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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

Kozo HIROTA*), Raymonde TOUROUDE*), Makoto MIYASAKA*)
and Chi MATSUMURA**)

(Received October 27, 1976)

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 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](image)

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, by whom the microwave spectral lines of deuterocyclopentanone (IV) (cf. Fig. 2) were determined. In the present paper, the main transition 4_11-3_13 was used for the analysis of the deuterated subspecies, while the transition 4_11-3_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-Cyclopenten-1-one (Tokyo Kasei Kogyo Co., Ltd., EP grade) was purified preparatively with a gaschromatograph.

Nickel catalyst was prepared from Raney alloy (Ni: ca. 48%, Wako Pure Chemical Ind., Ltd.) with the method proposed. 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**

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Temp. (°C)</th>
<th>Nickel Catalyst</th>
<th>39</th>
<th>40</th>
<th>48</th>
<th>49</th>
<th>52(\ast)</th>
<th>DAc+Mg</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reaction Time(min)</td>
<td></td>
<td>30</td>
<td>180</td>
<td>20</td>
<td>90</td>
<td>120</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Yield (mole %) of Cyclopentanone</td>
<td></td>
<td>5_4</td>
<td>42_4</td>
<td>4_8</td>
<td>20_3</td>
<td>72_9</td>
<td>3_9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d-distribution (%)</td>
<td></td>
<td>7_4</td>
<td>2_9</td>
<td>10_2</td>
<td>5_9</td>
<td>2_4</td>
<td>15_4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>41_4</td>
<td>40_8</td>
<td>26_8</td>
<td>33_7</td>
<td>29_4</td>
<td>33_4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>46_4</td>
<td>53_7</td>
<td>56_4</td>
<td>57_4</td>
<td>60_7</td>
<td>42_2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3_9</td>
<td>2_6</td>
<td>6_6</td>
<td>3_5</td>
<td>5_9</td>
<td>8_8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0_9</td>
<td>0_7</td>
<td>1_2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(d_5\sim d_8)</td>
<td></td>
<td>(d_8)/0_4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\phi = \Sigma id_i/\Sigma d_i)</td>
<td></td>
<td>1_5_9</td>
<td>1_5_9</td>
<td>1_5_9</td>
<td>1_6_1</td>
<td>1_7_5</td>
<td>1_4_4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\beta d_i/\alpha d_i)</td>
<td></td>
<td>3_1</td>
<td>3_5</td>
<td>2_5</td>
<td>3_6</td>
<td>3_2</td>
<td>1_3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cis-(\alpha\beta d_2/\alpha\beta d_2)</td>
<td></td>
<td>3_7</td>
<td>6_0</td>
<td>6_1</td>
<td>6_5</td>
<td>4_7</td>
<td>1_0</td>
<td></td>
</tr>
</tbody>
</table>

\(\ast\) The catalyst was pretreated with D_2 at 350°C for 3hr.
Hydrogenation of 2-cyclopenten-1-one on Ni with Deuterium

terium produced by the reaction between magnesium ribbon and CH₃COOD dissolved
in D₂O.

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 d₁-
and d₄-species, followed by d₅-species (except for No. 52). Therefore, mean deuterium
contents, ϕ's, are always less than two, even though the catalysts were treated with D₂.
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 D₂.

Three following relations are found from the microwave spectral data given in Table
1, where a denotes the deuterated positions at C(2) or C(5) while β at C(3) or C(4); 1°) The βd₁-subspecies is ca. three times more than the ad₁-subspecies. 2°) The cis-aβd₁-
subspecies is more than trans-aβd₁-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 d₂-subspecies only a trace
of fβd₂-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 D₂/CH₃COOD is so large that more than two
deuteron atoms can be introduced in the cyclopentanone, mean deuterium content ϕ is
below two in all the runs. This indicates that the exchange reaction between cyclopen-
tanone 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 prac-
tically 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 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 β·d₁/α·d₁ is nearly three irrespective
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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 αψ′δ-l-subspecies, C or C′ and βψ′δ-l-subspecies, ruling out possibility of double bond migration of the surface, as Eq. (1) shows:

\[
\begin{align*}
\text{A} & \rightarrow \text{B} \\
\text{D} & \rightarrow \text{C}
\end{align*}
\]

(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.

References


2) The details of the study will be published elsewhere.

