

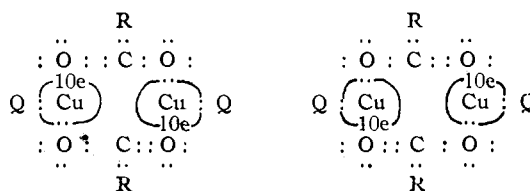
$$\text{with } k_2 > k_1' > k_1 > k_3$$

k_1' is set larger than k_1 since the equilibrium of (b) must be far to the left as evidenced by the only very small effect of cuprous acetate on the solubility of hydrogen in quinoline.

The temperature coefficient of the hydrogenation includes the shift of the equilibrium (a₂) as well as the change of the rate k_1 . This shift of equilibrium affects the rate in the opposite direction from the change in k_1 . If one makes a correction for this shift in equilibrium using the heat of dissociation of 10 kcal. previously calculated, one finds that the activation energy of k_1 is increased only slightly and probably is very close to 14,000 cal.

Thus it seems quite reasonable that the cu-

prous acetate is at least partially dimeric in solution, although the possibility of a higher polymer is not eliminated. The structure of this dimer analogous to that of other carboxylate dimers can be represented by a number of valence formulas containing chelated copper.



Any further speculation concerning the properties of such a dimer awaits an independent demonstration of its existence.

Summary

It has been shown that probably a dimer of a cuprous acetate-quinoline complex is responsible for the activation of molecular hydrogen in the homogeneous catalytic hydrogenation of quinone in solution.

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[CONTRIBUTION FROM THE JOHNSON CHEMICAL LABORATORIES, UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA]

The Composition of the Colloidal Platinum Micelle

BY S. W. PENNYCUICK

Evidence brought forward by the author^{1,2} has shown that the particles of colloidal platinum are composite in nature, containing platinum, platinum oxide and hexahydroxyplatinic acid.

This has now been confirmed by the microchemical analysis of the coagulated particles; and the relative amounts of the three constituents have been determined. The composition of the micelle in an average Bredig preparation is given by the formula $[3.9 \text{ Pt}, 1.16 \text{ PtO}_2, 1.0 \text{ H}_2\text{Pt}(\text{OH})_6]_n$.

Isolation of the Micelle.—The sols were prepared from conductivity water by the Bredig method,³ and the particles were isolated by coagulating the sol by freezing and then thawing the mixture.⁴ In the preparation of the sol and in the isolation of the micelle no foreign electrolyte was added, nor was any foreign matter allowed to

enter. The micelle was thus obtained in as pure a form as possible.

The particles in the frozen coagulum were sufficiently compact to settle readily; they were therefore washed free from the mother liquor by decantation, and allowed to drain and dry. Filtering was avoided.

Preliminary Observations.—In the previous work^{1,2} it was not possible to decide whether the self-formed acid which acted as stabilizing electrolyte was hexahydroxyplatinic acid or one of its dehydration products. Now, however, the indications are fairly clear that the acid in the micelle is in its most highly hydrated form, namely, $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$ or $\text{H}_2\text{Pt}(\text{OH})_6$. This is based on the following observations.

First, the weight of any one sample of the air-dried micelle varies slightly from day to day. The changes are not in one direction, but appear to follow variations in the atmospheric vapor pres-

(1) Pennykuick, *THIS JOURNAL*, **52**, 4621 (1930).

(2) Pennykuick, *J. Chem. Soc.*, 1447 (1930), and previous papers.

(3) Pennykuick, *Aus. J. Exptl. Biol.*, **4**, 99 (1927).

(4) Pennykuick, *J. Chem. Soc.*, 2108 (1928).

sure. This is in keeping with the behavior of the highest hydrate, $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$; for Wöhler⁵ and Bellucci⁶ have shown that it is the only hydrate of PtO_2 which suffers partial dehydration at low temperatures.

Second, when a sample of the micelle is placed in a desiccator over sulfuric acid there is a steady loss in weight, which after some weeks attains a maximum of 2.6% (see Table IA). Analysis (detailed later) shows that this loss is equal to approximately one-half the total water content. This again indicates that the highest hydrate is present in the micelle; for Wöhler⁵ has shown that $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$, when dehydrated by sulfuric acid, yields $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$, thereby losing half its water.

TABLE I

Loss in weight of the platinum micelle, (A) on standing in desiccator, (B) on heating.

(A) In desiccator			(B) On heating			
Time	Wt., mg.	% loss	Treatment °C.	Time	Wt., mg.	% loss
....	34,445	34,194	..
4 hours	33,890	1.61	100	10 min.	33,714	1.40
2 days	33,700	2.17	110	4 hrs.	33,291	2.60
6 days	33,625	2.38	160	4 hrs.	33,033	3.40
20 days	33,570	2.54	400	1 hr.	32,538	4.84
23 days	33,550	2.60	Ignited		31,130	8.96

Third, when the micelle is strongly heated, all the water is driven out. Actually it appears to come out in fractions (see Table IB). Approximately one quarter comes out readily at 100°; the next quarter less readily after heating at 110° for four hours; the third quarter requires a temperature of 160° for four hours; whilst the final quarter is difficult to remove, requiring to be kept for an hour at a temperature of 400°. (Analysis, details of which are given later, shows that the further loss on ignition which appears in the last line of the table is due to the decomposition of the oxide. All the water is given up at 400°.)

This fractional decomposition is in agreement with the behavior of $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$ as recorded by Wöhler, who has shown that under the action of heat the dehydration becomes progressively more difficult as the hydrate moves from $4\text{H}_2\text{O}$ to $3\text{H}_2\text{O}$ to $2\text{H}_2\text{O}$ to $1\text{H}_2\text{O}$, the last hydrate being very resistant to heat.

These three results taken together indicate that all the water in the micelle is in the form of the hydrate $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$.

Analysis of the Micelle.—The air-dried micelle was used in all cases. The slight variations in initial weight

were smoothed out by taking a series of analyses over several days. Constancy in weight could not be secured except at the cost of dehydrating the particles.

It proved desirable to separate the water estimation from that of the oxygen, since a quick heating was necessary to determine the former, and a slow ignition to obtain the latter.

In the water estimation, about 30 mg. of the air-dried micelle was heated rapidly to a temperature well over 400°, and the water quickly and completely expelled. The heating was carried out in a platinum boat in a shortened combustion tube using an adaptation of the microchemical combustion chain. A stream of purified nitrogen was passed continuously through the apparatus at the rate of one bubble every two seconds, and the expelled water was collected and weighed in a calcium chloride tube with the usual microchemical precautions. Two blank tests preceded each estimate, followed by a final blank.

In the oxygen estimation, on the other hand, a fresh sample of the micelle, from 10 to 15 mg., was heated very slowly to 600°, at which temperature, apart from the water being driven out, all the platinum oxide was completely decomposed into platinum and oxygen. The sudden decomposition of the oxide at about 550° was characteristic and rather striking. The micelle, with or without the water, was brown-black in color, but as the oxygen was expelled it changed almost instantaneously to light gray.

The heating was carried out slowly in order to avoid loss of weight by spluttering. The sample was then reweighed, the total loss in weight being made up of the water expelled together with that of the oxygen. As the former already had been determined, the oxygen content was at once obtained by difference. The micelle was finally ignited, but it seldom showed any further loss in weight.

A preliminary method in which the oxygen was determined as water after reduction with a stream of hydrogen was abandoned as it proved to be unreliable. The present method, however, has proved satisfactory and accurate.

The analyses of a number of different preparations are set out in Table II (i). From these it is seen that the micelle suffers a total loss in weight (at 600° or on ignition) of from 10.2 to 12.1%. Approximately one-half of this is due to the water given up by the complete dehydration of the hexahydroxy acid, and the remainder to the oxygen expelled by the decomposition of the platinum oxide.

Numerous freshly made sols (all prepared by the Bredig method) were analyzed. Four characteristic analyses (A, B, C and D in Table II (i)) are set out. Two very old samples of micelles that had been isolated ten years previously were also analyzed. One of these (F) had been kept under water, and the other (G) had been stored in the dry state. The analysis shows that over the ten-year period, although each suffered some slight variation, neither showed any abnormal change.

Calculation of the Formula.—A representative formula is quite sufficient. This can be obtained by using the average results for the micelles from the four freshly made sols, all of which were made under exactly the same conditions. These four sols (A, B, C and D in Table II) show an average water content of 5.4%, and an oxygen content of

(5) Wöhler, *Z. anorg. Chem.*, **40**, 423 (1904).

(6) Bellucci, *ibid.*, **44**, 168 (1905).

TABLE II

All sols made under the same set of conditions: 220 volts, 5 amps., 15 mins. arcing time.

Description	Weight, mg.	Loss at 600° (or on ignition) Loss	% loss	H ₂ O expelled		O ₂ expelled (by dif.)	
				H ₂ O	% H ₂ O	O ₂	% O ₂
(i) Analysis of the colloid micelle							
A Freshly made	27,680	2853	10.3	1440	5.20	1413	5.10
B Freshly made	29,536	3013	10.20	1500	5.09	1513	5.11
C Freshly made	24,056	2644	10.99	1364	5.66	1280	5.32
D Freshly made	25,449	2779	10.92	1433	5.63	1346	5.29
E Three months old	31,872	3870	12.14	1958	6.14	1912	6.00
F Ten years old (wet)	30,486	3199	10.50	1707	5.60	1492	4.89
G Ten years old (dry)	23,157	2452	10.58	1401	6.05	1051	4.53
(ii) Analysis of the precipitate formed on boiling or aging							
Fresh sol (unboiled)	25,980	1557	6.00	870	3.34	687	2.66
Fresh sol (boiled)	30,074	1224	4.15	627	2.09	617	2.06
(iii) Analysis of the residue in the Bredig vessel							
Gray residue	34,783	72	0.21	20	0.06	52	0.15

5.2%. One thousand parts by weight of the colloid micelles thus contain 894 parts of platinum, 52 of oxygen and 54 of water.

Writing the constitution of the micelle as $[xPt, yPtO_2, zH_2Pt(OH)_6]_n$, a simple calculation gives the values of x , y and z as 576, 199 and 225 g., respectively. Converting the values into gram molecules, the formula becomes $[3.9 Pt, 1.16 PtO_2, 1.0 H_2Pt(OH)_6]_n$.

The Free Hexahydroxyplatonic Acid.—Quite apart from the hexahydroxy acid in the micelle, there is a further quantity which exists in solution as free electrolyte and which is responsible for practically the whole of the conductivity of the sol. The amount so present can be calculated directly from the specific conductivity.

For example, the freshly prepared sols (A, B, C and D in Table II) have an average specific conductivity (after boiling) of 12.2 gemmhos measured at 25°. Using 349 and 43 as the respective mobilities of the hydrogen ion and the hexa acid anion (and assuming complete ionization), the concentration of the hexa acid is calculated as 0.0046 g. per liter.

One liter of the above sol is found (by analysis) to contain 97 mg. of the micelle. The free hexa acid is thus 4.7% of the weight of the micelle, whereas the combined acid (from the figures already given) is 22.5% of the micelle weight. There is thus five times as much hexahydroxyplatonic acid bound up in the micelle as there is in the free state.

On continued boiling, or even on aging, some of the combined acid passes into solution. The relative amounts can be calculated at any time from the conductivity figures and from the micelle analysis. These have been determined

in various cases and are set out in Table III.

TABLE III

DISTRIBUTION OF THE HEXAHYDROXYPLATONIC ACID BETWEEN THE PARTICLES AND SOLUTION

Total acid present is 27.2% of the weight of the particles.

Treatment	Acid combined in micelle, %	Acid free in solution, %	Spec. conduc. in gemmhos.
Freshly made	25.4	1.8	4.7
Boiled 0.5 hour	22.5	4.7	12.0
Boiled 30 hours	20.2	7.0	17.8 (max.)
Boiled 45 hours	(Unstable)		13.2

The results show that in the freshly made sol (before boiling) 1.8% of the acid is in solution, while 25.4% is in the micelle. After thirty minutes of boiling, the free acid content increases to 4.7%, leaving 22.4% in the micelle. After boiling for thirty hours in a reflux condenser, the free acid rises to a maximum of 7.0%, leaving 20.2% in the micelle. On further boiling, the sol becomes unstable. The fact that the greater part of the acid remains always in the micelle seems to indicate that some at least of the acid is in the interior of the particles from whence it is incapable of passing into solution.

Analysis of the Precipitate Formed on Boiling or on Aging.—When the sol is boiled or allowed to stand for some time a soft flocculate is thrown down. This can be isolated by drawing off most of the sol, then freezing and thawing the residue.

The analysis of this early precipitate is shown in Table II (ii), whence it is seen that both the oxygen and water content are low, being roughly one-half of the corresponding figures for the stable micelle. These low values are not unexpected seeing that the early precipitate would consist of the less stable particles, that is, those which contain less of the stabilizing material.

Analysis of the Residue in the Bredig Vessel.

—During the arcing process there is a moderate amount of wastage which collects in the bottom of the Bredig vessel. Part of this is light gray in color, and has the appearance of the ignited micelle. Analysis of this gray matter (Table II (iii)) shows that it is practically pure platinum. Evidently it consists of the metallic particles which for some reason have failed to collect any appreciable amount of stabilizing material during the arcing process.

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Summary

The colloidal platinum micelle, after isolation

by freezing from Bredig preparations, has been analyzed by microchemical methods. The composition of the micelle of an average preparation can be given by the formula $[3.9\text{Pt}, 1.16\text{PtO}_2, 1.0\text{H}_2\text{Pt}(\text{OH})_6]_n$.

There is evidence that the whole of the water in the micelle is present in the form of the highest hydrate, $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$, which is hexahydroxyplatinic acid.

The total amount of this acid (in the micelle and in solution) is 27.2% of the gross weight of the particles. On continued boiling the greater part of this remains in the micelle, where some appears to be in the interior.

The precipitate formed on aging is less rich in stabilizing material than is the ordinary micelle.

The light-gray wastage in the Bredig vessel is practically pure platinum.

ADELAIDE, SOUTH AUSTRALIA RECEIVED MAY 22, 1939

[CONTRIBUTION FROM MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Use of the Concentration Cell in Quantitative Analysis. II. The Determination of Fluoride¹

BY GEORGE W. LOW, JR.,² AND EVERETT H. PRYDE

The first paper in this series³ described in detail the procedure which may be used for the determination of traces of chloride by employing a simple concentration cell. It was pointed out that the technique involved should be perfectly general and should be applicable to the determination of any substance for which a suitable reversible electrode could be found. In the present paper is given a discussion of the application of this technique to the determination of fluoride. Detailed reviews of the literature on the subject of fluoride determination recently have been given⁴ and therefore need not be considered here.

Preliminary Measurements

Our first concern was to find an electrode which would behave reversibly toward fluoride ions. Allen and Furman⁵ have reviewed this subject in developing a potentiometric titration method for

fluorine. Treadwell and Köhl⁶ showed that the system $\text{Fe}^{+++}/\text{Fe}^{++}$ -Pt functions as a good fluoride electrode because of the formation of the complex iron cryolite, Na_3FeF_6 . This system seemed to offer the best possibilities for use in the concentration cell. Accordingly preliminary titrations were performed using the electrode pair, Pt-satd. calomel, in order to determine, if possible, the conditions of acidity and salt concentration which would be most suitable for the final concentration cell measurements and for what range of fluoride concentration the electrode would be expected to function. These titrations, the results of which are shown in Figs. 1, 2 and 3, give information, of a qualitative nature, which is of particular value to anyone who wishes to carry out concentration cell measurements under different conditions from those described in this paper.

Figure 1 shows typical curves for the titration of pure ferric chloride solutions of different concentrations with solutions of sodium fluoride, in the presence of a small amount of ferrous iron, potassium chloride of concentration 0.5 *M*, and hydrochloric acid 0.01 *M*. Under these condi-

(1) Presented at the 97th meeting of the American Chemical Society held at Baltimore, Md., April 3 to 7, 1939.

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(3) Furman and Low, *THIS JOURNAL*, **57**, 1585, 1588 (1935).

(4) (a) Reynolds and Hill, *Ind. Eng. Chem., Anal. Ed.*, **11**, 21 (1939); (b) McClure, *ibid.*, **11**, 171 (1939).

(5) Allen and Furman, *THIS JOURNAL*, **55**, 90 (1933).

(6) Treadwell and Köhl, *Helv. Chim. Acta*, **9**, 470 (1926).