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Catalytic Decomposition of Hydrogen Peroxide on Some Oxide Catalysts

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Decomposition of H_2O_2 on some oxide catalysts has been studied. It appears that the oxide of the element which may form a redox system involving two different oxidation states of the element, and having a higher standard potential (reduction) E_0 than the corresponding value E'_0 of the system $O_2 + 2H^+ + 2e = H_2O_2$ is a good catalyst. And the oxide system having potential E_0 lower than E'_0 is a poor catalyst. In the former case oxidation of H_2O_2 is the primary process of catalytic decomposition of H_2O_2, and in the latter case, reduction of H_2O_2 is the primary process.

INTRODUCTION

In catalytic decomposition of H_2O_2 in solution in the presence of Fe^{2+}, Haber and Weiss (*1*) suggested the mechanism as

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$
$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$
$$HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH$$
$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-$$

On the basis of this scheme the authors could explain that a local excess of Fe^{2+} would favor the chain termination, and a local excess of H_2O_2 would favor the chain propagation. In ferric ion catalysis the primary step suggested by them is

$$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + HO_2$$

Since then a number of authors (*2*) have reported results on decomposition of H_2O_2 in solution with different modifications of the mechanism. Uri (*3*) considers that an important reaction in the Haber-Weiss mechanism has been overlooked

$$Fe^{3+}OH^- + OH \rightarrow Fe^{2+} + H_2O_2$$

This is the back-reaction of the primary step of their mechanism.

Weiss (*4*) studied the decomposition of H_2O_2 on metal and postulated the general scheme as

(a) $H_2O_2 + M \rightarrow OH^- + OH + M^+$
(b) $M^+ + HO_2^- \rightarrow M + HO_2$

Cota (*5*) studied the decomposition of H_2O_2 in an aqueous solution of K_2CO_3 and KOH on different solid oxides. He observed that Co_2O_3, MnO_2, and Ag_2O were good catalysts in decomposition of H_2O_2.

As oxidation or reduction of H_2O_2 is involved in catalytic decomposition of H_2O_2, the present investigation was undertaken to find a relation between the potential of the oxide system with two different oxidation states of the element, and the catalytic activity of the oxide.

EXPERIMENTAL

Preparation of oxides. MnO was prepared by heating (*6*, p. 822) MnC_2O_4 at about 200°C, and Mn_2O_3 by heating MnO to redness (*6*, p. 825) in air. $Co(NO_3)_2$ was heated in air at 600–700°C to form Co_3O_4; the latter is reduced in an atmosphere of hydrogen at about 300°C to CoO which is partially reduced to metallic Co. Ag_2O was prepared from $AgNO_3$, by adding NaOH, washing the precipitate thoroughly with water, and subsequently drying in a desiccator. Pb_2O is said to be formed on heating (*6*, p. 524) lead oxalate below 300°C. PbO was prepared (*6*, p. 526) from $Pb(NO_3)_2$, and Pb_3O_4 from PbO. PbO_2 was E. Merck guaranteed reagent. NiO was prepared by strongly heating (*6*, p. 874) $Ni(NO_3)_2$, and Ni_2O_3 by moderate heating (*6*, p. 874) (340°C) of the same.

Black CuO was prepared by heating $CuSO_4$ at about 1000°C, and Cu_2O was obtained by reducing $CuSO_4$ with Rochelle's salt (Fehlings solution). All the chemicals used were either Analar BDH or E. Merck guaranteed reagent. The hydrogen peroxide used was of E. Merck quality Merckozone.

Kinetics of decomposition of H_2O_2. About 0.5 g of powdered oxide with 50 ml of water was taken in a flask provided with a stopper and a side tube connected to a gas burette. The flask was placed on a water bath (28° ± 0.5°C) and 2 ml of 0.36 *M* H_2O_2 solution added into it. The solution was stirred by a magnetic stirrer. Oxygen liberated was collected in a gas burette. The initial rate of reaction was determined by extrapolation of volume–time data to time equal to zero. Initial rate is expressed in volume of oxygen (at STP) per unit time.

Preparation of oxide electrodes. The oxides of the respective elements were electrodeposited from solutions of their salts on platinum foil (1 sq cm) sealed in a tube (Fig. 1). The composition of the electrolytic solutions and the quantity of electricity passed are shown in Table 1. The electrode potential was measured against a saturated calomel electrode with a Cambridge potentiometer. The pH of water measured before the addition of H_2O_2 was found to be approximately the same as that after the decomposition of H_2O_2 in the presence of a catalyst. Water was prepared by distillation from alkaline potassium permanganate solution using a Pyrex flask, and was collected in a Pyrex bottle. The slight variation of the pH of water (≈ 6) from the ideal value may be due to the presence of a little dissolved CO_2. Decomposition of H_2O_2 in that sample of water was not perceptible.

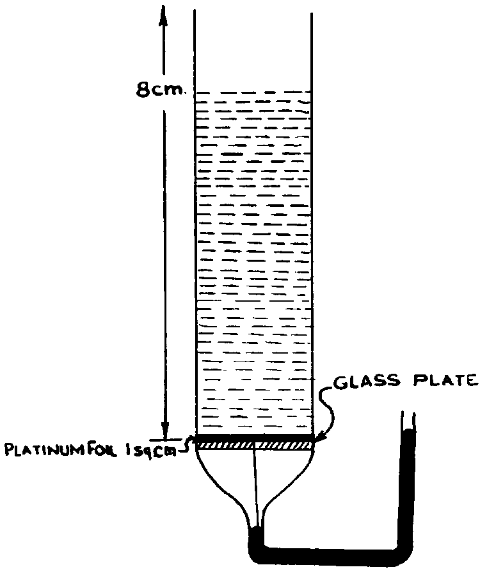

Fig. 1. Apparatus for preparation of oxide electrodes.

Results and Discussions

It is evident from the initial rates of decomposition of H_2O_2 (Table 2) that Mn_2O_3, MnO, PbO_2, Pb_3O_4, Co_3O_4, and Ag_2O are good catalysts in the decomposition of H_2O_2. In the study of decomposition of H_2O_2 in an aqueous solution of K_2CO_3 and KOH on some solids, Cota (*5*) observed that Co_2O_3, MnO_2, and Ag_2O, which were some of the solids used, were good catalysts. It appears that the oxide which may form a redox system with the oxide of the element at a lower valency state, and having a higher standard potential (reduction) of the system than the corresponding value of the O_2, $2H^+/H_2O_2$ system, is a good catalyst in decomposition of H_2O_2.

Vosburgh and his co-workers (*13*) in connection with "self-discharge of the manganese dioxide electrode" have extensively studied such electrodes which are represented as

$$Pt|MnO_2|MnO\quad OH|H^+$$

involving two sparingly soluble compounds in two valency states. Electrode potential is determined mainly by the surface composition of the deposits.

Nickel oxide electrodes are used in the Edison accumulator, and have been studied by Wynne-Jones (*14*) and co-workers with results of a similar kind.

According to Kozawa and Powers (*15*) the electrode potential of MnO_2 electrode is given by

$$E = E^\circ - \frac{RT}{F}\ln\frac{[Mn^{3+}]_{solid}}{[Mn^{4+}]_{solid}}$$

TABLE 1
Electrodeposition of Oxides

Electrodes	Composition of electrolytes	Current density (mA/cm²)	Time of passing current (hr)	References
MnO_2	1 *M* $MnSO_4$, 0.03 *M* H_2SO_4	0.2	1	*7*
PbO_2	0.006 *M* $Pb(NO_3)_2$	1.2	½	*8*
Cobalt oxide	1 *M* $Co(NO_3)_2$, 0.1 *N* HNO_3	1	1¼	—
NiO_2	0.1 *N* $Ni(NO_3)_2$, 0.1 *N* CH_3COONa, 0.001 *N* KOH	0.5	1¼	*9*
AgO (sample 1)	0.1 *N* $AgNO_3$, 0.1 *N* HNO_3	1.5	1½	—
AgO (sample 2)	Anodic polarization of Ag in 1 *N* NaOH	0.5	½	*10*
Pt oxide	0.1 *N* H_2SO_4	2.5	1½	—
Cu_2O-CuO	Mixture of Cu_2O and CuO in equal proportion by weight settled on Pt foil, dried at 90°C then at 120°C	—	—	—
Ag_2O	Ag_2O mixed with water, settled on Pt foil, dried at 120°C	—	—	*11*

corresponding to the reaction

$$MnO_2 + H_2O + e \rightarrow MnO\quad OH + (OH)^-$$

The reaction is assumed to take place in one phase of the oxide electrode system $[Mn^{3+}\text{-}Mn^{4+}\text{-}O^{2-}\text{-}OH^-]$ by the electron–proton mechanism (*16*) as proposed by Coleman, Vosburgh, and co-workers (*17*) and others. Other oxide electrodes, namely, PbO_2, cobalt oxide, NiO_2, and AgO, may be treated similarly.

From the experimental results (Table 3) it is found that the electrode potentials of the oxide electrodes (MnO_2, Co_2O_3, or Co_3O_4, Pt oxide, NiO_2, PbO_2, AgO) decrease in the presence of H_2O_2. These oxides form redox systems with the corresponding oxides of the elements at the lower valency state. As the concentration of the element at the higher valency state decreases by the reduction with H_2O_2, electrode potential falls. So it is evident that oxidation of H_2O_2 is the primary process of the catalytic decomposition of H_2O_2 on these oxides. Oxidation of H_2O_2 takes place through the step (*18*)

TABLE 2
Rate of Decomposition of H_2O_2 on Different Oxides[a]

Oxides	Initial rates (ml O_2/min)
Mn_2O_3	16
MnO	16
Co_3O_4	2.7
CoO	5.5
Ag_2O	17
PbO_2	16
Pb_2O	10
Pb_3O_4	8
PbO	0.4
Cu_2O	0.2
CuO	0.2
NiO	0.1
Ni_2O_3	0.2

[a] 0.5 g oxide, 0.014 *M* H_2O_2, temp. 28° ± 0.5°C.

$$H_2O_2 = HO_2 + H^+ + e$$

The free radical HO_2 sets off the chain reaction (*4*)

$$HO_2 + H_2O_2 = OH + H_2O + O_2$$
$$OH + H_2O_2 = HO_2 + H_2O$$

terminated by

$$OH + HO_2 = H_2O + O_2$$

In the case of the Ag_2O electrode there is no change of electrode potential in the presence of H_2O_2, though there is rapid catalytic decomposition over it. The standard potential of the system Ag^+/Ag couple is close to the value of that of the couple $O_2,2H^+/H_2O_2$. So probably oxidation and reduction of H_2O_2 take place simultaneously over Ag_2O. The free radicals, (OH) by reduction and HO_2 by oxidation of

TABLE 3

Change of Potential of Oxide Electrodes in the Presence of Hydrogen Peroxide[a]

Oxides	Electrode potential in water (against saturated calomel electrode) (V)	Electrode potential in the presence of H_2O_2 (0.01 M) against saturated calomel electrode (V)	Redox system	Standard potential[b] (reduction) (V)
MnO_2	0.65	0.20	MnO_2/Mn^{2+}	1.28
PbO_2	0.85	0.28	PbO_2/Pb^{2+}	1.456
Co_2O_3 or Co_3O_4	0.87	0.29	Co^{3+}/Co^{2+}	1.842
NiO_2	0.74	0.22	NiO_2/Ni^{2+}	1.75
AgO (sample 1)	0.85	0.45	Ag^{2+}/Ag^{+}	1.98
Pt oxide	0.67	0.41	Pt^{2+}/Pt	~1.2
Cu_2O-CuO	0.13	0.20	Cu^{2+}/Cu^{+}	0.167
Ag_2O	0.35	0.35	Ag^{+}/Ag	0.7995
—	—	—	O_2, $2H^{+}/H_2O_2$	0.682
—	—	—	Ni^{2+}/Ni	−0.25
AgO (sample 2)	0.60	0.25		

[a] pH of water and that of solution after decomposition of $H_2O_2 \approx 6$.

[b] Reference (*12*).

H_2O_2, both set off the chain reaction, and it is a very good catalyst, as is evident from the present investigation and that of Cota (*5*).

MnO as prepared in the atmosphere may contain some Mn_2O_3, forming the redox system Mn^{3+}/Mn^{2+}. Its standard potential (*12*) (reduction) is 1.51 V, indicating its good catalytic activity. Pb_3O_4 is a good catalyst because of its constituent PbO_2. NiO_2 is likely to be a good catalyst.

The oxides PbO, Cu_2O, CuO, NiO, and Ni_2O_3 may form redox systems with corresponding elements at different oxidation states. They appear to be poor catalysts in decomposition of H_2O_2. The standard potentials (*12*) (reduction) of such systems (M^{n+}/M or $M^{(n+1)+}/M^{n+}$) are lower than the corresponding value of $O_2,2H^{+}/H_2O_2$. So it is likely that H_2O_2 will be reduced primarily in the presence of such systems as

$$H_2O_2 + e \rightarrow OH + OH^-$$

leading to the formation of free radical OH which sets off the chain reaction (*1*, *4*). The electron will be available from the element (M) as

$$M \rightarrow M^{n+} + ne$$

and/or

$$M^{n+} \rightarrow M^{(n+1)+} + e$$

The chain reaction may be terminated (*1*), as in the presence of Fe^{2+}, by the local excess of M^{n+} which will react with free radical OH as

$$M^{n+} + OH \rightarrow M^{(n+1)+} + OH^-$$

This reaction explains the poor catalytic activity of these oxides. In support of the above mechanism it is to be noted that the potential of the CuO/Cu_2O system is slightly increased in the presence of H_2O_2 (Table 3).

However, CoO, which was partially reduced to metallic cobalt, and Pb_2O, which is supposed (*19*) to be a mixture of metallic lead and PbO, act as comparatively good catalysts. The excess metal present in these systems supply more electrons, because of their easy availability (*20*), to produce OH by reduction of H_2O_2. The reaction, $H_2O_2 + e \rightarrow OH + OH^-$ will compete with the chain-terminating reaction. $M^{n+} + OH \rightarrow M^{(n+1)+} + OH^-$, the former predominating over the latter in these cases.

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