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# Reactions of Alkyl Halides in Fused Salt Media<sup>1</sup>

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Passage of C<sub>1</sub> to C<sub>5</sub> haloalkanes through SnCl<sub>2</sub>-KCl melts results in halide exchange reactions, alkene formation, and rearrangement (including cyclization) reactions of the organic molecules. Relative reactivities, product distributions and melt composition effects are consistent with a carbonium ion mechanism in which the melt functions as a halide ion acceptor. Some control of product distribution by choice of Lewis acid character of the melt seems possible.

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While the physical properties of fused salts have been the subject of extensive investigations, reaction chemistry in such media has been studied much less systematically. However, a variety of reactions have been reported, including a number involving substitution, elimination, and other reactions of organic molecules; many of the known examples have been reviewed by Sundermeyer (1). These include halide and pseudohalide exchange, halogenation, and elimination reactions. For the most part they involve small aliphatic or aromatic systems. While some work has involved simple ionic salts such as the alkali halides, most reactions of this type have used low melting systems composed of salts employed as catalysts in more classical reactions, e.g. AlCl<sub>3</sub>alkali chloride melts and similar systems below 200 °C. These have established the catalytic action of such melts, although the behavior of the molten salt in other systems is not so evident. Generally, little has been done to establish the role of the molten salt in the overall mechanism, or the effect of varying reaction parameters (temperature, melt composition, etc.).

This report considers the reactions of several alkyl halides ( $C_1$  to  $C_5$ ) in molten KCl–SnCl<sub>2</sub> mixtures. Substitution, elimination, and rearrangement reactions were observed, and some

beginnings can be made to understand the basic mechanism of the reactions.

#### Experimental

The reaction system consisted of a vertical cylindrical tube 30 mm in diameter with a fritted Pyrex disc (normally fine porosity) some distance from the lower end. This was enclosed in a cylindrical furnace and the temperature maintained at the desired value by means of an electronic controller. Fisher SnCl<sub>2</sub>.2H<sub>2</sub>O was dehydrated with acetic anhydride (2), mixed with dry Baker Analyzed KCl, and placed above the frit in the reaction tube. Final purification was effected by passing HCl gas through the salt as the temperature was raised to the desired value. This was followed by a lengthy flush with dry  $N_2$ . The organic reactant was added to a flask attached to the lower end of the reaction system, and distilled through the melt aided by a slightly reduced pressure at the exit side. When a constant flow rate had been attained, samples were collected at the exit in liquid nitrogen traps and analyzed by gas chromatography. Care was taken to preheat the reactant vapors to the melt temperature, and to heat the exist system before the traps to prevent product condensation. Proton magnetic resonance and infrared spectroscopy were used when necessary to aid in product identification.

In comparing results, a number of factors must be considered. The melt height was fixed by weight of salt and tube diameter, and was 4.4 cm for the results reported here. The average size of the bubbles passing through the melt was reasonably reproducible for a frit of given porosity, but varied with flow rate. Photographs permitted the average bubble diameter to be estimated as a function of flow rate, and from this and the flow rate the number of collisions of a gas molecule with the melt could be estimated. This was greater at low flow rates, but was of the order of  $10^4$ . It varied somewhat with the reactants, as did the height of froth above the melt during a reaction

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Reactant	Flow rate $\times 10^2$ (mM s <sup>-1</sup> )	Product yield (%)			
		1-Chloroalkane	2-Chloroalkane	Alkene	Overall
Bromoethane	2 6	32 20		$\sim^4_{\sim 2}$	36 22
1-Bromopropane	2 7	17 7	$\sim^2_{-1}$	10 5	29 13
1-Chloropropane	2		<1	6	<7
1-Iodopropane	2 7	27 15	$\sim^3_{\sim 3}$	23 13	53 31
2-Bromopropane	2 10		68 50	30 25	98 75
2-Chloropropane	2	_	_	22	22
1-Bromobutane	2 7	15 6	~2 < 2	10 5	27 <13
1-Chlorobutane	2	_	< 1	6	<7
1-Iodobutane	2 5	15 12	~4~1	12 8*	31 21
2-Bromobutane	2 8		40 50	55 40	95 90
2-Chlorobutane	2			35	35
1-Bromopentane	2	7	<1	6†	< 14

TABLE 1. Reaction products of haloalkanes in 62 mole % SnCl<sub>2</sub>-KCl at 280 °C

\*1-Butene with small amount of 2-butene. †5% 1-pentene; 1% 2-pentene.

in which a significant amount of the overall process could occur. Therefore, the significance of the following data lies in the relative values and trends rather than in the absolute yield values. While a few reactions approached 100% under these conditions, in general we attempted to operate so as to have only partial reaction so that effects could be detected. Results by no means imply the maximum yield of any product. While a few compounds showed gross decomposition in the melt as evidenced by charring, most recoveries were close to 100%.

The data given in the accompanying Figures and Tables are averaged; variation of the moderate or high yields of  $\pm 5\%$  from the results given are typical for runs made under apparently identical conditions. This reflects primarily variation in bubble size. Certain systems showing apparent surface activity of the reactant as indicated by considerable frothing are more erratic.

### **Results and Discussion**

As discussed above, contact times and hence the extent of reaction depend upon flow rate, such that reactivities usually increase with decreasing flow rate. There are occasional exceptions to this, when the yield of one product decreases as a consequence of competition from another; overall reactivities invariably increase as expected. An indication of the magnitude of the flow rate effect is included in the following tables of data.

TABLE 2. Product yields of bromomethanes in 62 mole % SnCl<sub>2</sub>-KCl, at 280 °C; flow rate,  $2 \times 10^{-2}$  mM s<sup>-1</sup>

Reactant	Products			
CHBr <sub>3</sub>	CHBr <sub>2</sub> Cl 5%	CHBrCl <sub>2</sub> 17%	CHCl <sub>3</sub> 50%	Overall 72 %
CH <sub>2</sub> Br <sub>2</sub>	CH₂BrCl 10%	CH <sub>2</sub> Cl <sub>2</sub> 70%	_	80%
CH₂BrCl	CH <sub>2</sub> Cl <sub>2</sub> 72%			

#### Substitution and Reactivity Patterns

The relative reactivities of the various compounds studied can be observed from Tables 1-3. Studies on benzyl and allyl bromides were not fully successful due to considerable decomposition and quantitative data are not given, but results indicated the reactivity in the 62 mole %  $SnCl_2-KCl$  eutectic to be benzyl > allyl > alkyl > aryl (bromobenzene gave essentially no reaction). Within the bromobutanes, the reaction order is tertiary > secondary > iso > primary. These reaction patterns are generally observed with carbonium ion or  $S_N$ 1 mechanisms (3, 4). The formation of 1-chloroalkanes from the bromo compounds is in the order ethyl > propyl >

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	Products				
Reactant	2-Chloro- 2-methylpropane	1-Chloro- 2-methylpropane	2-Methylpropene	Methyl- cyclopropane	Overall
1-Bromo-2-methylpropane 1-Chloro-2-methylpropane 2-Chloro-2-methylpropane	22 % 7 %	3% <1%	10 % 10 % 30 %	5% <1% <1%	40 % 17 % 30 %

TABLE 3. Product yields from halo-methylpropanes; 62 mole % SnCl<sub>2</sub>-KCl, at 280 °C; flow rate,  $2 \times 10^{-2}$  mM s<sup>-1</sup>

butyl > pentyl. This is similar to the order of reactivity in the substitution of thiocyanate and cyanate for chloride in methyl, ethyl, and 1-propyl chloride using melts reported by Packham and Rackley (5), although this may be a very different situation as is indicated by the level of reactivity of benzyl bromide. At a flow rate of  $2 \times 10^{-2}$  mM/s, the ratios of chloride compound formation are 1.9 : 1.1 : 1.0 : 0.5 for bromoethane, 1-bromopropane, 1-bromobutane, and 1-bromopentane, respectively. As a comparison to reactions in more classical media, solvolysis rates in dioxane at 40 °C for the same compounds (6) are in the rather similar ratios 2.2 : 1.2 : 1.0 : 0.9.

The overall reactions of the halopropanes and -butanes follow the order I > Br > Cl. In both the propanes and butanes, product ratios for the substitution, elimination, and rearrangement products were similar for the bromo- and iodo compounds of each series, implying the possibility of a common intermediate. Considerably less rearranged product is formed from the 1-chloro compounds here than in the 1-bromo or 1-iodo systems. This may be explained, since both 2-chlorobutane and 2-chloropropane are more reactive than the 1-chloro compounds, resulting in their being reacted as formed from the latter. As they are less reactive than the parent bromides and iodides, however, they form in proportionately greater yields in these cases.

The completely chlorinated methanes are seen to be the predominant products from the reactions of di- and tri-bromomethane at all flow rates studied (Table 2). The order of reactivity of the individual compounds is  $CHBrCl_2 >$  $CHBr_2Cl > CHBr_3$ . In addition, bromochloromethane is somewhat more reactive than dibromomethane, although an apparent surface active behavior of the latter in the melt makes comparison difficult. Hine and co-workers found that the intermediates of a number of  $S_N$ 1 solvolysis reactions of halomethanes were stabilized more by chloride than bromide substituents, and thus the reactions were enhanced as observed here (3, 7, 8). All of the above reaction patterns are consistent with a carbonium ion intermediate in the melt or at the melt-vapor interface.

### **Rearrangement Products**

Most primary halides considered here gave some rearranged products (Tables 1 and 3); indeed, 1-bromo-2-methylpropane gave 5–10 times as much rearrangement product, 2-chloro-2-methylpropane, as the expected 1-chloro compound. Rearrangement of secondary halides to primary was slight. Such observations may be explained by the known stabilities of carbonium ions, which are tertiary > secondary > primary. This is indicated both from kinetic data and mass spectrometric formation energies (9). Hence, there would be a net loss in energy for a rearrangement such as

### $CH_3CH_2CH_2^+ \rightarrow (CH_3)_2CH^+$

This would be even greater in the 1-bromo-2methylpropane example. Thus, the observed rearrangements would not be surprising if the cation has a sufficient life-time in the melt.

#### Melt Effects

Variation of melt composition has an appreciable effect on reaction as shown in Table 4, particularly when melts rich in  $SnCl_2$  are used. This is understandable on the basis of Lewis acid behavior of the  $SnCl_2$ , and may be comparable to the behavior of silver and mercuric halides which are used to favor carbonium ion formation in solvolysis reactions of alkyl halides (3, 8). Pure stannous chloride appears readily to accept a halide ion; the pure melt has been shown to be slightly polymeric through chloride bridges (10) and on addition of KCl this structure may be broken down through formation of  $SnCl_3^-$  or  $SnCl_4^{2-}$  ions in the melt. Conceivably, the melt functions by abstracting a chloride (or bromide)

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#### Yield (%) Mole % SnCl<sub>2</sub> 1-Chloropropane Propene Reactant 2-Chloropropane 100 ca. 1 68 70 80 ca. 1 62 50 50 46 Undetected Undetected Yield (%) Mole% SnCl2 1-Chloropropane 2-Chloropropane Reactant Propene 15 15 15 1-Bromopropane 100 31 9 7 4 28 16 80 62

TABLE 4. Yield as a function of melt composition,  $SnCl_2$ -KCl melts, at 295 °C; flow rate,  $1 \times 10^{-2}$  mM s<sup>-1</sup>

TABLE 5. Reaction of halopropanes as a function of temperature, 62 mole % SnCl<sub>2</sub>-KCl; flow rate,  $2\,\times\,10^{-2}\,mM\,s^{-1}$ 

Reactant	Temperature (°C)	Yield (%)		
		1-Chloropropane	2-Chloropropane	Propene
1-Chloropropane	280 295 315		<1 <1 1	6 7 17
1-Bromopropane	280 295 317	17 15 22	$\sim^2_{\sim 3}_{\sim 4}$	10 12 20

ion from the organic molecule to produce the complex anion and a carbonium cation. The tendency for this to happen is reduced as the  $SnCl_2$  is satisfied by free  $Cl^-$  from the KCl, although it is not markedly effected until appreciable KCl has been added. It may be noted that products not detected in 62 mole%  $SnCl_2$  may appear with higher  $SnCl_2$  concentration, also implying that the carbonium ion has a longer lifetime for reaction in the latter media.

Data in Table 5 show that increasing temperature results in increased reaction. However, changes in melt properties with temperature (e.g. viscosity) and their resulting influence on contact times may be equally significant. At temperatures above 330 °C yields decreased, probably because of the change in flow properties of the melt.

#### Elimination Reactions

Most systems produced unsaturated products corresponding to loss of hydrogen halide from the original molecule, as shown in Tables 1 and 3. That these results are due to melt reactions and not purely thermal decomposition is shown by Fig. 1, which compares the conversion of 1-



FIG. 1. Comparison of gas phase and molten salt (62 mole % SnCl<sub>2</sub>-KCl; 317 °C) reaction of 1-bromopropane to give propene. *A*, melt reaction; *B*, gas phase reaction.

bromopropane to propene in a gas phase reaction studied by Aguis and Maccoll (11), with our results in the melt. Time refers to the total time in the heated region of our apparatus, which in these experiments was usually much longer than the melt contact time alone. Such results show that the elimination reaction observed in this case is essentially wholly due to reaction with the melt at any reasonable flow rate.

Six chloro-compounds were studied to evaluate the amount of  $\beta$ -elimination of hydrogen in the absence of substitution reactions (Tables 1 and 3). 2-Chloropropane and 2-chlorobutane both give more alkene than the 1-chloro compounds. Also, 2-chlorobutane yields more alkene than does 2-chloro-2-methylpropane, although the overall reactivity of the bromides is in the reverse order. The differences are accountable in terms of the ease of formation of the carbonium ion, since it is well established for  $S_N l$  mechanisms that a secondary carbonium ion is not as stable as a tertiary. Stabilization of the secondary may require a greater shift of electron density from the  $\beta$ -hydrogens, and the stability may then be dependent on the number of such hydrogens available; for example, nine on 2-chloro-2methylpropane, but five with 2-chlorobutane. If the electron delocalization is greater per hydrogen in the latter, these hydrogens become more acidic and hence more readily available to the bases in the solvent; *i.e.*  $Cl^-$ ,  $SnCl_3^-$  or  $SnCl_4^{2-}$ .

It is also noted that 1- and 2-butene are formed more readily than propene while ethylene is the most difficult to obtain. This reflects the known values of heats of formation in the series ethylene < propene  $\sim$  1-butene < 2-butene, which has been discussed in equivalent terms by Hughes, Ingold, and Shiner (12). While elimination reactions seem to be understandable on the basis of carbonium ion formation, more data would be required to elucidate all of the details of the reactivities observed.

# **Reaction Mechanism**

We have accounted for the various observations above by means of carbonium ion formation in the melt, or at the melt-vapor interface. Free radical formation should also be considered, particularly in view of the elevated temperatures. Other molten salt reactions in the literature, such as the formation of ethane from methanol and dimethylether (13), may arise through some type of free radical mechanism. A number of compounds investigated in this study, notably  $\alpha$ -bromotoluene, tetrabromomethane, and tribromomethane, gave considerable carbonaceous decomposition material in the melt, and produced Sn(IV) compounds which volatilized and were collected with the products. (Sn(IV) was not produced in detectable amounts in the other reactions.) These examples may be cases where homolytic dissociation is a competitive or even favored mode of reaction, but the majority of the reactions reported here are better described by the ionic mechanism.

The following reaction scheme shows the various steps which we believe take place in the reaction of 1-bromopropane



The steps should be reversible but the small bromide ion concentration in the melt ensures that bromide readdition will not be observed. This mechanism implies that 1-chloropropane should be formed from the 2-chloropropane produced, although this may be in small amount since the latter is energetically favored. It is interesting that while this was not seen in the 62% SnCl<sub>2</sub>-KCl melts it could be observed in

pure SnCl<sub>2</sub>, where the difficulty in removing the chloride from the melt may produce a longer lived cation with more chance for rearrangement.

A similar mechanism is shown below for the reaction of 1-bromo-2-methylpropane. The formation of methylcyclopropane is interesting. Previous preparations from isobutyl compounds have generally been regarded to involve carbanion intermediates (14–16). CANADIAN JOURNAL OF CHEMISTRY. VOL. 49, 1971



Removal of a proton from  $(CH_3)_2CHCH_2^+$  may involve two possible three-centered transition states, leading to methylcyclopropane or 1-butene with the latter being favored.

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From the discussion above, it is evident that a number of organic exchange, rearrangement, and elimination reactions can be accounted for by a mechanism involving abstraction of a halide ion from the organic molecule by the melt. To some extent at least, product yields can be controlled by suitable choice of melt and reaction time. Total reaction yields may be high; for most of the reactions discussed here essentially complete utilization of reactant could be achieved by increasing the melt-vapor contact time or introducing more efficient mixing. Yields were reasonably proportional to depth of melt.

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