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THE HOMOGENEOUS DECOMPOSITION OF
HYDROGEN PEROXIDE BY PLUTONIUM (IV)

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THE HOMOGENEOUS DECOMPOSITION OF HYDROGEN PEROXIDE
BY PLUTONIUM (IV)

Robert E. Elson

September 11, 1961

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ABSTRACT

The homogeneous decomposition of H_2O_2 by HNO_3 ; $\text{Pu}^{(\text{IV})}$; $\text{Pu}^{(\text{IV})}$ and Pt; $\text{Pu}^{(\text{IV})}$ with $\text{Cu}^{(\text{II})}$ and $\text{Fe}^{(\text{III})}$; and, $\text{Pu}^{(\text{IV})}$ with Pt and $\text{Cu}^{(\text{II})}$ with $\text{Fe}^{(\text{III})}$ in nitric acid solutions ($>1\text{M}$) as a function of temperature were investigated. The range of $[\text{H}_2\text{O}_2]$ was 10^{-2} to 10^{-1} M. $[\text{Pu}^{(\text{IV})}] \sim 1.25$ M. The evolution of gas was first order in all cases up to $[\text{HNO}_3] \sim 10$ M. Above $[\text{HNO}_3] \approx 10$ M, the reaction is no longer first order.

Approximate activation energies for the decomposition of H_2O_2 by the various catalysts are listed.

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Pursuant to a number of other problems, it was felt desirable to obtain some idea of the rate of decomposition of hydrogen peroxide by Pu(IV), both alone and in the presence of known catalysts for the decomposition. As Pu(IV) hydrolyzes in solutions of low acid concentration, nitric acid solutions of greater than 1 M were investigated.

The apparatus used was extremely simple. A round-bottom flask of 100 cc capacity was fitted with a magnetic stirrer and connected to a water-filled 10-ml burette through a condenser cooled with constant temperature water which also circulated around the 100-cc flask. The burette was attached to a leveling bulb through a stopcock and the O₂ evolved in the decomposition of H₂O₂ measured, as a function of time, by displacement of water from the burette. One hundred ml of acid was used and sufficient 30% H₂O₂ added to make the solution $\sim 10^{-2}$ M in H₂O₂.

The reaction between H₂O₂ + HNO₃ alone was studied first. The rate at room temperature was zero or exceedingly slow in 1, 2, 4, and 6 M HNO₃. At 8 M HNO₃, a first-order production of gas was obtained ($k = \sim 8 \times 10^{-6} \text{ sec}^{-1}$). At 12 and 16 M HNO₃, the reaction was more rapid, but not of first order. An analysis of the gas evolved indicated that at HNO₃ concentrations up to 10 M, only O₂ was obtained, but at higher concentrations of acid considerable amounts of the oxides of nitrogen were formed, indicating reaction between HNO₃ and H₂O₂. The rates for H₂O₂ - HNO₃ at higher temperatures were: for 4 M HNO₃, $k = 1.8 \times 10^{-5} \text{ sec}^{-1}$ at 40°C and $k = 5.6 \times 10^{-5} \text{ sec}^{-1}$ at 66°C; for 6 M HNO₃, $k = 6.1 \times 10^{-5} \text{ sec}^{-1}$ at 67°C.

A second series was run using only Pt at various acidities and temperatures. In spite of the well known catalytic effect of Pt on the decomposition of H₂O₂, no reference could be found in the literature to the rate of decomposition in moderate or concentrated acid solutions. The reaction was found to be first order. The results are summarized in Table I.

Table I. Decomposition of Hydrogen Peroxide by Platinum.

$[\text{HNO}_3]$, <u>M</u>	Temp, °C	$k \times 10^5 \text{ (sec}^{-1}\text{)}^*$
1	26.4	0.6
2	"	5.0 (average of 3 experiments)
"	29.7	6.4
4	0.7	0.6
"	26.4	2.83 ± 1.0 (average of 11 experiments)
"	48	11.1
"	67	14.1
6	26.4	5.5
"	37	11.8
"	47	34.5
"	57.8	54.5
8	26.4	12 (average of 3 experiments)

* Normalized to a surface area of $20 \text{ cm}^2/100 \text{ cc}$ of solution. Initial $[\text{H}_2\text{O}_2]$ 0.1-0.01 M.

There was no noticeable effect, on the rate, of the pretreatment of the Pt. Treatments used were: (1) washing in carbon tetrachloride and acetone, heating to red heat; (2) washing in 16 M nitric acid, water, carbon tetrachloride, and acetone, heating; (3) washing in 6 M nitric acid; (4) washing in 30% hydrogen peroxide; (5) washing in aqua regia, water and nitric; (6) bright new metal treated as in (1) compared to old, dull metal treated as in (1). The concentration of H_2O_2 was varied between 10^{-2} M and 10^{-1} M with no effect on the rate. It was found that the rate decreased 2-3 times if the solutions were not stirred, but there was no noticeable effect of stirring rate within moderate limits.

The effect of Fe^{+3} and Cu^{+2} , well known homogeneous catalysts, was looked at by the addition of $\sim 10^{-3}$ M Fe^{+3} and $\sim 10^{-3}$ M Cu^{+2} to solutions in contact with Pt. The reactions were first order and are summarized in Table II.

Table II. Decomposition of Hydrogen Peroxide
by Platinum, Cu^{++} , and Fe^{+++} .

$[\text{HNO}_3]$, <u>M</u>	Temp, °C	$[\text{Cu}^{++}] \times 10^3$, <u>M</u>	$[\text{Fe}] \times 10^3$, <u>M</u>	$k \times 10^5$ (sec ⁻¹)*
2.0	0.8	1.0	5.0	5.4
2.0	26.4	-	5.0	7.5
2.0	26.4	1.0	5.0	11.8 (average of 2 experiments)
2.0	36	1.0	5.0	21.8
2.0	66	1.0	5.0	101
2.0	26.4	2.0	10.0	0.19 (no Pt)
4.0	0.4	1.0	5.0	2.2
4.0	26.4	10.	-	0.18
4.0	26.4	-	5	5.0 (average of 2 experiments)
4.0	26.4	-	10	5.5 (average of 2 experiments)
4.0	26.4	-	20	4.5 (average of 2 experiments)
4.0	26.4	1.0	5.0	12.4 (average of 3 experiments)
4.0	26.4	10.	1.0	4.6
4.0	26.4	10.	3.0	7.2
4.0	26.4	10	5.0	8.2 (average of 2 experiments)
4.0	26.4	10.	10	12.4 (average of 2 experiments)
4.0	26.4	1.	20	7.9
4.0	26.4	2	20	8.6
4.0	26.4	7	20	7.7 (average of 2 experiments)
4.0	26.4	70	20	6.3
4.0	48.	1.0	5.0	69
4.0	67	1.0	5.0	346 (average of 2 experiments)
4.0	0.5	1.0	5.0	0.17 (no Pt)
4.0	0.5	2.0	10.0	0.29 (no Pt)
4.0	26.4	2.0	10.0	2.6 (no Pt)
4.0	67	1.0	5.0	87 (no Pt)

Table II. (continued)

$[\text{HNO}_3], \text{ M}$	Temp, °C	$[\text{Cu}^{++}] \times 10^3, \text{ M}$	$[\text{Fe}] \times 10^3, \text{ M}$	$k \times 10^5 (\text{sec}^{-1})^*$
6.0	0.7	1.0	5.0	2.7
6.0	16.3	1.0	5.0	10
6.0	26.4	1.0	5.0	15.5
6.0	37	1.0	5.0	25.5
6.0	47	1.0	5.0	118
6.0	57.8	1.0	5.0	155
6.0	67	1.0	5.0	227
6.0	26.4	2.0	10.0	3.6 (no Pt)

* Normalized to a surface area of $20 \text{ cm}^2 \text{ Pt}/100 \text{ cc}$ of solution. Initial $[\text{H}_2\text{O}_2] 10^{-1}$ to 10^{-2} M .

The effect of treatment of Pt was the same as before. Increasing Cu^{++} concentration increased the rate up to $\sim 10^{-2} \text{ M}$ and then decreased it. Increasing the Fe^{+++} concentration increased the rate at all concentrations used. The effect of ferric ion appears to be at least an order of magnitude greater than that of cupric.

The decomposition studies with Pu(IV) were conducted with Pu(IV) alone, and Pu(IV) in combination with Pt, with Pt, Cu^{++} and Fe^{+++} , and with no Pt but with added Cu^{++} and Fe^{+++} . The system was modified in that the solution volume was reduced to 10 cc. The $[\text{Pu(IV)}]$ was $\sim 1.25 \text{ M}$ and the $[\text{H}_2\text{O}_2]$ initially in the range of 5×10^{-2} to 10^{-1} M . All runs were made in 4.5 M HNO_3 . The solutions were not stirred. Again, the evolution of gas was first order. The results are tabulated in Table III.

Table III. Decomposition of Hydrogen Peroxide

by 1.25 M Pu(IV) .

A. No Pt

Temp, °C	$\text{Fe}^{+++} \times 10^3 \text{ M}$	$\text{Cu}^{++} \times 10^3 \text{ M}$	$k \times 10^3 \text{ sec}^{-1}$
-9.1	-	-	0.24
-8.1	-	-	0.30
-1.0	-	-	0.88
9.1	-	-	2.5 (average of 3 experiments)
17.8	-	-	4.1

Table III. (continued)

A. No Pt

Temp, °C	$\text{Fe}^{+++} \times 10^3 \text{ M}$	$\text{Cu}^{++} \times 10^3 \text{ M}$	$k \times 10^3 \text{ sec}^{-1}$
18.3	-	-	6.3
19.5	-	-	14
20.5	-	-	18
1.1	5.0	1.0	0.73
3.8	5.0	1.0	0.87
4.2	5.0	1.0	0.94
5.1	5.0	1.0	2.2
6.6	5.0	1.0	3.1
3.0	10	10	1.2 (average of 4 experiments)
12.9	10	10	1.9 (average of 2 experiments)
23.3	10	10	2.6 (average of 2 experiments)
24	10	10	3.5 (average of 2 experiments)

B. 9cm^2 Pt

Temp, °C	$[\text{Fe}^{+3}] \times 10^3 \text{ M}$	$[\text{Cu}^{+2}] \times 10^3 \text{ M}$	$k \times 10^3 \text{ sec}^{-1}$
-10.0	-	-	0.43
-8.4	-	-	0.47
5	5.0	1.0	3.3
13	5.0	1.0	6.5 (average of 3 experiments)
19	5.0	1.0	11 (average of 2 experiments)
-10.2	10	10	0.56
-7.2	10	10	0.66
-0.6	10	10	1.2
4.9	10	10	3.0
9.0	10	10	4.0
20	10	10	7.6 (average of 2 experiments)

The results indicate that Pt ($9\text{ cm}^2/10\text{ ml}$ of solution) added to Pu(IV) about doubles the rate whether Fe^{+3} and Cu^{+2} are present or not. Also the effect of Fe^{+3} and Cu^{+2} at 10^{-2} M each was to lower the rate as compared with lower concentrations of these ions.

An estimate of the energy of activation for the decomposition of H_2O_2 can be made from the temperature dependency of the rate under varying conditions. The results are, at best, only semiquantitative and are given in Table IV.

Table IV. Energy of Activation for the Decomposition of Hydrogen Peroxide.

Conditions		
[HNO ₃] M	Catalyst	E _A , (kcal)
2.0	Pt, Fe ⁺³ , Cu ⁺²	10
4.0	None	14
4.0	Pt	10
4.0	Pt, Fe ⁺³ , Cu ⁺²	13
6.0	Pt	14
6.0	Pt, Fe ⁺³ , Cu ⁺²	13
4.5	Pu(IV)	17
4.5	Pu(IV) + Fe ⁺³ + Cu ⁺²	10
4.5	Pu(IV) + Pt + Fe ⁺³ + Cu ⁺²	15

These values are to be compared with literature¹ values of the order of 40-50 kcal for the homogeneous gas phase decomposition, down to ~35 for Cu⁺² in solution, 13-25 for the halide ions, 28 for Fe⁺³ and 11 for Fe⁺².

The log of the rate was proportional to the acid concentration. For Pt alone this dependency appeared to be independent of temperature, but the combination of Pt plus Fe⁺³ and Cu⁺² showed a decreasing dependence on acid with decreasing temperature, so that at 26°C the rate was almost independent of acid concentration, while at 0°C there appeared to be an inverse dependency.

In general, the rate of Pu(IV) catalysis was about 10³ times that for Fe⁺³ and/or Cu⁺² at about 10³ times the concentration. One mechanism suggested for the catalytic effect of Fe⁺³ and Cu⁺² is an oxidation-reduction reaction involving hydrogen peroxide as both the oxidant and reductant.¹ This type of mechanism could also explain the catalytic behavior of Pu(IV).

¹ Walter C. Schumb, Charles N. Satterfield, and Ralph L. Wentworth, Hydrogen Peroxide (Reinhold Publishing Corp., New York, 1955).

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