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Studies on the Catalysis of Molten Metal

XII. A Stereochemial Study on the Reaction of Menthol

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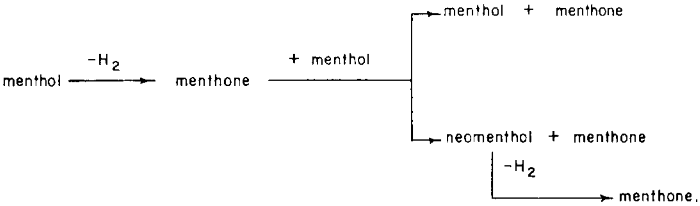
The conversion of *dl*-menthol and that of *l*-menthol have been measured by a rectangular duct-type reactor containing a liquid metal catalyst (Tl or In; the surface area is about 20 cm^2). The experimental result has shown that the total conversion of *dl*-menthol is higher than that of *l*-menthol. In order to explain this unusual result, the following reaction scheme has been assumed:



With the aid of stereochemistry and molecular interaction models, comparisons among the rate constants for the elementary steps have been carried out. It has been shown that the transfer hydrogenation step proceeds faster in the *dl*-menthol system than in the *l*-menthol system and, consequently, that the difference in the total conversion of the menthol isomers becomes observable.

INTRODUCTION

Although many aspects of the reaction of an alcohol over a liquid metal catalyst have been revealed (*1–10*), the stereochemical aspect of the catalysis has not yet been clarified. Recently, the present authors (*11*) have revealed that various terpene alcohols can be selectively dehydrogenated by a liquid metal catalyst. This finding has prompted the authors to study the reaction of optically active terpene alcohols over a liquid metal catalyst.

This paper reports the results of a stereochemical investigation on the reaction of menthol over a liquid metal catalyst. The experimental data show that *dl*-menthol reacts faster than *l*-menthol. This result seemingly contradicts the stereochemical principle, which states that optical isomers of a compound should have an identical reactivity. Thus, a plausible explanation for the experimental result is given in the discussion section.

EXPERIMENTAL

Materials. Indium (99.999%) and thallium (99.999%) obtained commercially were used as catalysts. *l*-Menthol of 98%

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purity and *dl*-menthol of 99% purity were obtained commercially and were used as reactants without further purifications. *p*-Cymene of 97% purity was commercially obtained to use as a solvent of menthol.

Procedures. The reaction was carried out in an apparatus equipped with a rectangular duct-type reactor. Since the advantages of the use of a rectangular duct reactor have been reported in the previous paper (*5*), only the dimensions of the reactor used in the present work are shown in Fig. 1. The geometrical surface area of the liquid metal catalyst contained in this reactor is about 20 cm^2.

In the activity measurement, a mixed solution of menthol and *p*-cymene (menthol/*p*-cymene = 0.15 in mole ratio) was supplied (0.004 mole/hr) from a microfeeder into the reaction apparatus. The solution was heated in the preheating region, and the evaporated menthol and *p*-cymene were led to the reaction zone, where menthol was subjected to the catalysis of a liquid metal. The effluent vapor from the reactor was cooled to separate condensable products from gaseous products. Finally, both gaseous products and liquid products were analyzed by means of a temperature-raising gaschromatograph (Hitachi Model 163; column = PEG-20M, 3 m; carrier gas = nitrogen; temperature = 60–180°C; programmed rate of temperature raising = 5°C/min; detector = FID).

RESULTS

The experimental results given in Table 1 show that the menthone yield from *dl*-menthol was larger than that from *l*-menthol. This fact deserves special mention. According to the stereochemistry, the reactivities of two optical isomers of a compound should be identical to each other, and hence, the reactivity of *dl*-menthol should be identical to that of *l*-menthol. Thus, the question of whether the experimental result mentioned above conforms to the stereochemical principle was raised. Initially, the present authors doubted if the experiment had been carried out adequately. Hence, the effect of solvent, the purity of reagent, and the reproducibility of the experimental result were checked carefully. However, no fault that might have yielded wrong data was found. Accordingly, the experimental result was accepted as a manifestation of the charac-

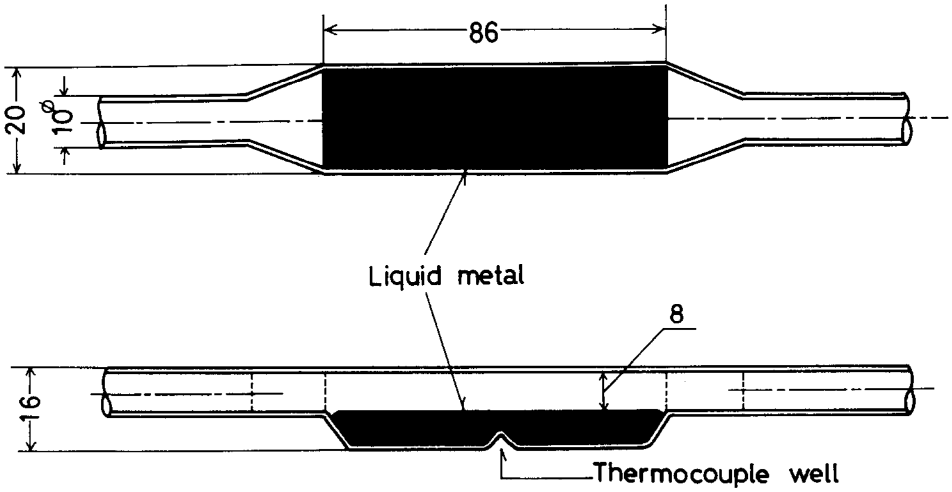

FIG. 1. Horizontal and vertical cross sections of the rectangular duct reactor used in the present work.

TABLE 1

Results of Reaction of *l*-Menthol and *dl*-Menthol on Liquid Metal Catalysts

Catalyst	Reaction temperature (°C)	*l*-Menthol		*dl*-Menthol	
		Conversion to menthone (mole%)	Conversion to neomenthol (mole%)	Conversion to menthone (mole%)	Conversion to neomenthol (mole%)
In	445	4.4	0.3	3.8	0.5
	476	6.0	0.6	12.9	2.5
	498	9.6	1.3	18.1	4.4
	523	19.8	5.0	27.0[a]	7.5[a]
Tl	440	3.7	0.4	5.3	0.8
	479	10.5	2.2	13.8	3.3
	500	13.8	2.8	19.2	5.7
	524	21.2	4.9	26.9	8.2

[a] At 530°C.

teristics of the reaction which had taken place on the liquid metal catalyst.

The data given in Table 1 again show that the yield of neomenthol from *dl*-menthol is higher than that from *l*-menthol. This fact indicates that a certain side reaction took place in addition to the main reaction which produced menthone. As can be seen in the following discussion, this information makes an essential contribution to the understanding of the reaction mechanism.

DISCUSSION

Reaction Scheme

The higher rate of formation of menthone from *dl*-menthol than from *l*-menthol cannot be explained in terms of a simple dehydrogenation mechanism. If we assume that the overall reaction consists of only one elementary reaction

$$\text{menthol} \rightarrow \text{menthone} + H_2, \qquad (1)$$

the conversion of *dl*-menthol should be identical to the conversion of *l*-menthol. On the other hand, if the overall reaction consists of several elementary steps, the conversion of *dl*-menthol may have a value different from that for *l*-menthol. Of course, the composite overall reaction must produce menthone as the main product.

It is probable that a transfer hydrogenation step,

$$\text{menthone} + \text{menthol} \rightarrow \text{menthol} + \text{menthone}, \qquad (2)$$

follows the dehydrogenation step (1). It must be remembered that the liquid metal catalyst had effectively promoted the transfer hydrogenation between alcohol and ketone (*10*). Furthermore, it must be pointed out that the transfer hydrogenation between menthol and menthone is capable of providing a route which forms neomenthol, i.e.,

$$\text{menthone} + \text{menthol} \rightarrow \text{neomenthol} + \text{menthone}. \qquad (3)$$

The formation of neomenthol was actually recognized in the experiment (Table 1).

Finally, it must be taken into consideration of a strong dehydrogenation activity of the liquid metal catalyst. In other words, neomenthol is considered to be dehydrogenated to form menthone, i.e.,

$$\text{neomenthol} \rightarrow \text{menthone} + H_2. \qquad (4)$$

It is easily seen that only menthone and neomenthol are formed in any overall reaction which can be derived by composing the elementary reactions described above. Since many steps are available to produce menthone, the main product of the overall reaction would probably be menthone.

The reaction schemes which are shown in Fig. 2 were based on the discussion above. Every elementary step is labeled and the rate constant for each elementary step is defined in the figure. This figure reveals that only one route, route (i), is possible for the reaction of *l*-menthol while four routes, (i), (ii), (iii), and (iv), are available for the reaction of *dl*-menthol.

Stereochemical Principle and Rate Constants

From the principles of stereochemistry, several important relations among the rate constants can be easily derived. For instance, it is obvious that

$$k_1 = k_{1'}, \quad k_4 = k_{4'}, \tag{I}$$

because *d*-menthol is an enantiomer of *l*-menthol and *d*-neomenthol is an enantiomer of *l*-neomenthol. It is also possible to show that

$$k_{2\mathrm{a}} = k_{2'\mathrm{a}}, \quad k_{2\mathrm{b}} = k_{2'\mathrm{b}} \tag{II}$$

and that

$$k_{3\mathrm{a}} = k_{3'\mathrm{a}}, \quad k_{3\mathrm{b}} = k_{3'\mathrm{b}}. \tag{III}$$

The enantiomer relation between the transition state (*l*-one – – – *l*-ol)$^{\neq}$ and the transition state (*d*-one – – – *d*-ol)$^{\neq}$ justifies relation (II), and the same relation between (*l*-one – – – *d*-ol)$^{\neq}$ and (*d*-one – – – *l*-ol)$^{\neq}$ justifies relation (III).

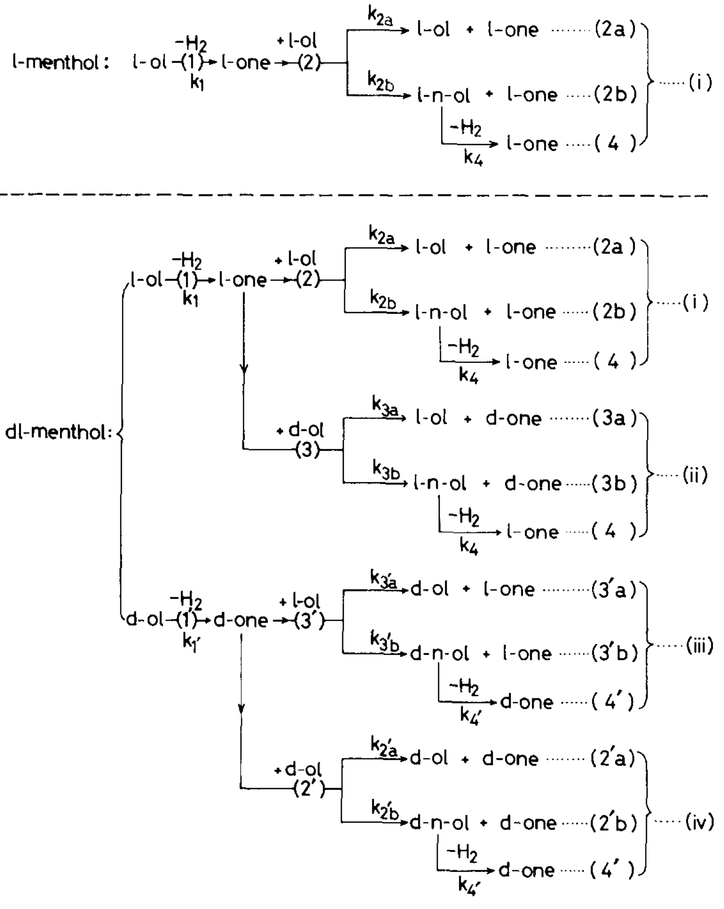

FIG. 2. The fine structure of the reaction pathway; ol, menthol; one, menthone; n-ol, neomenthol.

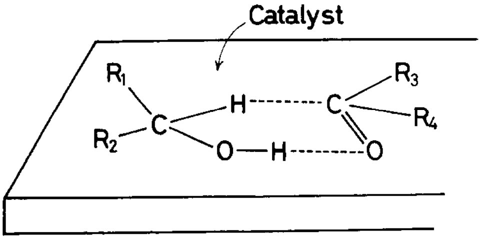

FIG. 3. A molecular interaction model for the hydrogen transfer between alcohol and ketone over a liquid metal catalyst.

Steric Hindrance and Rate Constants

Reasonable molecular interaction models are necessary to continue the discussion about the interrelations among the rate constants. Fortunately, the previously proposed transition state model (*10*), which is illustrated in Fig. 3, provides a basis for realistic interaction models, which are shown in Fig. 4.

Comparison of the models enables us to expect that the smallest steric hindrance would appear in transition state $3b^{\neq}$ because neither the axial hydrogen–hydrogen interaction nor the interaction between the isopropyl groups is seen in this model. Therefore, it is obvious that

$$k_{3b} > k_{2a},\quad k_{2b},\quad k_{3a} \tag{IV}$$

and that

$$k_{3'b} > k_{2'a},\quad k_{2'b},\quad k_{3'a}. \tag{IV'}$$

On the other hand, the largest steric hindrance would appear in transition state $3a^{\neq}$ because not only the interactions among axial hydrogen atoms but also the interactions between two bulky isopropyl groups are seen in this state. Therefore,

$$k_{3a} < k_{2a},\quad k_{2b},\quad k_{3b} \tag{V}$$

and

$$k_{3'a} < k_{2'a},\quad k_{2'b},\quad k_{3'b}. \tag{V'}$$

Since an isopropyl group is much bulkier than a hydrogen atom, the steric hindrance due to the interactions between isopropyl groups appears to be larger than the steric hindrance due to the axial hydrogen–hydrogen interaction. Therefore, it is reasonable to consider that

$$k_{2a} > k_{2b} \tag{VI}$$

and

$$k_{2'a} > k_{2'b}. \tag{VI'}$$

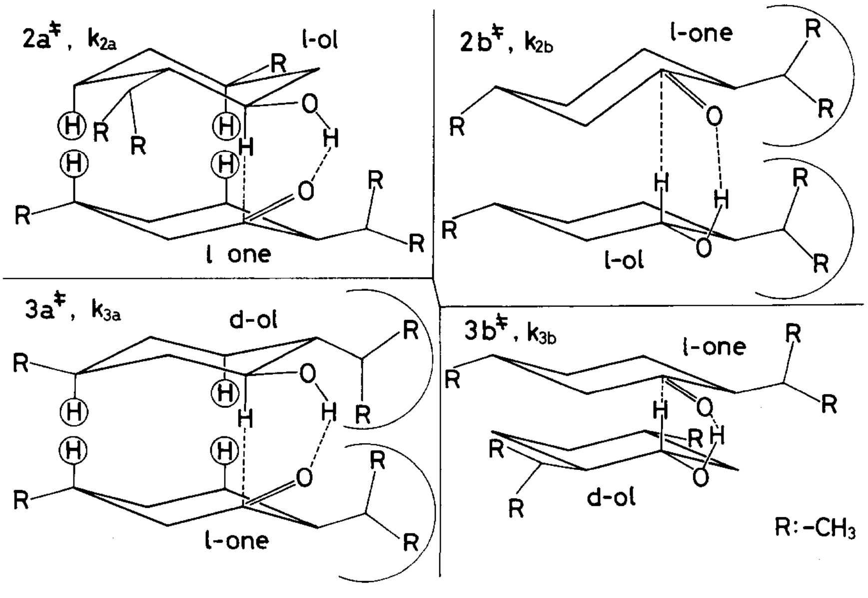

FIG. 4. Transition state models for the transfer hydrogenation steps 2a, 2b, 3a, and 3b.

By combining (IV), (V), and (VI), we obtain

$$k_{3b} > k_{2a} > k_{2b} > k_{3a}. \qquad \text{(VII)}$$

Similarly, by combining (IV′), (V′), and (VI′), we obtain

$$k_{3'b} > k_{2'a} > k_{2'b} > k_{3'a}. \qquad \text{(VII}'\text{)}$$

Interpretation of Experimental Results

Probably, in any of the dehydrogenation steps, such steric hindrances as those seen in the transfer hydrogenation steps would not appear. Therefore, compared with the transfer hydrogenation steps, the dehydrogenation steps would have higher rates. In other words, the transfer hydrogenation steps would limit the rate of overall reaction. The situation becomes more convincing if we consider that, in the transfer hydrogenation step, molecules of alcohol and ketone have to sit perpendicular to the surface, and hence, an additional large steric hindrance also participates to retard the reaction. Thus, the product distribution of the overall reactions would sensitively be affected by the relative rates of the transfer hydrogenation steps. This view provides a basis for the interpretation of the experimental results.

In the reaction of *l*-menthol, the transfer hydrogenation step 2 consists of two substeps, 2a and 2b. According to the relation (VI), step 2b, which produces neomenthol, is not as accessible to the reaction as step 2a. Therefore, the reaction occurs more frequently through 2a than through 2b, and the formation of neomenthol is suppressed. On the other hand, additional steps 2′a, 2′b, 3a, 3b, 3′a, and 3′b are available for the reaction of *dl*-menthol. According to the relations (II), (III), (VII), and (VII′), it is obvious that

$$k_{3b} = k_{3'b} > k_{2a} = k_{2'a} > k_{2b} = k_{2'b} > k_{3a} = k_{3'a}. \qquad \text{(VIII)}$$

Therefore, the reaction occurs most frequently through 3b and 3′b. This is favorable for the formation of neomenthol. This conclusion agrees with the experimental result that more neomenthol was formed from *dl*-menthol than from *l*-menthol.

Another experimental result that more menthone was formed from *dl*-menthol than from *l*-menthol can be explained as the consequence of the faster formation of neomenthol from *dl*-menthol. According to the reaction scheme, neomenthol is dehydrogenated to menthone. Probably, this reaction obeys first-order kinetics (*5*), i.e.,

$$R_{dl} = k_{dl}C_{\text{n-ol},dl}; \quad R_l = k_l C_{\text{n-ol},l}, \qquad \text{(IX)}$$

where R is the reaction rate, k is the rate constant, $C_{\text{n-ol}}$ is the concentration of neomenthol, and the subscripts *dl* and *l* specify whether the starting material (menthol) is *dl*- or *l*-. It is obvious that $k_l = k_4$ and $k_{dl} = (2k_4 + 2k_{4'})/4 = k_4$. Thus, $k_{dl} = k_l$. On the other hand, as mentioned in the preceding paragraph, more neomenthol was produced from *dl*-menthol than from *l*-menthol. Hence, $C_{\text{n-ol},dl} > C_{\text{n-ol},l}$. Consequently, $R_{dl} > R_l$. This means that more menthone is produced from *dl*-menthol than from *l*-menthol, provided that other factors play no roles.

It is possible to show that elementary steps other than (4) never result in the difference between the menthone yield from *dl*-menthol and that from *l*-menthol. For instance, the dehydrogenation step (step (1) or composite step (1) + (1′)) is available to produce menthone, but the amount of menthone to be produced from *dl*-menthol is equal to that to be produced from *l*-menthol because $k_1 = k_{1'}$. The transfer hydrogenation steps 2a, 2b, 2′a, 2′b, 3a, 3b, 3′a, and 3′b are also available to produce menthone. However, no change in the menthone concentration is brought about by these steps because the amount of menthone to be produced in each step is equal to the amount of menthone to be consumed in this step.

Now we have seen that the reaction scheme and the transition state models are probable. Unfortunately, however, the role of the catalyst yet remains to be clarified. Of course, it is not always impossible to guess that the catalyst might have played a role similar to that had been postulated for aluminum in the intermediate of Meerwein–Ponndorf–Verley reduction (*12*). However, it is said that the exact mechanism of this reaction is unknown (*12*). Thus, care must be taken not to place too much emphasis on the fact that both indium and thallium, which were used as catalysts in the present work, are also group VIIIA elements. Too little evidence is available to believe that the mechanism of the heterogeneous catalysis of a liquid metal is analogous to the mechanism of the homogeneous catalysis of an aluminum alkoxide. Further discussions about the role of the catalyst are beyond the scope of the present study.

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