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Decomposition of Concentrated Hydrogen Peroxide on Silver I. Low Temperature Reaction and Kinetics

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The decomposition of hydrogen peroxide (HP) at silver surfaces has been quantitatively investigated. Two distinct decomposition regions exist with an abrupt transition from one region to the other. At low temperatures the rate of HP decomposition, $d(H_2O_2)/dt$, is proportional to (Area)(H_2O_2). The rate of silver mass loss, $d(M)/dt$, is proportional to (Area)$(H_2O_2)^2$. The rate of silver loss is inhibited by the presence of silver and hydroxide ions in the HP solution. The data at low temperatures indicate that chemical reaction at the silver surface controls the rate of HP decomposition. A chain mechanism consistent with the experimental evidence has been postulated.

INTRODUCTION

The rapid silver-catalyzed decomposition of HP has been known for a long time and several kinetic studies have been reported (*1–6*). A review of earlier work by Schumb *et al.* (*5*) shows that the decomposition of HP is not influenced by Ag^+ even when 90 wt % HP is saturated with $AgNO_3$. Catalysis, however, does occur when a precipitate forms. Wiegel (*2*) suggests that the catalysis occurs when the solubility product of argentuous hydroperoxide is exceeded and proposed an oxidation-reduction cycle between the metal and the hydroperoxide. Based on Wiegel's work, Weiss (*3*) suggested that Ag^+ reacted with perhydroxyl ions on silver metal to form perhydroxyl radicals, resulting in a chain reaction. Wentworth (*4*) established, in agreement with Wiegel, that the precipitate in question is metallic silver and that Ag^+ is present in solution. Maggs and Sutton (*6*) investigated silver loss and HP decomposition rates at atmospheric pressure from -10 to 25°C. They indicated that an unspecified diffusion process was operative at the higher temperature while chemical reaction controlled the rates below 10°C. In the lower temperature region they reported that rates of silver loss and HP decomposition increased as a function of HP concentration.

In order to clarify the situation quantitative data were obtained concerning rates of HP decomposition and silver mass loss as a function of bulk solution temperature, silver surface temperature, HP concentration, and pressure. As a result of this study it is now certain that there is an abrupt change in the mechanism of decomposition which depends on a number of factors but it is convenient to speak of a low temperature regime where rates are chemically controlled and a high temperature regime where rates are limited by heat transfer. The low temperature regime is discussed here, while the transition and the high temperature regime are reported in the following paper (*10*).

EXPERIMENTAL

The low temperature reaction rates were studied with a static system at constant temperature and essentially constant HP concentration.

If oxygen is evolved from decomposing HP at a rate of 10 cc/sec, then heat is liberated at the rate of 21 cal/sec. With this high a rate of production of heat it is difficult to maintain constant temperature with ordinary laboratory apparatus. If the above rates are derived from 100 ml of 90% HP then the HP concentration decreases at a rate of 0.017%/sec. Consequently, rapid decomposition rates must be avoided.

For measurements at low temperature (0°C) a 125 ml Erlenmeyer flask having a thermocouple well for measurement of the solution temperature was placed in a well-stirred ice or ice-salt bath. The 90% HP (100 ml) was added to the flask and cooled to the reaction temperature. In a typical experiment a 30 mg piece of silver wire (0.035 cm diameter) was cleaned by rinsing at room temperature in 90% HP for a few moments until fizzing occurred, was weighed, and was then dropped into the HP under test. The flask was quickly closed with a ground glass joint connected to a water saturator and a 1-liter wet test meter. During the experiment the HP was vigorously stirred at 1500 rpm with a Teflon-covered magnetic stirrer. The oxygen evolution was followed for 4000 sec. Under the conditions described, constant temperature and HP concentration were maintained in most experiments. The silver was again weighed at the end of each experiment so that silver loss rates could be calculated.

In those experiments in which the silver surface temperature was measured, an iron-constantan thermocouple was imbedded in a piece of silver with the following technique. The iron-constantan thermocouple wires (28 gage) were silver-soldered into hypodermic tubing which in turn was silver-soldered into a 1-ft section of 0.32 cm, 20 gage stainless steel tubing. The hypodermic tubing was then threaded. A piece of 0.32 cm silver rod approximately 0.64 cm long was drilled and tapped to fit the threads on the hypodermic tubing. The threads on the silver rod and on the hypodermic tubing were such that the silver rod butted snugly against the stainless steel tubing. In this manner only the sides and one end of the silver rod were exposed to the HP solution.

The experimental procedure consisted of weighing and measuring the length and diameter of the 0.64 cm silver rod and threading it onto the hypodermic tubing. After the sample of HP was cooled to the reaction temperature, the test section was lowered into the solution and the solution temperature, silver surface temperature, and oxygen evolution rate were measured as a function of time. At the conclusion of the experiment the silver rod was again removed for weighing and measurement of length and diameter.

It was calculated that the error in the apparent silver surface temperature measured in this manner due to heat losses along the tubing and thermocouple wires was negligible.

The material used was 90 wt % commercial HP. Two different lots of unstabilized material together with a special purity (recrystallized) lot were tested. Absolute differences among the lots were noted (see Fig. 1). However, within a given lot excellent reproducibility was obtained. The effects have been ascribed to changes in trace impurity content which can influence the rate of decomposition at silver surfaces. HP concentrations less than 90 wt % were prepared by diluting the stock 90 wt % material with deionized distilled water.

The silver was obtained commercially as 99.9 wt % pure material in cylindrical diameters ranging from 0.035 cm to 0.32 cm.

All of the Pyrex glassware was degreased with hot 10% NaOH, washed with distilled water, and thoroughly cleaned with concentrated nitric acid. The glassware was then leached with hot distilled water and finally passivated with 90% HP.

RESULTS

The temperature coefficient of the HP decomposition rate and the silver loss rate in the low temperature reaction zone were measured with both commercial 90% HP and special purity 90% HP. The HP decomposition rate data are summarized in Fig. 1, where the logarithmic initial rate is plotted versus reciprocal temperature to form the usual Arrhenius plot. In these experiments it is obvious that the reaction mechanism changed completely at a solution temperature of about 18°C. The silver surface temperature in the low temperature regime was always in the range 3–10°C above the solution temperature. At temperatures

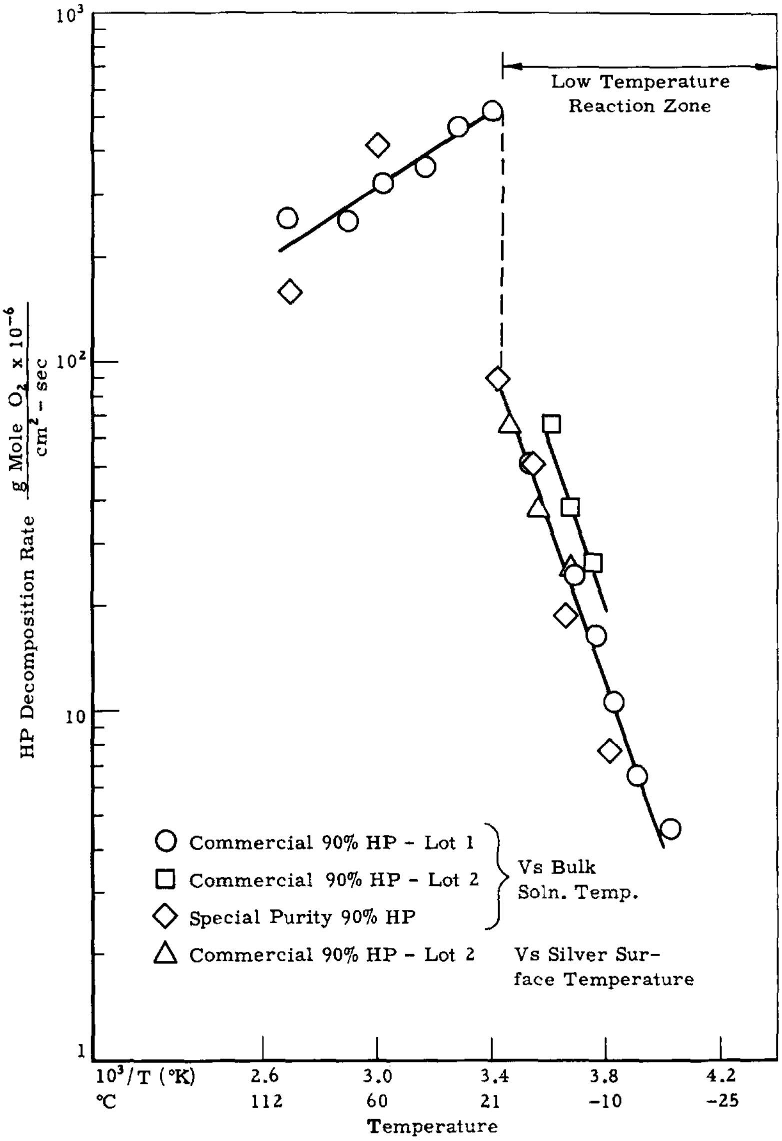

FIG. 1. Arrhenius plot for HP decomposition in low temperature reaction zone.

below 18°C the experiment was in the low temperature reaction zone while at about 18°C a transition to the high temperature zone was made (the silver surface temperature rose markedly at this point). The Arrhenius equation is obeyed in the low temperature reaction zone, as shown in Fig. 1. The slope common to all of the data yields an activation energy of 10.4 kcal/mole for the rate of HP decomposition on a pure silver surface in the low temperature reaction zone.

The change in mechanism from the low temperature reaction zone to the high temperature zone is also shown by the rate of silver loss given as a function of temperature in Fig. 2. In the low temperature reaction zone the rate of silver loss increases with temperature while in the high temperature zone the rate of silver loss decreases

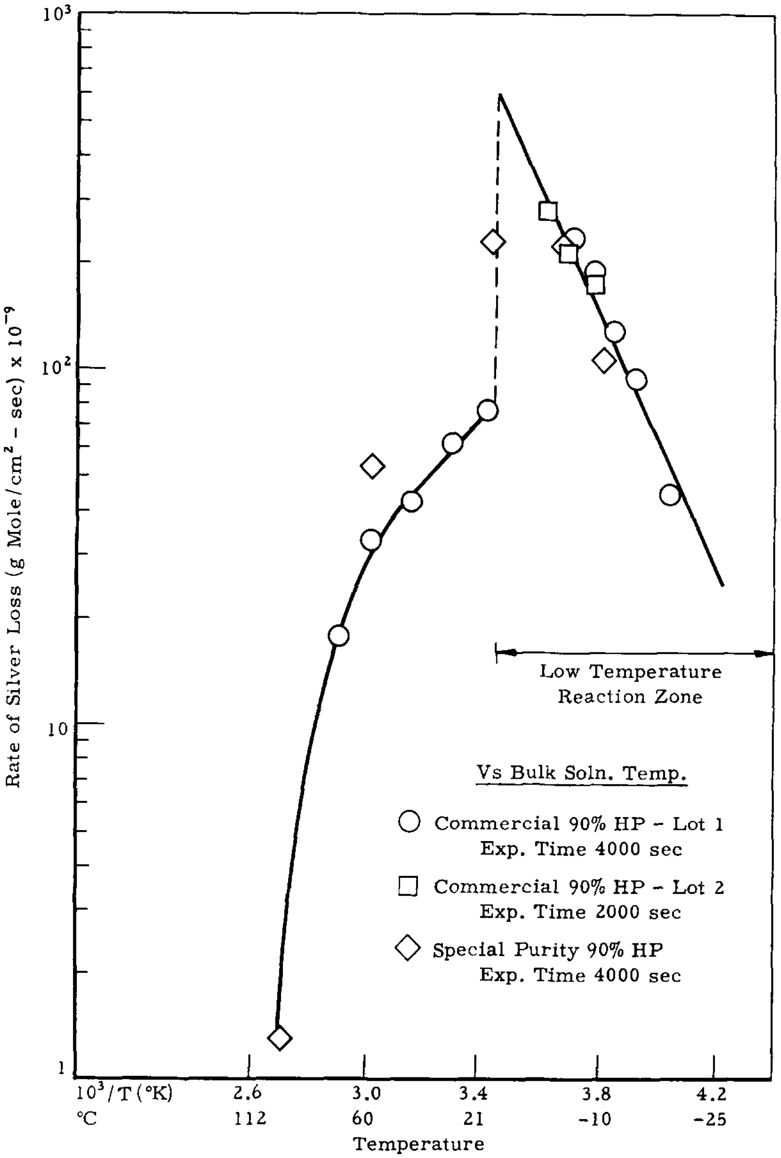

FIG. 2. Arrhenius plot for silver loss in low temperature reaction zone.

with temperature. The Arrhenius equation is obeyed in the low temperature reaction zone. The silver loss rate data when plotted versus the bulk solution temperature yield an activation energy of 8.2 kcal/mole.

The effects of HP concentration and silver surface area on the HP decomposition rate were determined with a bulk solution temperature maintained at 0°C. The data given in Table 1 show results over a threefold change in surface area and a twentyfold change in HP concentration. Analysis of the data yields the kinetic rate equation for the decomposition of HP:

$$-d[H_2O_2]/dt = 2d[O_2]/dt = k[A][X_{H_2O_2}] \quad (1)$$

where A = silver surface area, cm²; $X_{H_2O_2}$ = mole fraction HP*; k = rate constant, g moles (O_2) $sec^{-1}cm^{-2}X^{-1}$. The absolute value

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* The units given for the rate constant k are intentionally expressed as mole fraction rather than wt/vol.

TABLE 1

EFFECT OF SILVER SURFACE AREA AND HP CONCENTRATION ON THE RATE OF HP DECOMPOSITION[a]

HP Conc. ($X_{H_2O_2}$)		Silver area (cm²)		Rate of oxygen evolution $\left[\frac{\text{g mole } (O_2) \times 10^{-6}}{\text{cm}^2\text{-sec-}X_{H_2O_2}}\right]$	
Initial	Final	Initial	Final	Initial	Final
0.833	0.806	0.421	0.211	40.7	35.6
0.833	0.825	0.418	0.310	39.1	34.4
0.833	0.810	0.722	0.696	47.1	44.7
0.833	0.818	0.278	0.231	40.0	40.2
0.833	0.811	0.397	0.342	44.8	37.8
0.549	0.529	0.496	0.469	54.1	45.0
0.379	0.364	0.710	0.674	42.9	29.4
0.199	—	0.672	—	43.5	—
0.072	—	0.670	—	33.9	—
0.034	—	0.670	—	60.3	—

[a] Bulk solution temperature: 0°C; pressure: 1 atm; length of exposure: 4000 sec.

of the rate constant k depends somewhat on the purity of the HP under test.

In the low temperature regime at 0°C in 90 wt % HP the rate of silver loss was proportional to the silver surface area. This was demonstrated with experiments (Table 2) where the change in surface area was kept small compared with the change in mass so that:

$$k_a = -\frac{1}{\text{Area}} \frac{\Delta\text{Mass}}{\Delta t} \qquad (2)$$

TABLE 2

RATE OF SILVER LOSS[a]

Length of experiment (sec)	Ag wire area (cm²)		Loss in weight, (g moles × 10^{-6})	Rate constant k^a $\left(\frac{\text{g moles}}{\text{cm}^2\text{-sec}} \times 10^{-9}\right)$
	Initial	Final		
2000	0.722	0.697	303	−213
4000	0.278	0.231	220	−217
4000	0.397	0.341	304	−205
			k_{Ave}	−212

[a] HP: 90%; temp: 0°C; pressure: 1 atm.

It can also be shown that for long, thin cylinders:

$$k_a = -\frac{\rho}{2}\frac{dD}{dt} = -\frac{\rho}{(\pi\rho l)^{1/2}}\frac{(dM)^{1/2}}{dt} \qquad (3)$$

where ρ = silver density, 0.0973 g mole cm^{-3}; D = diameter; l = length; and M = mass. For silver wires 3.8 cm long and 0.035 cm in diameter, the data given in Table 3 were obtained.

TABLE 3

RATE OF SILVER LOSS[a]

Length of experiment (sec)	(Silver Mass)$^{1/2}$ (g moles)$^{1/2}$ × 10^{-3}		Rate constant k_a $\left(\frac{\text{g moles}}{\text{cm}^2\text{-sec}} \times 10^{-9}\right)$
	Initial	Final	
500	18.99	17.31	−301
1000	19.03	16.84	−195
2000	18.94	13.89	−227
2000	18.90	13.78	−230
2000	19.11	12.96	−273
4000	18.97	9.82	−205
		k_{Ave}	−238 ± 30

[a] HP: 90%; temp: 0°C; pressure: 1 atm.

The effect of HP concentration on the rate of silver loss was determined at 0°C and is plotted in Fig. 3. The rate of silver loss (over four orders of magnitude) is close to second order over a fiftyfold change in HP concentration. Thus the rate of silver mass loss is given by:

$$d(\text{M})/dt = k_a[\text{A}][X_{H_2O_2}]^2 \qquad (4)$$

The addition of up to 0.1 wt % $AgNO_3$ to the silver-90 wt % HP system at 0°C repressed the silver loss rate but did not affect the HP decomposition rate. The silver loss rate was inversely proportional to the Ag^+ concentration.

The effect of pH on the decomposition rate of 90% HP and on the silver loss rate was studied at 0°C. The pH values reported here are the direct readings of a glass electrode versus a calomel cell at 25°C. Neutral 90 wt % HP reads 2.15 on the pH scale at 25°C and the pH reading is directly proportional to the hydrogen ion content.

The data (Fig. 4) show that the decomposition was independent of pH (0 to 3.22) in the region investigated. The rate of silver loss was independent of the pH up to a pH of 1.5 and then apparently decreased as the pH was further increased. The decreased silver loss rate was actually due to the accumulated concentration of silver ions in the solution rather than the increased hydroxyl ion concentration. This was shown

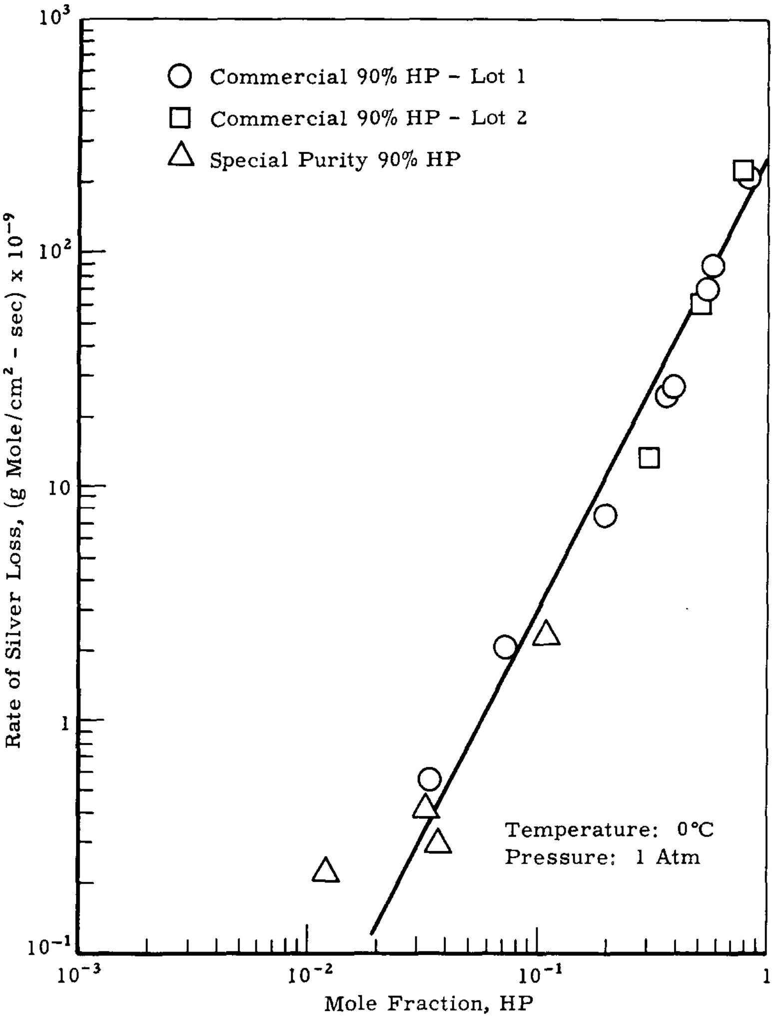

FIG. 3. Rate of silver loss as function of HP concentration.

by measuring the rate of silver loss as a function of time at two different constant pH levels (Fig. 5). The rates of silver loss obtained by extrapolation to zero time are the same as the rates obtained at lower pH levels (shown with the dashed line in Fig. 4). This indicates that the silver loss rate, in the absence of silver ions, is independent of pH in the range studied.

DISCUSSION

In any heterogeneous catalysis there are distinct phases in the reaction with diffusion of reactants to the surface, reaction, and diffusion of products occurring. The experimental data were analyzed with respect to limitation by the three possible steps and are most consistent with a chemical rate-controlled mechanism at the surface.

Considering for the moment only the rate of HP decomposition, the following mechanism is consistent with the experimental data:

$$Ag + H_2O_2 \xrightarrow{k_5} AgOH_{surf} + OH \qquad (5)$$

$$AgOH_{surf} + H_2O_2 \xrightarrow{k_6} Ag + HO_2 + H_2O \qquad (6)$$

$$OH + H_2O_2 \xrightarrow{k_7} H_2O + HO_2 \qquad (7)$$

$$AgOH_{surf} + HO_2 \xrightarrow{k_8} Ag + H_2O + O_2 \qquad (8)$$

$$2HO_2 + M \xrightarrow{k_9} H_2O_2 + O_2 + M \qquad (9)$$

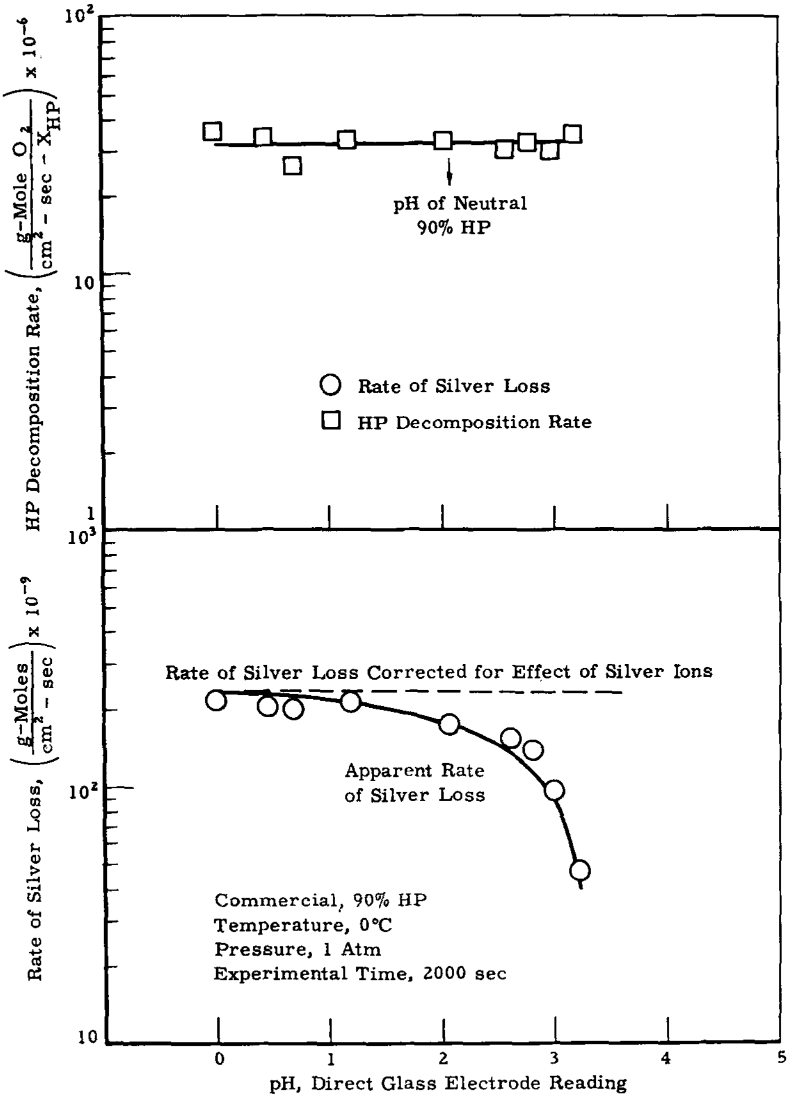

FIG. 4. Effect of pH on HP decomposition rate and silver loss rate.

Starting with fresh metallic silver the decomposition begins via the rate-limiting step (5), to generate silver hydroxide on the surface and OH radicals. The OH radicals react with HP to form water and HO_2 radicals. The surface silver hydroxide reacts either with HP via (6) or with HO_2 via (8)· Both reactions regenerate silver metal. Perhydroxyl radicals terminate the chain in the presence of a third body via (9) by forming HP and oxygen.

Of the steps given in the mechanism, (7) is well known (*3*). The rate-limiting step has also been postulated by Wiegel (*3*), Wentworth (*4*), and Maggs and Sutton (*6*); however, due to insufficient data, a complete mechanism has not previously been suggested.

With a steady state treatment for OH, HO_2, and surface AgOH two solutions are easily calculable. If reaction (8) is much more important than (6) [i.e., $k_8(HO_2) \gg k_6(H_2O_2)$], it can be shown that

$$\begin{aligned} OH &\propto Ag \\ HO_2 &\propto (Ag)^{1/3}(H_2O_2)^{2/3} \qquad (10) \\ AgOH_{surf} &\propto (Ag)^{2/3}(H_2O_2)^{1/3} \end{aligned}$$

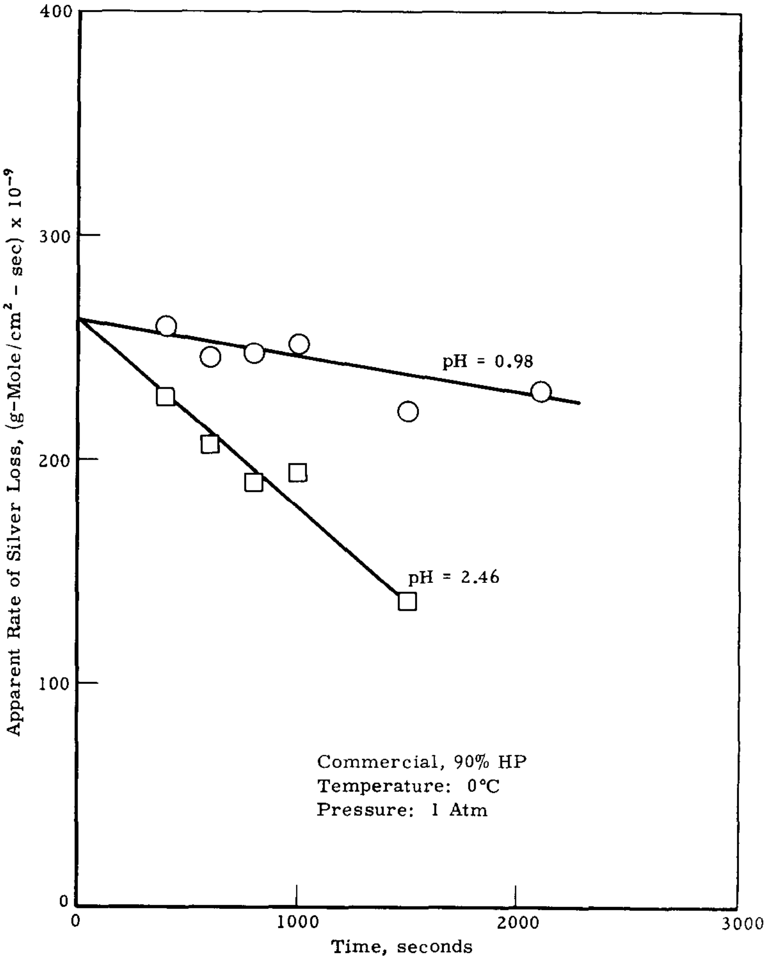

FIG. 5. Rate of silver loss as a function of time at constant pH.

The rate of decomposition is given by

$$-d(H_2O_2)/dt = k'(Ag)(H_2O_2) - k''(Ag)^{2/3}(H_2O_2)^{4/3} \quad (11)$$

where the first term must always be larger than the second. Thus, the deviation from direct proportionality to Ag and HP is minimal. If reaction (6) is more important than (8), it can be shown that

$$\begin{aligned} OH &\propto Ag \\ HO_2 &\propto (Ag)^{1/2}(H_2O_2)^{1/2} \quad (12) \\ AgOH_{surf} &\propto Ag \end{aligned}$$

For this approximation the rate of decomposition is simply given by

$$-d(H_2O_2)/dt = k'''(Ag)(H_2O_2). \quad (13)$$

Presumably, with (6) and (8) of comparable magnitude the HP decomposition rate is a combination of (11) and (13), which would also minimize deviation from direct proportionality to Ag and HP.

Of the reactions in the mechanism only (5) and (6) can be endothermic. The standard free energy of formation of the surface silver hydroxide is not known but can be estimated if it is assumed that the free energy of formation from Ag_2O and H_2O (7) is zero [this is not unreasonable since the free energy of formation of $Cu(OH)_2$ from CuO and H_2O (7) is only 1.8 kcal/mole]. With the above assumption the calculated free energy of AgOH is −30 kcal/mole. From the known free energy of formation of the other species (7), reaction (5) is endothermic by 6 kcal/mole and (6) is exothermic by no more than 3 kcal/mole. The mechanism thus indicates a low activation energy, as is observed experimentally.

Using the reaction

$$HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH \qquad (14)$$

in place of (8) leads to an HP decomposition rate proportional to Ag and HP and, therefore, is consistent with the experimental observations. Barb and Baxendale (*8*) have shown, in the homogeneous decomposition of dilute HP with ferric ion, that decomposition proceeds via Fe^{3+} in place of HP in (14). While this does not rule out (14) in concentrated HP, it does argue that it may not be important.

Of the three possible termination reactions

$$2\,OH + M \rightarrow H_2O_2 + M \qquad (15)$$

$$HO + HO_2 + M \rightarrow H_2O + O_2 + M \qquad (16)$$

and (9), reaction (9) appears most suitable. Due to the large HP concentration relative to the radicals present, reaction (7) should be the only important reaction for OH.

Reactions involving ionized perhydroxyl radicals, such as,

$$O_2^- + H_2O_2 \rightarrow O_2 + OH^- + OH \qquad (17)$$

do not appear to be important in the decomposition of nearly neutral 90% HP. No effect of pH on the rate of decomposition was observed over a three order of magnitude change in hydrogen ion content of 90% HP (Fig. 4).

To account for silver loss an additional reaction is necessary. The following equilibrium limited solvolysis reaction is postulated:

$$AgOH_{surf} + 2H_2O_2 \underset{k'_{18}}{\overset{k_{18}}{\rightleftharpoons}} Ag^+(H_2O_2)_2 + OH^-. \qquad (18)$$

The silver hydroxide on the surface is taken into solution by complexing with HP. Attack by two molecules of HP is not unreasonable since argentuous silver is known to form complexes with two ligands such as $Ag^+(NH_3)_2$ in aqueous solution.

The loss of silver by (18) is small compared with the rate of HP decomposition. From the experimental data it was calculated that, in 90% HP at 0°C, 135 moles of O_2 are formed per mole of silver lost. Thus, the rate of decomposition is at least 270 times faster than the rate of silver loss (1 mole O_2 = 2 moles HP).

From (18) the rate of silver mass loss is given by

$$d(M)/dt = k_{18}(AgOH)(H_2O_2)^2 - k'_{18}[Ag^+(H_2O_2)_2][OH^-] \qquad (19)$$

Considering only the forward reaction and substituting the steady state values for AgOH* derived in (10) and (12) yields

$$d(M)/dt = k^{IV}(Ag)^{2/3}(H_2O_2)^{7/3} \qquad (20)$$

$$d(M)/dt = k^{V}(Ag)(H_2O_2)^2 \qquad (21)$$

depending upon whether (8) or (6) is more important, respectively. Because (21) fits the experimental data better than (20), reaction (6) is probably more important than (8) in the decomposition mechanism. The mechanism of reaction indicates that (8) is not necessary to fit the experimental data; however, the reaction is included because it is highly exothermic and does occur at the surface. The other reactions, (7) and (9), which are strongly exothermic, need not occur at the surface. The radical termination step (9) probably occurs more readily in solution. The other reactions which are postulated to occur at the surface [i.e., (5) and (6)] are either endothermic or only weakly exothermic. A strongly exothermic reaction must occur at the surface to account for the transition to the high temperature regime (*10*).

Since (18) is equilibrium limited, the effect of added Ag^+ and OH^- is apparent. Silver and hydroxide ions decrease mass loss by increasing the rate of redeposition of silver hydroxide on the surface.

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* The use of the steady state value for AgOH derived in (10) and (12) is valid since (18) is much slower than the steps in the decomposition.

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