The Effect of Gases upon the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum.

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It was depicted in the foregoing papers(1),(2) that the catalytic decomposition of oxalic acid in its aqueous solutions by colloidal platinum-carbonyl as well as colloidal platinum would be definitely suppressed in case of deficient supply of air, and consequently, the scheme of the reaction might be assumed to be given by

$$C_2O_4H_2 + O_2 = 2\,CO_2 + H_2O_2 \qquad \text{(slow)}$$

$$H_2O_2 = H_2O + O \qquad \text{(rapid)}$$

$$O + C_2O_4H_2 = 2\,CO_2 + H_2O \qquad \text{(rapid)}$$

In the present experiments the influences of various gases, with which the reacting system was kept in contact throughout the course of reaction, upon the decomposition of the acid catalyzed by colloidal platinum were investigated with oxygen, nitrogen as well as air under reduced pressure as the charged gas.

The reactions were conducted under diffused day-light as it has been already confirmed to be of no influence upon the decomposition of the acid

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(1) I. Sano, this Bulletin, **14** (1939), 121.
(2) I. Sano, this Bulletin, **15** (1940), 196.

solution. The experimental procedures were quite the same as described in the previous paper⁽²⁾ except the contrast of the gases touching the medium of reaction. The reacting mixtures composed of 10 c.c. of a 0.05 N aqueous solution of oxalic acid and 2 c.c. of the platinum sol obtained from a 0.05% aqueous solution of chloroplatinic acid in the same way as stated formerly⁽²⁾ were put in test-tubes, which, immediately afterwards, were thoroughly filled with the gas in question and tightly sealed with rubber stopper, and consecutively, they were brought without delay in a thermostat to be kept at 50.0°C. under diffused day-light for the desired space of time. Oxygen now used was produced from sodium peroxide and water, and nitrogen from an aqueous solution of ammonium nitrite. The run of experiments with air under reduced pressure was performed in test-tubes furnished with rubber stopper through which a capillary tube was transfixed as a valve of exhaustion of air by means of water-pump. The degassing process was put, at intervals, in practice for some time at ordinary temperature.

Table 1.
Filled with oxygen.

t	c
0	5.99 (c_0)
3	4.76
6	3.58
12	1.99
18	2.03
24	1.83
30	1.80
40	1.79

Table 2.
Filled with nitrogen.

t	c
0	5.99 (c_0)
3	5.78
6	5.77
12	5.78
18	5.82
24	5.79
30	5.78
40	5.78

Table 3.
Filled with air under reduced pressure.

t	c
0	5.99 (c_0)
3	5.80
6	5.78
12	5.67
18	5.65
24	5.65
30	5.63
40	5.60

The results are given in Tables 1, 2 and 3, where t indicates the time elapsed from the start in hours and c the titre of the reacting solution titrated with a 0.1 N barium hydroxide solution at time t in c.c. The variation of $c_0 - c$ with t is graphically represented in Fig. 1, where the numeral accompanying the curve shows the number of the table referred to.

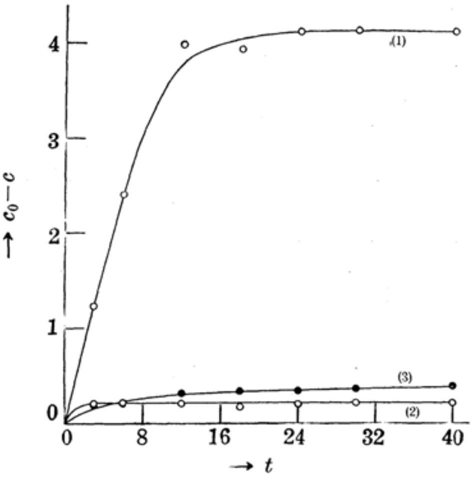

Fig. 1.

It can be seen from these that oxygen has a notable influence standing out in sharp contrast to those of nitrogen as well as air under reduced pressure. The retarding effect observed in the course of the reaction with oxygen may come from the increasing shortage of the gas with the progress of reaction. The appreciable decomposition of the acid at the incipient stage as seen in the runs with nitrogen as well as air under reduced pressure would be attributable to the air dissolving originally in the acid solution. Since a small quantity of air would effect an entrance into the vessel of reaction during the degassing steps conducted frequently with water-pump in the run, the reaction with air under reduced pressure might progress, though slow, with the lapse of time, and this is the actual case as indicated by Curve 3 in the figure.

The evacuation was intended to clear the reacting system of carbon monoxide which would be produced and adsorbed by the surface of catalyst to keep the reaction from the progress if the decomposition of the acid should occur unimolecularly on the surface of catalyst in accordance with

$$C_2O_4H_2 = CO + CO_2 + H_2O.$$

It would seem, in view of the results obtained, that circumstances are rather adverse for the unimolecular decomposition.

To infer from the informations which have hitherto been acquired, it will follow that oxalic acid should be decomposed, in the presence of oxygen as well as colloidal platinum, in line with the mechanism abovementioned.

Summary.

(1) The influences of gases such as oxygen, nitrogen as well as air under reduced pressure upon the decomposition of aqueous solution of oxalic acid (0.05 N) were, in the existence of colloidal platinum obtained from colloidal platinum-carbonyl through dialysis and under diffused daylight, examined at 50.0°C.

(2) Oxygen alone has a marked effect in accelerating the decomposition, but the two others none.

(3) This gives support to the mechanism of reaction previously discussed.

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