[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF BAKER & CO., INC.]

Hydrogenation of Quinone with Palladium and Platinum Catalysts

BY EDGAR F. ROSENBLATT

The hydrogenation of quinone has recently been studied by Otto Neunhoeffer and Willibald Pelz,[1] with the interesting result that hydrogenations with palladium catalysts are feasible also in a carbon monoxide atmosphere instead of the commonly used hydrogen. To compare it with hydrogen hydrogenations, they also studied[1] the hydrogenation of different quinones in a hydrogen atmosphere and found to their surprise that, in contrast to the results with carbon monoxide, palladium could not catalyze the reduction of quinone in a hydrogen atmosphere; from this experimental result they draw the conclusion that reversible systems cannot be hydrogenated with palladium and hydrogen. Such a conclusion conflicts with a publication by Donald T. Bonney and Wilbert J. Huff,[2] recommending the use of a solution of anthraquinone disulfonates and colloidal palladium for the absorption of hydrogen in gas analysis.

A clarification of this discrepancy seemed desirable, so the experiments described herein were undertaken. We may say at once that we have confirmed the experimental results of Neunhoeffer and Pelz, but only under their very special conditions, *i. e.*, in an aqueous hydrochloric acid solution. However, the general deduction that palladium is not a catalyst for reversible systems in a hydrogen atmosphere, is erroneous, as in aqueous as well as alcoholic solution the hydrogenation of quinone to hydroquinone proceeds with remarkable speed, *as long as no mineral acid is present.*

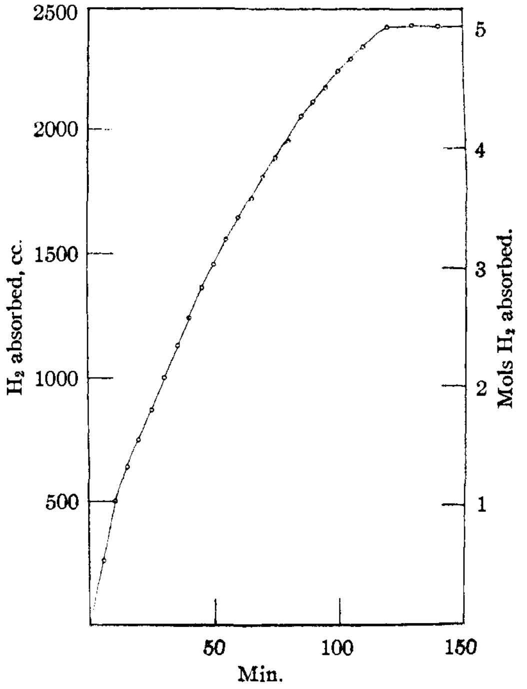

Fig. 1.—Hydrogenation of benzoquinone (2.16 g.) with platinum in HCl.

Our experiments are instructive also in another respect: though the platinum metals are quite generally recognized as excellent catalysts, due to their activity at low temperature and low pressure, there is considerable uncertainty regarding their relative activity, for instance that of palladium compared with platinum. From the following experiments, it can be seen that platinum, but not palladium, can catalyze the hydrogenation of quinone in a hydrochloric acid solution to cyclohexanol (as also found by Neunhoeffer and Pelz). However, in aqueous or alcoholic solution, the hydrogenation of quinone to hydroquinone takes place with either catalyst, and under these conditions the reaction with palladium charcoal is many times faster even than with platinum charcoal (see Fig. 3). Though it is not advisable to jump to hasty conclusions in such a complicated field as catalytic hydrogenation, it is suggestive that a similar result is obtained in many other instances, tending to show that palladium is a mild but extremely fast catalyst, while platinum is more powerful but slower.

Figure 1 shows the hydrogenation of 2.16 g. (0.02 mole) of quinone in 5% hydrochloric solution with the commercial platinum charcoal catalyst of Baker & Co., Inc. (1 g. charcoal was used containing 50 mg. Pt). The change of speed after the absorption of 1 mol of hydrogen is perceptible, especially if compared with normal hydrogenations, which run with undiminished speed almost to the reaction end. In one experiment, the hydrogenation was interrupted after the absorption of 1 mol of hydrogen, the catalyst filtered

---

[1] Neunhoeffer and Pelz, *Ber.*, **72**, 433 (1939).

[2] Bonney and Huff, *Ind. Eng. Chem., Anal. Ed.*, **9**, 157 (1937).

off and the filtrate evaporated; the residue was found to be hydroquinone, which therefore represents the first stage of the complete reaction leading to cyclohexanol.

Figure 2 shows how, in the absence of mineral acids, the hydrogenation of benzoquinone comes to a sudden stop after the hydroquinone stage has been reached. Curve 1 represents the hydrogenation of 2.16 g. of benzoquinone, with the same platinum catalyst as before, in acetic acid solution, curve 2 in ethyl alcohol. Curve 3 represents the hydrogenation in ethyl alcohol with the commercial palladium charcoal catalyst of Baker & Co., Inc. (1 g. charcoal containing 50 mg. Pd). Benzoquinone also can be hydrogenated with palladium in water, in which the quinone is not very soluble. This reduces the reaction speed considerably so that this hydrogenation curve lies between curves 1 and 2. The curve is not drawn as the reaction is not strictly comparable with the others.

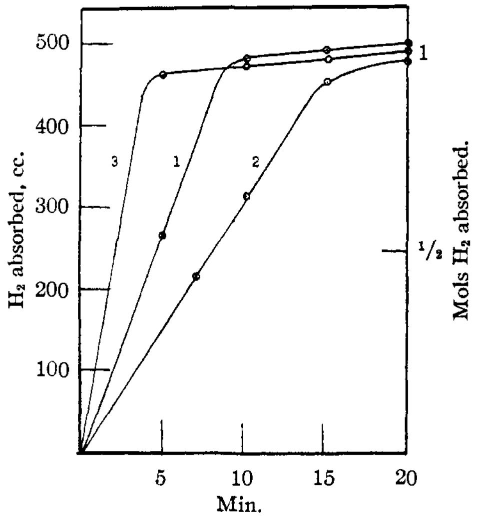

Fig. 2.—Hydrogenation of benzoquinone (2.16 g.): 1, Pt in acetic acid; 2, Pt in ethyl alcohol; 3, Pd in ethyl alcohol.

Figure 3 shows the greater speed of the reaction with a palladium catalyst; furthermore, it clearly indicates that there is no slowing down after the absorption of the 0.5 mol of hydrogen, *i. e.*, at the meriquinoid stage. In both cases 4 g. of benzoquinone was used, but in the case of platinum only a small part of the benzoquinone was hydrogenated when the experiment was interrupted.

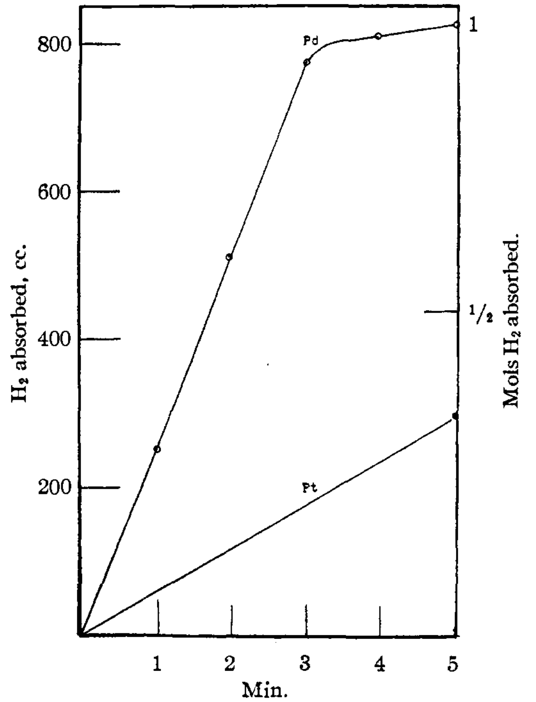

Fig. 3.—Hydrogenation of benzoquinone (4 g.) with platinum or palladium in methyl alcohol.

A few experiments were made relating to the hydrogenation of other quinones, *i. e.*, *p*-toluquinone and anthraquinone in alcoholic solutions. The hydrogenation of *p*-toluquinone proceeds with practically the same speed as benzoquinone. The hydrogenation of anthraquinone is much slower due to the restricted solubility in ethyl alcohol. The reverse reaction, the dehydrogenation of hydroquinone to quinone, could be observed only in the case of anthrahydroquinone, which partially reoxidized before the palladium catalyst could be filtered off.

Experimental

All hydrogenations were done at room temperature and at atmospheric pressure. The reaction vessel was a thick-walled Pyrex Erlenmeyer flask of 1000-cc. content, which was placed in a shaking machine (275 oscillations per minute, the lateral stroke 1$^1/_2$″ (3.7 cm.) long). The progress of the reaction could be followed by measuring the decrease in volume, due to the absorption of hydrogen. The results have not been corrected for barometer readings, temperature or humidity; since the last named factor is of the greatest relative importance, and is so difficult to evaluate accurately in the presence of different organic solvents, it seemed unnecessary to correct for pressure and temperature. Under our conditions the hydrogen absorption was around 24 liters per mole of hydrogen, instead of 22.4 liters. One hundred cc. of solvent was used in each experiment.

The catalyst was the commercial 5% platinum charcoal and 5% palladium charcoal (Baker & Co., Inc.), 1 g. of charcoal containing 50 mg. of platinum or palladium, respectively, being used. The same catalyst was used throughout, as it could be filtered and dried at 100° after each experiment without impairing its activity.

Summary

The hydrogenation of various quinones in a hydrogen atmosphere in the presence of palladium catalysts produces hydroquinone with great speed, provided mineral acids are absent. The same reaction takes place with platinum charcoal, but more slowly. Platinum charcoal is active even in the presence of mineral acid, hydroquinone being only the first stage of the reaction which has cyclohexanol as the final product.

NEWARK, N. J. RECEIVED FEBRUARY 12, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Kinetics of Neutralization

BY MARTIN KILPATRICK

In a recent paper Lewis and Seaborg[1] have reported the study of the rate of fading of the blue trinitrotriphenylmethide ion in acid solutions. They interpret their results in terms of their classification of acids and bases as primary and secondary.[2,3]

Another kinetic interpretation of their results merits consideration. Considering the reaction to be catalyzed by acids we may write

$$B_{S^-} \underset{k_{-1}A^-}{\overset{k_1\,HA}{\rightleftarrows}} B_{P^-} \qquad (1)$$

where B_{S^-} represents the blue ion, called the secondary base by Lewis, B_{P^-} the form called the primary base, HA any acid, and A^- its conjugate base. This reaction is followed by the reaction

$$B_{P^-} + HA \overset{k_2}{\rightleftarrows} HB + A^- \qquad (2)$$

In other words, equation (1) is step (a) in the paper of Lewis and Seaborg (who do not, however, consider the acid-base catalytic nature of the reaction) and equation (2) represents the second step. In equation (1) B_{S^-} is transformed to B_{P^-} by the catalyst HA, the reverse process being catalyzed by the base A^-. Now if the reaction $B_{P^-} + HA$ is much faster than the reaction $B_{S^-} \rightarrow B_{P^-}$, and if $k_2C_{HA} \gg k_{-1}C_{A^-}$, the rate equation would be

$$-\frac{dC_{B_{S^-}}}{dt} = k_1C_{B_{S^-}}C_{HA} \qquad (3)$$

and the reaction would be of the second order in agreement with the experimental findings of Lewis and Seaborg. Lewis and Seaborg consider that a small concentration of B_{P^-} is maintained in equilibrium with B_{S^-} and that the rate-determining step is the reaction of the primary base B_{P^-} with the acid HA. They conclude that ". . . the measured heat of activation should be the same for the several acids and equal to the difference in energy between the primary and secondary forms of the base." In the present paper it is assumed that the change from B_{S^-} to B_{P^-} requires an acid catalyst and that B_{P^-} reacts rapidly with the acid if it is sufficiently strong.

The measured energies of activation for the stronger acids are found to average 9.1 kcal., and the energy of activation is calculated to be 8.9 for alcohol. The constancy of this value is not in contradiction to a catalytic mechanism. For example, in the mutarotation of glucose the measured energies of activation for such different catalysts as water, pyridine, acetate ion, and hydrogen ion were found to be 17.6, 19.1, 18.0, and 19.3 kcal., respectively.[4] In the enolization of acetoacetic ester[5] and in the iodination of acetone[6] the measured energies of activation for different catalysts are practically the same. From the data it is evident that the statement of Lewis and Seaborg "The constancy of the heat of activation over the great range from chloroacetic acid to alcohol can hardly be explained by the theory of an activated complex" is hardly in accord with the facts for reactions showing general acid and basic catalysis.

Turning now to the alcohol reaction, Lewis and Seaborg state "Alcohol is itself an acid, and although its acid strength is not high

---

(1) Lewis and Seaborg, THIS JOURNAL, **61**, 1894 (1939).

(2) Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(3) Lewis and Seaborg, THIS JOURNAL, **61**, 1886 (1939).

(4) Kilpatrick and Kilpatrick, *Ibid.*, **53**, 3698 (1931).

(5) Pedersen, *J. Phys. Chem.*, **38**, 601 (1934).

(6) Smith, *J. Chem. Soc.*, 1774 (1934).