JOURNAL OF CATALYSIS 2, 415–420 (1963)

Decomposition of Concentrated Hydrogen Peroxide on Silver II. High Temperature Decomposition

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Received June 5, 1963

The heterogeneous decomposition of 90% hydrogen peroxide (HP) on silver has been investigated as a function of bulk solution temperature, silver surface temperature, and pressure. An abrupt transition between a region of lower rate of decomposition and one of higher rate occurs; the transition is strongly influenced by the rate of decomposition at low temperature.

At high temperature the decomposition of 90% HP is rate-limited by heat transfer. At constant bulk solution temperature, the silver surface temperature and the HP decomposition rate increase with increasing pressure in the manner expected for a heat-transfer-limited process. At constant pressure with increasing bulk solution temperature, the silver surface temperature slowly increases while the HP decomposition rate and the silver loss rate slowly decrease.

INTRODUCTION

In the foregoing paper (*1*) the chemical kinetics of the decomposition of concentrated HP on silver at low temperatures were described. As the temperature is increased, an abrupt transition to a different mechanism of decomposition occurs. Previous researchers (*2*, *3*) have encountered this effect but have not thoroughly investigated it. Maggs and Sutton (*3*) have shown that the high temperature decomposition of HP on silver is diffusion-controlled but have not quantitatively described the phenomenon. A consistent explanation of the transition and the decomposition at high temperatures has now been obtained by a study of the interrelationships among pressure, solution temperature, silver temperature, rate of HP decomposition, and rate of silver loss.

EXPERIMENTAL

Rates of HP decomposition at low temperatures were measured as described previously (*1*).

Transition temperatures were obtained by warming the vigorously stirred solution at a rate of about 1°C/min. The solution temperature at which suddenly accelerated HP decomposition began was taken as the transition temperature. The reproducibility of the transition temperature was $\leqslant 2°C$. The silver temperature and the HP decomposition rate were also measured during these experiments.

Because of the rapid rates of HP decomposition at temperatures above the transition, a dynamic rather than a static method of measuring rates was necessary. A detailed diagram of the equipment is shown in Fig. 1.

Liquid HP was pressured from a feed tank with nitrogen to an automatic valve controlled by an automatic feed rate balance. The flow rate used was 45 g/min. The HP entered the pressurized water bath and was warmed to the reaction temperature in a section of 1/8-inch stainless steel tubing. By upflow the liquid HP contacted the silver surface. The resultant mixture of liquid and gas was passed through an after-cooler, a back pressure regulator, and a liquid accumulator. The oxygen produced was separated from the liquid and passed through a gas meter.

Not shown in Fig. 1 were two thermocouples, one just ahead of the silver section and one just after the silver section. The average temperature from these thermo-

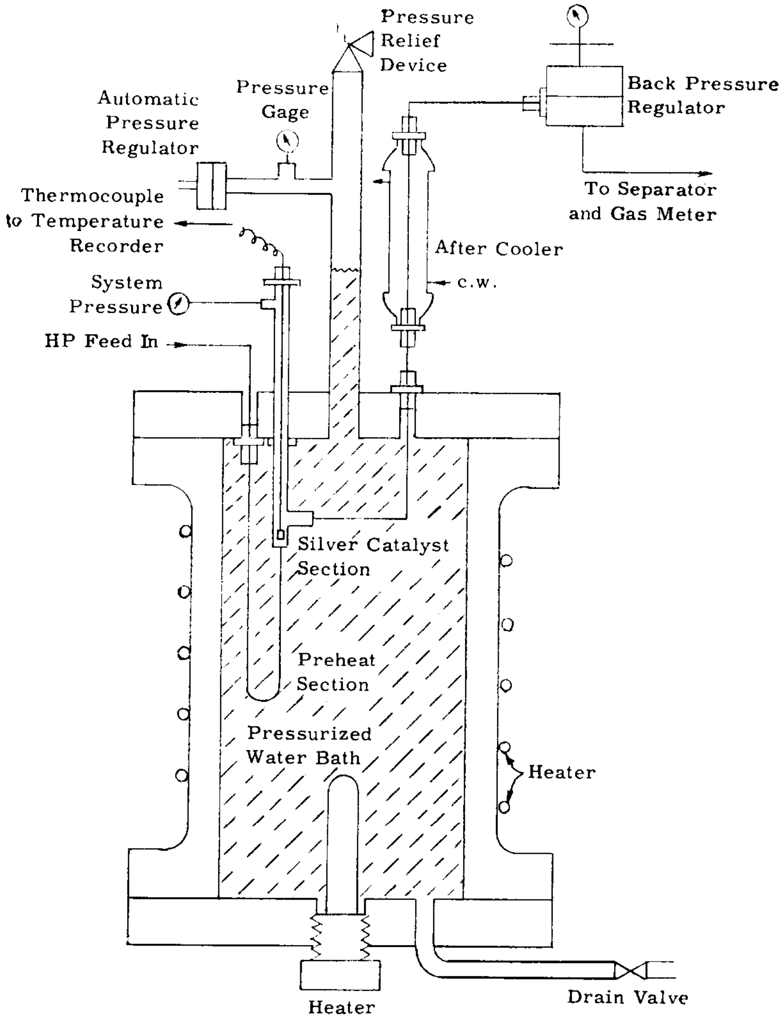

FIG. 1. Apparatus for measuring decomposition rates of 90% HP at elevated temperatures and pressures.

couples was used as the temperature of the HP stream.

The holder for the silver catalyst section was prepared by silver-soldering an iron-constantan thermocouple into a short section of hypodermic tubing. This tubing was soldered into another piece of larger sized hypodermic tubing which in turn was soldered into a long section of 1/8-inch stainless steel tubing.

The silver catalyst was a 1/4-inch long piece of 1/8-inch silver rod. One end was partially drilled out and threaded to fit over the hypodermic tubing. By this technique it was possible to measure the area and the weight of the silver section before and after each experiment.

With this apparatus HP decomposition rates and silver loss rates could be determined at constant temperature, constant pressure, and essentially constant HP concentration. The maximum working temperature of the system was about 150°C. Above this temperature the background homogeneous and stainless-steel–catalyzed decomposition rates became a substantial portion of the total decomposition rate.

The stainless steel surfaces in contact

with HP were degreased with 10% NaOH, rinsed with distilled H_2O, contacted with 30% HNO_3 at 40°C for 1 hr, rinsed again with distilled H_2O, and passivated with 90% HP for several hours before use.

RESULTS

Experimentally, it is possible to vary the HP decomposition rate in the low temperature zone by the addition of organic additives (for instance, acetic acid). The HP decomposition rates of a series of such solutions were determined at 0°C. The transition temperatures, in terms of the bulk solution temperature, were measured in separate experiments. A plot of the HP decomposition rates at 0°C versus the transition temperatures is given in Fig. 2. The transition temperature decreases as the specific decomposition rate at 0°C increases.

Above the transition temperature, decomposition rates, silver loss rates, and silver surface temperatures were measured as a function of bulk temperature and pressure. The results are plotted in Figs. 3, 4, and 5.

The 90% HP decomposition rates (Fig. 3) are high compared with those in the low temperature reaction zone. The rates are strongly dependent upon pressure and decrease slowly at constant pressure with increasing bulk temperature except for the indicated minimum at 1.7 atm pressure.

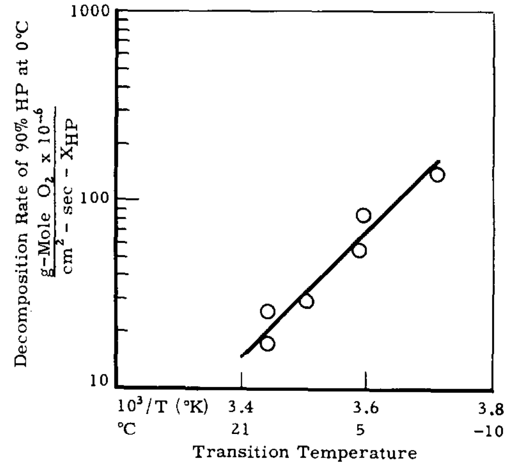

FIG. 2. Variation of transition temperature with 90% HP decomposition rate at 0°C.

The silver loss rates (Fig. 4) are low compared with those in the low temperature reaction zone. While the data scatter considerably due to experimental inaccuracies in measuring the low rates, the rates decrease with increasing bulk temperature, and increase slightly with increasing pressure.

The silver surface temperature (Fig. 5) is considerably above the bulk solution temperature and is a strong function of pressure. At any given pressure the surface temperature increases slowly with increasing bulk temperature. However, at low pressures a

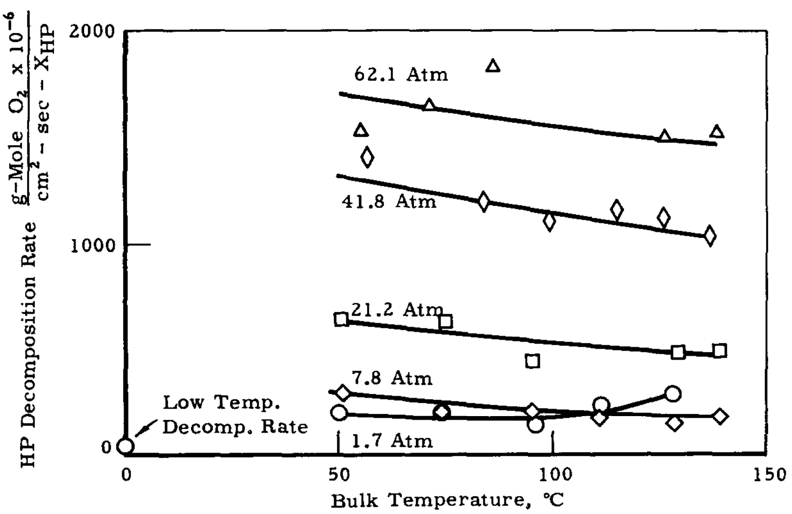

FIG. 3. Decomposition rate of 90% HP.

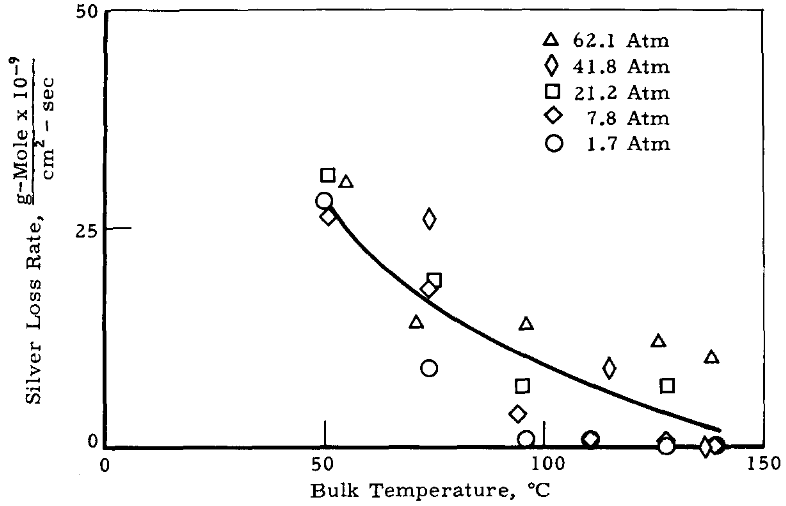

Fig. 4. Silver loss rate in 90% HP.

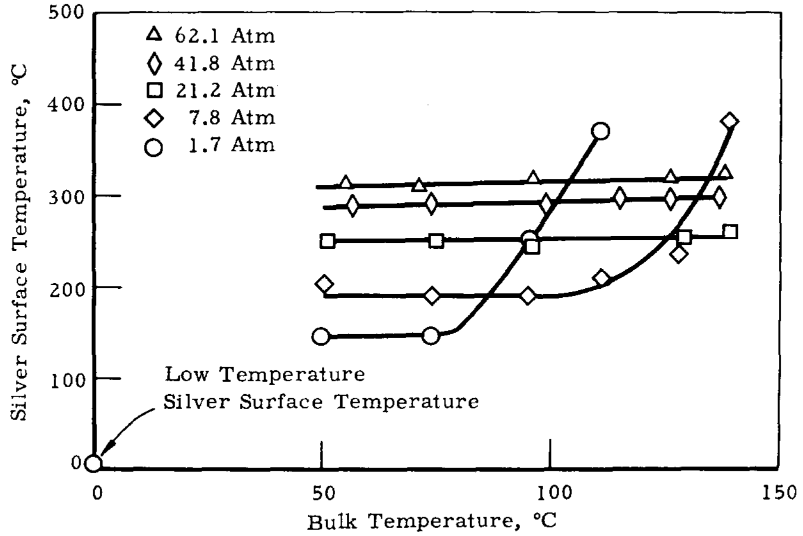

Fig. 5. Effect of pressure and bulk solution temperature of 90% HP on silver surface temperature.

further sharp increase in surface temperature is observed. The data show that the sharp increase in surface temperature occurs when the difference between the surface temperature and solution temperature reaches 75°C.

Discussion

The unusual HP decomposition rate data and silver loss data cannot easily be interpreted by standard kinetic analysis. However, the data are consistent with a mechanism dependent upon heat transfer from the surface.

In the decomposition of HP heat is generated. If the decomposition results in a net production of heat on the catalytic surface, the excess heat must be transferred to the surrounding liquid. In the low temperature reaction zone the heat transfer is by natural convection and the pumping action of the oxygen decomposition product leaving the surface. These processes, however, are capable of transferring only a limited amount of heat. At some temperature they fail to remove heat as fast as it is produced. The surface temperature now increases rapidly to a new equilibrium value where the heat produced can be removed by some other mechanism.

It is postulated that the rate of HP decomposition on silver surfaces at high temperature is determined by heat transfer to the solution via boiling with its associated surface blocking by bubbles. The surface is considered to be not in the moderate boiling region but in the transition boiling regime. The decomposition rate and surface temperature stabilize at the maximum in heat flux where an increase in surface temperature brings about a decrease in the area not blocked by bubbles and in the rate of heat transfer (*7*). Diffusion of HP to the surface and its reaction at the surface are fast compared with the phenomenon of heat removal by boiling.

The experimental evidence supports the above hypothesis. For instance, the abrupt transition in rate of decomposition (Fig. 2) occurs when natural convection can no longer transfer the heat being generated. The surface temperature increases to the vicinity of the HP boiling point where the boiling mechanism, more efficient than natural convection, can remove the heat. This contention is strengthened by the experimental observation (Fig. 2) that a higher rate of decomposition results in a lower transition temperature. Heat transfer in the transition boiling region is also indicated by the decrease in decomposition rate and increase in silver surface temperature resulting from an increase in bulk solution temperature at constant pressure (Figs. 3 and 5). This behavior may be explained in terms of the postulated mechanism as follows. At the experimental conditions of pressure and bulk solution, temperature equilibrium is established between the rate of decomposition and that of heat transfer by boiling. An increase in bulk solution temperature will initially cause a decrease in heat transfer due to the smaller driving force. This will cause an increase in surface temperature and a concomitant increase in the rate of bubble formation. Consequently the surface area not blocked by bubbles will decrease, i.e., there will be a shift in the direction of film boiling, and the rates of heat transfer and of decomposition will again be in balance at a lower level.

The effect at 1.7 atm pressure (Fig. 3), in which a minimum in the decomposition rate occurs, can also be attributed to a heat transfer phenomenon. The surface temperature increases very rapidly (Fig. 5) as the decomposition rate passes through the minimum. The high surface temperature may be associated with film boiling, i.e., complete blocking of the surface by vapor, in which radiant heat transfer and vapor phase decomposition are significant.

It is interesting that the bulk temperature at which a rapid rise in surface temperature occurs increases with increasing system pressure (Fig. 5). This is in accord with the expected behavior of the onset of complete film boiling. Higher pressure allows boiling to continue at higher bulk temperature due to the higher boiling point and delays the onset of complete film boiling, probably through its effect on bubble volume.

The postulated mechanism requires a strong correlation between surface temperature and system pressure. The surface temperature should be above the HP boiling point for effective heat transfer by boiling. Boiling point data for 90 wt % HP above the atmospheric boiling point are not available, however, the vapor pressure curve for 90 wt % HP was extrapolated from the data of Scatchard (*4*) using the Ramsey-Young (*5*) extrapolation method with water as the reference substance. The extrapolated curve together with the measured silver surface temperatures at various pressures is given in Fig. 6. The curves are parallel but the surface temperatures are too low. This is not unreasonable, however, since dilution of the HP near the surface by the water from the HP decomposition would result in lower boiling points. If the dilution is 20% the apparent inconsistency is resolved. There is also some uncertainty in the vapor pressure extrapolation.

Mechanistic details of the decomposition process itself are effectively obscured by the

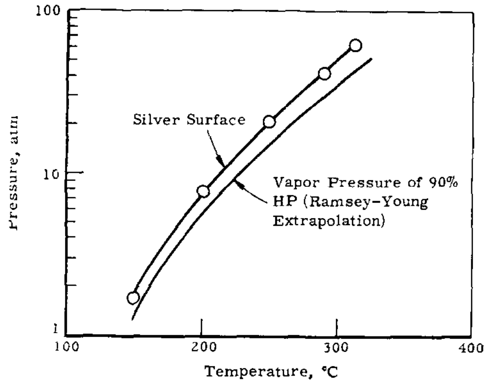

FIG. 6. Silver surface temperature as a function of pressure at 50°C bulk solution temperature.

rate-controlling phenomenon of heat transfer; however, the mechanism could be the same as the one postulated (*1*) at low temperature.

$$Ag + H_2O_2 \rightarrow AgOH_{surf} + OH \quad (1)$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (2)$$
$$AgOH_{surf} + HO_2 \rightarrow Ag + H_2O + O_2 \quad (3)$$
$$AgOH_{surf} + H_2O_2 \rightarrow Ag + HO_2 + H_2O \quad (4)$$
$$AgOH_{surf} + 2(H_2O_2) \rightleftarrows Ag^+(H_2O_2)_2 + OH^- \quad (5)$$
$$2HO_2 + M \rightarrow H_2O_2 + O_2 + M \quad (6)$$

At the higher surface temperatures in the heat transfer region reactions (1), (3), and (4) are much faster. Reactions (2) and (6) should not be strongly affected by changes in the surface temperature since they occur in the solution. With the activation energy (10.4 kcal/mole) observed (*1*) in the low temperature region, the rate of decomposition should increase by a factor of 100 between 20° and 150°C. Actually the rate increases by only a factor of 10, indicating that only a small fraction of the surface is available for decomposition at any given time.

Of the reactions given only the equilibrium-limited reaction (5) leads to silver loss. In the heat-transfer–limited region much of the surface is unavailable for reaction with HP; therefore, a lower silver loss rate would be effected. In our previous paper we have shown that the rate of silver loss decreases abruptly by about a factor of 8 as the transition from the low temperature to the heat transfer zone is made. While the apparent rate of decomposition is very sensitive to pressure, the rate of silver loss is only marginally affected. This result is in agreement with (5) as the step determining silver loss. The reaction between solid AgOH and liquid HP should not be much influenced by pressure.

ACKNOWLEDGMENTS

This work was supported by the U. S. Navy, Bureau of Aeronautics under Contract NOas 57-795d (1958). The authors gratefully acknowledge the assistance of T. J. Kellogg and A. F. Johnson, the guidance of G. J. Pierotti, and the advice of various people in the Shell Development Company.

REFERENCES

1. BAUMGARTNER, H. J., HOOD, G. C., MONGER, J. M., ROBERTS, R. M., AND SANBORN, C. E., *J. Catalysis* **2**, 405 (1963).
2. HEDGES, E. S., AND MYERS, J. E., "The Problem of Physico-Chemical Periodicity." Longmans Green, New York, 1926.
3. MAGGS, F. T., AND SUTTON, D., *Trans. Faraday Soc.* **54**, 1861 (1958) and *Trans. Faraday Soc.* **55**, 974 (1959).
4. SCATCHARD, G., KAVANAGH, G. M., AND TICKNOR, L. B., *J. Am. Chem. Soc.* **74**, 3715 (1952).
5. RAMSAY, W., AND YOUNG, S., *Phil. Mag.* **20**, 515 (1885), and *Phil. Mag.* **21**, 136 (1886).
6. SCHUMB, W. C., SATTERFIELD, C. N., AND WENTWORTH, R. L., "Hydrogen Peroxide," p. 602. Reinhold, London and New York, 1955.
7. McADAMS, W. H., "Heat Transmission," p. 380. London and New York, McGraw-Hill, London and New York, 1954.