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Author(s)	NAGAI, Ken-ichi; MIYAHARA, Koshiro
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HYDROGENATION OF ACETONE ON ZnO CATALYST^{*})

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

By

Ken-ichi NAGAI^{**}) and Koshiro MIYAHARA^{***})

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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 $\text{Zn}^{2+}\text{-O}^{2-}$ 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 α -carbon. The kinetics previously observed was well accounted for on this mechanism.

Introduction

In the preceding paper¹⁾ 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 observed¹⁾.

^{*}) Abstracted in part from the doctoral thesis of Ken-ichi NAGAI, Hokkaido University.

^{**}) Transferred to the Institute of Technology, Hitachi Shipbuilding & Engineering Co. Ltd., Konohana-ku, Osaka 554, Japan.

^{***}) Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan.

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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 for more than 10 hr, evacuated for several hours at 350°C similarly to the preceding work¹⁾ 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 work¹⁾.

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 results²⁾ with evident bands at 1515 and 1328 cm^{-1} .

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

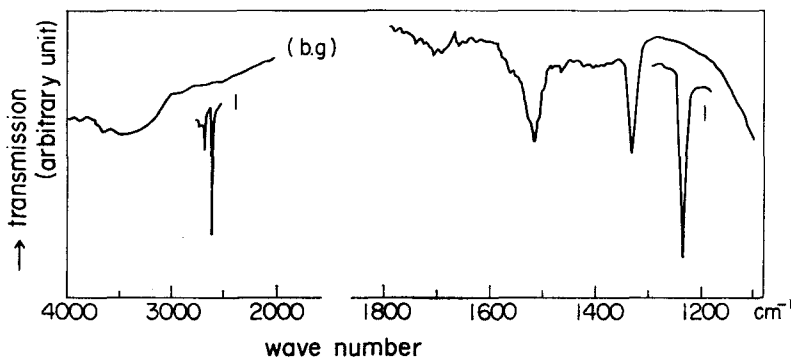


Fig. 1. ir Spectrum of deuterium (80 mmHg, 20°C) adsorbed on ZnO (Kadox-25).

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 disappeared by evacuation at a room temperature, while former two remained after evacuation at 100°C and coincide with those observed by ATHERTON⁴⁾ 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

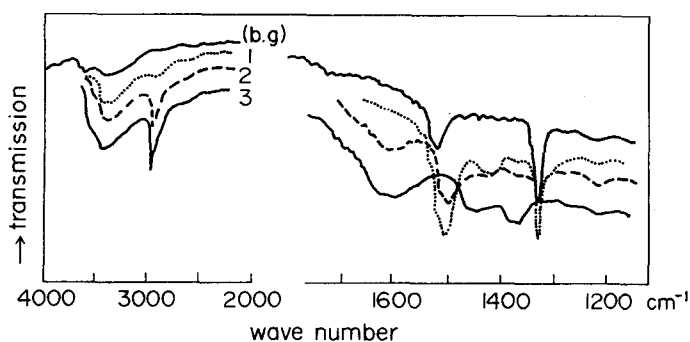


Fig. 2. ir Spectra of d_0 -acetone adsorbed on ZnO at a room temperature.

Curve 1: $45\text{ }\mu\text{l}$, 2: $100\text{ }\mu\text{l}$, 3: evacuated after treatment with 6 mmHg acetone.

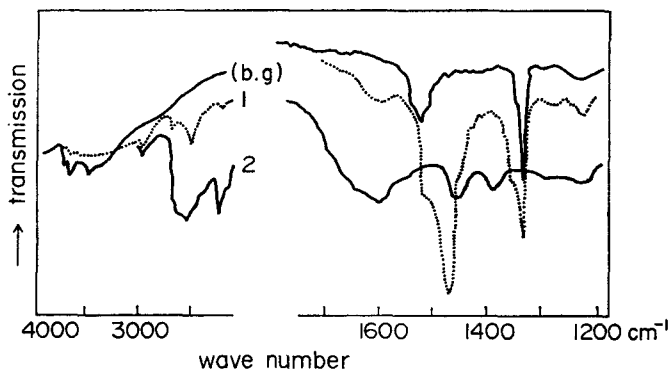


Fig. 3. ir Spectra of d_6 -acetone adsorbed on ZnO at a room temperature.

Curve 1: $55\text{ }\mu\text{l}$, 2: evacuated after treatment with 6 mmHg acetone.

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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 $25\text{ }\mu\text{l}$ 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 $\text{Zn}^{2+}\text{-O}^{2-}$ 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 $\text{Zn}^{2+}\text{-O}^{2-}$ 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.* $60\text{ }\mu\text{l}$, 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 these 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 acetylacetonate⁵⁾ as given in Table 1. Referring to these spectra, we assign the bands at 1600 and 1500 cm^{-1} of adsorbed acetone to $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{O})$ and a coupling of $\nu(\text{C}=\text{O})+\delta(\text{C}-\text{H})$ in plane.

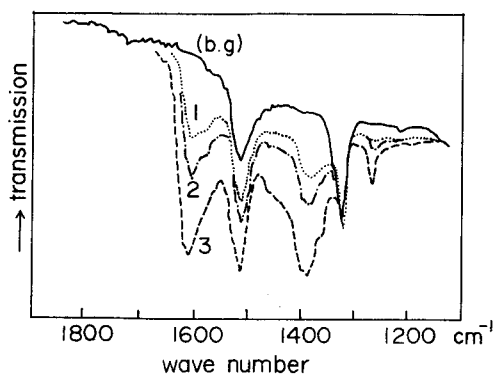


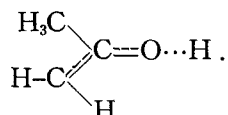
Fig. 4. ir Spectra of acetylacetone adsorbed on ZnO at a room temperature.
Curve 1: $24\text{ }\mu\text{l}$, 2: $47\text{ }\mu\text{l}$, 3: $95\text{ }\mu\text{l}$.

TABLE 1 Infrared Absorption spectra of acetylacetone adsorbed on ZnO.

Absorption band, cm^{-1}		Assignment ⁵⁾
Adsorption	Zn-Chelate ⁵⁾	
1600	1592	$\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{O})$
1520	1523 } 1464 }	$\nu(\text{C}=\text{O})+\delta(\text{C}-\text{H})$ in plane
1400	1394	$\delta_d(\text{C}-\text{H})$
	1361	$\delta_s(\text{C}-\text{H})$
1235	1261	$\nu(\text{C}=\text{C})+\delta(\text{C}-\text{CH}_3)$

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 $\delta_d(\text{C-H})$ and $\delta_s(\text{C-H})$ of ethylene coordinating to platinum atom are observed at 1428 and 1402 cm^{-1} , respectively, and, furthermore, those of $-\text{C}=\text{CH}_2$ 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 previously¹⁾ for the hydrogen randomization of acetone as



Adsorption of acetone with an enol-type configuration has been similarly reported with respect to $\text{NiO}^{7)}$ and $\text{SiO}^{8)}$ 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

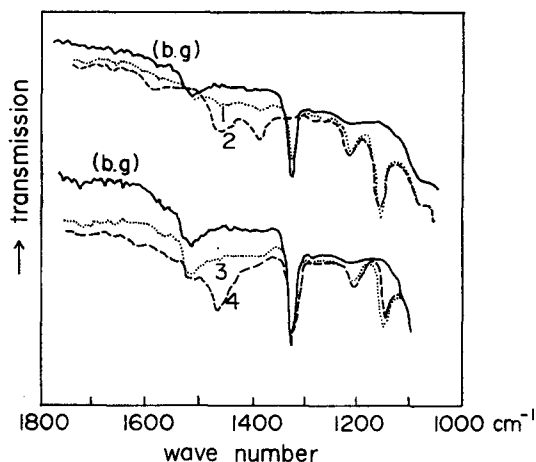


Fig. 5. ir Spectra of d_8 -2-propanol adsorbed on ZnO at a room temperature.

Curve 1: $80\text{ }\mu\text{l}$, 2: evacuated for 2 hr at 100°C ,
3: 35, 1, 4: evacuated for 1 hr at 100°C .

while those in formed acetone were completely redistributed¹⁾. 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 α -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 previously¹⁾ 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

$$V_H = v_{+s} - v_{-s}, \quad (2. V)$$

where

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

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 $a^{*(s)}$ of the initial, final and critical systems, $I(s)$, $F(s)$ and $\neq(s)$, of step s , respectively⁹⁾. The term (kT/h) has the usual meaning. Equation (2) is thus recast in the form of

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

where

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

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

Assuming the ideal gas law for a gaseous component, δ , we have

$$a^\delta = a_0^\delta P_\delta, \quad (4)$$

where P_δ is the partial pressure of δ and a_0^δ is constant at a given temperature. With respect to the overwhelmingly slow step 1 of scheme (1), we have

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

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

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

where

$$u_1 \equiv u'_1 a_0^{H_2} = (kT/h) a_0^{H_2} / a^{*(1)} \quad (6. u)$$

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

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

where

$$u_4 \equiv u'_4 a_0^A a_0^{H_2} = (kT/h) a_0^A a_0^{H_2} / a^{*(4)}$$

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

$$(1 - K P_I / P_A P_H) / V_H = 1 / u_1 P_H + 1 / u_4 P_A P_H. \quad (8)$$

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

$$(P_A + P_I) x / u_1 + 1 / u_4 P_H = (1 - K(1-x) / x P_H) x / (-\dot{x}). \quad (9)$$

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 KEMBALL¹⁰). 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 $u_1 P_H$ and $u_4 P_H$ 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, $V_{H,0}$, of acetone hydrogenation at $P_I = 0$ is given from Eq. (8) as

$$P_H/V_{H,0} = P_A/U_1 + 1/U_4 \quad (11)$$

with reference to Eq. (10). Equation

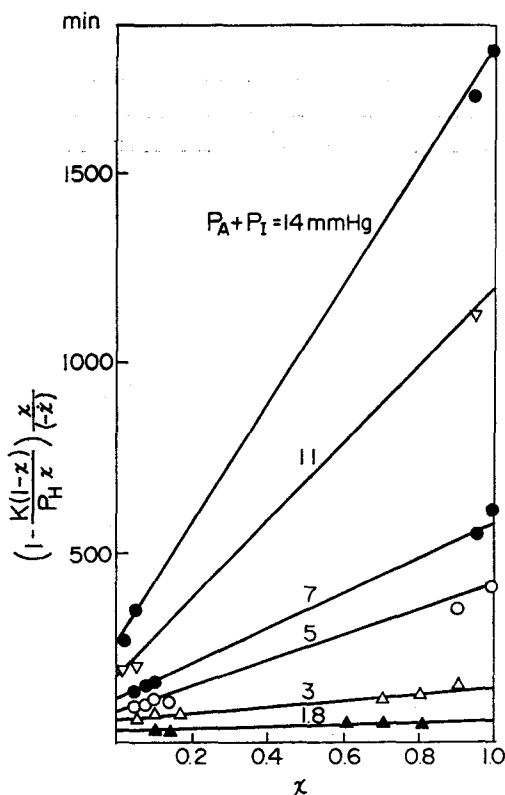


Fig. 6. Plots of the courses of acetone hydrogenation and dehydrogenation of 2-propanol according to Eq. (9) in the text.

$P_H = 500$ mmHg, $P_A + P_I = 1.8, 14$ mmHg, 140°C .

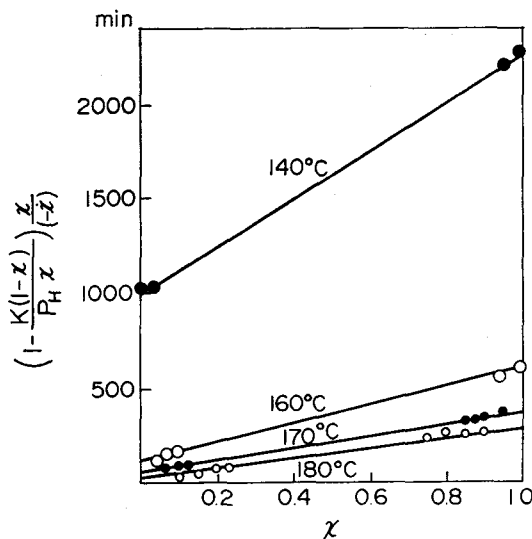


Fig. 7. Plots of the courses of acetone hydrogenation according to Eq. (9) in the text.

$P_H = 500$ mmHg, $P_A + P_I = 7$ mmHg, $140 \sim 180^\circ\text{C}$.

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(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 paper¹⁾. Figure 10 shows the temperature dependences of U_1

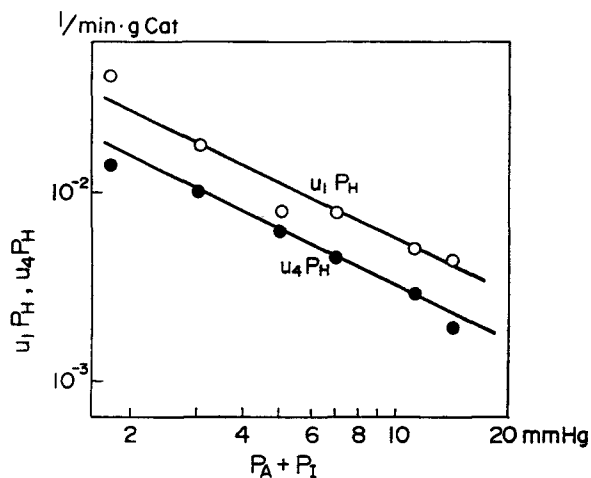


Fig. 8. Dependences of $u_1 P_H$ and $u_4 P_H$ upon $P_H + P_I$.
 $P_H = 500$ mmHg, 160°C .

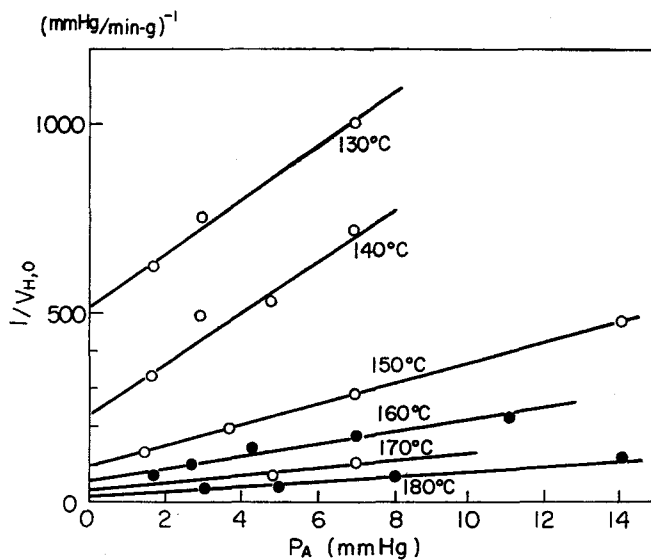


Fig. 9. Dependences of the initial rate of acetone hydrogenation upon acetone pressure (Cf. Eq. (11) in the text).

$P_A = 1.8 \sim 14$ mmHg, $P_H = 500$ mmHg, $130 \sim 180^\circ\text{C}$.

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 $V_{H,0}$ 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

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

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

$$V_{-H,0} = KU_4$$

which indicates that the initial rate of dehydrogenation is independent of P_I as well as P_H as observed previously¹⁾.

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

$$V_{-H,0} = KU_1 U_4 P_I / (P_A + P_I)(U_1 + P_A U_4), \quad (13)$$

which can be approximated as

$$V_{-H,0} = k_- P_I / P_A \quad (14)$$

in a case of $U_1 \ll P_A U_4$. The kinetics of Eq. (14) has been observed by DECHATER and TEICHNER¹¹⁾ 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 6×10^{-4} and 2.8×10^{-4} , respectively, and, thus, Eq. (13) is found to reproduce well the observed kinetics of Eq. (14).

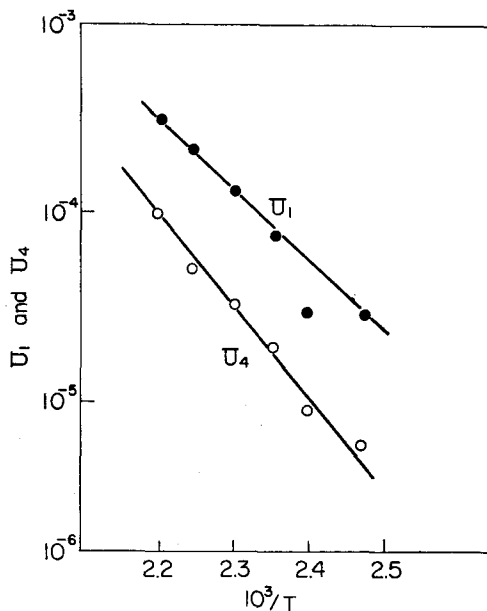


Fig. 10. Temperature dependences of U_1 and U_4 .

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