On the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum-carbonyl.

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Introduction. It is generally accepted through experiences⁽¹⁾ for a long time, although there have been raised a number of objections⁽²⁾ against the concept, that oxalic acid is decomposed in its aqueous solutions

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(1) G. Bizio, *Z. anal. Chem.*, **9** (1870), 392; A. Downes and T. P. Blunt, *Proc. Roy. Soc.* (London), **29** (1879), 219; E. Duclaux, *Compt. rend.*, **103** (1886), 1011; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; A. Richardson, *J. Chem. Soc.*, **65** (1894), 450; H. de Vries, *Z. angew. Chem.*, **1899**, 521; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521.

(2) T. Gigli, *Chem. Zentr.*, **64** (1893), I, 11.

by oxygen in the air to turn into carbon dioxide and water, if exposed to direct sun-light as well as (naturally in smaller extent) to diffused day-light for a certain space of time; while if not subjected to the agency of light (for instance, in the dark), it is quite stable.

It is thoroughly known as well, on the other hand, that oxalic acid is decomposed in its aqueous solutions by moulds,(3) no matter whether it may be present in the dark or in the light, and according to Wehmer(3) and Jorissen,(1),(3) the acid acts as a poison for the moulds if the concentration of the acid solution is greater than 2–3%. Dilute solutions can be conserved by means of sterilization or by adding 50 c.c. of concentrated sulphuric acid per litre, boric acid being scarcely effective. On the addition of manganese sulphate the decomposition of oxalic acid due to oxidation in its aqueous solutions is more accelerated in the presence of light.

S. Ishimaru(4) investigated the influences of purity of oxalic acid preparation, day-light, and sulphuric acid added on the preservation of aqueous solutions of oxalic acid during a long period extending over seven months, and established that a 0.01 N solution is stable when 50 c.c. of concentrated sulphuric acid per litre is added, irrespective of purity of preparation as well as day-light. A 0.1 N solution is decomposed in the light notwithstanding the addition of sulphuric acid, but stable in the dark without sulphuric acid. A 0.5 N solution is stable in the dark without sulphuric acid, solution of pure preparation being stable in the light.

O. Šulc(5) studied the effects of various metals in finely divided state such as palladium, silver, copper, and platinum on the decomposition of aqueous solutions of oxalic acid at room temperatures. The results obtained with palladium which was ascertained to be the most effective of the metals aforesaid, are tabulated below. A 100 c.c. of 0.1 N aqueous oxalic acid solution was mixed with 1.36 grams of palladium powder afresh ignited and cooled in the air prior to use in a closed flask in each run of the experiments and 10 c.c. was pipetted out from it at the desired inter-

Time elapsed in days	Titre of the oxalic acid solution in c c.			
	in the dark		in the light	
	without	with	without	with
	palladium		palladium	
0	10.05	10.05	10.04	10.04
4	—	—	9.92	8.62
8	10.03	8.79	—	—
9	—	—	9.00	6.78
19	10.00	8.24	6.40	3.75
26	9.90	8.31	—	—
38	—	—	0.34	0.25

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(3) C. Neubauer, *Z. anal. Chem.*, **9** (1870), 392; W. N. Hartley, *Chem. News*, **37** (1878), 9; G. Fleury, *Chem. Zentr.*, **14** (1883), 547; O. Warburg, *Untersuch. botan. Inst. Tübingen*, **2** (1886–8), 117; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521.

(4) S. Ishimaru, *J. Chem. Soc. Japan*, **43** (1922), 767; **53** (1932), 449; *Science Repts. Tôhoku Imp. Univ.*, Ser. I, **24** (1935), 411.

(5) O. Šulc, *Z. physik. Chem.*, **28** (1899), 719.

vals of time, mixed with a small quantity of sulphuric acid, warmed if necessary and titrated with a potassium permanganate solution.

In the preceding papers,(6) the author reported the formation and behaviour of a platinum-carbonyl sol of red colour obtainable from an aqueous solution of chloroplatinic acid by the action of carbon monoxide and the catalytic decomposition of hydrogen peroxide by the sol. The present communication deals with the experiments on the decomposition of oxalic acid in its aqueous solutions due to oxidation by the air, which is catalysed by the colloidal platinum-carbonyl as well as by the colloidal platinum obtainable from it.

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

Experimental Procedures and Results. The oxalic acid solutions used were prepared by dissolving oxalic acid purified by means of recrystallization in distilled water. The red sol was prepared by passing carbon monoxide through a 0.05% aqueous solution of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) with nearly a constant velocity throughout the experiments, carbon monoxide being obtained by heating the mixture of oxalic acid and concentrated sulphuric acid and purified by passing through alkaline hydroxide solutions. The black sol was obtained from the red one by standing it in the air as already mentioned. Accordingly the sol, red or black, was inferred from calculation to contain 0.188 grams of platinum in one litre.

In each run of the experiments described below, the red sol and the black one added as catalyst are respectively used immediately after its formation, the red sol being obtained from the aqueous solution of chloroplatinic acid and the black one from the red sol, and both of them being not dialyzed.

The reactions were carried out at 25.0°C. as well as 50.0°C. under diffused day-light. The vessels were cleand and steamed to the full before use. The results obtained are indicated in Table 1 to Table 12, where t denotes the time elapsed from the beginning in hours, c the titre of the reacting solution titrated with a 0.1 N barium hydroxide solution at time t in c.c., corrections being made for the portion of the titre attributable to hydrochloric acid in the sol added as catalyst, and t_r the time duration during which the sol remains red in the reaction mixture before it passes into black in hours. The meanings of c_k and t_k will be explained later. The procedures and results were as follows.

25.0°C.: A 20 c.c. of a 0.10 N oxalic acid solution was placed in a flask, 20 c.c. of the red sol was added to it and the solution thoroughly mixed by shaking. At the desired intervals of time, 10 c.c. was pipetted out from it and titrated with the barium hydroxide solution. The results are shown in Tables 1 and 2.

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(6) I. Sano, this Bulletin, **9** (1934), 320; **13** (1938), 118.

Table 1.

t	c	c_k ($t_k = 14$)
0	11.80 (c_0)	—
2	11.75	—
4	11.78	—
6	11.80	—
27	11.71	11.76
29	11.69	11.75
50	11.59	11.74
75	11.50	11.75
99	11.43	11.77
147	11.32	11.85
173	11.23	11.86
197	11.08	11.80
221	10.92	11.73
245	10.84	11.74
317	10.64	11.81
365	10.56	11.92
412	10.30	11.82
604	9.62	11.79
$t_r = 3$		

Table 2.

t	c	c_k ($t_k = 6$)
0	14.14 (c_0)	—
4	14.13	—
5	14.15	—
24	13.96	14.10
50	13.81	14.17
55	13.76	14.15
72	13.63	14.16
75	13.56	14.11
96	13.41	14.12
100	13.40	14.14
120	13.23	14.12
168	12.89	14.14
172	12.83	14.11
192	12.70	14.13
194	12.68	14.12
216	12.48	14.08
220	12.49	14.12
264	12.14	14.08
$t_r = 4$		

50.0°C.: The reacting mixtures consisting of 10 c.c. of aqueous solution of oxalic acid of a definite concentration and 2 c.c. of the red or black sol were placed in test-tubes provided with rubber stopper through which a capillary tube was inserted as a line of communication of the air. At the desired intervals of time, the test-tubes were, by turns, titrated with the barium hydroxide solution. The reacting solutions were, as in the other cases, agitated at short intervals. The results are given in Tables 3, 4, 5, 6, 7 and 8.

Table 3. Concentration of oxalic acid solution: 0.10 N
Sol added as catalyst: red

t	c	c_k ($t_k = 6$)
0	15.69 (c_0)	—
1.5	15.79	—
3	15.62	—
6	15.48	—
9	15.39	15.46
12	15.34	15.48
15	15.25	15.46
18	15.19	15.47
21	15.16	15.51
24	15.05	15.47
27	14.97	15.45
30	14.91	15.46
$t_r = 2$		

Table 4. Concentration of oxalic acid solution: 0.10 N
Sol added as catalyst: red

t	c	c_k ($t_k = 10$)
0	12.06 (c_0)	—
2	12.13	—
4	11.95	—
6	11.82	—
8	11.71	—
10	11.59	—
12	11.55	11.60
16	11.45	11.60
20	11.34	11.59
24	11.17	11.52
28	11.16	11.61
32	11.05	11.60
35	10.98	11.60
$t_r = 2$		

Table 5. Concentration of oxalic acid solution : 0.10 N
Sol added as catalyst : black

t	c	$c_k (t_k = 2)$
0	12.07 (c_0)	—
1	11.80	—
2.5	11.57	11.61
4	11.45	11.60
6	11.35	11.64
9	11.02	11.52
12	10.87	11.58
16	10.70	11.69
21	10.35	11.67
24	10.12	11.63
28	9.80	11.55
30	9.77	11.67
$t_r = -$		

Table 6. Concentration of oxalic acid solution : 0.05 N
Sol added as catalyst : red

t	c	$c_k (t_k = 2)$
0	5.65 (c_0)	—
2	5.69	—
4.5	5.42	5.61
6	5.32	5.60
8	5.25	5.69
10	5.10	5.68
12	4.91	5.62
16	4.73	5.71
21	4.39	5.67
24	4.11	5 53
27	4.05	5.67
32	3.76	5.64
$t_r = 2$		

Table 7. Concentration of oxalic acid solution : 0.05 N
Sol added as catalyst : black

t	c	$c_k (t_k = 2)$
0	6.12 (c_0)	—
1	5.88	—
2.5	5.64	5.70
4	5.54	5.76
6	5.30	5.73
9	4.97	5.70
12	4.78	5 81
16	4.33	5.70
21	4.02	5.83
24	3.73	5.74
27	3.52	5.74
30	3.38	5.85
$t_r = -$		

Table 8. Concentration of oxalic acid solution : 0.025 N
Sol added as catalyst : red

t	c	$c_k (t_k = 2)$
0	3.05 (c_0)	—
2	3.10	—
4	2.84	3.05
6	2.68	3.10
8	2.50	3.11
10	2.31	3.08
12	2.16	3 10
16	1.87	3.10
21	1.79	3.56
24	1.35	2.99
27	1.27	3.13
30	1.12	3.08
$t_r = 2$		

One run was carried out at 50.0°C. in hermetically sealed test-tubes. The results obtained are indicated in Table 9.

With the view of investigating the extent to which the light has influence upon the decomposition of oxalic acid in its aqueous solution, a number of runs were made under the conditions as already described without the sol being added. The results are shown in Tables 10, 11 and 12. From these results it can be concluded that aqueous solutions of oxalic acid are not decomposed in the least under the conditions concerned.

Table 9. Concentration of oxalic acid solution : 0.05 N
Sol added as catalyst : black

t	c	$c_k(t_k = 1.5)$
0	6.07 (c_0)	—
1	5.79	—
2.5	5.69	5.76
4	5.54	5.72
6	5.38	5.70
9	5.24	5.78
12	4.98	5.71
20	4.75	—
24	4.72	—
27	4.66	—
30	4.66	—
$t_r = -$		

Discussion of the Results. The above results indicated in the tables (Table 1 to Table 9 inclusive) are graphically depicted below in terms of the relationship between $\log(c_0/c)$ and t in Fig. 1, 2, 3 and 4 (Curve 1 to Curve 9 inclusive). If the decomposition of oxalic acid due to oxidation in its aqueous solutions, which is accelerated by colloidal platinum-carbonyl as well as colloidal platinum should, in the course of reaction, come to proceed in accordance with the formula for unimolecular reaction

$$-dc/dt = kc \quad \text{or} \quad \log(c_0/c) = kt,$$

where c_0 is the initial concentration and k the velocity constant, it may be anticipated that there must be a portion of straight line in the curve indicating the relation between $\log(c_0/c)$ and t.

Table 10.
Concentration of oxalic acid solution : 0.10 N
Temperature : 25.0°C.

t	c
0	14.32 (c_0)
20	14.31
24	14.31
43	14.28
68	14.27
72	14.36
92	14.40
96	14.37
116	14.35
164	14.35
188	14.38
216	14.38
260	14.36
356	14.35
358	14.34
456	14.29
457	14.30

Table 11.
Concentration of oxalic acid solution : 0.10 N
Temperature : 50.0°C.

t	c
0	12.17 (c_0)
4	12.16
9	12.12
12	12.16
18	12.15
24	12.17
30	12.12

Table 12.
Concentration of oxalic acid solution : 0.05 N
Temperature : 50.0°C.

t	c
0	6.14 (c_0)
4	6.15
9	6.22
12	6.16
18	6.18
24	6 16
30	6.16

In the case where the red sol is added as catalyst, the apparent concentration of oxalic acid solution remains nearly constant over a certain space of time and the reacting solution is of red tint throughout the period, suggesting the sol to exist unchanged. In time, however, the solution will lose the red colour to become tinged with black and then the decomposition will begin abruptly and proceed smoothly. The induction period

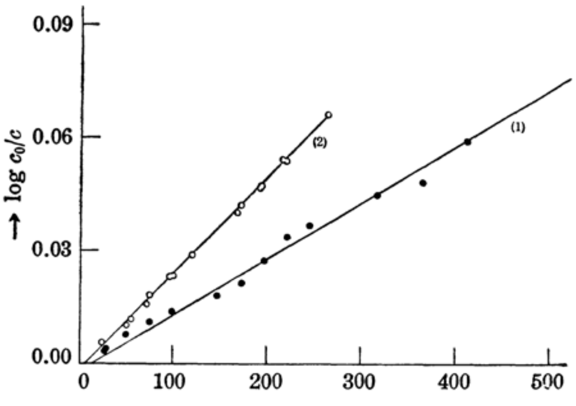

Fig. 1.

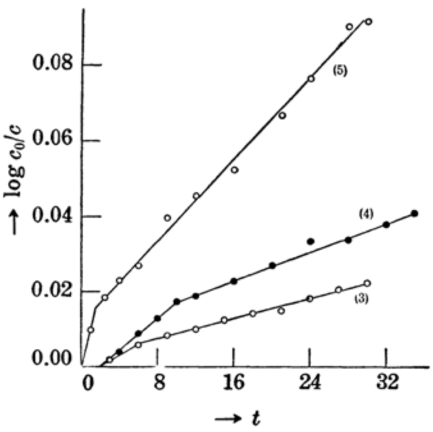

Fig. 2.

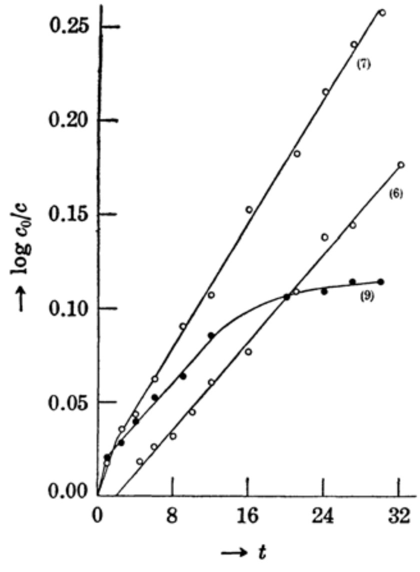

Fig. 3.

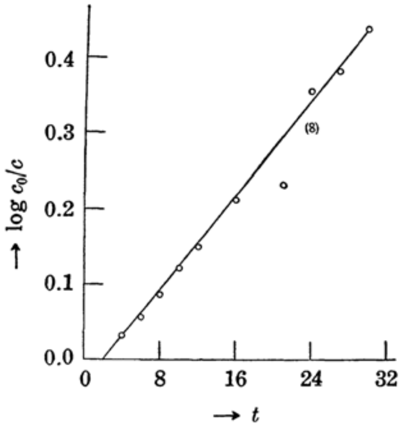

Fig. 4.

mentioned above is distinctly shown by the former parts of Curves 1, 2, 3, 4, 6 and 8; while the latter parts of the curves concerned are linear, indicating the reaction to proceed as unimolecular.

On adding the red sol to aqueous solutions of oxalic acid, carbon monoxide ratiocinated from various facts already established⁽⁷⁾ to be held in the colloidal particle as its essential constituent will vanish gradually from it through volatilization as well as oxidation, since the sol is diluted with oxalic acid solution loaded with dissolved oxygen. Sooner or later, carbon monoxide constituting the particle will reach a certain limiting amount, when the particle may be reasonably regarded as colloidal

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

platinum rather than as colloidal platinum-carbonyl; in other words, a sol of platinum of black colour will be formed and hereupon, the induction period will be over.

In the case where the black sol obtained from the red one is added as catalyst, the decomposition of oxalic acid in its aqueous solutions takes place immediately after mixing and proceeds without any delay. Although the former part of the curve standing for the relation between $\log(c_0/c)$ and t makes a bend in due course of time, the latter part of it assumes a rectilinear figure during the time duration concerned as shown by Curves 5, 7 and 9.

The transition period above mentioned—in the case of the red sol, it follows in the wake of the induction period as seen from Curves 3 and 4—may probably result from coagulation of the sol due to electrolyte. Since the sol under consideration is negatively charged, its coagulation must be caused by positive charge and in consequence, the catalytic activity of colloidal particles must be decreased to some extent. On passing this stage, there may scarcely occur any change in the catalytic activity of the particles. The coagulation may be assumed to proceed the more rapidly as well as strongly, the more concentrated the oxalic acid solution is.

This can be seen by comparing one another the magnitudes of the velocity constant, k, for the straight portion of the curve, calculated from the diagram. It is clear from the table that k increases definitely as the concentration of aqueous solution of oxalic acid decreases. It was observed, in fact, at 50.0°C. that in dilute solutions, the sol added is practically stable and remains black as it was throughout one run of the experiments; while in concentrated solutions, it coagulates to a marked degree in several hours from the commencement to settle at the bottom. Consequently, it appears that coagulation of the sol may be more influenced by electrolyte than by heat.

Number of table	Temperature at which the reaction was carried out (°C.)	Sol added as catalyst	t_r	Concentration of aqueous solution of oxalic acid (N)	k (hour^{-1})
1	25.0	red	3	0.10	0.000150
2	25.0	red	4	0.10	0.000249
3	50.0	red	2	0.10	0.000658
4	50.0	red	2	0.10	0.000956
5	50.0	black	—	0.10	0.00275
6	50.0	red	2	0.05	0.00586
7	50.0	black	—	0.05	0.00850
8	50.0	red	2	0.025	0.0157
9	50.0	black	—	0.05	0.00563

The value of c_k tabulated previously was calculated from k thus obtained in accordance with the formula for unimolecular reaction

$$\log(c_k/c) = kt,$$

where c is the concentration of oxalic acid solution at time t elapsed from a specified starting-point of reckoning indicated by t_k in the tables. It might be anticipated for c_k to assume a constant value in each run of the experiments if the reaction should proceed as unimolecular.

It has been stated already that oxalic acid is decomposed in its aqueous solutions in the presence of oxygen. The effect can be seen distinctly from Curve 9. In this run the reaction was carried out in test-tubes hermetically sealed in order to keep out the air from the outside. It can be seen that drift occurs in the final stage from want of oxygen.

In connection with what has been mentioned above, some theoretical consideration will be made as follows.

It may be supposed on the whole that chemical reactions will occur between molecules adsorbed on adjacent spaces of the catalyst surface, and the rate of reaction is slow in comparison with the rate at which molecules of reactants condense upon and evaporate from the surface; that is to say, the rate of reaction will not affect to any appreciable extent the equilibrium between the adsorbed layer and the surrounding medium.

If θ_1 represents the fraction of the available surface covered unimolecularly with molecules of oxalic acid and θ_2 with molecules of oxygen at any instant, it will follow that for equilibrium between the adsorbed layer consisting of both molecules of oxalic acid as well as oxygen and those in the surrounding medium, under the assumption that each molecule of these may occupy one elementary space of the surface and the presence of solvent may be left out of consideration,

$$\alpha_1\mu_1(1-\theta_1-\theta_2) = \nu_1\theta_1 \quad \text{and} \quad \alpha_2\mu_2(1-\theta_1-\theta_2) = \nu_2\theta_2\,,$$

α_1 and α_2 being the fractions of the numbers of molecules of oxalic acid and oxygen, μ_1 and μ_2, striking the surface in unit time which condense, and $\nu_1\theta_1$ and $\nu_2\theta_2$ the numbers of molecules of oxalic acid and oxygen which evaporate from the surface in unit time. Reference must be made to that oxalic acid may be treated as non-electrolyte for the sake of simplicity, the state of the molecule adsorbed on the catalyst surface being not taken into consideration both for dissociated as well as undissociated molecule.

If the surface is covered so sparsely by molecules of both of them that $\theta_1 \ll 1$ and $\theta_2 \ll 1$ and accordingly $\theta_1+\theta_2 \ll 1$, then $1-\theta_1-\theta_2$ may be put as approximately equal to unity; hence, it follows that

$$\alpha_1\mu_1 = \nu_1\theta_1 \qquad \text{and} \qquad \alpha_2\mu_2 = \nu_2\theta_2$$

or

$$\theta_1 = \mu_1 \cdot \alpha_1/\nu_1 \qquad \text{and} \qquad \theta_2 = \mu_2 \cdot \alpha_2/\nu_2\,.$$

Since it may be presumed for the rate of reaction, v, to be proportional to the amounts of reactants adsorbed on the available surface, it will be given by

$$v = k\theta_1\theta_2\,,$$

k being the velocity constant. Substituting the valeus for θ_1 and θ_2, it follows that

$$v = k\mu_1\mu_2 \cdot \alpha_1\alpha_2/\nu_1\nu_2 \,.$$

Considering μ to be proportional to the concentration, c, of the reactant, this may be written in the form

$$v = k'c_1c_2 \,,$$

k' being made up of a combination of various constants such as k, α and ν. The formula thus obtained reduces to the formula for unimolecular reaction

$$v = k''c_1 \,,$$

where $k'' = k'c_2$, provided that c_2 is constant throughout the experiment, and this is actually the case as the reacting system is supplied with oxygen from the outside.

On studying the influence of light on the decomposition of oxalic acid in its aqueous solutions due to oxidation by oxygen in the air, Richardson⁽¹⁾ concluded that during the decomposition of the acid in the presence of light and oxygen, the carbon in each molecule is oxidized to carbon dioxide and the hydrogen to hydrogen peroxide, if oxygen is in excess, in accordance with the equation

$$C_2O_4H_2 + O_2 = 2\,CO_2 + H_2O_2 \,,$$

although the peroxide found by analysis falls, in general, far short (it rarely reaching one-tenth) of that calculated from the equation, on account of the docomposition of the acid occurring at the expense of the peroxide to some extent.

From the above-mentioned, the decomposition of oxalic acid due to oxidation in its aqueous solutions by colloidal platinum will be explained in the following manner. Whenever oxalic acid is decomposed by oxygen on the catalyst surface to produce carbon dioxide and hydrogen peroxide, atomic oxygen will be liberated then and there from hydrogen peroxide since it is readily decomposed by colloidal platinum as a well-known fact, and in quick succession, this will act on molecules of oxalic acid adsorbed on adjacent spaces of the catalyst surface and oxidize them; namely,

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

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

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

Hence, the reaction

$$2\,C_2O_4H_2 + O_2 = 4\,CO_2 + 2\,H_2O$$

will proceed unimolecularly.

Summary.

(1) The decomposition of aqueous solutions of oxalic acid (0.10, 0.05, 0.025 N) due to oxidation accelerated by colloidal platinum-carbonyl of red colour as well as colloidal platinum of black colour obtainable from

it was, in the presence of oxygen and diffused day-light, studied during a period extending several hundred hours at 25.0°C. and thirty hours at 50.0°C.

(2) In the case where the red sol is added as catalyst, the reaction proceeds as unimolecular after it passed through an induction period and subsequently a transition period, while in the case where the black sol is added, it proceeds as the above after a transition period, no induction period presenting itself.

(3) The more dilute the acid solution, the more stable is the sol throughout the course of the experiment and consequently, the larger is the velocity constant.

(4) The mechanism of the reaction was discussed on these facts.

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