1526 PRICE AND FRIEND: THE EFFECT OF COLLOIDAL

CLIII.—The Effect of Colloidal Platinum on Mixtures of Caro's Persulphuric Acid and Hydrogen Peroxide.

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MANY investigations have been carried out with the object of determining the composition of Caro's acid, and the results show that its formula is probably either H_2SO_5 or $H_2S_2O_9$ (see Price, Trans., 1903, 83, 543; Mugdan, Zeit. Elektrochem., 1903, 9, 980).

When colloidal platinum is added to mixtures of Caro's acid and hydrogen peroxide, oxygen is rapidly evolved. The authors thought that, by studying this reaction, it might be possible to decide between the two formulæ suggested. If the formula were H_2SO_5 , a reaction of the second order might be anticipated, according to the equation

 $H_2SO_5 + H_2O_2 = H_2SO_4 + H_2O + O_2$,

but if it were $H_2S_2O_9$, one would expect a reaction of the third order, as represented by the equation

 $H_2S_2O_9 + 2H_2O_2 = 2H_2SO_4 + H_2O + 2O_2.$

As will be seen from the results obtained, the formula cannot be determined in this way, as it has not been found possible to obtain constants of any order.

Preparation of Caro's Acid.—Pure, dry, and finely-powdered potassium persulphate was placed in an evaporating basin, imbedded

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in a mixture of ice and salt, 5 c.c. of concentrated sulphuric acid were then added, drop by drop, from a pipette; this operation required about 10 minutes and the mixture was well stirred the whole time. After about an hour, the mixture was slowly poured on to broken ice, contained in a large evaporating basin, also imbedded in ice and salt, and the diluted mixture was left for three or more hours and made up to 250 c.c. with distilled water. When left for a few hours longer, the solution was ready for use. It was then free from hydrogen peroxide, for it gave no coloration with a solution of titanium sulphate. This method of preparation was essential, since hydrogen peroxide, in the presence of Caro's acid, cannot be estimated by titration with potassium permanganate (Price, Trans., 1903, 83, 543; Friend, Trans., 1904, 85, 597) and it is obviously necessary to know the strength of the two components in the mixtures used.

The colloidal platinum was prepared in the usual way (Bredig, Zeit. physikal. Chem., 1899, 31, 258). The hydrogen peroxide (30 per cent. solution) was obtained from Merck and guaranteed to be pure.

As the progress of the reaction cannot be measured by titration of the hydrogen peroxide with permanganate, an attempt was made to estimate the hydrogen peroxide colorimetrically by means of titanium sulphate. It was found, however, that the results could not be depended on to within 8 per cent.

The velocity of reaction was finally determined by measuring the rate at which the oxygen was evolved from the mixture, all the determinations being carried out at 25° . The apparatus used is represented in the figure. The mixture was contained in the tube, A. The evolved oxygen escaped through B to the burette, C, which was surrounded by a water-jacket, through which a slow stream from the thermostat was caused to circulate. The level of the water in C was adjusted by means of the india-rubber tube, D, and reservoir, E; the tube, A, was closed by an india-rubber cork through which passed a stirrer, the whole being made air-tight by means of a mercury seal.

The strength of the Caro's acid was determined by the liberation of iodine from potassium iodide; that of the hydrogen peroxide by titration with permanganate.

The two solutions were then mixed in A and left for 10 minutes, before the addition of platinum. It was only after numerous experiments that we found this to be the only means by which we could obtain two comparable series of results. At present we are unable to explain this action, for in the absence of platinum, as will be seen from the following table, no appreciable reaction takes place between the two substances in so short a time.

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TABLE I.

Mixtures of Caro's acid and hydrogen peroxide were employed, quantities of 5 c.c. being titrated at intervals with $N/50 \text{ KMnO}_4$.

Time of titration.	Mixture I.	Mixture II.	Mixture III.
Directly after mixing	13.06 c.c.	10.80 c.c.	12.70 c.c.
15 mins. ,, ,,	13.28 "	10.82 ,,	12.78 "
30 mins. ", "	13.30 "	10.79 "	12·90 "
60 mins. ", "	13.31 "	10.81 "	13.00 "
18 hours ", "	13.36 "		12.93 "



The small differences are probably due to experimental error (Friend, loc. cit.).

In the following series, the stirring was vigorous, and Bredig and Walton have since shown (*Zeit. physikal. Chem.*, 1904, 47, 185) that under these conditions accurate results may be obtained. Table II shows how nearly two comparable experiments agree.

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TABLE II.

Time in minutes.	Volume I in c.c.	Volume II in c.c.	Time i n minutes.	Volume I in c.c.	Volume II in c.c.
15	3.12	3.06	41	7.23	7.10
19	3.87	3.88	45	7.67	7.56
22	4.38	4.40	55	8.70	8.58
28	5.38	5.38	65	9.18	9.07
34	6.30	6.23			

In the following tables:

t = time in minutes after adding the platinum.

v = volume of oxygen evolved at N.T.P.

 Λ = concentration of peroxide, measured as the no. of c.c. of oxygen present in the mixture.

B = concentration of Caro's acid similarly expressed.

 $k_2 =$ velocity constant of the second order.

 k_3 = velocity constant of the third order.

R = extent to which the action has proceeded (approximately).

The concentration of the platinum in the mixture was in all cases 1 gram-atom in 227,000 litres.

TABLE III.

(Feb.	25) $A = 9.34$.	B = 20.29.	(Feb.	26) $A = 23.37$.	B = 20.29.
t.	v.	k_{2} .	t.	v.	k_2 .
16	4.71		16	5.54	
20	5.88	0.000542	20	6.69	0.000180
24	7.00	0.000563	25	7.90	0.000169
29	8.38	0.000283	31	9.14	0 000161
35	9.63	0.000597	37	10.24	0.000154
42	10.97	0.000613	44	11.38	0.000149
50	12.39	0.000650	53	12.55	0.000140
55	13.12	0.000665	63	13.70	0.000133
60	13.89	0.000698	77	15.10	0.000127
70	15.13	0.000760	92	16.43	0.000121
80	16.27	0.000848	100	16.99	0.000118

TABLE IV.

	A.	В.	k_2 .	R.
(Feb. 10)	16.24	12.65	0.000354 - 0.000362	1/4
(Feb. 10)	7.26	12.65	0.000695 - 0.000840	1/3
(Feb. 13)	5.29	29.23	0.000448-0.000490	1/4
(Feb. 13)	13.71	29.23	0.000295 - 0.000377	1/2

Only two series are given in full, it being deemed sufficient to give merely the general nature of the others. It will be observed that there is no approach to constancy in the values for k_2 . The constants rise gradually, except in the case of the series for February 26. Ex-VOL. LXXXV. 5 I

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periments carried out after this date with the same platinum solution likewise showed a decrease in the values for k_2 . It occurred to us that this was probably due to some of the platinum being thrown out of the colloidal solution by the electrolytes present. To test this, we made a solution of platinum containing about 0.5 grams of gelatin per litre (Zsigmondy, Annalen, 1898, 301, 387; Zeit. physikal. Chem., 1901, 40, 697; Bredig, Zeit. angew. Chem., 1898, 953; Kuspert, Ber., 1902, 35, 2815 and 4066; Paal and Amberger, Ber., 1904, 37, 124; Bredig and Fortner, Ber., 1904, 37, 798), and kept it in a steriliser at $80-90^{\circ}$ to prevent bacterial or fungoid growth.

The results obtained with this solution are given in the following tables:

TABLE	v.
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A = 28.74. $B = 19.72$.				A = 1	15.93. $B = 5$	20 ·93	
t.	v.	k.2.	k_3 .	t.	v.	$k_{2^{\bullet}}$	k_3 .
16	3.10			15	2.52		<u> </u>
18	3.62	0.000124		18	3.00	0.000123	0.0000195
20	4.20	0.000126	0.0000109	21	3.48	0.000122	0.0000198
26	5.88	0.000132	0.0000116	27	4.42	0.000127	0.0000204
32	7.52	0.000135	0.0000122	34	5.47	0.000128	0 0000212
38	9.16	$0 \ 000142$	0.0000129	42	6.62	0.000131	0.0000222
44	10.71	0.000146	0.0000135	50	7.90	0.000137	0.0000239
50	12.08	0.000147	0.0000139	60	9.20	0.000139	0.0000250

TABLE VI.

А.	B_*	k_2 .	R_{\bullet}
17.54	19.72	0.000183 - 0.000224	2/5
16.97	14.02	0.0000916 - 0.000136	3/5
16.97	22.12	0.0000865-0.0000972	2/5
27.98	14.24	0.0000735-0.0000865	3/10
27.98	24.95	0.0000446 - 0.0000508	1/3
13.99	27.58	0.000194 - 0.000242	3/7
21.09	21.09	0.0000143-0.0000210	5/14

A glance at the foregoing tables shows that the addition of gelatin has caused all the constants to rise gradually. As neither k_2 nor k_3 shows any approach to constancy, it is impossible to determine to which order the action belongs.

The gradual rise in the constants might be attributed to separate catalytic decomposition of the Uaro's acid and peroxide, each taking place independently; but the following results negative this view. Colloidal platinum was allowed to act on separate solutions of Caro's acid and hydrogen peroxide.

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	TABLE VII.				
	A = 9.34.	B=20	0.29.		
t.	v.	t.	v.		
12	0.18	12	0.28		
16	0.26	16	0.36		
22	0.34	22	0.39		
29	0.42	29	0.44		
38	0.61	38	0.47		
50	0.69	50	0.20		
65	0.88	65	0.52		
92	1.09	92	0.54		

If these results are compared with those in Table III, it will be seen that the sum of the volumes of oxygen evolved from the independent decomposition of the peroxide and Caro's acid is much less than that evolved from a mixture of the two.

That the hydrogen peroxide and Caro's acid both disappear will be evident from a consideration of the following results: 5 c.c. of a mixture were titrated with N/50 permanganate, some potassium iodide solution was then added, and the Caro's acid present estimated by titration of the liberated iodine with N/50 sodium thiosulphate solution. The titrations were effected under the same conditions, so that they might be comparable with each other (Friend, *loc. cit.*).

The columns headed x and y represent the diminution in the titration values.

TABLE	VIII.

t.	Permanganate.	x.	Thiosulphate.	y.	y/x.
3	14·20 c.c.	_	16.01 c.c.		
23	10.70 ,,	3.20	12.84 ,,	3.12	0.91
28	9.53 ,,	4.67	11.70 ,,	4.31	0.93
33	8.68 ,,	5.52	10.98 ,,	5.03	0.91
39	7.80 ,,	6.40	10.17 ,,	5.84	0.91
45	7.08 ,,	7.12	9.44 ,	6.57	6.92
51	6.48 ,,	7.72	8.91 ,,	7.10	0.95
58	5.90 ,,	8.30	8.38 ,,	7.63	0.92
65	5.30 ,,	8.90	7.79 ,,	8.22	0.95

Since the ratio y/x remains constant, it is clear that the amounts of the two substances decomposed are connected with each other. We have carried out a number of similar experiments with precisely the same results.

The increase in the velocity constants is probably due to two causes :—

(1) Increase in the activity of the platinum during the reaction, a phenomenon noticed by Bredig and his fellow workers (compare Liebermann, Ber., 1904, 37, 1519; Vondráček, Zeit. anorg. Chem., 1904, 37, 1519; Bredig and Fortner, loc. cit.).

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(2) The independent catalytic decomposition of the peroxide superposed on the reaction between the two reagents.

Using a large excess of one of the components, we have carried out a number of experiments to see if the order of the reaction could be determined in this way, but no definite conclusions can be drawn from the results.

Concentration of Platinum.

The following table gives the results obtained by varying the concentration of the platinum, that of the hydrogen peroxide and Caro's acid being kept constant. The series are not given in full, this being deemed unnecessary.

Pt = number of gram-atoms of platinum in 764,000 litres.

 t_1 and t_2 = times in minutes for evolution of 5 and 10 c.c. of oxygen respectively.

Pt.	t_1 .	t ₂ .	Pt.	t_1 .	t_{2} .
1	204	_	6	55	106
2	141	300	7	49	93
3	77	162	8	40	73
4	66	133	9	31	57
5	57	111	_		

It will be observed that there is no simple connection between the concentration of the platinum and the volume of oxygen evolved. It should be borne in mind, however, that the results are not strictly comparable, the experiments having been carried out on different days, so that the catalytic effect of the platinum had probably undergone a slight change. Moreover, the platinum solution was, of necessity, diluted to a different extent in each case, and this would have an influence on the catalytic effect (Bredig and Müller von Berneck, Zeit. physikal. Chem., 1899, 31, 258).

Effect of Acidity.—The alteration in the concentration of sulphuric acid has apparently little effect, as will be seen from the following results:

	v ₁ , total	v_2 , total	v_3 , total
t.	acidity 0.5 m.*	acidity m.	acidity 1.5 m.
10	1.52	1.42	1.40
18	3.20	3.62	3.60
26	5.90	5.70	5.82
34	8.16	7.80	7.95
42	10.10	9.78	9.90
60	13.83	13.72	13.80

* m=molecular weight of acid in grams per litre of solution.

Effect of Alkalinity.—We could not obtain any satisfactory results, since the velocity of decomposition seemed to depend on the rate of stirring.

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Effect of Poisons.—We have made a few experiments, using hydrocyanic acid and sulphuretted hydrogen as poisons, and obtained results similar to those of Bredig (Bredig and Ikeda, Zeit. physikal. Chem., 1901, 31, 1).

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