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The Elimination Reaction of Chlorobutane over Some Molten Salts*

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Synopsis. The elimination reactions of hydrogen chloride from 1-chlorobutane and 2-chlorobutane over molten salts ($ZnCl_2$, $SnCl_2$, CuCl melts) have been studied by using both a microreactor and a conventional flow reactor. The preferential formation of *cis*-2-butene in the reaction of 2-chlorobutane can be explained in terms of the stereochemistry of the surface-adsorbed carbonium ion.

Some molten salts, such as $SnCl_2$–KCl and $ZnCl_2$-containing melts, are known to assist the dehydrohalogenation of alkyl halides.[1–4] However, little is known about the stereochemistry of dehydrohalogenation over molten-salt catalysts. The present investigation was undertaken in order to obtain stereochemical information about the dehydrochlorination of chlorobutanes over $ZnCl_2$–KCl–NaCl melts, $SnCl_2$–KCl melts, and CuCl–KCl melts from the butene isomer-distribution and in order to discover a convenient method of using the pulse technique[5] for such a dehydrochlorination.

Results and Discussion

Elimination by Microcatalytic Reaction. The contact time of reactants with molten-salt catalysts was arbitrarily defined to be the reciprocal of the flow rate of hydrogen (F^{-1} s/ml), where various flow velocities were attained by varying the flow rate of the hydrogen carrier gas. The conversion percentage of 2-chlorobutane is plotted as a function of F^{-1} at 250 °C and 280 °C in Fig. 1, where the ratio of % conv with the $ZnCl_2$ melts to that with the $SnCl_2$ melts is shown to be about 10 to 1 (at 250 °C), while this conversion ratio is about 2—3 to 1 in the case of the ratio of the $SnCl_2$ melts to the CuCl melts (280 °C). Therefore, the relative activities for dehydrochlorination are $ZnCl_2 \gg SnCl_2 >$ CuCl melts.

The distribution of butene isomers over three kinds of molten salts are shown in Table 1, where the values of the thermal reaction and the equilibrium values are also cited for comparison. Although the % conv varied markedly from melt to melt, the *cis*/*trans* ratios (cited in Table 1) of 2-butene produced are much the same (1.3—1.4) over the series of melts. To examine the possibility of the isomerization of the olefins after elimination, the pulses of 1-butene and 2-butene isomers were passed over the $ZnCl_2$ melts.[6] However, no isomerization among the 1-, *cis*-2-, and *trans*-2-butenes was observed. The *cis*/*trans* ratio of the 2-butene produced over these salts is larger than the equilibrium values; this preferable formation of *cis*-2-butene is considered to be characteristic of this reaction.

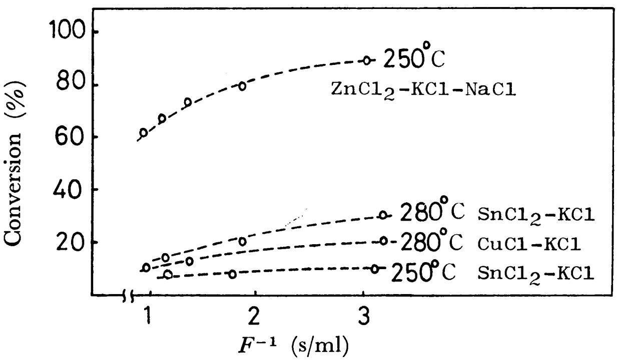

Fig. 1. Plots of % conv. of 2-chlorobutane *vs.* F^{-1}.

The reactivity of 1-chlorobutane over these molten salts becomes considerably lower than that of 2-chlorobutane. With $ZnCl_2$ melts, the % conv of 2-chlorobutane is 25 times as large as that of 1-chlorobutane, while the reactivity ratio of 2-chlorobutane/1-chlorobutane becomes about 9 in the case of the $SnCl_2$ melts. The relative catalytic activity of these melts for the de-

TABLE 1. ELIMINATION REACTION OF 2-CHLOROBUTANE

Melts[a)]		$ZnCl_2$-KCl-NaCl[b)] (3 : 1 : 1)		$SnCl_2$–KCl[c)] (1.5 : 1)		CuCl–KCl[d)] (1.8 : 1)		Homogeneous reaction in gas phase[e)]		Equilibrium		
Temp (°C)		205	250	290	350	280	320	400	450	200	300	400
Products (%)	1-butene (%)	9.8	10.8	7.9	12.8	11.1	11.9	39.3	37.4	13	19	23
	trans-2-butene (%)	37.4	37.3	39.8	38.6	38.1	37.3	38.6	36.3	55	50	46
	cis-2-butene (%)	52.8	51.9	52.3	48.6	50.8	50.7	22.1	26.3	32	31	31
cis/*trans*		1.4	1.4	1.3	1.3	1.3	1.4	0.57	0.72	0.58	0.62	0.67

a) The figures in parentheses indicate the molar ratio of the components. Hereafter, the melts will be denoted $ZnCl_2$ melts, $SnCl_2$ melts, and CuCl melts respectively. b) F^{-1}: 2.2 s/ml. c) F^{-1}: 3.3 s/ml. d) F^{-1}: 2.5 s/ml. e) F^{-1}: 2.5 s/ml.

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* Organic Reaction in Fused Salts. XI.
Part X: S. Kikkawa, M. Nomura, and M. Shimizu, *Chem. Lett.*, **1977**, 317.

Table 2. Elimination reaction of 1-chlorobutane

Melts		ZnCl$_2$ Melts[a]		SnCl$_2$ Melts[b]	
Temp (°C)		350	400	370	400
Products (%)	1-butene (%)	15.9	18.7	15.3	16.9
	trans-2-butene (%)	39.7	38.6	39.1	39.5
	cis-2-butene (%)	44.4	42.7	45.6	43.6
Conv (%)		18.8	51.0	15.5	31.9
cis/*trans*		1.1	1.1	1.2	1.1

a) F^{-1}: 2.78 s/ml. b) F^{-1}: 3.22 s/ml.

Table 3. Elimination reaction of 1-chlorobutane and 2-chlorobutane[a]

Melts		ZnCl$_2$ Melts	SnCl$_2$ Melts	CuCl-KCl-NaCl (3 : 1 : 1)
1-Chlorobutane (400 °C)				
Products (%)	1-butene (%)	22.2	31.1	41.2
	trans-2-butene (%)	39.4	32.3	27.3
	cis-2-butene (%)	38.4	36.6	31.5
Conv (%)		43.3	21.8	13.0
cis/*trans*		1.0	1.1	1.2
2-Chlorobutane (300°C)				
Products (%)	1-butene (%)	14.5	12.4	16.7
	trans-2-butene (%)	39.2	38.5	34.8
	cis-2-butene (%)	46.3	49.1	48.5
Conv (%)		62.8	20.9	0.7
cis/*trans*		1.2	1.3	1.4

a) Flow rate of Ar: 0.056 mol/h. Feed rate of reactant: 0.12 mol/h.

hydrochlorination of 1-chlorobutane was found to be different from that for 2-chlorobutane; that is, the ratio of % conv with the ZnCl$_2$ melts to that with the SnCl$_2$ melts is 2.5 to 1 (at 310 °C).

Table 2 shows the distribution of butene isomers resulting from the reaction of 1-chlorobutane over molten salts. In the last row of Table 2, the *cis*/*trans* ratios of 2-butene are presented. The preferable formation of 2-butene from 1-chlorobutane indicates that this elimination proceeds *via* a carbonium-ion mechanism involving rearrangement.[3,4]

The finding that *cis*-2-butene is formed in preference to *trans*-2-butene in the reaction of 2-chlorobutane over a series of molten salts can be explained in terms of the stereochemistry of the surface-adsorbed carbonium ion proposed by Noller, with the elimination of chlorobutane over CaO solid catalysts.[7] The secondary carbonium ion is attached to the molten-salt surface, where its most favorable conformation is as is shown in Fig. 2. Accordingly, *cis*-2-butene is preferably formed by sharing a free-electron pair resulting from the removal of H$_b$(by the chloride ion), with the vacant p orbital at C$_2$ (preferred path of the lower-energy barrier).

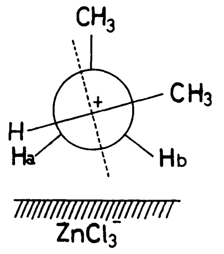

Fig. 2. Molten salts surface-adsorbed carbonium ion. Dotted line shows the vacant p orbital.

Elimination by Conventional Flow Method. Since the present elimination reaction is considered to be first-order, it was expected that the results from the pulse technique would be in agreement with those from the flow method. Table 3 shows the distribution of butene isomers obtained from both 1- and 2-chlorobutane, along with the values of % conv and the *cis*/*trans* ratios. As Table 3 clearly indicates, no notable differences were observed in the product distribution, the *cis*/*trans* ratio, or the % conv between the microcatalytic and the steady-state-flow reaction data. That is, in the study of such an elimination reaction over molten salts, the application of this microcatalytic method is of use experimentally. However, with the flow method, there was a tendency for the ZnCl$_2$ melts to have lower *cis*/*trans* ratios of the elimination of 2-chlorobutane compared with the results of the pulse method. This tendency may be explained by considering the small amount of the isomerization of products assisted by the considerable amounts of HCl dissolved in ZnCl$_2$ melts.

Experimental

Reagents. The 1-chlorobutane and 2-chlorobutane were obtained from Wako Pure Chemical Industries, Ltd. along with the three isomers of butene. The metal halides were guaranteed reagents from Nakarai Chemicals.

Apparatus and Procedure. A commercial gas chromatograph was arranged so as to record the amount of the pulse of the reactant (injected by means of a microsyringe, 1 µl) with a Silicone DC 550 column (75 cm) and to separate the products obtained after the reactant had passed over the melts in the reactor using a BMEE column (6 m) at 0 °C. A Pyrex-tube reactor containing the molten salts, immersed in a temperature-controlled salt bath, was connected to the gas chromatograph by means of a six-port valve which also served to dry the molten salt media by passing N$_2$ through before carrying out the pulse reaction.

For conventional flow experiments,[8] a vapor mixture of Ar and chlorobutane was bubbled up through dry molten salts for a period of 30 min. An Ar flow containing vaporized products was introduced, from the exit side, to the gas sampler once every 15 min. The gas-chromatographic separation of the products was done with a BMEE column (6 m).

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