THE REPUTED DEHYDROGENATION OF HYDROQUINONE BY PALLADIUM BLACK

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In the course of his work on hydrogenation as distinguished from oxidation, Wieland found in 1912 that palladium, containing appreciable quantities of hydrogen, is able to remove hydrogen from hydroquinone, even when an appreciable quantity of quinone is also present in the final mixture. The following experiment is mentioned among others.[2]

"Six-tenths gram of hydroquinone in 8 cc. of water was shaken for fourteen hours with about 0.5 g. of palladium. After this time, characteristic crystals of quinhydrone were precipitated; the solution contained free quinone in addition. In 0.42 g. of palladium, there was 6 cc. of hydrogen, which contained 40% carbon monoxide." From the discussion it appears that the attempt was made to exclude air; if this was not in fact accomplished, the experiment gives of course no evidence bearing on the distinction between oxidation and dehydrogenation.

Since that time evidence of two sorts has been brought forward which bears on the possibility of such a reaction taking place in the absence of air.

Biilmann,[3] in his study of the quinhydrone electrode, has shown that the pressure of hydrogen, at which hydrogen would be in equilibrium with a saturated solution of quinhydrone, is about 10^{-24} atm. at 18 or 25°. The figure would still be of the same order of magnitude, whether or not the solution is saturated, and whether excess of hydroquinone or of quinone is also present. Under the conditions of Wieland's experiment, in which hydrogen (in palladium) is a *product* of the reaction, the pressure of hydrogen, at which dehydrogenation of hydroquinone could take place, must be even smaller.[4]

But the experiments of Holt, Edgar and Firth and of Lambert and Gates[5] show that the vapor pressure of hydrogen in palladium is at least a centimeter of mercury at ordinary temperatures when 0.42 g. contains any such quantity as 6 cc. of hydrogen. These experimenters measured the pres-

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[1] From the thesis of T. H. Liu for the M.S. degree (1929) from the Massachusetts Institute of Technology.

[2] Wieland, *Ber.*, **45**, 484 (1912).

[3] Biilmann, *Ann. chim.*, [9] **15**, 109 (1921).

[4] Smaller, because of the direction of the reaction, and also because of the presence of free quinone, which decreases the equilibrium pressure of hydrogen.

[5] (a) Holt, Edgar and Firth, *Z. physik. Chem.*, **82**, 513 (1913); (b) Lambert and Gates, *Proc. Roy. Soc.* (London), **A108**, 456 (1925).

sure at which hydrogen could be removed from palladium, as well as the pressure at which it could be absorbed. The work of Gillespie and Hall[6] locates the equilibrium pressure more closely, but this is not necessary for present purposes.

A violation of the second law of thermodynamics is suggested. But from a thermodynamic standpoint the possibility cannot be denied that hydrogen is able to enter reversibly into combination with palladium at two distinct pressure levels, enormously different. The possibility exists, because the organic substances were not present in the physical measurements, and they might conceivably act catalytically, inducing a change of state in the palladium. But common sense would suggest that so important a change of state ought to attract attention, and one is naturally reluctant to admit such a curious state of affairs without the clearest proof.

No such very clear proof has been presented. Wieland gave two other experiments with hydroquinone, which had perhaps accumulative effect in arriving at his conclusion. It is not altogether easy to explain in detail the other experiments, and we shall content ourselves with the experiment quoted above, which after all is quite sufficient, if satisfactorily verified, to establish the existence of two distinct pressure levels.

Palladium black was prepared by Wieland as follows: A 0.5% solution of palladium chloride is quickly brought to 80° by passing in steam; then one neutralizes with 20% sodium hydroxide (but) until no precipitate of hydroxide forms, adds one-half the theoretical quantity of formic acid, makes (the solution) distinctly alkaline at the moment of the most vigorous evolution of carbon dioxide and pours in immediately twice the amount of formic acid used the first time; the reaction should remain weakly alkaline. Details are given for washing and protecting the preparation against oxygen by the use of nitrogen and carbon dioxide.

Cautions are given, to work rapidly, and that a suitable preparation, free from oxygen, can be obtained after some practice. He states that he used for the experiments only palladium black that contained 5–10 cc. of hydrogen per gram.

The conditions of preparation are such as to make it difficult to guarantee the absence of palladium hydroxide, which might itself oxidize hydroquinone, as pointed out by Wieland. Now that there are thermodynamic reasons for demanding strictness of experimental proof, one can hardly use the absence of a brown color in a black precipitate as guarantee of the absence of such a substance. Palladium so prepared may well contain carbon monoxide, or other desirable products.

A very clean method of preparation is that of Gutbier,[7] consisting of the (very smooth) reduction of palladosammine chloride in a current of hydro-

[6] Gillespie and Hall, THIS JOURNAL, **48**, 1207 (1926).

[7] Gutbier, *J. prakt. Chem.*, (N. F.) **79**, 235 (1909).

gen at about 150,° followed by a current of carbon dioxide and cooling in an atmosphere of carbon dioxide. The worst contamination to be feared seems to be the relatively innocent ammonium chloride, the last traces of which are difficult to remove.

Experimental

Experiment 1.—A simple apparatus, shown in Fig. 1, was used. It was provided with good stopcocks. Seven-tenths gram of palladium black prepared by the method of Gutbier was placed in B and thoroughly reduced by successive evacuation and treatment with hydrogen. It was then exhausted, finally for seven hours at 380–400° with a mercury-vapor diffusion pump, the final pressure being 0.0015 mm. as read on a McLeod gage. A 6% solution of hydroquinone, prepared by dissolving a good grade of the substance in freshly boiled water, was then placed in C, and freed from dissolved gas by shaking under diminished pressure until about 30% of the water was distilled off. It was allowed to stand for fourteen hours, when no change of appearance was observable with the aid of a freshly prepared control solution. The solution was then transferred into B by inverting the vessel and opening the stopcock E. The apparatus was shaken a few times and allowed to stand. As soon as the solids settled, the solution was observed to be deprived of the faintly pink color still present in the control. Upon intermittent shaking and standing for eighteen hours no further change was observed—the solution remained colorless.
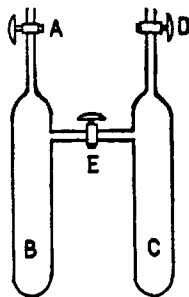

Fig. 1.

This preparation of palladium black was therefore not only unable to dehydrogenate hydroquinone, but was able immediately to remove a coloration probably due to a trace of quinone.

Further experiments showed that this preparation was able (1) to reduce quinone in the presence of hydrogen, (2) to cause the formation of quinone from hydroquinone in the presence of air, and (3) to cause the formation of water from hydrogen and air. Before each of these experiments the palladium was thoroughly washed, first with acetone and then with water. These experiments show that the palladium preparation used for experiment (1) has catalytic activity.

Experiments were now made with palladium black prepared by the method of Wieland. The formation of a precipitate in the neutralization was avoided, and the palladium came down as a black flocculent precipitate, that was quickly washed with hot water until the wash water came chloride free.

Experiment 2.—About 1 g. of this palladium was placed in the tube B of Fig. 1. It was not treated with hydrogen. The apparatus was exhausted overnight until the pressure was 0.0002 mm. of mercury. It was then treated with a solution of hydroquinone free from dissolved gas, as in experiment 1. A fairly intensely colored solution was obtained, although no quinhydrone precipitated even after three days.

Further experiments showed that treatment of this palladium with hydrogen or with hydroquinone deprived it of the ability to produce color in a solution of hydroquinone.

Experiment 3.—In one of these experiments the palladium, having been treated with hydroquinone, was washed with acetone and then with water and dried in a vacuum. It was then exposed to air, and successively exhausted and treated with air, finally being exhausted for three hours. The object of this treatment with air was to remove hydrogen that might be bound in the palladium. According to our experience this would be accomplished, and Wieland also states that exposure to air for one to two hours renders it gas free. In the treatment with air no rise of temperature was detected. When this palladium was then treated with gas-free hydroquinone solution there was no color developed.

This experiment 3 seems fairly conclusive. If palladium that contains a few cubic centimeters of hydrogen per gram of palladium can dehydrate hydroquinone, then there should be no difficulty in securing the reaction when we make use of palladium cleansed of hydrogen by thorough exposure to air.

We can perhaps explain our positive results in Experiment 2 by reference to the conditions of the precipitation of palladium black by the method of Wieland, which conditions appear favorable to the formation of palladium hydroxide. Even if not separately precipitated, this might be occluded in the precipitate of palladium and subsequently act on hydroquinone. Wieland states that brownish precipitates should not be used. According to our experience, when something is done to remove such an oxidizing substance from the palladium, or to avoid its formation, the palladium has no power to dehydrogenate hydroquinone.

Summary

Catalytically active palladium prepared by the method of Gutbier failed to dehydrogenate hydroquinone. Palladium black prepared by the method of Wieland reacted with hydroquinone, but the presence of an important suspected impurity was not excluded. When this impurity was removed, or its presence avoided, the palladium was unable to act on hydroquinone.

Since the original statement, that palladium can dehydrogenate hydroquinone, other evidence has been published which makes such a reaction very curious, if not highly improbable. We have been unable to secure any evidence that the reaction occurs, and believe that there is in fact no valid evidence, and that the original work is to be explained otherwise than on the basis of such a reaction.

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