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DECOMPOSITION OF ALIPHATIC SULFIDES IN MOLTEN SALT MEDIA

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The decomposition reaction of aliphatic sulfides was carried out in molten salt media employing a flow system. $ZnCl_2$-LiCl, $ZnCl_2$-KCl (or $ZnCl_2$-KCl-NaCl), and $ZnCl_2$-$SnCl_2$ eutectics showed strong activity in decomposition of the sulfide with the predominant formation of olefin corresponding to the alkyl group of the sulfide and the fixation of sulfur as ZnS in the molten salts.

Although some work has been reported on the catalytic cracking of sulfides over solid acids$^{1,2)}$, the decomposition reaction of sulfides in molten salts has not yet been reported. The present paper deals with the decomposition of a series of aliphatic sulfides in molten salts(binary eutectics $ZnCl_2$-KCl, $ZnCl_2$-LiCl, $ZnCl_2$-$SnCl_2$ and $SnCl_2$-KCl and ternary eutectics $ZnCl_2$-KCl-NaCl and CuCl-KCl-NaCl).

The reaction was carried out using apparatus similar to that described in a previous paper$^{3)}$ except that the reactant was supplied to the vaporizer by means of microfeeder(feed rate; 7.2 ml/hr). The molten salts in the reactor were dried for 1 hr by bubbling dry N_2 prior to use. Argon was employed as both diluent gas and internal standard gas for determination of the gaseous products by gas chromatographic analysis.

The activities of the above mentioned molten eutectics and the distribution of the products are listed in Table 1. Conv.(%) shows the mole % of the decomposed sulfides calculated from the normalization of carbon numbers of the resulting gaseous products. Accordingly the material balance of each run with respect to carbon numbers of starting reactants is presented as the sum of % conv. and % recovery of sulfide. The comparison of % conv. of each run shows that the activity order of molten eutectics for the decomposition of sulfide is $ZnCl_2$-KCl-NaCl melts $>$ $SnCl_2$-KCl melts $\geq$ CuCl-KCl-NaCl melts. In this decomposition, the corresponding thiol was not found in the recovered liquid. One characteristic of the gaseous products is the ratio of olefin to paraffin of the hydrocarbon corresponding to the alkyl group of the sulfide. This olefin to paraffin ratio was high in $ZnCl_2$-KCl-NaCl and $SnCl_2$-KCl melts, and decreased in the order $ZnCl_2$-KCl-NaCl melts $>$ $SnCl_2$-KCl melts $>$ CuCl-KCl-NaCl melts. The reactivity of the sulfides followed the order: iso-Pr_2S $>$ n-Bu_2S $>$ n-Pr_2S. Isopropyl sulfide showed a markedly larger value of % conv. than the n-alkyl sulfides. As described in the footnote to Table 1, the sulfur atom of the decomposed sulfide was mostly fixed as ZnS in the case of $ZnCl_2$-KCl-NaCl melts$^{4)}$.

Since the distribution of the butene isomers obtained from the decomposition of n-Bu_2S was expected to give some information about the reaction mechanism, the

Table 1. Decomposition of some aliphatic sulfides in some molten eutectics(400°C)

Run No	Melt a)	Reactant Sulfide	Conv.(%) of Sulfide	Recv.(%) b) of Sulfide	Gaseous products(mole %)							
					H_2	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10} iso-	C_4H_{10} n-	C_4H_8
1	3 $ZnCl_2$ + 1 KCl + 1 NaCl	n-Pr_2S	7.0	86.0	6.7	0.3	1.7	2.5	10.2	-	-	-
2 c)		iso-Pr_2S	32.7	62.3	4.5	0.1	1.9	2.2	60.9	-	-	-
3		n-Bu_2S	9.1	82.4	5.9	3.7	3.9	0.7	3.7	1.1	1.3	8.7
4 d)		n-Pr_2S	5.6	89.1	4.5	0.1	0.2	0.7	10.2	-	-	-
5 d,e)		iso-Pr_2S	13.5	79.9	2.8	t	1.2	2.3	25.9	-	-	-
6 d)		n-Bu_2S	6.3	83.0	2.1	0.2	0.4	t	2.1	1.1	0.6	8.9
7	3 $SnCl_2$ + 2 KCl	n-Pr_2S	6.5	92.8	0.5	0.2	2.4	3.6	7.7	-	-	-
8		iso-Pr_2S	9.8	84.3	0.7	t	0.3	3.9	15.5	-	-	-
9		n-Bu_2S	6.2	88.1	0.2	4.7	4.4	0.1	1.5	-	1.8	4.8
10	3 CuCl + 1 KCl + 1 NaCl	n-Pr_2S	6.4	86.7	-	0.6	2.3	6.1	4.8	-	-	-
11		iso-Pr_2S	8.7	86.0	-	t	1.2	4.2	13.0	-	-	-
12		n-Bu_2S	6.4	84.9	-	5.4	5.6	0.2	0.9	-	3.0	3.5
13 f)	1 KNO_3 + 1 $NaNO_3$	n-Pr_2S	3.5	89.8	-	0.4	2.4	2.6	2.6	-	-	-
14 f)		iso-Pr_2S	4.5	89.4	-	t	0.2	3.1	5.7	-	-	-
15 f)		n-Bu_2S	3.1	87.8	-	3.0	3.7	t	0.5	-	0.7	1.6

a) Figures show the number of moles of each component. The gas inlet tube was immersed 8 cm in the melts.

b) % Recovery= [recovered reactant(g)/starting reactant(g)]×100

c) An aqueous solution of the resultant melt was heated with 1N HCl and yielded 30.2 mole % of H_2S. Since the % conv. of sulfide was 32.7 mole %, this indicated that the sulfur of the decomposed sulfide was fixed preferentially as ZnS in the melts. H_2S content in gaseous products was 1.2 mole %, and HCl was 11.4 mole %.

d) Reaction temperature; 300°C.

e) Treatment of the resultant melt as described in footnote c) gave the following results: ZnS, 11.7 mole %; H_2S , 0.7 mole %; HCl, trace.

f) The reaction of sulfide at 300°C was also attempted but no decomposition occurred.

analysis of these isomers was undertaken using a gas chromatograph with a 4.5 m column of BMEE at 0°C. Table 2 indicates the distribution of butene isomers obtained from n-Bu_2S(see Table 1).

With $ZnCl_2$-KCl-NaCl melts, about half of the butene produced was 2-butene, whereas formation of 2-butene was not observed with CuCl-KCl-NaCl melts and KNO_3-$NaNO_3$ melts. $SnCl_2$-KCl melts showed an intermediate value of 2-butene. This suggests that the decomposition of sulfide through $ZnCl_2$-KCl-NaCl melts and $SnCl_2$-KCl melts proceeds mainly via a carbonium ion mechanism.

Table 2. Distribution of three isomers of butene from the reaction of n-Bu_2S

Melt	$ZnCl_2$-KCl-NaCl (3 : 1 : 1)		$SnCl_2$-KCl (1.5 : 1)	CuCl-KCl-NaCl (3 : 1 ; 1)	KNO_3-$NaNO_3$ (1 : 1)
Temperature(°C)	300	400	400	400	400
1-Butene (%)	50.3	55.1	74.4	100	100
trans-2-Butene (%)	26.8	23.4	13.0	-	-
cis-2-Butene (%)	22.9	21.5	12.6	-	-

Table 3. Decomposition of n-Pr_2S (350°C)

$ZnCl_2$-KCl melts Mole % $ZnCl_2$	Conv.(%)	Recov.(%)	$ZnCl_2$-LiCl melts Mole % $ZnCl_2$	Conv.(%)	Recov.(%)
54	2.9	88.7	40	4.4	89.1
60	4.9	85.5	50	12.6	71.1
71	12.2	80.2	60	26.6	-[a]

a) In this case, after 10 min from the start of reaction, a bit of melts gushed out because of increased viscosity of melts so that % recv. of reactants could not be obtained.

As for the structure of $ZnCl_2$-KCl melts, it is well known that the addition of KCl to molten $ZnCl_2$ causes the depolymerization of the network structure of $ZnCl_2$ and the formation of complex ions($ZnCl_3^-$ or $ZnCl_4^{2-}$)$^{6,7)}$, which are considered to show much less activity in decomposition of sulfide than molecular $ZnCl_2$. According to the Raman spectra of $ZnCl_2$-KCl melts, the amount of $ZnCl_2$ species decreases remarkably when the molar ratio of KCl/$ZnCl_2$ approaches unity. So, in order to examine the effect of melt composition on the reactivity of sulfides, the decomposition of n-Pr_2S was performed with some binary melts of different composition(Table 3).

As shown in Table 3, the melts with 71 mole % $ZnCl_2$ showed higher activity (12.2 % conv.) than expected from extrapolation of the two lower points in the plot of % conv. vs. $ZnCl_2$ content. On the other hand, addition of LiCl to $ZnCl_2$ did not decrease % conv. of n-Pr_2S to such an extent as the addition of KCl(or NaCl) did. This is thought due to the lower polarizing strength of LiCl and smaller propensity of LiCl to form complex ions$^{8-10)}$. As for the product distribution, the olefin to paraffin ratio of C_3 hydrocarbon increased with the increase of $ZnCl_2$ contents in both melts.

Using $ZnCl_2$-$SnCl_2$ melts as the reaction media, a relatively higher % conv. was attained as shown in Table 4. This was attributed to the fact that the both components of the melts were Lewis acids which assist the decomposition complementarily.

The finding that % conv. of sulfide increased as the $ZnCl_2$ content was increased strongly suggested that molecular $ZnCl_2$ promotes the decomposition of sulfides through the formation of a complex. This led us to study the addition compounds of $ZnCl_2$ with sulfides. Only in the case of isopropyl sulfide, a white crystalline precipitate successfully$^{11)}$ separated when dry $ZnCl_2$ was dissolved in the sulfide

Table 4. Decomposition of aliphatic sulfides using $ZnCl_2$(44 mole %)-$SnCl_2$ (56 mole %) melts (300°C)

Sulfide	Conv.(%)	Recv.(%)	Gaseous products(mole %)							
			H_2	C_2H_6	C_2H_4	C_3H_8	C_3H_6	iso-C_4H_{10}	n-C_4H_{10}	C_4H_8
n-Pr_2S	26.6	73.4	41.4	0.8	0.8	8.0	16.5	11.9	1.7	7.1
iso-Pr_2S	59.0	38.6	19.8	1.7	1.1	3.8	82.5	12.4	3.3	3.8
n-Bu_2S	27.3	71.9	39.9	1.5	0.7	5.2	7.3	20.4	4.7	19.0

under dry nitrogen atmosphere. Due to its very hygroscopic and sublimating properties, accurate analysis of the complex could not be attained. However, judging from the results of its microanalysis, this addition compound is suggested to have the composition of (iso-$Pr_2S)_3(ZnCl_2)_2$, this structure being also confirmed by the microanalysis of the dibromo and diiodo analogs.

The properties of these complexes (iso-$Pr_2S)_3(ZnX_2)_2$ were as follows. X=Cl, Mp: 83°C, Anal. Calcd for $(C_6H_{14}S)_3(ZnCl_2)_2$; Zn; 20.85 %, Found: Zn; 19.72 %. X=Br, Mp: 102°C, Anal. Calcd for $(C_6H_{14}S)_3(ZnBr_2)_2$: C; 26.85, H; 5.26 %. Found: C; 27.47, H; 5.75 %. X=I, Mp: 92°C, Anal. Calcd for $(C_6H_{14}S)_3(ZnI_2)_2$; C; 21.77, H; 4.75 %, Found: C; 22.94, H; 4.67 %.

Though it remains uncertain whether addition compounds are intermediates in the decomposition of sulfides through $ZnCl_2$ melts, it is reasonable to consider that the present decomposition reaction of sulfides proceeds via a carbonium ion mechanism through the formation of an alkyl sulfide-$ZnCl_2$ complex.

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