29. *The Mechanism of the Contact Hydrogenation of Carbonyl Groups in the Presence of Metallic Catalysts.*

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It is the object of the present research to establish the mechanism of the contact hydrogenation of carbonyl groups in the presence of nickel and platinum catalysts with special reference to acetone and acetaldehyde. All possible sequences of intermediate states for the elementary reaction,

may be written as below, if one admits that all possible states of aggregation of hydrogen at the surface of the metallic catalyst are H, H⁺, H₂¹⁾²⁾ and H₂ and neglects the probability of termolecular reaction among statistically independent atoms or atom groups at the surface compared with that of bimolecular ones;

$\begin{array}{c} \diagup \\ \text{C} \\ | \\ \dot{\text{O}} \end{array}$ denotes the carbonyl group and [H] or [H]' one of H⁺ and H, each being ready for reaction under the influence of the catalyst, perhaps chemisorbed by the latter. The sequence of intermediate states I will represent all possible alternatives obtained by commuting the order of addition to C- and O-atom and by substituting [H] and [H]' in each state with H and H⁺.

A hydrogenation reaction may proceed by any one of the sequences of states, which will simply be called processes in what follows, and any step of transition from a state to the subsequent one may govern the rate thus giving rise to various possible mechanisms.

On the premise that one and the same mechanism is responsible for the hydrogenation of acetone and acetaldehyde, the present authors

1) Horiuti and Okamoto; Sc. Pap. Inst. Phys. Chem. Res. Tokio, **28** (1936), 231.

2) Horiuti and Ikusima; Proc. **15** (1939), 39-44.

proceeded to decide the mechanism from results (1) to (9) of experiments (i) to (vi), of which brief accounts are given below.

(i) Thirty three % C_2H_5OD was shaken with 0.3 gm platinum black in a hydrogen atmosphere for 18 days at room temperature. It was found *that the deuterium content in the ethyl group after the treatment was less than 0.02 %*, Res. (1) by converting the ethyl alcohol into ethyl iodide, and by analysing the water obtained by burning the latter.

(ii) Four cc acetone was shaken with 0.07 gm platinum black in hydrogen atmosphere of 200 to 500 mm Hg pressure in a sealed vessel of 100 cc capacity for about 10 min. at $0^\circ C$. It was found *that about 10 to 20 % hydrogen was consumed in each case, the rate of consumption being approximately proportional to the hydrogen pressure*, Res. (2)

(iii) Two cc of ca. 10 % CH_3COD was shaken at room temperature with normal hydrogen of 200 to 2000 mm Hg pressure in a vessel of 100 cc capacity in the presence of 2 gm reduced nickel or 0.07 gm platinum black. The result was *that in the case of platinum the deuterium content in hydrogen was less than 0.02 % after 60 min. of shaking while approximately half the hydrogen was consumed*,... Res. (3) *that in the case of nickel the deuterium content became about 1 % after shaking for 5 hours while 30 % of the hydrogen was consumed*,..... Res. (4) *and that in the case of nickel the rate of consumption of hydrogen was increased by 40 % as the pressure was tenfolded*,..... Res. (5)

(iv) The rate of hydrogenation was similarly observed as in cases (ii) and (iii) with acetone acidified by $\frac{N}{1}HCl$ or basified by $\frac{N}{1}N(C_2H_5)_3$ in the presence of platinum or nickel catalyst. *In the case of platinum the rate was doubled by HCl but reduced to one-fourth by $N(C_2H_5)_3$* , Res. (6) *whereas in the case of nickel no such effect was observed*, Res. (7)

(v) Seven % heavy acetone (mixture of CH_3COCH_2D and, perhaps, of higher isotopic substitution products) was similarly hydrogenated with normal hydrogen in the presence of platinum catalyst at $0^\circ C$. *The deuterium content in hydrogen was found to be less than 0.02 % after 10 min. of shaking while half the hydrogen was consumed*, Res. (8)

(vi) Normal Acetone was similarly hydrogenated with 2.33 % heavy hydrogen in the presence of platinum catalyst at $0^\circ C$. *The deuterium content in the gas decreased as the hydrogenation proceeded, the monomolecular rate of the decrease being found to be approximately equal to that of the hydrogen pressure*, Res. (9)

It will be taken for granted that we are dealing in the above observations with rates of genuine chemical reactions not controlled by some physical process like diffusion, reserving arguments therefor to later papers.

Res. (1) and the order of magnitude of observed rates of hydrogenation show that the catalysed hydrogenation is practically irreversible, since otherwise deuterium must have penetrated into the ethyl groups. The conclusion obtained with platinum may be extended to the case of nickel because of the invariance of the hydrogenation-dehydrogenation equilibrium. It can be inferred now from Res. (2) and (5) that the irreversible reaction can not be governed by the step

the case, the rate would decrease rather than increase with increasing hydrogen pressure due to occupation of space by hydrogen molecules or atoms at the interface.

For nickel catalyst Res. (4) shows now that hydrogen molecule and aldehyde group exchange their constituent hydrogen atoms, which is only possible when the reaction follows process I and is governed by the step of addition of [H] or [H]' to O-atom, or alternatively by the addition to C-atom but accompanies the interchange reaction of the type,

where * distinguishes the origin of [H]: Res. (8) excludes the interchange reaction of such mechanism as involving hydrogen atoms of the methyl group, for instance that suggested by Farkas.¹⁾

In the case of platinum, Res. (3) excludes process I governed by the addition of [H] or [H]' to O-atom, which necessarily implies the exchange reaction and Res. (9), when combined with the experimental result obtained by A. and L. Farkas¹⁾ that the monomolecular rate of para-hydrogen conversion observed at the similar condition as Exp. (vi) is even larger than that of decrease of deuterium content in the gas,* excludes any process governed by a transition from molecular hydrogen

Further restrictions are derived for the mechanism of nickel and platinum from Res. (6) and (7) on the basis of the following consideration.

Since the acid or base is competent with the metallic catalyst loaded with hydrogen or a hydrogen electrode as a proton donator or acceptor, the acetone side of the catalyst-liquid interface is more electro-negative when acidified than when basified. Assuming that this is the only effect of contaminating acid or base, it follows for platinum that

1) Trans. Faraday Soc. **33** (1937), 678.

* The decrease of deuterium content in the course of hydrogenation indicates when incorporated with Res. (8) a higher reactivity of deuterium in hydrogenation compared with that of protium rather than the exchange reaction, as concluded by A. and L. Farkas. This point will be treated in detail in a later paper.

the rate of hydrogenation is affected by the potential at the interface, where the elementary system involved in the governing step is situated and henceforth that the elementary system is charged at the appropriate critical state, which is generally only possible when it is charged in either or both states before and after the governing transition. Similarly it follows for nickel that the elementary system is neutral before and after the governing transition.

It is hence concluded for the hydrogenation with the nickel catalyst that the hydrogen molecule catalytically dissociates to form pairs of hydrogen atoms, perhaps chemisorbed on the catalyst, which are successively combined to C- and O-atom of the carbonyl group, either of the latter two acts governing the rate.

For platinum only possible mechanism is now that of process I governed by the addition of $[H]$ or $[H]'$ to the C-atom, where $[H]$ or $[H]'$ should be such one of H and H^+ that the elementary system is charged at either or both states before and after the governing reaction (Mechanism *Pt-1*), or that of process II governed by the addition of H_2^+ to the carbonyl group (Mechanism *Pt-2*).

The latter mechanism is acceptable even with regard to the observation of Farkas on the para-hydrogen conversion since, according to the theoretical result obtained by Kotani,* a hydrogen molecule ion possibly undergoes the ortho-para conversion when adsorbed at the interface, if not dissociated into constituent particles.

We might go further with the mechanism *Pt-1* by incorporating knowledge of the interatomic forces and of the hydrogen electrode process,¹⁾ identifying the rôle of water of the hydrogen electrode process with that of acetone or aldehyde in this case in stabilizing H^+ or H_2^+ at the interface.

The hydrogen molecule will thus dissociate after the hydrogen electrode process,

so far as to result in a pair of statistically independent particles $H + H^+$ or $2H^+$, either of which is to react with the carbonyl group. In the case of $H + H^+$, H^+ will preliminarily be attached at the negative end of the dipole, i. e., O-atom of the carbonyl group when H attacks C-atom to complete the hydrogenation, whereas the alternative process with $2H^+$ is hardly probable because of the Coulomb repulsion.

The mechanism *Pt-1* assumes now a more concrete form that the reaction follows the process,

being governed by the last step. This is however identical with *Pt-2* except that H and H^+ are separated at the intermediate states instead

* Our best thanks are due to Dr. M. Kotani of Tokyo Imperial University who has communicated us his unpublished results.

1) Horiuti and Ikusima; Proc. **15** (1939), 39-44.

of being coherent with each other. Combining the two it is now concluded for the platinum catalyst that a hydrogen molecule ionises to form a hydrogen molecule ion, which subsequently combines the carbonyl group to yield alcohol, the latter act governing the rate; the hydrogen molecule ion may possibly be dissociated into constituent particles at the intermediate state.

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