On the Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum-carbonyl.

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There have already been published a number of reports⁽¹⁾ on the catalytic decomposition of hydrogen peroxide by colloidal platinum. In the previous paper,⁽²⁾ the author described the formation and behaviour of the platinum-carbonyl sol of red colour obtainable from the aqueous solution of chloroplatinic acid by the action of carbon monoxide. The present paper deals with the experiments on the catalytic decomposition of hydrogen peroxide by the colloidal platinum-carbonyl mentioned above and the colloidal platinum obtainable from it.

On passing carbon monoxide through the aqueous solution of chloroplatinic acid at ordinary temperature for some time, the colour of the solution changes from yellow to red, the platinum carbonyl sol being thus obtained. By dialyzing or standing in the air the red sol, it turns black to produce a platinum sol as prepared by Bredig's method.

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(1) G. Bredig and M. v. Berneck, *Z. physik. Chem.*, **31** (1899), 258; G. Bredig and K. Ikeda, *Z. physik. Chem.*, **37** (1901), 1; T. S. Price and A. D. Denning, *Z. physik. Chem.*, **46** (1903), 89; D. A. MacInnes, *J. Am. Chem. Soc.*, **36** (1914), 878; M. A. Heath and J. H. Walton, *J. Phys. Chem.*, **37** (1933), 977, etc.

(2) I. Sano, this Bulletin, **9** (1934), 320.

Experimental. The hydrogen peroxide solution was obtained from "Oxyfull" by distillation under reduced pressure (50–60 mm. Hg, 85°C.) in a thoroughly steamed hard glass system, diluted with water to 20 times of volume and kept in a Pyrex flask. The reaction was carried out at 30.0°C. in a Erlenmeyer flask which was cleaned and steamed before use. Ninty-five c.c. of the hydrogen peroxide solution was placed in the flask, a definite volume of the red or black sol was added to it, and the solution thoroughly mixed by shaking. At the desired intervals of time, 5 c.c. was taken out from it, added to a mixture of 50 c.c. of water and 10 c.c. of dilute sulphuric acid (1:3), and titrated with a 0.10 N potassium permanganate solution. The sol added as catalyst, red or black, was inferred from calculation to contain 0.075 grams of platinum in one liter.

The results obtained are given in Tables 1, 2, 3, 4 and 5, where t denotes the time elapsed from the beginning in minutes, c the volume of the potassium permanganate solution equivalent to 5 c.c. of the reacting solution at time t in c.c. and k the velocity constant in the formula for unimolecular reaction, $k=(1/t)\log(c_0/c)$, c_0 being the initial concentration. k_p and k_{τ} will be explained later.

Table 1. Five c.c. of red sol was added to 95 c.c. of hydrogen peroxide solution.

t	c	k
0	4.28 (c_0)	—
2	4.39	—
6	4.36	—
10	4.28	—
16.25	4.29	—
23.25	4.28	—
30	4.31	—
45	4.20	—
55	4.15	(0.000236)
60	4.08	(0.000350)
75	3.94	(0.000480)
90	3.82	0.000544
120	3.72	0.000508
150	3.55	0.000540
180	3.38	0.000569
240	3.16	0.000550
270	3.02	0.000559
450	2.39	0.000562

Table 2. Five c.c. of red sol was added to 95 c.c. of hydrogen peroxide solution.

t	c	k
0	4.31 (c_0)	—
2	4.27	—
6	3.37	(0.0178)
10	2.43	0.0249
18	1.53	0.0249
30	0.79	0.0246
45	0.36	0.0240
60	0.15	0.0243

Table 3a. Five c.c. of red sol was added to 95 c.c. of hydrogen peroxide solution.

t	c	k
0	4.25 (c_0)	—
2	4.24	—
5	4.09	(0.00340)
10	3.74	0.00560
15	3.53	0.00540
20	3.28	0.00565
30	2.90	0.00553
45	2.45	0.00531
75	1.71	0.00527

Table 3b. Two c.c. of red sol was added to 95 c.c. of hydrogen peroxide solution.

t	c	k
0	4.39 (c_0)	—
2	4.49	—
5.5	4.37	—
10	4.32	—
20	4.08	(0.00160)
30	3.93	0.00150
51	3.79	0.00124
60	3.70	0.00123
75	3.55	0.00123
90	3.43	0.00118
120	3.15	0.00120

Table 4a. Five c.c. of red sol was added to 95 c.c. of hydrogen peroxide solution.

t	c	k
0	4.27 (c_0)	—
2.17	4.35	—
5	4.25	—
10	4.30	—
15	4.18	—
20	4.08	—
25	3.91	(0.00152)
30	3.69	(0.00210)
35	3.38	(0.00300)
45	3.09	0.00311
60	2.72	0.00327
75	2.38	0.00339
90	2.06	0.00352
120	1.61	0.00353
150	1.32	0.00340
180	1.05	0.00338
210	0.83	0.00338
240	0.67	0.00335

Table 4b. Five c.c. of black sol (not dialyzed) was added to 95 c.c. of hydrogen peroxide solution.

t	c	k	k_p (p: -0.2)	k_γ (γ: 0.0706)
0	4.28 (c_0)	—	—	—
2.2	2.91	0.0762	0.136	0.0322
5.3	1.99	0.0627	0.117	0.0322
12	1.00	0.0526	0.105	0.0333
20	0.54	0.0450	0.096	0.0318
30	0.24	0.0417	0.097	0.0322
45	0.08	0.0384	0.101	0.0318

Table 4c. Two c.c. of black sol (not dialyzed) was added to 95 c.c. of hydrogen peroxide solution.

t	c	k	k_p (p: -0.3)	k_γ (γ: 0.0730)
0	4.44 (c_0)	—	—	—
2	3.61	0.0450	0.0683	0.0146
5.25	3.14	0.0287	0.0446	0.0106
10	2.58	0.0236	0.0377	0.0100
20	1.74	0.0203	0.0346	0.0105
30	1.24	0.0185	0.0331	0.0107
60	0.50	0.0158	0.0329	0.0110
123	0.11	0 0131	0.0352	0.0105

Table 5a. Five c.c. of red sol was added to 95 c.c. of hydrogen peroxide solution.

t	c	k
0	4.27 (c_0)	—
2	4.40	—
5	4.31	—
10	4.27	—
15	4.10	—
20	3.76	(0.00275)
30	3.02	(0.00500)
45	2.25	0.00618
60	1.74	0.00658
75	1.41	0.00641
90	1.14	0.00637
120	0.70	0.00654
150	0.46	0.00645

Table 5b. Five c.c. of black sol (dialyzed) was added to 95 c.c. of hydrogen peroxide solution.

t	c	k	k_p (p: -0.3)	k_γ (γ: 0.0523)
0	4.28 (c_0)	—	—	—
2.5	2.90	0.0676	0.107	0.0387
5	2.05	0.0639	0.107	0.0406
10.2	1.11	0.0553	0.106	0.0412
20	0.40	0.0515	0.112	0.0413
30	0.21	0.0436	0.106	0.0364

Table 5c. Two c.c. of black sol (dialyzed) was added to 95 c.c. of hydrogen peroxide solution.

t	c	k	k_p (p: -0.4)	k_γ (γ: 0.0719)
0	4.44 (c_0)	—	—	—
2	3.82	0.0327	0.0426	0.0104
5.1	3.22	0.0274	0.0370	0.0102
10	2.60	0.0232	0.0329	0.0100
20	1.80	0.0196	0.0300	0.0101
30	1.29	0.0179	0.0294	0.0103
45	0.80	0.0165	0.0301	0.0107
60	0.59	0.0146	0.0285	0.0100
90	0.29	0.0132	0.0303	0.0099

The red or black sols added as catalysts in the above experiments are summarized in Table 6.

Table 6. Carbon monoxide was passed through a 0.02% aqueous solution of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) with nearly a constant velocity throughout the experiment. The red sol thus obtained contains 0.075 grams of platinum in one liter as described before.

Number of table	Time duration during which the gas was continually passed through the chloroplatinic acid solution in hours before the colour change	Time duration during which the gas was continually passed through the chloroplatinic acid solution in hours after the colour change	Time duration during which the red sol was left in the air in hours	Volume of sol added in c.c. red	Volume of sol added in c.c. black
1	0.5	0	2	5	—
2	1	0.5	2.5	5	—
3a	0.5	0.5	3.5	5	—
3b	0.5	0.5	2	2	—
4a	0.5	2.5	0	5	—
4b	0.5	2.5	one night	—	5 (not dialyzed)
4c	0.5	2.5	one night	—	2 (not dialyzed)
5a	0.5	4	0	5	—
5b	0.5	4	one night	—	5 (dialyzed)
5c	0.5	4	one night	—	2 (dialyzed)

Discussion. The above results are graphically represented in terms of the relationship between $\log(c_0/c)$ and t in Fig. 1, 2, 3, 4 and 5. If the catalytic decomposition of hydrogen peroxide by colloidal platinum proceeds in accordance with the formula for unimolecular reaction $-dc/dt = kt$ as exemplified by Bredig and his co-workers, it might be expected, particularly in Fig. 4 and 5, that there should exist a linear relation between $\log(c_0/c)$ and t.

In the case where the red sol is added as catalyst, the apparent concentration of hydrogen peroxide solution remains nearly constant—and sometimes even increases slightly—over a short time of the earlier stage and the reacting solution is of red tint throughout the period, suggesting the sol to exist unchanged. In time, the solution, however, will lose the red colour to become slightly tinged with black, and then, the decomposition reaction begins abruptly and proceeds rapidly. The induction period mentioned above is distinctly shown by the former parts of the curves 1, 2, 3a, 3b, 4a and 5a in Fig. 1, 2, 3, 4 and 5; while the latter

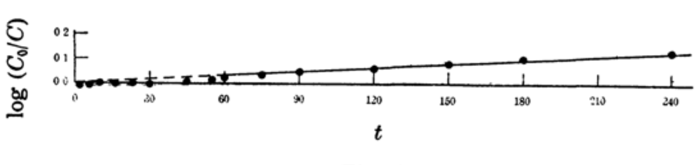

Fig. 1.

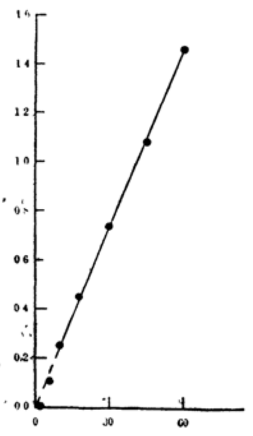

Fig. 2.

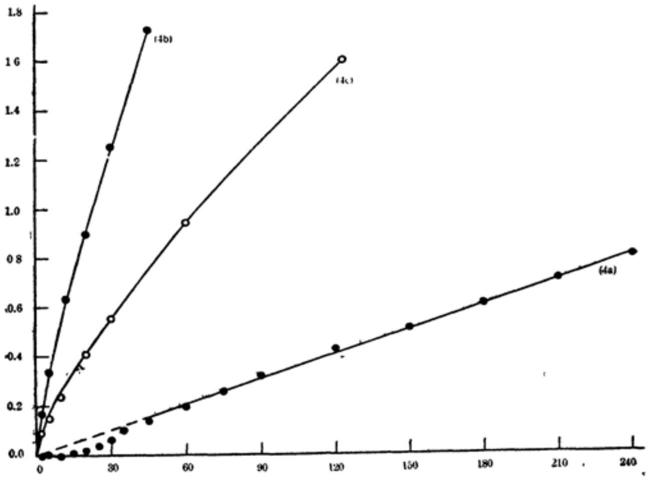

Fig. 4.

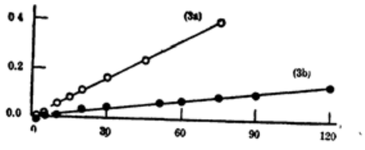

Fig. 3.

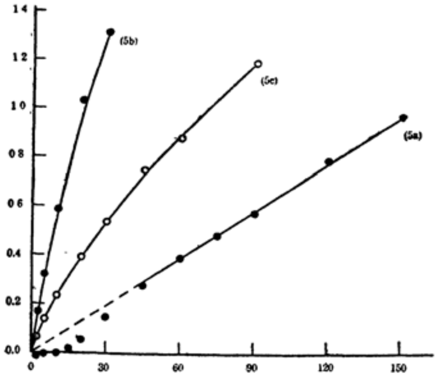

Fig. 5.

parts of these curves are linear and their extension lines passes through the origin, this indicating the reaction to proceed as unimolecular.

On adding the red sol to hydrogen peroxide solution, carbon monoxide considered to be retained in the colloidal particle as its essential constituent may be gradually set free, since the sol is diluted with hydrogen peroxide solution, and on subsequent titration, oxidized with potassium permanganate.(3) The apparent increase in the concentration of hydrogen peroxide solution during the induction period might probably be ac-

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(3) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, 943.

counted for from such a point of view. Sooner or later, a certain limiting amount of carbon monoxide constituting the particle will be reached, when the particle may be more reasonably regarded as colloidal platinum rather than as colloidal platinum-carbonyl; that is to say, a sol of black colour as prepared by Bredig's method will be formed and hereupon, the induction period will be over.

Carbon monoxide remaining in the particle will, thenceforward, play the part of maintaining the catalytic activity of the colloid unaltered, as it may be considered for the gas either to volatilize from, or to act on oxygen⁽⁴⁾ adsorbed by, the surface of the colloidal particle (The influence of oxygen adsorbed by the particle on the catalysis will be discussed below.), and thus render the portion of available surface covered with these free. The fact that, on adding the red sol to hydrogen peroxide solution as catalyst, the decomposition reaction proceeds as unimolecular after it passed through the induction period, may be explained by such a supposition.

In the case where the black sol obtained from the red one is added as catalyst, the decomposition reaction takes place immediately and proceeds rapidly, a curved line, instead of straight, being obtained between $\log(c_0/c)$ and t as shown in Fig. 4 and 5.

The velocity constants for unimolecular reaction k are given in the above tables. The constants, k_p and k_γ, are defined by the formulæ obtained by Freundlich⁽⁵⁾ (1) and by the present author (2):

$$-\frac{dc}{dt} = k_p \cdot c^{1-p} \quad \text{or} \quad k_p = \frac{1}{p \cdot t}(c_0^p - c^p) \qquad (p \text{ a constant}) \quad (1),$$

and

$$-\frac{dc}{dt} = k_\gamma \frac{c}{1-\gamma c} \quad \text{or} \quad k_\gamma = \frac{1}{t}\left\{\log \frac{c_0}{c} - \gamma(c_0 - c)\right\} \quad (\gamma \text{ a constant}) \quad (2).$$

The above-mentioned fact that the reaction deviates from unimolecular may probably be attributed to the retarding influence of oxygen evolved from hydrogen peroxide and subsequently adsorbed by colloidal platinum on the catalysis, subdivided platinum having a definite tendency to absorb oxygen.⁽⁶⁾ From this point of view, the above formula (2) has been derived in the following manner: If θ represents the fraction of the available surface covered with molecules of oxygen, it follows,

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(4) C. Paal, *Ber.*, **49** (1916), 548.

(5) H. Freundlich, "Kapillarchemie," Vol. 2, (1932).

(6) L. Woehler, *Ber.*, **36** (1903), 3492; C. Paal and C. Amberger, *Ber.*, **40** (1907), 2202; D. O. Shiels, *J. Phys. Chem.*, **33** (1929), 1181, etc.

according to Langmuir,(7) that for equilibrium between the adsorbed layer of molecules of oxygen and those in the surrounding medium, under the assumption that one molecule of oxygen occupies one elementary space of the surface,

$$a\mu(1-\theta) = \nu\theta \,,$$

a being the fraction of the number of molecules of oxygen μ striking the surface in unit time which condense and $\nu\theta$ the number of molecules of oxygen which evaporate from the surface in unit time. On the other hand, the rate of decomposition of hydrogen peroxide $-dc/dt$ should be proportional to the number of molecules of hydrogen peroxide μ' striking the surface in unit time; hence

$$-\frac{dc}{dt} = k\mu'(1-\theta) \,,$$

k being the velocity constant. Eliminating θ from these, it follows that

$$-\frac{dc}{dt} = \frac{k\mu'\nu}{\nu+a\mu} \,.$$

Although it might be assumed for μ to be proportional to c_0-c provided the oxygen evolved from hydrogen peroxide was wholly kept in the solution and adsorbed only to a small extent by the particles, the reaction was carried out in an open vessel as described above, and accordingly, it may be assumed for the present under the introduction of a constant β that μ should be proportional to $\beta(c_0-c)$, β being the average fraction of the amount of oxygen evolved which remains in the solution. Considering μ' to be proportional to the concentration of hydrogen peroxide solution c, the velocity of its decomposition should then be given by

$$-\frac{dc}{dt} = k_{\tau}\frac{c}{1-\gamma c}$$

which is the formula previously shown. k_{τ} and γ are the constants containing a , β , ν and k.

As seen in Fig. 4 and 5, the catalytic decomposition of hydrogen peroxide proceeds more rapidly with the black sol than with the red one. This fact may be rendered clear by the following consideration: As already described, the red sol turns black on account of the volatilization

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(7) I. Langmuir, *J. Am. Chem. Soc.*, **38** (1916), 2286; **40** (1918), 1361.

of carbon monoxide retained in the particles of the sol and becomes catalytically active during the course of an induction period. The colloidal particles of platinum in the black sol thus formed might be considered to be contaminated with carbon monoxide more profoundly than those in the black sol obtainable by standing in the air over-night or dialyzing the red sol; hence, there should be a difference between the areas of active surface available for catalysis, from which may probably result the diversity in the rate of decomposition.

Summary.

(1) The catalytic decomposition of hydrogen peroxide by colloidal platinum-carbonyl as well as colloidal platinum obtainabe from it was examined.

(2) In the former case, the reaction proceeds as unimolecular after it passed through an induction period, while in the latter case, it deviates apprecialy from unimolecular throughout the course of the reaction concerned.

(3) Some considerations were made on these facts.

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