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The Dehydrogenation of Amines by Molten Metal Catalysts[1]

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In order to investigate the catalytic activity of molten metal, experiments were carried out using the dehydrogenation of *n*-butylamine, benzylamine, and cyclohexylamine as test reactions. The molten zinc catalyst was thus found to show specially high activities and selectivities in all test reactions. The activity of the molten gallium catalyst for the dehydrogenation of *n*-butylamine was also considerable. However, the selectivity of this catalyst was somewhat lower than that of the molten zinc catalyst, and considerable amounts of dibutylamine were produced at lower reaction temperatures. The other molten metals were found to be almost inactive. That is, Pb, Cd, Sn, and Bi were inactive, while Tl and In were only slightly active.

The present authors have undertaken a systematic study of the catalysis of liquid metals and have found that some liquid metals, such as zinc and indium, efficiently dehydrogenate methanol,[2] *n*-butanol,[3] *iso*-butanol,[3] and *sec*-butanol.[3] Further studies of the dehydrogenation of the other alcohols, including cyclohexanol and benzyl alcohol, are now proceeding.

Although the details of the mechanism of the catalysis by the liquid metal have not yet been clarified, it is assumed that the interaction between lone-pair electrons around the oxygen atom of alcohol causes the dehydrogenation of alcohol. By extending this idea, it can be expected that the dehydrogenation of amine is catalyzed by the liquid metal. The present work has been undertaken to confirm this expectation.

Experimental

Catalysts. The liquid zinc (Zn-L) was mainly used as a catalyst in the present work. However, in some cases, other liquid metals, *i.e.* In-L, Tl-L, Ga-L, Pb-L, Cd-L, and Bi-L, were also examined.

Reactants. The *n*-butylamine, benzylamine, and cyclohexylamine were obtained commercially. They were of the highest quality among the available reagents.

Activity Test. The method of the activity test was similar to that described in previous papers.[2,3] The reaction products were analyzed mainly by gas chromatography, but the results were supplemented by chemical analysis and by infrared spectroscopic analysis.

Results and Discussion

Dehydrogenation of n-*Butylamine.* According to the experimental results, Zn-L and Ga-L showed considerably high catalytic activities for the dehydrogenation of *n*-butylamine. The activities of In-L and Tl-L were too low to be measured accurately, and Pb-L, Sn-L, Cd-L, and Bi-L were inactive. Therefore, only the details of the activities of Zn-L and Ga-L will be presented below.

Catalytic Activity of Zn-L for the Dehydrogenation of n-*Butylamine.* The experimental results showed that the catalytic activity of Zn-L persisted for a long period (more than 10 hr). The gaseous products were mainly hydrogen, and the contents of methane, ethane, and ethylene were very small. The main liquid product was *n*-butyronitrile (II). In addition to the main product, a small amount of a liquid by-product was also detected on the gas-chromatographic chart. The retention time of this peak agreed with that of the product of the following reaction[4]:

$$\mathrm{CH_3CH_2CH_2CH_2NH_2 + CH_3CH_2CH_2CHO \longrightarrow}$$
$$\mathrm{CH_3CH_2CH_2CH{=}N{-}CH_2CH_2CH_2CH_3 + H_2O}$$

Thus, the by-product was identified as Schiff's base, *i.e.* $\mathrm{CH_3CH_2CH_2CH{=}N{-}CH_2CH_2CH_2CH_3}$ (III). The infrared spectra shown in Fig. 1 support this view. The absorption peak appearing at 1660 $\mathrm{cm^{-1}}$ indicates the presence of a $-\overset{|}{\mathrm{C}}{=}\mathrm{N}-$ group.

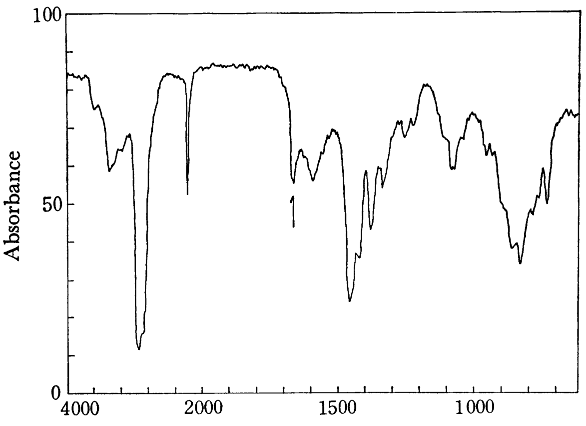

Fig. 1. Infrared spectra of the liquid products obtained by dehydrogenating *n*-butylamine in the presence of the Zn-L catalyst.

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[1] Studies on Catalysis by Molten Metal. III.

[2] Y. Saito, A. Miyamoto, and Y. Ogino, *Kogyo Kagaku Zasshi*, **74**, No. 8, 1521 (1971).

[3] K. Kashiwadate, Y. Saito, A. Miyamoto, and Y. Ogino, This Bulletin, **44**, 3004 (1971).

[4] The procedures for obtaining Schiff's base (III) (*i.e. N*-butyliden-*n*-butylamine) by a reaction such as that described in the text had been reported by K. N. Campbell *et al.* (*J. Amer. Chem. Soc.*, **66**, 82 (1944)), and by C. W. C. Stein *et al.* (*ibid.*, **64**, 2569 (1942)). In the present research, the products of this reaction was distilled in a nitrogen stream. The isolated material showed a definite boiling point of 142—143°C, which agreed well with the literature values of 141—145°C. Therefore, the isolated material may be identified as *N*-butylidene-*n*-butylamine and may be used as a standard material for the gas-chromatographic analysis, which was carried out under the following conditions: column; 20% PEG20M+10% KOH on cellite 2.25 m, carrier gas; He 8.10 m*l*/min, temperature; 80°C.

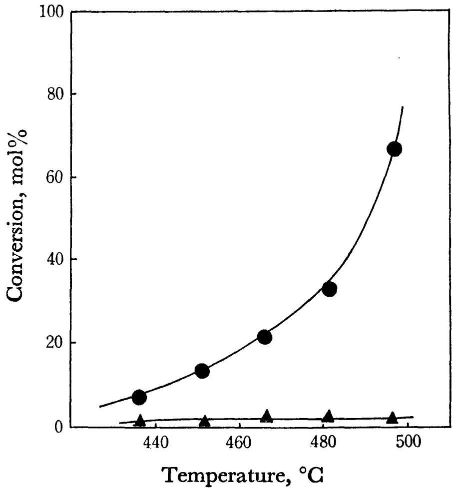

Fig. 2. The temperature dependency of the catalytic activity of Zn-L for the dehydrogenation of *n*-butylamine: —●— conversion to *n*-butyronitrile, —▲— conversion to Schiff's base. (Zn 70 g, Feed 0.089 mol/hr).

The conversion-*vs*-temperature relation is shown in Fig. 2. As can be seen in this figure, the conversion of *n*-butylamine to *n*-butyronitrile increased steeply with the increase in the reaction temperature, whereas the conversion to Schiff's base increased only a little.

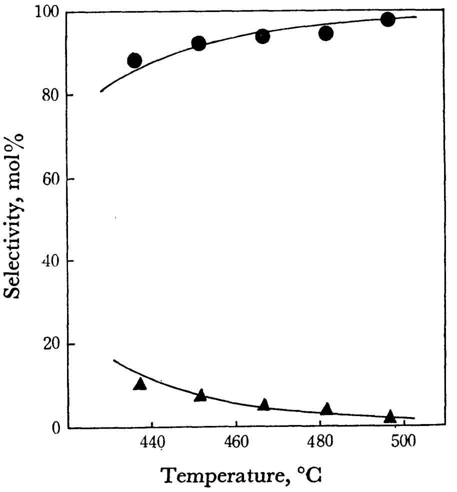

Fig. 3. The temperature dependency of the selectivity of the Zn-L catalyst in the dehydrogenation of *n*-butylamine: —●— for *n*-butyronitrile, —▲— for Schiff's base. (Zn 70 g, Feed 0.089 mol/hr).

The selectivity-*vs*-temperature relation is shown in Fig. 3. It can be seen in this figure that, with an increase in the reaction temperature, the selectivity for the formation of *n*-butyronitrile increased, while the selectivity for the formation of Schiff's base decreased. Further, it must be noted that the selectivity of the Zn-L catalyst for the formation of nitrile was generally high and that an especially high selectivity (~100%) was obtainable at high reaction temperatures (~500°C).

According to Dolgow,[5] Schiff's base can be regarded as an intermediate product in the catalytic hydrogenation of nitrile. Therefore, the same base may be produced by the reverse reaction, *i.e.*, the dehydrogenation of amine. Presumably, the primary product of the dehydrogenation would be aldimine, *i.e.*, $CH_3CH_2CH_2CH{=}NH$ (I), which is unstable and which can easily be subjected to further dehydrogenation to form nitrile (II). In addition, the aldimine (I) may react with *n*-butylamine to form Schiff's base in the following way:

$$\underset{\text{I}}{CH_3CH_2CH_2CH{=}NH} + CH_3CH_2CH_2CH_2NH_2 \longrightarrow$$

$$\underset{\text{III}}{CH_3CH_2CH_2CH{=}N\text{-}CH_2CH_2CH_2CH_3} + NH_3$$

Thus, the over-all reaction scheme for the Zn-L catalyzed dehydrogenation of *n*-butylamine may be expressed as follows:

$$\begin{tikzcd}
n\text{-butylamine} \arrow[r, "-H_2", "\text{Zn-L}"'] & \text{aldimine (I)} \arrow[r, "-H_2", "\text{Zn-L}"'] \arrow[d, "\text{Zn-L}"', "+n\text{-butylamine}"] & n\text{-butyronitrile (II)} \\
 & \text{Schiff's base (III)} + \text{ammonia} &
\end{tikzcd}$$

According to this reaction scheme (the parallel formation of II and III), when the total conversion of *n*-butylamine reaches zero, the concentrations of both II and III should be extraporated to values which are larger than 0% and smaller than 100%. As can be seen in Fig. 4, the experimental results supported this expectation. If II is consecutively formed *via* III the concentration of II should be extraporated to 0% and the concentration of III should be extraporated to 100%.

Catalytic Activity of Ga-L for the Dehydrogenation of Butylamine. As can be seen in Fig. 5, Ga-L showed a persistent activity for the dehydrogenation of *n*-butylamine. As in the dehydrogenation by the Zn-L catalyst, the main gaseous product was hydrogen, but very small amounts of methane, ethane, and ethylene were also

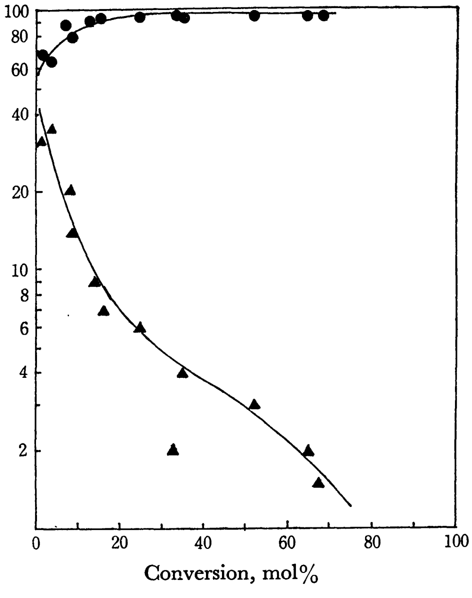

Fig. 4. Relations between the total conversion and the selectivities of the Zn-L catalyst for the formation of *n*-butyronitrile (-●-) and for the formation of Schiff's base (-▲-). (Zn 70 g, Feed 0.089 mol/hr).

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[5] B. N. Dolgow, "Die Katalyse in der organischen Chemie" VEB Deutscher Verlag der Wissenschaften (1963), p. 285.

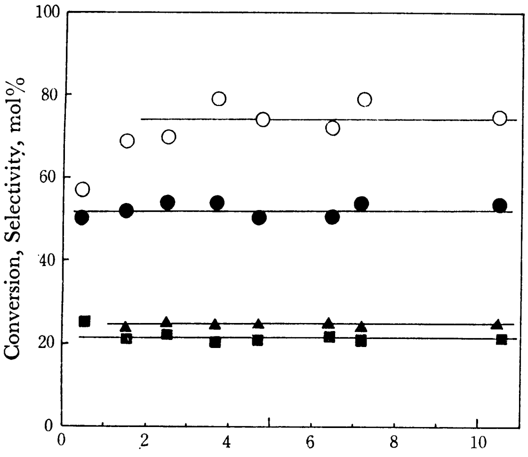

Fig. 5. Relations between the reaction time and the activity of the Ga-L catalyst for the dehydrogenation of *n*-butylamine: -○- total conversion, -●- selectivity for *n*-butyronitrile, -▲- selectivity for dibutylamine, -■- selectivity for Schiff's base. (Ga 40 g, Feed 0.089 mol/hr, Temperature 500°C).

produced. On the other hand, the liquid product[6] contained considerable amounts of dibutylamine, $(CH_3CH_2CH_2CH)_2NH$ (IV), in addition to *n*-butyronitrile (II) and Schiff's base (III).

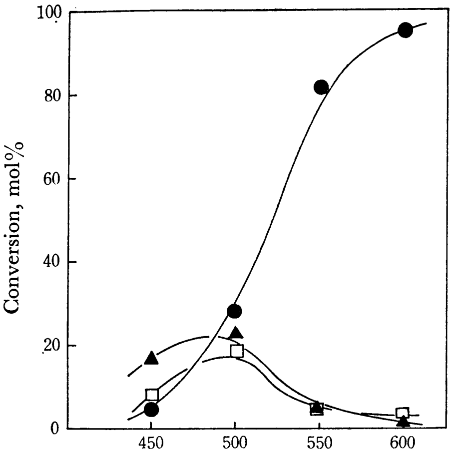

Fig. 6. The temperature dependency of the catalytic activity of the Ga-L catalyst: -●- conversion to *n*-butyronitrile, -▲- conversion to dibutylamine, -☐- conversion to Schiff's base. (Ga 40 g, Feed 0.089 mol/hr).

The temperature dependency of the catalytic activity of Ga-L is given in Fig. 6. At lower reaction temperatures, the conversion to nitrile (II) was rather low and the conversion to Schiff's base (III) or the conversion to dibutylamine (IV) was found to be high. However, the conversion to nitrile (II) increased steeply with the increase in the reaction temperature, whereas the conversion both to Schiff's base (III) and to dibutylamine (IV) decreased markedly with the increase in the reaction temperature. Thus, the selectivity for the formation of *n*-butyronitrile (II) increased steeply with the increase in the reaction temperature and reached ~95% at a temperature of 600°C.

As can be seen in Fig. 6, the curve which expresses the relation between the reaction temperature and the conversion of *n*-butylamine to Schiff's base (III) is nearly parallel with the curve which expresses the relation between the reaction temperature and the conversion to dibutylamine (IV). This means that the formation of III is intimately related to the formation of IV. Further information about this point was obtained by plotting each of the fractions, III/III+IV and IV/III+IV, against the conversion of *n*-butylamine to III+IV. As can be seen in Fig. 7, th eIII/III+IV fraction approaches unity, while the IV/III+IV fraction approaches zero, as the conversion is reduced to zero. These facts indicate that IV is formed consecutively from III.

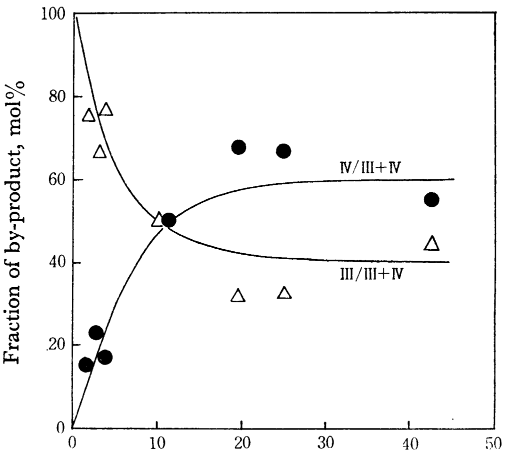

Fig. 7. Relations between the conversion of *n*-butylamine to by-products (dibutylamine and Schiff's base) and the respective fraction of each component in the by-products obtained in the presence of the Ga-L catalyst: -△- fraction of Schiff's base, -●- fraction of dibutylamine. (Ga 40 g, Feed 0.089 mol/hr).

The above-mentioned features of the Ga-L-catalyzed dehydrogenation of *n*-butylamine are somewhat different from those of the Zn-L-catalyzed dehydrogenation, which were described in the previous section; the following reaction scheme[7] seems to be applicable to the Ga-L-catalyzed dehydrogenation:

$$\begin{tikzcd}
\text{n-butylamine} \arrow[r, "-H_2", "\text{Ga-L}"'] & \text{aldimine (I)} \arrow[r, "-H_2", "\text{Ga-L}"'] \arrow[d, "\text{Ga-L}"', "+\text{n-butylamine}"] & \text{n-butyronitrile (II)} \\
& \text{Schiff's base (III)} + \text{ammonia} \arrow[d, "\text{Ga-L}"', "+H_2"] & \\
& \text{dibutylamine (IV)} &
\end{tikzcd}$$

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[6] Ammonia was also detected, in addition to negligibly small amounts of ethylamine, diethylamine, *n*-propylamine, dipropylamine, acetonitrile, propionitrile, and acrylonitrile. These materials were also found in the products obtained by the use of the Zn-L catalyst.

[7] W. S. Brey *et al.* (*Ind. Eng. Chem.*, **51**, 1031 (1959)) dehydrogenated butylamines by using an alumina catalyst and obtained dibutylamine, *N*-butylidenbutylamine, and some other compounds. They proposed a reaction scheme. However, because of the complicated product distribution, their reaction scheme was more complex than the present one.

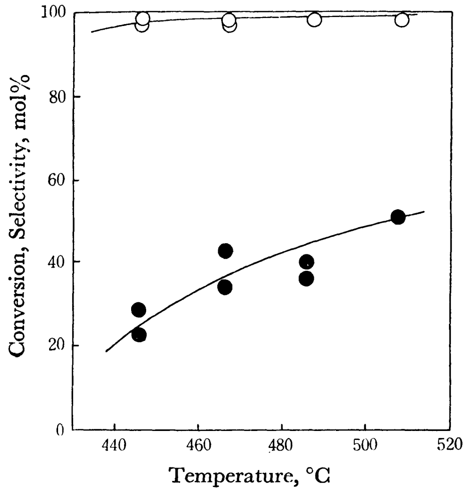


Fig. 8. The temperature dependencies of the catalytic activity and the selectivity of the Zn-L catalyst for the dehydrogenation of benzylamine: -●- total conversion, -○- selectivity for the formation of benzonitrile. (Zn 50 g, Feed 0.068 mol/hr).

Dehydrogenation of Benzylamine. In the dehydrogenation of benzylamine, only Zn-L was used as a catalyst. As can be seen in Fig. 8, Zn-L showed catalytic activity in the dehydrogenation of benzylamine. The reaction products were mainly hydrogen and benzonitrile, and the selectivity of the dehydrogenation was nearly 100% under the present experimental conditions. Thus, the over-all reaction may be expressed simply by:

$$C_6H_5CH_2NH_2 \xrightarrow{\text{Zn-L}} C_6H_5CN + 2H_2$$

Dehydrogenation of Cyclohexylamine. Also in this reaction, only Zn-L was used as a catalyst. According to the experimental results, cyclohexylamine decomposed and evolved hydrogen and ammonia, together with very small amounts of cyclohexene, cyclohexane, and a trace of unidentified compound. The mole ratio of hydrogen to ammonia was nearly 1: 1. Further, the liquid products gave the infrared spectra shown in Fig. 9. This figure shows the presence of the $-\overset{|}{C}=N-$ group in the the liquid products.

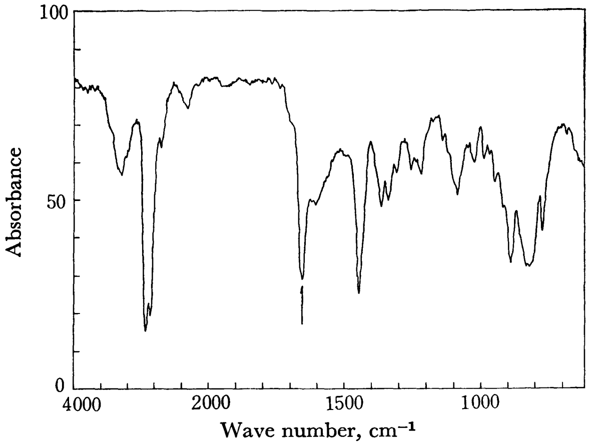
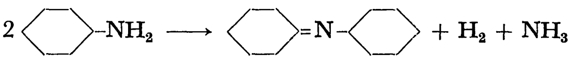


Fig. 9. Infrared spectra of the liquid products obtained by dehydrogenating cyclohexylamine in the presence of the Zn-L catalyst.

Thus, it was suspected that the dehydrogenation product (V) was *N*-cyclohexylidencyclohexylamine, which had been obtained by Pasek *et al.*[8] in the cyclohexylamine decomposition over alumina. To confirm this suspicion, *N*-cyclohexylidencyclohexylamine was prepared by the procedure reported by Pasek *et al.*[8] and properties of this compound were compared with those of the dehydrogenation product. That is, the reaction product (V′) of the following reaction:

was isolated by means of distillation in a nitrogen stream at a pressure of 20 mmHg. Further, the dehydrogenation product (V) was also isolated by distillation. Then, the properties of V′ and V were compared. The results were as follows; i) both V′ and V crystallized at a given temperature of 26°C and boiled at 132°C (20 mmHg), and ii) the gas-chromatographic retention time[9] of V agreed well with that of V′. These facts indicate that the dehydrogenation product (V) is *N*-cyclohexylidencyclohexylamine. Considering these facts, the over-all reaction may be expressed as follows;



(1)

In the present work, the reaction (1) was assumed to be the main reaction and the conversion of cyclohexylamine was calculated on the base of this scheme. The results are given in Fig. 10.

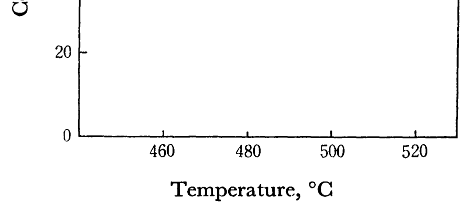


Fig. 10. The temperature dependency of the catalytic activity of the Zn-L catalyst for the dehydrogenation of cyclohexylamine. (Zn 50 g, Feed 0.072 mol/hr).

Presumably, the primary reaction is a dehydrogenation of cyclohexylamine to ketimine, *i.e.*, $C_6H_{10}NH$ (VI). However, because of the high reactivity of this compound, a further reaction between this compound and cyclohexylamine occurs. Therefore, it is not unlikely that the compound (VI) was not detected.

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[8] J. Pasek, J. Tyrpekl, and M. Machova, *Collect. Czech. Chem. Commun.*, **31**, 4108 (1966).

[9] Except for the temperature (135°C), the conditions of the gas-chromatographic analysis were identical with those described in the foot note of the previous section.

Summary

The present work has demonstrated that some liquid metals catalyze the dehydrogenation of amine. Especially, the high activity and the high selectivity of the Zn–L catalyst must be noted. The dehydrogenation of amine by solid catalysts has been said to be difficult,[5] and it has been considered that specially-prepared catalysts[10] are necessary for the selective dehydrogenation of amine. On the contrary, the liquid metal catalysts can be prepared without difficulty. Therefore, the use of the liquid-metal catalyst seems to give a useful tool not only for a scientific study of the dehydrogenation of amine, but also for the industrial dehydrogenation of amine.

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[10] G. Zuby, C. E. Johonson, and T. D. Nevitt, U. S. 2849478 (1958).