

Catalytic Decomposition of Hydrogen Peroxide by Metals and Alloys of the Platinum Group

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The catalytic decomposition of dilute aqueous solutions of hydrogen peroxide has been studied on a number of Group VIII metals and binary alloys, including palladium-gold. The kinetics were measured at 27° as a function of catalyst composition and pH of the solution. In neutral solution, the activity of the individual metals of Group VIII² was generally greater than those of Group VIII¹, the order of specific activity (per unit surface area) decreasing in the sequence Pt > Os > Ir > Pd > Ru > Rh. Alloys of Pt-Pd, Pt-Ru and Pt-Rh showed activities intermediate between those of the constituent metals. Alloys of Pt-Ir and Pd-Au exhibited maximum activities at intermediate alloy compositions. The kinetics depended strongly on the pH of the solutions, the rate rising to a sharp maximum at pH values of 10-11, in accordance with the radical-chain mechanism for the decomposition.

INTRODUCTION

The metal-catalyzed decomposition of aqueous hydrogen peroxide has certain unique features which distinguish it from most other heterogeneous reactions. Although the mechanism is by no means established, the reaction appears to be electrochemical in nature, involving electron transfer from metal to adsorbate and a chain reaction at the surface of the metal (1). As the direction of electron transfer is the reverse of that normally encountered in metal-catalyzed reactions, the trend of catalytic activity should be quite different from that found, for example, in hydrogenation reactions, where electron donation to unfilled levels in the metal generally occurs. Thus, the s-metal, silver, is an active catalyst for hydrogen peroxide decomposition (2) but inactive for ethylene hydrogenation. Also the activity for peroxide decomposition shown by copper-nickel foils has been found to decrease with increasing nickel content (3), whereas the reverse trend has been observed for ethylene hydrogenation (4).

The decomposition of hydrogen peroxide is of considerable interest from an electrochemical standpoint, in view of the possible role of this species as an intermediate in the cathodic reduction of oxygen at metal electrodes. Although the mechanism of this electrochemical reaction appears to vary in a complex manner with the nature and surface condition of the metal, the pH of the electrolyte, and the potential applied to the electrode, it is generally agreed that the formation and decomposition of peroxide plays a central role in the reaction scheme (5). For this reason the ability to catalyze hydrogen peroxide decomposition has often been used to test potential cathode materials for fuel cells and batteries (6).

In spite of the importance of this reaction and the detailed studies that have been made with active individual metals such as silver (7), few attempts have been made to use this reaction in the systematic study of alloy catalysts. The results of kinetic measurements on the platinum group metals and selected binary alloys over a

broad range of catalyst composition are described in the present paper.

EXPERIMENTAL

Catalyst Preparation

The metal and alloy powders were prepared by reduction of suitable mixed salt solutions with 5% sodium borohydride solution as described previously (8). The salts used included Engelhard $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, PdCl_2 , $\text{RhCl}_3 \cdot 2.74\text{H}_2\text{O}$ (9), $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{OsCl}_3 \cdot x\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ [probably an oxychloride (9)], and Fisher Reagent Grade $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and silver nitrate. The reduction was carried out slowly at room temperature by adding the reducing agent dropwise to the stirred salt solutions and the resulting metal powders were washed thoroughly before being dried in air. After being ground and sieved through a 400-mesh nylon screen, the catalysts were characterized by x-ray diffraction, x-ray emission, and chemical analysis and their surface areas were measured by the BET method using nitrogen as adsorbate at -195°C .

The surface areas of the catalyst samples were generally in the range 5–30

m^2/g , although, in the case of pure iridium and ruthenium, the reduction reaction was slow and the resulting metal blacks were very finely divided and showed abnormally high surface areas. The slow reduction of iridium salts by borohydride has been noted previously by Holt (10). On reduction of silver nitrate, the silver particles coagulated to coarse lumps with very low surface area ($<0.2 \text{ m}^2/\text{g}$) and no catalytic measurements were made with this material.

Lattice parameters and surface areas for the Pt-Pd, Pt-Rh, Pt-Ru, and Pd-Au alloy series are summarized in Table 1. Owing to the effects of line broadening, it was only possible to determine lattice parameters to within 0.01 \AA for the last three series. Alloys of Pt-Pd were of lower surface area and the x-ray lines were less diffuse so that lattice parameters could be estimated to $\pm 0.001 \text{ \AA}$. In general the alloys were homogeneous solid solutions (with the exception of the Pt-59.7% Ru sample) and the measured lattice spacings agreed quite well with literature values (11).

A few Pd-Au samples were prepared by fusing the dry mixed chlorides with excess sodium nitrate at 500°C for 3 hr. After thorough washing to remove soluble salts

TABLE 1
PROPERTIES OF ALLOY CATALYSTS

Alloy compn. (wt %)	Lattice spacing (a_0 (Å))	Surface area (m^2/g)	Alloy compn. (wt %)	Lattice spacing (a_0 (Å))	Surface area (m^2/g)
100 Pt	3.916	4.9	Pt-8.9 Ru	3.90	12.0
Pt-20.0 Pd	3.904	3.6	Pt-16.3 Ru	3.90	13.1
Pt-33.0 Pd	3.899	3.3	Pt-19.9 Ru	3.89	9.7
Pt-49.3 Pd	3.894	6.0	Pt-28.2 Ru	3.88	13.7
Pt-65.2 Pd	3.892	6.2	Pt-59.7 Ru	3.87 + Ru	18.3
100 Pd	3.890	14.3	100 Ru	2.70	74.4
Pt-10 Rh	3.89	13.7	Pd-10.9 Au	3.90	16.8
Pt-15.8 Rh	3.90	34.9	Pd-15.5 Au	3.89	8.3
Pt-27.3 Rh	3.86	16.2	Pd-19.7 Au	3.89	8.6
Pt-49.9 Rh	3.85	21.7	Pd-25.7 Au	3.89	18.0
Pt-72.6 Rh	3.82	23.6	Pd-29.2 Au	3.92	10.7
Pt-90.1 Rh	3.81	25.7	Pd-33.5 Au	3.92	8.0
100 Rh	3.80	28.1	Pd-50.5 Au	3.94	12.4
			Pd-59.0 Au	3.98	12.9
			Pd-79.0 Au	4.02	10.4
			100 Au	4.08	5.0

the suspensions of mixed oxides were treated with bubbling hydrogen at room temperature. This treatment did not, however, result in complete reduction to the metals and the resulting materials were inactive for peroxide decomposition. Attempts were made to achieve complete reduction by gas phase reduction with flowing hydrogen at 100°C. Although the catalytic activity of the samples was increased as a result of this treatment, extensive sintering took place during the hydrogen reduction. As it appeared unlikely that homogeneous alloys would be formed by this method, no further experiments were carried out with materials of this type.

Procedure

The method used to study the catalytic decomposition of hydrogen peroxide was essentially the same as that described recently by Keating, Rozner, and Youngblood (12). The reaction was carried out in a 1-liter Erlenmeyer flask immersed in an Aminco constant temperature water bath, controlled to $\pm 0.02^\circ\text{C}$ by means of a mercury filled thermoregulator. 500 ml of a 0.3% hydrogen peroxide solution (prepared from Fisher Certified 3% hydrogen peroxide, without stabilizer) was placed in the flask, and the required quantities of acid or alkali were added. The pH of the solution was then measured by means of a Beckman Model H2 pH meter. The contents of the flask were then stirred vigorously with a glass stirrer provided with flat vanes. The speed of the stirrer was adjusted stroboscopically to 400 rpm before each catalytic run. After the solution had attained thermal equilibrium with the bath, a sample was withdrawn and analyzed for peroxide by titration with standardized 0.1 *N* potassium permanganate (13). For this purpose the sample was acidified with 20% sulfuric acid and titrated until a pink endpoint was reached. By this method concentration changes of 2×10^{-5} g $\text{H}_2\text{O}_2/\text{ml}$ could be readily determined. A weighed sample of catalyst (generally 0.2 g) was then added to the solution and samples were withdrawn for analysis at measured intervals during the

course of the reaction. A blank run of peroxide decomposition rate in the absence of catalyst was also carried out as a function of the pH of the solution. The homogeneous decomposition rate was found to be negligible compared with the catalyzed rate in both neutral and acid solutions. In solutions of pH greater than 10 the homogeneous decomposition was rapid enough for a correction to be applied. All the catalytic measurements reported were carried out at a temperature of $27.0 \pm 0.2^\circ\text{C}$.

RESULTS AND DISCUSSION

Noble Metals

Preliminary experiments carried out in neutral 0.3% peroxide solution indicated that the individual metals of Group VIII varied widely in their ability to catalyze the decomposition reaction. With initial concentrations of less than 3×10^{-3} g $\text{H}_2\text{O}_2/\text{ml}$, the reaction invariably followed first order kinetics, a plot of $\log_{10} c_0/c$ showing a linear variation with time until at least 90% of the reaction had been completed. Linear plots of this type were used to evaluate the rate constant of the reaction as a function of catalyst composition.

Table 2 shows values for the specific rate constants ($\text{min}^{-1} \text{cm}^{-2}$ of catalyst surface), for the various platinoid metals and gold, determined in neutral solution with 0.3% peroxide initially. The activity of the metals of Group VIII³ was generally much

TABLE 2
DECOMPOSITION OF H_2O_2 ON NOBLE METALS

0.3% neutral H_2O_2 :		27°C
Metal	Surface area (m^2/g)	Rate $k \times 10^6$ ($\text{min}^{-1}\text{cm}^{-2}$)
Platinum	4.9	19.4
Osmium	17.2	16.2
Iridium	57.3	6.2
Palladium	14.3	2.2
Ruthenium	74.4	0.91
Rhodium	28.1	0.66
Gold	5.0	0.079

greater than those of Group VIII², the sequence of activities showing no correlation with the variation of surface area of the samples. In experiments conducted below 31°C, Stroganova *et al.* (14) have also shown that the order of activity of metal blacks falls in the sequence Pt > Ir > Pd > Rh. Although the sample of gold had about the same surface area as the platinum black sample, the latter was more than 200 times more active than the gold sample under the same conditions.

Noble Metal Alloys

The behavior of Pt-Pd, Pt-Ru, and Pt-Rh alloy catalysts in the decomposition of neutral 0.3% peroxide solution is summarized in Fig. 1, in which the logarithm of the specific rate constants (in min⁻¹ cm⁻²) are plotted against alloy composition for the three catalyst series. In spite of considerable scatter of the data, alloying of platinum with Pd, Ru, or Rh resulted in a steady decrease in the activity of the catalyst for this reaction. In the case of the Pt-Pd series, the activity decreased smoothly with palladium content. With Pt-Ru and Pt-Rh alloys no synergistic effects similar to those observed for CH₄-D₂ exchange (15) were found.

In other alloy series, however, synergistic effects were observed. Alloys of platinum-iridium, containing 10–20% Ir, were much more active than platinum black for the decomposition of peroxide in neutral solution. In these cases the decomposition rate appeared to vary little with the amount of catalyst added, suggesting that the kinetics were diffusion limited. With the Pt-Ir catalysts, 90% of the reaction was complete after 1-min contact. As meaningful kinetic measurements could not be made under these conditions, no further experiments were carried out with Pt-Ir catalysts. It is interesting, however, that Pt-Ir catalysts have been claimed to be superior cathodes for oxygen reduction in fuel cells (16), presumably as a result of their activity as peroxide decomposition catalysts.

Marked synergistic effects were also observed in the palladium-gold alloy series

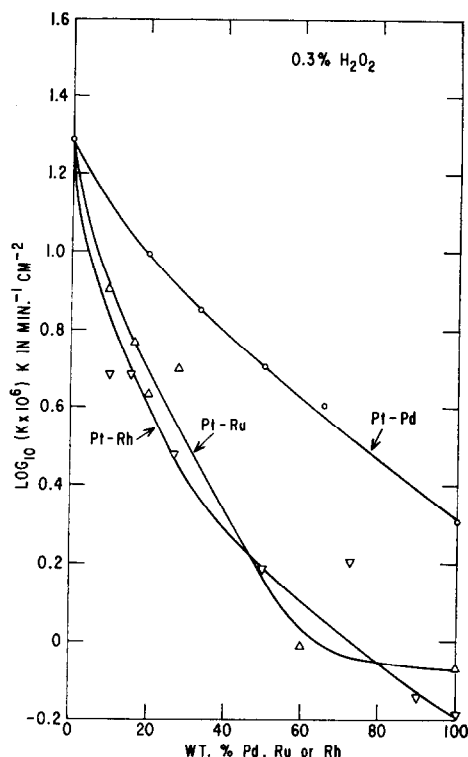


Fig. 1. H₂O₂ decomposition on Pt-Pd, Pt-Ru, and Pt-Rh alloy catalysts. 27°C, 0.3% neutral H₂O₂ solution initially.

which was studied in more detail, as described in the following sections.

Palladium-Gold Alloys

The variation in specific rate for 0.3% peroxide decomposition in neutral solution is shown in Fig. 2 for the palladium-gold alloy series. Although gold is very much less active than palladium, addition of 15–20% gold resulted in a marked maximum activity, the specific rate for the Pd–15.5% Au alloy corresponding to a 20-fold increase over that found for pure palladium and a 2-fold increase over that of platinum black. A similar, though less marked, maximum rate has been previously observed for CH₄-D₂ exchange (17) and para-H₂ conversion on Pd-Au alloys (18), the corresponding bulk alloy compositions being about 17 wt% and 44 wt% in the two cases. With both these reactions, however, further increase in gold content resulted in

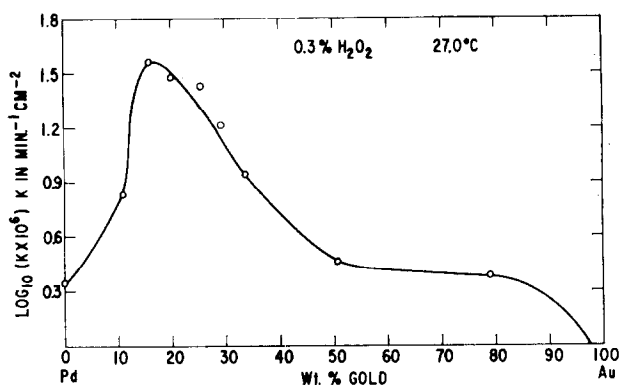


Fig. 2. H_2O_2 decomposition on Pd-Au alloy catalysts. 27°C , 0.3% neutral H_2O_2 solution initially.

a rapid decrease in catalytic activity, attributed to the filling of the Pd d band by s electrons from the gold. No such effect was observed in the case of hydrogen peroxide decomposition.

The rate of the catalytic decomposition of peroxide in aqueous solution was very strongly influenced by the pH of the solution. The effect of added sodium hydroxide and sulfuric acid on the activity of the palladium catalyst is illustrated in Fig. 3. Although the decomposition rate was generally more rapid in alkaline than in acid media, a very sharp maximum at low alkali concentrations was observed. Figure 4 shows similar data for a Pd-79% Au alloy. Although the position of maximum activity was about the same as for palladium, with increasing gold content the activities of the alloys diminished rapidly with increasing acid strength. The pH required for maxi-

mum activity is defined more closely for a Pd-50.5% Au alloy in Fig. 5, which summarizes a series of measurements in weakly acid and alkaline solutions. The optimum pH value was found to be around 10.5. Early measurements on the decomposition of hydrogen peroxide by colloidal gold and palladium and platinum also indicated a maximum rate at a well-defined hydrogen ion concentration, the rate being greatest at around $\text{pH} \sim 12$ (19). However, more recent measurements on Mn_2O_3 have also indicated a maximum rate at $\text{pH} = 10.5$ (20). Experimental values for the pH corresponding to maximum rate do not seem to be strongly dependent on catalyst composition.

The decomposition of peroxide in strong acid and base is shown in Fig. 6 for the Pd-Au alloy series. In both 5 N sulfuric acid and 30% potassium hydroxide the

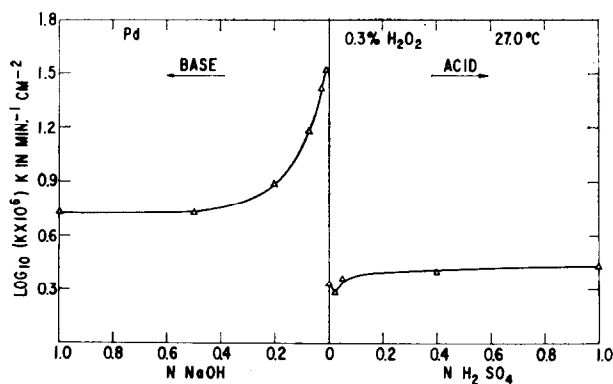


Fig. 3. Catalytic decomposition of 0.3% H_2O_2 solution by palladium. Effect of added acid and base.

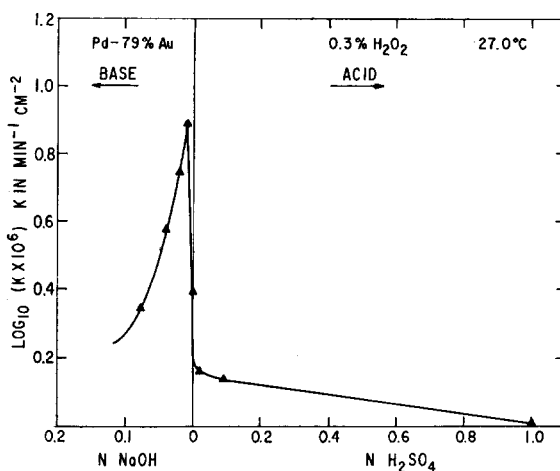


FIG. 4. Catalytic decomposition of 0.3% H_2O_2 solution by Pd-79% Au alloy. Effect of added acid and base.

rates showed maxima at bulk alloy compositions in the range 15–20% gold. Such electrolytes are in common use in fuel cells and batteries. Although the activity of pure palladium was slightly greater in strong

acid than in base, the activity of gold-rich alloys decreased rapidly with increasing acid strength. No decomposition of peroxide in 5 N sulfuric acid could be detected on pure gold, whereas in 30% potassium

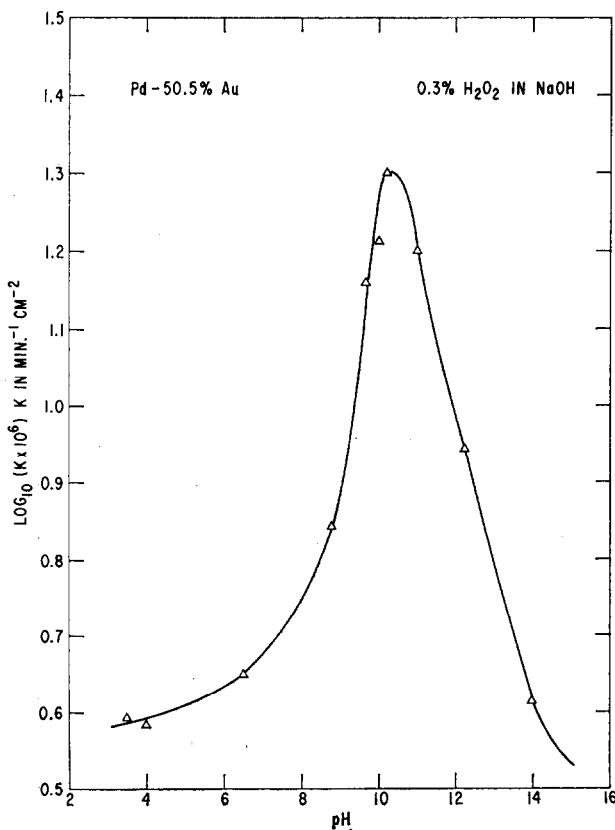


FIG. 5. Catalytic decomposition of 0.3% H_2O_2 solution by Pd-50.5% Au alloy. Effect of pH.

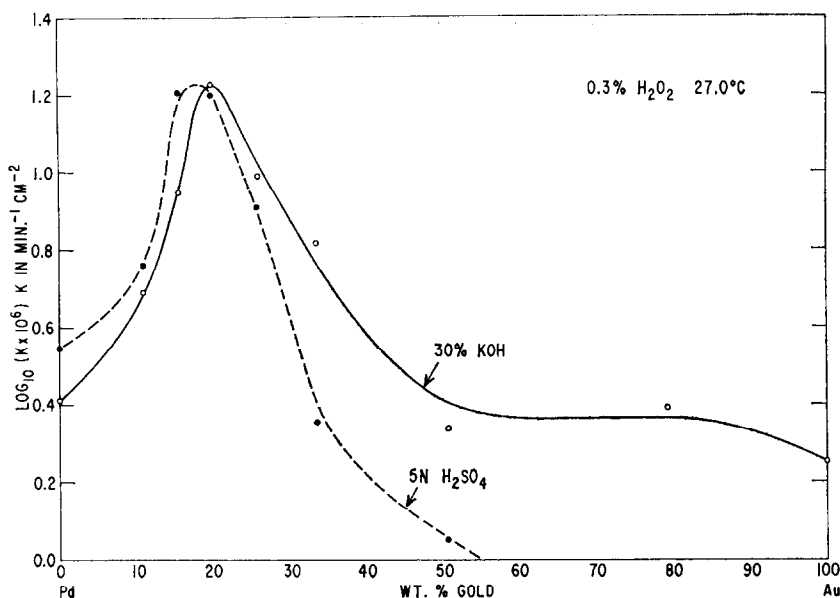


FIG. 6. Catalytic decomposition of H_2O_2 by Pd-Au alloys in 30% KOH and 5 N H_2SO_4 · 0.3% H_2O_2 solution initially.

hydroxide solution gold was reasonably active.

The effect of initial hydrogen peroxide concentration on the kinetics of the decomposition reaction are illustrated in Fig. 7 for a Pd-29.2% Au alloy catalyst. In this case the pH was adjusted with sulfuric acid to lie in the range 4-5 where the kinetics were relatively insensitive to pH (Fig. 5). The initial rate of peroxide decomposition was found to be a linear function of initial H_2O_2 concentration up to 3×10^{-3} g H_2O_2 ml. The slight falling off in the rate at higher peroxide concentrations may be an indication of diffusion controlled processes in the solution.

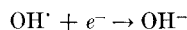
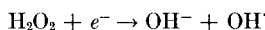
It was also observed that active Pd-Au catalysts tended to redisperse and become colloidal during the course of the reaction, probably as a result of charging of the metallic particles by adsorbed ions, whereas inactive catalysts remained in the agglomerated state.

Mechanism

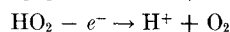
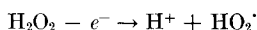
Although almost every conceivable mechanism for the catalytic decomposition of hydrogen peroxide has been proposed at one time or another, the most popular

schemes involve either a process of electron exchange between metal and reactant or the intermediate formation of oxide or oxygenated species on the metal surface.

The classical Haber-Weiss mechanism for the homogeneous decomposition (21) was elaborated by Gerischer (22) to explain the electrochemical process at platinum electrodes. Dissociation of the H_2O_2 molecule was believed to occur as a result of electron donation from the metal substrate. Cathodic reactions:



Formation of perhydroxyl radical could also occur by electron transfer to the metal. Anodic reactions:



The relative rates of these reactions depend on potential but both may occur simultaneously during the heterogeneous decomposition. As cathodic polarization of the electrode was found to give rise to an increase in the overall decomposition rate, it seems likely that the chain reaction:

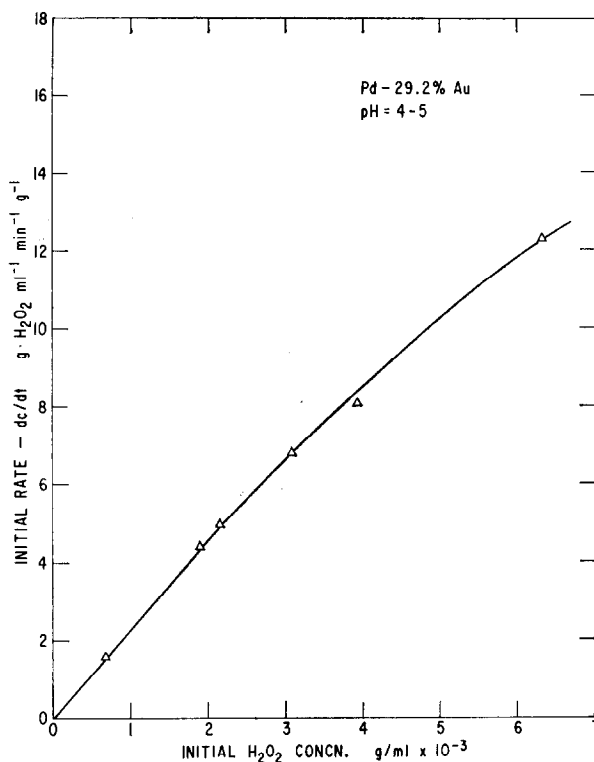
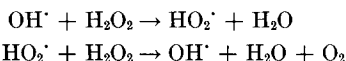
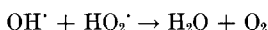


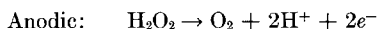
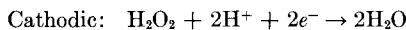
FIG. 7. Catalytic decomposition of H_2O_2 by Pd-29.2% Au alloy. Effect of initial H_2O_2 concentration.



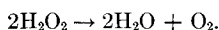
could also occur, with the termination step:



The overall electrode reactions were then:



giving the overall stoichiometry:



By using such a sequence of reaction steps, Weiss (21) showed that it was possible to predict the existence of an optimum pH at which the decomposition rate is a maximum.

According to this scheme, the rate of catalytic decomposition in the stationary state is of the form:

$$\begin{aligned} \text{Rate} &= - \frac{dC_{\text{H}_2\text{O}_2}}{dt} \\ &= \text{const.} \frac{[\text{H}^+]}{[\text{H}^+] - K'_{\text{HO}_2}} \cdot [\text{H}_2\text{O}_2], \end{aligned}$$

where K'_{HO_2} is the dissociation constant of the HO_2^\cdot radical in the surface phase. The analytical concentration of peroxide $C_{\text{H}_2\text{O}_2}$, will be related to the actual concentration $[\text{H}_2\text{O}_2]$ by the equation:

$$[\text{H}_2\text{O}_2] = \frac{C_{\text{H}_2\text{O}_2} \cdot [\text{H}^+]}{K_{\text{H}_2\text{O}_2} + [\text{H}^+]},$$

where $K_{\text{H}_2\text{O}_2}$ is the dissociation constant of hydrogen peroxide in the adsorbed phase. By differentiation it can be shown that the rate should be a maximum at a hydrogen ion concentration given by:

$$[\text{H}^+]_{\text{max}} = \frac{K_{\text{H}_2\text{O}_2} \cdot K'_{\text{HO}_2}}{K_{\text{H}_2\text{O}_2} - K'_{\text{HO}_2}}.$$

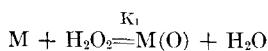
Using the experimental pH value of 10.5 for maximum activity and assuming a value of 1.7×10^{-12} for $K_{\text{H}_2\text{O}_2}$ as in the homogeneous phase (23), a value of about 1.6×10^{-12} is obtained for K'_{HO_2} . This is much less than the value of 10^{-6} measured in aqueous solution (21) and suggests that

the $\text{HO}_2\cdot$ radical is stabilized by adsorption on the metal surface.

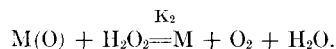
The role of the metal catalyst as both electron donor and acceptor can be used in a general way to interpret the observed differences in the activity of the noble metals and gold. Thus, as with copper-nickel alloys (3), addition of the s-metal gold would be expected to increase the activity of the d-metal palladium. If the slow step in the peroxide decomposition reaction involves electron transfer from the catalyst to the adsorbate, then the variations in activity of the alloys should be accompanied by corresponding changes in the work function and a minimum value at the optimum alloy composition. Unfortunately no work function measurements of Pd-Au alloys are available to test this hypothesis.

On the other hand, the addition of small amounts of gold to palladium results in enhanced activity, not only for peroxide decomposition, but also to a lesser extent, for para- H_2 conversion (18), CH_4 - D_2 exchange (17) and H-atom recombination (24), suggesting that the direction of electron transfer at the interface may not be of major importance in determining the trend of activity. In the case of the para- H_2 conversion, the effect appears to be due more to changes in the pre-exponential factor than in the activation energy, whereas the reverse is true for CH_4 - D_2 exchange. The variation of these kinetic parameters with alloy composition for the hydrogen peroxide reaction has not yet been measured.

The presence of surface oxide of chemisorbed oxygen on the active metal surface has frequently been suggested as an alternative mechanism for the peroxide decomposition. The formation of oxide on a platinum catalyst during the decomposition was suggested by Haber and Grinberg (25) and this idea has been revived recently in more general form by Bianchi, Mazza, and Mussini (26). It is likely that oxide films can arise by the chemical reaction of hydrogen peroxide at the metal surface



followed by the reduction of oxide by



In the steady state, the coverage of oxide on the metal will be given by the ratio of the rate constants for these two processes,

$$\frac{[\text{M(O)}]}{[\text{M}]} = \frac{K_1}{K_2}.$$

In acid solutions oxide phases will be less stable and the decomposition rates will be generally lower than in alkaline media, as found experimentally. In sulfuric acid, gold will not form an oxide layer owing to the formation of $\text{AuH}(\text{SO}_4)_2$ and this metal will be generally inactive under these conditions. In agreement with this prediction, the activities of gold-rich Pd-Au alloys showed a much more rapid decrease in activity with increasing acid strength than did the palladium rich alloys. The coverage of oxide on a palladium surface during the peroxide decomposition reaction probably does not exceed a monolayer as bulk palladium oxide is inactive.

Although the presence or absence of oxide films may influence the general level of activity of the various metals in acid and alkaline media, it is not clear how the complex dependence of rate on hydrogen ion concentration can be explained on this basis. As it is likely that many different species, such as $\text{OH}\cdot$, OH^- , HO_2^- , $\text{HO}_2\cdot$, O , O_2^- , etc., may exist on the metal surface during the course of the reaction, the detailed mechanism will depend in a complex manner on the pH, composition of the adlayer and the potential of the metal surface. In the absence of this information, electronic interpretations of the observed behavior of the various metal catalysts must remain highly speculative.

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