

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## CATALYTIC HYDROGENATION AND THE POTENTIAL OF THE HYDROGEN ELECTRODE

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The addition of hydrogen to certain classes of substances, such as quinones, is a strictly reversible reaction. It may be brought about in acid solution by such reducing agents as titanous chloride. By measuring the oxidation-reduction potential of the reducing agent on the one hand and the organic compound on the other, it is possible to state accurately the equilibrium between them in terms of the general principles of electrochemistry.<sup>1</sup> In the same way the equilibrium between such an organic substance and gaseous hydrogen in the presence of a metallic catalyst in aqueous solution will depend on the oxidation-reduction potential of the substance and the potential of the hydrogen in this solution. This potential of the "catalytic hydrogen" is, of course, easily determined by the usual methods of measuring the hydrogen-electrode potential. Thus, the catalytic hydrogenation of all substances (organic or inorganic) whose reduction is *reversible* can be clearly stated in electrochemical or thermodynamical terms.

The question arises whether or not the *irreversible* catalytic hydrogenation of many organic substances can be similarly formulated. The very fact that a certain process of reduction or hydrogenation is irreversible prevents our applying the usual thermodynamical equations and we cannot at present measure or define its oxidation-reduction potential. Nevertheless, we know in a rather qualitative way that in many instances the possibility of bringing about a certain irreversible reduction depends on the oxidation-reduction potential of the reagent employed. Thus, if we compare the irreversible reduction of two related substances,—maleic acid,  $\text{HOOCCH}=\text{CHCOOH}$ , and dibenzoyl-ethylene,  $\text{C}_6\text{H}_5\text{COCH}=\text{CHCOC}_6\text{H}_5$ ,—we find that the former is rapidly reduced to succinic acid by chromous chloride in aqueous solution but is not affected by sodium hydrosulfite or titanous chloride. Dibenzoyl-ethylene, however, is reduced to dibenzoyl-ethane by all these reagents.<sup>2</sup>

Even without a quantitative method of expressing these facts, we can confidently predict that another reducing agent of nearly the same oxidation-reduction potential as sodium hydrosulfite will reduce the diketone

<sup>1</sup> Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904). Granger and Nelson, *THIS JOURNAL*, **43**, 1401 (1921). W. M. Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920). Billman and Lund, *Ann. chim.*, **16**, 321 (1921). Conant, Kahn, Fieser and Kurtz, *THIS JOURNAL*, **44**, 1382 (1922).

<sup>2</sup> Experimental portion of this paper.

but not the acid, whereas a reducing agent with as low a potential as chromous chloride will reduce both substances.

Can a similar line of reasoning be applied to catalytic hydrogenation? A great many ethylene derivatives, which are not reduced by sodium hydrosulfite, are hydrogenated catalytically,—for example, cinnamic acid. Is this well-known fact to be accounted for by the statement that the reduction potential of the hydrogen is greater (more negative) under the conditions of the experiment than sodium hydrosulfite? The results of our experiments with dimethyl-acrylic acid seem to give a definite negative answer to these questions. We have found that dimethyl-acrylic acid dissolved in 0.1 *N* hydrochloric acid is hydrogenated by hydrogen and a catalyst *but is not reduced by a solution of chromous chloride* even after standing for several months. The potential of the hydrogen in this experiment is, obviously, about  $-0.05$  volts on the normal hydrogen electrode scale; the potential of a mixture of equivalent amounts of chromous and chromic ions is  $-0.40$  volts.<sup>3</sup> Thus the reducing agent employed was about *0.3 volts more powerful* than the hydrogen-catalyst combination and yet did not accomplish the reduction. The conception of reduction potential as applied to *irreversible catalytic hydrogenation* does not seem to be of value in correlating the known facts.

We have performed these simple experiments with dimethyl-acrylic acid because most recorded instances of catalytic hydrogenation have involved the use of neutral or alkaline solutions. Under these conditions the value of the potential of the hydrogen electrode is so negative that no clear-cut distinction could be made between it and a reducing agent such as hydrosulfite.

### Hydrogenation and Reduction

From our experiments with maleic acid and dibenzoyl-ethylene it seems as if certain cases of irreversible reduction of ethylene derivatives could be qualitatively expressed in terms of reduction potentials. In the light of the experiments with dimethyl-acrylic acid, it appears that irreversible cases of catalytic hydrogenation cannot be so expressed. This being the case it is, perhaps, reasonable to suppose that the two cases represent different types of processes. We should like to present the hypothesis that in the first instance the process involves the addition of electrons and hydrogen ions, and in the second case the addition of hydrogen atoms only. The process involving electron addition is, from this point of view, a special case of the phenomenon of *reduction* such as we deal with in inorganic chemistry; the addition of hydrogen atoms can best be expressed by the term often used,—*hydrogenation*. Equations 1 and 2 represent



the two processes. It is evident that Equation 1 represents a case of elec-

<sup>3</sup> Forbes and Richter, *THIS JOURNAL*, **39**, 1140 (1917).

tronic reduction of the inorganic type which is peculiar for two reasons: first, because it is irreversible; and second, because it involves addition of hydrogen ions as well as electrons. Irreversible reduction without the addition of hydrogen ions is met with in certain steps in the reduction of nitro compounds and the conception of reduction potentials has long been applied to such processes which take place at a cathode in aqueous solution.<sup>4</sup>

These irreversible reductions are usually accomplished by such chemical reagents as sodium hydrosulfite, titanous chloride and stannous chloride, all of which bring about rapid inorganic reductions in aqueous solution but which are not capable of reducing most ethylene derivatives, ketones, aldehydes and nitriles.

If the point of view here presented is correct, it is of great importance to extend this distinction between reduction and hydrogenation and to determine the factors governing both processes. This we hope to do in a subsequent paper. It will also be a matter of importance to decide whether the changes brought about by such reagents as zinc and acid or sodium amalgam are to be classed as reductions or hydrogenations. We are at present engaged in a thorough study of the types of reduction brought about by a very powerful inorganic *reducing agent*,—chromous chloride. With the information thus gained we hope to be able to make certain generalizations in regard to *irreversible reductions* as distinct from *irreversible hydrogenations*. We are also studying these reactions from an electrochemical standpoint.

### Experimental<sup>5</sup>

**Catalytic Reduction of Dimethyl-acrylic Acid.**—In a typical experiment 3.0 g. of  $\beta,\beta$ -dimethyl-acrylic acid was dissolved in a mixture of 100 cc. of 0.1 *N* hydrochloric acid and 3 cc. of a 10% solution of chloroplatinic acid, and 6 cc. of 5% gum arabic was added together with a few drops of a colloidal solution of platinum as "seed." The solution was placed in a suitable apparatus for hydrogenation and shaken at room temperature until the absorption ceased. The amount of hydrogen absorbed was 658 cc. (N. T. P.); calculated for one molecule, 678 cc. The solution no longer decolorized bromine water. The product was isolated in the usual way and was identified as *iso*-valerianic acid by its odor and boiling point.

**Experiments with Chromous Chloride and Dimethyl-acrylic Acid.**—A solution of 5 g. of dimethyl-acrylic acid in water was treated with a solution containing 25 g. of chromous chloride (100% excess) and considerable free hydrochloric acid; the total volume was about 200 cc. Suitable precautions were taken to avoid the access of air to the solutions. The characteristic blue of the chromous solution was unchanged; and after standing overnight 4.8 g. of the dimethyl-acrylic acid was recovered unchanged by extraction with ether. In a similar experiment the mixture was heated for 12 hours at

<sup>4</sup> Haber, *Z. Elektrochem.*, **4**, 506 (1898). *Z. physik. Chem.*, **32**, 193 (1900).

Reductions during electrolysis are complicated by the heterogeneous system which is present as Haber and other workers have pointed out.

<sup>5</sup> The experiments with dibenzoyl-ethylene were performed by Mr. R. E. Lutz.

60°; no color change occurred and the organic acid was recovered unchanged. Similar mixtures were sealed up and allowed to stand for several months; no reduction took place.

**Reduction of Maleic Acid and Dibenzoyl-ethylene.**—Five g. of maleic acid dissolved in water was added to 250 cc. of a solution of chromous chloride containing 25 g. of chromous salt (100% excess) and hydrochloric acid contained in a suitable apparatus free from air. The mixture at once became purple and then green, showing that reduction had taken place. By extracting 6 times with ether, 3.2 g. of succinic acid (64%) was obtained. Due to the difficulty in extraction considerable succinic acid was probably lost; the actual yield may well have been quantitative.

A solution of maleic acid in the equivalent quantity of aqueous sodium hydroxide was treated with a 100% excess of sodium hydrosulfite, heated for 15 min. on the steam-bath and allowed to stand for 2 hours. After the solution was acidified it was repeatedly extracted with ether, but no trace of succinic acid was found.

Dibenzoyl-ethylene (both *cis* and *trans* forms) was reduced by dissolving in hot alcohol and adding a slight excess of sodium hydrosulfite in concentrated aqueous solution. The light yellow color of the unsaturated ketone instantly disappeared, and on dilution of the mixture with water dibenzoyl-ethane was precipitated. The precipitate was recrystallized from alcohol and identified by its melting point. The reduction could also be accomplished by mixing a suspension of the ketone in alcohol at room temperature with the sodium hydrosulfite solution. In this case the reduction took a little time due to the heterogeneous system involved.

Dibenzoyl-ethylene was also reduced by adding a chromous chloride solution to a hot alcoholic solution of the compound. The product obtained after dilution with water was dibenzoyl-ethane.

### Summary

1. Dimethyl-acrylic acid has been hydrogenated in 0.1 *N* hydrochloric acid solution by means of hydrogen and a catalyst.

2. Chromous chloride in aqueous solution does not reduce dimethyl-acrylic acid although its reducing power, as measured by its oxidation-reduction potential, is 0.3 volts greater than that of gaseous hydrogen and a catalyst in 0.1 *N* hydrochloric acid.

3. Maleic acid is reduced by chromous chloride in aqueous solution but not by sodium hydrosulfite; dibenzoyl-ethylene is reduced by both reagents.

4. It is apparent that the process of catalytic hydrogenation cannot be successfully formulated in terms of oxidation-reduction potentials. The reductions with chromous chloride and sodium hydrosulfite can be so formulated in a qualitative manner. It is suggested that in one case we are dealing with a process of hydrogenation and in the other with a case of reduction (electron transfer) of an irreversible type.