The Kinetics and Mechanism of the Oxidation of Hypophosphorous Acid by Cerium(IV) in Perchloric Acid Solution

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Abstract: The kinetics of oxidation of hypophosphorous acid by Ce(IV) in strong acid solution was studied using Ce^{144} as a radioactive tracer. The observed rate is about $^1/_{200}$ of that expected by the Mitchell strong acid catalysis mechanism. The results indicate that the reaction takes place by way of cerium(IV) hypophosphite complex ions. The observed rates can be described in terms of the reacting species by the rate expression

$$\frac{-{}^1/_2\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = [\mathrm{H}^+]\sum_{n=1}^{n=3} k_{\mathrm{H}^+(n)}[\mathrm{Ce(H_2PO_2)}_n{}^{+(4-n)}]$$

Values for the catalytic coefficients are estimated, and these along with estimated association constants for the three Ce(IV) complex ions yield a calculated rate curve which fits the experimental data reasonably well over the full range of concentrations investigated. A mechanism consistent with the experimental rate law has been proposed.

The kinetics of reactions of hypophosphorous acid with oxidizing agents has been studied by several investigators.[2-5] The reactions in acid solution have the singular characteristic that they show the same rate constants and the rates become independent of the concentrations of the oxidizing agent above moderate values of the latter. The reactions in acid solution are generally described by the rate equation devised by Mitchell

$$-\frac{\mathrm{d}[\mathrm{H_3PO_2}]}{\mathrm{d}t} = \frac{k_{\mathrm{H}^+}[\mathrm{H_3PO_2}][\mathrm{H}^+]}{1 + \dfrac{k'_{\mathrm{H}^+}[\mathrm{H}^+]}{k_{\mathrm{OX}}[\mathrm{OX}]}} \quad (1)$$

In some cases modification is needed since the reaction is subject to general acid catalysis and the k_{H^+} and k'_{H^+} terms are replaced by sums of terms with catalytic coefficients for each Brønsted acid present in significant concentration. The mechanism consistent with this rate equation consists of a reversible tautomeric shift, catalyzed by acid, between the predominant inactive species of H_3PO_2 and the active form

$$\mathrm{H_3PO_2\ (inactive\ form)} + \mathrm{H}^+ \underset{k'_{\mathrm{H}^+}}{\overset{k_{\mathrm{H}^+}}{\rightleftharpoons}} \mathrm{H_3PO_2\ (active\ form)} + \mathrm{H}^+ \quad (2)$$

followed by the reaction of the active form with the oxidizing agent

$$\mathrm{H_3PO_2\ (active)} + \mathrm{OX} \xrightarrow{k_{\mathrm{OX}}} \mathrm{H_3PO_3} + \mathrm{reduction\ product} \quad (3)$$

The inactive form has been represented as $H_2PO(OH)$ and the active form as $HP(OH)_2$.[6] As the concentration of oxidizing agent is increased to moderate values, the kinetics is described by only the numerator of eq 1. The reactions with various oxidizing agents show the same k_{H^+} which is the catalytic coefficient for the tautomeric shift for strong acids. The reality of the tautomeric shift (2) as the primary step in the reaction has been verified by experiments on the isotopic exchange rates between tritiated[6] and deuterated water[7] and H_3PO_2.

Experimental Section

A. **Materials.** Cerium(IV) perchlorate solution was prepared from G. F. Smith reagent grade solution (0.5 *M* Ce(IV) in 6 *M* $HClO_4$). Ce^{144} ($t_{1/2}$ = 282 days) was obtained from Oak Ridge National Laboratory and purified by the method of Glendenen, *et al.*[8] The Ce(IV) stock solution was brought to the desired specific activity by adding the Ce^{144}, and the resulting solution was standardized against iron wire using diphenylamine sulfonate as indicator. To avoid end point troubles the acidity of the solution was determined by titrating a measured portion to approximately pH 3 with standard NaOH, diluting to a known volume, and determining the acidity by a pH meter.

Stock solutions of hypophosphorous and phosphorous acids were prepared by diluting Baker and Adamson U.S.P. grade acids to approximately 4 *M*. The densities were determined and known weights of the acids were standardized against carbonate-free NaOH using a pH meter. The acid concentrations were checked by the Bernhart method.[9] Reagent grade $HClO_4$ was diluted to the desired concentration and standardized against carbonate-free NaOH solution.

Constant ionic strength was maintained with sodium perchlorate. Solutions of this were prepared from twice-recrystallized Fisher "Purified" grade. Standard solutions were made by taking known weights of sodium perchlorate monohydrate.

For extraction of the unreacted Ce(IV) Fisher "Purified" grade tributyl phosphate (TBP) was used. It was further purified of reducing materials by shaking with cerium(IV) perchlorate prior to use.

B. **Procedure.** The reaction vessel consists of a 200-ml tube with a $^{55}/_{50}$ standard taper top and a side tube at an acute angle for access to the reacting solution. The vessel was partially immersed in a thermostat bath held to ±0.02° of the value chosen, and the reaction solution was agitated by a glass stirrer.

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[2] A. D. Mitchell, *J. Chem. Soc.*, **117**, 957 (1920); **117**, 1322 (1920); **119**, 1266 (1921); **121**, 1624 (1922); **123**, 629 (1923).

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[5] P. Hayward and D. M. Yost, *J. Am. Chem. Soc.*, **71**, 915 (1949).

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[9] D. N. Bernhart, *ibid.*, **26** 1798 (1954),

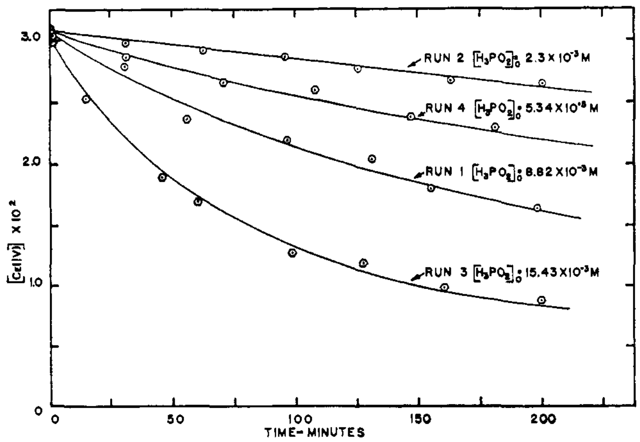

Figure 1. Cerium(IV) concentration *vs.* time for four initial H_3PO_2 concentrations.

The reaction was started by sliding a weighed amount of H_3PO_2 solution (0.1 to 1 ml) in a small Teflon cup down the side tube to the temperature-equilibrated Ce(IV) solution, where mixing was essentially instantaneous. At uniform intervals during the ensuing reaction, seven to nine pipets of the reacting mixture were withdrawn by way of the side tube. The unreacted Ce(IV) was separated by extraction in tributyl phosphate, following the method of Warf,[10] by emptying the withdrawn samples into separatory funnels containing 50 ml of TBP. A 4 *M* HNO_3-2 *M* NH_4NO_3 solution (50 ml) was immediately added and the contents of the funnel shaken for 30 sec. After separation of the phases the aqueous layer was withdrawn. The remaining TBP phase, which contained the Ce(IV), was shaken twice with 25-ml portions of the HNO_3–NH_4NO_3 solution to remove the remaining Ce(III). The time of separation was taken as the time of addition of the HNO_3–NH_4NO_3 solution to the separatory funnel. It was found necessary to increase the HNO_3 and NH_4NO_3 concentrations above those of Warf[10] to obtain a good Ce(IV) extraction. This is apparently due to necessity for breaking down complexes formed by cerium(IV) hypophosphite. At the concentrations used, good reproducibility was obtained.

The Ce(IV) in the TBP phase was made up to a specified volume, and the γ-activity of the 134-kev transition of the Ce^{144} was measured with a Picker 2804E well-type scintillation detector with discriminator set to count energies between 100 and 175 kev. Samples were counted long enough to bring the statistical error within 1%.

Chemical shifts were measured by a 24.3-Mc nmr spectrometer, relative to 85% H_3PO_4 as an external reference, contained in a 1-mm capillary inserted in a 5-mm o.d., nonspinning sample tube.

Results and Discussion

The rate data were analyzed graphically and by a least-squares method using a 1620 IBM computer. Representative concentration *vs.* time plots for runs 1 to 4 are shown in Figure 1. Initial concentrations are shown in Figure 1 and the initial rate constants, k_0, are listed in Tables I to V with the respective run numbers. The "k" used throughout this paper is defined with regard to a stoichiometry of 2Ce(IV) oxidizing $1H_3PO_2$ as $k = (-{}^1/_2 d[Ce(IV)]/dt)(1/[Ce(IV)])$. The "$k_0$" is the same for the initial rate and concentration. Concentrations are all in moles per liter and the time unit is minutes. The system is prone to precipitation, and to avoid this over as wide a range as possible the experiments were carried out in solutions of high perchloric acid concentration, *i.e.*, greater than 1 *M* in $HClO_4$. Even at such acidities the study was complicated by precipitate formation at high [Ce(IV)] and at high $[H_3PO_2]/[Ce(IV)]$ ratios.[11]

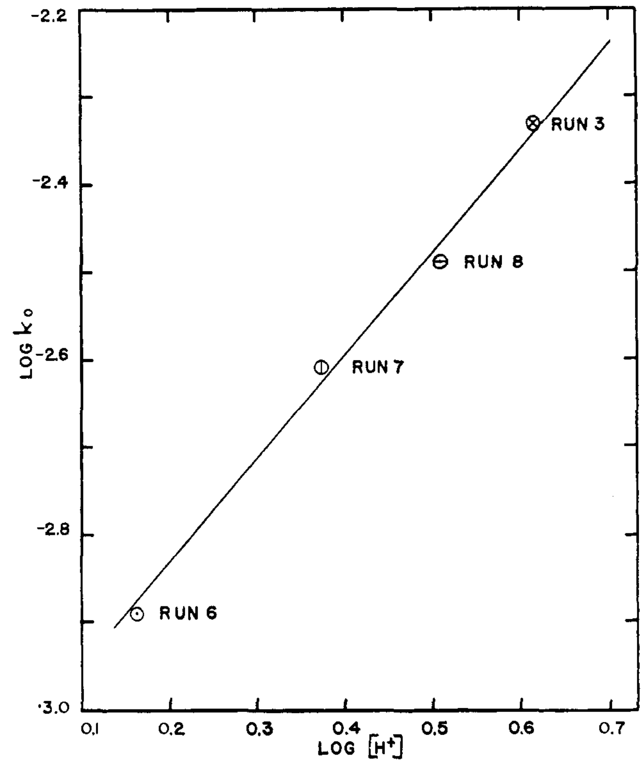

Figure 2. Log k_0 *vs.* log $[H^+]$ showing first-order $[H^+]$ dependence. $[H_3PO_2]_0$, $[Ce(IV)]_0$, and μ are the same for each run (25°).

Like the Mitchell reactions,[2–5] this reaction exhibited a first-order rate dependence on hydrogen ion concentration, observed for all ranges of [Ce(IV)] and $[H_3PO_2]$ tested. The acid dependence was studied in series of runs at fixed $[Ce(IV)]_0$ and $[H_3PO_2]_0$ by varying the perchloric acid concentration but keeping the ionic strength the same for the series. Figure 2 is a plot of log k_0 *vs.* log $[H^+]$ for such a series. The slope is unity, indicating a first-order dependence of the rate on the hydrogen ion concentration.

A series of runs given in Table I isolates the effect of varying $[Ce(IV)]_0$ on the initial rates and on the initial rate constant, k_0, over $[Ce(IV)]_0/[H_3PO_2]_0$ ratios from 2.3 to 15.5. Table II gives a similar series except that the above ratio is varied from 0.083 to 0.33. In both series the initial rates fail to indicate a first-order dependence on $[Ce(IV)]_0$ as shown by the diminishing values of k_0 with ascending $[Ce(IV)]_0$ values. In Table I the rates actually show an over-all decrease[12] with increasing $[Ce(IV)]_0$, falling to about half for a four-to sixfold increase of $[Ce(IV)]_0$, averaging runs 11 and 13. The

Table I. Variation of k_0 with Varying Concentration of Ce(IV) When $[Ce(IV)]_0$ Is in Excess of $[H_3PO_2]_0$[a]

Run	$[Ce(IV)]_0$ $\times 10^2$	$[H_3PO_2]_0$ $\times 10^3$	$[H^+]$	$k_0 \times 10^3$	Initial rate $\times 10^5$
9	1.005	4.38	2.185	2.14	2.15
10	2.035	4.33	2.185	0.65	1.32
11	3.390	4.37	2.185	0.29	0.98
13	6.780	4.33	2.185	0.18	1.22

[a] Ionic strength = 2.6; temperature, 25.00°.

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[10] J. C. Warf, *J. Am. Chem. Soc.*, 71, 3257 (1941).

[11] Brackets about formulas indicate molar concentrations.

[12] The increase in rate shown from run 11 to run 13 may not be real, in view of overlap of probable errors of these runs.

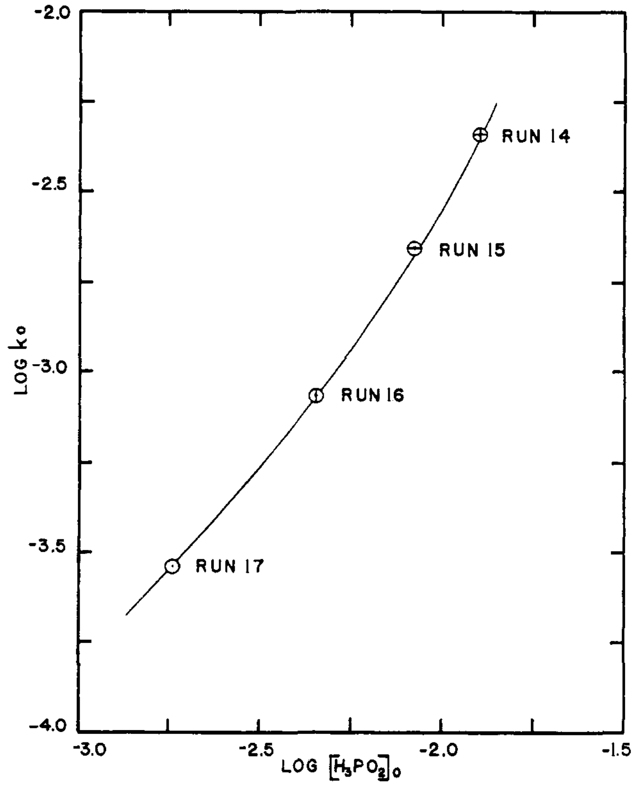

Figure 3. Log k_0 *vs.* log $[H_3PO_2]$ showing variation of apparent order with respect to $[H_3PO_2]_0$; $[Ce(IV)]_0$, $[H^+]$, and μ are the same for each run (25°).

initial rates in Table II vary roughly with the square root of $[Ce(IV)]_0$. It is apparent that the reaction cannot be assigned a simple order with respect to $[Ce(IV)]$ over the ranges studied.

Table II. Variation of k_0 with Varying Ce(IV) Concentration When $[Ce(IV)]_0$ Is Less Than $[H_3PO_2]_0$[a]

Run	$[Ce(IV)]_0 \times 10^3$	$[H_3PO_2]_0 \times 10^3$	$[H^+]$	$k_0 \times 10^2$	Initial rate $\times 10^5$
39	0.77	9.27	4.815	4.27	3.67
37	1.54	9.30	4.815	3.15	4.85
38	2.30	9.30	4.815	2.56	5.88
40	3.08	9.27	4.815	2.43	7.48

[a] Ionic strength = 4.9; temperature, 25.00°.

Series of runs were also made to isolate the effect of varying the $[H_3PO_2]_0$ on k_0, holding all other initial concentrations constant. In Figure 3, run 17 (Table IV) and runs 16 to 14 (Table V) are plotted as log k_0 *vs.* log $[H_3PO_2]_0$. The $[H_3PO_2]_0/[Ce(IV)]_0$ ratios vary from 0.18 to 1.3, respectively, for the points plotted, and the slopes (apparent orders) vary from approximately 1 to 2 over this range. A like plot of the series in Table III in which the $[H_3PO_2]_0/[Ce(IV)]_0$ ratios vary from 2.2 to 8.3 shows a line of slope about 0.15, and hence an apparent order approaching zero. Again it is seen that a rate law for this reaction cannot be written in terms of a simple order dependence on the $[H_3PO_2]_0$. It should be emphasized that the $[H_3PO_2]_0$ is the concentration the H_3PO_2 would have if that added were to exist as such in the solution, and it is not necessarily even close to the actual concentration of this species. It will be shown below that a satisfactory basis for the observed kinetics can be had on the assumption of complex ion formation between ceric and hypophosphite ions, with reduction of Ce(IV) occurring within the various cerium(IV) hypophosphite complex ions.

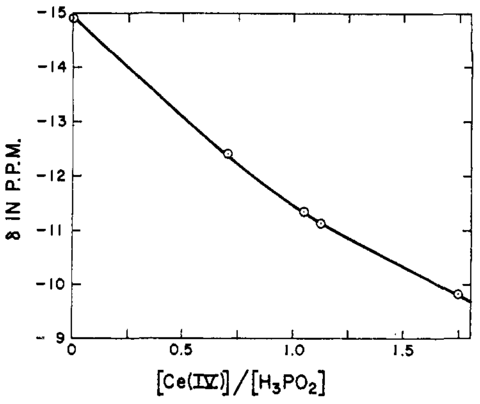

Figure 4. Variation of the P^{31} chemical shift for H_3PO_2 as Ce(IV) ion is added; external reference is 85% H_3PO_4.

Table III. Variation of k_0 When $[H_3PO_2]$ Is in Excess of $[Ce(IV)]$[a]

Run	$[Ce(IV)]_0 \times 10^3$	$[H_3PO_2]_0 \times 10^3$	$[H^+]$	$k_0 \times 10^2$
44	1.54	3.41	4.815	2.76
43	1.54	5.32	4.815	2.97
37	1.54	9.30	4.815	3.15
36	1.54	12.92	4.815	3.36

[a] Ionic strength = 4.9; temperature, 25.00°.

We find no mention of cerium(IV) hypophosphite complex ions or compounds in the literature. However, it is evident from visual, spectrophotometric, nmr, and kinetic evidence that such complexes are formed in the systems studied. The fading and disappearance of the characteristic yellow-orange color of ceric ion as hypophosphorous acid is added (before reduction has had time to occur appreciably) and the appearance of intense absorption bands (ϵ >5 × 10^3) in the 230–260-mμ range indicate complex formation between the constituents. As pointed out earlier, a precipitate forms readily if $[Ce(IV)]$ and $[H_3PO_2]$ are increased beyond the highest concentrations reported in the tables at the specified $[H^+]$ values. Commercial analyses of samples of the precipitate for phosphorus agree with the formulas $Ce(H_2PO_2)_4 \cdot 4H_2O$ for the unheated, dried precipitate and $Ce(H_2PO_2)_4 \cdot 2H_2O$ for a sample dried at 65° *in vacuo*. This again indicates culmination of the complex ion formation process by precipitation of the neutral species expected.

Nmr evidence for complex ion formation is indicated in Figure 4 where large upfield shift of the P^{31} nmr signal is shown as cerium(IV) perchlorate is added to a fixed amount of 1 *M* H_3PO_2 in 2 *M* $HClO_4$. The chemical shift, δ, in ppm, is plotted against the ratio $[Ce(IV)]/[H_3PO_2]$ put in the sample solution. The spin coupling constant, J_{H-P}, was found to be independent of the Ce(IV) concentration. The lack of broadening of the nmr signal observed upon passing from the H_3PO_2 to the complexed $H_2PO_2^-$ is taken to indicate that the rate of exchange of the hypophosphite from the complexes is very rapid. A large chemical shift of the phosphorus resonance line in polyphosphate ion upon forming complexes in solution has been observed by others,[13] giving a basis for interpretation of the shift reported here as due to complex formation, with the $Ce(H_2PO_2)^{+3}$ becoming the favored species at high abscissa ratio in Figure 4.

The results of all the runs at 25° listed in Tables I to V, plotted as $k_0/[H^+]$ *vs.* $[H_3PO_2]_0/[Ce(IV)]_0$, fall in the regular pattern shown in Figure 5. Run numbers are located by the points. In regions where the density of points is too great to plot, the run numbers in those regions are shown. Deviation of points taken from runs not included in Figure 5 are within the limits typical of those plotted. The curve, regarded for the moment as a reasonable best fit to the points, steepens from its initial slope at the origin and then flattens in the region of abscissa concentration ratio about 2 and continues with a much diminished slope above this. The mechanism of the reaction leading to this relatively uniform display of kinetic data is assumed to involve the rapid establishment of the following equilibria

Table IV. Values Obtained for $k_{H^+(1)}$ with [Ce(IV)] in Large Excess of $[H_3PO_2]^a$

Run	$[Ce^{+4}]_0 \times 10^2$	$[H_3PO_2]_0 \times 10^3$	$[H^+]$	$k_0 \times 10^4$	$k_{H^+(1)} \times 10^3$	Ionic strength
2	3.08	2.32	4.195	3.92	1.24	4.4
4	3.03	5.34	4.195	7.48	1.03	4.4
10	2.04	4.38	2.185	6.52	1.39	2.6
11	3.39	4.38	2.185	2.91	1.03	2.6
13	6.78	4.38	2.185	1.80	1.28	2.6
17	1.01	1.83	1.185	2.84	1.32	1.3

[a] Temperature, 25°.

Table V. Summary of Data Not Included in Other Tables

Temp, °C	Run	$[Ce^{+4}]_0 \times 10^2$	$[H_3PO_2]_0 \times 10^3$	$[H^+]$	$k_0 \times 10^3$	Ionic strength
25.00	1	3.08	8.82	4.195	1.59	4.4
	3	3.07	15.43	4.188	4.75	4.4
	5	3.07	15.43	1.461	1.23	4.5
	6	3.07	15.47	1.461	1.30	4.4
	7	3.07	15.44	2.370	2.48	4.4
	8	3.07	15.44	3.279	3.29	4.4
	14	1.02	13.18	1.186	4.52	1.3
	15	1.02	8.64	1.186	2.18	1.3
	16	1.02	4.50	1.186	0.85	1.3
	18	0.99	12.93	1.186	4.13	4.4
	19	0.99	12.93	2.183	7.97	4.4
	20	0.99	12.93	3.184	9.36	4.4
	21	0.99	12.93	4.187	14.83	4.4
	41	0.154	9.12	3.652	26.00	4.9
10.00	27	0.244	8.64	2.353	1.39	2.4
	29	0.124	4.32	2.078	0.97	2.2
	30	0.244	4.50	2.130	0.47	2.2
	31	0.122	12.74	2.078	2.15	2.2
0.05	22	1.572	8.31	2.203	0.15	2.3
	23	1.540	13.29	2.228	0.18	2.3
	25	0.122	8.70	2.078	0.68	2.3
	26	0.122	5.72	2.078	0.48	2.3

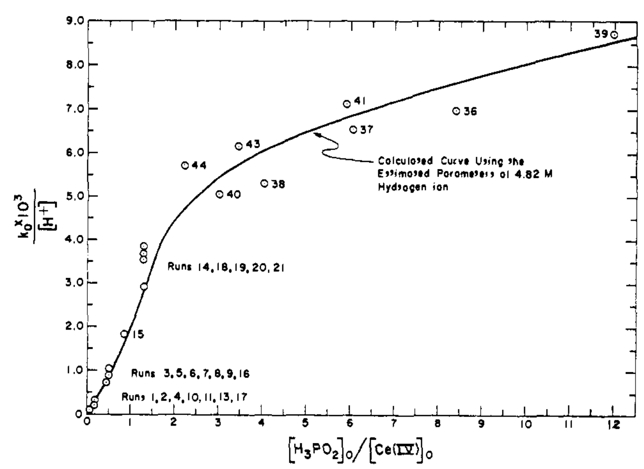

Figure 5. A plot of $k_0/[H^+]$ *vs.* $[H_3PO_2]_0/[Ce(IV)]_0$ over the complete range studied.

$$Ce^{+4} + H_3PO_2 \overset{K_1}{\rightleftarrows} Ce(H_2PO_2)^{+3} + H^+ \tag{4}$$

$$Ce(H_2PO_2)^{+3} + H_3PO_2 \overset{K_2}{\rightleftarrows} Ce(H_2PO_2)_2^{2+} + H^+ \tag{5}$$

$$Ce(H_2PO_2)_2^{+2} + H_3PO_2 \overset{K_3}{\rightleftarrows} Ce(H_2PO_2)_3^{+1} + H^+ \tag{6}$$

Analysis of the kinetic data indicates that K_1 and K_2 are sufficiently large that very little H_3PO_2 remains as such when the total H_3PO_2 added is less than twice the Ce(IV) concentration. This is indicated by the fact that no decrement from first-order hydrogen ion rate dependence due to reversal of reactions 4 or 5 with a fourfold increase in $HClO_4$ concentration was observed. K_3 for reaction 6, estimated from the kinetic data to lie between 0.8×10^2 and 1.5×10^2, is much smaller than K_1 or K_2. It follows that, in the region of abscissa ratio above 2 in Figure 5, one would expect the concentration of $Ce(H_2PO_2)_3^{+1}$, one of the complexes in which reaction is postulated to occur, to be diminished by increasing the perchloric acid concentration and to give lowered ordinate values in Figure 5. Unfortunately, all of the runs except 41 in this region are at the maximum H^+ ion concentration (4.815 *M*) to assure avoidance of precipitation of the neutral complex. Runs 41 and 37 at an abscissa ratio about 6 show ordinate values trending in the direction predicted by this effect, but data are not available over a H^+ concentration range to test it adequately. The equilibria, reactions 4 to 6, give the following in the solutions. When Ce(IV) is in excess, *i.e.*, at abscissa ratios less than 1 (Figure 5), the predominant complexes are $Ce(H_2PO_2)^{+3}$ and $Ce(H_2PO_2)_2^{+2}$. At the abscissa ratio about 2 the Ce(IV) is predominantly present as $Ce(H_2PO_2)_2^{+2}$, and at ratios above 2 this is partially converted to $Ce(H_2PO_2)_3^{+1}$. With the above equilibria the following rate expression appears able to account formally for the observed kinetics over the full concentration range studied

$$-{}^1/_2 \frac{d[Ce(IV)]}{dt} = k_{H^+(1)}[Ce(H_2PO_2)^{+3}][H^+] + k_{H^+(2)}[Ce(H_2PO_2)_2^{+2}][H^+] + k_{H^+(3)}[Ce(H_2PO_2)_3^{+}][H^+] \tag{7}$$

in which the indicated $k_{H^+(n)}$ are the catalytic coef-

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[13] M. M. Crutchfield and R. R. Irani, *J. Am. Chem. Soc.*, **87**, 2815 (1965).

ficients for the decomposition of the 1, 2, and 3 cerium(IV) hypophosphite complex ions shown.

Values of $k_{H^+(1)}$ have been estimated from the kinetic data at small $[H_3PO_2]/[Ce(IV)]$ ratios (<0.2), where the principal reaction is the catalytic decomposition of the $Ce(H_2PO_2)^{+3}$ complex. Table IV contains pertinent data from six runs suitable for determining the first catalytic coefficient and the resulting values. The $k_{H^+(1)}$ values are obtained assuming all of the H_3PO_2 added is present as $Ce(H_2PO_2)^{+3}$, since Ce(IV) is present in large excess.

It is of interest to compare the rate of this reaction with that expected by the Mitchell mechanism, assuming that Ce(IV) is present as ceric ion and H_3PO_2 is present as the acid. The larger concentrations of Ce(IV) in Table IV are presumed to be above the minimum required in the Mitchell reactions for nondependence of rate on oxidizing agent concentration (see introductory paragraph). Using the Mitchell rate constant as 0.256 l. mole^{-1} min^{-1}, run 4 would show an initial rate 5.74 × 10^{-3} mole l.$^{-1}$ min^{-1} and run 13 an initial rate 2.45 × 10^{-3}. Our comparable observed rates are 2.3 × 10^{-5} and 1.2 × 10^{-5}, respectively, as found by multiplying k_0 by $[Ce(IV)]_0$. Our rates are seen to be about 0.5% of those expected in the absence of our proposed complex formation. Since the Ce(IV) ion must be present in the runs of Table IV owing to the large excess of Ce(IV) over H_3PO_2 added to make up these solutions, the slow rates observed indicate that the H_3PO_2 has been removed, as such, to the extent that the Mitchell type reaction, if occurring in this system at all, is insignificant compared to that expected from the amounts of H_3PO_2 added.

The second catalytic coefficient, $k_{H^+(2)}$, for the reaction involving $Ce(H_2PO_2)_2^{+2}$ ion was estimated using runs in which the $[H_3PO_2]/[Ce(IV)]$ ratios were between 0.2 and 2.0 by equating the rate to the sum of the first two terms on the right-hand side of eq 7 and taking $k_{H^+(2)} = 1.3 \times 10^{-3}$. Essentially all of the H_3PO_2 is assumed to be bound as $Ce(H_2PO_2)^{+3}$ or $Ce(H_2PO_2)_2^{+2}$, in keeping with the association constants of these species being large. A reiterative procedure, assuming large values of K_1 and K_2 and adjusting $k_{H^+(2)}$ for most consistent agreement between observed and calculated rates for all runs in the region, gave $k_{H^+(2)} = 4.75 \times 10^{-3} \pm 0.5 \times 10^{-3}$ l. mole^{-1} min^{-1}.

For abscissa ratios above 2 (Figure 5), the points do not define a curve as well as at lower ratios, but it is evident that the slope is sharply diminished. The data of Table III show the $[H_3PO_2]_0/[Ce(IV)]_0$ ratio increasing from 2.3 to 8.3, but k_0 increasing only 22%. At ratios above 3, or possibly 4, there is no mechanism to tie up hypophosphite other than as H_3PO_2, so its concentration as such must rise by a tremendous factor over this range, *i.e.*, 2.3 to 8.3, yet there is no great increase in rate. The oxidation–reduction reaction apparently does not involve H_3PO_2 directly in this region. On the assumption that reaction in this region involves the $Ce(H_2PO_2)_2^{+2}$ and $Ce(H_2PO_2)_3^{+1}$ ions, and taking $k_{H^+(2)}$ to be 4.75 × 10^{-3} and the association constant K_3 to be in the range mentioned, $k_{H^+(3)}$ is estimated to be 11 × 10^{-3} ± 1 × 10^{-3} l. mole^{-1} min^{-1} at 25°. The curve of Figure 5 was calculated for 4.82 *M* H$^+$ concentration using $K_1 = K_2 = 4 \times 10^5$ and the values for K_3 and the three catalytic coefficients obtained above. The activation energies for the reactions of the second and third complex ions are 23 ± 3 and 21 ± 3 kcal, respectively. Efforts were made also to determine the activation energy for the first complex ion, but the lack of adequate data, due in part to the very slow rates at temperatures below 25° and at the very low $[H_3PO_2]/[Ce(IV)]$ ratios necessary to determine $k_{H^+(1)}$, precluded a reliable result.

A proposed mechanism for our reaction, then, which is consistent with the observations involves first the rapid establishment of the equilibria which maintain the various cerium hypophosphite complexes as represented in eq 4, 5, and 6. A reasonable extension of the hydrogen ion catalyzed tautomeric shift concept used in other reductions by H_3PO_2 can be applied to the hypophosphite ion bound in the complexes, which also is assumed to undergo a hydrogen ion catalyzed tautomeric shift to an active form. These shifts within the various complex ions provide the rate-controlling parallel steps which may be represented

$$[Ce(H_2PO_2)_n]^{+(4-n)} + H^+ \underset{k'_{H^+(n)}}{\overset{k_{H^+(n)}}{\rightleftarrows}} [Ce(H_2PO_2)^*(H_2PO_2)_{n-1}]^{+(4-n)} + H^+ \quad (8)$$

where the asterisk denotes an "active" hypophosphite group. The complex ions containing the active species then undergo rapid transformation to the primary product

$$[Ce(H_2PO_2)^*(H_2PO_2)_{n-1}]^{+(4-n)} \xrightarrow{k_{d(n)}} \text{products} \quad (9)$$

The ion systems must evidently call upon the environment to complete the reaction to the final products which are considered to be Ce(III) and phosphite in acid or cerium complex form. We are not in a position to speculate profitably on the nature of these processes.

Another mechanism to accomplish reaction 8 without having to assume a tautomeric shift in the bound hypophosphite ions in the complexes, but utilizing the known tautomeric shift in the free acid, appears possible. The several cerium hypophosphite complex ions must exchange hypophosphite ions with the hypophosphorous acid in solution, *i.e.*, reverse and forward reactions of eq 4, 5, and 6, and the recombination could be expected to incorporate a certain fraction of active form hypophosphite ions in the complexes. The catalytic coefficients would then be directly related to the rates of reactions 4, 5, and 6, considered as dynamic equilibria.

The derived rate law consistent with the proposed mechanism is

$$\frac{-{}^1/_2 d[Ce(IV)]}{dt} = \frac{[H^+]\sum_{n=1}^{n=3} k_{H^+(n)}[Ce(H_2PO_2)_n{}^{+(4-n)}]}{1 + \dfrac{[H^+]\sum_{n=1}^{n=3} k'_{H^+(n)}}{\sum_{n=1}^{n=3} k_{d(n)}}} \quad (10)$$

If $k_{d(n)} >> k'_{H^+(n)}$, the derived rate law reduces to the experimental rate law already given (eq 7).

The kinetics of the reaction described is unique among those reported for hypophosphorous acid. The kinetics of the latter have been described either by the rate law given in eq 1 or a bimolecular reaction between the oxidizing agent and hypophosphite ion. Rates of these were much faster than those found in this study.

The Ce(IV)–H_3PO_3[14] reaction has been found to have common characteristics with this reaction, *e.g.*, complex formation and first-order hydrogen ion catalysis, but to proceed at much slower rates.

(14) R. L. Carroll, unpublished results.

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The Kinetics and Mechanism of the Hydrolysis of Pyrophosphite

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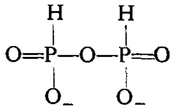
Abstract: The kinetics of the hydrolysis of pyrophosphite has been investigated over an extensive pH range. The rate law for the reaction can be expressed as

$$-\text{rate}/[H_2P_2O_5^{-2}] = k_0 + \sum_{a} k_a(HA)_a + \sum_{b} k_b(B)_b$$

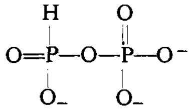
where k_a and k_b are the catalytic coefficients and $(HA)_a$ and $(B)_b$ are the concentrations of all Brønsted acids and Lewis bases, respectively. The catalytic coefficients for several carboxylic acids and a variety of bases are reported along with the temperature coefficients for the specific rate constants for the hydrogen ion and hydroxide ion. Evidence for the formation of intermediate species by the base catalysis reaction was obtained by high resolution P^{31} nmr spectra of partially hydrolyzed pyrophosphite solutions. On the basis of the kinetics and nmr studies and previously reported observations, the mechanism of the hydrolysis reaction is discussed.

Although the sodium salt of pyrophosphorous acid, $Na_2H_2P_2O_5$, has been known[1] since 1888, the kinetics of its hydrolysis has never been satisfactorily defined. The disodium salt is very soluble in water and the pH of its aqueous solution is about neutral. This is the only evidence at present regarding the acid strength of pyrophosphorous acid.[2] The symmetrical pyrophosphite anion undergoes hydrolysis[3–6] to 2 moles of orthophosphite, and the structure has been shown to be[7]



$$O{=}\overset{H}{\underset{O^-}{P}}{-}O{-}\overset{H}{\underset{O^-}{P}}{=}O$$

The complexity of the hydrolysis reaction is indicated by the study of Blaser and Worms,[6] where they reported large effects due to certain salts, and by the studies of other investigators[1,3–5] who did not arrive at a rate law defining the reaction. Several of these salts react with the pyrophosphite ion to give products other than the orthophosphite ion; *e.g.*, the fluoride ion reacts to give the monofluorophosphite ion, and the orthophosphate ion reacts in neutral solution to give the isohypophosphate ion



$$O{=}\overset{H}{\underset{O^-}{P}}{-}O{-}\overset{O}{\underset{O^-}{\overset{\|}{P}}}{-}O^-$$

a process called transanhydrization by Blaser.[6,8] We have found other examples of this type which will be reported in this paper.

The pyrophosphite ion, unlike the condensed phosphates, has been reported to show very weak complexing ability with cations in aqueous solution,[9] indicating an absence of chelation stabilization. This difference has been interpreted in terms of less π bonding in the P–O–P linkage of the pyrophosphite ion which should relate to the hydrolytic instability.

The pyrophosphite species is of special interest to the field of phosphorus chemistry because its behavior typifies much of the chemistry of condensed species of the lower oxidation states of phosphorus. Because of the importance of the hydrolysis reaction itself in understanding the nature of the P–O–P linkage, and the sparsity of thorough kinetics studies in this realm of phosphorus chemistry, contributions in this area are sorely needed.

Experimental Section

Materials. Sodium pyrophosphite was prepared by the method described by Amat.[1] The material was assayed by iodine titration, the results of which were confirmed by P^{31} nmr spectra of concentrated water solutions. Of the phosphorus present, 95.5% was in the form of pyrophosphite and 4.5% was present as phosphite. All other chemicals were of reagent grade quality.

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