

Figure 2. Infrared spectra in the bridging $\nu(\text{CO})$ region of $\text{Co}_4(\text{CO})_{12}$ in heptane (for peak assignment see ref 7): (A) natural-abundance ^{13}CO sample; (B) ^{13}CO -enriched sample (>75%) for exchange reaction at 24.6 °C for 90 h;⁷ (C) ^{13}CO -enriched sample for exchange reaction in the presence of 1 equiv of $(n\text{-Bu})_3\text{P}=\text{O}$ at 0 °C for 18 h.

the form $[\text{Co}(\text{CO})_3(\text{PR})_2][\text{Co}(\text{CO})_4]$.⁴³ Similar reactions have also been reported of vanadium carbonyls with nitrogen and oxygen donor bases, including $(\text{C}_6\text{H}_5)_3\text{P}=\text{O}$ where $[\text{V}(\text{Ph}_3\text{P}=\text{O})_4][\text{V}(\text{CO})_6]_2$ is produced.⁴⁴ We have isolated a lavender, crystalline salt from the reaction of $\text{Co}_4(\text{CO})_{12}$ with $(\text{CH}_3)_3\text{P}=\text{O}$ (the product of the analogous reaction with $(n\text{-Bu})_3\text{P}=\text{O}$ provided a blue oil), which is best formulated as $[\{(\text{CH}_3)_3\text{P}=\text{O}\}_6\text{Co}][\text{Co}(\text{CO})_4]_2$ on the basis of total elemental analyses and infrared spectroscopy ($\nu(\text{CO})$ 1980 cm^{-1} , $\nu(\text{P}=\text{O})$ 1156 cm^{-1}).⁴⁵⁻⁴⁷ A complete characterization of this species by X-ray crystallographic analysis is planned.

It was nonetheless possible to observe $(n\text{-Bu})_3\text{P}=\text{O}$ -induced CO lability by carrying out the reaction of $\text{Co}_4(\text{CO})_{12}$ with 1 equiv of $(n\text{-Bu})_3\text{P}=\text{O}$ in a ^{13}CO atmosphere at 0 °C. Under these conditions ^{13}CO uptake into the cluster was substantial (a control experiment in the absence of $(n\text{-Bu})_3\text{P}=\text{O}$ showed

little, if any, ^{13}CO incorporation). Within 18 h a level of ^{13}CO enrichment in $\text{Co}_4(\text{CO})_{12}$ similar to that requiring 90 h via thermolysis at 24.6 °C in the absence of $(n\text{-Bu})_3\text{P}=\text{O}$ was observed (see Figure 2). Because of the mild conditions under which ^{13}CO exchange occurs in $\text{Co}_4(\text{CO})_{12}$ in the presence of $(n\text{-Bu})_3\text{P}=\text{O}$ it is highly likely that a radical chain pathway is operative in this instance.⁴³ Analogous reactions employing the substitutionally more inert $\text{Ir}_4(\text{CO})_{12}$ cluster, however under much more rigorous conditions (80 °C for 20 h), were unsuccessful at providing ^{13}CO -enriched species. Similarly, whereas $\text{Mn}_2(\text{CO})_{10}$ readily incorporated ^{13}CO in the presence of $(n\text{-Bu})_3\text{P}=\text{O}$, $\text{Re}_2(\text{CO})_{10}$ did not.

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Registry No. $(n\text{-Bu})_3\text{P}=\text{O}$, 814-29-9; $(\text{H}_3\text{N})_3\text{Cr}(\text{CO})_3$, 14974-11-9; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $\text{Co}_4(\text{CO})_{12}$, 17786-31-1; $\text{pyFe}(\text{CO})_4$, 53317-88-7; $\text{K}^+(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2$, 61453-56-3; $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Co}_2(\text{CO})_8$, 10210-68-1; ^{13}CO , 1641-69-6; Me_3NO , 1184-78-7; $\text{Cr}(\text{CO})_6$, 25941-09-7; $[\{(n\text{-Bu})_3\text{P}=\text{O}\}_6\text{Co}][\text{Co}(\text{CO})_4]_2$, 76721-78-3; $[\{(\text{H}_3\text{C})_3\text{P}=\text{O}\}_6\text{Co}][\text{Co}(\text{CO})_4]_2$, 76721-80-7.

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Redox Behavior of the $[\text{Rh}_2(1,3\text{-diisocyanopropane})_4]_2^{6+}$ Ion at the Rotating Glassy Carbon Electrode

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During the last several years the chemistry of the family of $\text{Rh}_2(\text{bridge})_4^{2+}$ (bridge = 1,3-diisocyanopropane, $n = 2,3,4$) ions has been an area of intense interest to us.²⁻¹¹ The initial synthesis of $\text{Rh}_2(\text{bridge})_4^{2+}$ led to subsequent studies of the structural chemistry^{2b-4} and the photochemistry⁴⁻⁹ of these ions. Recently, the structure of the $[\text{Rh}_2(\text{bridge})_4]_2\text{Cl}^{5+}$ ion, which is implicated in the visible-light production of hydrogen from aqueous acid solutions, has been determined.¹⁰ The rich redox chemistry, as well as the need for a further understanding of the thermodynamics of the reactions of the $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ ion, has prompted us to examine the electrochemical behavior of this ion in acidic aqueous media. The limited solubility and the highly surface-active nature of some oxidation states of the ion (vide infra) were a hindrance in obtaining reproducible cyclic voltammetric data at stationary electrodes. However, a rotating electrode has several advantages over a stationary electrode. It provides a larger steady-state current proportional to the square root of the rotation velocity for species that undergo mass transport and currents independent of rotation velocity for surface species. It can also provide information about the electron-transfer kinetics of a redox system.¹² Herein we report the results of both the oxidation and reduction of the $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ ion in acidic media at a rotating glassy carbon disk electrode.

Experimental Section

Materials. $\text{Rh}_2(\text{bridge})_4(\text{BF}_4)_2$ was prepared by a standard method.^{2a,4} All reagents were analytical grade. Solutions 0.5 mM in $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ were made up by weighing a proper amount of $\text{Rh}_2(\text{bridge})_4(\text{BF}_4)_2$ into a volumetric flask, adding the correct amount of concentrated sulfuric or methanesulfonic acid, and diluting to volume with quadruply distilled water. Air oxidation of $\text{Rh}_2(\text{bridge})_4^{2+}$ to

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 (47) The $\nu(\text{P}=\text{O})$ band in $[(\text{HMPA})_4\text{Co}][\text{Co}(\text{CO})_4]_2$ occurs at 1188 cm^{-1} .⁴²

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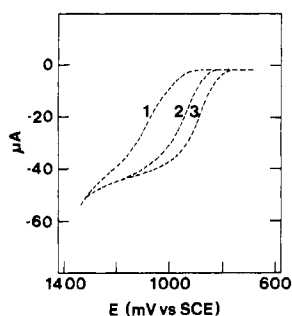


Figure 1. Shifts in the position of the oxidation wave as a function of chloride ion concentration of 4.86×10^{-4} M Rh_4^{6+} in 1 M H_2SO_4 at the rotating glassy carbon electrode at a rotation speed of 1000 rpm. The voltammograms are the average of the anodic and cathodic scans at a rate of 20 mV/s. Curve 1 corresponds to no added chloride, curve 2 to 8.1×10^{-4} M added chloride, and curve 3 to 2.7×10^{-3} M added chloride.

$[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ took place on mixing. These solutions were stored in the dark overnight to decompose the H_2O_2 formed during the preparation of the solutions.¹¹ A final check of the concentration of $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ was made by measuring the absorbance of the solutions at 558 nm ($\epsilon = 8.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

Apparatus. The rotating electrodes were constructed from vitreous carbon rod (V-20) obtained from Atomegic Chemetals Corp., Plainview, NY. Disks cut from the rod (area 0.32 cm^2) were mounted on the end of precision $1/4$ in. steel rods with conductive epoxy and then potted in inert plastic and machined to cylindrical form. The carbon surface was then polished to a mirror finish. The rotator was a Model ASR 2 from Pine Instrument Co., Grove City, PA, which was adapted to accommodate the $1/4$ in. shafts of the homemade electrodes. Electrochemical instrumentation consisted of standard potentiostats and ramp generators. The two-compartment cell was flushed continuously with nitrogen, which was scrubbed with a V(II) solution to remove the last traces of oxygen and saturated with water before entering the cell. All potentials are quoted with respect to the saturated calomel electrode (SCE).

Results and Discussion

Solutions of the purple $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ ion (abbreviated Rh_4^{6+}) in sulfuric or methanesulfonic acid exhibit an oxidation wave near the onset of water oxidation on the rotating glassy carbon disk electrode. The addition of small amounts of chloride ion, which binds to Rh_4^{6+} to form the complex $\text{Rh}_4\text{Cl}^{5+}$,¹⁰ shifts the wave to more negative potentials, effectively resolving the wave from the anodic background (Figure 1).

This negative shift in the oxidation wave arises from the

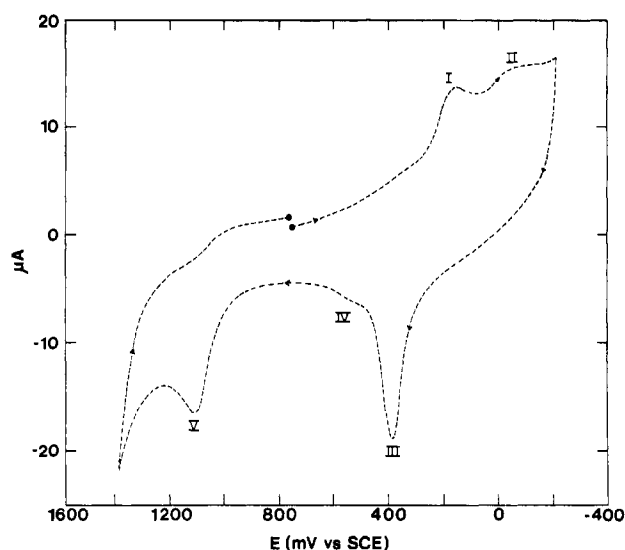


Figure 2. Cyclic voltammogram of 4.86×10^{-4} M Rh_4^{6+} in 1 M H_2SO_4 at a stationary glassy carbon electrode at a scan rate of 20 mV/s. Peaks I and II are reductions, and peaks III, IV, and V are oxidations.

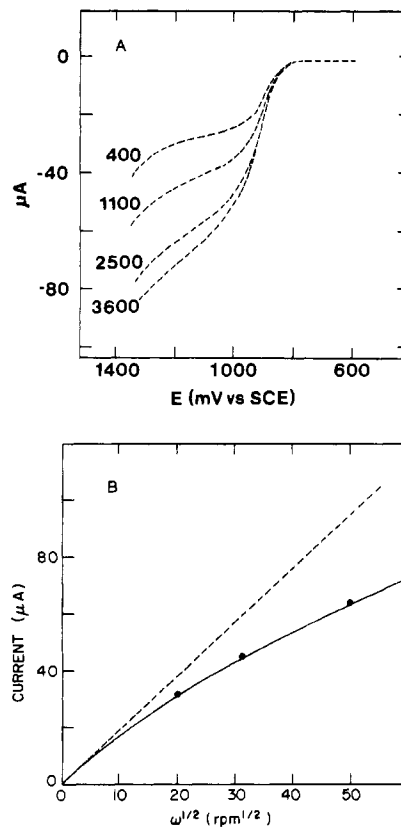


Figure 3. (A) Rotating-electrode voltammograms for the oxidation of 4.86×10^{-4} M Rh_4^{6+} in 1 M H_2SO_4 containing 3.2 mM KCl. The voltammograms are the average of the anodic and cathodic scans at a rate of 20 mV/s. The rotation velocity is indicated to the left of the voltammograms in revolutions per minute. (B) Levich plot analysis of the data presented in part A for the oxidation of Rh_4^{6+} in 1 M H_2SO_4 containing 3.2 mM KCl. The dashed line in the Levich plot is a theoretical line plotted with a diffusion coefficient of $1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ assumed for Rh_4^{6+} .

stronger bonding of chloride ion by the oxidized complex (Rh_2^{4+}) than by the reduced complex (Rh_4^{6+}). The oxidation was determined to be a two electron per Rh_4^{6+} unit process by measuring the disappearance of the oxidation wave as

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known amounts of cerium(IV) were added to the solution. The overall stoichiometry for the oxidation reaction at the electrode in the presence of chloride ion is



Analysis of the data obtained for the oxidation of Rh_4^{6+} in the presence of $8 \times 10^{-4} \text{ M Cl}^-$ (a plot of $\log(i/(i_d - i))$ vs. E) yielded a slope of -130 mV/decade , which indicates the electron transfer at the electrode exhibits non-Nernstian behavior. Further evidence for the irreversibility of this process is demonstrated by the absence of a reduction peak corresponding to this oxidation (V) in the stationary-electrode cyclic voltammogram presented in Figure 2.

The rotation-speed dependence of the oxidation wave (Figure 3A) shows a negative deviation from the expected Levich current (Figure 3B) at fast rotation speeds, suggesting that the heterogeneous electron-transfer rate is controlled by a slow step preceding the electron transfer. The identity of this step is not known, but it could be either cleavage of the Rh-Rh bond between the binuclear units or a very large Franck-Condon barrier to the electron transfer from the tetranuclear unit (vide infra).

The reduction of the Rh_4^{6+} ion is distinctly more complex than its oxidation. The stationary-electrode cyclic voltammogram in 1 M sulfuric acid (Figure 2) reveals reduction peaks at $+160 \text{ mV}$ (peak I) and at -70 mV (peak II). On the reverse scan, a very sharp oxidation peak is observed at $+385 \text{ mV}$ (peak III) with a shoulder (peak IV) at about $+530 \text{ mV}$. This behavior is indicative of the formation of a surface film upon reduction of the complex. Indeed, the height of the anodic stripping peak is proportional to the amount of charge passed while the potential is held negative of peak I. Somewhat surprisingly, the film can be deposited in amounts corresponding to very thick layers (100 monolayers or more) with no indication of passivation, suggesting that the film is conductive. At a rotating glassy carbon electrode in 1 M methanesulfonic acid, the formation of a thick film is not observed; however, we believe that a small amount of the film is present due to the steepness and the hysteresis observed in the reduction wave even at the low scan rates used in Figure 4A (1 mV/s). Because a limiting current plateau is not reached (Figure 4A) at the rotating electrode and a peak corresponding to the poorly resolved reduction peak (Figure 2, peak II) at the stationary electrode is not observed, we believe that the film may contain partially reduced oligomeric Rh complexes similar to those observed in both methanesulfonic and sulfuric acids upon partial reduction of Rh_4^{6+} with chromous ion.¹¹ The sharp oxidation peak at $+385 \text{ mV}$ is likely due to resolubilization of the oligomeric surface species via oxidative cleavage of the Rh-Rh bonds holding the binuclear units together. The Levich plot behavior of the reduction wave (Figure 4B) also begins to deviate from linearity above 1000 rpm, again indicating a slow step controlling the electron-transfer reaction. This step may be related to the formation of Rh-Rh bonds in the oligomers or to slow charge transport through the film.

Figure 5 shows the current-voltage curve obtained at the rotating-disk electrode for a sulfuric acid solution of the oxidized form of the complex (Rh_2^{4+}). The reduction of the Rh_2^{4+} species does not commence until about $+200 \text{ mV}$, the approximate reduction potential of the Rh_4^{6+} species, suggesting that the formation of the surface film is required to reduce the oxidized complex, although this reduction wave is not as steep as is the one observed in methanesulfonic acid solutions. The large, sharp stripping peak, associated with the dissolution of the surface film, is clearly seen (Figure 5) at $+435 \text{ mV}$.

The sluggishness of the heterogeneous oxidation and reduction reactions of the redox forms of $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ was

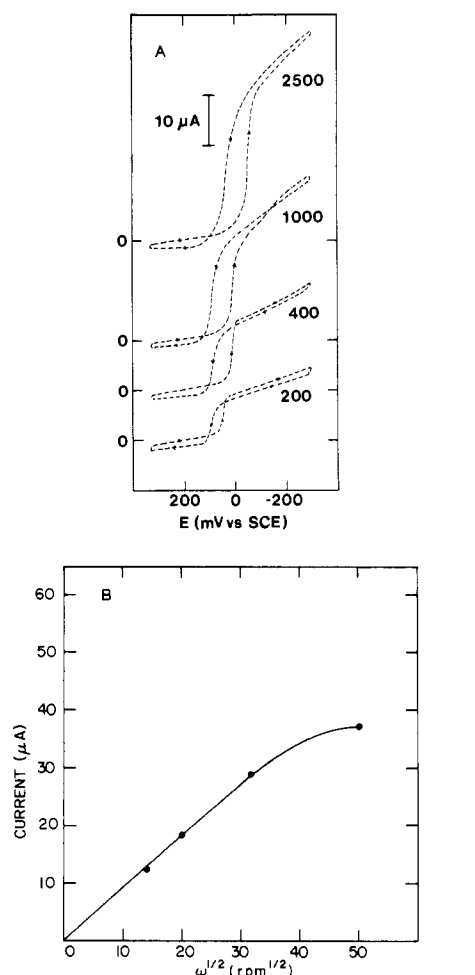


Figure 4. (A) Rotating-electrode voltammograms for the reduction of $5.1 \times 10^{-4} \text{ M Rh}_4^{6+}$ in 1 M methanesulfonic acid at the rotating glassy carbon electrode at a scan rate of 1 mV/s. The rotation velocity is indicated to the right of the voltammograms in revolutions per minute. (B) Levich plot analysis of the data presented in part A for the reduction of Rh_4^{6+} in 1 M methanesulfonic acid.

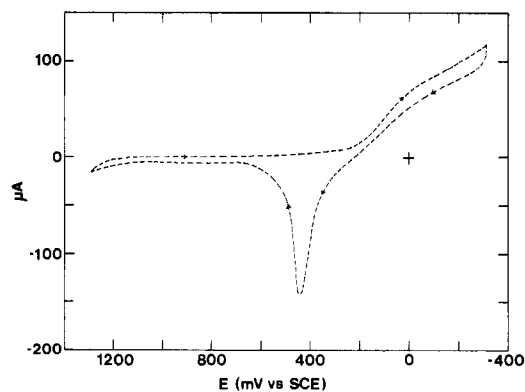


Figure 5. Voltammogram for a solution of $9.7 \times 10^{-4} \text{ M Rh}_2^{4+}$ in 1 M H_2SO_4 at a glassy carbon electrode rotated at 1000 rpm with a scan rate of 20 mV/s.

not unexpected on the basis of a simple molecular-orbital treatment of the important metal-metal bonding levels in $[\text{Rh}_2(\text{bridge})_4]_2^{6+}$ (Figure 6). Oxidation of Rh_4^{6+} results in removal of an electron from the $2a_1$ level, which is bonding with respect to the two inner Rh atoms. The removal of electrons from this level leads to severe weakening of the bond holding the two Rh_2^{3+} units together. Dissociation then occurs to yield a Rh_2^{4+} ion containing a strong Rh-Rh single bond³

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

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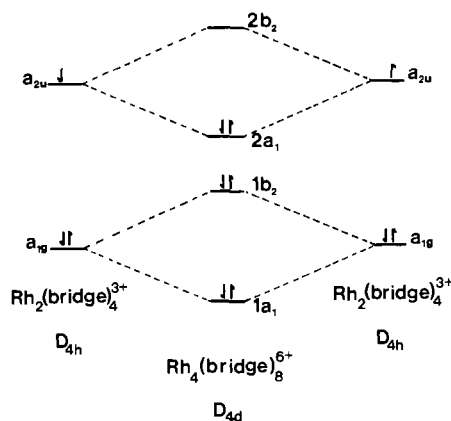


Figure 6. Relative energies of the molecular orbitals derived from the $a_{1g}(d_{z^2})$ and $a_{2u}(d_{z^2})$ $Rh_2(\text{bridge})_4^{3+}$ binuclear complex functions in D_{4d} $[Rh_2(\text{bridge})_4]_2^{6+}$.

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 oxidized¹³ 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 ion¹¹ 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 $[Rh_2(\text{bridge})_4]_2^{6+}$ 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.

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

- (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.

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 alcohol⁸ 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 titration¹¹ by adding the desired quantity of sodium bicarbonate. The reproducibility was better than $\pm 10\%$.

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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