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HYDROGENATION OF ACETONE ON ZnO CATALYST*

Part 1—Kinetics and hydrogen exchanges

By

Ken-ichi NAGAI**) and Koshiro MIYAHARA**

(Received March 30, 1975)

Abstract

Hydrogenation of acetone on ZnO catalyst took place with a large excess of hydrogen and its rate depends upon the first order of hydrogen pressure and a negative order of acetone pressure varying from -0.3 at 130°C to -0.8 at 180°C. The reversed reaction, i.e. dehydrogenation of 2-propanol was zero order of both hydrogen and alcohol pressures.

Hydrogen exchanges were investigated between (CH₃)₃CO-D₂, (CH₃)₃CO-(CD₃)CDOD, (CH₃)₂CHOH-(CD₃)₂CHOH and (CH₃)₂CHOH-(CD₃)CDOD and, furthermore, H₂-D₂ under coexistence of acetone or 2-propanol. The results are; (1) hydrogen in methyl group of acetone mixed rapidly with each other and with those of hydroxyl group of alcohol, suggesting the presence of adsorbed acetone with an enol-type configuration, while hydrogens in methyl group of alcohol mixed hardly, (2) isotopic effect on the rate of codehydrogenation of d₀- and d₅-2-propanol is responsible to the slow process of hydrogen abstraction from α-carbon and (3) isotopic mixing in hydrogen gas proceeds probably via Rideal-Eley mechanism between D₂ gas and adsorbed hydrogen atoms, but not the H₂-D₂ equilibration of liberated hydrogen gas.

Introduction

Many works have been reported on hydrogenation of acetone with metal catalysts but a little with metal oxide catalysts. Metal oxides, especially zinc oxide, are known to be active for the reverse of this reaction, i.e., dehydrogenation of 2-propanol, and its kinetic behaviour has been studied¹-³ with a conclusion that the dehydrogenation is rate-controlled by some surface process affected by coexisting acetone³.

In the present works, hydrogenation of acetone and dehydrogenation of 2-propanol catalyzed by zinc oxide is studied with respect to their
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kinetics and accompanying hydrogen exchanges (part 1), a mechanism of the reaction is proposed by taking account of the results of these exchanges as well as infrared spectroscopy of adsorbed intermediates and the observed kinetics are discussed according to the treatment of steady rate of reaction⁶ (part 2).

**Experimental**

**Apparatus:** The reaction was carried out with a closed, circulation system made of Pyrex glass as shown in Fig. 1. The volume of circulation system, A including the reaction vessel (1.8 cmφ × 5 cm), was ca. 250 ml. Reactant gases and argon of known amounts were mixed in the another circulation system, B, and introduced into the part A to start the reaction.

![Diagram of apparatus](image)

**Fig. 1.** Diagram of apparatus.


Reacting gas was circulated with a rate of ca. 500 ml/min through a preheater tube around the reaction vessel. During the reaction, the reaction vessel and preheater tube were immersed in an oil bath at a reaction temperature and 1 ml of reacting gas was sampled at times for mass spectrometric measurements.

**Materials:** Two grams of powdered and highly pure ZnO from Wako-Junyaku Co. was kneaded with glass wool and a little of water and dried in air. Prior to use, the catalyst was treated in the reaction vessel with 10 mmHg oxygen at 450°C for more than 10 hr and successively evacuated for 3 hr at 350°C.

Hydrogen or deuterium gas from cylinder was purified with Pd–Ag thimble. Acetone and 2-propanol of high purity from Wako-Junyaku Co. were passed through a CaCl₂-tube and distilled in vacuum repeatedly.

$d_τ$-Acetone ((CD₃)₂CO) and $d_τ$-2-propanol ((CD₃)₂CDOD) were obtained
from Merck Co. and of D-atomic fraction above 95%. 2-Propanol of which 70% was $d_6$ ((CD$_3$)$_2$CHOH) was prepared by hydrogenation of $d_6$-acetone with H$_2$ over nickel catalyst at 0°C; the remaining part of the alcohol consisted of deuterioisomers less than $d_6$. Argon gas was of 99.99% purity.

Analysis: Argon was admixed in the reactant as an internal reference for the mass spectrometric measurement of reacting gas. A part of reacting gas sampled in the vessel S with the sampling cock SC of Fig. 1 was introduced into a mass spectrometer (Hitachi RMU-6). In the case of hydrogenation of $d_6$-acetone with H$_2$, the relative amounts of acetone and 2-propanol were estimated from the relative heights of peaks at $m/e=40$ (Ar$^+$), 43 (C$_2$H$_3$O$^+$) and 45 (C$_2$H$_5$O$^+$) with reference to the individual mass spectra of argon, acetone and 2-propanol. In the case of reaction traced with deuterium, hydrogen gas alone was analyzed at first by introducing the sampled gas into the mass spectrometer through a liquid nitrogen trap. The trap was then warmed up to $-45^\circ$C and vaporized part, of which majority is acetone, was analyzed. The rest in the trap was finally vaporized and 2-propanol was admitted in the spectrometer by separating it from acetone with a Porapak Q column (1 m at 130°C) with He carrier. This treatment of sampled gas was necessary because hydrogen redistribution in acetone was caused considerably with this column, while hydrogen exchange of 2-propanol was absent.

Ionization voltage of the spectrometer was 70 v. The relative amounts of H$_2$, HD and D$_2$ were estimated with reference to those of a standard, equilibrated mixture of H$_2$ and D$_2$. Distribution of $d_6$-acetones was evaluated from the peaks at $m/e=58\sim64$ consisting exclusively of parent peaks of $d_6$-acetones.

Only a profile of distribution of $d_6$-2-propanol was took into account as rapid hydrogen exchange was caused between H$_2$O remaining in the mass spectrometer and hydroxyl group of the alcohol.

Results

(A) Kinetics

Dehydration of 2-propanol over ZnO was found to accompany with its dehydrogenation considerably above 250°C and further to decompose into CO$_2$ above 300°C and hence reactions were carried out at temperatures from 100 to 200°C to observe the single reaction,

\[(\text{CH}_3)_2\text{CO} + \text{H}_2 \rightarrow (\text{CH}_3)_2\text{CHOH} .\] (1)
Hydrogenation of acetone: The reaction was observable with a large excess of hydrogen. Figures 2 and 3 show that \( m = 1 \), while \( n \) varies from \(-0.3\) at \(130^\circ \text{C}\) to \(-0.8\) at \(180^\circ \text{C}\) for the initial rate of hydrogenation, \( V_{\text{H,0}} \), expressed as

\[
V_{\text{H,0}} = k_m P_H^m P_A^n,
\]

where \( P_H \) and \( P_A \) are the partial pressure of hydrogen and acetone, respectively.

Dehydrogenation of 2-propanol: Time courses of the dehydrogenation of 2-propanol at \(7\) mmHg of its initial pressure, \( P_I \), was followed at various \( P_H \) as shown in Fig. 4, which indicates that the dehydrogenation with a conversion as low as \(10\%) \) is not affected by coexisting hydrogen. Time courses at various \( P_I \) are given in Fig. 5, showing that the initial rate of dehydrogenation,
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$V_{-\text{H,O}}$ is independent of $P_1$. Slowing down of the dehydrogenation at its later stage is due to the equilibrium of the reaction (1). Consequently, we have the rate equation,

$$V_{-\text{H,O}} = k_{-} P_1^0 P_1^0,$$

in agreement with the result observed by Dechater and Teichner\(^2\).

(B) Deuteration and Hydrogen Exchanges.

**Deuteration of $d_n$-acetone:** $d_n$-Acetones of $n \leq 3$ and HD were formed by reaction of $(\text{CH}_3)\text{CO}$ with $\text{D}_2$ at 160°C as shown in Fig. 6. The

![Fig. 4. Time courses of dehydrogenation of 2-propanol.](image)

$P_1 = 7 \text{ mmHg}, 160^\circ\text{C},$

$P_H = 0 (\triangle), 150 (\bigcirc), 210 (\bullet), 360 (\Delta)$ and $500 (\triangle)$ mmHg.

![Fig. 5. Time courses of dehydrogenation of 2-propanol.](image)

$P_H = 500 \text{ mmHg}, 160^\circ\text{C}, P_1 = 1.8 \sim 14 \text{ mmHg}.$
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increasing rate of D-atoms in acetone at the initial stage of reaction was evaluated as $5 \times 10^{-2}$ mmHg/min, which is ca. ten times as large as the initial rate of 2-propanol formation and close to $5.3 \times 10^{-2}$ mmHg/min of the rate of HD evolution, showing the rapid hydrogen exchange between $D_2$ and $d_0$-acetone. Relative amounts of $d_n$-acetones coincide with those of the random distribution of D atoms at the observed D-atomic fraction of acetone, $y_A$, indicating a rapid hydrogen redistribution among methyl group of acetone.

Reaction of $d_0$-acetone with $d_2$-2-propanol: Meerwein-Ponndorf reduction of acetone having been known to take place with ZnO catalyst at 400°C was checked with the present reaction mixture at 160°C. As shown in Fig. 7, the hydrogen exchange of acetone was nearly completed during the initial ten minutes as seen from the random distribution of D
Fig. 7. Time courses of deuteroisomers of acetone formed by dehydrogenation of \(d_0\)-2-propanol under coexistence of \(d_0\)-acetone. \(P_A = P_I = 3.5\) mmHg; 160°C.

atoms. Mass spectrum of 2-propanol was unchanged during 60 minutes as shown in (A) of Table 1, suggesting the absence of Meerwein-Ponndorf reduction.

### Table 1. Mass spectra in the course of dehydrogenation of iso-propanol

<table>
<thead>
<tr>
<th>Reaction</th>
<th>React. time min.</th>
<th>Conversion</th>
<th>59</th>
<th>60</th>
<th>61</th>
<th>62</th>
<th>63</th>
<th>64</th>
<th>65</th>
<th>66</th>
<th>67</th>
<th>68</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) (d_0)-2-propanol mixed with (d_0)-acetone (1:1) 160°C, 7 mmHg, 2 gr ZnO.</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>18.2</td>
<td>6.2</td>
<td>2.1</td>
<td>3.2</td>
<td>5.2</td>
<td>61.6</td>
<td>4.2</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>6.1</td>
<td>100</td>
<td>22.5</td>
<td>10.6</td>
<td>3.7</td>
<td>1.0</td>
<td>4.0</td>
<td>76.0</td>
<td>1.7</td>
<td>7.8</td>
<td></td>
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<tr>
<td></td>
<td>60</td>
<td>9.0</td>
<td>100</td>
<td>26.8</td>
<td>13.4</td>
<td>5.4</td>
<td>1.2</td>
<td>4.2</td>
<td>78.5</td>
<td>2.2</td>
<td>6.4</td>
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<td>(B) (d_0) and (d_0)-2-propanol (3:1) 160°C, 7 mmHg, 2 gr ZnO.</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>20.3</td>
<td>2.8</td>
<td>5.1</td>
<td>13.7</td>
<td>18.8</td>
<td>87.5</td>
<td>14.9</td>
<td>1.7</td>
<td></td>
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<tr>
<td></td>
<td>60</td>
<td>4.7</td>
<td>100</td>
<td>18.1</td>
<td>5.0</td>
<td>5.0</td>
<td>11.7</td>
<td>18.3</td>
<td>84.6</td>
<td>12.8</td>
<td>1.9</td>
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<td></td>
<td>120</td>
<td>7.5</td>
<td>100</td>
<td>22.2</td>
<td>6.3</td>
<td>5.2</td>
<td>12.6</td>
<td>18.1</td>
<td>84.5</td>
<td>14.6</td>
<td>2.9</td>
<td></td>
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<tr>
<td>(C) (d_0) and (d_0)-2-propanol (1:1) 160°C, 7 mmHg, 2 gr ZnO.</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>20.3</td>
<td>2.8</td>
<td>5.1</td>
<td>13.7</td>
<td>18.8</td>
<td>87.5</td>
<td>14.9</td>
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<td>19.2</td>
<td>83.7</td>
<td>10.7</td>
<td>4.1</td>
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**Hydrogenation of Acetone on ZnO Catalyst**

**Codehydrogenation of \( d_0 \)- and \( d_\tau \)- or \( d_\phi \)- and \( d_\phi \)-2-propanol:** The reaction with a mixture of \( d_\tau \)- and \( d_\phi \)-2-propanol was carried out to investigate the hydrogen randomization in methyl groups of 2-propanol and acetone formed by dehydrogenation. Relative amounts of deuteroisomers in produced acetone and hydrogen shown in Fig. 8 are in agreement with those of random distribution of D atoms with \( y_A = 0.32 \) for acetone and \( y_H = 0.27 \) for hydrogen, respectively. The mass spectrum of unreacted 2-propanol was changed a little as given in (B) of Table 1, suggesting that the mixing of hydrogen atoms in methyl groups of \( d_\tau \)- and \( d_\phi \)-2-propanol is considerably slow.

The D-atomic fractions of produced acetone and hydrogen are evidently smaller than that of 2-propanol (ca. 0.4), and this suggests an isotopic effect on dehydrogenation rate, that is, \( d_\phi \)-alcohol was much consumed as compared with \( d_\tau \)-alcohol. There are three types of hydrogen in 2-propanol, that is, those in methyl group, attached to \( \alpha \)-carbon and in hydroxyl group; the last one is not responsible to the present isotopic effect because of its rapid ramdomization as found in the preceding experiment.

![Fig. 8. Time courses of deuteroisomers of acetone and hydrogen formed by codehydrogenation of \( d_\phi \)- and \( d_\phi \)-2-propanol.](image)

\( P_1 = 7 \text{ mmHg (} d_0/d_\phi = 3/2) \), 160°C.
The results of codehydrogenation of \(d_6\)- and \(d_6\)-2-propanol are shown in (C) of Table 1. The relative height of peak at \(m/e=65\) due to ion \([\text{CD}_2\text{COH}]^+\) was changed a little with the progress of codehydrogenation (C), while it was evidently increased in reaction (B). Taking account of the rapid hydrogen exchange between hydroxyl group of alcohol and that the mass spectra in (B) and (C) of Table 1 are given in terms of ratios of respective peak heights to that at \(m/e=59\) due to ion \([\text{CH}_3\text{COH}]^+\), the above result indicates that \(\text{CD}_3\text{CHOH}\) is much consumed as compared with \(\text{CD}_3\text{CDOH}\), while \(\text{CD}_3\text{CHOH}\) is dehydrogenated as rapid as \(\text{CH}_3\text{CHOH}\). We can thus conclude that the isotopic effect observed in the codehydrogenation of \(d_6\)- and \(d_6\)-2-propanol is caused by hydrogen atoms attached to \(\alpha\)-carbon of alcohol.

**H\(_2\)-D\(_2\) equilibration during the reactions:** Cohydrogenation of \(d_6\)- and \(d_6\)-acetone and codehydrogenation of \(d_6\)- and \(d_6\)-2-propanol were carried out in the presence of \(H_2\) and \(D_2\). In these reactions, the D-atomic fraction of hydrogen was made equal to that of acetone or alcohol so as

![Fig. 9](image-url). Time courses of \(H_2\)-D\(_2\) equilibration during the cohdrogenation of \(d_6\)- and \(d_6\)-acetone (C) or the codehydrogenation of \(d_6\)- and \(d_6\)-2-propanol (C). \(P_H=210\) mmHg \((H_2/D_2=3/2)\), \(P_A=5\) mmHg \((d_6/d_6=3/2)\), \(P_T=5\) mmHg \((d_6/d_6=3/2)\).
to make the D-atomic fractions of gaseous and adsorbed hydrogen equal to each other. From the results shown in Fig. 9, the initial rates are estimated as $3.5 \times 10^{-2}$, $5 \times 10^{-3}$ and $2 \times 10^{-2}$ mmHg/min for the evolution of HD, hydrogenation of acetone and dehydrogenation of alcohol, respectively. HD formation is faster than hydrogenation and dehydrogenation, however, it attained after 60 minutes reaction to only ca. 6% of the equilibrium amount (48%).

Retardation of the H$_2$–D$_2$ equilibration by coexisting acetone or 2-propanol was additionally examined as given in Fig. 10, where $r$ is the rate constant of the exchange obeying the first order rate equation,

$$P_H \frac{dw}{dt} = r(w_\infty - w);$$

$w$ denotes the mol-fraction of HD in hydrogen gas and $w_\infty$ the special value of $w$ at the equilibrium of exchange. The rate, 10 mmHg/min·g Cat., of the exchange at 0°C is much large as compared with $1.75 \times 10^{-2}$ or $2.5 \times 10^{-2}$ mmHg/min·g Cat. observed during hydrogenation of acetone or dehydrogenation of 2-propanol, respectively. It decreased linearly with the amount of added acetone or alcohol and was almost quenched by addition of ca. 60 $\mu$l/g Cat. This amount for quenching is only 4% of 1.5 ml/g Cat. of acetone saturating the catalyst surface at 0°C.
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Discussion

The initial rate of hydrogenation of acetone depends upon the partial pressure of acetone with a negative order varying from $-0.3$ at $130^\circ$C to $-0.8$ at $180^\circ$C. This fact cannot be interpreted as being caused by occupation of active sites with adsorbed acetone, because the positive heat of acetone adsorption on ZnO$^5$ should result in the temperature dependence opposite to the observation. This kinetics will be discussed in the next paper as being due to a mechanistic factor, that is, changes of relative rates of constituent steps.

Meerwein-Ponndorf reduction of acetone was denied by the reaction of $d_0$-acetone with $d_2$-2-propanol. In this reaction, the value of $y_A \approx 0.09$ as given in Fig. 7 is expected for the randomization of D atoms in hydroxyl group of 2-propanol with whole hydrogen atoms in acetone. Accordingly, it is concluded that deuteroisomers of acetone are formed by a rapid hydrogen exchange between methyl group of $d_0$-acetone and hydroxyl group of $d_2$-alcohol.

It has been suggested$^5$ that the rapid hydrogen randomization between $d_0$- and $d_2$-acetone over ZnO catalyst takes place via acetone adsorbed on a pair sites, Zn$^{2+}$–$O^{2-}$, with an enol-type configuration and dissociatively adsorbed hydrogen atom. Similar rapid randomization of hydrogen in acetone was observed in the present experiments on acetone hydrogenation and dehydrogenation of 2-propanol, suggesting the presence of dissociative adsorption of hydrogen and the reversible change of adsorbed acetone into an enol-type configuration.

Isotopic effect on the dehydrogenation of 2-propanol is found to be attributed to the process of hydrogen abstraction from $\alpha$-carbon. This process is slow and before it the fission of C–H bond in methyl group does not occur as seen from the absence of hydrogen exchange of 2-propanol except its hydroxyl group.

Isotopic mixing in hydrogen gas formed from $d_0$- and $d_2$-2-propanol mixture was similarly random as shown in Fig. 8. This randomization may not be responsible to the $H_2$–$D_2$ equilibration in hydrogen once liberated into gas phase but to the random recombination of adsorbed hydrogen atoms on the catalyst surface, because the equilibration was markedly retarded by coexisting 2-propanol as shown in Fig. 10. The evolution of HD alone during the deuteration of $d_0$-acetone is similarly not responsible to the $H_2$–$D_2$ equilibration in deuterium gas diluted by a little of H atoms. According to the rapid hydrogen exchange between adsorbed
acetone and hydrogen atom\textsuperscript{5)}, the D fraction of adsorbed hydrogen atoms during the deuteration of \textit{d\textsubscript{5}}-acetone may be ca. 0.15 at most as shown by a broken line in Fig. 6, and hence HD and H\textsubscript{2} should be evolved in a ratio of 0.25/0.72 by random recombination of adsorbed hydrogen atoms, far differing from the observed result. The evolution of HD alone may be attributed to the Rideal-Eley mechanism,

$$D_2 + H(a) \rightarrow HD + D(a),$$

as proposed by TAMARU \textit{et al}\textsuperscript{6).}

On reference to the practically complete retardation of H\textsubscript{2}–D\textsubscript{2} equilibration by coexisting acetone or 2-propanol amounting to only ca. 4\% of saturation of catalyst surface, the active sites for the equilibration and the hydrogenation-dehydrogenation disperse sparsely on the catalyst surface, probably consisting of vacancies of O\textsuperscript{2–} ions.

\textbf{References}

4) K. MIYAHARA and S. YOKOYAMA, This Journal 19, 127 (1971).