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# HYDROGENATION OF ACETONE ON ZnO CATALYST*)

## Part 2. Infrared spectroscopy of adsorbed intermediates and mechanism of the reaction

By

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**Abstract**

The adsorbed states of hydrogen, acetone and 2-propanol over ZnO catalyst were studied with ir spectroscopy. Chemisorption of deuterium on the pair sites $Zn^{2+}$-$O^{2-}$ was proved with ZnO pretreated with acetone. Acetone was adsorbed with an enol-type configuration loosening the double bond in carbonyl group and an another type, X, of adsorbed acetone was found with increase of adsorbed amount or with heating adsorbed 2-propanol at 100°C.

On the bases of these results of ir spectroscopy and the hydrogen exchanges in the preceding work, a mechanism of acetone hydrogenation was proposed as that the reaction is rate-controlled by the step of hydrogen chemisorption as well as the step of addition of hydrogen atom to $\alpha$-carbon. The kinetics proviously observed was well accounted for on this mechanism.

## Introduction

In the preceding paper[1] intermediates of acetone hydrogenation and its reverse catalyzed by zinc oxide were suggested to include adsorbed hydrogen atoms and adsorbed acetone with an enol-type configuration. Furthermore, hydrogen of hydroxyl group of 2-propanol was found to be released easily on the catalyst surface. In the present work the states and behaviors of these intermediates are investigated with infrared spectroscopy and the mechanism proposed on these bases was shown to be in good agreement with the kinetics previously observed[1].

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## Experimental

*Materials*: Powdered ZnO (Kadox-25 from New Jersey Zinc Co.) was pressed into a disk of 2 cm diameter and 0.16 mm thick and mounted at the center of the ir cell. Prior to use the catalyst was heated in 10 mmHg oxygen at 450°C fro more than 10 hr, evacuated for several hours at 350°C similarly to the preceding work[1] and, furthermore, oxidized and evacuated again at 350°C each for 30 min to obtain a sufficient ir transmission.

Hydrogen, deuterium, $d_0$- and $d_6$-acetone and $d_8$-2-propanol were treated similar to the preceding work[1].

*Apparatus*: The ir cell was a conventional one made of glass tube of 3 cm diameter and 10 cm length, of which both ends were sealed with KBr windows. Catalyst disk at the center of cell can be heated up to 500°C with a nichrome heater wrapped around the cell and the both ends of the cell were cooled by water jackets. All of spectra were observed at a room temperature.

## Results and Discussions on ir Spectroscopy

Zinc oxide well evacuated at 350°C after oxygen treatment has a poor ir transmission and, hence, it was reoxidized and evacuated at 350°C as short as 30 min. Zinc oxide catalyst with such a pretreatment revealed a sufficient ir transmission and activity for the acetone hydrogenation. The ir spectrum of catalyst itself is shown by (b. g.) of Fig. 1 in agreement with reported results[2] with evident bands at 1515 and 1328 $cm^{-1}$.

*Adsorbed deuterium*: Curve 1 in Fig. 1 is the spectrum obtained in contact

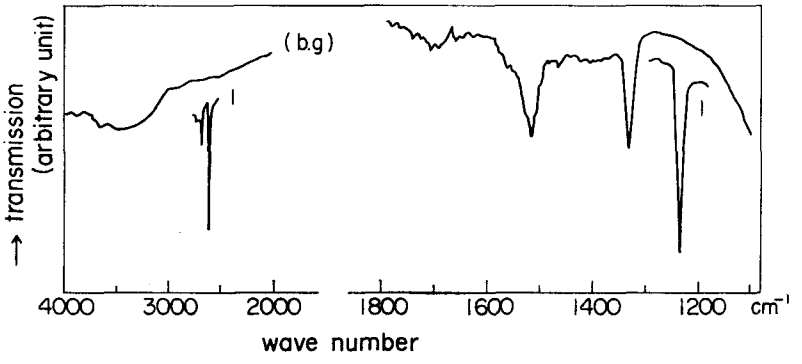



**Fig. 1.** ir Spectrum of deuterium (80 mmHg, 20°C) adsorbed on ZnO (Kadox-25).

with 80 mmHg $D_2$. New sharp bands appeared at 2700, 2660, 2580 and 1230 $cm^{-1}$. The latter two bands were assigned by EISCHENS *et al.*[3] to deuterium dissociatively adsorbed on the pair sites, $Zn^{2+}$–$O^{2-}$, and dissappeared by evacuation at a room temperature, while former two remained after evacuation at 100°C and coincide with those observed by ATHERTON[4] with $D_2O$ adsorbed on ZnO. The bands at 2700 and 2660 $cm^{-1}$ are thus assigned to −OD group formed on the catalyst surface.

*Adsorbed acetone*: Spectra of $d_0$- and $d_6$-acetone adsorbed at room temperature with various amounts are shown in Figs. 2 and 3. In Fig. 3, the

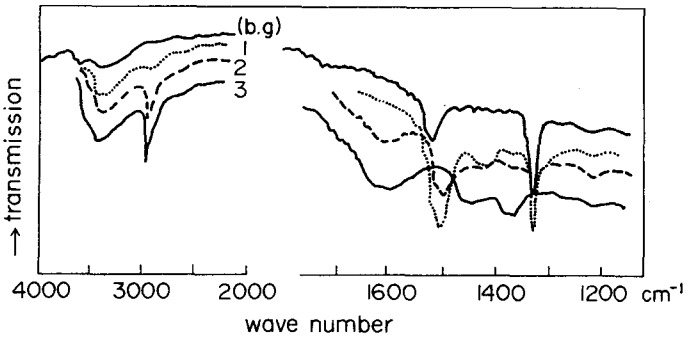



**Fig. 2.** ir Spectra of $d_0$-acetone adsorbed on ZnO at a room temperature.
Curve 1: 45 $\mu$l, 2: 100 $\mu$l, 3: evacuated after treatment with 6 mmHg acetone.

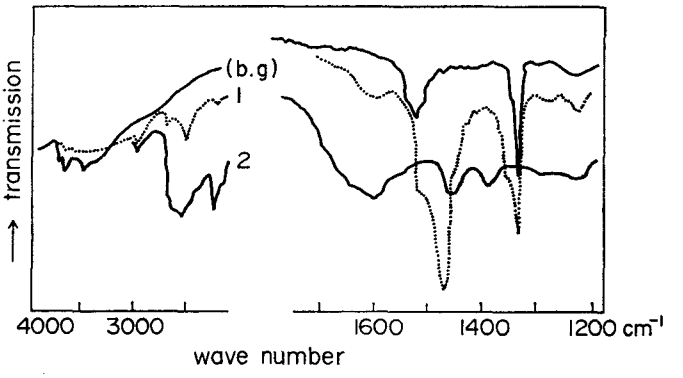



**Fig. 3.** ir Spectra of $d_6$-acetone adsorbed on ZnO at a room temperature.
Curve 1: 55 $\mu$l, 2: evacuated after treatment with 6 mmHg acetone.

bands of (b. g.) around 3500 $cm^{-1}$ disappeared by adsorption of $d_6$-acetone and new bands around 2500 $cm^{-1}$ grew, of which form resembles to those above 3000 $cm^{-1}$ in the spectrum of $d_0$-acetone. With admission of 80 mmHg $D_2$ at room temperature over ZnO preadsorbed with 25 $\mu$l $d_0$-acetone, the bands due to $d_0$-acetone did not change and new bands grew at 2580 and 1230 $cm^{-1}$, showing the chemisorption of deuterium on $Zn^{2+}$–$O^{2-}$ pair sites. These bands did not vary as long as an hour with none of HD evolution into gas phase. These facts indicate that, at a room temperature, hydrogen atoms of acetone are easily exchanged with hydroxyl group on the catalyst surface, but hardly with hydrogen atoms chemisorbed on the $Zn^{2+}$–$O^{2-}$ pair sites.

The spectra below 1800 $cm^{-1}$ in Figs. 2 and 3 were unchanged with evacuation at 100°C and lacking in the band at *ca.* 1700 $cm^{-1}$ characteristic for carbonyl group, suggesting that adsorption of acetone on ZnO is so strong as to lose the double bond in this group.

Bands at 1500 and 1420 $cm^{-1}$ of $d_0$-acetone and 1470 $cm^{-1}$ of $d_6$-acetone increased with increase of adsorbed amount, however, they as well as the band at 1330 $cm^{-1}$ due to catalyst itself disappeared with further increase of amount beyond *ca.* 60 $\mu$l, and at the same time a band at 1600 $cm^{-1}$ and new ones at 1460 and 1380 $cm^{-1}$ grew for both of $d_0$- and $d_6$-acetone. For the assignment of thesee bands, ir spectrum of acetylacetone adsorbed on ZnO were observed as shown in Fig. 4, which is in good agreement with the spectrum of zinc acetylacetonate[5] as given in Table 1. Referring to these spectra, we assign the bands at 1600 and 1500 $cm^{-1}$ of adsorbed acetone to $\nu$(C=C), $\nu$(C=O) and a coupling of $\nu$(C=O)+$\delta$(C–H) in plane.

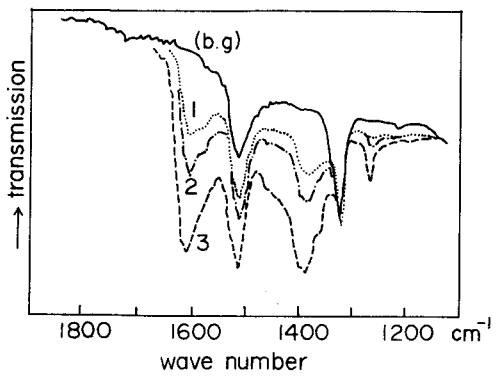
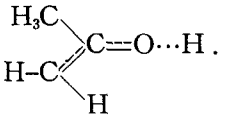



**Fig. 4.** ir Spectra of acetylacetone adsorbed on ZnO at a room temperature.
Curve 1: 24 $\mu$l, 2: 47 $\mu$l, 3: 95 $\mu$l.

TABLE 1 Infrared Absorption spectra of acetylacetone adsorbed on ZnO.

| Absorption band, $cm^{-1}$ | | Assignment[5] |
|---|---|---|
| Adsorption | Zn-Chelate[5] | |
| 1600 | 1592 | $\nu$(C=C), $\nu$(C=O) |
| 1520 | 1523<br>1464 | $\nu$(C=O)+$\delta$(C–H) in plane |
| 1400 | 1394 | $\delta_d$(C–H) |
| | 1361 | $\delta_s$(C–H) |
| 1235 | 1261 | $\nu$(C=C)+$\delta$(C–$CH_3$) |

A band corresponding to 1420 $cm^{-1}$ of adsorbed $d_0$-acetone was absent in the region above 1200 $cm^{-1}$ of spectrum of adsorbed $d_6$-acetone, suggesting it is due to some vibrations of bonds with hydrogen. Bending bands $\delta_d$(C–H) and $\delta_s$(C–H) of ethylene coordinating to platinum atom are observed at 1428 and 1402 $cm^{-1}$, respectively, and, furthermore, those of $-\overset{|}{\underset{O}{C}}=CH_2$ are ranged from 1440 to 1400 $cm^{-1}$. Consequently, we assume for the adsorbed state of acetone the following enol-type configuration in conformity with one proposed previously[1] for the hydrogen randomization of acetone as



Adsorption of acetone with an enol-type configuration has been similarly reported with respect to NiO[7] and SiO[8] catalysts.

The bands at 1600, 1460 and 1380 $cm^{-1}$ were intensified with increase of adsorbed acetone irrespective of $d_0$ and $d_6$, suggesting that these bands should be assigned to groups of atoms excluding hydrogen. The assignments of these bands are ambiguous for the present, however, the configuration of adsorbed acetone may be concluded to change with increase of adsorbed amount from an enol-type into another type X, in which the

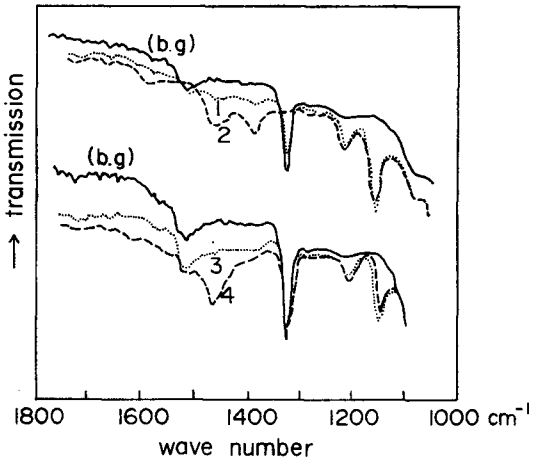


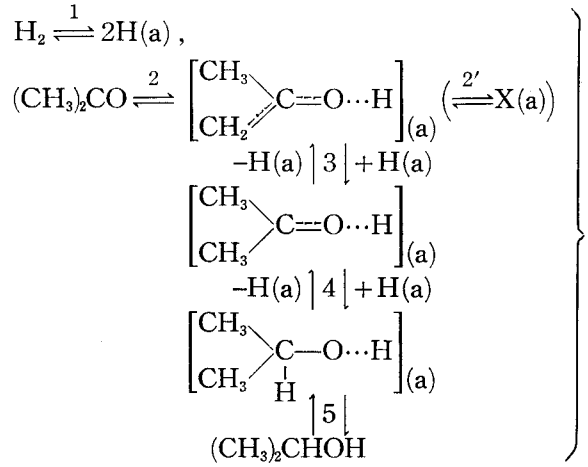

**Fig. 5.** ir Spectra of $d_8$-2-propanol adsorbed on ZnO at a room temperature.
Curve 1: 80 $\mu$l, 2: evacuated for 2 hr at 100°C, 3: 35, 1, 4: evacuated for 1 hr at 100°C.

double bond in carbonyl group and the coupling of $\nu(C{=}O)+\delta(C{-}H)$ are absent as shown by the absence of bands at 1700 and 1500 $cm^{-1}$.

The ir spectrum of 2-propanol adsorbed on ZnO at room temperature was similar to that of liquid 2-propanol except a little broadening of the band of hydroxyl group around 3500 $cm^{-1}$ to the lower side of wave number, indicating formation of hydrogen bond. Figure 5 shows the spectra of adsorbed $d_8$-2-propanol. The bands at 1460 and 1390 $cm^{-1}$ grew with heating at 100°C for an hour, indicating the formation of adsorbed acetone with the configuration of X.

## Mechanism of Acetone Hydrogenation

Summerizing the results of hydrogen exchanges[1] and ir spectroscopy of adsorbed species, we propose the following steps for reversible hydrogenation of acetone over zinc oxide catalyst.



(1)

Step 1 is the chemisorption of hydrogen on the pair sites $Zn^{2+}$–$O^{2-}$ as observed by ir spectroscopy of deuterium admitted on ZnO treated with acetone. This step is strongly retarded by coexisting acetone or 2-propanol. Hydrogen atoms on $Zn^{2+}$ and $O^{2-}$ are not discriminated from each other with respect to their reactivity. Step 2 is the adsorption of acetone into an enol-type or X-type configuration, through which hydrogens in methyl group of acetone are redistributed rapidly[6]. During the dehydrogenation of 2-propanol, hydrogen isotopic effect was observed with respect to hydrogen at $\alpha$-carbon but not to hydrogen of methyl group and, furthermore, hydrogen in methyl group of 2-propanol were not redistributed,

while those in formed acetone were completely redistributed[1]. On these bases, steps 3, 4 and 5 are proposed, among which step 4 should be overwhelmingly slow because of the isotopic effect of hydrogen attached to $\alpha$-carbon. Step 3 causes the hydrogen exchange of acetone during deuteration of $d_0$-acetone.

## Discussions on the Kinetics of Hydrogenation and Dehydrogenation

The kinetics previously[1] observed with respect to the initial rate of acetone hydrogenation and that of dehydrogenation of 2-propanol are well interpreted as follows on the basis of scheme (1) with overwhelmingly slow steps 1 and 4.

The steady rate, $V_H$, of acetone hydrogenation is given as

$$V_H = v_{+s} - v_{-s}, \tag{2. V}$$

where

$$\left.\begin{aligned} v_{+s} &\equiv (kT/h)\, a^{I(s)}/a^{\ddagger(s)} \\ \text{and} \\ v_{-s} &\equiv (kT/h)\, a^{F(s)}/a^{\ddagger(s)} \end{aligned}\right\} \tag{2. v}$$

are the forward and backward unidirectional rate of step $s(=1, 2, 3, 4$ or $5)$ expressed in terms of the absolute activities $a^{I(s)}$, $a^{F(s)}$ and $a^{\ddagger(s)}$ of the initial, final and critical systems, I(s), F(s) and $\ddagger$(s), of step $s$, respectively[9]. The term $(kT/h)$ has the usual meaning. Equation (2) is thus recast in the form of

$$V_H = u'_s(a^{I(s)} - a^{F(s)}) \tag{3. V}$$

where

$$u'_s \equiv (kT/h)/a^{\ddagger(s)} \tag{3. u}$$

is a function of temperature and the surface coverage of the catalyst.

Assuming the ideal gas law for a gaseous component, $\delta$, we have

$$a^{\delta} = a_0^{\delta} P_{\delta}, \tag{4}$$

where $P_{\delta}$ is the partial pressure of $\delta$ and $a_0^{\delta}$ is constant at a given temperature. With respect to the overwhelmingly slow step 1 of scheme (1), we have

$$a^{I(1)} = a_0^{H_2} P_H \quad \text{and} \quad a^{F(1)} = (a^{H(a)})^2, \tag{5}$$

where $P_H$ is the partial pressure of hydrogen. Introducing Eqs. (5) into (3. V), we have

$$V_H = u_1 P_H \left(1 - \frac{(a^{H(a)})^2}{a_0^{H_2} P_H}\right), \tag{6. V}$$

where

$$u_1 \equiv u_1' a_0^{H_2} = (kT/h)\, a_0^{H_2}/a^{\neq(1)} \tag{6. u}$$

is the forward unidirectional rate of step 1 at an unit pressure of $H_2$.

With regard to step 4, we have similarly

$$V_H = u_4' a_0^A P_A (a^{H(a)})^2 \left(1 - \frac{a_0^I}{a_0^A (a^{H(a)})^2} \cdot \frac{P_I}{P_A}\right),$$

where $P_A$ or $P_I$ is the partial pressure of acetone or 2-propanol, respectively, and the practical equilibria of steps other than 1 and 4 are took into account. $V_H$ is further recast with reference to Eq. (6. V) in the form of

$$V_H = u_4 P_A P_H \left(1 - \frac{V_H}{u_1 P_H} - K \frac{P_I}{P_A P_H}\right), \tag{7}$$

where

$$u_4 \equiv u_4' a_0^A a_0^{H_2} = (kT/h)\, a_0^A a_0^{H_2}/a^{\neq(4)}$$

is the forward unidirectional rate of step 4 in a special case where the initial system of the step, I(4), is equilibrated with gaseous acetone and hydrogen both at an unit pressure, and

$$K \equiv a_0^I/a_0^A a_0^{H_2}$$

is the equilibrium constant of acetone hydrogenation into 2-propanol. It follows from the above expression of $V_H$ that

$$(1 - KP_I/P_A P_H)/V_H = 1/u_1 P_H + 1/u_4 P_A P_H . \tag{8}$$

In the present experiments, acetone was hydrogenated with a large excess of hydrogen, and hence $P_H$ is practically constant and Eq. (7) can be rewritten in terms of $x \equiv P_A/(P_A + P_I)$

as

$$(P_A + P_I)\, x/u_1 + 1/u_4 P_H = \left(1 - K(1-x)/xP_H\right) x/(-\dot{x}) . \tag{9}$$

The right-hand side of Eq. (9) observed at various $(P_A + P_I)$ and temperature was plotted versus $x$ as shown in Figs. 6 and 7, where the value of $K$

was introduced from the observed results of KEMBALL[10]. The linearity of plots proved with reactions at 1.8 and 3 mmHg of $(P_A+P_I)$ was assumed for the reactions with $(P_A+P_I)$ larger than 3 mmHg. The linearity indicated that $u_1$ and $u_4$ are constant independent of $x$.

Logarithmic $u_1P_H$ and $u_4P_H$ evaluated from Fig. 6 are plotted in Fig. 8 versus logarithmic $(P_A+P_I)$, and the result indicates that $u_1$ and $u_4$ are given as

$$u_1=U_1/(P_A+P_I) \text{ and } u_4=U_4/(P_A+P_I) \quad (10)$$

where $U_1$ or $U_4$ is a function of the activation energy of step 1 or 4, respectively, as seen from the definition of $u_1$ and $u_4$, and is constant at a given temperature.

The initial rate, $V_{H,O}$, of acetone hydrogenation at $P_I=0$ is given form Eq. (8) as

$$P_H/V_{H,O}=P_A/U_1+1/U_4 \quad (11)$$

with reference to Eq. (10). Equation

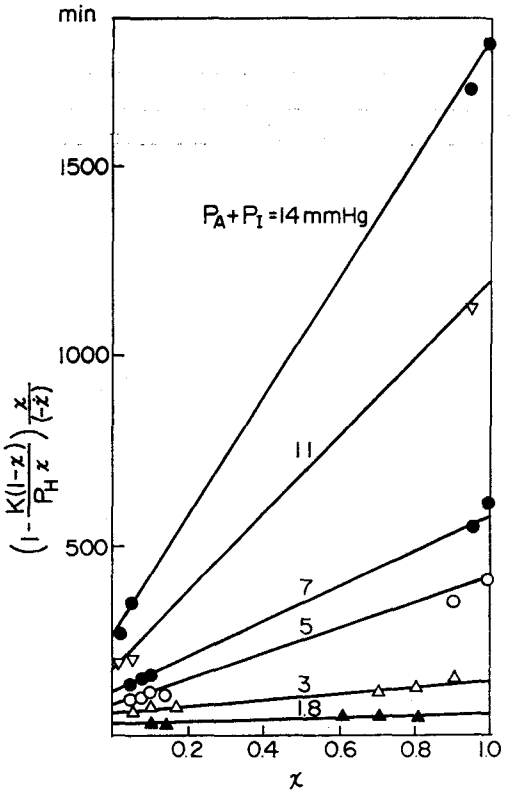



**Fig. 6.** Plots of the courses of acetone hydrgenation and dehydrogenation of 2-propanol according to Eq. (9) in the text.

$P_H$ = 500 mmHg, $P_A+P_I$ = 1.8, 14 mmHg, 160°C.

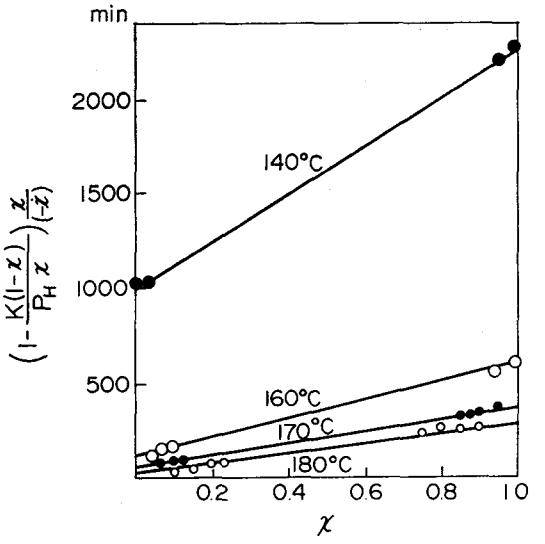



**Fig. 7.** Plots of the courses of acetone hydrogenation according to Eq. (9) in the text.

$P_H$=500 mmHg, $P_A+P_I$=7 mmHg, 140~180°C.

(11) agrees with the observed results that $V_{H,0}$ is first order of $P_H$ and $1/V_{H,0}$ depends linearly upon $P_A$ as shown in Fig. 9 reproduced from the preceding paper[1]. Figure 10 shows the temperature dependences of $U_1$

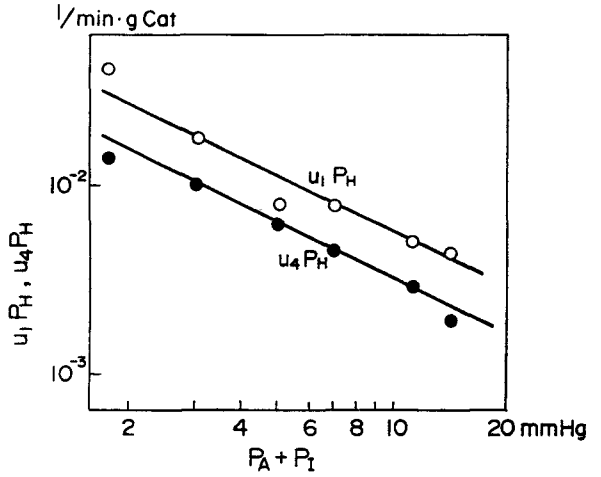



**Fig. 8.** Dependences of $u_1 P_H$ and $u_4 P_H$ upon $P_H + P_I$.
$P_H = 500$ mmHg, 160°C.

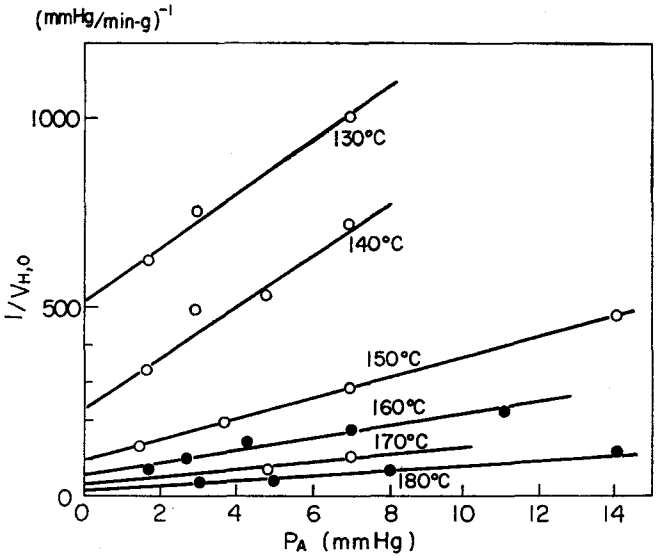



**Fig. 9.** Dependences of the initial rate of acetone hydrogenation upon acetone pressure (Cf. Eq. (11) in the text).
$P_A = 1.8 \sim 14$ mmHg, $P_H = 500$ mmHg, 130~180°C.

and $U_4$, from which the activation energy of step 1 or 4 is evaluated as 17 or 22 kcal/mol, respectively. Drop in the reaction temperature makes $U_4$ to be more smaller than $U_1$ and, hence, the dependence, $n$, of $V_{H,O}$ upon $P_A$ shifts from $-1$ toward zero.

The rate of steady dehydrogenation of 2-propanol is given as

$$V_{-H} = v_{-s} - v_{+s}$$

and, accordingly, it follows similarly to $V_H$ that

$$P_A(P_A+P_I)/U_1+(P_A+P_I)/U_4 = (KP_I-P_AP_H)/V_{-H}. \quad (12)$$

At the initial stage of the dehydrogenation, where $P_A=0$, we have

$$V_{-H,O} = KU_4$$

which indicates that the initial rate of dehydrogenation is independent of $P_I$ as well as $P_H$ as observed previously[1].

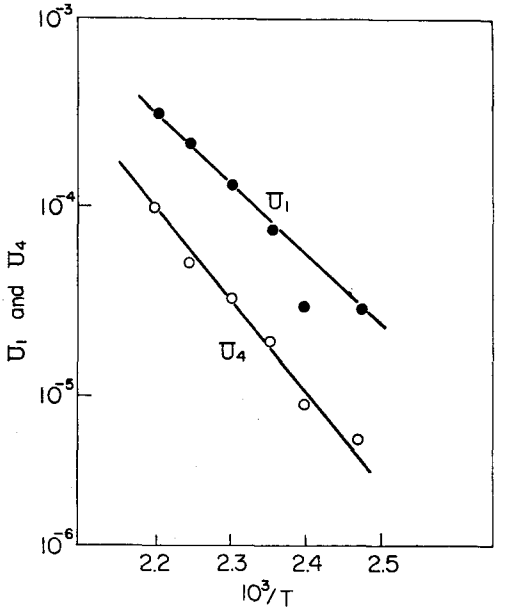



**Fig. 10.** Temperature dependences of $U_1$ and $U_4$.

With the dehydrogenation of 2-propanol mixed with acetone but not with hydrogen, it follows from Eq. (12) that

$$V_{-H,O} = KU_1U_4P_I/(P_A+P_I)(U_1+P_AU_4), \quad (13)$$

which can be approximated as

$$V_{-H,O} = k_-P_I/P_A \quad (14)$$

in a case of $U_1 \ll P_AU_4$. The kinetics of Eq. (14) has been observed by DECHATER and TEICHNER[11] with a mixture of 16 mmHg 2-propanol and 2~16 mmHg acetone at 200°C. $U_1$ and $U_4$ at 200°C are now evaluated according to Fig. 10 as $6\times10^{-4}$ and $2.8\times10^{-4}$, respectively, and, thus, Eq. (13) is found to reproduce well the observed kinetics of Eq. (14).

**Acknowledgement**

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