

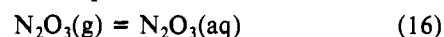
Equilibrium 2 was studied by Grätzel et al.,<sup>13</sup> as noted above. In that study NO<sub>2</sub> was formed in solution rapidly after the pulse; the equilibrium constant  $K_2$ , determined from the decrease in NO<sub>2</sub> absorbance as equilibrium 2 was established, was found to be  $1.4 \times 10^4 \text{ M}^{-1}$  (20 °C).

The magnitude of  $K_1$  evaluated by eq 16,  $(2.3 \pm 1) \times 10^{-3} \text{ M}^{-1}$ , agrees within the estimated error bound with that determined in this study  $((3.03 \pm 0.23) \times 10^{-3} \text{ M}^{-1})$ . This agreement lends support to the present interpretation of the measurements made in dilute acid, viz., that the species responsible for the quadratic component of the UV absorption in the present study is the same species (presumably N<sub>2</sub>O<sub>3</sub>) that gives rise to the UV absorption spectrum in the pulse radiolysis studies. This close agreement contrasts with the strong disagreement (70-90-fold) between the value of  $K_1$  evaluated by eq 15 and that determined by Turney<sup>4</sup> (in  $\sim 5 \text{ M}$  perchloric acid) or that given by Schmid and Krenmayr<sup>5</sup> (based on the value of Turney but corrected to dilute solution). As noted above, it was this disagreement that stimulated the present investigation. The present results establish that this disagreement is a consequence of the shift in the empirical association constant  $K_D'$  with increasing acidity. We have suggested above that this shift is due to the formation of a species whose concentration is dependent upon hydrogen ion activity as well as exhibiting a quadratic dependence on [HNO<sub>2</sub>]. Since the shift in  $K_D'$  is observed in studies both in the UV (this work) and in the visible regions (Bunton and Stedman,<sup>3</sup> as well as the qualitative observations noted above), we infer that the absorption at  $\lambda$  500-800 nm that gives rise to the blue color of the acidic solutions also arises from the acidic species, rather than from the neutral N<sub>2</sub>O<sub>3</sub> as has been supposed in the previous studies. A study of the dependence of the weak visible absorption band upon acid concentration might give further insight into the identity of the species responsible for the blue color. We note in this context that the presence of "blue nitrous acid" is generally associated with highly acidic media.<sup>11,28,29</sup>

The low value of  $K_1$  found in the present study would appear also to resolve an anomaly in the interpretation of the kinetics

of diazotization of amines via N<sub>2</sub>O<sub>3</sub> intermediate. As pointed out by Ridd,<sup>2</sup> the apparent reaction rate between N<sub>2</sub>O<sub>3</sub> and amines is far less than the encounter rate of the species when [N<sub>2</sub>O<sub>3</sub>] is evaluated by using Turney's value for  $K_1$ , whereas for diazotization via nitrosyl halide intermediates the rate coefficients approach those of encounter reactions. However, for the lower value of [N<sub>2</sub>O<sub>3</sub>] calculated by using  $K_1$  obtained in the present study, the rate coefficient for reaction between N<sub>2</sub>O<sub>3</sub> and, e.g., aniline is found to be  $7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, within 1 order of magnitude of the encounter rate of the species and much more in keeping with the rate constants obtained for reaction with nitrosyl chloride and nitrosyl bromide.

Determination of  $K_1$  permits the free energy of formation of N<sub>2</sub>O<sub>3</sub>(aq) to be evaluated, making use of the known<sup>30</sup> free energies of formation of HNO<sub>2</sub> and H<sub>2</sub>O(l); the resulting value is  $\Delta G_f^\circ(\text{N}_2\text{O}_3(\text{aq})) = 33.53 \pm 0.05 \text{ kcal/mol}$ , where the error bar represents the propagated uncertainty in  $K_1$ . This value may be used in turn to evaluate the physical (Henry's law) solubility of N<sub>2</sub>O<sub>3</sub> as the equilibrium constant of reaction 16.



Making use of the known<sup>30</sup> free energy of formation of N<sub>2</sub>O<sub>3</sub>(g), one obtains  $K_{16} = 0.70 \pm 0.05 \text{ M atm}^{-1}$ , where again the uncertainty reflects the uncertainty in the present value of  $K_1$ . Because of the reactivity of N<sub>2</sub>O<sub>3</sub>,  $K_{16}$  cannot be directly measured. The value of  $K_{16}$  derived here agrees as well as may be expected with the value (1 M atm<sup>-1</sup>) estimated by Turney and Wright<sup>31</sup> on the basis of physical properties of N<sub>2</sub>O<sub>3</sub> in analogy with other molecules whose solubility coefficients are known.

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**Registry No.** HNO<sub>2</sub>, 7782-77-6; N<sub>2</sub>O<sub>3</sub>, 10544-73-7.

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## Kinetics and Mechanism of Oxidation of Hypophosphorous Acid with Silver(II) in Aqueous Perchloric Acid Solutions

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The title reaction at constant [HClO<sub>4</sub>] and [ClO<sub>4</sub><sup>-</sup>] follows the rate law  $-d[\text{Ag}(\text{II})]/dt = 2k_2[\text{Ag}(\text{II})][\text{H}_3\text{PO}_2]/(1 + K_5[\text{Ag}(\text{I})])$ , where  $k_2$  was found to be  $(7.6 \pm 0.7) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , at 30 °C and  $I \approx 4.0 \text{ M}$ , and  $K_5$  is the formation constant of AgH<sub>3</sub>PO<sub>2</sub><sup>+</sup>, and its value from kinetics results was  $38 \pm 2.5 \text{ M}^{-1}$  at 30 °C and [HClO<sub>4</sub>] = 4.0 M. There is evidence for the complexes AgClO<sub>4</sub><sup>+</sup> and Ag(ClO<sub>4</sub>)<sub>2</sub> in perchlorate solutions of Ag(II). Silver(II) oxide appears to disproportionate to Ag(III) even in the solid state.

The authors recently studied<sup>1</sup> the silver(I)-catalyzed oxidation of hypophosphorous acid with cerium(IV) to ascertain the role of the catalyst. Though no evidence for the Ag(I)/Ag(II) cycle was obtained, a study of the reaction of Ag(II) with hypophosphorous acid seemed desirable to confirm the absence of this cycle in the catalyzed reaction. The kinetic

studies made with silver(II) have been few, owing to its reaction with water in acidic solutions of HClO<sub>4</sub>,<sup>2,3</sup> H<sub>2</sub>SO<sub>4</sub>,<sup>4</sup> H<sub>3</sub>PO<sub>4</sub>,<sup>5</sup> and HNO<sub>3</sub>,<sup>6</sup> and some of them are incomplete from

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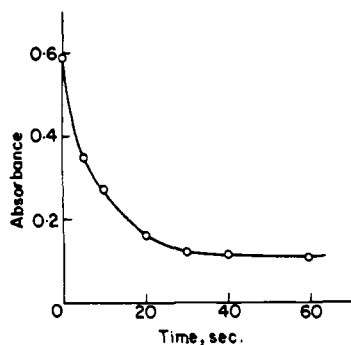
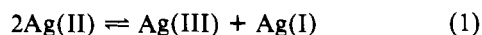


Figure 1. Typical plot of absorbance and time for the oxidation of  $\text{H}_3\text{PO}_2$  by  $\text{Ag(II)}$  ( $[\text{Ag(II)}] = 2.5 \times 10^{-3} \text{ M}$ ;  $[\text{H}_3\text{PO}_2] = 1 \times 10^{-3} \text{ M}$ ;  $[\text{HClO}_4] = 4.0 \text{ M}$ ;  $[\text{Ag(I)}] = 0.20 \text{ M}$ ;  $30^\circ \text{C}$ ;  $\lambda = 470 \text{ nm}$ ).

the viewpoint of the mechanism.

Several papers have appeared on the oxidation of hypophosphorous acid. The central theme of these oxidations in acidic solutions has been the existence of tautomeric equilibrium between the normal and active forms of hypophosphorous acid. Complexation with the metal ions is another feature of these reactions.

Apart from the motivation with which this work was started, the reaction has not been studied so far, and the interest lies in knowing whether the tautomeric equilibrium is the bottleneck of the reaction and whether disproportionation<sup>7</sup> of  $\text{Ag(II)}$  as given by eq 1 is important in this reaction since in some



cases (exchange reaction<sup>8</sup> and decomposition<sup>2,6</sup>)  $\text{Ag(III)}$  has been reported to be the oxidizing species.

### Experimental Section

**Materials.** Silver nitrate and peroxydisulphate were S. Merck GR quality, and hypophosphorous acid was Riedel AR grade (32%). Perchloric acid was Riedel 60%. All other chemicals were either BDH AnalaR or E. Merck GR quality. Corning glass vessels were employed for storing the solution and for carrying out the reactions. Doubly distilled water was used for all solutions and in the reaction mixture, second distillation being made from alkaline potassium tetraoxo-permanganate.

**Preparation of  $\text{Ag(II)}$  Solutions.** Concentrated solutions of silver nitrate and potassium peroxydisulphate were mixed to yield a black solid<sup>9</sup> which was filtered, washed with water, and dried. Solutions of  $\text{Ag(II)}$  were prepared by weighing the required quantity of this solid and dissolving it in a mixture of solutions of 0.2 M silver perchlorate and 4.0 M  $\text{HClO}_4$ . Solutions were prepared whenever required since  $\text{Ag(II)}$  reacts with water yielding oxygen. Dried solid older than 2 h was not used for reasons mentioned later. The decomposition<sup>2,3</sup> is sufficiently slowed down in about 4.0 M  $\text{HClO}_4$  and in the presence of about 0.2 M  $\text{AgClO}_4$ .

**Extinction Coefficient of  $\text{Ag(II)}$  in Perchloric Acid Solutions.** Solutions of  $\text{Ag(II)}$  so prepared were determined cerimetrically. Excess iron(II) was added to a solution of  $\text{Ag(II)}$ , and excess iron(II) was back-titrated with cerium(IV) in the presence of about 1.0 M  $\text{H}_2\text{SO}_4$ . Absorbance of solutions of silver(II) perchlorate was measured on a Coleman colorimeter with a 470-nm filter, and the molar extinction coefficient was found to be  $139 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$ . Other reported values of extinction coefficients are  $140 \pm 7 \text{ M}^{-1} \text{ cm}^{-1}$  at  $475 \text{ nm}$ ,  $140 \pm 7 \text{ M}^{-1} \text{ cm}^{-1}$  at  $474 \text{ nm}$ ,<sup>10</sup> and  $138 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$  at  $470 \text{ nm}$ .<sup>11,12</sup>

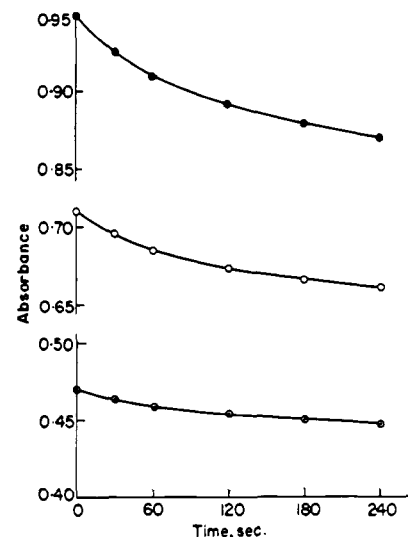


Figure 2. Plot of absorbance and time for the decomposition of  $\text{Ag(II)}$  ( $[\text{Ag(II)}] = 2 \times 10^{-3} \text{ M}$  (○);  $3 \times 10^{-3} \text{ M}$  (○);  $4 \times 10^{-3} \text{ M}$  (●);  $[\text{HClO}_4] = 4.0 \text{ M}$ ;  $[\text{Ag(I)}] = 0.20 \text{ M}$ ;  $\lambda = 470 \text{ nm}$ ;  $30^\circ \text{C}$ ).

Table I. Stoichiometry of the Reaction of  $\text{Ag(II)}$  and  $\text{H}_3\text{PO}_2$  in 4.0 M  $\text{HClO}_4$  and 0.2 M  $\text{AgClO}_4$  at  $30^\circ \text{C}$

$10^4 \times$ $[\text{H}_3\text{PO}_2]/\text{M}$ taken	$10^4 \times$ $[\text{Ag(II)}]/\text{M}$ taken	$10^4 \times$ $[\text{Ag(II)}]/\text{M}$ left over	$10^4 \times$ $[\text{Ag(II)}]/\text{M}$ consumed	$[\text{Ag(II)}]_{\text{used}}/$ $[\text{H}_3\text{PO}_2]_{\text{used}}$
2.0	5.0	0.96	4.04	2.02
2.0	15.0	10.94	4.06	2.03
2.0	20.0	16.06	3.94	1.97
3.0	25.0	19.07	5.93	1.98
5.0	25.0	14.83	10.17	2.03
7.0	25.0	11.00	14.00	2.00
10.0	25.0	5.00	20.00	2.00
				av 2.00 $\pm$ 0.02

Although in general the absorbance is reported to be independent of the concentration of  $\text{HClO}_4$ , complexing of  $\text{Ag(II)}$  with perchlorate is reported by Kirwin and co-workers.<sup>2</sup> However at about 475 nm the various perchlorate complexes of  $\text{Ag(II)}$ , even if formed, have the same extinction coefficients. The quantity of solid silver(II) oxide weighed and the cerimetric assay corresponded to the empirical formula  $\text{AgO}$ .<sup>13</sup>

**Kinetics Procedure.** The reactions were studied colorimetrically at 470 nm in 4.0 M  $\text{HClO}_4$  and 0.2 M  $\text{AgClO}_4$ . A weighed amount of solid silver(II) oxide was quickly dissolved in a 10-mL mixture of  $\text{HClO}_4$  and  $\text{AgClO}_4$ , yielding the above final concentrations at  $30 \pm 0.1^\circ \text{C}$ , and the solution was added to a known quantity of a temperature-equilibrated solution of  $\text{H}_3\text{PO}_2$  in the colorimeter tube. Mixing and the first measurement of absorbance took from 2 to 3 s. The reaction was very fast for this conventional method of analysis and not more than three to four measurements were possible within 15–20 s. There was no variation in the temperature of the reaction mixture during this interval since the air temperature was  $30 \pm 2^\circ \text{C}$  for the period during which this study was made. A typical plot of absorbance and time is given in Figure 1. Initial rates were calculated by the plane mirror method.<sup>14</sup> Duplicate measurements were reproducible to  $\pm 15\%$ .

**Decomposition of  $\text{Ag(II)}$  Solutions.** Though the decomposition of  $\text{Ag(II)}$  is fast, the title reaction is much faster, and, further, the decomposition reaction is slowed down in the presence of  $\text{Ag(I)}$  and by employing a suitable concentration of  $\text{HClO}_4$ . Thus during the period in which the title reaction occurs, decomposition reactions can be neglected. This is also obvious from the nature of the curve in Figure 1. Some decomposition reactions were also studied, and the

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**Table II.** Rates ( $v$ ) of Ag(II) Dependence in the Ag(II)-H<sub>3</sub>PO<sub>2</sub> Reaction<sup>a</sup>

$10^3$ [Ag(II)]/M	0.5	1.0	1.5	2.0	3.0	4.0	5.0
$10^5 v$ /M s <sup>-1</sup>	1.8	4.1	5.6	7.25	11.0	13.2	17.8

<sup>a</sup> [H<sub>3</sub>PO<sub>2</sub>] = 2.0 × 10<sup>-4</sup> M; [HClO<sub>4</sub>] = 4.0 M; [Ag(I)] = 0.2 M; 30 °C.

**Table III.** Variation of H<sub>3</sub>PO<sub>2</sub> in the Ag(II)-H<sub>3</sub>PO<sub>2</sub> Reaction<sup>a</sup>

$10^3$ [H <sub>3</sub> PO <sub>2</sub> ]/M	1.0	2.0	3.0	5.0	7.0	10.0
$10^5 v$ /M s <sup>-1</sup>	4.5	9.6	13.7	26.0	34.0	48.5

<sup>a</sup> [Ag(II)] = 2.5 × 10<sup>-3</sup> M; [HClO<sub>4</sub>] = 4.0 M; [Ag(I)] = 0.2 M; 30 °C.

**Table IV.** Effect of Ag(I) in the Ag(II)-H<sub>3</sub>PO<sub>2</sub> Reaction<sup>a</sup>

	[H <sub>3</sub> PO <sub>2</sub> ] = 2.0 × 10 <sup>-4</sup> M					
[Ag(I)]/M	0.06	0.1	0.15	0.20	0.25	0.30
$10^5 v$ /M s <sup>-1</sup>	17.3	11.3	10.3	6.34	5.55	4.07

	[H <sub>3</sub> PO <sub>2</sub> ] = 4.0 × 10 <sup>-4</sup> M				
[Ag(I)]/M	0.15	0.20	0.25	0.30	
$10^5 v$ /M s <sup>-1</sup>	17.8	14.7	11.3	9.26	

<sup>a</sup> [Ag(II)] = 2.0 × 10<sup>-3</sup> M; [HClO<sub>4</sub>] = 4.0 M; 30 °C.

results are given in Figure 2. If one divides the rate (decomposition of Ag(II) of the first reaction by the concentration of Ag(II), a first-order rate constant of about 6 × 10<sup>-4</sup> s<sup>-1</sup> is obtained whereas a similar treatment of the rate of the title reaction with the same concentration of Ag(II) and the lowest concentration of H<sub>3</sub>PO<sub>2</sub> would yield a value of about 4 × 10<sup>-2</sup> s<sup>-1</sup> for the so-called first-order rate constant. The value for the decomposition reaction would be still less in the presence of Ag(I).

**Stoichiometry.** The conventional method of determining the stoichiometry with excess Ag(II) was not possible owing to its reaction with water. With excess H<sub>3</sub>PO<sub>2</sub>, cerimetry<sup>15</sup> appears to be the least troublesome method, but even this would fail in the presence of Ag(I) owing to the reaction of Ce(IV) with H<sub>3</sub>PO<sub>3</sub> catalyzed by Ag(I). Fortunately in all the kinetics experiments employing excess Ag(II), almost constant absorbance is obtained after the title reaction is over, and from this the concentration of leftover Ag(II) can be calculated. Some of those results given in Table I show that 2 mol of Ag(II) are required for each mole of H<sub>3</sub>PO<sub>2</sub>. Obviously the reaction of Ag(II) with H<sub>3</sub>PO<sub>3</sub> seems to be slow, and it is so.<sup>16</sup>

**Reactions with Aged Solid Oxide of Ag(II).** If reactions are carried out with different samples of solid oxide of Ag(II), the rate of title reaction is almost unchanged, but the rate of decomposition (reaction of Ag(II) with water) increases with the aging of the sample. Even 1 day old samples result in a 100% increase in the rate. Such old samples when dissolved in aqueous HClO<sub>4</sub> immediately yielded a precipitate of AgCl with a solution of NaCl whereas fresh samples yielded a precipitate after a few seconds. These findings are in conformity with the earlier reports that solid samples of formula Ag<sub>2</sub>O<sub>2</sub> are really Ag<sup>I</sup>Ag<sup>III</sup>O<sub>2</sub>.

## Results

**Silver(II) and H<sub>3</sub>PO<sub>2</sub> Dependences.** The concentration of Ag(II) was varied in the range 5 × 10<sup>-4</sup>–5 × 10<sup>-3</sup> M with a fixed concentration (2 × 10<sup>-4</sup> M) of H<sub>3</sub>PO<sub>2</sub>, and the concentration of H<sub>3</sub>PO<sub>2</sub> was varied in the range (1–10) × 10<sup>-4</sup> M at a fixed concentration (2.5 × 10<sup>-3</sup> M) of Ag(II), in 4.0 M HClO<sub>4</sub> and 0.2 M AgClO<sub>4</sub>. The results are given in Tables II and III. The plots of rate vs. [Ag(II)] and also [H<sub>3</sub>PO<sub>2</sub>] yielded straight lines passing through the origin in both cases. The reaction is thus first order in each. The apparent second-order rate constants were found to be 1.74 × 10<sup>2</sup> and 1.96 × 10<sup>2</sup> M<sup>-1</sup> s<sup>-1</sup> at 30 °C in the variation of Ag(II) and H<sub>3</sub>PO<sub>2</sub>, respectively.

**Reactions in Presence of Ag(I) and H<sub>3</sub>PO<sub>3</sub>.** Since the products of the reaction are Ag(I) and H<sub>3</sub>PO<sub>3</sub>, systematic

**Table V.** Effect of HClO<sub>4</sub> in the Ag(II)-H<sub>3</sub>PO<sub>2</sub> Reaction<sup>a</sup>

[HClO <sub>4</sub> ]/M	2.5	3.0	3.5	4.0
$10^5 v$ /M s <sup>-1</sup>	5.8	6.15	6.55	6.7

<sup>a</sup> [Ag(II)] = 2.0 × 10<sup>-3</sup> M; [H<sub>3</sub>PO<sub>2</sub>] = 2.0 × 10<sup>-4</sup> M; [Ag(I)] = 0.2 M;  $I$  = 4.2 M; 30 °C.

**Table VI.** Effect of Ionic Strength or Perchlorate Ions in the Ag(II)-H<sub>3</sub>PO<sub>2</sub> Reaction<sup>a</sup>

[LiClO <sub>4</sub> ]/M	0	0.5	0.7	1.0	1.3
[ClO <sub>4</sub> <sup>-</sup> ] <sub>T</sub> /M	3.2	3.7	3.9	4.2	4.5
$I$ /M	3.2	3.7	3.9	4.2	4.5
$10^5 v$ /M s <sup>-1</sup>	3.8	4.7	5.4	6.3	7.3

<sup>a</sup> [Ag(II)] = 2.0 × 10<sup>-3</sup> M; [H<sub>3</sub>PO<sub>2</sub>] = 2.0 × 10<sup>-4</sup> M; [Ag<sup>I</sup>ClO<sub>4</sub>] = 0.2 M; [HClO<sub>4</sub>] = 3.0 M; 30 °C.

**Table VII.** Absorbance of Ag(II) in Different Perchlorate Solutions at 380 nm<sup>a</sup>

	[ClO <sub>4</sub> <sup>-</sup> ] <sub>T</sub> /M			
time/s	3.0	3.5	4.5	5.0
20	0.65	0.66	0.690	0.695
30	0.635	0.64	0.655	0.670
60	0.625	0.625	0.635	0.650
100	0.615	0.618	0.625	0.635
140	0.605	0.615	0.618	0.625
extrapolated abs at zero time	0.655	0.680	0.725	0.745

<sup>a</sup> [Ag(II)] = 4.0 × 10<sup>-3</sup> M; [HClO<sub>4</sub>] = 2.0 M.

studies in their presence were also made. The concentration of Ag(I) was varied from 0.05 to 0.3 M, and the rate was found to decrease with the increase of [Ag(I)]. The results are given in Table IV. If a plot of (rate)<sup>-1</sup> vs. [Ag(I)] is made, a straight line with an intercept results. The concentration of H<sub>3</sub>PO<sub>3</sub> varied in the range (1–10) × 10<sup>-3</sup> M had no effect.

**Effect of Perchloric Acid.** The reaction was studied with different concentrations (2.5–4.00 M) of HClO<sub>4</sub> at a constant ionic strength of 4.2 M adjusted with lithium perchlorate. The results given in Table V show a little increase in the rate with the increase of [HClO<sub>4</sub>].

**Effect of Ionic Strength/Perchlorate Ions.** The ionic strength was varied in the range 3.2–4.2 M by employing LiClO<sub>4</sub> at a fixed [HClO<sub>4</sub>] = 3.0 M. The results given in Table VI show an increase of rate with the increase of ionic strength or [ClO<sub>4</sub><sup>-</sup>]. However, the effect of ionic strength in such concentrated solutions in general is not much, and the increase in rate probably occurs owing to the variation in the concentration of the reactive species of Ag(II) with perchlorate. A plot of rate vs. [ClO<sub>4</sub><sup>-</sup>] yields a curve with the increase of [ClO<sub>4</sub><sup>-</sup>]. Two complexes of Ag(II), AgClO<sub>4</sub><sup>+</sup> and Ag(ClO<sub>4</sub>)<sub>2</sub>, appear to be formed as in the case of sulfate solutions.<sup>4</sup> The formation constant of AgClO<sub>4</sub><sup>+</sup> appears to be large enough to convert all of the Ag(II) into this complex, but the formation constant of Ag(ClO<sub>4</sub>)<sub>2</sub> appears to be small.

**Spectrophotometry of Perchlorate Solutions.** Absorbance of 4.0 × 10<sup>-3</sup> M Ag(II) in 2.0 M HClO<sub>4</sub> and different perchlorate solutions at 380 nm<sup>2</sup> was measured at different times. The results are reported in Table VII. A plot of absorbance vs. time yielded a curve which is extrapolated to obtain absorbance at zero time.

Since the extinction coefficient of Ag<sup>2+</sup> without perchlorate cannot be determined, the formation constants of AgClO<sub>4</sub><sup>+</sup> and Ag(ClO<sub>4</sub>)<sub>2</sub> separately cannot be calculated by the Yatsimirskii method.<sup>17</sup> If all of the Ag(II) is considered to be

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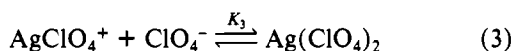
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converted into  $\text{AgClO}_4^+$  in 2.0 M  $\text{HClO}_4$ , the formation constant of  $\text{Ag}(\text{ClO}_4)_2$  can be calculated by Ramette's method<sup>18</sup> from the data of Table VII, and it was found to be  $0.077 \pm 0.011 \text{ M}^{-1}$  at 30 °C.

### Discussion

Since the acid dissociation constant<sup>19</sup> of  $\text{H}_3\text{PO}_2$  is about 0.135 at 25 °C and  $I = 1.0 \text{ M}$ , the predominant form of hypophosphorous acid would be  $\text{H}_3\text{PO}_2$ . With regard to  $\text{Ag}(\text{II})$  species, since perchlorate solutions have been employed and since the rate increases with the increase of perchlorate ion, a possibility of complexes<sup>2,3</sup>  $\text{AgClO}_4^+$  and  $\text{Ag}(\text{ClO}_4)_2$  being reactive exists (see eq 2 and 3).



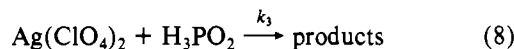
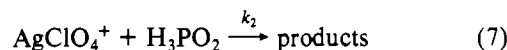
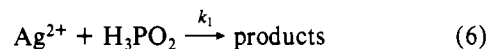
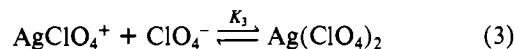
Another possibility for  $\text{Ag}(\text{II})$  species to exist in the hydrolyzed form has been indicated in the oxidation of hydroxylamine,<sup>20</sup> vanadium(IV),<sup>21</sup> and aliphatic organic compounds<sup>12,22</sup> (eq 4). The value of  $K_H$  has been found<sup>23</sup> to vary



from 0.1 to 0.7 at  $I = 5.6 \text{ M}$ . Hence the predominant form of  $\text{Ag}(\text{II})$  in 4.0 M  $\text{HClO}_4$  would be  $\text{Ag}^{2+}$ , but  $\text{AgOH}^+$  would also be present. If  $\text{Ag}^{2+}$  is reactive, there would be small changes in the concentration of  $\text{Ag}^{2+}$  with the increase of  $\text{HClO}_4$ , and consequently there would be a small increase in the rate as found in the present investigation. Thus  $\text{Ag}(\text{II})$  is likely to be present as  $\text{Ag}^{2+}$ ,  $\text{AgClO}_4^+$ ,  $\text{Ag}(\text{ClO}_4)_2$ , and  $\text{AgOH}^+$  in perchloric acid solutions.

There is yet another possibility for a complex of  $\text{Ag}(\text{II})$ . A number of complexes of  $\text{Ag}(\text{II})$  with organic ligands containing nitrogen donor atom are known, viz., pyridine,<sup>24</sup> *o*-phenanthroline,<sup>25</sup>  $\alpha, \alpha'$ -dipyridyl,<sup>26</sup> oxime,<sup>27</sup> picolinic acid,<sup>28</sup> nicotinic and isonicotinic acids,<sup>29</sup> and other pyridinecarboxylic acids,<sup>30</sup> but inorganic complexes so far reported are those of nitrate,<sup>31</sup> sulfate,<sup>4</sup> and perchlorate.<sup>2,3</sup> Hypophosphorous acid is likely to complex with  $\text{Ag}^{2+}$  through oxygen, but there is no evidence of any kind. On the other hand for  $\text{Ag}(\text{I})$  there is kinetics as well as spectrophotometric evidence<sup>32</sup> for its complexing with hypophosphite, and as a consequence of this, the concentration of free  $\text{H}_3\text{PO}_2$  in the present system decreases.

In view of the various types of dependences described earlier, mechanism (2)–(8) for the reaction may be suggested.



The rate law for the decrease of  $\text{Ag}(\text{II})$  is given by eq 9.

$$v = -d[\text{Ag}(\text{II})]/dt = 2[\text{Ag}(\text{II})][\text{H}_3\text{PO}_2] \times \frac{(k_1 + k_2K_2[\text{ClO}_4^-] + k_3K_2K_3[\text{ClO}_4^-]^2)/(1 + K_5[\text{Ag}(\text{I})](1 + K_H/[\text{H}^+] + K_2[\text{ClO}_4^-] + K_2K_3[\text{ClO}_4^-]^2))}{(9)}$$

Since  $K_H$  is reported to be small,  $K_2$  is large (greater than at least 10), and  $K_3$  is  $0.077 \text{ M}^{-1}$ , the predominant form of  $\text{Ag}(\text{II})$  would be  $\text{AgClO}_4^+$  in  $\text{HClO}_4$  solutions used, but  $\text{Ag}(\text{ClO}_4)_2$  would also be present in significant amounts and contribute to the rate. The rate law thus is given by eq 10. A plot of

$$-d[\text{Ag}(\text{II})]/dt = \frac{2[\text{Ag}(\text{II})][\text{H}_3\text{PO}_2](k_2 + k_3K_3[\text{ClO}_4^-])}{(1 + K_5[\text{Ag}^+])(1 + K_3[\text{ClO}_4^-])} \quad (10)$$

$v(1 + K_3[\text{ClO}_4^-])$  vs.  $[\text{ClO}_4^-]$  yields a straight line, but with a negative slope on the rate function axis. This is not possible, and it appears that the straight line may pass through the origin. Hence  $K_3$  is still smaller, and the only species predominant and contributing to the rate appears to be  $\text{AgClO}_4^+$ . The rate law thus reduces to eq 11. A plot of  $(\text{rate})^{-1}$  vs.

$$-d[\text{Ag}(\text{II})]/dt = \frac{2k_2[\text{Ag}(\text{II})][\text{H}_3\text{PO}_2]}{1 + K_5[\text{Ag}(\text{I})]} \quad (11)$$

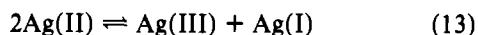
$[\text{Ag}(\text{I})]$  would yield a straight line with intercept, and from these  $K_5$  and  $k_2$  were found to be  $38 \pm 2.5 \text{ M}^{-1}$  and  $(6.8 \pm 0.2) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, at 30 °C and  $[\text{HClO}_4] = 4.0 \text{ M}$ . The value of  $K_5$  recently found<sup>32</sup> in the oxidation of  $\text{H}_3\text{PO}_2$  with  $\text{Ag}(\text{I})$  was  $138 \pm 19 \text{ M}^{-1}$  at  $[\text{H}^+] = 0.1 \text{ M}$  and 30 °C. The difference in the values of  $K_5$  may perhaps be explained by its dependence on hydrogen ions. At constant  $[\text{Ag}(\text{I})]$  the rate law further reduces to eq 12.

$$-d[\text{Ag}(\text{II})]dt = 2k_2'[\text{Ag}(\text{II})][\text{H}_3\text{PO}_2] \quad (12)$$

The apparent second-order rate constants from the  $\text{Ag}(\text{II})$  and  $\text{H}_3\text{PO}_2$  dependences were found to be  $1.74 \times 10^2$  and  $1.96 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , respectively;  $k_2'$  values are thus  $87$  and  $98 \text{ M}^{-1} \text{ s}^{-1}$ . If these values are multiplied by  $(1 + K_5[\text{Ag}(\text{I})])$ , one obtains  $7.5 \times 10^2$  and  $8.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  for the values of  $k_2$ . These values are fairly comparable to the one obtained from the  $\text{Ag}(\text{I})$  variation. An average value of  $k_2$  is thus  $(7.6 \pm 0.7) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . The same rate law (10) would be obtained at constant  $[\text{ClO}_4^-]$  and  $[\text{HClO}_4]$ , if one assumes only one complex,  $\text{AgClO}_4^+$ , along with  $\text{Ag}^{2+}$ , to be the reactive species, the latter being predominant.

The reaction is conspicuous by the fact that the  $\text{Ag}(\text{II})$  dependence is first order and not second order,<sup>2,6,8,16</sup> and hence it appears that the  $\text{Ag}(\text{III})$  species is not reactive in this system. Moreover, the disproportionation step (eq 13), which would

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exist any way, becomes insignificant in the presence of large concentration of Ag(I). The reaction appears to be somewhat similar to the oxidation of formic acid,<sup>22,31</sup> involving three terms in the rate law which, however, could not be proved in the present case on account of high concentrations of Ag(I) and HClO<sub>4</sub> employed to check the decomposition.

There is no evidence for a tautomeric equilibrium between the normal and active forms of hypophosphorous acid in the present system since under the conditions employed the rate

is not independent of Ag(II). This mechanism becomes significant only when the direct reaction with the hypophosphorous acid and the oxidant is very slow. Direct reaction between the oxidant and reductant is the preferred path in the present case.

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**Registry No.** H<sub>3</sub>PO<sub>2</sub>, 6303-21-5; Ag<sup>2+</sup>, 15046-91-0.

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## Hydrogen Ion Dependence of the Oxidation of Iron(II) with Peroxydisulfate in Acid Perchlorate Solutions

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The title reaction has been studied in the [H<sup>+</sup>] range of 0.01–1.0 M at different ionic strengths and temperatures. Unlike previous reports, the rate is dependent on the concentration of the hydrogen ions, if it is larger than 0.2 M. The rate laws are  $d[\text{Fe(III)}]/dt = 2k_1[\text{S}_2\text{O}_8^{2-}][\text{Fe(II)}]$  for [H<sup>+</sup>] < 0.2 M and  $d[\text{Fe(III)}]/dt = (k_1 + k_2K[\text{H}^+])[\text{S}_2\text{O}_8^{2-}][\text{Fe(II)}]$  for [H<sup>+</sup>] > 0.4 M. In the [H<sup>+</sup>] range of 0.4–1.0 M and at  $I \approx 1.0$  M,  $k_1$  (M<sup>-1</sup> s<sup>-1</sup>) and  $k_2K$  (M<sup>-2</sup> s<sup>-1</sup>) were found to be  $25 \pm 1.2$  and  $83 \pm 8$ ,  $18 \pm 1.2$  and  $63 \pm 4$ , and  $11.5 \pm 0.6$  and  $55 \pm 4$  at 40, 35, and 30 °C, respectively. A plot of  $\log k_{\text{obs}}$  (second-order rate constant) vs.  $I^{1/2}$  for  $I < 0.02$  M yields a straight line with a slope of -3.83. The slope decreases numerically with the increase in the range of ionic strength investigated. The energy of activation (kcal mol<sup>-1</sup>) was found to be  $14.7 \pm 1$  and  $7.6 \pm 2$  for the  $k_1$  and  $k_2$  paths, respectively. The value for the  $k_1$  path is dependent on the ionic strength showing ion pairing.

Recently the authors have studied<sup>1</sup> the iron(II)-catalyzed oxidation of hydrazine with peroxydisulfate in aqueous perchloric acid solutions. The study necessitated the investigation of the oxidation<sup>2</sup> of hydrazine with iron(III) and the oxidation of iron(II) with peroxydisulfate under the conditions employed in the catalyzed reaction. Although the catalyzed oxidation<sup>1</sup> operates through the Fe(II)/Fe(III) cycle, the mechanism is not simple, and it involves mixed complexes of iron(III) with peroxydisulfate and hydrazine, and there is no evidence for a complex of iron(II) or iron(III) with hydrazine. The second reaction<sup>2</sup> substantiates this finding. The reaction of iron(II) and peroxydisulfate is much faster than the catalyzed reaction<sup>1</sup> and also the oxidation of hydrazine with iron(III). The title reaction has been studied by several workers<sup>3-8</sup> in the past, and all of them suggest the same mechanism. The stoichiometry was studied in detail by Kolthoff and co-workers.<sup>9</sup>

Table I. Stoichiometry of the Reaction between Fe(II) and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> at Different [H<sup>+</sup>]

[HClO <sub>4</sub> ]/ M	10 <sup>5</sup> × [Fe(II)]/ M taken	10 <sup>5</sup> × [S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]/ M taken	10 <sup>5</sup> × [Fe(II)]/ M remaining	[Fe(II)] <sub>reacted</sub> / [S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ] <sub>reacted</sub>
0.01	5.0	2.0	1.0	2.0
0.01	10.0	2.0	6.05	1.975
0.01	20.0	4.0	12.0	2.0
0.01	40.0	4.0	32.0	2.0
0.01	10.0	1.0	7.95	2.05
0.50	5.0	2.0	1.60	1.70
0.50	8.0	2.0	4.5	1.75
1.0	5.0	2.0	2.0	1.5
1.0	8.0	2.0	4.9	1.55

Most of the workers<sup>3,8</sup> studied the reaction in buffered solutions and found the rate to be unaffected by the change in hydrogen ion concentration. In the present investigation, when the study is extended to higher acid concentrations, significant dependence on [H<sup>+</sup>] was found. The reaction therefore, has been fully reinvestigated from the viewpoint of hydrogen ion dependence.

### Experimental Section

**Materials and Solutions.** The chemicals employed in the investigation were either BDH AnalaR or E. Merck GR quality. The solutions were prepared in doubly distilled water, the second distillation

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