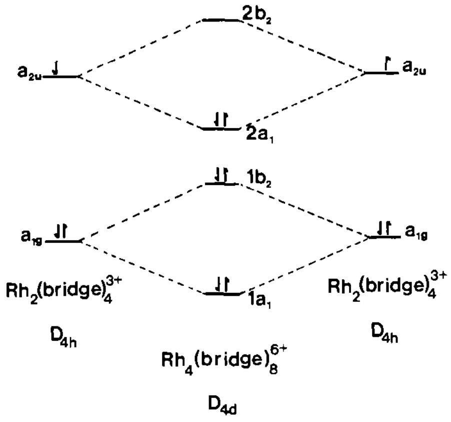

Figure 6. Relative energies of the molecular orbitals derived from the $a_{1g}(d_{z^2})$ and $a_{2u}(d_{z^2})$ $Rh_2(bridge)_4{}^{3+}$ binuclear complex functions in D_{4d} $[Rh_2(bridge)_4]_2{}^{6+}$.

and a $Rh_2{}^{3+}$ ion, which has a formal Rh–Rh bond order of 0.5. $Rh_2{}^{3+}$ has been shown to be more easily oxidized[13] than $Rh_4{}^{6+}$. Clearly, the one-electron-level energies are very sensitive to their occupation by electrons, effectively coupling the dissociative chemical reactions to the electron transfer upon oxidation.

Similar arguments apply to the reduction of $Rh_4{}^{6+}$, except that in this case an electron goes into the $2b_2$ level, which is antibonding with respect to all three Rh–Rh interactions. An odd electron in this level can be greatly stabilized by the formation of an additional Rh–Rh bond via further aggregation to form partially reduced oligomeric species similar to $Rh_6{}^{8+}$ or $Rh_8{}^{10+}$, which have been observed in the aqueous solution reduction of $Rh_4{}^{6+}$ by chromous ion[11] or hydrogen gas.[14] The film formed upon reduction of $Rh_4{}^{6+}$ at the electrode surface is probably related to these insoluble oligomeric species observed in the homogeneous solution chemical reductions. Further studies are in progress to elucidate the properties and structure of this oligomeric surface film.

It is interesting to speculate about the relationship between the extreme irreversibility of the oxidation–reduction reactions and the photochemical production of hydrogen gas from hydrogen ions which have been observed for the $Rh_4{}^{6+}$ system. Due to the high-energy requirement for the reduction of hydrogen ions to hydrogen gas via hydrogen atom intermediates and the related back-electron-transfer problem encountered in excited-state electron-transfer reactions, systems such as the $[Rh_2(bridge)_4]_2{}^{6+}$ system, which are capable of undergoing irreversible two-electron-transfer reactions, will have distinct advantages in the production of hydrogen gas from aqueous solutions. Clearly, systems which display "normal" behavior (i.e., undergo reversible one-electron transfers) are systems which are unlikely to be able to cause H–H bond formation since they will be unable to supply the second electron to complete the formation of the H_2 bond before a back-electron-transfer step regenerates hydrogen ions.

Acknowledgment. Support of this research through a Dupont Young Faculty Grant and a University of Minnesota Faculty Summer Research Appointment (K.R.M.) are gratefully acknowledged. We also wish to thank Mr. David A. Bohling for drawing the figures presented here.

Registry No. $Rh_4{}^{6+}$, 76900-21-5; $Rh_2{}^{4+}$, 71375-02-5.

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[13] The rapid oxidation of $Rh_2{}^{3+}$ by Fe^{3+}, observed in ref 8, suggests that the reduction potential of $Rh_2{}^{3+}$ is more negative than that of $Rh_4{}^{6+}$.

[14] Mann, K. R.; Bell, R. A., unpublished result.

Contribution from the Department of Chemistry,
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Kinetics and Mechanism of Oxidation of Hypophosphorous Acid with Silver(I) in Aqueous Perchloric Acid Solutions

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Received June 18, 1980

Silver(I)-catalyzed oxidation of hypophosphorous acid with cerium(IV) in aqueous perchloric acid has been recently studied,[1] and the role of silver(I) was not well defined. This prompted us to study the oxidation of hypophosphorous acid with Ag(I) itself to know how far these results can explain the catalyzed reaction. Mitchell,[2] studied this reaction in 1923 and found the reaction to have the same characteristics as reported in the other oxidations of H_3PO_2 with iodine,[3] chlorine,[4] Hg(II),[5] and copper(II).[6] The reaction was independent of the concentration of oxidant for its larger concentrations and two forms of hypophosphorous acid (normal and active) were suggested to exist in a tautomeric equilibrium.[7] However, Mitchell did not give the mechanism of the reaction, and the role of silver(I) was not defined clearly under all possible conditions of acidity. Rate constants were calculated only under the conditions when excess silver(I) was present. The present investigation has been made under all possible conditions limited by experimental procedure. Another point of interest was to know whether any complex of Ag(I) with H_3PO_2 is formed in view of the reported Ag(I) adducts in the Ag(I)-catalyzed oxidations of isopropyl alcohol[8] and other oxygen-containing compounds.[9,10]

Experimental Section

Materials. Hypophosphorous acid was Riedel AR grade (32%), and all other reagents were either BDH AnalaR or E. Merck GR quality. Corning glass vessels were employed for storing the solution and for carrying out the reactions. Silver nitrate was stored in black painted bottles. Doubly distilled water was used for all solutions, and in the reaction mixtures, the second distillation being from the neutral potassium permanganate.

Kinetics Procedure. Reactions were carried out at 30 ± 0.1 °C in a thermostat. They were initiated by adding a temperature-equilibrated solution of silver nitrate to the reaction mixture containing the desired amounts of hypophosphorous acid, perchloric acid, and other reagents or water at 30 °C. The kinetics were followed by removing 5-mL aliquots after suitable intervals of time and quenching the reaction by adding it to a known excess of a solution of sodium bromide. Since silver(0) is formed as a product, the reaction mixture was thoroughly shaken before taking out the aliquots. The excess bromide was determined by titration against a standard solution of silver nitrate with potassium chromate as indicator. The pH of the solution was made nearly 7 before titration[11] by adding the desired quantity of sodium bicarbonate. The reproducibility was better than ±10%.

Initial rates were determined by the plane mirror method.[12] It was not possible to make plots conforming to an integrated equation since the reaction is complicated and it is further made complicated

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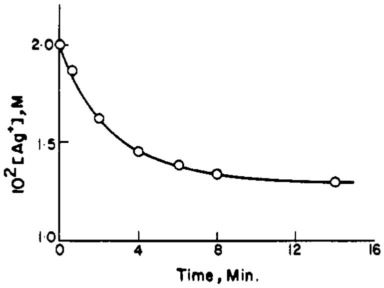

Figure 1. Typical concentration–time curve for the oxidation of H_3PO_2 by Ag^+ ($[Ag^+] = 0.02$ M; $[H_3PO_2] = 0.02$ M; $[HClO_4] = 1.0$ M; 30 °C).

Table I. Variation of $[Ag^+]$ in the Oxidation of H_3PO_2 with Ag^+ at 30 °C[a]

	10^5v/M s^{-1}			
	$[H_3PO_2] = 0.02$ M		$[H_3PO_2] = 0.04$ M	
$10^2 \times [Ag^+]$/M	$[H^+] =$ 0.0635 M	$[H^+] =$ 1.0 M	$[H^+] =$ 0.0325 M	$[H^+] =$ 1.0 M
1.0	0.53	1.95	0.512	4.05
2.0	0.63	3.94	0.678	8.02
2.5		4.95		
3.0	0.63	4.42	0.71	12.0
4.0	0.615	3.98	0.752	16.0
5.0	0.525	3.50	0.72	16.9
6.0		2.91	0.71	14.4
7.0	0.487			12.0
8.0		2.58		10.8
10.0	0.465	2.43		9.84
12.0		2.29		9.41

[a] The rates are given as 10^5v in M s^{-1}

by the separation of solid Ag(0) which inhibits the reaction. Another complication is the presence of H_3PO_3 which is formed as a product and which increases the rate. The decrease in the rate due to the adsorption of Ag^+ on solid Ag(0) is more predominant than the increase in the rate by H_3PO_3. The net result is that the concentration time curves typical of Figure 1 are obtained.

Optical measurements were made with a Beckmann spectrophotometer using 1-cm cell. pH titrations were made on an EC Digital (pH 5651) pH meter.

The stoichiometry was found to be in accordance with eq 1.

$$2Ag(I) + H_3PO_2 + H_2O \rightarrow 2Ag(0) + H_3PO_3 + 2H^+ \quad (1)$$

Results

Silver(I) Dependence. At higher acid concentration (1.0 M $HClO_4$) and at two different $[H_3PO_2]$ (0.04 and 0.02 M), silver(I) was varied by (1–12) × 10^{-2} M. The rate is first order in Ag(I) for its range of lower concentrations, attains a maximum, and then becomes limiting for large concentrations of Ag(I). This behavior with respect to Ag(I) was missed by Mitchell.[2] These results are shown in Table I. Since the rate profile has a maximum, there must be at least two reactive species of Ag(I)—most likely Ag^+ and AgH_2PO_2, the latter being less reactive.

At lower $[H^+]$ (0.05 M $HClO_4$), the rate appears to be independent of Ag(I). The same type of behavior is obtained even in the absence of added $HClO_4$, and the only source of hydrogen ion (0.032 M) was the dissociation of H_3PO_2. These results are also given in Table I. The results obtained by Mitchell[2] pertain to low acidity.

Hypophosphorous Acid Dependence. Hypophosphorous acid was varied in the range 4.0×10^{-3}–1.0×10^{-1} M at two concentrations of Ag(I) and three different concentrations of perchloric acid. The results are given in Table II. It was also varied without any addition of perchloric acid. This resulted in the simultaneous variation of $[H^+]$ too. The latter was calculated in such solutions from the known dissociation constant[13] of 0.135 for H_3PO_2 at $I = 1.0$ M and 25 °C and $\Delta H = -2970$ cal mol^{-1} obtained from the values at 16 and 30 °C given by Griffith.[14] The value of 0.124 at 30 °C and $I = 1.0$ M was employed for calculation. $[H^+]$ was also calculated in solutions of 0.05 M $HClO_4$, and these values are shown in parentheses in Table II. For approximately $[H_3PO_2] > {}^1/_2[Ag^+]$, a plot of rate vs. $[H_3PO_2]$ is a straight line showing first-order dependence on $[H_3PO_2]$. For lower concentrations of H_3PO_2 the same plot gives a curve passing through the origin. For a certain range of concentration of H_3PO_2, the rate for 0.05 M [Ag(I)] is less than that for 0.02 M [Ag(I)], suggesting again that at least two species of Ag(I) are reactive and that one with larger content of Ag(I) is less reactive.

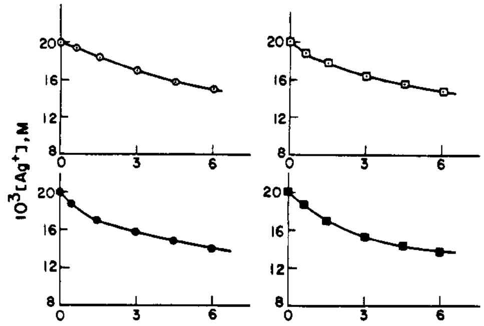

Figure 2. Concentration–time curves showing the effect of addition of Ag^0 at different times ($[Ag^+] = 0.02$ M; $[H_3PO_2 = 0.02$ M; $[HClO_4] = 1.0$ M; 30 °C): ⊙, Ag^0 added in the begining; □, Ag^0 added after 45 s; ●, Ag^0 added after 95 s; ■, Ag^0 not added.

Hydrogen Ion Dependence. Hydrogen ion concentration was varied by employing perchloric acid at constant ionic strength adjusted with lithium perchlorate under three different conditions: (1) excess H_3PO_2, (2) excess Ag(I), and (3) a little excess of Ag(I). The total hydrogen ion concentration was calculated by taking into account the dissociation of H_3PO_2. The results are given in Table III. The rate has first-order dependence on $[H^+]$ for the condition $[H^+]/[H_3PO_2] < 10$. It is probably connected with the dissociation of H_3PO_2. The rate tends to attain a limiting value with the increase of $[H^+]$. The limiting rate depends on the concentrations of Ag(I) and H_3PO_2 in a complex way or perhaps on the concentrations of Ag(I) species and free $[H_3PO_2]$.

Effect of Ionic Strength. Ionic strength was varied with lithium perchlorate at constant concentrations of other reagents and under two conditions: (1) $[H_3PO_2] > [Ag(I)]$ and (2) $[Ag(I)] > [H_3PO_2]$. The results are given in Table IV. Under the first condition the rate is independent of ionic strength whereas, when $[Ag(I)] > [H_3PO_2]$, the rate increases with the increase of ionic strength. It is obvious that the reacting species are different under the two conditions.

Reaction in the Presence of Added Ag(0). Silver(0) was prepared by allowing the title reaction to proceed for sometime. The solid was filtered and washed thoroughly with water. The washings gave a positive test of Ag(I) with NaCl showing adsorption of Ag(I) on the precipitate of Ag(0). A suspension of Ag(0) was prepared in distilled water, and a known quantity after thorough shaking was removed and was added to the reaction mixture either initially or was added at suitable intervals of time. Typical plots showing decrease in the rate are given in Figure 2. It is obvious that the rate decreases to a large extent if Ag(0) is added.

Reaction in the Presence of H_3PO_3. Several reactions with different initially added phosphorous acid were also studied

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Table II. Variation of H_3PO_2 in Its Oxidation with Ag^+ at 30 °C and $I = 1.0$ M[a]

	10^5v/M s^{-1}				
	$[Ag^+] = 0.02$ M				$[Ag^+] = 0.05$ M, $[HClO_4] = 1.0$ M
$10^2[H_3PO_2]$/M	$[HClO_4] = 0.0$ M	$[HClO_4] = 0.05$ M	$[HClO_4] = 0.5$ M	$[HClO_4] = 1.0$ M	
0.4		0.040 (0.0528)		0.162	
0.5	0.0101 (0.00485)	0.061 (0.0535)	0.231	0.258	0.196
0.6		0.081 (0.0545)		0.37	
0.7			0.442		0.384
0.8	0.0275 (0.0077)	0.137 (0.0556)		0.72	
1.0	0.0412 (0.0095)	0.197 (0.057)	0.85	1.08	0.77
1.2		0.258 (0.058)	1.41	1.58	1.15
1.5	0.091 (0.014)	0.386 (0.06)	2.11	2.41	1.82
2.0	0.166 (0.018)	0.635 (0.0635)	3.3	3.66	3.52
2.5			4.35		5.66
3.0	0.376 (0.025)		5.67	6.20	8.72
4.0	0.682 (0.0325)		7.75	8.1	16.8
5.0				11.0	25.1
6.0				13.6	32.6
8.0				18.0	45.4
10.0					55.0

[a] The rates are given as 10^5v in M s^{-1}. Figures in parentheses are the molar hydrogen ion concentrations. In other cases $[H^+]$ is equal to $[HClO_4]$.

Table III. Variation of $[H^+]$ in the Oxidation of H_3PO_2 with Ag^+ at 30 °C and $I = 1.0$ M Adjusted with $LiClO_4$[a]

			10^5v/M s^{-1}				
			$[H_3PO_2] = 0.04$ M			$[H_3PO_2] = 0.02$ M	
$[HClO_4]$/M	$[H^+]$/M for $[H_3PO_2] = 0.04$ M	$[H^+]$/M for $[H_3PO_2] = 0.02$ M	$[Ag^+] = 0.0025$ M	$[Ag^+] = 0.020$ M	$[Ag^+] = 0.050$ M	$[Ag^+] = 0.100^b$ M	$[Ag^+] = 0.050$ M
0.0		0.018				0.122	0.147
0.02		0.035				0.242	
0.05		0.0635				0.433	
0.08		0.092				0.624	
0.1	0.122	0.11	0.298	2.44		0.87	1.30
0.2	0.216	0.207	0.510	3.75	6.65	1.51	2.35
0.3	0.312	0.305	0.75	5.4	9.7	1.62	3.04
0.4	0.408	0.40	0.98	7.3	12.8	1.68	3.30
0.5	0.50	0.50	1.08	7.8	14.1	1.75	3.42
0.6	0.60	0.60			15.2		
0.7	0.70	0.70	1.20	8.4			
0.8	0.80	0.80			15.7		3.48
1.0	1.0	1.0	1.32	8.6	16.8		3.58

[a] The total $[H^+]$ was calculated from a K_d value of 0.124 for H_3PO_2; 10^5v/M s^{-1} is the rate. [b] The ionic strength was 0.5 M.

Table IV. Effect of Ionic Strength in the Reaction between Ag^+ and H_3PO_2 at 30 °C

$10^2[Ag^+] = 5.0$ M; $10^2[H_3PO_2] = 2.0$ M; $[HClO_4] = 0.5$ M

I/M	0.57	0.77	1.07	1.27	1.57	2.07
10^5v/M s^{-1}	3.25	3.38	3.56	3.75	3.95	4.28

$10^2[Ag^+] = 2.0$ M; $10^2[H_3PO_2] = 4.0$ M; $[HClO_4] = 1.0$ M

I/M	1.06	2.06	3.06
10^5v/M s^{-1}	8.6	8.4	8.55

to notice how the rate is affected in the presence of H_3PO_3. The concentration of phosphorous acid was varied in the range 1×10^{-2}–8×10^{-2} M at three different sets of reactant concentrations as given in Table V. For reactant ratios $[Ag(I)]/[H_3PO_2] > 1$, the rate increases and attains a limiting value, but for ratios $[Ag^+]/[H_3PO_2] < 1$, the rate concentration profile gives a straight line with an intercept. A separate experiment of Ag(I) with H_3PO_3 showed that no reaction occurs.

Reaction at Different Temperatures. The reactions were carried out at 30, 35, 40, and 45 °C under two different ratios of the reactants. The overall energy of activation for the condition $[H_3PO_2] > [Ag^+]$ was 10.6 ± 0.1 kcal mol^{-1}, and for the condition $[Ag^+] > [H_3PO_2]$, it was 17.4 ± 0.1 kcal mol^{-1}.

Spectrophotometric Work. The spectra of Ag^+, of mixtures of Ag^+ and H_3PO_2, and of Ag^+ and H_3PO_3 (all in 0.10 M

Table V. Effect of Phosphite in the Reaction between Ag^+ and H_3PO_2 at 30 °C[a]

$10^2[Ag^+] = 2.0$ M; $10^2[H_3PO_2] = 4.0$ M

$10^2[HPO_3^{2-}]$/M	0	1.0	2.0	4.0	5.0
10^5v/M s^{-1}	8.43	8.75	9.25	9.87	10.0

$10^2[Ag^+] = 5.0$ M; $10^2[H_3PO_2] = 2.0$ M

$10^2[HPO_3^{2-}]$/M	0	1.0	2.0	3.0	4.0	5.0	6.0	8.0	10.0
10^5v/M s^{-1}	3.32	5.47	6.95	8.0	8.33	8.55	8.60	8.70	8.75

$10^2[Ag^+] = 5.0$ M; $10^2[H_3PO_2] = 1.0$ M

$10^2[HPO_3^{2-}]$/M	0	1.0	2.0	3.0	4.0	5.0	6.0	8.0
10^5v/M s^{-1}	0.75	1.52	2.02	2.30	2.67	2.70	2.72	2.75

[a] $[HClO_4] = 1.0$ M.

$HClO_4$) show that the absorbance of both the mixtures slightly decreases as compared to that of Ag^+. Absorbance of 1×10^{-4} M [Ag^+] with different concentrations of H_3PO_2 and H_3PO_3 at 202 and 206 nm, respectively, were measured at 30 °C, and the formation constant for the 1:1 complex was calculated by the method of Ramette.[15] The formation constants for H_3PO_2 and H_3PO_3 with the assumption of a 1:1 complex were found to be 138 ± 19 and 510 ± 30 M^{-1}, respectively.

pH Measurements. Titration of 0.05 M [H_3PO_2] with and without 0.0025 M [Ag^+] against 0.11 M [NaOH] indicated complex formation, but the stability constants could not be determined.

Discussion

The kinetics and spectrophotometric results of the present work indicate complex formation between Ag^+ and H_3PO_2 (eq 2). This is in line with the coordinating properties of H_3PO_2

$$Ag^+ + H_2PO_2^- \xrightleftharpoons{K_1} AgH_2PO_2 \qquad (2)$$

with other metal ions[16] with concentration equilibrium constants between 150 and 10. Important observations from the mechanistic point of view are the limiting rates at high [H^+] and high [Ag(I)] and the dependence of the rate on their relative values. Mixed up with this is the question of free concentration of H_3PO_2 which is controlled by the dissociation equilibrium (eq 3), with a K_d value[13] of 0.135 at 25 °C and

$$H_3PO_2 \xrightleftharpoons{K_d} H_2PO_2^- + H^+ \qquad (3)$$

$I = 1.0$ M and the complex formation equilibrium (2). Two things are further to be noted. (1) At high [H^+], $v/[H_3PO_2][Ag^+]$ gives a constant value of 0.104 ± 0.004 M^{-1} s^{-1}. (2) At low [H^+] or at high [Ag^+], $v/H_3PO_2][H^+]$ gives a constant value of $(4.27 \pm 0.12) \times 10^{-3}$ M^{-1}. This would imply a rate law of the form in eq 4, where A, B, and C are

$$v = -d[Ag(I)]/dt = \frac{A[H_3PO_2][H^+][Ag^+]}{B[Ag^+] + C[H^+]} \qquad (4)$$

constants. Considering one situation for a simple reaction between Ag^+ and H_3PO_2, the mechanism and the rate law are given by

$$Ag^+ + H_2PO_2^- \xrightleftharpoons{K_1} AgH_2PO_2 \qquad (2)$$

$$H_3PO_2 \xrightleftharpoons{K_d} H_2PO_2^- + H^+ \qquad (3)$$

$$Ag^+ + H_3PO_2 \xrightarrow{k} \text{products} \qquad (5)$$

Hence

$$v = -d[Ag(I)]/dt = \frac{2k[H_3PO_2][Ag^+][H^+]}{[H^+] + K_d + K_dK_1[Ag^+]} \qquad (6)$$

If at high [H^+] (≈1.0 M) $K_d + K_dK_1[Ag^+]$ could be neglected, the rate law reduces to eq 7. The value of k is (5.2 ± 0.2)

$$v = 2k[H_3PO_2][Ag^+] \qquad (7)$$

$\times 10^{-2}$ M^{-1} s^{-1}. Similarly if at low [H^+], [H^+] + K_d could be neglected as compared to $K_dK_1[Ag^+]$ (which is not very true), the rate law reduces to eq 8. The value of k using K_d

$$v = \frac{2k[H_3PO_2][H^+]}{K_dK_1} \qquad (8)$$

= 0.124 and K = 138 was found to be 3.65×10^{-2} M^{-1} s^{-1}. The two values are fairly similar. The value of 4.27×10^{-3} M^{-1} s^{-1} at 30 °C is comparable to the value 1.3×10^{-3} M^{-1} s^{-1} at 25 °C reported by Mitchell.[2]

One more way to test rate law 6 is to plot $1/v$ vs. $1/[H^+]$. From the slope:intercept ratio, the values of K_d $(1 + K_1[Ag^+])$ can be calculated, and from the K_d value of 0.124, the value of K_1 was found to be 170 ± 44 M^{-1}. The order of magnitude of K_1 is the same as determined spectrophotometrically.

Another way to explain these results is to assume the much talked about tautomeric equilibrium[7] through mechanism (9)–(11). This would lead to rate law 12. The verification

$$H_3PO_2 \text{ (normal)} + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_3PO_2 \text{ (active)} + H^+ \qquad (9)$$

$$H_3PO_2 \text{ (active)} + Ag^+ \xrightarrow{k_3} \text{products} \qquad (10)$$

$$H_3PO_2 \text{ (active)} + AgH_2PO_2 \xrightarrow{k_3'} \text{products} \qquad (11)$$

$$v = \left(\frac{2k_1k_3[Ag^+][H_3PO_2][H^+]}{k_3[Ag^+] + k_2[H^+]} + \frac{2k_1k_3'[AgH_2PO_2][H_3PO_2][H^+]}{k_3'[AgH_2PO_2] + k_2[H^+]} \right) \left(\frac{[H^+]}{[H^+] + K_d} \right) \qquad (12)$$

of this rate law is still more difficult, and it can be tested only qualitatively by reducing the rate law under different limiting conditions. Different ionic strength effects and different overall energies of activation under two different conditions of relative concentrations of Ag^+ and H_3PO_2 clearly show that the reactive species are different under the two conditions. The increase in the rate in the presence of phosphorous acid supports the facts of reactive free H_3PO_2 and the complexing of Ag^+ with H_3PO_2.

Acknowledgment. A.K.I. is thankful to M. D. College, Sri Ganganagar for the study leave, and the UGC for providing the finances and the fellowship to carry out this work.

Registry No. H_3PO_2, 6303-21-5; Ag^+, 14701-21-4.

Supplementary Material Available: Initial rates at temperatures of 35, 40, and 45 °C under two different conditions, absorption data of mixtures of Ag^+ and H_3PO_2 and of Ag^+ and H_3PO_3, values of constants under two limiting conditions of eq 4, and the values of K_1 from kinetics results (5 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of a New Layered Compound, $V(CH_3CS_3)_2$

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Received January 3, 1980

Many layered inorganic compounds are known to act as host lattices and react with a variety of guest atoms or molecules to give intercalation compounds in which the guest is inserted between the host layers. Recently these materials have attracted considerable attention for such different reasons as the observation that the superconducting transition temperature of some hosts increases on intercalation of amines[1] and the

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