tively the data afforded by the absorption measurements of Warburg lead to a value of the equilibrium constant K_p = 1.2 g./cc. Probably this is significant only in order of magnitude owing to the approximations entering into the treatment of the data.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

THE INFLUENCE OF ACIDS AND BASES ON THE INHIBITORY EFFECT OF GELATIN UPON THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY COLLOIDAL PLATINUM

BY H. V. TARTAR AND N. K. SCHAFFER

RECEIVED MARCH 15, 1928 PUBLISHED OCTOBER 6, 1928

Introduction

Both Groh[1] and Iredale[2] have stated that the inhibitory effect of protective colloids upon the catalytic decomposition of hydrogen peroxide by colloidal platinum is approximately proportional to their protective properties as measured by Zsigmondy's "gold number." Tartar and Lorah[3] and later Reinders,[4] using proteins as protective colloids, investigated the influence of different degrees of acidity and alkalinity on the "gold number" and concluded that the variation of the protective action was in accordance with the known amphoteric character of the proteins.

The work presented herein is a study of the influence of different degrees of acidity and alkalinity on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide by colloidal platinum. It was undertaken in order to determine whether or not under these conditions the variation of the inhibitory effect is similar to that of the protective effect, as shown by Zsigmondy's "gold number."

Experimental Part

(a) **Preparation of Materials.**—The colloidal platinum was prepared by Bredig's arc method using a direct current, 110 volts and 8 amperes. The platinum was dispersed in a solution of 0.001 *M* potassium hydroxide as a peptizer. After standing for a few weeks in clean Pyrex flasks to permit the larger platinum particles to settle, the sol was carefully decanted and made uniform by mixing. The concentration then determined was 12.5 mg. of platinum per liter.

The gelatin ("Silver Label" brand) was purified and made isoelectric according to the procedure recommended by Loeb[5] and dried *in vacuo* at 65–70°. The gelatin sol used was prepared by adding 0.05 g. of gelatin to 100 cc. of water and heating the mixture

---

[1] Groh, *Z. physik. Chem.*, **88**, 414 (1914).

[2] Iredale, *J. Chem. Soc.*, **119**, 109 (1921); *ibid.*, **121**, 1536 (1922).

[3] Tartar and Lorah, *J. Phys. Chem.*, **29**, 792 (1925).

[4] Reinders, *Chem. Weekblad*, **22**, 481 (1925).

[5] Loeb, "Proteins and Theory of Colloidal Behavior," McGraw-Hill Book Co., New York City, **1922**, p. 35.

at 50° for four hours to permit the sol to come to "equilibrium."[6] The sol was then diluted to 250 cc. and allowed to cool slowly to 25°. Five cc. of this sol in 100 cc. of the reaction mixture gave a concentration of 0.001% of gelatin. This concentration was used in all experiments. The gelatin sol was used a few hours after its preparation to eliminate any effects due to aging.

The hydrogen peroxide (Merck's) was purified by distillation under reduced pressure.

(b) **Method of Procedure.**—The reactions were run in uniform, calibrated, 100cc. volumetric flasks, kept in a thermostat at 25°. The desired quantity of platinum sol was pipetted into the flask and the gelatin, acid, or base added; then the mixture was immediately diluted to 95 cc. and shaken. At this time the flask was placed in the thermostat and after exactly fifteen minutes, 5 cc. of the hydrogen peroxide solution was added, the time observed and the mixture shaken. The initial concentration of the hydrogen peroxide was determined in a separate flask containing none of the catalyst. At subsequent intervals 5 cc. of the reaction mixture was pipetted into dilute sulfuric acid and titrated rapidly with potassium permanganate, 0.03 *N*.

It was found expedient to express the results in terms of the time required for half of the peroxide used to decompose, the half period, since the velocity constant is inversely constant proportional to the time for 50% decomposition.

Although the order of the reaction is uncertain, reaction constants using the unimolecular formula, $K = 1/t \log_{10} (a/(a - x))$, were calculated for a few typical acid and alkali runs with and without gelatin, to afford some idea of the progress of the reactions. The data are given in Table I. With

TABLE I

TYPICAL ACID AND ALKALI RUNS WITH AND WITHOUT GELATIN AND THE CALCULATED REACTION CONSTANTS

t = time in minutes. $a-x$ = cc. of potassium permanganate

Sulfuric Acid at P_H of 3.3

	Without gelatin			With gelatin	
t	$a-x$	K	t	$a-x$	K
0.0	12.40	....	0.0	12.40	...
2.5	9.42	0.047	9.0	9.67	0.0119
5.5	7.01	.045	16.0	8.05	.0117
8.0	5.41	.045	22.5	6.85	.0116
11.0	4.02	.044	28.0	5.91	.0115
			31.0	5.50	.0114

Sodium Hydroxide

	Without gelatin, $P_H = 8.4$			With gelatin, $P_H = 11.85$	
t	$a-x$	K	t	$a-x$	K
0.0	4.05	....	0.0	3.89	...
39	3.05	0.0031	4.0	3.19	0.021
65	2.45	.0034	6.5	2.74	.023
81	2.13	.0035	11.0	2.15	.023
85	2.05	.0035	12.5	2.01	.023
90	1.90	.0037	14.0	1.78	.024
			15.5	1.66	.024

---

[6] Elliott and Sheppard, *J. Ind. and Eng. Chem.*, **13**, 699 (1921).

sulfuric acid without gelatin the value for K fell rapidly, showing that the colloidal platinum quickly became less active as a catalyst. At this same acid concentration in the presence of gelatin, however, the value for K decreased very much more slowly, indicating a stabilizing action of the gelatin. With the alkalies, K increased both in the presence and absence of gelatin.

The hydrogen-ion concentration was determined electrometrically. Very little difficulty was experienced from the presence of the gelatin and the colloidal platinum.

Results and Discussion

(a) **Reproducibility.**—In general, under carefully controlled conditions the reproducibility of the experimental results was excellent with alkalies, but only fair with acids. It was better with than without gelatin. Preliminary experiments showed that the period during which the platinum sol remained diluted and the time that the acid or alkali was in contact with the platinum, before the addition of hydrogen peroxide, had to be controlled. Immediate dilution of the platinum sol and addition of hydrogen peroxide gave extremely poor results. Bredig and Muller von Berneck[7] have reported like findings in their studies of the catalysis of the decomposition of hydrogen peroxide. It was found that the method given above gave the best results with acids; however, the half period even in this method had to be shortened (by increasing the concentrations of platinum and hydrogen peroxide) to give results of quantitative significance. The smaller the time of the catalysis, the less the time for the action of foreign influences.

Reproducibility of results with acids below a P_H of 3.5 equaled that with alkalies; however, from a P_H of 3.5 to 8,[8] deviations of 15% or more occasionally occurred. Similar discrepancies have also been noted by Bredig and Ikeda,[9] who in studying the effect of various substances on the hydrogen peroxide catalysis with platinum, report that, "between parallel runs sometimes there occur errors of more than 20 per cent. in the velocity constants, which by no means are accounted for by errors of manipulation; but are explained by very slow changes in the condition of the platinum sol, due to its extremely great sensitiveness toward traces of certain poisons, which cannot be excluded from the air of a large chemical laboratory."

(b) **Experiments with Acids.**—The results are given in Table II and presented graphically in Fig. 1 for acetic, sulfuric and phosphoric acids, respectively. In all these runs, 50 cc. of the platinum sol was used, the concentration in 100 cc. of the reaction mixture being 6.25 mg. of platinum

---

[7] Bredig and von Berneck, *Z. physik. Chem.*, **31**, 286 (1899).

[8] Since the platinum sol contained sodium hydroxide, it was possible to add acids and yet the sol react alkaline.

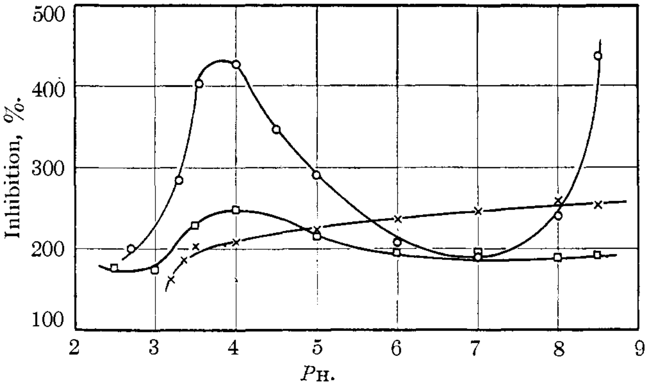
[9] Bredig and Ikeda, *Z. physik. Chem.*, **37**, 3 (1901).

per liter. The initial concentration of the hydrogen peroxide was 0.075 *N*. The per cent. of inhibition at any *P*H was calculated by subtracting the half period without gelatin from that with gelatin, dividing the result by the half period without gelatin and multiplying by 100.

TABLE II

VARIATION OF THE INHIBITORY EFFECT OF GELATIN WITH CHANGE OF *P*H WITH DIFFERENT ACIDS

*P*H	Half period, without gelatin, T minutes	Half period, with gelatin, T_G minutes	Inhibition, $\frac{T_G - T}{T}$ 100, %
	Acetic Acid		
3.20	10.5	27.7	164
3.35	10.6	30.5	188
3.50	10.7	32.5	204
4.00	10.9	33.5	207
5.00	11.1	36.0	224
6.00	11.3	38.0	236
7.00	11.5	40.0	248
8.00	11.7	42.0	259
8.50	11.9	43.0	254
	Sulfuric Acid		
2.70	6.2	18.6	200
3.30	6.8	26.2	285
3.55	7.5	37.6	402
4.00	9.5	50.0	427
4.50	11.4	51.0	347
5.00	13.0	51.0	292
6.00	17.0	51.0	209
7.00	18.0	51.0	191
8.00	15.0	51.0	240
8.50	9.5	51.0	437
	Phosphoric Acid		
2.50	7.8	21.5	176
3.00	8.0	22.0	175
3.50	8.5	28.0	229
4.00	9.5	33.0	247
5.00	11.5	36.5	217
6.00	13.5	40.0	196
7.00	14.5	43.0	197
8.00	16.0	46.5	191
8.50	16.5	48.5	194



○, sulfuric acid. □, phosphoric acid; ×, acetic acid.

Fig. 1.—Influence of acids on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide.

Inspection of the curves for the acids shows that in all cases the inhibition increases rapidly to a *P*H of 3.5 to 4, but beyond this *P*H it constantly increases with acetic acid, decreases with phosphoric acid and first decreases then increases with sulfuric acid. However, the noteworthy conclusion to be drawn from these results is that the inhibitory effect in the acid range is not completely comparable to the protective effect, for if it were, we should expect the inhibitory effect to increase not at a *P*H of 3.5 but at 4.7, the isoelectric point of gelatin, as was the case of the "gold number."[3] Apparently the acids affect not only the gelatin but also the catalysis. The different shapes of the curves are perhaps attributable to the specific effects of the acid anions.

(c) **Experiments with Alkalies.**—The experiments with alkalies convincingly disclose a dissimilarity between inhibition and protection. The data are presented in Table III and Fig. 2 for potassium hydroxide, barium hydroxide and sodium hydroxide, respectively. Reinders[4] has shown that the protective effect of gelatin from a *P*H of 5.5 to 11 is large and constant, whereas it is here shown that the inhibitory effect in the alkaline range is small, variable and even becomes accelerative at certain concentrations. The smallest recorded inhibition in the acid range is even greater than the largest inhibition in the alkaline range. Groh[1] reported less efficient protective action of gelatin in 0.1 *N* sodium hydroxide than in neutral solution. Rocasolano,[10] studying inhibition, found an increase of catalytic power beyond a certain concentration of sodium protalbinate, which he attributed to its alkaline reaction.

TABLE III

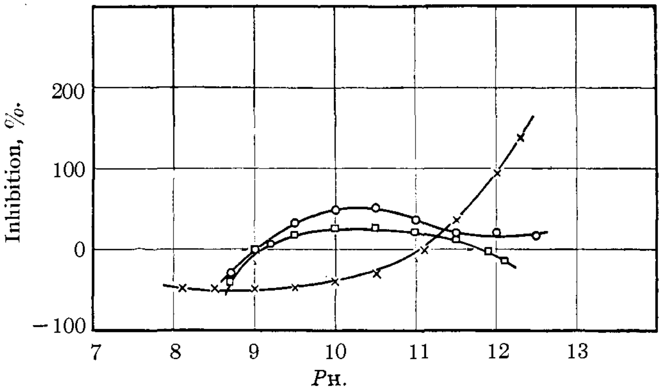
VARIATION IN THE INHIBITORY EFFECT OF GELATIN WITH CHANGE OF *P*H WITH DIFFERENT ALKALIES

*P*H	Half period, without gelatin, T, minutes	Half period, with gelatin, T_G, minutes	Inhibition, $\frac{T_G - T}{T}$ 100, %
	Potassium Hydroxide		
8.7	160.0	116.0	−27.5
9.0	95.0	95.0	0.0
9.5	52.0	70.0	34.6
10.0	35.0	51.0	50.0
10.5	23.0	35.5	52.1
11.0	16.0	22.0	37.5
11.5	11.0	13.3	20.9
12.0	8.4	10.3	22.6
12.5	8.1	9.6	18.5
	Barium Hydroxide		
8.7	173.0	106.0	−38.7
9.0	86.0	86.0	0.0
9.2	71.0	77.0	8.5
9.5	56.0	66.0	17.9
10.0	38.0	48.0	26.3
10.5	26.5	33.5	26.4
11.0	17.5	21.5	22.8
11.5	11.0	12.5	13.6
11.9	8.0	8.0	0.0
12.1	7.0	6.2	−11.4
	Sodium Hydroxide		
8.1	176.0	90.0	−48.8
8.5	76.0	40.0	−47.4
9.0	50.0	26.0	−48.0
9.5	34.0	18.0	−47.0
10.0	23.0	14.0	−39.1
10.5	15.0	10.7	−28.7
11.1	10.0	10.0	0.0
11.5	8.0	11.0	37.5
12.0	8.2	16.0	95.1
12.3	10.0	24.0	140.0

---

[10] Rocasolano, *Compt. rend.*, **173**, 41 (1921).

The potassium hydroxide and barium hydroxide curves are very similar, indicating that the hydroxyl ion is the dominant factor in the catalysis. The hydroxyl ion apparently promotes the catalysis by its peptizing action on the platinum and also by directly decomposing the hydrogen peroxide.[11] Since in alkaline solution the reaction is markedly accelerated, a smaller quantity of platinum sol had to be used. With potassium hydroxide and barium hydroxide, 10 cc. of the platinum sol was used, giving a concentration of 1.25 mg. of platinum per liter. The initial concentration of the hydrogen peroxide was 0.075 *N*. In the runs with sodium hydroxide only 5 cc. of the platinum sol was used, a concentration of 0.625 mg. of platinum per liter. The initial concentration of the hydrogen peroxide was 0.0077 *N* and titrated with 0.001 *N* potassium permanganate. The divergencies between the potassum hydroxide and barium hydroxide curves on the one hand and the sodium hydroxide on the other are undoubtedly chiefly due to the different proportions of the materials used. Thus from Fig. 2 barium hydroxide at a *P*H of 9.5 and potassium hydroxide at a *P*H of 9.6 give per cent. inhibitions of 17.9 and 37.5, respectively, whereas using the concentrations of hydrogen peroxide and platinum as in the sodium hydroxide runs and keeping the *P*H the same, the per cent. inhibitions were found to be −7.9 and −20.9, respectively.



○, potassium hydroxide; □, barium hydroxide; ×, sodium hydroxide.

Fig. 2.—Influence of bases on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide.

In conclusion the writers wish to point out that the catalysis of hydrogen peroxide by colloidal platinum will be markedly influenced by the extent and character of the platinum surface. Zsigmondy[12] specifies very fully how the gold sol must be prepared for the determination of the "gold

---

[11] Lemoine, *Compt. rend.*, **161**, 47 (1915).

[12] Zsigmondy, *Z. anal. Chem.*, **40**, 687 (1901).

number." In any use of the catalysis by platinum of the decomposition of hydrogen peroxide for the measurement of protective action, there should be a careful standardization of the method.

Summary

1. A study has been made of the influence of different concentrations of acid and alkalies on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide by colloidal platinum.
2. In the acid range the variation of the inhibition is evidently a function of the specific effect of the acid anion as well as of the hydrogen-ion concentration.
3. In the alkaline range the variation of the inhibition depends chiefly upon the hydroxyl ion concentration.
4. At any P_H the inhibition depends upon the concentration of the hydrogen peroxide and platinum used.
5. The results indicate that not only the gelatin but also the catalysis itself is influenced by the acids and alkalies; therefore the variation of the inhibitive effect is not similar to the protective effect as shown by the "gold number."

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

THE EQUILIBRIUM BETWEEN HYDROGEN-CARBON MONOXIDE AND METHANE-CARBON DIOXIDE IN THE CORONA DISCHARGE

BY GERALD L. WENDT AND GREGG M. EVANS

RECEIVED MAY 2, 1928 PUBLISHED OCTOBER 6, 1928

Introduction

The subject of chemical reaction in the electrical discharge has long been of interest. Andrews and Tait,[1] Brodie,[2] Thenard,[3] and Berthelot[4] seem to have been the earliest workers. Since then a large number of investigators[5] have studied various reactions, and many others have worked on

---

[1] Andrews and Tait, *J. Chem. Soc.*, **13**, 344 (1861).

[2] Brodie, *Phil. Mag.*, [4] **44**, 470 (1872).

[3] Thenard, *Compt. rend.*, **75**, 118 (1872).

[4] Berthelot, *ibid.*, **82**, 1357 (1876); *Bull. soc. chim.*, [2] **26**, 101 (1876).

[5] Anderegg, THIS JOURNAL, **39**, 2581 (1917); **47**, 2429 (1925); *Trans. Am. Electrochem. Soc.*, **44**, 203 (1923); *Proc. Indiana Acad. Sci.*, **1921**, p. 157; (b) Briner, Meiner and Rothen, *Helv. Chim. Acta.*, **9**, 409 (1926); (c) Collie, *J. Chem. Soc.*, **79**, 1149 (1901); (d) Comanducci, *Rend. accad. sci. Napoli*, **15**, 15 (1909); (e) Crespi and Lunt, *J. Chem. Soc.*, **127**, 2051 (1925); (f) Crocker, *Phys. Rev.*, **8**, 344 (1916); (g) Dem'yanov and Pryanishnikov, *J. Russ. Phys.-Chem. Soc.*, **58**, 462 (1926); (h) Elliott, Joshi and Lunt, *Trans. Faraday Soc.*, **23**, 57 (1927); (i) Elliott, *ibid.*, **23**, 60 (1927); (j) Grubb, *Thesis.*