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# A STUDY ON THE HYDROGENATION OF 2-CYCLOPENTEN-1-ONE ON NICKEL CATALYST WITH DEUTERIUM BY THE USE OF MICROWAVE SPECTROSCOPY

By

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Reaction scheme of a catalytic hydrogenation of $\alpha$-olefins on the group VIII metals can be clarified precisely by the aid of the microwave spectroscopy[1] in addition to the mass spectrometry. As an example, the classical Horiuti-Polanyi scheme *via* the *di*-adsorbed state (I) in Fig. 1 was confirmed on the catalytic hydrogenation over nickel. However, the discrimination between the eclipsed (II) and the staggered (III) conformations of the adsorbed state was still difficult on the basis of this new isotopic analysis. Though the deuterated positions of the produced deuteropropanes can be determined, the analytical result does not give any answer to the problem, due to the capability of free rotation of their C–C bonds.

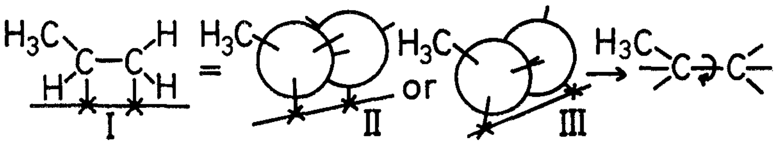

**Fig. 1.** Adsorbed states of propene

To solve the above unsettled question, cyclic unsaturated ketone is very suitable to be hydrogenated with deuterium, because the ring structure hinders the free rotation of the C–C bonds and the location of the double bond in the reactant can be identified with respect to the carbonyl group, so that the deuterated positions of the products will reflect the conformation of the adsorbed state. Therefore, we used 2-cyclopenten-1-one as the olefin to be hydrogenated, and applied this new technique to the analysis of the

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produced deuterocyclopentanones.

This attempt was put into practice by the recent research of MATSUMURA and TOUROUDE,2) by whom the microwave spectral lines of deuterocyclopentanone (IV) (*cf.* Fig. 2) were determined. In the present paper, the main transition $4_{04}$–$3_{03}$ was used for the analysis of the deuterated subspecies, while the transition $4_{14}$–$3_{13}$ was used in some cases as a reference. The spectrometer used was a conventional 100 kHz Stark modulation type and was constructed by MATSUMURA in National Chemical Laboratory for Industry (Tokyo Kogyo Shikensho).

2-Cylopenten-1-one (Tokyo Kasei Kogyo Co., Ltd., EP grade) was purified preparatively with a gaschromatograph.

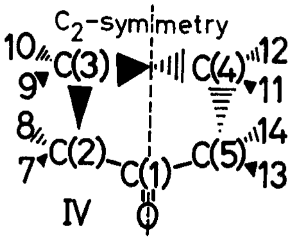


**Fig. 2.** Structure of cyclopentanone

Nickel catalyst was prepared from Raney alloy (Ni: *ca.* 48%, Wako Pure Chemical Ind., Ltd.) with the method proposed3). The catalyst was pretreated with deuterium before each measurement at 80°C for 3hr, to remove the occluded hydrogen. The measurement was carried out in a glass vessel of 200 mℓ, which contains 0.1 mℓ cyclopentenone, deuterium gas of *ca.* 99.9%, and 50 mg nickel catalyst. Initial molar ratio of $D_2$: cyclopentenone was six. The reaction temperature was 25°C or 40°C. As a reference (see the last column in Table 1), cyclopentenone was hydrogenated with "atomic" deu-

TABLE 1. Reaction of Cyclopentenone with Deuterium

| Run | Nickel Catalyst | | | | | DAc+Mg |
|---|---|---|---|---|---|---|
| | 39 | 40 | 48 | 49 | 52*) | 20 |
| Reaction Temp. (°C) | 25 | 25 | 40 | 40 | 40 | 23 |
| Reaction Time(min) | 30 | 180 | 20 | 90 | 120 | 60 |
| Yield (mole %) of Cyclopentanone | $5._4$ | $42._4$ | $4._8$ | $20._9$ | $72._9$ | $3._9$ |
| *d*-distribution (%) | | | | | | |
| $d_0$ | $7._4$ | $2._9$ | $10._2$ | $5._0$ | $2._4$ | $15._6$ |
| $d_1$ | $41._4$ | $40._8$ | $26._8$ | $33._7$ | $29._4$ | $33._4$ |
| $d_2$ | $46._4$ | $53._7$ | $56._4$ | $57._1$ | $60._7$ | $42._2$ |
| $d_3$ | $3._9$ | $2._6$ | $6._6$ | $3._5$ | $5._9$ | $8._8$ |
| $d_4$ | $0._9$ | | | $0._7$ | $1._2$ | |
| $d_5 \sim d_8$ | | | | | $(d_5)\,0._4$ | |
| $\phi = \Sigma i d_i / \Sigma d_i$ | $1.5_0$ | $1.5_6$ | $1.5_9$ | $1.6_1$ | $1.7_5$ | $1.4_4$ |
| $\beta d_1/\alpha d_1$ | 3.1 | 3.5 | 2.5 | 3.6 | 3.2 | 1.3 |
| *cis*-$\alpha\beta d_2$/*trans*-$\alpha\beta d_2$ | 3.7 | 6.0 | 6.1 | 6.5 | 4.7 | 1.0 |

*) The catalyst was pretreated with $D_2$ at 350°C for 3 hr.

terium produced by the reaction between magnesium ribbon and $CH_3COOD$ dissolved in $D_2O$.

All the experimental runs are summarized in Table 1. The run of No. 52 gave the highest conversion of the reactant (95.3% by weight). Main product was cyclopentanone whose yield is seen in Table 1. The others were cyclopentanol, 2-cyclopenten-1-ol and cyclopentane. Though the reaction temperature and time are different in each run, the results have a similar tendency in the distributions determined by the mass spectrometry. This relation, therefore, exists irrespective of the yield of cyclopentanone.

According to the mass spectral data, the deuterated products consist mainly of $d_2$- and $d_1$-species, followed by $d_0$-species (except for No. 52). Therefore, mean deuterium contents, $\phi$'s, are always less than two, even though the catalysts were treated with $D_2$. This means that the hydrogen cannot be excluded perfectly from the catalysts by the above treatment, and also that the double bond in the cyclopentenone accepts one or two H atoms from other adsorbed cyclopentenones directly or indirectly *via* the adsorbed H atom, besides D atoms, which exist abundantly on the surface by the dissociative adsorption of $D_2$.

Three following relations are found from the microwave spectral data given in Table 1, where $\alpha$ denotes the deuterated positions at C(2) or C(5) while $\beta$ at C(3) or C(4); 1°) The $\beta d_1$-subspecies is *ca.* three times more than the $\alpha d_1$-subspecies. 2°) The *cis*-$\alpha\beta d_2$-subspecies is more than *trans*-$\alpha\beta d_2$-subspecies (the last line of the Table), where *cis* and *trans* denote the two deuterium atoms locating at the same side and at the opposite side of the carbon ring, respectively. 3°) Among all the other $d_2$-subspecies only a trace of $\beta\beta d_2$-subspecies was detected in some runs.

As ought to be expected, the result with "atomic" deuterium (No. 20) does not give the above three findings, suggesting that the double bond is hydrogenated successively with H or D atoms from independent directions.

Even though the initial molar ratio of $D_2/C_5H_6O$ is so large that more than two deuterium atoms can be introduced in the cyclopentanone, mean deuterium content $\phi$ is below two in all the runs. This indicates that the exchange reaction between cyclopentanone and deuterium does not proceed so fast as the hydrogenation. The run of No. 52 gave the highest conversion of the reactant, but the $d$-distribution was similar to the others. Hence, we can find that hydrogen atoms occluded by nickel do not affect practically our observation, and will discuss the results, neglecting the occluded hydrogen.

Result 2°) indicates that cyclopentenone is adsorbed on the catalyst surface as the eclipsed (II) rather than as the staggered conformation (III) [see Fig. 1]. This conclusion is very interesting, because it coincides with BURWELL's proposition[4] that the carbon atoms bonded to the surface are more likely to be eclipsed.

Result 1°) can be explained, assuming that the half-hydrogenated state A in Fig. 3 is more stable than B. However, that the ratio $\beta$-$d_1/\alpha$-$d_1$ is nearly three irrespective

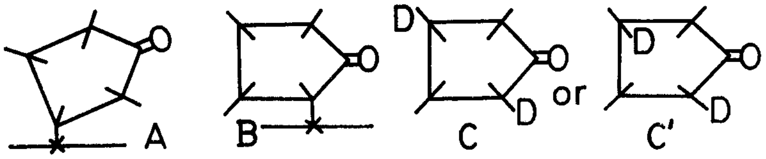
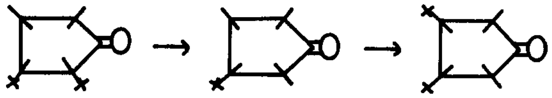


**Fig. 3.** Intermediate states of hydrogenation of cyclopentenone and its deuterogenated products

of the reaction conditions cannot be explained fully by the present data alone.

Result 3°) indicates the absence of $\alpha\beta' d_2$-subspecies, C or C' and $\beta\beta' d_2$-subspecies, ruling out possibility of double bond migration of the surface, as Eq. (1) shows:


(1)

The absence of the double bond migration was explained by comparison of the stability of 2-cyclopentenone and 3-cyclopentenone, because 2-cyclopentenone, whose double bond is conjugated to the carbonyl group, is more stable than 3-cyclopentenone.

The above tendencies were confirmed according to our unpublished data, also over a reduced nickel catalyst. It will be interesting to extend this research further from the stereochemical viewpoint, especially if the above result 2°) can be applied to the group VIII metal catalysts other than nickel.[5]

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