the less

$$HOPH_2O \rightleftharpoons (HO)_2PH \qquad (7)$$

stable; various estimates[20,21] give the equilibrium quotient of this structural change reaction as $10^{-9}$–$10^{-12}$.

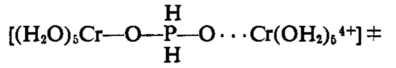
A postulated isomeric structure $Cr(OPHOH)^{2+}$ for the complex raises questions both of its rate of formation and of its stability. The rate of reaction of $Cr^{3+}$ and $H_2PO_2$ is sufficiently low to be consistent[22] with estimates of the rate of reaction 7, but the intrinsic stability required to enable the species $(H_2O)_5Cr(OPHOH)^{2+}$ to form in preference to $(H_2O)_5Cr(OPH_2O)^{2+}$ in spite of the ~15 kcal by which $HOPH_2O$ is favored over $(HO)_2PH$ seems larger than the free energies available for most Cr(III) complexes. It is difficult to rule out the form $(H_2O)_5(OPHOH)^{2+}$ on this basis, however, since stability constants for species of known structure are not available. The noncommittal representation $CrH_2PO_2^{2+}$ will be used in the discussion that follows except when points of detailed structure must be raised.

**Exchange Mechanism.** Electron exchange of chromium(II) and hypophosphitochromium(III) ions proceeds without release of hypophosphite ion from the primary coordination sphere of chromium(III). The reaction necessarily involves bridging by this anionic ligand similar to other exchange reactions of $(H_2O)_5CrX^{2+}$.[3–7] Replacement of $X^-$ by a water molecule (eq 8) is in most instances (including $X^- = H_2PO_2^-$)

$$(H_2O)_5CrX^{2+} + H_2O = (H_2O)_6Cr^{3+} + X^- \qquad (8)$$

a thermodynamically favored process, but its spontaneous rate is so low that it is not a major reaction during the time in which Cr(II)–(III) exchange occurs.[16] The feature that electron transfer and $X^-$ transfer proceed at identical rates constitutes an interesting and significant aspect of the mechanism of these reactions.

The energy of the two exchange sites must first become equivalent before electron exchange occurs.[23] A mechanism for this energy equalization is the formation of a symmetrical transition state. The exchange reaction of $(H_2O)_5CrH_2PO_2^{2+}$ and $Cr(H_2O)_6^{2+}$ would appear to have available an inner-sphere transition state that maintains symmetry at each chromium atom



$$[(H_2O)_5Cr\text{—}O\text{—}\overset{H}{\underset{H}{P}}\text{—}O\cdots Cr(OH_2)_5{}^{4+}]^{\ddagger}$$

---

[18] Alternative dependences on $[H^+]$ were considered including term(s) proportional to $[H^+]^0$ and/or $[H^+]^{-2}$. The fit of the data was not greatly improved by such terms, and the values of the rate constants for these terms were generally within a standard deviation of zero. In 22 runs at 25.0°, the rate law $k[H^+]^{-1} + k'$ had values $10^4k = 6.04 \pm 0.26$ sec$^{-1}$ and $10^5k' = -1.1 \pm 5.2$ $M^{-1}$ sec$^{-1}$. The same data in the equation $k[H^+]^{-1} + k''[H^+]^{-2}$ gave values $10^4k = 5.8 \pm 0.23$ sec$^{-1}$ and $10^6k'' = 1.6 \pm 1.5$ $M$ sec$^{-1}$. For these three equations, the weighted variance of the fit was as follows: $k$ only, 0.32; $k$ and $k'$, 0.32; $k$ and $k''$, 0.30 These results led us to conclude that a single term in $[H^+]^{-1}$ was consistent with these data.

[19] A tabulation of the individual exchange experiments listing concentrations and time, fraction exchange has been deposited as Document No. 9357 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[20] (a) R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **30**, 530 (1934); (b) R. O. Griffith, A. McKeown, and R. P. Taylor, *ibid.*, **36**, 752 (1940); (c) P. Hayward and D. M. Yost, *J. Am. Chem. Soc.*, 71, 915 (1949).

[21] W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11**, 297 (1959). This article contains a review of $H_3PO_2$ reaction mechanisms and demonstrates the interrelation of H exchange and oxidation–reduction reactions.

[22] The rate of the transformation in eq 7 is of the form $k_{HA}[H_3PO_2]\cdot[HA]$ in which HA is an acid catalyst.[21] If the complex formation rate constant[10] $k_f[H_3PO_2][Cr^{3+}]$ is regarded as a rate constant of this type, its value (0.2 $M^{-1}$ hr$^{-1}$) does not appear unreasonable for $Cr^{3+}$ = HA in view of the acid strength of $Cr^{3+}$ relative to other HA catalysts studied previously.[21]

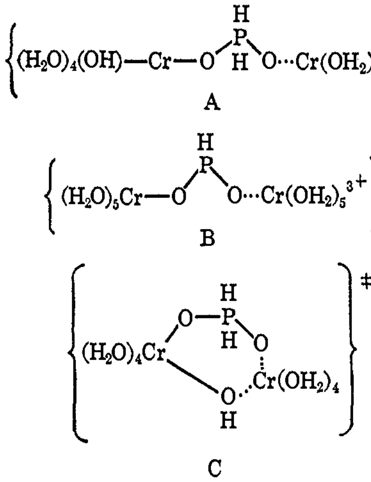
[23] W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

This transition state could be formed from the reactants with an apparent minimum of structural reorganization. Over the entire range of [$H^+$] studied here, even at 1 *M* $H^+$, *this symmetrical transition state remains quite an unimportant pathway,*[16] relative to a configuration containing one proton less. The net activation process, written to ignore the role of solvent molecules, is given by eq 9.

$$CrH_2PO_2^{2+} + Cr^{2+} + H_2O = \{Cr_2(H_2PO_2)(OH)^{3+}\}^{\ddagger} + H^+ \quad (9)$$

Three reasonable formulations for this transition state that we wish to consider are shown in Scheme I. Since during exchange hypophosphite ion is transferred, and not replaced by water, only transition states with a bridging hypophosphite ion are considered. The three formulations are a nonsymmetrical transition state (A) containing a nonbridging hydroxide ion ligand, a symmetrical configuration (B) involving (formally, at least) proton loss from phosphorus, and a symmetrical double-bridged structure (C). The kinetic results we have obtained do not alone allow us to eliminate any of the kinetically equivalent alternatives; the discussion that follows is based largely on analogy with other exchange reactions and on the properties of hypophosphite ion.

**Scheme I**



The nonsymmetrical transition state (A) has no known counterpart in other Cr(II)–Cr(III) exchanges. Rate laws of this form were noted[7–9] for some reactions of $(H_2O)_5CrX^{2+}$ and $Cr^{2+}$. These reactions result in aquation of X and not its transfer, however; presumably hydroxide ion is a bridging ligand in these cases, and the nonbridging $X^-$ group aquates upon electron transfer. Formulation A suffers from the further disadvantage that is not symmetrical. Symmetry is not a criterion for a suitable exchange transition state, but it generally does provide the best mechanism for bringing about energy equivalence of the two electron exchange sites.[23] On the basis of these arguments we are inclined to regard A as a relatively improbable configuration for the transition state.

Formulation B involves a significant structural change in the reactant hypophosphite complex. The phosphorus protons in the free acid are nonlabile, and it seems unlikely those on the coordinated anion are substantially more so. Thus this mechanism *cannot* be a rapid acid dissociation equilibrium of a P–H proton in the complex $(H_2O)_5Cr(OPH_2O)^{2+}$. Were the previously considered isomeric complex $Cr(OPHOH)^{2+}$ the predominant form, the symmetric formulation B would be easily understood. Since this structure for the hypophosphite complex was deemed the less likely, B seems relatively improbable unless further studies on the complex reveal its structure.

Formulation C, a double-bridged transition state involving the anion $H_2PO_2^-$ and one *cis* hydroxide ion, is also consistent with all evidence now at hand. This formulation preserves symmetry in the transition state, accounts for the observed rate dependence on $[H^+]^{-1}$, and would involve a rapid preequilibrium loss of a labile proton from coordinated water.

Direct evidence for double-bridged transition states has been found only for *cis*-diazido complexes.[24,25] They have been shown to be unimportant in some other instances, including difluoro[3] and diaquo complexes.[26] Doubly bridged transition states employing hydroxide ion analogous to C have also been suggested for the rate terms varying as $[H^+]^{-1}$ in the reaction of $CrSCN^{2+}$ and $Cr^{2+}$,[27] and in the reaction of *cis*-$Co(NH_3)_4(OH_2)(O_2CCH_3)^{2+}$ and $Cr^{2+}$.[28] Preliminary work on *cis*-$Cr(H_2PO_2)_2^+ + Cr^{2+}$ indicates important contributions of a double-bridged transition state.[29]

**Related Reactions.** Since the form of the rate law for this reaction differs from that in previously studied Cr(II)–Cr(III) exchange reactions involving $Cr^{III}$–$X^-$ complexes, a comparison of the kinetic parameters cannot be made. The exchange reactions $Cr^{3+}$–$Cr^{2+}$ and $CrNH_3^{3+}$–$Cr^{2+}$ each have a rate law of the form $[Cr^{III}][Cr^{2+}]/[H^+]$, analogous to the present results.[7–9] In those instances, however, presumably the transition states involve hydroxide ion bridging, which is certainly not the case in the present reaction.

Further information on the mechanism of the exchange reaction will be obtained from studies on the kinetics and equilibrium of iron(III)–hypophosphite ion complex formation. Since complex formation would be rapid relative to isomerization of hypophosphorous acid, the kinetics and equilibrium of this reaction may point up some important differences related to the structural features. In addition, alternate syntheses of chromium(III) hypophosphite complex using relatively rapid reactions (*e.g.*, oxidation–reduction techniques) may clarify the question of the possibility of two forms of the monohypophosphite complex.

More directly, the use of labeled hypophosphorous acid (*i.e.*, titrium labeling of $H_3PO_2$ as in the studies of Jenkins and Yost[21]) may clarify many points. An answer to the question of whether one of the two "nonexchangeable" hydrogens is exchanged on complex formation or on electron exchange or not at all can provide valuable information both on the structure of the complex and on the exchange mechanism not available at present. The preferred formulation (C) causes transfer of one water oxygen as well, but oxygen-18 labeling will not be a useful technique since repeated exchange will cause all *cis* and *trans* oxygens in the complex to exchange.

---

(24) R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962).

(25) A. Haim, *ibid.*, **88**, 2324 (1966).

(26) W. Kruse and H. Taube, *ibid.*, **82**, 526 (1960).

(27) A. Haim and N. Sutin, *ibid.*, **88**, 439 (1966).

(28) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

(29) K. A. Schroeder and J. H. Espenson, unpublished experiments.