none were observed. The observation of Feustel that the ortho compound has always the highest surface tension, while the para gives the smallest, is borne out by our work on the toluidine—and also by the Morgan-Daghlian work on the xylenes.

LABORATORY OF PHYSICAL CHEMISTRY.

[FROM THE BIOCHEMICAL LABORATORY OF HARVARD MEDICAL SCHOOL, BOSTON.]

THE EFFECT OF ULTRA-VIOLET LIGHT UPON THE CATALYTIC ACTIVITY OF COLLOIDAL PLATINUM.

BY CHESTER J. FARMER AND FREDERIC PARKER, JR.

Received July 31, 1913.

The experiments described in this paper were suggested by the results obtained in certain experiments by Bovie and Farmer. These experimenters exposed cystin to the ultra-violet light and found that hydrogen sulfide and ammonia were set free. The ammonia was determined quantitatively by the new Folin method. Hydrogen sulfide was evolved after acidifying the exposed liquid with sulfuric acid.

It is known that the catalytic action of colloidal platinum on hydrogen peroxide is destroyed by boiling the colloidal platinum solution. If heat and ultra-violet light have a similar effect, it seemed reasonable to expect that the light would destroy the catalytic activity of the colloidal platinum. Such, indeed, was found to be the case, as is described below.

Preparation of Colloidal Solution.—A solution of colloidal platinum was prepared by the Bredig method, *i. e.*, by producing an arc between platinum electrodes under distilled water.

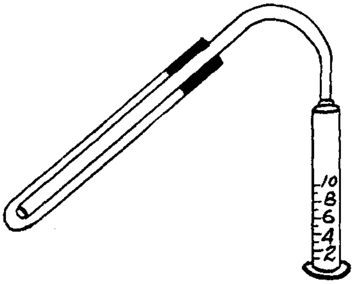
Source of Light.—The ultra-violet light used for these experiments was obtained from mercury vapor. The lamp was loaned to us by Mr. Bovie of the Department of Plant Physiology, Harvard University. It was constructed of transparent quartz tubing 1 cm. in diameter. The lamp carried $1^1/_2$ amperes of current. The voltage across the terminals was 45 volts. The arc was 10 cm. long.

Exposure of the Colloidal Platinum.—The surface of the platinum solution was directly exposed to the rays of the lamp in the following manner:

Thirty-five cc. of colloidal platinum solution were put into a shallow crystallizing dish. This dish was placed in a larger Petri dish, which contained water. In this way evaporation was reduced to a minimum, and the possibility of the destruction of the colloid by heat was guarded against. Any water lost by evaporation was replaced.

Preparation of a Dilute Hydrogen Peroxide Solution.—The hydrogen peroxide used to measure the activity of the colloidal platinum was obtained by diluting a 3% solution of Merck's hydrogen peroxide with an equal volume of distilled water. This solution was kept at a constant temperature by being immersed in running tap water.

Mode of Experimentation.—At stated intervals, 5 cc. of colloidal platinum solution were removed from under the light and placed in a fermentation tube. The tube was completely filled with the dilute hydrogen peroxide solution, and the stopper, carrying the bent delivery tube, was inserted, the liquid completely filling all parts of the apparatus. After quickly inverting the tube to mix the colloidal platinum and hydrogen peroxide solutions, the delivery tube was placed in the neck of a 10 cc. graduated cylinder. The water displaced during a period of five minutes was collected and measured. This decomposition of hydrogen peroxide was taken as an index of the activity of the colloidal platinum solution. Two controls were run; one with unexposed colloidal platinum to serve as a measure of its normal activity, and a second with the hydrogen peroxide solution alone, to give a base line representing the rate of spontaneous decomposition of the solution. The apparatus used is shown in the accompanying sketch.



Experiment No. 1.

Time of exposure to ultra-violet light.	Amount water displaced.
1 hour	10.0 cc.
2 hours	7.0 cc.
4 hours	4.5 cc.
5 hours	4.3 cc.
Colloidal platinum unexposed to light at first	8.5 cc.
Colloidal platinum unexposed to light after standing four hours	6.5 cc.
Hydrogen peroxide solution alone spontaneously	0.5 cc.

The above figures seemed to show that the catalytic activity of the colloidal platinum was seriously impaired, if not destroyed, by the action of the ultra-violet light. The light caused the platinum to be precipitated out of solution as a black, flocculent precipitate.

It will be noted that the activity of the colloidal platinum is decreased considerably after an exposure of five hours. It occurred to us that the large amount of flocculent platinum, on account of its large surface, might be responsible for considerable decomposition of the hydrogen peroxide solution. This idea was strengthened by the two following experiments:

1. The liquid above the precipitated platinum was clear and colorless, differing from the original brown color of the colloidal platinum solution. Five cc. of this clear liquid were added to the hydrogen peroxide solution, and the amount of water displaced after the usual five minutes was found to be only five-tenths of a cubic centimeter, an amount equal to the amount displaced by the spontaneous breaking down of the hydrogen

peroxide as is shown in the above table. Thus it was demonstrated that no colloidal platinum remained in the clear solution.

2. A little powdered barium carbonate was added to the hydrogen peroxide solution, and 1.5 cc. of water were displaced, thus proving that the presence of finely divided particles of matter, not necessarily of colloidal nature, may cause an increased liberation of oxygen, probably due to a change in surface tension.

EXPERIMENT NO. 2.—SAME CONDITIONS AND APPARATUS AS IN EXPERIMENT NO. 1.

Time of exposure to ultra-violet light.	Amount. water displaced.
1 hour	7.2 cc.
2 hours	6.0 cc.
4 hours	5.5 cc.
7 hours	4.4 cc.
Colloidal platinum unexposed to the light at first	7.0 cc.
Colloidal platinum unexposed to the light after standing 7 hours	6.0 cc.

The amount of water displaced by the liberation of oxygen due to the catalytic activity of the platinum exposed seven hours to the light was probably due to the same cause as that in the first experiment.

The results of these two experiments are in accordance with those of eight others performed in a similar manner.

A possible explanation for the long time of exposure, which was necessary to completely destroy the activity of the colloidal platinum, may be found in the inability of the ultra-violet rays to penetrate to any great depth of liquid. It is evident therefore that only those particles of colloidal platinum which are on the surface of the liquid, or so near to it as to be within the possible depth of penetration, can be acted upon by the light.

In Experiment 3, a stirring device was introduced into the crystallizing dish to insure uniform exposure of the colloidal platinum.

The following results were obtained:

EXPERIMENT NO. 3.

Time of exposure to ultra-violet light.	Amount water displaced.
$^1/_2$ hours	7.6 cc.
1 hour	6.5 cc.
2 hours	5.6 cc.
3 hours	4.8 cc.
4 hours	3.9 cc.
5 hours	2.0 cc.
6 hours	0.6 cc.
Colloidal platinum unexposed to the light at first	9.5 cc.
Colloidal platinum unexposed to the light after standing 4 hours	9.5 cc.

It will be noted that in this experiment the catalytic activity of the colloidal platinum was almost completely destroyed after an exposure of six hours, the activity observed being no greater than that of the spontaneous decomposition of hydrogen peroxide itself. The platinum, after precipitation by the light, was in the form of large, mossy clusters.

To show more conclusively that the ultra-violet light is capable of destroying the catalytic activity of colloidal platinum in a short period of time, the following experiment was performed:

Five cc. of colloidal platinum solution were placed in a dish of such a size that the depth of the liquid was not more than 3 mm. This solution was exposed to the ultra-violet light for one hour. On testing the catalytic activity of this platinum solution, only 0.5 cc. of water was displaced. This was undoubtedly due to the spontaneous decomposition of the hydrogen peroxide solution.

EXPERIMENT No. 4.

Time of exposure to ultra-violet light.	Amount water displaced
1 hour	6.5 cc.
2 hours	6.0 cc.
3 hours	3.2 cc.
4 hours	2.6 cc.
5 hours	1.1 cc.
6 hours	1.2 cc.
Colloidal platinum unexposed to light at first	5.0 cc.
Colloidal platinum unexposed to light after standing 5$^1/_2$ hours	3.5 cc.

In all cases, with one exception, the colloidal platinum solution was stimulated to greater activity by a short exposure to the light. This fact is shown by the increased decomposition of the hydrogen peroxide solution after 1 hour of exposure to the light. This is in harmony with observations by Mr. Bovie in his work.

We believe that the above experiments clearly demonstrate the fact that ultra-violet light destroys the catalytic activity of colloidal platinum.

THE INCREASE IN THE OXIDIZING POTENTIAL OF DICHROMATE ION ON PLATINUM CAUSED BY CERTAIN REDUCING AGENTS. AN IMPROVED METHOD FOR THE ELECTROMETRIC TITRATION OF FERROUS SALTS.

BY GEORGE SHANNON FORBES AND EDWARD PAYSON BARTLETT.

Received August 14, 1913.

During a research begun last year on the reduction of chromic acid at a platinum cathode, the electrolyzed solutions were titrated with ferrous salts. The end point, as determined by potassium ferricyanide, proving useless in concentrated solutions, owing to the intense color of the chromic salts, recourse was had to the electrometric determination of the end point, as proposed by Crotogino,[1] by Ostwald, Luther, and Drucker,[2]

---

[1] *Z. anorg. Chem.*, **24**, 225 (1900).

[2] *Physiko-chemische Messungen*, p. 454.