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CATALYTIC HYDROGENATION WITH PROTECTED HYDROSOLS.

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Applications of colloidal platinum and more especially of colloidal palladium as catalytic hydrogenating agents have now become general in many organic syntheses. The hydrosols prepared by reduction with hydroxylamine salts are usually protected by Paal's method with the sodium salts of protalbic and lysalbic acids. These colloids have been used by Paal and his co-workers[1] in a great variety of reduction processes but other protective colloids possessing low gold numbers such as gelatine, gum arabic, or casein may be employed.

Catalysts prepared according to Paal's method are found to be extraordinarily stable both towards temperature changes and to the presence of electrolytes, but they are very variable in activity. It was formerly thought[2] that the protective effect of the colloid was due to mutual absorption, resulting in the formation of a coating over the metal surface by the protective colloid, while Bancroft[3] identifies protective action with peptization, indicating the disintegrating or peptizing action of the protective colloid in a great number of instances.

When colloidal sols are employed for catalytic purposes the choice between Freundlich's theory and that of Bancroft as to the mechanism of protection becomes one of great importance. According to Freundlich's point of view the activity of a colloidal catalyst should fall on the addition of the protecting agent since the active surface of the catalyst become covered with the inert protector. On the theory of peptization, on the other hand, the addition of small amounts of the protective agent should peptize the colloid metal and thus increase its surface and consequently its activity should *rise*; after the addition of the optimum amount of peptizing agent, this amount being governed by various factors such as the magnitude of the various interfacial surface tensions and the viscosity of the medium which affects the Brownian movement, the metal sol is peptized as far as possible. Subsequent addition of the peptizing agent can now no longer increase the surface of the sol but will commence to cover up the free surface of the metal, with a consequent decrease in catalytic activity.

It appeared probable that this preliminary rise and subsequent fall in catalytic activity on the progressive addition of a protective colloid, which was to be anticipated on Bancroft's hypothesis should be capable of experimental determination; such was found to be the case in the cata-

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[1] *Ber.* (1902); especially *Ber.*, **39**, 26 (1904); **41**, 818 and 2281 (1908); **42**, 2239 (1909); **48**, 994 (1915).

[2] Freundlich, "Kapillarchemie," p. 455.

[3] *J. Phys. Chem.*, **20**, 85 (1916).

lytic reduction of phenyl propiolic acid utilizing both platinum and palladium hydrosols with gum arabic as protective colloid.

Influence of Concentration of Peptizing Agent.

The general method of procedure was as follows. Ten cc. of a solution of palladium or platinum chloride containing 10 mg. of the metal was carefully neutralized with sodium carbonate and to the solution a known amount of gum arabic was added in the form of a solution containing one mg. per cc.; the salt was subsequently reduced with hydroxylamine prepared from hydroxylamine sulfate. To the protected sol 10 cc. of a solution of the sodium salt of phenyl-propiolic acid was added, the salt being prepared from the pure acid and the solution containing 14.8 g. per liter of the acid. The mixture of protected sol and sodium phenylpropiolate was then run into an Erlenmeyer flask and shaken continuously in an atmosphere of hydrogen, prepared by electrolysis of a solution of sodium hydroxide and from which all traces of oxygen had been carefully removed. The rate of absorption of the hydrogen was measured by the rate of flow of water from a buret into a small Erlenmeyer flask connected with the absorption vessel and a manometer. The experiments were conducted at 15° and a blank run of 4 hours duration indicated that the rate of diffusion of the hydrogen through the flexible rubber connection was negligible. The rates of absorption with various amounts of gum arabic as protective colloid are indicated in the following curves, each representing the mean of 3 experiments. As typical of one determination the following may be cited:

Catalyst, 10 mg. Palladium Protected with 2 mg. of Gum Arabic. Temp. 15°.

Time.				
H.	m.	s.	t.	Cc. of water run into compensate for contraction.
1	2	50	0	0
	27	20	2.2	10
	28	36	3.6	15
	30	0	5.0	20
	31	42	6.7	25
	33	30	8.5	30
	35	0	10.0	35
	36	54	11.9	39
	38	48	13.8	43
	40	54	15.9	47
	43	18	18.3	51
	46	0	21.0	55
	50	18	25.3	60
	54	30	29.5	64
	58	30	33.5	68
2	3	0	38.0	72
	8	30	43.5	76
	16	18	51.3	80
	31	18	66.3	84

It will be noted that there is an optimum concentration of gum arabic for each catalyst, 2 mg. per 10 mg. for palladium and for the like amount of platinum 4 mg. is required; since the atomic weight of platinum is practically twice that of palladium this latter metal is peptized 4 times as easily as the former. It seems probable however that the phenylpropiolic acid assisted in the peptizing of the colloid, since, when only small concentrations of gum arabic were employed, the sol would usually flocculate toward the end of the run, an indication that the unsaturated acid took part in the peptization but that the saturated acid was less active in this respect, an hypothesis in accord with the accepted views on the chemical nature of adsorption phenomena.

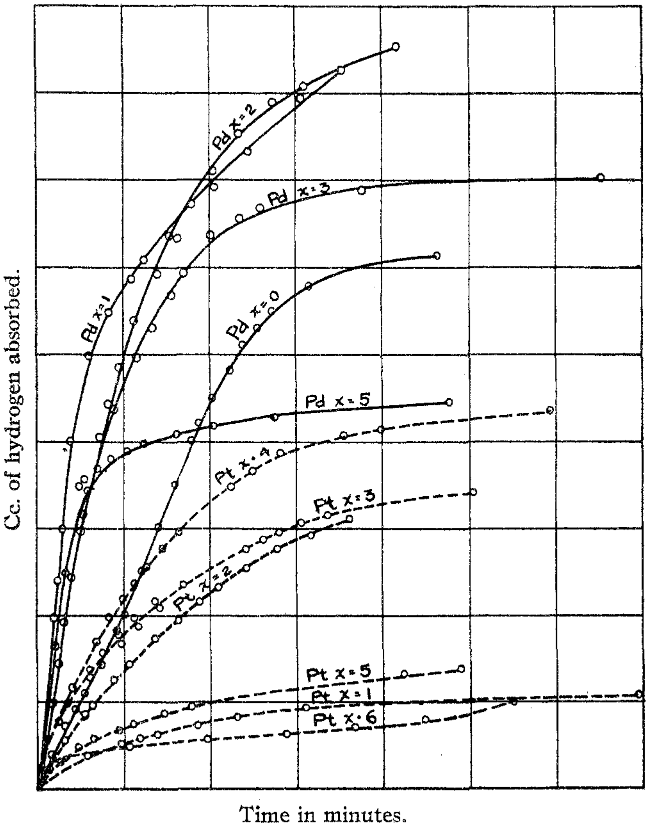

Fig. 1.

x = mg. of gum arabic per 10 mg. of metal.

Influence of Promoters.

It has long been known that the addition of small quantities of similar substances to a catalyst considerably augments its catalytic activity.

For this so-called promoter action there is as yet no adequate explanation and the study of the phenomenon has been confined chiefly to massive catalysts. It was, therefore, thought of interest to investigate the mutual effect of 2 somewhat similar substances platinum and palladium when reduced together in the sol form.

A series of runs was made in which 10 mg. of the mixed metals in various proportions were precipitated together in the sol form. As stabilizing colloid 3 mg. of gum arabic was employed, this concentration permitting each metal in the pure state to exert almost its maximum activity. The results of these experiments are depicted in Fig. 2.

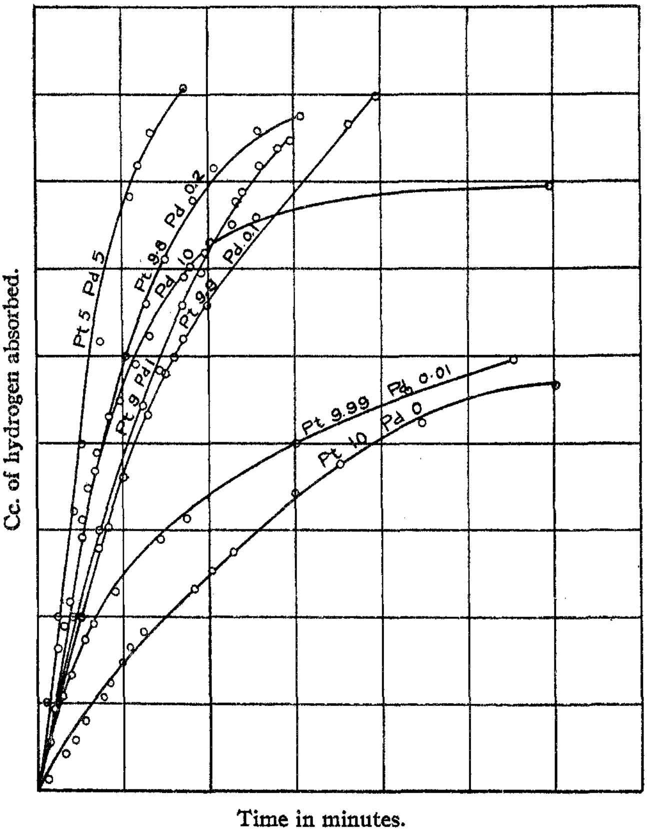

Fig. 2.

It was noted in all cases where the sol was prepared from the mixed metals, especially from platinum containing small quantities of palladium that there was a very marked improvement in stability and resistance to age over those prepared from the pure salts. This suggests the hypothesis that promoters may in part function as peptizing agents for colloidal catalysts, or for catalysts which pass through a colloidal stage at some point in their preparation.

For this reaction there is a steady increase in the catalytic activity of platinum sol on the addition of small quantities of palladium until a concentration by weight of 9.8 mg. of platinum to 0.2 mg. of palladium is reached. At this point it would appear that there is a slight decrease in activity until a ratio of 9 mg. of platinum to one mg. of palladium is reached followed by a rise to the ratio 5 mg. to 5 mg. which appears to be a maximum, the activity then slightly sinking for pure palladium. These latter differences are, however, so slight as to be within the region of experimental error, since such factors as the partial or complete removal of the carbon dioxide resulting from the neutralization of the acid chloride by means of sodium carbonate, the temperature of reduction and the age of the sol, all exert by no means inappreciable effects on the catalytic activity. It is evident, however, that a mixed sol containing about 9.8 mg. of platinum to 0.2 mg. of palladium (atomic ratio 26 to 1) is practically as active as a pure palladium sol in the hydrogenation of phenyl-propiolic acid.

The curves obtained in the first 2 series of experiments represent the combined effects of 2 reactions, the absorption of hydrogen by the metal and the hydrogenation of the acid. The experiments of Paal and Gerum[1] indicated that the precipitated sol protected with sodium protalbate and brought into the sol form again with a trace of alkali took up relatively small quantities of hydrogen, the figures obtained approximating to the composition PdH for palladium black to $Pd(H)_2$ for the protected sol under a pressure of one atmosphere of hydrogen. Experiments with the sols of palladium and platinum protected with small quantities of gum arabic, and which had not been precipitated and repeptized indicated that under these conditions very much larger quantities of hydrogen could be taken up: thus a mixture of 9 mg. of platinum and one mg. of palladium prepared by direct reduction in the presence of 3 mg. of gum arabic absorbed 80 cc. while 5 mg. of platinum and 5 mg. of palladium absorbed 106 cc. of hydrogen, equivalent to the formation of the hypothetical compounds $Pd(H_2)_{65}$ and $Pt(H_2)_{65}$ under one atmosphere pressure. (A large excess of hydroxylamine was not used in the precipitation of the sols.) It is interesting to note that the atomic absorption of both platinum and palladium under these conditions is identical.

A number of experiments in which the hydrogen absorption curves were obtained first for the metal sol and then for the hydrogenation of the sodium phenyl-propiolate which was subsequently added to the hydrogenated sol indicated that the hydrogenation of the sol took place relatively quickly and at the same speed for both platinum and palladium while the subse-

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[1] *Ber.*, 41, 818, 2281 (1908).

quent hydrogenation of the unsaturated acid proceeded rapidly in the case of palladium and but slowly in the presence of platinum, as is instanced by the following figures.

Catalyst:	10 Mg. Platinum.			10 Mg. Palladium.			
Time. Min.	Cc. H_2 absorbed by catalyst.	Time. Min.	Cc. H_2 absorbed by acid.	Time. Min.	Cc. H_2 absorbed by catalyst.	Time. Min.	Cc. H_2 absorbed by acid.
0	0	0	0	0	0	0	0
1.5	4	6.5	2	1.5	12	1	20
3	8	14	4	3.0	24	2.5	28
4.3	12	20.5	6	4.1	36	3	35
5.5	16	29	8	5	40	4	40
7.3	20	37	10	5.5	48	7.5	43
11.5	28	....	..	9	56	15	45
16	36	....	..	11.5	60	20	45.7
21	44	....	..	20	68	...	....
26	52	....	..	32	74	...	....
34	60	....	..	41	78	...	....
42.5	68	....	..	48.5	80	...	....
52.5	76	....	..	....	..	...	....
Catalyst:	5 Mg. Palladium.		5 Mg. Pt.	9 Mg. Platinum.		1 Mg. Palladium.	
0	0	0	0	0	0	0	0
1.2	8	1.5	8	2	12	2	8
4.5	20	3.2	16	4.75	20	3.5	12
7.5	28	5	24	7.75	28	5.5	16
10.5	36	7.3	32	11.25	36	7.5	20
13.5	44	9.5	40	16	44	15	28
17.3	52	11.7	48	22.3	52	20	32
22	60	15	51	30.75	60	27	36
27	68	20	52	44	68	31	38
34	76	30	53	52	70	36	40
43.5	84	....	..	....	..	...	....

It will be noted that all the curves are of the same type, linear over a great part of their course approaching logarithmic towards the end. This type of curve appears to be general for a large number of colloidal catalytic processes. Bredig and von Bernick and Groh[1] found in the decomposition of hydrogen peroxide with colloidal platinum, both unprotected and protected that the family of decomposition-time curves obtained could be represented by the relationship $dx/dt = K(a - x)$ where a is the initial and x the concentration of peroxide at a time t. This expression holds for a monomolecular chemical reaction or for a process in which diffusion is operative. That the diffusion is an important factor is seen from the work of Groh who found that the K values lessened with progressive addition of gelatin to the platinum sol, but showed, however, the usual irregularities noted above. Paal's values for the hydrogenation of cinnamic acid[2]

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

[2] *Ber.*, **41**, 2276 (1908).

in a constant pressure hydrogen atmosphere also show a general approximation to a curve of the above type, while if his values for the combination of hydrogen and ethylene (equal volumes) in the presence of colloidal platinum and palladium[1] be plotted, it will be found that the curve, in the case of a fresh palladium sol, approximates to a bimolecular reaction, and with platinum between a bi- and a monomolecular reaction.

F. Armstrong and Hilditch[2] found that the absorption time curves for the hydrogenation of various unsaturated glycerides in the presence of colloidal nickel, were nearly linear and showed distinct curvature only when saturation was nearly completed. These observers came to the conclusion that a great part of the absorption curve could be represented by the expression $dx/dt = K$ and inferred that a nickel oleate adsorption complex of constant active mass was formed, the observed rate of reaction being that of the less reactive hydrogen under constant pressure reacting with the complex; the subsequent falling off in the rate being due to the interference by the saturated glyceride formed in the process. The following figures indicated a few of the values of K as calculated from the expression $dx/dt = K(a - x)$ for the hydrogenation of phenylpropiolic acid.

Catalyst, 10 Mg. of Platinum. 10 Mg. of Palladium. 9.5 Mg. of Platinum, 0.5 Mg. of Palladium protected with 3 Mg. of Gum Arabic.

Time, M.	*x*.	*K*.	Time.	*x*.	*K*.	Time.	*x*.	*K*.
10	0	0.0090	5	20	0.0183	5	14	0.0129
20	16.2	0.0089	10	32	0.0158	10	20.5	0.0130
30	21.6	0.0086	15	41.5	0.0162	15	36	0.0127
40	26	0.0085	20	46.7	0.0128	20	44	0.0124
50	30.7	0.0088	30	57	0.0112	30	53.5	0.0109
60	35	0.0094	40	64	0.0102	50	62.3	0.0085
70	37.5	0.0094	50	66.7	0.0089	60	64.9	0.0060
80	41.2	0.0099	60	68.2	0.0076	70	66.5	0.0067
100	44.8	0.0176	80	69	0.0066	80	67.5	0.0060
			80	69.5	0.0060			

It would appear from an analysis of these various examples that the rate of chemical reaction at the protected colloid surface is not governed so much by the formation of a colloid-reactant complex to which the other reactant diffuses and reacts with it but primarily by the rate of diffusion of both of the reactants to the colloid surface, thus in the case of the decomposition of hydrogen peroxide or in the various hydrogenating reactions under constant hydrogen pressure the reactions approximate to a monomolecular chemical reaction in form, being in reality a diffusion process. In the ethylene hydrogen reaction, where the reaction is governed by the rate of diffusion both reactants a pseudochemical bimolecular

[1] *Ber.*, **48**, 994 (1915); **42**, 2239 (1909).

[2] *Proc. Roy. Soc.*, **96A**, 137 (1919).

reactant results. The values of K, the reaction velocity coefficient or the diffusion coefficient can, however, be made extremely small by coating the colloid with a relatively thick layer of protective colloid.[1] by using as reaction medium a very viscous substance having a low diffusion coefficient such as oil, or by employing reactants which diffuse very slowly.

For small values of K the alteration in the reaction velocity dx/dt with the alteration in the concentration of the reactant in the environment $(a - x)$ will be inappreciable, and the curves will degenerate into the limiting form $dx/dt = K$ over a very considerable range of their existence. This phenomenon is likewise noted with old colloidal sols where the active surface is presumably well coated. A progressive deterioration in the type of curve is noted in the following cases, hydrogen peroxide, ethylene, cinnamic acid, phenylpropiolic acid and glyceryl oleate, coinciding with a decrease in the value of the diffusion coefficients.

The values of K obtained in this manner are, however, only very approximate, since there may ensue an alteration in the effective surface of the catalyst during the reaction, either an increase[2] due to continued peptization of the colloid during the reaction or more generally a decrease, as noted in a variety of reactions. This decrease is in part due to the presence of the products of the reaction lowering the rate of diffusion of the reactants to the surface[3] but it may also be due to the products of the reaction becoming absorbed to the surface of the catalyst as suggested by Langmuir, and thus decreasing the effective catalytic area. It is, however, to be expected, that the form of curves obtained may be interpreted on either of these hypotheses with equal facility.

Summary.

The effect of a protective colloid on the reaction velocity of a hydrogenation process in the presence of colloidal platinum and palladium has been studied and the results lead to the conclusion that the protective colloid functions as a peptizing agent, in agreement with Bancroft's hypothesis.

The addition of a small quantity of a palladium sol to a platinum sol greatly enhances is activity, and it is suggested that promoter action may in part be due to peptization.

The mechanism of catalytic actions in the presence of colloidal metal appears to conform rather to the diffusion hypothesis than to the colloid reactant complex theory. Abnormalities are equally explicable on the single layer theory as on the view that the retardation of diffusion is caused by the products of the reaction.

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[1] See Groh, *loc. cit.*, and Fig. 1.

[2] Expt. 1; and Groh, *loc. cit.*

[3] Armstrong and Hilditch, *loc. cit.;* Fink, on the oxidation of SO_2; Bodenstein and Ohlmer on the oxidation of CO.