A π-Complex Mechanism for the Catalytic Deuteration of Cyclohexene

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An additional explanation is given for the catalytic exchange and deuteration of cyclohexene on iron films.

The hypothesis was drawn up that in certain cases cyclic hydrocarbons, which during their adsorption have formed more than two bonds with the surface, may react with hydrogen and deuterium on both sides of the ring. It is possible that the bonding of these adsorbed molecules on the metal is analogous to the bonding in organometallic complexes.

The catalytic exchange and deuteration of cyclohexene on transition metal and gold films has been the subject of investigations by Erkelens, Galwey, and Kemball (1, 2). However, in these publications no mention was made of an additional mechanism, described in the thesis of this author (3, pp. 68, 96–99). It seems therefore useful to discuss this mechanism separately.

When iron was used as a catalyst for the deuteration of cyclohexene, two maxima occurred in the distribution of the reaction products, one at about d_2-cyclohexane, the other at about d_{10}-cyclohexane. The position and the height of the maxima were dependent on the reaction temperature. It seemed reasonable to assume that the first maximum originated from the type of process we discussed in detail for platinum and which is schematically shown in Fig. 1.

However, the question arose which process was responsible for the second maximum. In other words: Why can preferentially more than six hydrogen atoms exchange?

The latter question has been posed before by Anderson and Kemball (4) in a study on the exchange of cyclohexane and deuterium on various evaporated metal films at different temperatures. The authors came to the conclusion that ring-shaped molecules—adsorbed perpendicularly to the catalyst surface—could "turn over" by using two bonds to one carbon atom (A).

The uptake of a deuterium atom in the right place has as a consequence that now the other side of the molecule comes into contact with the surface. It is clear that in this way more than six hydrogen atoms can easily be exchanged.

Burwell *et al.* (5, 6) sought the explanation in the presence of a carbon atom with
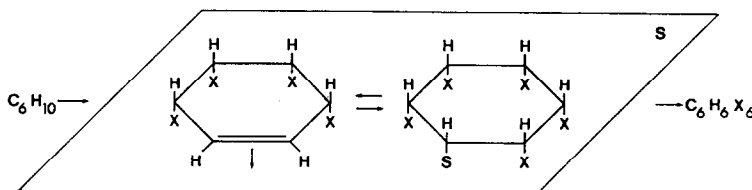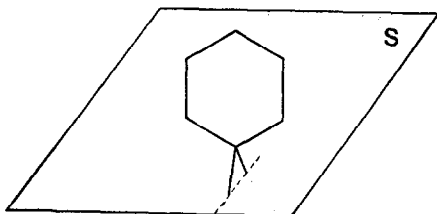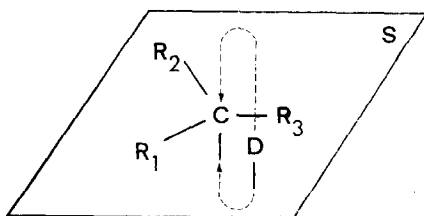

Fig. 1. The redistribution process for cyclohexene. X is a hydrogen or deuterium atom which participates in this process; S represents the surface of the catalyst.

**Anderson
and
Kemball
(A)**

**Burwell
(B)**

**Anderson
(C)**

threefold coordination or a free radical (B), adsorbed perpendicularly to the surface and symmetrically orientated with respect to the surface hydrogen atoms. This might at the same time account for the racemization which they found to occur in the reaction between optically active 3-methylhexane and deuterium on nickel and palladium catalysts.

Anderson (7) explains Burwell's problem by assuming that at the top as well as at the bottom of the optically active carbon atom a reaction may occur (*C*). Anderson, however, has not drawn the conclusion (*3*, p. 20) that this might be an alternative explanation for exchange on both sides of the cyclohexane ring instead of "turning over" as postulated by himself and Kemball. At any rate it is clear that when chemisorbed molecules on either side could react with deuterium, the assumption of turning over of the rings is not necessary at all.

For a further discussion of the reaction of cyclohexene on iron it is now necessary to consider some experimental facts published earlier. In the first place it should
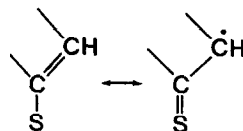
be mentioned that when the evaporated film was slightly sintered with the purpose of reducing the surface area, a slower reaction was obtained—which is self-evident—and the second maximum in the deuterium distribution no longer occurred. Secondly it is important to know that on a sintered iron film the disproportionation reaction which is displayed by cyclohexene on exclusion of hydrogen according to the reaction equation

$$3C_6H_{10} \rightarrow 2C_6H_{12} + C_6H_6$$

no longer occurred at $0°C$. It seemed reasonable to suppose that adsorption of the cyclohexene molecule with more than two bonds—essential for the formation of benzene—was no longer possible.

It was obvious to combine the two data and assume that during the reaction of cyclohexene with deuterium on nonsintered iron films the second maximum in the deuterium distribution originated from the molecules which had formed more than two bonds with the surface. For that reason the following hypothesis was made by the author (*3*, pp. 68, 96–99): molecules which have formed more than two bonds with the surface can also react with deuterium at the upper side of the ring. This deuterium probably reacts in the molecular form from the gas phase. A reaction with adsorbed atoms, with as result a deuterium at the upper side of the ring must not be excluded. This hypothesis was drawn up because for the "turn over" mechanism of Anderson and Kemball only *one* carbon atom may be bound to the surface.

It was supposed that the three-point or multi-point adsorbed molecules which are adsorbed on iron could be the catalytic equivalent of organometallic compounds such as ferrocene,* a molecule in which an iron atom is placed between two cyclo-pentadiene rings (so called π-bonding). Sintering of the iron film would result in removal of the sites which are necessary for forming these ferrocene-resembling compounds. It is of course also possible that in our case the degree of the vacuum was such that poisoning of these sites with residual gases had occurred.

Although it appeared to be quite difficult to prove this attractive hypothesis within the scope of the investigation, some efforts were made. The most obvious experiment was the catalytic deuteration of cyclohexadiene on iron since the surface was offered a molecule which is able to form directly more than two bonds on the surface without dissociation. At 20.4°C only the second maximum was found, which means that excessive exchange occurred on either side of the ring. Another idea was to use a cyclic molecule with a double bond outside the ring, namely 4-methylmethyl-enecyclohexane. If a relatively stable condition should occur in which three carbon atoms are bound on the surface, in the ring only two atoms would be bound, so that little exchange could take place. This molecule behaved indeed differently from cyclohexene.

* The chemical bonding in ferrocene has been treated by Moffitt (8) and by Ruch and Fischer (9). The "molecular orbital" method by Moffitt has also been discussed in detail in a survey article of Kragten (10).

In this publication it is shown that the explanation for the catalytic deuteration and exchange of cyclohexene, given in the author's thesis has led to the concept of the π-complex mechanism. An excellent review of recent developments has been given by Rooney (11). It should, however, be emphasized that the suggestion of π-bonding between the adsorbed hydrocarbon species and the metal surface was introduced for reasons of analogy with organo metallic complexes. From this analogy it should not be concluded that the bonding in the two cases—absorbed species and complex—is necessarily identical.

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