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Chlorination of Methylcyclohexane in Molten Salt Media

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The chlorination of methylcyclohexane in several molten metal chloride mixtures ($ZnCl_2$/KCl/NaCl, CuCl/KCl/NaCl, $AlCl_3$/KCl/NaCl, and $CuCl_2$/KCl/NaCl) has been carried out, using nitrogen gas as a diluent, at three levels of temperature (250, 350, and 450 °C). The reactions in both $ZnCl_2$ and CuCl melts were studied extensively, the former representing the molecular-type melt and the latter standing for the partially-ionic-type one. These reactions gave 1-, 2-, 3-, and 4-chloro-methylcyclohexanes and 1-, 3-, and 4-methylcyclohexenes as primary products, along with smaller amounts of toluene and methylcyclohexadiene. The formation of these olefins were interpreted by the subsequent elimination (by a carbonium-ion mechanism) of HCl catalytically enhanced by these melts from the methyl-chlorocyclohexane derivatives. The difference observed in the product distributions between $ZnCl_2$ and CuCl melts was also explained by the studies of the effect of hydrogen chloride produced in these reactions over molten salts.

A great many studies have been carried out on the chlorination of hydrocarbons in the liquid and gas phases, and many detailed data on the reactivities and reaction mechanism are available. However, the chlorination employing molten salts as a reaction medium[1] has been investigated much less systematically. Melts have the advantages of a high solubility of chlorine and of good thermal conductivity, which effects the removal of the local heat, accompanied by exothermic chlorinations.

The present authors have carried out the chlorinations of ethylbenzene,[2] alicyclic hydrocarbons (C_3–C_4),[3] and cyclohexane[4] in molten salts and found that molten salts act not only as thermally stable reaction media, but also show catalytic activities. The present paper deals with the reaction of methylcyclohexane with chlorine in molten salts.

Since this compound has primary, secondary, and tertiary hydrogen in the molecule, useful information about their relative reactivities and about the reaction mechanism of chlorinations in molten salts can be expected to be obtained by analyzing the isomer distribution of the products.

Experimental

Materials. Commercial methylcyclohexane (I) was distilled after sulfuric acid washing. Commercially-available 4-methylcyclohexene (V) was employed without further purification. The 1-methylcyclohexene (III)[5] and 3-methylcyclohexene (IV) [contaminated with (V)] were prepared according to the reported methods.[6] The 1-chloro- (VI),[7] 3-chloro- (VIII)[8] and 4-chloro-methylcyclohexane (IX),[9] and chloromethylcyclohexane (X)[10] were synthesized by the procedures cited in the literature.

The samples prepared had the following physical constants: III, bp 110—113 °C (108—111 °C); I, bp 100—101 °C (100 °C); V, bp 56—57 °C/28.5 mmHg (50—52 °C/12 mmHg); VIII, bp 45.5 °C/18 mmHg (43.8—44.0 °C/14 mmHg); IX, bp 41—41.5 °C/12 mmHg (41 °C/10 mmHg); X, bp 66—69 °C/20 mmHg (67—68 °C/20 mmHg).

Reagent-grade zinc chloride, cuprous chloride, cupric chloride, and aluminum chloride (Wako Pure Chemical Industries, Ltd., Osaka) were used without further purification.

Apparatus. The apparatus used for the chlorination is shown schematically in Fig. 1. A vertical cylindrical Pyrex tube 30 mm in diameter, equipped with a gas inlet tube (inner diameter of the nozzle of the inlet tube: 1.0—1.5 mm) some distance from the lower end, was heated by means of a coil heater connected to an electric controller (the gas inlet tube was immersed 10 cm in the melts). The mixture of salts was melted and dried with N_2 for 60 min before carrying out the chlorination. After constant flow rates of the nitrogen (0.2 mol/hr) and chlorine (0.1 mol/hr) had been attained, the supply[11] of the reactant was started; the reaction products were collected at the exit in an acetone–Dry Ice trap and analyzed by gas chromatography after the removal of the chlorine by washing with a sodium hypochlorite solution. A blank test on the gas-phase reaction (non-catalytic) was carried out in a U-glass tube covered with aluminum foil to avoid the influence of diffused daylight and immersed 10 cm in a fused salt bath.

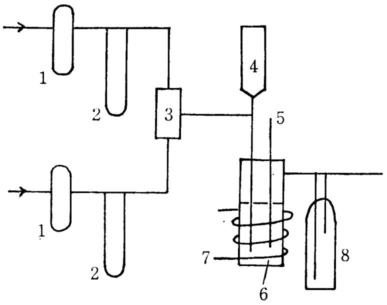

Fig. 1. Block diagram of the apparatus used.
1: $CaCl_2$ tube, 2: flow meter, 3: mixing chamber, 4: starting material, 5: thermocouple, 6: molten salt, 7: heater, 8: Dry Ice–acetone trap

Analysis of Reaction Products. The isomeric products were analyzed by means of gas chromatography [on a Shimadzu-GC-3AH gas chromatograph equipped with TCD using a combined column of Pluronic L-84 (4.5 m × 3.0 mm) and Apiezone grease (0.75 m × 3.0 mm) at 85 °C]. The oven temperature was fixed at 85 °C to avoid dehydrochlorination in the injection port of the gas chromatograph. Hydrogen was used as the carrier gas at a flow rate of about 46 ml/min.

Preparative gas chromatography and proton magnetic resonance were used when necessary for product identification.

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Results and Discussion

Identification of Chlorination Products. A gas chromatogram of the GC-Mass analysis of products obtained in the $ZnCl_2/KCl/NaCl$ (3: 1: 1 mole ratio)[12] melt is shown in Fig. 2.

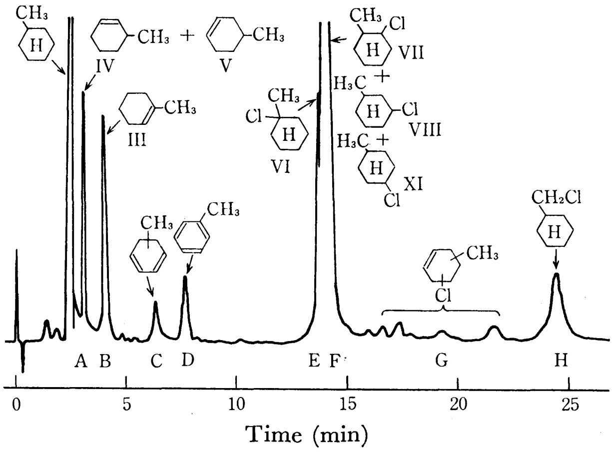


Fig. 2. Glc fractionation of chlorination products of methylcyclohexane in $ZnCl_2/KCl/NaCl$ melt.
Conditions of GC-MS (Hitachi K 53 GC-Hitachi RMU-60 MS) analysis: PEG-1540 (0.02′×50 feet), 70 °C, He (0.5 kg/cm^2).

The mass spectra of Peak A and Peak B (shown in Fig. 2) indicated the parent peak at $m/e=96$ [Peak A, m/e 96, M^+ (13), 81, M^+-CH_3 (100), 68, retro Diels Alder fraction of 3-methylcyclohexene, (39), 54, retro Diels Alder fraction of cyclohexene. Peak B, m/e 96, M^+ (46), 81 (100), 68 (75), 67 (43), 55 (50). The number in brackets indicates the relative intensity].[13,14] Both peaks had retention times corresponding to 3-methylcyclohexene(IV) or 4-methylcyclohexene(V) and 1-methylcyclohexene(III) respectively. Since, under these conditions, IV and V were not separated on our columns, Peak A was regarded as a mixture of V and IV. Peak D was confirmed as toluene(XIII) by mass spectral studies (m/e 92, M^+ (63), 91 (100), 65 (27), 63 (32)). The mass spectra of Peak C indicated the presence of methylcyclohexa-1,3-diene derivatives(XII) (m/e 94, M^+ (25), 91 (25), 79 (100), 77 (75)). Peak E and Peak F showed the following mass spectra [m/e 97, M^+-Cl, 81, $96-CH_3$ (most abundant in both peaks), 68, 67, retro Diels-Alder fraction of methylcyclohexene (secondarily abundant in Peak F), 55, retro Diels-Alder fraction of C_6H_{10} (secondarily abundant in Peak E)] and corresponded to the identical retention times of VII, VIII, and IX on the PEG 1540 column, while VI showed a bit of separation, as is shown in Fig. 2. However, using a serially-combined column of Pluronic L-84 and Apiezone glease L, VI was separated distinctly from VII, VIII, and IX (when still had identical retention times), while the fraction of VI was obtained by preparative gas chromatography and was confirmed as 1-chloro-methylcyclohexane by means of its NMR datum (τ, 8.30, CH_3, singlet in CCl_4). The small peaks between Peak F and Peak H were estimated to correspond to methylchlorocyclohexene derivatives (XI) by mass spectral studies (m/e 132, 134, M^+, 94 (base peak), 77, 53). Peak H was confirmed to be due to chloromethylcyclohexane by means of mass spectral studies (m/e 134,

Table 1. Chlorination of methylcyclohexane in the presence of various melts[a)]

Exp. No.	Melts	Temp. (°C)	Recv.[b)] Liq. (g)	Conv.[c)] (%)	IV and/or V	% Yields							
						III	XII	XIII	VI	VIII | IX	XI	X	Others[d)]
1[e)]	$ZnCl_2+KCl$ $+NaCl$	250	10.1	11.8	t	t	—	22.4	t	60.8	t	16.8	—
2		350	10.2	45.0	23.0	8.7	3.1	9.2	43.4	3.6	3.2	4.7	0.6
3		450	10.1	52.5	25.1	7.4	2.1	16.4	44.4	3.0	t	0.4	1.2
4	$CuCl+KCl$ $+NaCl$	250	9.8	4.1	t	14.9	—	—	t	71.0	t	14.1	—
5		350	9.2	48.6	10.3	6.8	—	5.9	10.8	53.2	5.5	7.4	0.5
6		450	8.1	50.6	26.1	7.8	3.3	11.6	21.6	22.7	1.0	5.5	0.4
7	$AlCl_3$[g)]	250	8.1	19.8	39.7	34.7	—	7.5	11.7	—	—	—	6.9
8[f)]	$CuCl_2$[h)]	350	10.6	40.8	16.7	t	—	12.1	8.1	40.9	3.5	6.4	—
9[f)]	$CuCl_2$[i)]	350	11.1	26.7	9.6	t	—	7.4	7.2	61.0	0.9	7.2	—
10[f)]		450	9.9	31.6	3.6	0.8	—	16.4	19.5	27.0	5.2	9.8	—
11	no melts[j)]	350	8.9	53.8	3.8	2.3	t	1.9	7.4	75.9	1.1	7.6	—
12[f)]		450	8.0	46.8	13.0	1.4	3.5	10.4	12.6	41.9	2.3	6.4	1.0

a) Duration of reaction; 1 hr, Starting material; 0.1 mol/hr, $C_6H_{11}CH_3: Cl_2: N_2=1:1:2$ (mole ratio). See Fig. 4 for structures of the products. b) Recv. Liq. implies the recovered liquid products including the reactant. c) $\text{Conv. (\%)}=\dfrac{\text{Recv. Liq.}-\text{Recovered methylcyclohexane}}{\text{Recv. Liq.}}\times 100$. d) Low boiling hydrocarbon. e) A large amount of polymeric products was obtained. The polymer obtained by means of the reprecipitation in methanol of their benzene solution was analyzed to give molecular weight (by Mechrolab Osmometer Model 301) 1040—1100 and C, 79.56; H, 6.45% ($C_{1.04}H_1$). f) The %yield of XIV was as follows. 11.6% (Exp. No. 8), 6.5% (No. 9), 16.7% (No. 10), and 7.5% (No. 12). The formation of dichloromethylcyclohexane was estimated by mass spectral studies of the fraction obtained by the preparative gas chromatography. g) $AlCl:KCl:NaCl=3:1:1$ (mole ratio). h) $CuCl_2:KCl:NaCl=3:1:1$ (mole ratio). i) In this experiment chlorine was not supplied because $CuCl_2$ acts as chlorinating reagent. j) At 250 °C, no reaction.

132, M^+, 83, M^+-CH_2Cl) and because its retention times were identical with those of the authentic compound.

Reaction of Methylcyclohexane with Chlorine in Molten Salts. The distribution of chlorination products for I is summarized in Table 1, together with the reaction conditions. With both the $ZnCl_2$ melt and the CuCl melt,[15] the conversions at 250 °C were low, but higher conversions were attained at both 350 and 450 °C. In the melt of $AlCl_3$, it was found difficult to carry out chlorination above 300 °C because of the sublimation of $AlCl_3$. A marked difference in the product distribution can be seen between a catalytic reaction in molten salts and a non-catalytic thermal reaction. In the catalytic reaction, the yield of olefin derivatives including toluene shows a high value, while the formation of these is small in the thermal reaction.

The values of f_0 (representing the sum of olefin yields) and f'_0 (f_0+toluene yields) are plotted against the reaction temperatures in Fig. 3.

In the case of the $AlCl_3$ melt, a high % yield of olefin in the recovered liquid products was observed. The small amount of recovered liquid products containing the reactant is due to the formation of a considerable amount of intractable polymeric products remaining on the surface of molten salt in the reactor.

Both the $CuCl_2$ melt and the CuCl melt showed nearly the same olefin yields, whereas, with the $CuCl_2$ melt, a higher yield of dichloro compounds was observed; this fits the finding by Kunugi[16] that the chlorine addition to olefin was predominant with the $CuCl_2$ melt. Figure 3 also indicates that the relative activities for olefin formation are $ZnCl_2$ melt>CuCl melt. It is interesting to note that toluene formation was accompanied by no olefin derivatives in the $ZnCl_2$ melt at 250 °C.

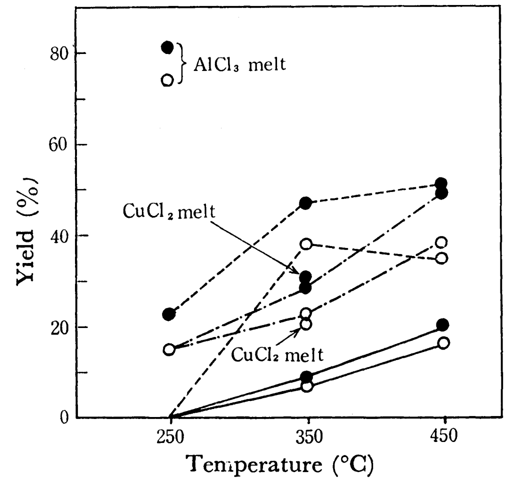


Fig. 3. Olefin yields (f_0 and f'_0) obtained from chlorination of methylcyclohexane in various fused salts at different temperatures.
—○—; f_0, —●—: f_0', ——: non catalytic reaction, ------: $ZnCl_2$ melt. -·-·-: CuCl melt.

As is shown in Table 1, the formation of VI was favored over that of VII, VIII, and IX in the melt of $ZnCl_2$ at both 350 and 450 °C, while the reverse was true with the CuCl melt. These observations will be discussed later.

Reaction of Methyl-Chlorocyclohexanes in Molten Salts. The results of the reaction are shown in Table 2. Three methyl-chlorocyclohexane isomers showed nearly

TABLE 2. DEHYDROCHLORINATION OF 1-CHLORO-, 3-CHLORO-, AND 4-CHLORO-METHYLCYCLOHEXANE

A) 1-CHLORO-METHYLCYCLOHEXANE[a]

Exp. No.	Melts	Temp. (°C)	Recv. Liq. (g)	Conv. (%)	% Yield					f[c]
					II[b]	III	XIII	VI	VII—IX	
13	$ZnCl_2$+KCl +NaCl	250	1.9	84.4	6.3	75.4	1.8	15.6	0.6	0.08
14		350	2.0	99.4	10.1	89.3	t	0.6	—	0.1
15		450	2.0	98.8	9.3	89.5	t	1.2	—	0.1
16	CuCl+KCl +NaCl	250	2.1	46.5	0.5	42.1	3.9	53.5	—	0.01
17		350	2.1	53.4	1.0	50.3	2.1	46.6	—	0.02
18		450	2.0	52.3	1.3	46.2	4.8	47.7	—	0.03

a) Duration of reaction; 20 min, 1-Chloro-methylcyclohexane; 3.0 g, Gas N_2; 0.1 mol/hr, Depth of melts; 5 cm.
b) NMR spectra of products (Exp. No. 14) in CCl_4 showed the presence of III (=CH 4.7 ppm, lit,[17] 4.72 ppm) and II (=CH_2 5.5 ppm, lit,[17] 5.45 ppm). c) f=II/III.

B) 3-CHLORO-METHYLCYCLOHEXANE[a]

Exp. No.	Melts	Temp. (°C)	Recv. Liq. (g)	Conv. (%)	% Yield				Others	f_{iso}[b]
					IV and/ or V	III	VI	VII—IX		
19	$ZnCl_2$+KCl +NaC	250	1.8	89.1	47.9	22.7	17.1	10.9	1.4	0.7
20		350	1.9	100	53.0	44.6	1.6	t	1.0	0.8
21		450	1.7	100	64.3	33.6	1.0	—	1.1	0.5
22	CuCl+KCl +NaCl	250	2.1	8.9	4.4	3.2	0.3	92.1	—	0.03
23		350	2.2	31.3	23.0	6.5	1.0	69.5	—	0.08
24		450	2.0	78.8	60.9	7.9	7.7	22.1	2.3[c]	0.2

a) Duration of reaction; 18 min, 3-Chloro-methylcyclohexane; 2.0 g, Flow rate of N_2; 0.1 mol/hr, Depth of melts; 5.0 cm. b) f_{iso}=(III+VI)/(IV+V+VIII) c) All toluene, in this case.

C) 4-CHLORO-METHYLCYCLOHEXANE$^{a)}$

Exp. No.	Melts	Temp. (°C)	Recv. Liq. (g)	Conv. (%)	% Yield					Others$^{b)}$	$f_{iso}$$^{c)}$
					IV and/or V	III	XIII	VI	VII—IX		
25	$ZnCl_2$+KCl +NaCl	250	1.5	72.5	23.8	29.3	2.0	12.9	27.5	2.4	0.9
26		350	1.3	93.5	55.3	33.9	1.0	6.5	1.6	1.7	0.7
27		450	1.3	100	75.4	25.3	1.2	t	t	1.1	0.3
28	CuCl+KCl +NaCl	250	1.8	5.9	3.1	1.1	0.7	t	95.1	t	0.01
29		350	1.7	16.8	12.9	2.5	1.4	t	83.2	t	0.09
30		450	1.5	66.2	54.8	1.3	3.0	7.1	33.8	—	0.09

a) Reaction condition was the same as described in B). b) Low boiling compounds containing cyclohexane.
c) f_{iso}=(III+VI)/(V+IX).

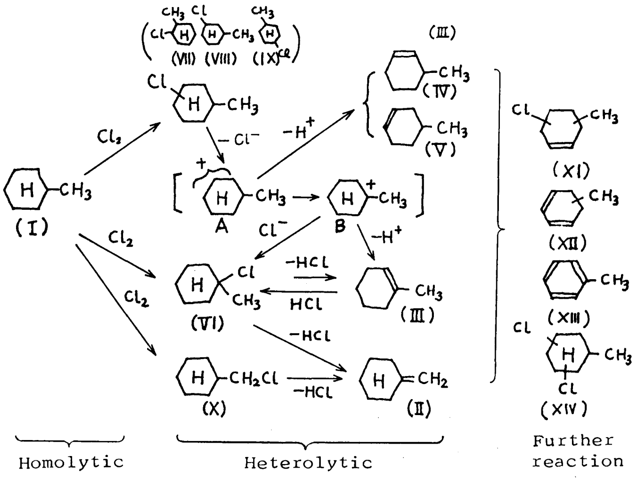
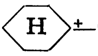


Fig. 4. Reaction scheme.

a 100% conversion at 350 and 450 °C in the $ZnCl_2$ melts, while they indicated a lower conversion in the CuCl melt. The catalytic activity difference between these melts is particularly pronounced at 250 °C with VIII and IX as reactants.[18] In the reaction of VI, the primary elimination products were confirmed to be methylene-cyclohexane (II) and 1-methylcyclohexene (III) [see Footnote b) in Table 2A)]. The ratio of II/III, which represents the preference between the "Hofmann" and "Saytzeff" orientations, was 0.1 in the melt of $ZnCl_2$, but 0.01—0.03 in the melt of CuCl. The higher ratio of the $ZnCl_2$ melt compared with that of the CuCl melt may be explained as follows. Since the $ZnCl_2$ melt is known to have a more molecular character[19] than the CuCl melt, the presence of the ( $\overset{+}{-}CH_3$ $ZnCl_3^-$) complex is seemingly possible in the melt of $ZnCl_2$, where $ZnCl_3^-$ (base) may be well situated to abstract more acidic CH_3 protons, thus leading to the formation of the thermally-unstable olefin II in the higher ratio of II/III compared with the case of the CuCl melt,[21] though 1-methylcyclohexene remains as the primary product.

In the reaction of VIII and IX, considerable amounts of VI and III were formed, together with direct dehydrochlorination products (particularly in the melt of $ZnCl_2$). Table 4 indicates that the direct dehydrochlorination products of VIII and IX, *i.e.*, IV and V, hardly isomerize even in the presence of HCl to III, which is expected to react with HCl to give VI. Therefore, these findings can be explained in terms of rearrangements of the secondary carbonium ion[22] produced by chloride-ion abstraction from VIII or IX to the most stable tertiary carbonium ion (see Fig. 4 for the structures of probable intermediates). The value of f_{iso}(=rearranged products/direct dehydrochlorination products) was used here as a measure of the extent of isomerization. The melts of $ZnCl_2$ showed a higher f_{iso} value than that of CuCl; this can also be explained by the molecular character[19] of the $ZnCl_2$ melt.

TABLE 3. DEHYDROCHLORINATION OF METHYL-CHLOROCYCLOHEXANE DERIVATIVES IN THE PRESENCE OF HCl GAS THROUGH FUSED SALTS$^{a)}$

Reactant	Exp.$^{b)}$ No.	Temp. (°C)	Recv. (g)	Conv. (%)	% Yield					f_{iso}
					VI and/or V	III	XIII	VI	VII—IX	
VI	31*	350	1.7	19.5	3.7$^{c)}$	13.6	2.2	80.5	—	0.2
	32	350	1.8	—	—	t	—	100	—	—
VIII	33*	350	1.8	95.2	43.4	3.8	5.4	42.6	4.8	1.0
	34	350	1.7	26.2	18.5	—	1.8	5.9	3.8	0.06
IX	35*	350	1.9	95.2	48.6	2.3	7.1	37.2	4.8	0.7
	36	350	1.7	19.8	15.5	—	1.7	2.6	80.2	0.03
VIII	37*	450	1.7	92.6	46.2	2.8	6.9	36.6	7.4	0.7
	38	450	1.7	58.4	44.3	t	3.0	11.1	41.6	0.1

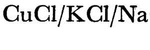
a) Starting material; 2.0 g, Duration of reaction; 17—18 min, Flow rate of N_2; 0.1 mol/hr, HCl:  = 1:0.5 (mole ratio). b) Remark of * indicates use of $ZnCl_2$/KCl/NaCl. Another used a melt of CuCl/KCl/NaCl. c) Methylene cyclohexane in this case.

Table 4. Reaction of methylcyclohexene with HCl gas in the presence of melts[a)]

Reactant	Exp.[b)] No.	Temp. (°C)	Recv. Liq. (g)	Conv. (%)	% Yields						Others
					IV and/ or V	III	XIII	XII	VI	VII—IX	
III	39*	350	1.7	94.2	3.0	5.8	7.0	7.3	75.4	—	1.5
	40	350	1.8	64.5	—	35.5	4.3	7.9	50.8	—	1.5
IV+V	41*	350	1.6	11.1	88.9	1.2	3.3	—	3.6	3.0	—
	42	350	1.7	0.5	99.5	—	—	—	—	—	0.5

a) Starting material; 2.0 g. Duration of reaction; 20 min, Flow rate of HCl; 0.1 mol/hr, HCl: olefin = 1:0.7, Depth of salts; 5.0 cm. b) Remarks are the same as described in Table 3.

Reaction of Methyl-Chlorocyclohexane and Methylcyclohexene with HCl in Molten Salts. In the reaction of methylcyclohexane with chlorine in molten salts, chlorine substitution and the subsequent elimination of HCl occurred; both reactions produced corresponding amount of HCl, whose effects on the reaction in molten salts should be noted. Therefore, the following experiments in the presence of added HCl were carried out; the results are listed in Tables 3 and 4. As is shown in Table 3, the reaction of VI shows a substantial recovery of the reactant in the presence of HCl, even in the $ZnCl_2$ melt, which can be expected to assist the dehydrochlorination reaction. This indicates that the olefins formed readily reacted with HCl to give the starting material. This is also confirmed by the experimental results cited in Table 4. That is, the addition of HCl to III took place preferentially with $ZnCl_2$ melts.

However, with VIII and IX as the reactants, a large amount of VI was obtained, along with direct dehydrochlorination products (IV and V), especially in the melt of $ZnCl_2$. In the $ZnCl_2$ melt, the reaction of VIII and IX afforded VI in a yield of about 40%, while the yield of VI reached only a small percentage in the CuCl melt. The preferred formation of these rearranged products with the $ZnCl_2$ melt may be considered to be due to the rearrangement of the Intermediate A to the Intermediate B (in Fig. 4), which is favored in the molecular $ZnCl_2$ melt.

Accordingly, the finding that, in the chlorination of I in molten salts, VI was a main product in the $ZnCl_2$ melt, while a mixture of VII, VIII, and IX was the primary product in the CuCl melt, could be explained by such experimental results. That is, in the $ZnCl_2$ melt, which favors carbonium-ion formation, most of the products, VII—IX, formed by the chlorination of I are converted to III *via* the carbonium-ion mechanism; they then reacts extensively with HCl to afford VI. On the other hand, these rearrangements were not assisted to such an extent by the CuCl melt. In addition, the reaction of IV and V with HCl in the $ZnCl_2$ melt gave slight addition products (3% yield), while the addition of HCl to III took place extensively with the $ZnCl_2$ melt. This is explained by the known stabilities of the carbonium ions (formed by the addition of protons to olefins), which are tertiary (from III)> secondary (from IV—V).

Reaction Process of Methylcyclohexane with Chlorine in the Presence of Molten Salts. In a previous paper[2,4)](the chlorination of cyclohexane in molten salts), the chlorination (substitution reaction) was assumed to proceed by means of a homolytic mechanism, and the subsequent elimination, by means of a heterolytic mechanism. The experimental evidence in favor of this assumption is the observation that the overall reaction was remarkably retarded by the addition of a radical inhibitor (cyclohexene), but the product distribution showed much the same distribution as that in the absence of cyclohexene. Similar observations were made in the reaction of I with chlorine in molten salts; therefore, in these studies, we also considered chlorination to follow a homolytic mechanism and the subsequent elimination and isomerization to follow a heterolytic mechanism.

The most important results obtained here (especially at 350 and 450 °C) may be summarized as follows: 1) The chlorination of I in both the $ZnCl_2$ melt and the CuCl melt affords mono-chlorinated products, VI—IX, along with olefin products, III—V. 2) The reactions of VIII and IX in both melts also give dehydrochlorination products (IV and V), along with III. The relative activities for dehydrochlorination are $ZnCl_2$ melt>CuCl melt. 3) The addition of HCl to III (to form VI) occurs more extensively in the $ZnCl_2$ melt than in the CuCl melt. The addition of HCl to IV and V hardly occurs over either melt. 4) The $ZnCl_2$ melt assists the abstraction of a chloride ion from the organic molecule to a greater extent than the CuCl melt; *i.e.*, the $ZnCl_2$ melt favors carbonium-ion formation from chloro compounds. 5) III and VI are formed from VIII—IX, especially in the $ZnCl_2$ melt, *via* a carbonium-ion mechanism involving the rearrangement of Intermediate A (from VIII—IX) to Intermediate B and the subsequent substitution by chloride ions or the removal of the protons. These results lead us to the reaction scheme shown in Fig. 4, where the inferred intermediates are also given.

References

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11) The reactant was supplied to the gas inlet tube through capillary of the resevoir and instantly evaporated. The contact time of a bubble of flow gas with the melt may be estimated less than 1 s.

12) Hereafter denoted $ZnCl_2$ melt. CuCl melt also denoted CuCl/KCl/NaCl (3: 1: 1 mole ratio) eutectic.

13) American Petroleum Institute Res. Project. 44, "Catalog of Mass Spectra Data," Carnegie Institute of Technology, Pittsburgh Pa. No. 1174 (1955) and No. 1491 (1958).

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15) The alkali metals serve to form eutectic solutions with the active constituents and thus lower the melting point, and reduce the vapor pressure.

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18) A possible explanation for this is as follows. As the thermal contribution becomes more significant in the elimination reaction in CuCl melt (owing to its low catalytic activity), the reaction is reluctant to proceed at such a low temperature as 250 °C even in the presence of CuCl melt, whereas the reaction shows a considerable high conversion in the presence of $ZnCl_2$ melt due to its strong catalytic activity. This probably caused the considerable difference between both conversions, being also affected by the fact that lower reactive secondary chloride (VII, VIII, and IX) may be more sensible to the change of reaction condition than the reactive tertiary chloride (VI).

19) N. E. Norman[20)] divided inorganic salts roughly into two groups, molecular melts and ionic melts. This simple classification may be considered useful in analyzing the catalytic activities of different molten salts.

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21) In the melt of CuCl, both the cuprous and chloride ion believed to exist, as well as undissociated cuprous chloride.

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