Isomerization Reactions of Cyclohexene over Molten Salt Catalysts

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We have already reported that catalytic activity for hydrocracking of polyaromatic compounds of ZnCl_2 - CuCl binary melts is more outstanding than that of ZnCl_2 melt alone. In order to further study the catalytic activity of these melts, isomerization of cyclohexene at 400°C using a continuous flow method was carried out. ZnCl_2 melt showed only 2% conversion while a ZnCl_2 - CuCl melt containing 30 mol % of CuCl realized as high as 43.7% conversion. These observations strongly suggest that some active species formed in the binary melts effectively enhance the isomerization reaction.

1. Introduction

Kenney et al.¹⁾ found that the catalytic activity of molten ZnCl_2 for the elimination of hydrogen chloride from isopropyl chloride was lowered by addition of metal chlorides, such as KCl , NaCl , and AgCl . Through intensive studies of catalytic activities of ZnCl_2 -containing melts for some organic reactions²⁾ including hydrocracking of coal related substances^{3),4)}, we found a remarkable catalytic activity of binary molten mixtures of ZnCl_2 and CuCl when it was compared with that of ZnCl_2 alone. In order to study this observation further in detail, we carried out isomerization of cyclohexene over molten salts.

2. Results and Discussion

The results observed are shown in **Table 1**. A small quantity of the proton source (H_2O , HCl) existing in the reaction system acts as a co-catalyst for Lewis acid in the isomerization of cyclohexene to methylcyclopentenes that proceeds via the carbonium ion mechanism. Accordingly, the total yield of isomerized products (1-methylcyclopentene, 3-methylcyclopentene, methylcyclopentane, and 1-chloro-1-methylcyclopentane) could be a measure of the acid strength of the molten salts. The yield of 1-methylcyclopentene was always higher than that of 3-methylcyclopentene because of the stability of the carbonium ion formed in the course of reaction. The ratio of 1-methylcyclopentene/3-methylcyclopentene was in the range of 3.5—5.5 (in Runs 2—8).

Runs 1—8 revealed the influence of composition of ZnCl_2 - CuCl melts on product distribution. The

addition of CuCl to ZnCl_2 raised the catalytic activity, and the extent of isomerization varied remarkably depending upon the composition-change in the molten salt. The melt of ZnCl_2 : CuCl = 70 : 30 (Run 4) gave the maximum yield of isomerized products. This increase in catalytic activity by addition of CuCl to ZnCl_2 seems to indicate the presence of new active species.

The detection of HCl addition products (chloro-cyclohexane and 1-chloro-1-methylcyclopentane) led us to examine the influence of HCl on the isomerization (in Runs 9 and 10). The addition of hydrogen chloride to the reaction system increased the yields of isomerized products as expected; the addition of large amounts of HCl increased the yields of addition products remarkably. These findings indicate that the cause of rise in the catalytic activity by addition of CuCl to ZnCl_2 is not attributable to the change in the amounts of proton sources in the reaction system.

The catalytic activity of ZnCl_2 for several acid-catalyzed reactions^{1),5)} is lowered by addition of alkali metal chlorides because of the formation of some stable complex salts. Runs 11 and 12 showed the influence of addition of the alkali metal salts on the catalytic activities of the binary molten salts. In comparison with the result of Run 5, the addition of KCl or LiCl lowered the yields of isomerized products. The extent of the lowering of the catalytic activity was greater with ZnCl_2 / CuCl / KCl . ZnCl_2 salts tend to form stable complex ions with KCl more than LiCl because the partial interaction between small Li^+ and Cl^- is very strong in LiCl . These results can not be explained by diluent effect and would demonstrate the destruction of the active species resulting from the interaction of ZnCl_2 and CuCl .

The Hammett indicator method⁷⁾ and the IR method using xanthone⁸⁾ did not show any dif-

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Table 1 Product Distribution of Isomerization of Cyclohexene

Run No.	1	2	3	4	5	6	7	8	9	10	11	12
Molten Salt Composition	ZnCl ₂	ZnCl ₂ : CuCl							ZnCl ₂ ^{a)}	ZnCl ₂ ^{b)}	ZnCl ₂ ^{c)} /CuCl /KCl	ZnCl ₂ ^{c)} /CuCl /LiCl
		90:10 ^{d)}	80 : 20	70 : 30	60 : 40	50 : 50	40 : 60	30 : 70				
Recovery (%) ^{e)}	73.5	89.2	96.8	88.5	79.2	88.0	87.6	91.4	85.9	107.9	87.8	79.0
Yield (%) ^{f)}	2.0	4.3	11.8	43.7	29.3	25.9	19.5	13.4	2.8	9.8	1.4	8.6
-Me	1.5	3.4	9.3	32.0	22.0	18.5	16.4	10.5	2.1	5.5	1.2	6.7
-Me	t ^{g)}	0.8	2.2	8.5	5.7	5.3	3.0	2.1	0.6	1.1	t	1.2
-Me	t	t	t	2.2	0.8	1.5	t	0.5	t	t	t	t
( )	97.4	95.1	87.4	51.5	68.2	71.0	79.3	85.4	94.0	36.1	98.1	90.3
-Me -Cl	—	—	—	0.8	0.8	t	t	t	t	3.1	t	0.6
-Cl	0.6	0.6	1.2	0.9	0.9	1.0	t	0.5	1.3	50.4	t	0.9
Others ^{h)}	—	—	—	3.9	1.5	2.1	0.9	0.7	1.9	3.7	—	t

Reaction conditions : Temperature 400°C, Cyclohexene 0.068 mol/hr, Ar 0.089 mol/hr; a) HCl gas (0.019 mol/hr) was bubbled for 1 hr before reaction. b) HCl gas (0.019 mol/hr) was added to the reaction system. c) 48 : 32 : 20 d) mol % : mol % e) (weight of recovered compounds/weight of feed) × 100 f) Total yield of isomerized products g) “t” indicates the yield being less than 0.5%. h) Higher boiling products

ference of the observed acid strength between ZnCl₂ alone and the binary mixture of ZnCl₂ and CuCl in solid state.

3. Experimental

1) Materials Zinc chloride, copper(I) chloride, potassium chloride, and lithium chloride all obtained from Nakarai Chemicals, Ltd. were guaranteed reagents. The cyclohexene (G. R.) obtained from Wako Pure Chemical Industries, Ltd. was used without further purification after its purity was found satisfactory by GLC.

2) Apparatus and procedure The bubbler type reaction apparatus and the procedures used in the experiments were reported in detail in our previous paper⁹⁾. The molten salt was dried for 1 hr in the argon atmosphere. Cyclohexene was introduced into the vaporizer with a microfeeder and it was then bubbled along with a stream of argon into the molten salt. The product distribution was determined by GLC (Shimadzu GC-4BPTF, 4.5 m × 3 mm column packed with 20% SE-30 on Uniport B 60—80 mesh, 30—270°C, 5 °C/min, TCD, H₂ carrier). Mass spectra of all

products were obtained by means of GC-MS. 1-Methylcyclopentene and 3-methylcyclopentene were isolated by preparative GLC and identified by ¹H and ¹³C NMR spectra. Small quantities of benzene and 1,3-cyclohexadiene, which were dehydrogenated products of cyclohexene, were found in all runs. Also only small amounts of gaseous products were observed.

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要 旨

溶融塩触媒を用いたシクロヘキセンの異性化反応

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著者らはすでに多環芳族化合物の水素化分解において、 $\text{ZnCl}_2\text{-CuCl}$ の 2 元系溶融塩が ZnCl_2 単独の溶融塩触媒に比べ著しく高い活性を示すことを見出し報告した^{2),4)}。上記 2 元系溶融塩の触媒活性上昇の要因をさぐる一つの手段として、本論文ではシクロヘキセンの異性化反応を検討した。反応はシクロヘキセンをアルゴンガスと共に気相で 400°C に加熱した溶融塩中にふき込んで行う流通法によった。生成物は 1-メチルシクロペンテン、3-メチルシクロペンテン、メチルシクロペンタンおよび 1-クロロ-1-メチルシクロペンタンで 1-メチルシクロペンテンが主要生成物であることやこれまでの結果から、本反応はカルボニウムイオン機構で進むと考えられる。ここではこれらの 4 つの生成物の総和を転化率としたが、これは

溶融塩媒体の本反応に対する活性の尺度ともなる。生成物中に HCl の付加物と考えられる 1-クロロ-1-メチルシクロペンタンを認めたので、 ZnCl_2 中で HCl 共存下に反応を行ったところ、上記化合物の他に多量のクロロシクロヘキサンが生成した。**Table 1** から明らかなように、 $\text{ZnCl}_2\text{-CuCl}$ の組成を変化させると転化率は著るしく変動し、 $\text{ZnCl}_2\text{-CuCl}$ が 7:3 のモル比の時最も高い転化率 43.7% を示した。このことは ZnCl_2 に CuCl を添加することにより本反応を促進する活性種が新たに生成していることを強く示唆する。しかし固体状態の ZnCl_2 および $\text{ZnCl}_2\text{-CuCl}$ 塩のハメット指示薬⁷⁾ やキサントンを用いる IR 法等⁸⁾ による酸強度の測定を行ったが両者の間に何ら差異がみられなかった。

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Keywords

Isomerization, Cyclohexene, Molten salt catalyst, Zinc chloride, Cuprous chloride