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Kinetics of the Reaction between Hypophosphite and Perruthenate Ions in Alkaline, Aqueous Solutions

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The reaction between hypophosphite ion, $H_2PO_2^-$, and perruthenate, RuO_4^-, has been studied in basic solutions at several temperatures. The reaction is first order in each of $[H_2PO_2^-]$, $[RuO_4^-]$, and $[OH^-]$. The rate constant is 248 ± 14 M^{-2} sec^{-1} at 24.8°. The enthalpy of activation is 1.86 ± 0.2 kcal/mol, and the entropy is −41 ± 7 eu. The process is believed to involve a rapid reaction between OH^- and $H_2PO_2^-$ to form some P(I) species such as $\bar{H}_2PO_2^-$ or HPO_2^- which then reacts with RuO_4^- to form a P(II) intermediate or a P^I–RuO_4^- complex in the rate-determining step. A final fast reaction between a second RuO_4^- and the P(II) or complex then completes the process. The mechanism is discussed briefly in the light of previous studies of $H_2PO_2^-$ reduction mechanism investigations.

Few studies on the oxidation of hypophosphite ($H_2PO_2^-$) in alkaline solution have been published. Sieverts and Loessner[1] studied the decomposition of $H_2PO_2^-$ in aqueous alkali at 91 and 100°. Ben-Zvi[2] reported a radical chain mechanism for the oxidation by peroxydisulfate up to pH 11. Roper, Haas, and Gillman[3] reported a proton nmr study of the base-catalyzed hydrogen–deuterium exchange between hypophosphite ion and water. The authors suggest the observed rate of exchange is due to the production of a reactive intermediate, analogous to Mitchell's[4] inactive and active forms of hypophosphorous acid (H_3PO_2). This study was designed to determine whether there is a reactive phosphorus intermediate in basic solution.

Experimental Section

Reagents. Except for 99.9% ruthenium metal (K & K Laboratories, Inc.) reagent grade chemicals were used throughout this investigation. Water, used for preparation of solutions, was passed through and mixed-bed ion-exchange resin, was distilled from alkaline permanganate, and then was redistilled. Glassware was washed with hot commercial bleach, soaked in alcoholic KOH, rinsed with dilute HCl, rinsed thoroughly with distilled water, and then air-dried.

Potassium perruthenate was prepared according to the directions of Larsen and Ross[5] except that KOH was substituted for NaOH and the catch solution was cooled to 7°. The shiny black crystals were removed by filtration, washed with distilled water, and stored in a desiccator. *Anal.* Calcd for $KRuO_4$: Ru, 49.50. Found: Ru, 49.77. Potassium hypophosphite was recrystallized from distilled water. Analyses by the methods of Ogawa[6] and Jones and Swift[7] agreed well and indicated that no phosphite was present. Fresh potassium hydroxide (0.300 M) solutions were prepared for each set of experiments. The concentration (0.300 M) was calculated from results of a titration of the base against potassium hydrogen phthalate. All solutions were made up to ionic strength of 0.30 (molar basis). Solutions for varying pH studies were made from tri- and dibasic potassium phosphate mixed in appropriate concentrations.

Procedure. The pseudo-first-order reaction (observed with large excesses of hypophosphite) was too fast for conventional techniques. Stopped-flow studies were conducted on two apparatus differing mainly in construction detail and light path length. One instrument, with a 2.0-cm path length, is described elsewhere,[8] and the other, an instrument constructed by Dewald,[9] has a light path length of 2.0 mm. The increase in concentration of ruthenate (RuO_4^{2-}) was followed at 465 nm and concentration was calculated by means of absorptivities given by Luoma and Brubaker.[10] Traces of absorbance *vs.* time were stored on an oscilloscope and recorded on self-developing photographic film. Perruthenate concentrations were then calculated from total ruthenium and RuO_4^{2-} concentrations. Reaction half-lives were estimated from graphs of the log of the calculated perruthenate concentration *vs.* time.

Experiments in which the concentrations of $H_2PO_2^-$ and RuO_4^- which were comparable were monitored at 465 nm by use of a Cary Model 14 spectrophotometer. The cylindrical Pyrex spectrophotometric cell had a path length of 5.0 cm. For each experiment, aliquots of each stock solution were pipetted into separate beakers in a controlled-temperature water bath. When the solutions reached thermal equilibrium, the two reactants were removed from the bath and poured back and forth from one beaker to another; then the cell was filled. The spectrophotometer was started 30 sec after the two solutions were mixed. (Mixing time was taken as zero time.) The reaction was monitored until all RuO_4^- was reduced to RuO_4^{2-} (less than 2000 sec under these conditions).

Ruthenate is not reduced to a significant extent by hypophosphite in these concentrations and reaction times. Several experiments indicated the rate of reduction of RuO_4^- by phosphite (HPO_3^{2-}) is slow compared to reduction by $H_2PO_2^-$. Analysis of reaction mixture by the method of Jones and Swift[7] (after removal of Ru by the method of Gilchrist[11]) indicated the production of 2 mol of RuO_4^{2-} for each mole of $H_2PO_2^-$ (±15%) used. No difference in the reaction was noted when it was examined in the absence of light or in deoxygenated solutions. Thin-layer chromatography[12] on Bakerflex R 0-4468 sheets showed that the oxidation product was HPO_3^{2-} (R_f 0.75 compared to that of $H_2PO_2^-$).

Results

Extensive stopped-flow studies were designed to observe the effects of an equilibrium between inactive and active forms of $H_2PO_2^-$. Table I presents the half-lives for the disappearance of RuO_4^- under various conditions. The $t_{1/2}$ values are consistent and all plots are linear for at least 2 half-lives, for solutions in which pseudo-first-order conditions prevail.

Data from dilute solution studies were analyzed by the curve fitting computer program of Dye and Nicely.[13] The second-order equation

$$\frac{dx}{dt} = k_2([Ru] - x)\left([P] - \frac{x}{2}\right) \qquad (1)$$

was intergrated and rearranged to the form

$$x = \frac{2[Ru](e^{yk_2t} - 1)}{\frac{[Ru]}{[P]}e^{yk_2t} - 2} \qquad y = \frac{[Ru] - 2[P]}{2} \qquad (2)$$

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Table I. Half-Lives for RuO_4^- Disappearance

$10^4[H_2PO_2^-]$, M	$t_{1/2}$, sec ± 7%					
	$10^4[RuO_4^-]_{initial}$, M					
	12.3	5.56	4.55	3.52	0.745	0.73
1000	0.080[a]	0.089		0.10	0.13	
500	0.18	0.17				
250	0.355	0.37	0.40	0.40	0.40	0.48
125			0.81			0.88
50			2.1			2.7
25			4.25			4.3
12.5			8.3			8.7
5.0			20.5[a]			19

[a] Pseudo-first-order conditions do not apply.

where [Ru] and [P] represent initial concentrations of RuO_4^- and $H_2PO_2^-$, k_2 is the second-order rate constant, t is time, and x is the extent of reaction (the concentration of RuO_4^{2-} calculated from RuO_4^- at any time t). The input data are x and time, and k is optimized to give minimum residuals between the input x and the calculated x. Results of these calculations from data taken at 24.8° appear in Table II. All errors listed are standard deviations, unless otherwise noted.

All temperature dependence studies were carried out at 0.300 M KOH. The results are listed in Table II. The activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) are 1.86 ± 0.2 kcal/mol and −41 ± 7 eu, respectively, and the Arrhenius activation energy, E_a, is 2.46 ± 0.2 kcal/mol.

A positive hydroxide ion dependence for the rate constant was expected. The reaction was studied over a wide range of hydroxide concentrations. At the lowest pH (10.3), the reaction solution was turbid when removed from the Cary 14. It was obvious other reactions interfered at lower pH. Table III presents rate constant results from pH studies. A plot of k_2 *vs.* [OH$^-$] has a slope of 248 ± 14 and an intercept of 0.2 ± 1.8. Thus $k_2' = k_2/[OH^-] = 248 \pm 14\ M^{-2}\ sec^{-1}$.

Discussion

Roper, Haas, and Gillman's[2] rate data for the exchange reaction in D_2O

$$H_2PO_2^- \rightleftharpoons HDPO_2^- \rightleftharpoons D_2PO_2^-$$

obeyed the rate law

$$\text{rate} = k[OD^-][H_2PO_2^-] \qquad (3)$$

with $k = 3 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 25°. They concluded this rate "is actually the rate of production of the reactive intermediate." If this reactive intermediate is the species proposed by Mitchell (*i.e.*, the form that is readily oxidized), then it should be easily oxidized by RuO_4^-. If the reactive intermediate concentration is substantially less than that of the inactive form (say 10%) and considering observed rates, the reaction should deviate from pseudo-first-order kinetics before the initial $H_2PO_2^-$ to RuO_4^- ratio falls below 20:1. The $t_{1/2}$ values in Table I do not deviate from the expected pattern. Therefore, the reactive species is either equal to the hypophosphite ion concentration at all times or the reactive intermediate is formed at a rate that is rapid compared to the rate-determining step.

When the ratio of $H_2PO_2^-$ to RuO_4^- is near 1, the data conform to the second-order expression

$$\frac{dx}{dt} = k_2([Ru] - x)\left([p] - \frac{x}{2}\right)$$

with $k_2 = 58.5\ M^{-1}\ sec^{-1}$ at 25°. Stopped-flow data fitted to eq 2 give a second-order rate constant, k_2, equal to 72.7 ± 4.0 M^{-1} sec^{-1}. The OH$^-$ dependence leads to a rate law of the form

Table II. Rate in 0.300 M KOH at Various Temperatures

Temp, °C	Initial concn × 10^4, M		k_2, M^{-1} sec^{-1}
	$H_2PO_2^-$	RuO_4^-	
4.3	2.49	1.70	43.9 ± 0.4
	1.25	1.77	45.5 ± 0.6
	2.49	1.77	45.3 ± 0.3
	1.25	1.71	43.3 ± 1.2
			Av 44.5 ± 1.0
14.7	2.49	1.81	48.5 ± 0.3
	1.25	1.79	54.1 ± 0.6
	2.49	1.79	49.1 ± 0.4
	1.25	1.80	45.1 ± 0.6
			Av 49.2 ± 1.0
24.3	2.50	1.72	56.6 ± 0.4
	2.00	1.73	59.1 ± 0.5
	1.50	1.69	59.1 ± 0.5
	1.00	1.69	59.9 ± 0.9
	0.500	1.66	57.8 ± 1.1
			Av 58.5 ± 1.8
34.3	2.53	1.57	64.1 ± 0.7
	1.90	1.56	70.0 ± 0.7
	1.27	1.50	73.1 ± 1.0
	0.633	1.47	66.3 ± 1.7
			Av 68.4 ± 2.0
42.8	2.53	1.65	73.7 ± 1.0
	1.90	1.65	66.3 ± 0.9
	1.27	1.61	84.9 ± 1.4
	2.53	1.45	73.6 ± 0.6
			Av 74.6 ± 5.0

Table III. Dependence of the Rate on [OH$^-$] at 24.3°

Initial concn × 10^4, M		[OH$^-$], M	k_2, M^{-1} sec^{-1}
$H_2PO_2^-$	RuO_4^-		
2.64	2.76	0.0833	16.5 ± 0.1
3.08	1.98	0.0158	5.15 ± 0.09
2.58	2.89	0.00851	4.17 ± 0.03
3.49	2.55	0.00363	3.78 ± 0.07
2.53	2.28	0.000200	3.00 ± 0.05

$$\text{rate} = k_2'[RuO_4^-][H_2PO_2^-][OH^-]$$

and suggest a fast preequilibrium between OH$^-$ and (probably) $H_2PO_2^-$ followed by the rate-determining step between RuO_4^- and the P(I) species produced in the previous step.

Ben-Zvi[2] proposed the formation of a hypophosphite radical in the oxidation of $H_2PO_2^-$ by peroxydisulfate. He found the activation energy for the formation of the radical was 6.6 kcal/mol. The rate equation is not simple and the observed rate constant decreased to a plateau (about 10^3 M^{-1} sec^{-1}) at pH 11. Although a free-radical chain mechanism for oxidation by RuO_4^- cannot be excluded, it could not be substantiated, and the data conform well to the second-order rate law.

Roper, Haas, and Gillman[3] reported an E_a of about 19 kcal/mol which is similar to activation energies from other studies on the oxidation of hypophosphite. The low E_a from this study (2.46 kcal/mol) and the small entropy of activation (−41 eu) indicates the rate-determining step is other than the inactive-active tautomerism. The data can be explained by the formation, in a fast equilibrium, of a P(I) species

$$H_2PO_2^- + OH^- \rightleftharpoons H_3PO_3^{2-}\ (P(I))$$

and then

$$P(I) + RuO_4^- \xrightarrow{k_2'} P(II) + RuO_4^{2-}$$

which is rapidly oxidized to form phosphite

$$P(II) + RuO_4^- + 3OH^- \xrightarrow{fast} HPO_3^{2-} + RuO_4^{2-} + 2H_2O$$

The results might also be rationalized in terms of the formation of a [RuO_4^--PI] intermediate. The latter might be more in accord with the large negative $\Delta S^{\ddagger}$ if an intermediate, which contains both tetrahedral P and Ru and a water or -OH bridge, is formed. But where the observed rate constant is a product of a rate and a preequilibrium constant, such speculation is probably unwarranted.

Registry No. $H_2PO_2^-$, 15460-68-1; RuO_4^-, 14333-21-2.

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Reduction of Vanadium(V) by L-Ascorbic Acid[1]

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The stoichiometry of the reduction of vanadium(V) by L-ascorbic acid (H_2A) has been experimentally determined to be $H_2A + 2V(V) \rightarrow A + 2V(IV) + 2H^+$. The kinetics of this reaction has been studied by stopped-flow procedures at 25° and ionic strength of 1 *M* ($LiClO_4$) in acid media (0.20-1.0 *M* $HClO_4$). Upon mixing acidic solutions of V(V) and L-ascorbic acid a transient appears, the uv-vis spectrum of which has a maximum at 425 nm. The observed pseudo-first-order rate constant, k_{obsd}, which was not acid dependent, is related to the concentration of the reagent in excess, V(V), according to the equation $k_{obsd} = kK[V(V)]/(1 + K[V(V)])$. This equation is the familiar one for rapid formation of a complex followed by its rate-limiting decomposition. The experimentally determined constants are the intermediate complex formation constant, $K = 488 \pm 28\ M^{-1}$, and the decomposition rate constant, $k = 12.1 \pm 0.2\ sec^{-1}$. On the basis of the measured value of k_{obsd} and the known value for the reaction $V(III) + V(V) \rightarrow 2V(IV)$, the two-electron reduction mechanism can be ruled out; an inner-sphere, one-electron reduction of vanadium(V) by L-ascorbic acid seems to be the most plausible mechanism.

Vanadium was discovered in the blood of certain marine invertebrates (*Ascidia*) in 1911,[2] yet neither the mechanism of vanadium extraction from the sea water nor the metabolic role of the element has been established. More recently,[3] it has been shown that vanadium is present in ascidians chiefly as V(III) within specific blood cells called vanadocytes. Unlike the animal's blood plasma (pH ≃7) or sea water (pH ≃8), these cells are about 1 *M* in sulfuric acid. In the course of our investigations into the mechanism of vanadium incorporation by ascidians,[4] specifically regarding the reduction of oceanic V(V) to V(III) by the animal, we have conducted studies of the kinetics of the reduction of V(V) by L-ascorbic acid in acidic media.

The reduction of V(V) by a variety of two-electron reductants has been the object of numerous studies. In a qualitative survey of the reduction of V(V) by a multitude of organic species,[5] Littler and Waters have shown that most, if not all, such reactions proceed *via* a free-radical mechanism wherein V(V) undergoes only a one-electron reduction. Thus these reactions appear to occur according to the sequence

$$V(V) + R \rightarrow V(IV) + R\cdot$$

$$R\cdot + V(V) \rightarrow V(IV) + P \quad \text{(rapid)}$$

where R, R·, and P represent the reductant, a free radical, and the oxidized product, respectively. The alternative sequence

$$V(V) + R \rightarrow V(III) + P$$

$$V(III) + V(V) \rightarrow 2V(IV) \quad \text{(rapid)}$$

wherein V(V) undergoes two-electron reduction, followed by rapid V(V) oxidation of the V(III) intermediate to V(IV) was ruled out by detection of the free-radical intermediate.

Littler and Waters have also studied the stoichiometry and kinetics of V(V) reduction by pinacol,[5] cyclopentanone,[6] and cyclohexanone.[6] In all cases indirect evidence for a free radical was observed, and the one-electron reduction of V(V) to V(IV) was demonstrated. The rate of V(V) reduction by cyclopentanone was observed to be first order with respect to hydrogen ion concentration in perchlorate media at an ionic strength of 6.0 *M*. The rate of V(V) oxidation of pinacol in sulfate media showed virtually no hydrogen ion dependence below 1.0 *M* in hydrogen ion. Above this level an increase in the electron-transfer rate was ascribed to either a more reactive form of V(V), possibly $V(OH)_3^{2+}$ or a vanadium(V) sulfate complex such as $[V(OH)_3HSO_4]^+$.

Wells and Kuritsyn have suggested[7] that the reduction of V(V) by hydroquinone (QH_2) may proceed *via* an inner-sphere mechanism, giving the products V(IV) and *p*-benzoquinone. The rate is first order in [V(V)] overall but becomes less than first order in [QH_2] at higher concentrations of the reductant, suggesting complexation of V(V) prior to the electron-transfer step. The rate increases with increasing hydrogen ion concentration, further suggesting that the equilibrium constant for complexation is dependent upon [H^+].

Cooper, *et al.*, have studied[8] the reduction of V(V) by hypophosphorous acid, which also involves complexation

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