to exist: $KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$, $2KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$ and $KC_2H_3O_2 \cdot 2Pb(C_2H_3O_2)_2$.

3. The analogy between these compounds and the hydroxyl plumbites has been shown.

4. It is suggested that the solvate $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$ is a complex acetoplumbous acid.

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Catalysis of Nitramide Decomposition by Colloidal Platinum and Gold

BY CECIL V. KING

In a previous study, it was found that the decomposition of nitramide in aqueous solution

$$H_2N_2O_2 \longrightarrow H_2O + N_2O$$

was accelerated by platinized electrodes.[1] This suggested an investigation of the catalysis by colloidal and finely divided metals, and experiments with platinum and gold are reported in this paper.

At 20° the "spontaneous" (water-catalyzed) pseudo-unimolecular decomposition of nitramide has a half-time of about six hours. In dilute solutions of strong acids the rate is practically independent of the acid concentration, although a very small acid catalysis has been reported.[2] The colloidal metal catalysis can then be studied in dilute acid solutions, but not in alkaline media because of the large catalytic effect of bases.

In many respects the catalysis reported here resembles the colloidal metal catalysis of hydrogen peroxide decomposition, studied extensively by Bredig and his collaborators and by many investigators since. Brief reviews of this work are found in a number of publications.[3] The catalysis is now ascribed to a rapid decomposition of hydrogen peroxide adsorbed on the surface of the colloidal particles.[4] The inhibiting effect of many substances is ascribed to their preferential adsorption and partial or complete displacement of the hydrogen peroxide. The mechanism of the decomposition in the adsorbed phase has been studied and discussed by Weiss.[5]

Materials and Method

Nitramide was prepared by the customary method,[6] the final extraction being made as described by Marlies and La Mer.[7] It was recrystallized by dissolving in ether, adding chloroform and partly evaporating the solution *in vacuo*.

Six preparations of colloidal platinum were used. These were made by striking a direct current arc between platinum wires immersed in well-stirred distilled water, cooled in an ice-bath. In preparing sols I–V, inclusive, the current was kept at approximately four amperes; in making sol VI, three amperes. Two gold sols were made with a current of three amperes: sol I in 0.0001 *M* hydrochloric acid, sol II in 0.0002 *M* acid. Gold sol IIA consisted of residues from experiments in which sol II was diluted with water only (15 cc. sol II to 50 cc.), nothing else being added except nitramide samples.

Metal Content of the Sols.—No attempt was made to analyze the sols with great accuracy. The metal content was determined as indicated in Table I, 50-cc. samples being used in most cases. The evaporation residue was dissolved in aqua regia and finally converted to the chloro salt by adding a weighed amount (in excess) of potassium chloride. The gold sols showed no discrepancy between the weight of the residue from evaporation and the gold content of the chloroaurate. The metal content of the platinum sols, however, varies from 10 to 30% less than the weight of the residue from evaporation, indicating that this residue contains other material than the metal. It has been known that some of the platinum is oxidized in preparing such sols; Pennycuick[8] has estimated that about

TABLE I

COMPOSITION OF THE SOLS

Sol. no.	Residue on evaporation g./l.	Metal from chloro salt
	Platinum	
I	0.050[a]	...
II	.106	0.092
III	.068	.058
IV	.038	.022
V	.114	.104
VI	.070	.053
	Gold	
I	.204	.205
II	.204	.205
IIA	.0612[b]	...

[a] Determined by precipitating with hydrochloric acid.
[b] Calculated from dilution of sol II.

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[1] Brönsted and King, THIS JOURNAL, **49**, 193 (1927).

[2] Marlies and La Mer, *ibid.*, **57**, 1812 (1935).

[3] Freundlich, "Colloid and Capillary Chemistry," English translation of 3d German edition, Methuen and Co., London, 1926. Weiser, "Inorganic Colloid Chemistry," John Wiley and Sons, Inc., New York, 1933. A volume of the series "Kolloidforschung in Einzeldarstellungen" to deal exclusively with this subject has not appeared.

[4] MacInnes, THIS JOURNAL, **36**, 878 (1914).

[5] Weiss, *Trans. Faraday Soc.*, **31**, 1547 (1935).

[6] Thiele and Lachman, *Ann.*, **292**, 317 (1896).

[7] Marlies and La Mer, THIS JOURNAL, **57**, 2008 (1935).

[8] Pennycuick, *ibid.*, **52**, 4621 (1930), and previous papers.

4% of the metal exists as $H_2Pt(OH)_6$ dissolved in the intermicellar liquid. The amount of this or other compounds associated with the colloidal particles has been unknown.

The liquid obtained by precipitating the platinum with very dilute hydrochloric acid and filtering showed little or no catalytic effect. It did, however, contain enough dissolved metal to leave a black residue on evaporation. In the case of sol VI this dissolved platinum was determined by the chloroplatinate method, to be 0.035 g./l. If present as $H_2Pt(OH)_6$, this would account for the difference between the values of columns 2 and 3 of Table I for this sol.

The platinum sols were slightly acid but their exact acidity was not determined. These sols were filtered through paper to remove sludge formed in the preparation; Pennycuick[8] reports that this usually reduces the original acidity. The sols were considered to contribute nothing to the acidity when acids were added for the catalytic experiments. The gold sols were considered to have the acidity of the solutions used in their preparation.

Method of Following the Reaction.—The decomposition rates were measured by observing the pressure increase above the solution in an apparatus similar to that described by Brönsted and Bell.[9] The solution (50 cc. unless otherwise stated) was introduced into the 100-cc. reaction flask, and the nitramide sample suspended in the flask neck until the apparatus was evacuated. The shaking speed was kept uniform by a centrifugal governor. All experiments were carried out at 20°.

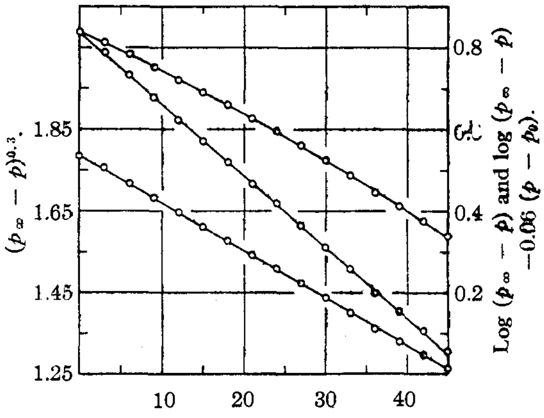

Fig. 1.—Plots of log $(p_\infty - p)$, upper curve; log $(p_\infty - p)$ -0.06 $(p - p_0)$, middle; and $(p_\infty - p)^{0.3}$, lower. Solution: 10 cc. Pt sol I in 50 cc., 0.00008 M HCl, 0.0090 M $H_2N_2O_2$ at start.

Measurements of the "spontaneous" decomposition rate in dilute hydrochloric acid solutions gave an average value of $k = 0.00162$, calculated from the unimolecular rate equation

$$k = \frac{2.3}{t}\log\frac{c_0}{c}$$

where t = time in minutes, c_0 and c = concentration initially and at time t, respectively. Interpolation from measurements of Baughan and Bell[10] gives $k = 0.00152$–0.00156 at 20°. In these and other calculations pressure values proportional to concentrations were used; if p_0 = initial pressure, p = pressure at time t, p_∞ = pressure at end of reaction, then $(p_\infty - p)$ is proportional to c, $(p_\infty - p_1)$ to c_0, $(p - p_0)$ to $(c_0 - c)$, etc.

Colloidal Platinum Catalysis

Order of the Reaction.—The catalyzed reaction was found to be between zero and first order, except in a few experiments in which the catalytic activity of the metal was decreasing rapidly enough with time to affect the measurements. Assuming the amount of nitramide adsorbed to be given by the Freundlich isotherm

$$y = \beta c^m$$

where β and m are constants, and the decomposition rate to be proportional to y, the integrated rate equation becomes

$$kt = c_0^{1-m} - c^{1-m} \qquad (1)$$

An equation based on the Langmuir adsorption isotherm can be derived similarly. If the amount of nitramide adsorbed is given by

$$y = abc/(1 + bc)$$

where a and b are constants, the integrated rate equation becomes

$$kt = \ln(c_0/c) + b(c_0 - c) \qquad (2)$$

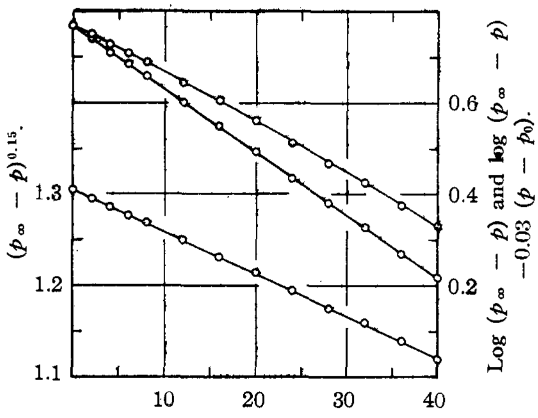

Fig. 2.—Plots of log $(p_\infty - p)$, upper curve; log $(p_\infty - p)$ -0.03 $(p - p_0)$, middle; and $(p_\infty - p)^{0.15}$, lower. Solution: 12 cc. Pt sol III in 50 cc., 0.00007 M HCl, 0.0000024 M I_2, 0.0087 M $H_2N_2O_2$ at start.

In Figs. 1 and 2 plots of log $(p_\infty - p)$ *versus* time for two typical experiments are not linear as they would be for a unimolecular reaction. On the other hand, plots of $(p_\infty - p)^{0.3}$ *versus* time in

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[9] Brönsted and Bell, THIS JOURNAL, 53, 2478 (1931).

[10] Baughan and Bell, *Proc. Roy. Soc.* (London), A158, 464 (1937).

Fig. 1, and of $(p_\infty - p)^{0.15}$ in Fig. 2 are seen to give straight lines. Likewise plots of $\log (p_\infty - p) - 0.06\,(p - p_0)$ *versus* t (Fig. 1) and of $\log (p_\infty - p) - 0.03\,(p - p_0)$ *versus* t (Fig. 2) are seen to be linear. The exponent of equation (1) and b of equation (2) must be determined by trial; for most experiments with sols I, II, IV and VI the value of $(1 - m)$ is approximately 0.30. The same value was found for some of the experiments with sol III, although 0.15 is better for others; 0.20 satisfies most of the rate curves with sol V. In general $b = 0.2\,(1 - m)$ when pressure units and decadic logarithms are used.

Variation of Initial Nitramide Concentration.—To make certain that the increasing values of $(\mathrm{d}c/\mathrm{d}t)/c$ with time in each experiment were caused by the changing nitramide concentration and not by changing activity of the catalyst or some other factor, a series of experiments was carried out in which the initial nitramide concentration was varied. Details of these experiments are shown in Fig. 3, where values of $(p_\infty - p)^{0.3}$ and of $\log (p_\infty - p) - 0.06\,(p - p_0)$ are plotted *versus* t. The rate constants are given in Table II.

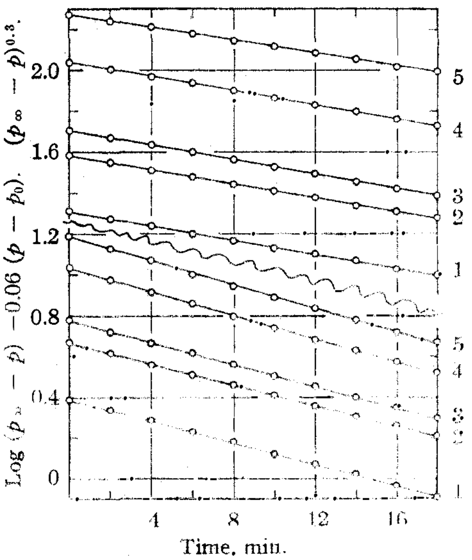

Fig. 3.—Data from which the constants of Table II are obtained. Numbers on right refer to experiment numbers in Table II.

Exact values of $(1 - m)$ and b are not determined easily and may vary in different experiments even with the same sol. For comparative purposes, therefore, it was thought best to use a first order rate "constant" from the first part of each experiment. This was obtained by plotting $\log (p_\infty - p)$ *versus* t and drawing a straight line through the first few points. The negative slope, times 2.3, gives a value k' which is comparable dimensionally to the spontaneous rate constant and can be corrected by subtracting the latter when desirable. This correction was not made in the experiments of Table II since the catalytic effect was relatively high.

TABLE II

EFFECT OF INITIAL NITRAMIDE CONCENTRATION. 10 cc. OF PT SOL III IN 50 cc.; 0.0001 *M* HCl

	$C_{H_2N_2O_2}$, *M*	$k(1)$	$k(2)$
1	0.00323	0.0173	0.0614
2	.00645	.0174	.0600
3	.0090	.0180	.0607
4	.0161	.0171	.0658
5	.0235	.0156	.0665

$$(1)\quad k = \frac{1}{t}\,(p_\infty - p_0)^{0.3} - (p_\infty - p)^{0.3}$$

$$(2)\quad k = \frac{2.3}{t}\log\frac{p_\infty - p_0}{p_\infty - p} - 0.06\,(p - p_0)$$

Reproducibility of Rate Experiments.—Platinum sols of this type are not very stable. The catalytic activity decreases slowly with time, and for this reason each series of experiments reported was completed within a few days to make the results as nearly comparable as possible. Experiments with the sols diluted with water only were found to be less reproducible than when definite and higher concentrations of various reagents were present. Many of the earlier experiments were discarded because of poor reproducibility, which in part may be ascribed to lack of uniformity in the method of mixing the solutions. No entirely satisfactory method was found but most of the solutions were mixed as follows: the reagent to be added was diluted with nearly the requisite amount of water; the sol was run in from a buret while the flask was swirled, and finally the dilution with water was finished.

Variation of Platinum Concentration.—The experiments of Table IIIA were carried out with samples of sol I, with 0.0002 *M* hydrochloric acid added; the platinum coagulated, partly at least, in eight to twelve hours. With the lowest platinum concentration, the value of k' decreased from 0.00444 at the start to 0.00360 after sixty minutes. Thereafter it remained constant for three hours instead of rising as it would if equation (1) were valid.

As shown in Fig. 4, a plot of k' *versus* platinum concentration is concave upward. This is ascribed to the fact that the platinum was in a stage of incipient precipitation, and the longer the time necessary for measurement, the lower the value of k' obtained. A second series run with samples of Pt sol II with 0.0001 M added hydrochloric acid did not show this effect. Values of k' are given in Table IIIB, and in Fig. 4 it is seen that the catalysis is proportional to the platinum concentration. The solutions used for these experiments were allowed to stand for one hour after mixing; the solutions of series A were used fifteen to twenty minutes after mixing.

TABLE III

VARIATION OF PLATINUM CONCENTRATION. INITIAL $C_{H_2N_2O_2} = 0.0090\ M$

A. Pt sol I 0.0002 M HCl		B. Pt sol II 0.0001 M HCl	
Cc. Pt sol in 50 cc.	k'	Cc. Pt sol in 50 cc.	k'
0	0.00162	0	0.00162
2.5	.00444	1	.00906
5	.0123	2	.0200
5	.0124	3	.0282
7.5	.0157	4	.0301
10	.0221	5	.0363
12.5	.0329	6	.0449
12.5	.0325	7	.0465
15	.0417	7	.0508
		8	.0614
		9	.0676
		10	.0725

Effect of Time after Mixing the Solutions.—A series of experiments was run with Pt sol II with 0.0001 M hydrochloric acid added, a concentration of acid which alone did not cause visible coagulation of the platinum during twenty hours, but which after addition of the nitramide sample sometimes caused partial precipitation during this time. The nitramide samples were introduced at various time intervals after the solutions had been mixed, as indicated in Table IV. The catalysis falls off only slowly with time, but there is undoubtedly some effect. In the two experiments marked (*) a slight precipitate was visible three hours after the nitramide was introduced, and these rates were somewhat lower than in other comparable experiments. That coagulation alone does not decrease the catalytic activity is shown by the last experiment of Table IV, in which the platinum was coagulated by warming the solution for ten or fifteen minutes. In this and other experiments which are not reported, coagulation of the platinum by heating seems to increase the activity which then, however, falls off rapidly with time.

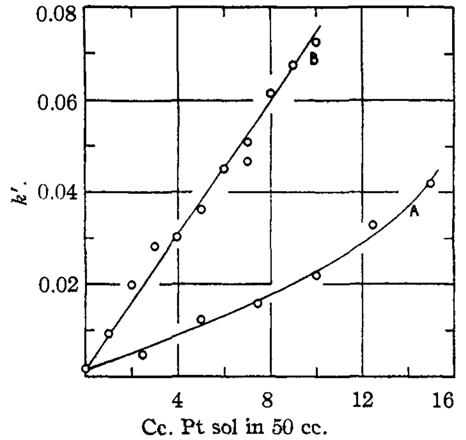

Fig. 4.—Effect of platinum concentration: A, Pt sol I, 0.0002 M HCl; B, Pt sol II, 0.0001 M HCl.

Another series in which the decrease in activity with time after precipitation of the platinum by hydrochloric acid was measured is described later.

TABLE IV

EFFECT OF TIME AFTER MIXING THE SOLUTIONS. 8 CC. PT SOL II IN 50 CC.; 0.0001 M HCl. INITIAL $C_{H_2N_2O_2} =$ 0.0090 M

Time after mixing, min.	k'
6	0.0621
11	.0633
30	.0600
45	.0590*
65	.0550*
80	.0614
80	.0614
101	.0614
18.8 hrs.	.0538
21.5 hrs.	.0544
a	.0638

[a] Pt ppt. by warming the solution. * Pt partly ppt. in three hours.

Variation of Acid Concentration.—Several series of experiments were run in which the platinum and initial nitramide concentrations were kept constant and varying amounts of hydrochloric acid were added. Three such series with various platinum sols are not reported because of poor reproducibility and because the acid concentration was not varied widely. The experiments of Table VA and B are typical of the results, however. The similarity of the results with hydrochloric and nitric acids indicates that the hydrogen ion has more influence than the negative ion. This is also indicated by the influence of salts to be discussed later.

TABLE V

THE EFFECT OF HYDROCHLORIC AND NITRIC ACIDS ON THE RATES

Initial $C_{H_2N_2O_2} = 0.0090$ *M*

A. HCl. 16 cc. Pt sol VI diluted to 50 cc.		B. HNO_3. 10 cc. Pt sol V diluted to 50 cc.	
C_{HCl} *M*	k'	C_{HNO_3} *M*	k'
0	0.1202	0	0.1053
0.00002	.1017	0.000036	.1003
.00002	.1012	.000072	.0874
.00005	.0971	.000108	.0888
.00005	.0941	.000144	.0837
.00010	.0874	.00018	.0828
.00010	.0803	.00036	.0748
.00020	.0720	.00054	.0713
.00030	.0621	.00072	.0676
.00040	.0610	.00090	.0626
.00050	.0495		
.00060	.0453		

The decrease in catalysis in the presence of acids or other "poisons" may be ascribed to a decrease in the amount of nitramide adsorbed. Assuming that this decrease is proportional to the amount of "poison" adsorbed, a rate equation based on the Freundlich isotherm becomes

$$-\frac{dc}{dt} = k_0\,(1 - \beta' C^n_{\text{poison}})\; C^m_{H_2N_2O_2}$$

where β' and n are the constants of the acid adsorption isotherm, and k_0 the rate constant when $C_{\text{poison}} = 0$. Whether β and m are affected by the presence of the "poison" or β' and n change with nitramide concentration will be discussed later. If none of these are affected

$$k = k_0\,(1 - \beta' C^n_{\text{poison}})$$

The equation actually tested is

$$k' = k_0\,(1 - \beta' C^n_{\text{poison}}) \qquad (3)$$

which would be influenced only by changes in β and m, since the same initial nitramide concentration was used in each series of experiments.

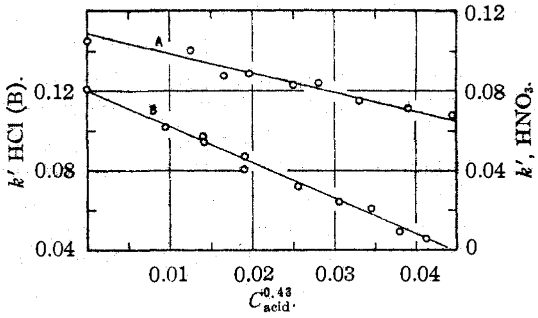

Fig. 5.—Rate constants *versus* acid concentration to 0.43 power: A. HNO_3. 10 cc. Pt sol V in 50 cc. B, HCl. 16 cc. Pt sol VI in 50 cc.

Equation (3) was tested by plotting k' *versus* C^n_{acid}, trying various values of n until the best straight line was obtained. In Fig. 5 straight lines are obtained for hydrochloric and nitric acids with $n = 0.43$.

In the above experiments the platinum precipitated before or during the experiment when the acid concentration was 0.0002 *M* or higher, and in such cases the catalytic effect was decreasing more or less rapidly with time. In these experiments the nitramide samples were introduced ten to fifteen minutes after the solutions were mixed.

In a series of experiments with Pt sol II this decrease in activity with time was measured. The solutions, made up of 7 cc. of platinum sol in 40 cc. with 0.00025 *M* hydrochloric acid, were left in the reaction flasks and new nitramide samples were introduced from time to time. The platinum precipitated when the first nitramide was dissolved. After seventy hours, more hydrochloric acid was added, the catalysis measured, and then enough potassium hydroxide added to neutralize the additional acid. This increased the catalytic effect approximately to the value it would have had if no additional acid had been added. Salts have little effect on the rate.

Two such series were carried out with identical concentrations, and, while the rates did not check, the relative effect of the added acid is nearly identical. The rate constants k' for these and other similar experiments are given in Table VI and the values of series A are plotted *versus* time in Fig. 6. In this figure, interpolated (or extrapolated) values of k' without additional acid are marked * and the vertical lines indicate the decrease in catalysis due to the acid. These interpolated rate constants were taken as unity and the values of k' on addition of acid calculated relative to them. The spontaneous rate constant, 0.00162, was subtracted in each case before this calculation. The results are summarized in Table VII and in Fig. 7 it is seen that when they are plotted *versus* the added hydrochloric acid concentration raised to the 0.23 power, a linear relation is obtained. In this case since the relative rates are all based on the values in 0.00025 *M* acid, it is equally useful to plot log $(k'_0 - k')$ *versus* log $(C_{HCl} - C^0_{HCl})$, where $C^0_{HCl} = 0.00025$ *M*, and the exponent 0.23 was actually obtained by making this plot.

TABLE VI

EFFECT OF TIME AFTER MIXING WHEN PLATINUM IS PRECIPITATED; EFFECT OF HCl ADDITION

7 cc. Pt sol II in 40 cc. Initial $C_{H_2N_2O_2}$, 0.0090 *M*

Total vol., cc.	C_{HCl}, *M*	Time, hours	k'(A)	k'(B)
40	0.00025	1.0	0.0313	0.0414
40	0.00025	4.5	.0253	.0317
40	.00025	22.4	.0207	.0262
40	.00025	27.7	.0193	.0227
40	.00025	46.8	.0160	.0196
40	.00025	53.8	.0147	.0166
40	.00025	(70.5)	(.0123)*	(.0136)*
45	.0112	70.5	.00352	.00368
49.6	.0002	95.2	.00891	.00887
..	...	(117.1)	(.0058)*	...
51.1	.0031	117.1	.00322	...
49.6	.0002	(117.1)	...	(.0058)*
52.6	.0058	117.1	...	.00286
40	0.00025	45.7	0.0269	0.265
..	...	(51.0)	(.0255)*	...
41.5	.0038	51.0	.00991	...
42.9	.00023	69.8	.0210	...
40	.00025	(51.0)	...	(.0248)*
43.5	.00815	51.0	...	.00607
46.7	.00021	69.8	...	.0202
10 cc. of Pt sol III in 40 cc.				
40	0.00025	42.6	.0163	.0174
..	...	(49.7)	(.0128)*	...
40.3	.00098	49.7	.00792	...
40.6	.00024	65.9	.00719	...
40	.00025	(49.7)	...	(.0136)*
40.7	.00194	49.7	...	.00651
41.4	.00024	65.9	...	.00842

* Values from curves as shown in Fig. 6.

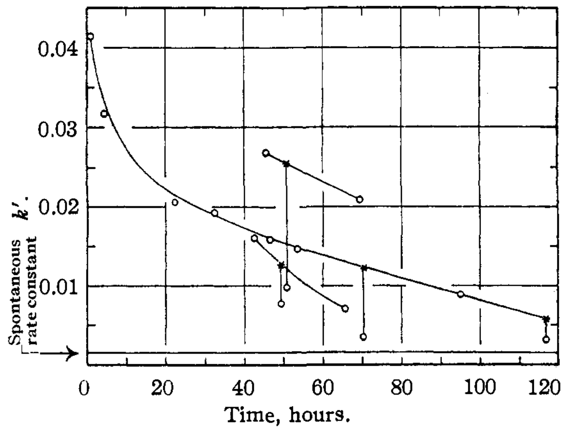

Fig. 6.—Decrease in catalysis by precipitated platinum with time; effect of addition and neutralization of acid. The points * and vertical lines indicate HCl additions.

It is interesting to note that the exponent 0.23 is much lower than the value 0.43 found previously. However, it is not surprising that different platinum preparations should give different exponents, just as was found for variations of nitramide concentration with different sols.

TABLE VII

EFFECT OF HYDROCHLORIC ACID ON CATALYSIS BY PRECIPITATED PLATINUM

$(C_{HCl} - C^0_{HCl})$, *M*	Relative values, k'
0	1
0.00073	0.56
.00169	.41
.00285	.38
.00355	.35
.00555	.30
.00785	.20
.01095	.175

C^0_{HCl} = 0.00025 *M*

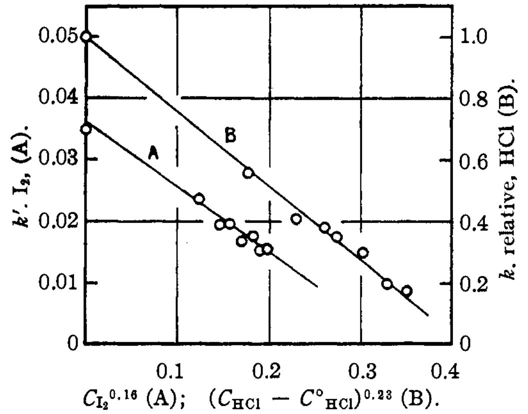

Fig. 7.—Effect of iodine; effect of HCl on precipitated platinum.

Other "Poisons."—Many substances have a large effect on colloidal platinum catalysis of hydrogen peroxide decomposition, especially ions or molecules which can form chemical complexes with platinum ion, and "protective" colloids such as gelatin. From this list iodine, dextrin and glucose were chosen for study as substances having a wide range of effects. A dilute solution of iodine in distilled water was made up, and portions were diluted quantitatively to use in the experiments. The dextrin used had been purified by precipitation with methanol. It was found difficult to reproduce the experiments with dextrin accurately. Fresh solution was made each day, and diluted quantitatively immediately before each experiment. The concentrations are given in grams/100 cc. The experiments with iodine, dextrin and glucose are summarized in Table VIII.

In Fig. 7 values of k' plotted *versus* $C_{I_2}^{0.16}$ give a satisfactory linear relation. In Fig. 8 the plot of k' *versus* $C_{\text{dextrin}}^{0.05}$ indicates a linear relation,

TABLE VIII

EFFECT OF IODINE, DEXTRIN AND GLUCOSE. INITIAL $C_{H_2N_2O_2}$ = 0.0090 M

Iodine 12 cc. Pt sol. III in 50 cc.: 0.00007 M HCl		Dextrin 15 cc. Pt sol V in 50 cc.: 0.00007 M HCl		Glucose 10 cc. Pt sol V in 50 cc.: 0.00007 M HCl	
C_{I_2}, M	k'	$C_{dextrin}$, g./100 cc.	k'	$C_{glucose}$, M	k'
0	0.0350	0	0.1311	0	0.0840
0.0000024	.0235	0.00004	.0626	0.03	.0821
.0000064	.0195	.00004	.1205	.3	.0658
.0000096	.0196	.00004	.1134	.8	.0511
.000016	.0166	.00008	.1242	1.4	.0407
.000024	.0177	.0004	.0796		
.000024	.0175	.004	.0624		
.000032	.0152	.004	.0557		
.000040	.0152	.004	.0621		
		.04	.0672		
		.04	.0662		
		.4	.0552		
		2.4	.0515		

although values at the lowest concentrations are quite undependable. The experiments with glucose give a straight line with $C_{glucose}^{0.70}$ (Fig. 8). The effect of glucose on the catalysis is comparatively small, but seems to be similar in principle to the other cases.

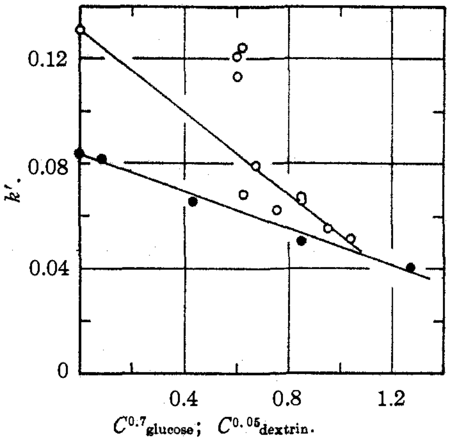

Fig. 8.—The effect of glucose (●) and dextrin (○).

The Effect of Salts.—A number of experiments were carried out in which various salts were added to the catalyzing solution. These are summarized in Table IX, where comparisons are made with solutions which were identical except for the salt addition. It will be seen that salts have no great effect on the catalysis. Their addition probably increases the catalytic effect temporarily; if the platinum is precipitated quickly, the catalysis falls off rapidly with time and a lower rate is obtained.

Colloidal Gold Catalysis

Order of the Reaction.—The gold catalyzed reaction was also found to be between zero and first order (approximately 0.5 order) with low concentrations of nitramide, but reached a maximum, zero order rate at sufficiently high nitramide concentrations. Two series of experiments were carried out with varying nitramide concentrations, one with samples of gold sol II diluted with water only, the other with gold sol IIA with 0.0001 M hydrochloric acid added. Pressure readings are plotted *versus* time for the latter series in Fig. 9. The slopes of the straight lines of Fig. 9, divided by $(p_\infty - p_0)$, are equal to $-(dc/dt)/c_0$ and are taken as rate constants k. The values for both series are given in Table X.

In Fig. 10, log k is plotted *versus* log c. The straight lines drawn through the points at low concentrations have the slopes -0.53 and -0.67 for sols IIA and II, respectively. In both cases the slope -1 is satisfactory for the higher concentrations, which is another way of indicating

TABLE IX

EFFECT OF SALTS ON THE CATALYSIS

Initial $C_{H_2N_2O_2}$ = 0.0090 M

Solution (50 cc.)	C_{HCl}, M	C_{salt}, M	k'	Remarks
30 cc. Pt sol V 0.2 g. dextrin	0.00008	......	0.0909	
0.2 g. dextrin	.00008	0.001 $Ba(NO_3)_2$	.0987	No ppt.
15 cc. Pt sol V	.00007	......	.1453	
15 cc. Pt sol V	.00007	.0005 $Ba(NO_3)_2$	.1380	Immed. ppt.
15 cc. Pt sol V 0.00002 g. dextrin	.00007	......	.1134	
0.00002 g. dextrin	.00007	.005 $Ba(NO_3)_2$	.1242	Immed. ppt.
10 cc. Pt sol V	.00007	....	.0840	
10 cc. Pt sol V	.00007	.01 KNO_3	.0840	Immed. ppt.
10 cc. Pt sol V	.00007	.002 $La(NO_3)_3$	.0833	Immed. ppt.
10 cc. Pt sol V	.00007	.004 $La(NO_3)_3$	.0750	Immed. ppt.
16 cc. Pt sol VI	0	......	.1202	...
16 cc. Pt sol VI	0	.0002 $KClO_4$	.1190	Some ppt.

TABLE X

EFFECT OF NITRAMIDE CONCENTRATION ON THE RATE

15 cc. Au sol II in 50 cc.; 0.00006 M HCl		30 cc. Au sol IIA in 50 cc.; 0.000136 M HCl	
$C_{H_2N_2O_2}$, M	k^a	$C_{H_2N_2O_2}$, M	k^a
0.00333	0.186	0.00333	0.0338
.00571	.126	.00667	.0237
.010	.0823	.010	.0191
.0133	.0613	.0133	.0144
.0167	.0571	.0167	.0109
.020	.0437	.020	.0091

[a] Corrected by subtracting spontaneous rate constant, 0.00162.

that the rates are independent of the concentration.

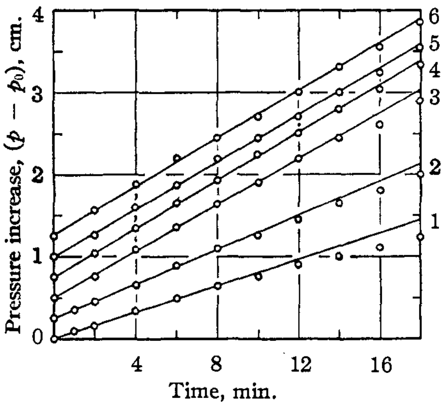

Fig. 9.—Expts. with Au sol IIA (Table X). Curves 2, 3, 4, 5, 6 (see numbers at right) are shifted upward 0.25, 0.5, 0.75, 1.0 and 1.25 cm., respectively.

In all the following experiments the "rate constant" k was determined as above, *i. e.*, the slope of the straight line drawn through the first few points of the plot of $(p - p_0)$ *versus* time was divided by $(p_\infty - p_0)$ for the experiment in question.

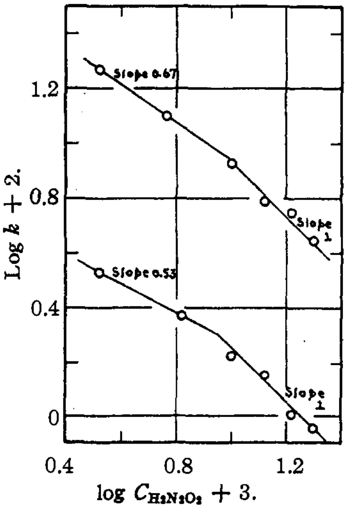

Fig. 10.—Dependence of rate constant on initial nitramide concentration.

Variation of Gold Concentration.—Two series were run with varying gold concentrations, as shown in Table XI. Values of k are plotted *versus* gold concentration in Fig. 11. The measured catalytic effect increases somewhat with the gold concentration, and the ratio of the rates decreases with increasing gold content (5.3 at 5 cc., 4.4 at 30 cc.). These effects cannot be accounted for by uncertainty in the acid concentration, especially in the second series; nor is it logical to assume that an appreciable fraction of the acid is removed from the solution by adsorption.

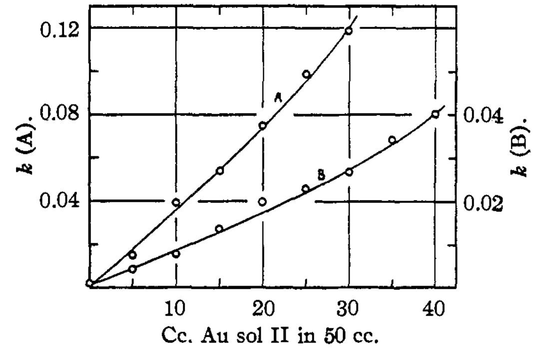

Fig. 11.—Variation of gold concentration: (A), 0.0002 M HCl; (B), 0.0007 M HCl.

TABLE XI

EFFECT OF GOLD CONCENTRATION

C_{HCl} = 0.0002 M, $C_{H_2N_2O_2}$ = 0.01 M		C_{HCl} = 0.0007 M, $C_{H_2N_2O_2}$ = 0.01 M	
Cc. Au sol II in 50 cc.	k	Cc. Au sol II in 50 cc.	k
0	0.00162	0	0.00162
5	.0146	5	.00417
10	.0386	10	.00765
15	.0538	15	.0136
20	.0746	20	.0196
25	.0991	25	.0229
30	.1189	30	.0267
		35	.0342
		40	.0403

Effect of Hydrochloric Acid Concentration.—Experiments were carried out, with Au sol I, in which various concentrations of acid were added with a fixed concentration of gold. Rate constants are given in Table XII. The effect of the acid is seen to be very similar to that with the platinum sols. In Fig. 12, values of k are plotted *versus* $(C_{HCl} - C^0_{HCl})^{0.4}$ and a satisfactory linear

TABLE XII

EFFECT OF HYDROCHLORIC ACID CONCENTRATION

40 cc. Au sol I in 50 cc. 0.01 M $H_2N_2O_2$

C_{HCl}, M	k^a
0.00008	0.0213
.00008	.0228
.00013	.0160
.00018	.0159
.00028	.0110
.00048	.00753
.00068	.00615
.00108	.00535
.00208	.00401

[a] Corrected for spontaneous rate.

relation is obtained except for the two highest concentrations. These two points will be discussed later.

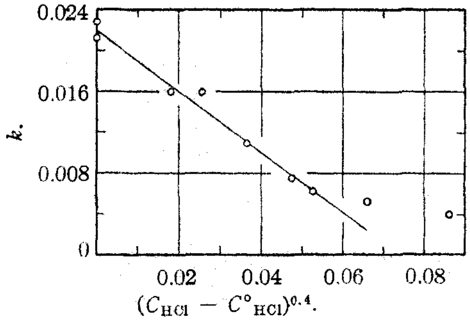

Fig. 12.—Effect of hydrochloric acid on catalysis by gold sol I.

Effect of Salts.—One series in which varying amounts of potassium perchlorate were added to solutions containing no added acid was discarded because the rates were very erratic, varying as much as 100% with the same salt concentration. Another series with 15 cc. sol II and sufficient hydrochloric acid added to make the total 0.0002 M gave much more consistent results. These rate constants are given in Table XIII. Experiments with added barium nitrate are shown in the same table. The effect of these salts is definitely different from the effect of acids and the other "poisons." Here the effect is a diminution of the rate (10% by potassium perchlorate, 20–30% by barium nitrate) at very low concentrations with little further effect until concentrations are reached which make the sols definitely unstable and cause their catalytic activity to fall off with time.

TABLE XIII

EFFECT OF ADDED SALTS

15 cc. Au Sol II in 50 cc. 0.0083 M $H_2N_2O_2$ initially. 0.0002 M HCl.

C_{KClO_4}, M	$C_{Ba(NO_3)_2}$, M	k	Remarks
..	..	0.0556	......
..	..	.0553	......
0.0001	..	.0502	No color change
.0005	..	.0516	No color change
.001	..	.0487	No color change
.003	..	.0371	Deeper red[a]
.005	..	.0273	Deeper red[a]
..	0.000025	.0402	No color change
..	.000025	.0374	No color change
..	.00005	.0374	Tinge of purple
..	.00005	.0387	Tinge of purple
..	.0001	.0465	Dark purple, no ppt.
..	.0001	.0407	Dark purple, no ppt.
..	.0005	.0216	Immed. ppt.
..	.005	.0171	Immed. ppt.

[a] After twenty hours there was no further change noticeable in the color. New nitramide samples in the same solutions gave k = 0.0327, 0.0137, respectively.

Discussion

It has been assumed in the foregoing that all adsorption equilibria involved were reached so rapidly as not to affect the rates. In the extreme, slow attainment of a "steady state" of adsorption or of decomposition in the adsorbed film would lead to autocatalytic rate curves. There was no evidence of such behavior, though the method used for following the reaction precluded investigation of the behavior during the first ninety to one hundred and twenty seconds after the reaction was started.

While the Freundlich adsorption isotherm is of such a nature that it can be made to fit experimental data in a variety of systems, the Langmuir expression has no such wide applicability. However, the fact that equation (2) can be used to express the rates of the experiments described here does not, of course, indicate that adsorption in these systems is of the type for which the isotherm was derived. Little is known of the nature of adsorption by colloidal particles, and experiments of this type offer no conclusive test.

While equation (3) expresses the action of "poisons" on the catalysis fairly well, its derivation is not very satisfactory. Although there has been little work on the influence of one adsorbable solute on the adsorption of another, there is evidence that while the Freundlich isotherm is still valid, both constants are changed.[11] The only test of this point available in these experiments lies in the constancy of the exponent

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(11) Freundlich, "Kapillarchemie," Akad. Verlagsges., 1930, Vol. 1, pp. 276–278. Freundlich and Masius, J. M. van Bemmelen Gedenkboek, Helder, 1910, pp. 88–101.

of equation (1) when various concentrations of "poison" are added to the solution.

None of the "poisons" added changed the value of m, so far as can be determined from the data of the individual experiments. However, measurements were taken over little more than the time of half decomposition in most of the experiments, and a variation of at least ten times in the concentration is needed to determine the exponent accurately.

An equation based on the Langmuir isotherm can be derived in the same manner as equation (3). It is

$$k' = k_0'\left(\frac{1}{1 + b' C_{\text{poison}}}\right) \qquad (4)$$

A plot of $1/k'$ *versus* C_{poison} should be linear if this equation is valid. Such plots are approximately linear for some of the systems studied, but usually there is a wide divergence at low concentrations. In Fig. 13 values of $1/k'$ for the data of Table V are plotted *versus* hydrochloric and nitric acid concentrations. While straight lines represent the results fairly well at concentrations above 0.0001 M there is a definite divergence below this value.

For the addition of hydrochloric acid to gold sol, Fig. 12 indicates a linear relation except for the points at 0.001 and 0.002 M acid. A plot of $1/k$ *versus* C_{HCl} is likewise approximately linear except for these two points. It seems probable that the upper limit of acid adsorption has been reached at these concentrations, but that nitramide can still be adsorbed to some extent. Neither equations (3) nor (4) would be valid under these conditions. Addition of 0.001 M acid changed the color of this sol little if any; 0.002 M acid changed its color to a clear purple, but caused no visible precipitation in twenty-four hours. These experiments were rather slow (half time eighty and one hundred and forty minutes) and coagulation or increase in particle size presumably would result in rates decreasing with time and lower than predicted rather than higher.

Since the nitramide decomposition is so sensitive to bases one might wonder if the effect of colloidal platinum and gold were not a basic catalysis. This does not seem to be the case; although acids reduce the catalysis, similar reduction is caused by many other reagents. Further, this reaction resembles the hydrogen peroxide catalysis, which is not sensitive to general acid or basic catalysis. Also, while the platinum sol particles contain oxide or hydroxy anions, these are anions of strong acids and consequently are exceedingly weak bases; the corresponding ions in the gold sol (as perhaps $AuCl_4^-$) are also anions of strong acids. The possibility remains that the catalysis is initiated by the the free electrons of the metal, as suggested by Weiss for hydrogen peroxide.[5]

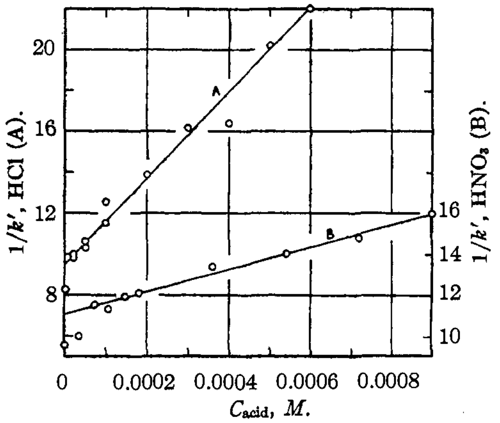

Fig. 13.—Reciprocal of rate constant *versus* acid concentration: A, HCl; B, HNO_3.

The results obtained parallel those in the literature on the hydrogen peroxide catalysis when the latter are not too fragmentary or obviously too irreproducible to allow a comparison. Bredig and Ikeda[12] found an exponential equation for the effect of "poisons"

$$g = \alpha C_{\text{poison}}^{\beta}$$

where α and β are constants, and g the relative increase in half-time of the decomposition caused by the "poison." Iredale[13] states that with gelatin present a plot of log % inhibition *versus* log % gelatin is linear, which suggests an equation similar to (3). Bredig and Müller[14] found that the catalytic activity of a platinum sol decreased with time in the presence of 0.01 or 0.02 M hydrochloric acid, potassium chloride or sodium hydroxide. The effect of acids has not been studied thoroughly; Bredig and Müller reported a 30% decrease in catalysis by 0.01 M nitric acid, 90% decrease by 0.01 M hydrochloric acid, while Bredig and Ikeda found nitric acid to increase the catalysis.

Bredig and Müller also found that the catalysis was not proportional to the platinum concentration, but increased relative to the latter (*cf.*

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(12) Bredig and Ikeda, *Z. physik. Chem.*, **37**, 1 (1900).

(13) Iredale, *J. Chem. Soc.* (London), **121**, 1536 (1922).

(14) Bredig and Müller, *Z. physik. Chem.*, **31**, 255 (1899).

Figs. 4 and 11). For some of their results they found the following equation to hold

$$\frac{k_1}{k_2} = \left(\frac{C_{\mathrm{Pt.}\,1}}{C_{\mathrm{Pt.}\,2}}\right)^b$$

The experiments reported here indicate a fundamental difference in the action of acids and of salts on platinum and gold sols. They indicate that acids (or hydrogen ion) may be adsorbed in a manner similar to iodine and other substances of molecular or ionic nature; in sufficiently high concentration they coagulate the colloid by virtue of their ionic charges much as salts do. If the salts can be said to be adsorbed, it seems to be another type of adsorption which has relatively little effect on the portion of the surface active in catalysis.

The role played by the particle size of the colloid is rather obscure. Gold sol II showed a much greater catalysis per unit of gold than sol I in spite of the greater acidity; this was presumably due to greater dispersion of the gold. On the other hand, coagulation would be expected to decrease the surface area, but it seems that the initial coagulation may actually lead to a temporarily greater active surface.

The author takes this opportunity to express his gratitude to Professor J. N. Brönsted, who suggested this work and whose interest and aid made possible its completion.

Summary

Colloidal and finely divided platinum and gold have been shown to have a pronounced catalytic effect on the decomposition of nitramide in aqueous solution. In suitable solutions 10^{-6} g./cc. of these metals may increase the normal decomposition rate two to ten times. The platinum sols used were more active catalysts than the gold sols, but the activity varies a great deal with the history of the individual sol and especially its content of acids and other reagents.

The mechanism of the catalysis has been explained as a rapid decomposition of nitramide adsorbed by colloidal particles. The effect of "poisons," including strong acids, iodine, dextrin and glucose has been explained as due to preferential adsorption with displacement of the nitramide. The colloidal metal catalysis has been shown to resemble similar catalysis of hydrogen peroxide decomposition.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF YALE UNIVERSITY]

Viscosity and Chemical Constitution

BY MOTT SOUDERS, JR.[1]

Previously, the most successful attempts to define relationships between the viscosity and the chemical constitution of organic liquids have been based on comparisons at constant temperature,[2] at the temperature of equal viscosity–temperature slope,[3] or at equal fluidity.[4] These restrictions have made viscosity comparisons difficult and have limited seriously the usefulness of the relationships between viscosity and chemical constitution.

Viscosity Density Constant.—For a wide range of organic liquids, plotting the logarithm of the logarithm of the viscosity at constant pressure (in millipoises) against the density (in grams per cc.) gives substantially a straight line for each compound. The curvature usually increases in the vicinity of the melting point or boiling point, but over the intermediate range the function is nearly linear. An examination of such plots for a large number of compounds shows that although the slopes vary widely among the different liquids, the intercepts are nearly equal so that an average value of -2.9 may be used for all organic liquids. These observations lead to a general viscosity–density equation

$$\log_{10} (\log_{10} \eta) = md - 2.9 \qquad (1)$$

in which η is viscosity in millipoises at atmospheric pressure; m is a constant characteristic of each liquid; and d is density in grams per cc.

Although an equation of the general type

$$\eta = Ae^{Be^{Cd}} \qquad (2)$$

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[1] Sterling Fellow in Chemical Engineering.

[2] Dunstan and Thole, "The Viscosity of Liquids," Longmans, Green and Company, London, 1914, p. 36.

[3] Thorpe and Rodger, *Phil. Trans.*, **A185**, 397 (1894); *Proc. Roy. Soc. (London)*, **A60**, 152 (1896).

[4] Bingham and Harrison, *Z. physik. Chem.*, **66**, 1 (1909); E. C. Bingham, THIS JOURNAL, **33**, 302 (1910).