THE ACTION OF CARBON MONOXIDE ON CHLORO-PLATINIC ACID SOLUTION.

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The preparation of the colloidal solutions of noble metals such as gold, palladium, and platinum by the action of carbon monoxide on the solutions of their salts was studied by J. Donau.(1) He obtained a red colloidal solution of gold from auric chloride and a black colloidal solution of palladium from palladium chloride. As for the platinum, however, F. C. Phillips(2) observed that the blackening of aqueous solutions of platinum chloride by the action of the gas was followed subsequently by slow deposition of metallic platinum.

The present author has obtained red-coloured colloidal solutions of platinum by the action of carbon monoxide on the aqueous solutions of chloroplatinic acid. The present paper describes the experiment on this subject.

Carbon monoxide was prepared by heating the mixture of concentrated sulphuric acid and either formic acid or oxalic acid, the latter being mostly used for the sake of convenience. The gas thus obtained was freed from carbon dioxide by passing through tubes containing caustic alkali. The chloroplatinic acid solution was made by dissolving the acid $H_2PtCl_6.6H_2O$ from Kahlbaum in ordinary distilled water.

On passing carbon monoxide through the aqueous solution of chloroplatinic acid at ordinary temperature for a while, the colour of the solution changes from yellow to red. If a comparatively concentrated solution is used a black solution, instead of red, is obtained. The relation between the concentration of the starting solution and the colour of the resulting solution is shown in Table 1.

It seems, however, that the colour is influenced by the conditions such as temperature, material of the vessel, purity of the gas, etc..

Red solutions thus obtained are always transparent, and have been proved to be colloidal by the Tyndall effect and the experiment of electrophoresis. The particles have the negative charge, and the coagulation values are greatly affected by the valency of the positive ions. Some of the results obtained are tabulated in Table 2.

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(1) Donau, *Monatsh.*, **26** (1905), 525; **27** (1906), 59, 71.

(2) Phillips, *Am. Chem. J.*, **16** (1894), 255.

Table 1.

Concentration of $H_2PtCl_6.6H_2O$(%)	Colour of resulting solution observed by	
	reflected light	transmitted light
0.2	black	brownish black
0.1	black	brownish black
0.07	black	reddish brown
0.05	black	purplish red
0.04	reddish black	purplish red
0.02	reddish black	purplish red
0.01	reddish black	somewhat light red
0.005	reddish purple	light red

Table 2.

Electrolyte	Coagulation values (milli-mol / litre)	
	Red sol (Author) 0.038 g. Pt per litre	Black sol (Freundlich) 0.14 g. Pt per litre
NaCl	100	2.5
$^1/_2$ Na_2SO_4	100	—
$^1/_2$ H_2SO_4	—	0.24
$BaCl_2$	1.5	0.058
$MgSO_4$	1.5	—
$Al(NO_3)_3$	0.02	—
$^1/_2$ $Al_2(SO_4)_3$	0.02	0.013

In order to get the sol free from electrolytes it was dialyzed in distilled water, but the colour always changed to black by this process. The coagulation values were determined in the following manner. Ten cubic centimeters of the aqueous solutions of an electrolyte at various concentrations were mixed, respectively, with 10 c.c. of the sol, and, thus, the minimum amount of that electrolyte sufficient to cause coagulation observable by the naked eye within two hours was decided as the coagulation value of the electrolyte. Table 2 indicates the result with a red sol obtained from a 0.02 per cent. solution of chloroplatinic acid, and accordingly, containing 0.038 gram of platinum in one litre. The third column in the table shows the result obtained by H. Freundlich(3) under nearly the same conditions as the above with a black sol of platinum prepared by Bredig's method. Thus the red sol is more stable than the black one to the action of electrolytes. From Table 2, moreover, it can be seen that the sol is more sensible to the valency of the cation than that of the anion, and, accordingly, the particles in the sol are charged negatively.

In order to get informations of the composition of the colloidal particles in the red sol, the following experiments have been undertaken. The colour of the sol changes from red to black by the following various treatments. (a) On standing the sol in the air, blackening takes place at the surface of the sol and it spreads to the bottom, generally, in less than a few days, producing a black sol of the ordinary appearance. (b) By bubbling oxygen through the sol blackening occurs more rapidly. Hydrogen and nitrogen, however, show no action on the red sol. (c) On the addition of hydrogen peroxide the sol immediately undergoes the same colour change as the above, bubbles being evolved actively. (d) If the sol is kept in an large evacuated vessel the colour change from red to black is slow, taking a period of several days; and on taking it out subsequently to the outer atmosphere, it turns black in a short time. (e) If the sol is kept in a sealed test tube the red colour is stable during a considerable period. Some of the samples have been kept unchanged for the period of nine months already.

From these experiments it was ascertained that the colour of the sol is affected by the oxidizing action of oxygen. The blackening of the red sol might probably occur as a result of the disappearance of carbon monoxide in the sol due to the action of oxygen. This can be confirmed by the following observations. (f) If heated on a water bath, the red sol, turning brown at moderate temperature, becomes black at about 95°C., slight bubble-formation being sometimes observed. (g) On mixing alcohols or aceton with the red sol, bubbles are produced immediately, and then the colour changes to black within a few hours or so. Carbon monoxide, thus, seems to be one of the essential components of the red sol.

Some considerations of the structure of these colloidal particles have been made as follows. Since carbon monoxide is an essential component of the sol, an intuitive model representing the structure of the colloidal particles in the sol may be such as shown by Fig. 1a. According to this model, particles are constructed with a great number of platinum atoms surrounded by platinum carbonyl molecules $Pt(CO)_n$. According to the

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(3) Freundlich *Z. physik. Chem.*, **44** (1903), 152.

studies of Schützenberger and others,⁽⁴⁾ there exists such a compound as $Pt(CO)Cl_2$, which is so unstable in dilute aqueous solution that it decomposes immediately into platinum, carbon dioxide, and hydrochloric acid, but is considerably stable in concentrated hydrochloric acid as it forms a compound such as $[Pt(CO)Cl_3]H$. Therefore, another structure expressed by Fig. 1 b might be expected in the presence of concentrated hydrochloric acid. According to this model, a group of platinum atoms forms the centre of a particle and is surrounded by $[Pt(CO)Cl_3]$-ions. Since chloroplatinic acid solutions used were always dilute throughout the experiment, such a complex compound as described above must have been unable to exist as a stable one, and the decomposition of it must have been inevitable. Moreover, if the red sol were given by the particles of this structure, the red sol must have been obtained with a concentrated chloroplatinic acid solution which might afford concentrated hydrochloric acid. The experimental results are contrary to this supposition as can be seen from Table 1.

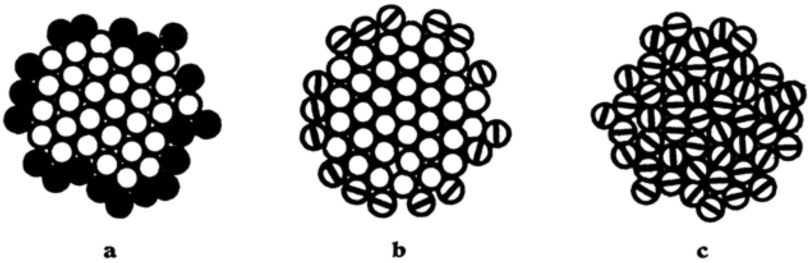

Fig. 1.

Now the following experiments have been undertaken. On the addition of a small quantity of very dilute bromine water to the red sol, it became at once discoloured to be faintly yellow. The solution thus obtained never displays the Tyndall effect even immediately after mixing. But, if a suitable amount of bromine water is added, the solution proves to show the Tyndall effect distinctly after heated for a while or left over night at room temperature. Again, if an excess of bromine water is added the Tyndall effect is never observed. These phenomena may be accounted for in the following manner by assuming that the particles in the red sol are of the structure represented by Fig. 1 c.

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(4) Schützenberger, *Ann. chim. phys.*, [4], **21** (1870), 350; *J. prak. Chem.*, [2], **4** (1871), 159. Pullinger, *Ber.*, **24** (1891), 2291; *J. Chem. Soc.*, **59** (1891), 598. Mylius and Foerster, *Ber.*, **24** (1891), 2424.

Some experimental facts have been reported to indicate the formation of platinum carbonyl such as $Pt(CO)_n$, though this compound has not yet been isolated.⁽⁵⁾ From the general properties of the metal carbonyls, the compound may be sparingly soluble or insoluble in water and decomposed by the aqueous solution of halogens. The insolubleness in dispersing medium is, of course, the essential condition of colloid formation.

Thus, the following reactions may be considered as showing the mechanisms of the formation of colloidal particles of the sol. Platinous chloride may be formed by the reaction,

$$H_2PtCl_6 + CO + H_2O = PtCl_2 + CO_2 + 4HCl\,,$$

and, subsequently, platinum carbonyl chloride may be formed by the reaction,

$$PtCl_2 + CO = Pt(CO)Cl_2\,,$$

which is immediately decomposed by water, depositing platinum of molecular dimension. This may combine, as soon as it is formed, with carbon monoxide existing excessively around it to produce platinum carbonyl $Pt(CO)_n$. The carbonyl molecules thus formed have a strong tendency to condense themselves for colloid formation, and produce the red sol. Hence, the following equilibria may be established in the solution.

$$H_2PtCl_6 + 2CO + 2H_2O \rightleftarrows Pt + 6HCl + 2CO_2\,,$$
$$Pt + nCO \rightleftarrows Pt(CO)_n\,.$$

The following observations support the above assumptions. The electrical conductivities of chloroplatinic acid solutions were measured at 25°C. by means of a Wheatstone bridge with simultaneous recording of time. The carbon monoxide gas was passed through the solution with constant velocity. The reaction vessel was used, at the same time, as the conductivity cell as shown in Fig. 2. The capacity of the vessel was about 30 c.c. The blank platinum electrodes were used. Some of the results obtained are given in Table 3 and Fig. 3. The concentration of the chloroplatinic acid solution was 0.02 per cent. and the rate of passage of the carbon monoxide gas was 3.0–3.5 litres per hour.

Fig. 2.

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(5) Mond, Langer, and Quincke, *Chem. News*, **62** (1890), 97.
Harbeck and Lunge, *Z. anorg. Chem.*, **16** (1897), 50.

Table 3.

Time (min.)	Specific conductivity (mho.)	Colour of solution
0	367.8×10^{-6}	faintly yellow
30	376.6	——
60	403.2	——
90	454.2	slightly dark
99	906.2	dark red
102	941.6	red
120	993.0	——
150	998.7	——
270	1012.0	——
The gas bubbling was discontinued, and the sol was left in the air.		
48 hrs.	1012.1×10^{-6}	upper part black, lower part red
72 hrs.	1011.4	black uniformly

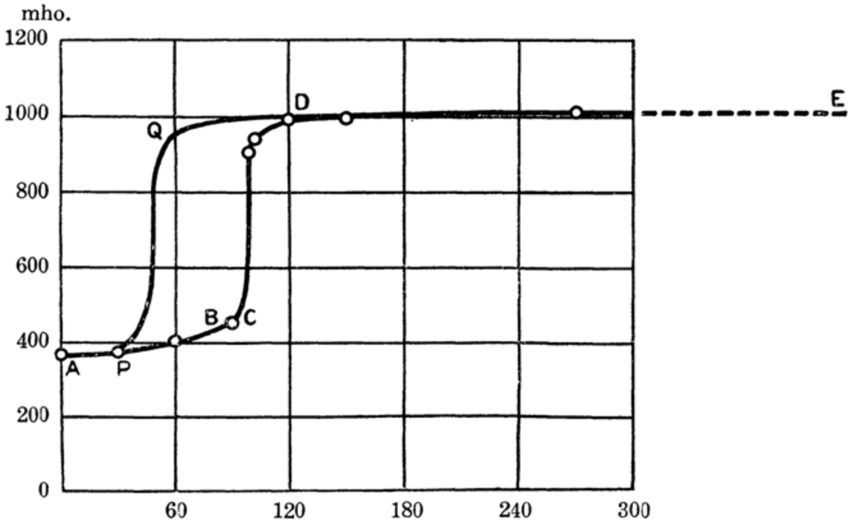

Fig. 3.

The solution is of yellow tint at the period of AB in Fig. 3. At point B it begins to become somewhat dark, at C it becomes red suddenly, and then at D the sol takes the deepest colour. If the bubbling of carbon monoxide is discontinued at point D, and the red sol obtained is exposed to the air for a few days, it turns black at its upper layer, though it shows the same electrical conductivities as before. This is represented by point E in Fig. 3. If the rate of passage of the gas is changed, another curve as shown by APQDE is obtained.

Moreover, the following facts were observed. If bubbling of carbon monoxide is interrupted at point B, the solution of a black tint thus obtained does not or hardly show the Tyndall effect then and there. But in a few minutes it turns orange and at the same time proves to display the Tyndall effect distinctly. The more distinct the Tyndall effect becomes, the deeper the colour turns. At last a solution of brown colour is obtained. This brown solution cannot be turned to red by the passage of carbon monoxide. The brown solution is considered to be a mixed sol of platinum and its carbonyl.

It will be seen from the above observation that if bubbling of carbon monoxide is once interrupted, it fails to obtain a red solution. This may be explained as follows: It is not possible for platinum molecules to form carbonyl owing to the strong tendency of the formation of platinum colloid, if the amount of carbon monoxide is not sufficient to produce the carbonyl. Thus it may be concluded that most of the particles in the red sol have the structure represented by Fig. 1 c.

Summary.

(1) By passing carbon monoxide gas through the dilute aqueous solution of chloroplatinic acid, a red-coloured colloidal solution was obtained.

(2) The red sol was more stable than the ordinary black platinum sol against electrolytes.

(3) The red sol changed to the black one evolving some gas bubbles by the action of air, oxygen, hydrogen peroxide, alcohols, and aceton, or by the process of evacuation or heating.

(4) The action of bromine water on the red sol is described.

(5) The change of the electrical conductivity was measured in the process of formation of the red sol.

(6) The structure of the colloidal particles of the red sol is discussed. They consist, probably, of groups of platinum carbonyl molecules.

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