The Dehydrogenation of Butyl Alcohols by the Molten-metal Catalysts

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(Recieved May 29, 1971)

In order to investigate the catalytic activity of molten metals, the dehydrogenation reactions of *n*-butyl alcohol, *iso*-butyl alcohol, and *sec*-butyl alcohol were carried out in the presence of molten zinc and molten indium (molten gallium was also used for the dehydrogenation of *iso*-butyl alcohol). According to the experimental results, all of these molten metals showed persistent catalytic activities and high selectivities for all the test reactions, and the decreasing order of the reactivity of the butyl alcohol isomers was found to be *sec*-butyl alcohol > *iso*-butyl alcohol > *n*-butyl alcohol. Among the three molten metals, *i.e.* Zn, Ga, and In, the activity and the selectivity of the molten zinc catalyst was outstandingly high. Further, kinetic analyses of the data showed that a compensation effect exists between the apparent activaiton energy, E_a, and the logarithmic frequency factor, log A.

Since the pioneer work of Ipatiew[1] was published, only a few works[2,3] about the catalysis of molten metals have appeared in the literature. However, it was expected that the use of molten metals as catalysts would have many advantages in studying the catalysis. Thus, the present authors undertook a systematic study of the catalysis of the molten metal. According to the preceding work,[4] which is the first of this series, some molten metals, such as zinc, gallium, aluminum, indium, and thallium, showed considerable activities for the dehydrogenation of methanol. This finding prompted an investigation with some other alcohols as reactants. It is the purpose of the present paper to show the catalytic activities of such molten metals as zinc and indium for the dehydrogenation of *n*-butyl alcohol (*n*-butanol), *iso*-butyl alcohol (*iso*-butanol), and *sec*-butyl alcohol (*sec*-butanol).

Experimental

Catalysts. Molten zinc (Zn-L) and molten indium (In-L) were used as catalysts (sometimes molten gallium was also used). They were of the highest quality among the commercially available metals, and no purifications were carried out.

Alcohols. *n*-Butanol, *iso*-butanol, and *sec*-butanol were obtained commercially. The gas chromatographic analyses showed that no significant amounts of impurities were present in these alcohols. Therefore, the purifications of these alcohols were not carried out.

Apparatus. The apparatus shown in Fig. 1 was used in the measurement of the catalytic activity of the molten metal. The reactor was made from Pyrex glass; its dimensions are given in Fig. 2.

Procedures. After a given amount (50 g) of a desired metal was charged into the reactor, ③, the air in the reactor as well as in the whole reaction system was driven out by streaming helium. Then, the temperature of the reactor was raised and the melting of the catalyst metal was confirmed directly by sight. (The electric furnace was constructed from two concentric Pyrex tubes, with a nichrome heater wound on the outer wall of the inner tube. Therefore, the interior of the reactor could be observed.) After the desired temperature was reached, the stream of helium was stopped and alcohol was fed in at a rate of 0.088—0.094 mol/hr from a micro-feeder, ①. The preheater, ②, which was packed with glass-wool and maintained at a temperature of ~200°C, served for the vaporization of alcohol. The vapor of alcohol

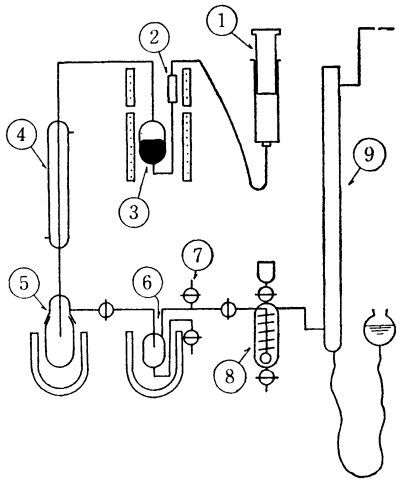

Fig. 1. Flow diagram of the reaction apparatus:
①: microfeeder, ②: preheater, ③: reactor,
④: condenser, ⑤: first separator, ⑥: second separator,
⑦: port for gas sampling, ⑧: scrubber,
⑨: soap film flow meter.

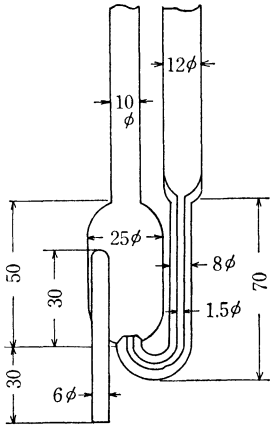

Fig. 2. Details of the reactor (dimensions are given in mm).

* Studies of Catalysis by Molten Metals. II.

1) W. Ipatiew, *Ber. Deut. Chem. Ges.*, **34**, 3579 (1901).
2) E. W. R. Steacie and E. M. Elkin, *Proc. Roy. Soc.*, **A142**, 457 (1933).
3) G. M. Schwab, *Dechema Monographiën*, **38**, 205 (1960).
4) Y. Saito, A. Miyamoto, and Y. Ogino, *Kogyo Kagaku Zasshi*, **74**, 1521 (1971)

was led to the bottom of the reactor and made to bubble from a small opening into the molten metal. The effluent containing the reaction products and unreacted alcohol was cooled by a condenser, ④; the condensable materials were separated from the gaseous products and collected in separators, ⑤ and ⑥, which were immersed in ice baths. The gaseous products were led to a scrubber, ⑧. Then, the flow rate of the gas was measured by means of a soap film-meter, ⑨. Finally, the gas was purged into the atmosphere.

The liquid products collected in the separators were weighed and analyzed by gas chromatography. The gaseous products were collected from a port, ⑦, and analyzed by gas chromatography.

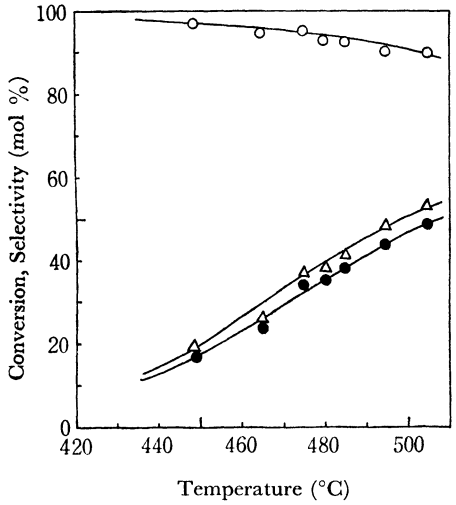

Fig. 3. Temperature dependencies of the catalytic activity of Zn-L for the dehydrogenation of *n*-Butanol:
-○- selectivity for the formation of *n*-butyraldehyde,
-△- total conversion of *n*-butanol,
-●- conversion to *n*-butyraldehyde.

Results and Discussion

Dehydrogenation of n-*Butanol.*

Activity of Zn-L. As can be seen in Fig. 3, molten zinc (Zn-L) showed a catalytic activity for the dehydrogenation of *n*-butanol. The main liquid product was *n*-butyraldehyde, but very small amounts of butylbutyrate, butyl ether, and water were also obserbed. From these results, the following reactions were considered to occur;

$$n\text{-}C_4H_9OH \longrightarrow H_2 + n\text{-}C_3H_7CHO \quad (I)$$

$$2n\text{-}C_4H_9OH \longrightarrow C_4H_9OC_4H_9 + H_2O \quad (II)$$

$$2C_3H_7CHO \longrightarrow C_3H_7CO_2C_4H_9 \quad (III)$$

Reaction I is the main reaction, while Reaction II and III are the side reactions.

The compositions of the gaseous products are given in Fig. 4. As can be seen in this figure, the hydrogen content was very high. This fact supports the idea that Reaction I is the main reaction. Further, the existence of CO, CH_4, C_2H_4, and C_2H_6 in the gaseous products suggests that the following decomposition reaction;

$$C_3H_7CHO \longrightarrow CH_4 + C_2H_4 + CO \quad (IV)$$

occurred together with the reaction;

$$C_2H_4 + H_2 \longrightarrow C_2H_6 \quad (V)$$

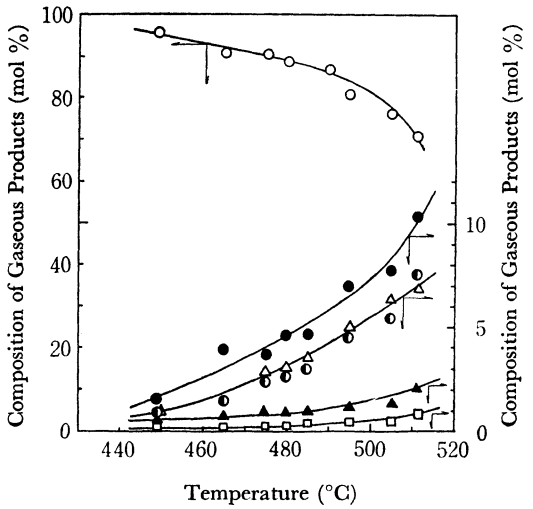

Fig. 4. Temperature dependencies of the compositions of gaseous products produced by the Zn-L catalyst from *n*-butanol:
-○- H_2, -●- CO, -△- CH_4, -◐- C_2H_4,
-▲- C_2H_6, -□- CO_2.

According to these reactions, *i.e.* IV—V, the ratio of CO: CH_4: $C_2H_4+C_2H_6$ should be 1: 1: 1. The experimental results shown in Fig. 4 indicate a somewhat higher CO content than the above-mentioned stoichiometric ratio. In addition, the existence of small amounts of CO_2 in the products seems to suggest that some unknown side reactions also occurred. At any rate, however, the side reactions were small, and the selectivity of the main reaction was higher than 90%.

Activity of In-L. As can be seen in Fig. 5, molten indium (In-L) also showed a catalytic activity for the butanol dehydrogenation, though the conversion was considerably smaller than the value obtained by the use of Zn-L catalyst (Fig. 3). The main liquid product was *n*-butyraldehyde, and the same sorts of by-products as those produced by the Zn-L catalyst were also found in the liquid products. Therefore, the main reaction may be I, and the same sorts of side reactions as for the Zn-L catalyst may be considered to occur.

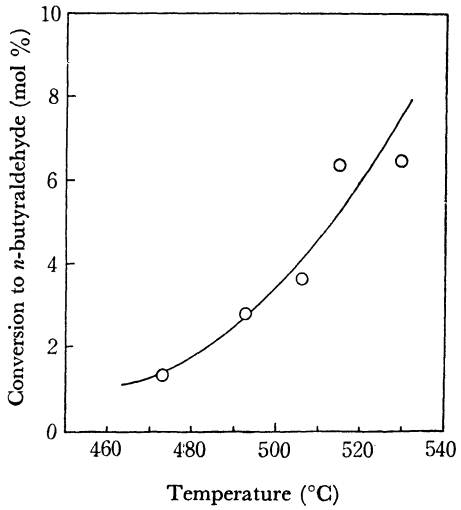

Fig. 5. Temperature dependency of the catalytic activity (conversion to *n*-butyraldehyde) of In-L for the dehydrogenation of *n*-butanol.

Comparison with Solid Catalysts. Dunbar[5] investigated the dehydrogenation of *n*-butanol, using copper chromite as a catalyst. According to his work, the conversion of *n*-butanol was 30—60% in the temperature range of 330—350°C. As can be seen in Fig. 3, nearly the same conversion value as above was obtained in the present work by employing the Zn-L catalyst. However, the reaction temperature employed in the present work is about 150°C higher than that employed by Dunbar. Thus, with respect to the reaction temperature, the copper chromite catalyst is preferable to the Zn-L catalyst. On the contrary, according to Dunbar, the selectivity for the formation of *n*-butyraldehyde was 40—80%, while the selectivity obtained in the present work was higher than 90%.

Excellent copper-containing catalysts have also been proposed by some other workers.[6,7] It is said that the catalysts are effective at temperatures lower than 300°C, and that selectivities higher than 90% are obtainable with these catalysts. However, it must be noted that the activities of copper-containing catalysts are specially sensitive to sintering and poisons. Further, great care is necessary for the preparation of a highly effective solid catalyst. On the contrary, no such difficulties as those described above are encountered in the use of a molten-metal catalyst. Of course, efforts to make more active molten metal catalysts are necessary. The application of molten-alloy catalysts seems to be hopeful.

Dehydrogenation of iso-*Butanol.*

Activity of Zn-L. As can be seen in Fig. 6, molten zinc (Zn-L) showed a catalytic activity for the dehydrogenation of *iso*-butanol, and this activity was found to persist for a long time. Figure 7 shows the relations between the reaction temperature and the degree of conversion as well as the composition of gaseous products. As can be seen in this figure, the conversion increased with the increase in the reaction temperature and reached ~80% at 500°C. Isobutyraldehyde was the main product, while the content

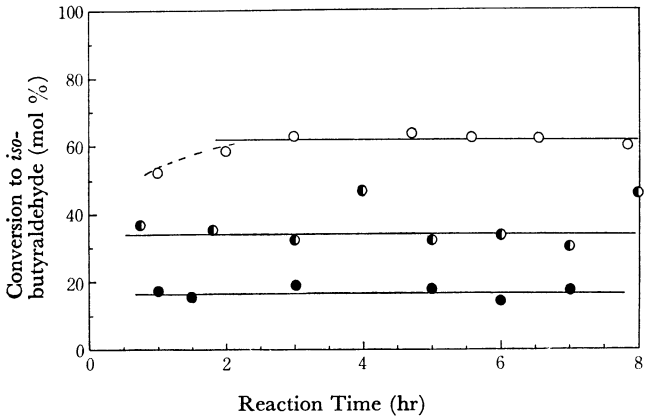

Fig. 6. Relations between the conversion to *iso*-butyraldehyde and the reaction time: -○- Zn-L 500°C, -◐- Zn-L 450°C, -●- In-L 550°C. (Zn 50 g, butanol feed rate=0.089 mol/hr, In 50 g, butanol feed rate=0.089 mol/hr).

5) P. E. Dunbar, *J. Org. Chem.*, **3**, 242 (1938).

6) "Monograph on the Science and Engineering of Catalysis." edited by the Catalysis Society of Japan, Vol. 7, Chijinshokan Co. Ltd., Tokyo, Japan (1964), p. 209.

7) S. Yata and S. Kudo, *Kagaku Kogaku*, **28**, 687 (1964).

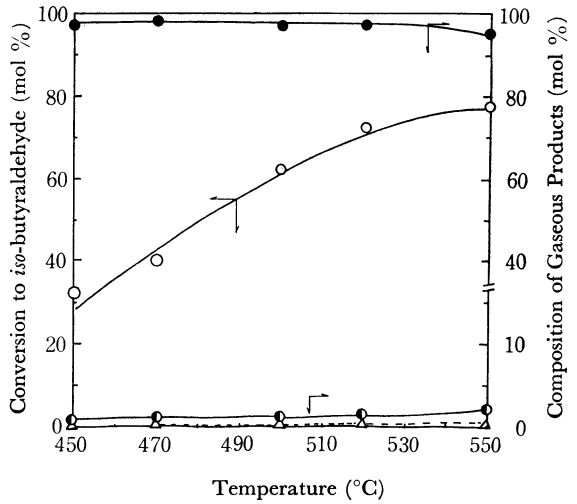

Fig. 7. Temperature dependencies of the catalytic activity of the Zn-L catalyst for the dehydrogenation of *iso*-butanol and the compositions of the produced gas; -○- conversion to *iso*-butyraldehyde, -●-H_2, -◐- CO, -△- CH_4.

of the other products in the liquid products was very small (smaller than 2%). Further, the hydrogen content in the gaseous products was very high, while the contents of CO and CH_4 were very small. On the basis of these results, the selectivity for the reaction;

$$iso\text{-}C_4H_9OH \longrightarrow iso\text{-}C_3H_7CHO + H_2$$

was calculated in order to obtain Fig. 8. This figure demonstrates a very high selectivity (higher than 95%) of the Zn-L catalyst.

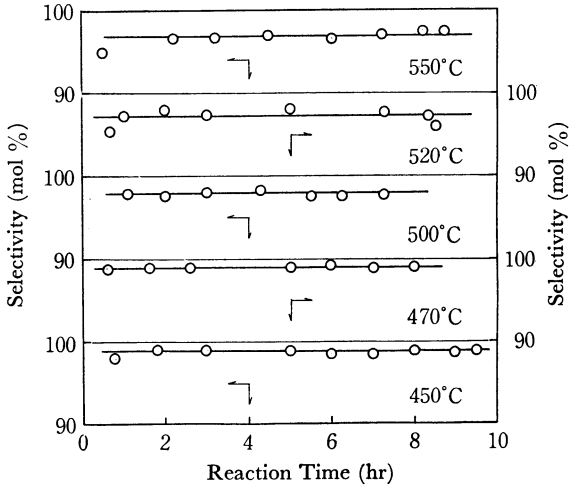

Fig. 8. Selectivities of the Zn-L catalyst for the *iso*-butyraldehyde at various temperatures.

Activity of In-L. As can be seen in Fig. 6, molten indium (In-L) also gave a persistent catalytic activity for the dehydrogenation of *iso*-butanol. The relation between the conversion and the reaction temperature is given in Fig. 9. Over the whole range of reaction temperatures, the conversion value was considerably lower than the value obtained by the use of the Zn-L catalyst.

Further, a comparison of Fig. 7 with Fig. 9 shows that the hydrogen content in the gaseous products for

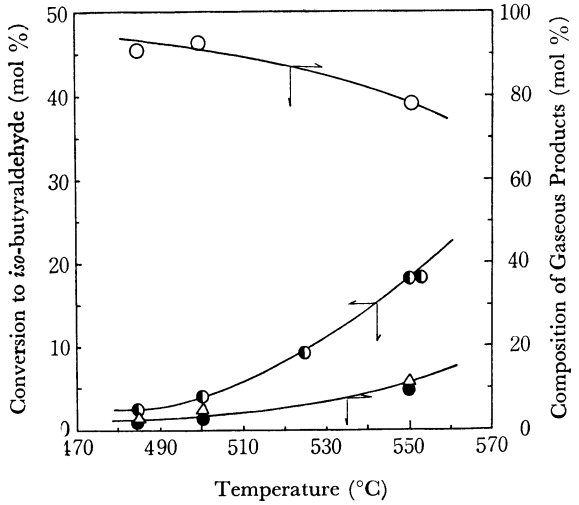

Fig. 9. Temperature dependencies of the catalytic activity of the In-L catalyst for the dehydrogenation of *iso*-butanol and the compositions of the produced gas:
-◐- conversion to *iso*-butyraldehyde, -○- H_2, -△- CO, -●- CH_4.

the In-L catalyst is lower than the content for the Zn-L catalyst. This is due to the higher contents of CO and CH_4 in the gaseous products for the In-L catalyst. From these facts, it can be said that the selectivity of the In-L catalyst is somewhat lower than that of the Zn-L catalyst.

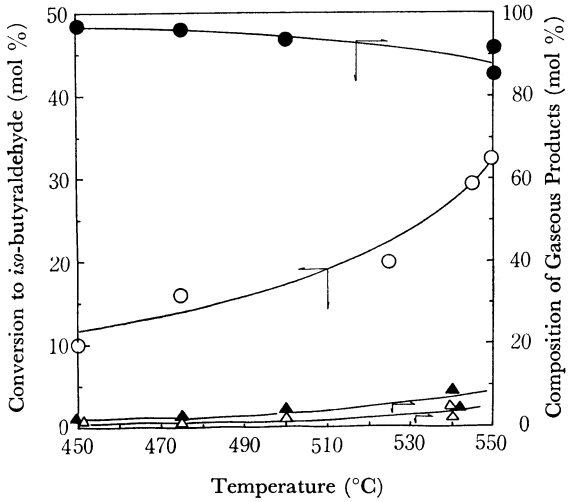

Fig. 10. Temperature dependencies of the catalytic activity of the Ga-L catalyst for the dehydrogenation of *iso*-butanol and the compositions of the produced gas:
-○- conversion to *iso*-butyraldehyde, -●- H_2, -▲- CO, -△- CH_4.

Activity of Ga-L. As can be seen in Fig. 10, Ga-L also showed a catalytic activity. The conversion value was higher than that obtained by the use of the In-L catalyst, while it was lower than the conversion value obtained by the use of the Zn-L catalyst. The hydrogen content in the gaseous products was somewhat higher than the value obtained by the use of the In-L catalyst. Further, the CO content and the CH_4 content were both lower than the corresponding values obtained by the use of the Zn-L catalyst. From these results, it was expected that the *iso*-butyraldehyde content in the liquid products would be higher than that obtained by the use of the In-L catalyst. However, as can be seen in Fig. 11, the selectivity for the formation of the *iso*-butyraldehyde of the Ga-L catalyst was the lowest among the three molten metal catalyst, *i.e.*, Zn-L, In-L, and Ga-L. This may be attributed to the higher content of an unidentified component (presumably isobutylene dissolved in the liquid phase) in the liquid products produced by the Ga-L catalyst.

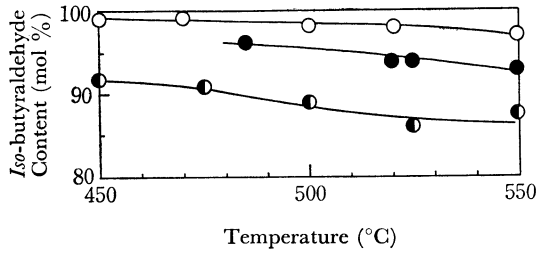

Fig. 11. Temperature dependencies of *iso*-butyraldehyde contents in the liquid products produced by dehydrogenating *iso*-butanol by the molten metal catalysts:
-○- Zn-L, -●- In-L, -◐- Ga-L.

Dehydrogenation of sec-*Butanol.*

Activity of Zn-L. As can be seen in Fig. 12, and

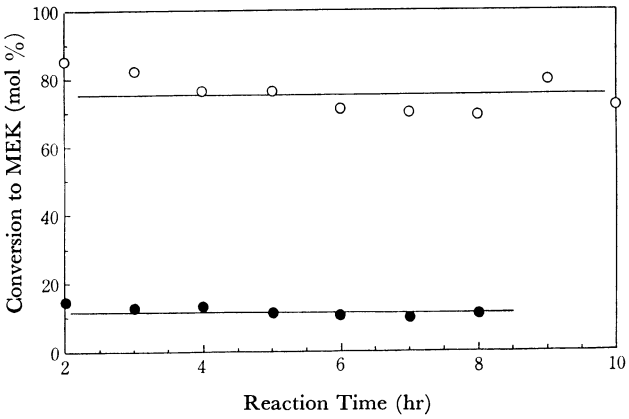

Fig. 12. Relations between the reaction time and the catalytic activities (conversion to MEK) of the Zn-L catalyst (-○-, 462°C) and the In-L catalyst (-●-, 500°C).

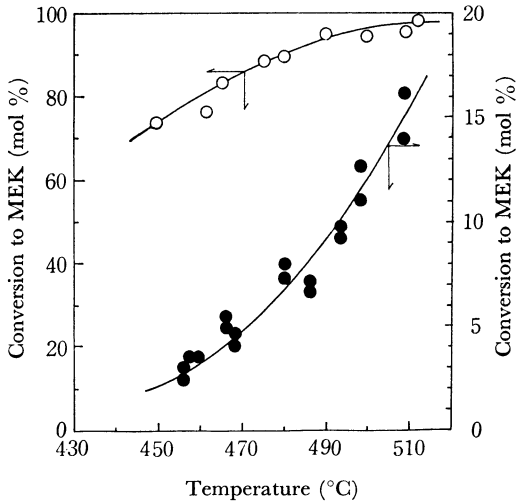

Fig. 13. Temperature dependencies of the catalytic activities (conversion to MEK) of the Zn-L catalyst (-○-) and the In-L catalyst (-●-).

Fig. 13, Zn-L showed a persistent and very high catalytic activity for the dehydrogenation of *sec*-butanol. Further, the liquid products were mainly methylethylketone (MEK). The by-products were acetone and propionaldehyde, and the total content of these materials was less than 1%. Further, the hydrogen content in the gaseous products was very high, and only a small amount of CH_4 was produced at reaction temperatures higher than 500°C. All of these facts indicate that the main reaction may be written as;

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CHOH \longrightarrow \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CO + H_2$$

and that the selectivity of the Zn-L catalyst for the dehydrogenation of *sec*-butanol is satisfactory.

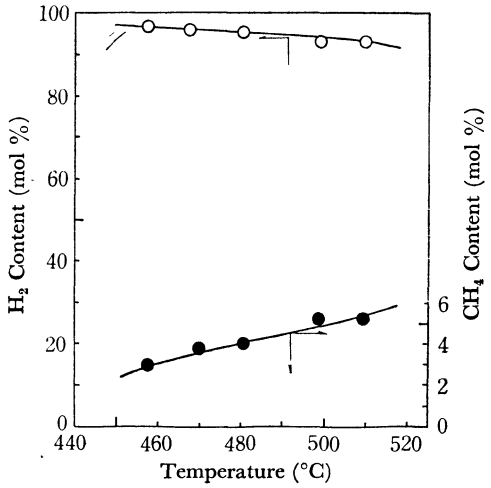

Fig. 14. Temperature dependencies of the composition of the gaseous products produced by the In-L catalyst:
-○- H_2, -●- CH_4.

Activity of In-L. As can be seen in Fig. 12, and Fig. 13, In-L also showed a persistent activity for the dehydrogenation of *sec*-butanol. The main liquid product was MEK, and the main gaseous product was hydrogen, as in the case of the Zn-L catalysts. However, compared with the Zn-L catalyst, the activity of the In-L catalyst was quite low. In addition, the selectivity of the In-L catalyst was somewhat lower than that of the Zn-L catalyst. That is, the content of CH_4 in the gaseous products was considerable (Fig. 14). Further, 2—3% of acetone was found in the liquid products. In addition, a small amount of propionaldehyde was also contained in the liquid products. Considering from these facts, the over-all reaction may be written as follows:

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CHOH \longrightarrow \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CO + H_2 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO + CH_4$$

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CO \longrightarrow CH_3CH{=}CO + CH_4$$

$$CH_3CHCO + H_2 \longrightarrow CH_3CH_2CHO$$

Comparison with Solid Catalyst. The manufacturing of MEK by the dehydrogenation of *sec*-butanol is an industrially important reaction. Thus, several catalysts which can be used for this process have been proposed. For instance, Dunbar and his co-workers[8] proposed the copper chromite catalyst. According to their data, the conversion of *sec*-butanol to MEK was ~68% at 300—325°C. Kolb and his co-workers[9] used the Ni-Cu catalyst, which converted 84% of *sec*-butanol at a pressure of 308 mmHg and at a temperature of 472.2°K. As can be understood from these

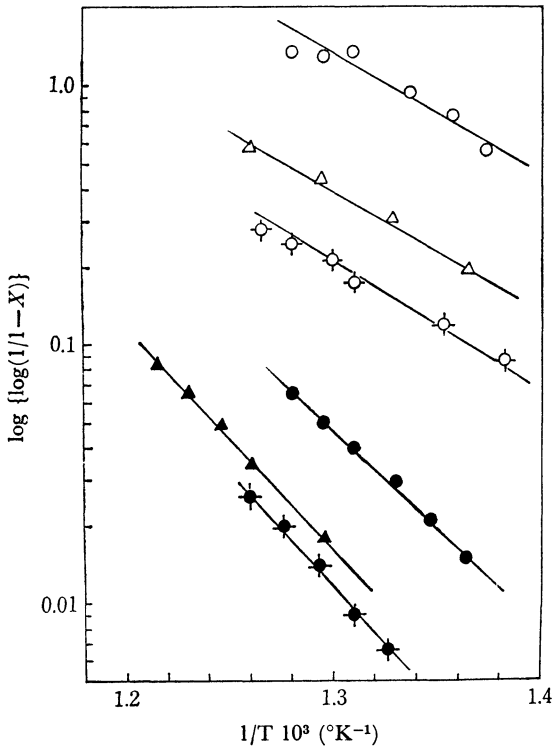

Fig. 15. Arrhenius plots for various reactions:
-○- Zn-L, *n*-butanol, -△- Zn-L, *iso*-butanol,
-○- Zn-L, *sec*-butanol, -◆- In-L, *n*-butanol,
-▲- In-L, *iso*-butanol, -●- In-L, *sec*-butanol.

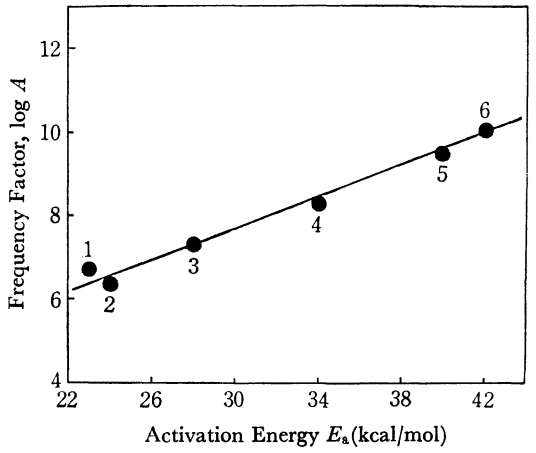

Fig. 16. Compensation effect between the apparent activation energy and the logarithmic frequency factor:
1; Zn-L, *sec*-butanol, 2; Zn-L, *iso*-butanol,
3; Zn-L, *n*-butanol, 4; In-L, *sec*-butanol,
5; In-L, *iso*-butanol, 6; In-L, *n*-butanol.

8) P. E. Dunbar and M. R. Arnold, *J. Org. Chem.*, **10**, 501 (1945).
9) H. J. Kolb and K. Z. Burwell, *J, Amer. Chem. Soc.*, **67**, 1084 (1945).

data, the reaction temperature for the solid catalyst is lower than that for the molten-metal catalyst.

At first sight, this seems to indicate a superiority of the solid catalysts. However, it must be noted that the selectivity of the molten metals, especially the Zn-L catalyst, was very high. Further, the merit of the easier method of the preparation of the molten-metal catalyst must also be taken into consideration.

Kinetic Treatments. As has been described in the preceding sections, the selectivities of the molten-metal catalysts were generally high. This permits us to assume that the side reactions can be disregarded for an approximate kinetic treatment. Further, it may be assumed that the dehydrogenation of alcohol on the metallic catalyst is first order with respect to alcohol,[10] and that the reaction will be approximately irreversible under the present experimental conditions. Thus, the first order rate constant, k, will be proportional to $\log(1/1-X)$, where X is the conversion.

On the basis of the above considerations, $\log\{\log(1/1-X)\}$ was plotted against $1/T$. The results are shown in Fig. 15. As can be seen in this figure, good linear relationships were obtained, and it was possible to evaluate the apparent activation energies, E_a, as well as the frequency factors, A. Interestingly, the apparent activation energy, E_a, was found to be proportional to the logarithmic frequency factor, $\log A$ (Fig. 16). That is, the so-called "compensation effect"[11] was observed. This relation seems to suggest that the catalysis of the liquid metal obeys a simple rule; Schwab's work[3] seems to throw some light on this problem. However, considering the qualitative nature* of the present experiments, this effect will not be discussed further.

10) A. C. Neish, *Can. J. Res.*, **23**, 49 (1945).

11) E. Cremer, "Advances in Catalysis," edited by W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Vol. 7, Academic Press, New York (1955), p. 75.

* In order to discuss the kinetic data further, the following problems must be clarified: i) the relations between the catalytic activity and the size of the bubble, which is affected by the experimental conditions (temperature, pressure, feed rate, catalyst, etc.); ii) the catalysis of metal vapor; iii) the catalysis of the metal film which is formed on the inner wall of the reactor, and iv) the extent of the oxidation of the molten metal and the catalysis of the oxide.

The i) problem is important not only from the scientific point of view but also from the engineering point of view, in which the practical use of the molten-metal catalyst is taken into consideration. Unfortunately, however, little information on this point is available at present, separate investigations to solve the problem seem to be necessary.

Concerning the ii)—iv) problems, somewhat detailed discussions have been given in the preceding paper;[4] these effects have been considered to be minor, though they can not be ignored. The reasons are given briefly in the following table.

Catalyst	Reasons which support to consider the minor effects of		
	ii	iii	iv
In-L	Very low vapor pressure.	Very low vapor pressure and little formation of the film.	Easily-reduible property of indium oxide.
Ga-L	Very low vapor pressure.	Very low vapor pressure and little formation of the film.	No significant oxidation was detected by X-ray diffraction study.
Zn-L	Comparison of the data with the data of Cd vapor and Zn vapor (a).	High activities observed at the initial reaction stage, wherein little metal films were found.	No significant oxidation was detected by X-ray diffraction. Different selectivity of ZnO from that of Zn-L.

(a) N.I. Kobozev and M.N. Danchevskaya, *Zhur. Fiz. Khim.*, **34**, 1728 (1960).