Notes

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Thermal decomposition of some metal mercaptides, $M(SC_6Hal_5)$, Hal = F, Cl

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INTRODUCTION

ALTHOUGH many metal mercaptides are thermally unstable and decompose before melting, few studies of their thermal stability have been made. Recently various lead mercaptides derived from aromatic thiols have been reported to decompose at about 300° in nitrogen, forming lead sulfide and the corresponding aromatic sulfide[1]. Various alkyltin mercaptides, $R_2Sn(SR')_2$ decompose at 270° forming hydrocarbons, alkylsulfides, thiols, and tin (IV) sulfide[2]. Mercury, mercury (II) sulfide, and alkyl sulfides were among the photochemical decomposition products of mercury mercaptides[3]. In continuation of a study of the derivatives of pentafluoro- and pentachloro-thiophenols[4, 5], the thermal stability and decomposition products of various metal mercaptides derived from these thiols, $M(SC_6-Hal_s)_x(Hal = F, CI)$, have been examined.

M(SC ₆ Ha	$l_5)_x$	÷			Decomposition
M	Hal	Nature	Product*	Method§	temp (°C)
Li(I)	F 1.5H₂O	Ionic	LiF	TGA	300
Li(I)	Cl 2H ₂ O	Ionic	LiCl H2O	TGA	350
K(I)	Cl	Ionic	KCl	TGA	450-500
Cs(I)	F	Ionic	Not identified [†]	TGA	450-500
Ag(1)	F	Polymeric	Ag ₂ S	ST	350
Ag(1)	Cl	Polymeric	AgCl	ST	350-400
Au(I)	F	Polymeric	Au	ST	350
Au(I)	Cl	Polymeric	Au	ST	350-400
TI(I)	F	Polymeric	Tl ₂ S‡	ST	350
Cu(I)	F	Polymeric	CuS·4Cu ₂ S	ST	300
Ni(II)	F	Polymeric	α-NiS	TGA	385
Ni(II)	Cl	Polymeric	Not identified [†]	ST	350-400
Pd(11)	F	Polymeric	Amorphous	ST	350-400
Pd(II)	Cl	Polymeric	Mainly PdS	ST	350-400
Pt(II)	F	Polymeric	Pt	ST	450
Zn(II)	F	Partially Ionic	ZnF ₂ , trace ZnS	ST	350
Zn(II)	Cl	Polymeric	Not identified [†]	ST	450
Cd(II)	F	Partially Ionic	CdF ₂ , trace CdS	ST	350
Hg(II)	F	Partially Ionic	HgS, cinnabar	ST	300-350
Pb(II)	F	Partially Ionic	PbS	TGA/ST	250-350
Pb(II)	Cl	Polymeric	PbS	TGA	327, 382

Table 1. Thermal decomposition products	Table 1	. Thermal	decomposition	products
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*All products identified by X-ray diffraction.

†The product from $CsSC_6F_5$ was not Cs or CsF, and assumed to be Cs_2S_2 .

 $The products from M(SC_6Cl_5)_2$ (M = Zn, Ni) were not M, MCl₂ or MS.

Product contains unreacted TISC₆F₅.

TGA = thermogravimetric analysis, ST = sealed tube.

1. R. A. Shaw and M. Woods, J. chem. Soc. (A), 1569 (1971).

2. Y. Yamaji, Y. Nakagawa, S. Matsuda, Kogyo Kagaku Zasshi, 73, 2009 (1970).

3. R. J. Kern, J. Am. chem. Soc. 75, 1865 (1953).

4. R. J. Neil and M. E. Peach, J. Fluor. Chem. 1, 257 (1971).

5. C. R. Lucas, M. E. Peach and K. K. Ramaswamy, J. inorg. nucl. Chem. 34, 3267 (1972).

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DISCUSSION

The mercaptides may decompose thermally to the corresponding sulfide, halide or the metal:

$$M(SC_{6}Hal_{5})_{2} \rightarrow MS + (C_{6}Hal_{5})_{6}S$$

$$M(SC_{6}Hal_{5})_{2} \rightarrow MHal_{2} + (C_{6}Hal_{4}S)_{x}$$

$$M(SC_{6}Hal_{5})_{2} \rightarrow M + (C_{6}Hal_{5}S)_{2}.$$

If the metal sulfide or halide is unstable, further decomposition could occur resulting in the formation of the metal. The sulfides, $(C_6Hal_5)_2S$, and the disulfides, $(C_6Hal_5S)_2$, are well known, as is polyfluorophenylene sulfide, $(C_6F_4S)_x$ [6], but polychlorophenylene sulfide, $(C_6Cl_4S)_x$ has not yet been characterized[7]. If the decomposition temperature is too high, the sulfides, disulfides, and polyhalophenylene sulfides may decompose. The disulfide, $(C_6Cl_5S)_2$, decomposes at 450° in a sealed tube, as does the thiol, C_6Cl_5SH .

The decompositions were studied either by T.G.A. or in evacuated sealed tubes. Due to the similarity in the molecular weights of MF_2 and MS, and even M or MCl_2 and large molecular weight of $M(SC_6Hal_5)_2$, T.G.A. will not distinguish between the possible products. The inorganic products were identified by X-ray diffraction. The organic products could not be identified with certainty due to partial pyrolysis. T.G.A. data indicate that the compounds do not decompose sharply, but over a temperature range. In general the mercaptides derived from pentafluorothiophenol are somewhat more thermally stable than those from pentafluorothiophenol. The results are summarized in the table.

The thermal decomposition gives the metal, its halide or sulfide. Various metal thiolates are totally



These are indicated in the table as polymeric, and it is seen that sulfide, or the metal, is generally formed in its decomposition. The halides are more often formed by mercaptides which are ionic, or partially ionic.

If the mercaptide is ionic, its decomposition to the metal sulfide or halide can be represented diagrammatically as:

$$2M^+ \mathrm{SC}_{\theta} Hal_{5}^{-}{}_{(s)} \tag{1}$$

$$2M^{+}_{(g)} + 2SC_{\theta}Hal_{5} \cdot _{(g)} + 2\epsilon_{(g)}$$
⁽²⁾

$$2M^{+}_{(g)} + (C_{6}Hal_{5})_{2}S_{(g)} + S_{(g)} + 2\epsilon_{(g)} \qquad 2M^{+}_{(g)} + (C_{6}Hal_{4}S)_{2x(g)} + 2Hal_{(g)} + 2\epsilon_{(g)}$$
(3)

$$2M^{+}_{(g)} + (C_{6}Hal_{5})_{2}S_{(g)} + S^{2-}_{(g)} \qquad 2M^{+}_{(g)} + (C_{6}Hal_{4}S)_{2x(g)} + 2Hal^{-}_{(g)} \qquad (4)$$

$$M_{2}^{+}S^{2-}(\mu) + (C_{6}Hal_{5})_{2}S_{(\mu)} \qquad 2M^{+}Hal^{-}(\mu) + (C_{6}Hal_{4}S)_{2}S_{(\mu)} \qquad (5)$$

The difference between the two pathways at stage $2 \rightarrow 3$ depends on the difference in bond strengths, at $3 \rightarrow 4$ on the difference in electron affinities, and at $4 \rightarrow 5$ on the difference in lattice energies.

Although some of the bond strengths are not known very accurately [8], using known values of the lattice energies and electron affinities [9], it can easily be shown that the favored reaction is:

- 6. M. E. Peach, Can. J. Chem. 46, 2699 (1968).
- 7. C. R. Lucas and M. E. Peach, Can. J. Chem. 48, 1869 (1970).
- 8. T. L. Cottrell, Strength of Chemical Bonds, Butterworths, London (1958).
- 9. T. C. Waddington, Adv. inorg. chem. Radiochem. 1, 157 (1959).

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Notes

$MSC_6Hal_5 \rightarrow MHal + (C_6Hal_4S)_x$

when M is an alkali metal (Hal = F, M = Li; Hal = Cl, M = Li, K). Insufficient data are available when M(I) = Cs. Difficulty may be encountered with non alkali metal halides in deciding whether they are ionic or not, but the same general reasoning for stages $2 \rightarrow 5$ can be applied provided that ionic sulfides or halides are formed. Little data on the lattice energies are available and various values are reported[9]. This reasoning would predict that CdF_2 , ZnF_2 , PbS (borderline) and Cu_2S are formed in the thermal decomposition of $M(SC_6F_5)_x$, but cannot explain why HgS is formed.

EXPERIMENTAL

The metal thiolates were prepared by literature methods [6, 7]. T.G.A. measurements were made on a Du Pont 950 Thermogravimetric Analyzer in a nitrogen atmosphere (100 ml/min) with the sample in a Pt boat and heating rate 5°C/min (Yardsley Research Laboratories). X-ray diffraction data were obtained on a Metropolitan-Vickers "Raymax 100" using CuK_{α} radiation with a Ni filter (Yardsley Research Laboratories) or Phillips Norelco X-ray powder diffractometer using FeK_{α} radiation with a Mn filter.

Some decompositions were studied in sealed evacuated pyrex sealed tubes at $350-450^\circ$. At 450° pyrolysis of $(C_6Cl_5S)_2$ and C_6Cl_5SH was observed giving unidentified crystalline products.

The solid residues from the sealed tube reactions were washed with benzene or methanol. The insoluble material, and the solid residues from the T.G.A. were identified by X-ray diffraction. Evaporation of the solvent left an organic residue, which, due to partial pyrolysis, could not be positively identified. Heating the decomposition products of $M(SC_6Cl_5)_2$, M = Ni, Pt, in air at 500° gives the oxide, indicating that the sulfide MS is the probable first decomposition product.

The molar conductivities (mho cm²/mol) of 0.1 M methanol solutions of $M(SC_6F_5)_2$ were M = Cd (1.81), Pb(1.07), Zn(0.48), Hg(0.15), and that of 0.1 M CaCl₂ 11.67. These mercaptides are assumed to be partially ionic, at least in methanol solution.

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Photo-induced formation of copper(II)porphyrins

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THE REACTION of porphyrins with certain copper(II)1,3-diketonates in a variety of solvents was found to be accelerated by light.

EXPERIMENTAL

Etioporphyrin I[1]; tetraphenylporphin[2]; phyllo-type petroporphyrins[3]; bis(2,4-pentanedionato)copper(II), $Cu(AA)_2[4]$; bis(2,6-dimethyl-3,5-heptanedionato)copper(II), $Cu(DIBM)_2[4]$;

1. D. J. Rislove, A. T. O'Brien, and J. M. Sugihara, J. chem. Engng Data 13, 588 (1968).

- 2. A. D. Adler, F. R. Lonzo, J. O. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, J. org. Chem. 32, 476 (1967).
- 3. Isolated by J. F. Branthaver from Boscan crude oil.

4. W. C. Fernelius and B. E. Bryant, Inorg. Synth. 5, 105 (1957).