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Comparative Thermal Stability and Synthesis of Group IVB Polythioethers

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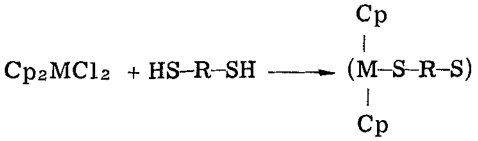
ABSTRACT

A comparison of the synthetic and thermal characteristic of Group IVB polythioethers is made. In general, yield follows the trend interfacial systems > aqueous solution systems and Hf > Ti > Zr.



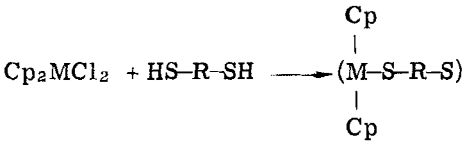
$$\mathrm{Cp_2MCl_2 + HS{-}R{-}SH \longrightarrow (\overset{\overset{\textstyle Cp}{|}}{\underset{\underset{\textstyle Cp}{|}}{M}}{-}S{-}R{-}S)}$$

Degradation initially begins about 150 to 200°C with as much as 80% weight retention above 1000°C. Initial degradation in air

and nitrogen occur through similar routes, but above 250° C degradation occurs through oxidative routes in air.

INTRODUCTION

We recently announced the synthesis of Group IVB polythioethers of Form I [1-3]. Here we report on the comparative synthesis of these polythioethers along with a comparative study of their thermal stabilities.



$$Cp_2MCl_2 + HS{-}R{-}SH \longrightarrow (\overset{\overset{Cp}{|}}{\underset{\underset{Cp}{|}}{M}}{-}S{-}R{-}S)$$

I

EXPERIMENTAL

The following organometallic reagents were used without further purification: Dicyclopentadienylhafnium dichloride (Strem Chemicals, Inc., Danvers, Massachusetts), and dicyclopentadienyltitanium dichloride and dicyclopentadienylzirconium dichloride (Alfa Inorganic, Inc., Beverly, Massachusetts). Ethylenebis(3-mercaptopropionate) (EMPAT) and dimercaptoacetate were obtained as gifts from Evans Chemetics, Inc., Darien, Connecticut. All other thiols were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, and used without further purification.

The polymerization apparatus and detailed polymerization procedure are described elsewhere [1-4]. Briefly, the phase containing the base and dithiol was added through a large-mouthed funnel to the stirred Cp_2MCl_2 solution. Polymer precipitated rapidly from the polymerization system and was recovered by utilizing suction filtration. The titanium polythioethers are light yellow to dark orange in color, the zirconium polythioethers white to light cream, and the hafnium polythioethers white to cream. Some were originally tacky and all dried to give electrostatic solids which could be ground to give powders.

Infrared and elemental analyses results appear elsewhere [1-3] and are in agreement with a repeating unit of Form I.

Thermal gravimetric analysis was conducted employing a 950 DuPont TGA. Air and nitrogen flows were about 0.3 L/min. Samples were ground to a fine powder to aid in obtaining reproducible results (for use in both DSC and TGA).

Differential scanning calorimetry was carried out by employing a DuPont 900 DSC cell fitted on a DuPont Thermal Analyzer console employing a flow rate of about 0.2 L/min of air or nitrogen. A linear baseline compensator was used with the DSC cell to insure a constant energy baseline. A Mettler H20 semimicrobalance was employed for the weighing of the DSC samples. Measurements were obtained on samples contained in open aluminum cups to allow the free flow away from the solid of volatilized gases, thus more closely simulating the conditions under which TGA studies were conducted.

RESULTS AND DISCUSSION

Group IVB organometallic dihalides of the form Cp_2MCl_2 were chosen as the metal-containing reactant for several reasons. First, all three undergo ionization in water to form the corresponding Cp_2M^{2+} moiety (see, for example, Ref. 5). After a time, Cp_2M^{2+} undergoes mono- and finally dihydroxylation, forming insoluble $Cp_2M(OH)_2$. The order of this hydroxylation is Ti $<$ Zr $<$ Hf. Cp_2Hf^{2+} is stable under reaction conditions for greater than 3 min. To avoid such hydroxylation, aqueous solutions of Cp_2MCl_2 were made up just prior to conducting the reaction. All values given here are from systems where hydroxylation is not critical to product yield. Second, the homologous series of Cp_2MCl_2 compounds where M = Ti, Zr, or Hf are commercially available. Third, all three are stable in air, alleviating the need for special reaction conditions. Fourth, all have already shown industrial uses as catalysts, etc., and such properties could be incorporated into polymer chains containing the Cp_2M moiety.

As noted in previous work, many organometallic polymers are either insoluble in all solvents or achieve solubility in a limited number of solvents followed by subsequent degradation. All of the Group IVB polythioethers synthesized thus far have been insoluble in all solvents tried [1-3]. This is disappointing and precludes many possible applications of such products. Further, it prevents molecular weight determination, leaving yield as the major "sensing device."

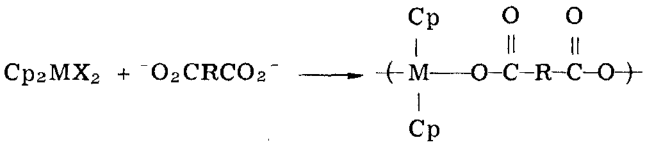
Table 1 displays yield as a function of reaction system, thiol, and metal reactant. Several trends are apparent. First is a general trend of yield being of the order IF $>$ Soln (where IF is interfacial systems and Soln is aqueous solution systems). Second, yield follows the order Hf $>$ Ti $>$ Zr for a given thiol for both reaction systems. The reason(s) for this trend are currently unknown. For the analogous synthesis of Group IVB polyesters of Form II, the yield trend was Hf $>$ Zr $>$ Ti [6]. This was explained by utilizing arguments of polarizability. Even though Hf and Zr are of similar size, Hf presents a more disperse electron density and empty "orbital" array, resulting in a more disperse outer shell.

TABLE 1. Yield as a Function of Reaction System and Reactants[a]

		Metal-containing reactant		
Dithiol	System	Cp_2HfCl_2 Yield (%)	Cp_2ZrCl_2 Yield (%)	Cp_2TiCl_2 Yield (%)
EMPAT	IF	78	6	36
EMPAT	Soln	35	5	17
1,6-Hexanedithiol	IF	58	4	48
1,6-Hexanedithiol	Soln	31	3	28
1,2-Ethanedithiol	IF	51	1	33
1,2-Ethanedithiol	Soln	57	5	12
1,3-Propanedithiol	IF	59	8	40
Dimercaptoacetate	IF	78	-	23
Dimercaptoacetate	Soln	53	-	23
EMPAT[b]	IF	-	4	25
EMPAT[b]	Soln	-	0	35
1,6-Hexanedithiol[b]	IF	-	31	30
1,6-Hexanedithiol[b]	Soln	-	0	20
1,2-Ethanedithiol[b]	Soln	-	0	22

[a] Reaction conditions: For interfacial systems (IF), the dithiol (0.0005 mole) with Et_3N (0.001 mole) in 15 mL water was added to rapidly stirred solutions of Cp_2MCl_2 (0.0005 mole) in 15 mL chloroform at 0.27 °C with a stirring rate of 23,000 rpm for 1 min. For aqueous solution systems (Soln), the same as for IF except Cp_2MCl_2 is contained in 15 mL of water instead of chloroform.

[b] Reaction conditions. The same as for footnote a except with the dithiol (0.001 mole) with NaOH (0.002 mole) contained in 25 mL water with Cp_2MCl_2 contained in 25 mL of water (for Soln) or chloroform (for IF).



$$Cp_2MX_2 + {}^{-}O_2CRCO_2^{-} \longrightarrow \left(\overset{Cp}{\underset{Cp}{M}} - O - \overset{O}{\overset{\|}{C}} - R - \overset{O}{\overset{\|}{C}} - O \right)$$

II

The yield trend for the polyester systems can be rationalized using Pearson's hard-soft acid-base (HSAB) concept where the RCO_2^- is considered to be soft electrophilic centers giving an expected kinetic trend of Hf > Zr > Ti which is the trend observed for the polyester systems [7-11]. The $R\text{-}S^{\ominus}$ and R-SH are soft bases [10, 11]. Again, treating Cp_2M^{2+} and Cp_2MCl_2 as intermediate or soft bases, a bonding trend of Ti > Zr > Hf would be predicted which is consistent with the Ti > Zr portion of the observed trend with polythioethers but not with the position of Hf. Thus, while the HSAB theory is adequate to rationalize much of the data involving condensation of Group IVB Cp_2MCl_2's with dithiols and salts of diacids, it does not permit the rationalization of all the observed trends.

There may be several objections to applying the HSAB treatment to the present systems. First, Pearson's theory mainly applies to nucleophilic displacement reactions though the treatment has been applied to a wide variety of reactions including simple addition reactions (see, for example, Refs. 10 and 11). In aqueous solutions the chemical rate-determining step probably involves addition of Cp_2M^{2+} to $R\text{-}S^{\ominus}$ and $RCO_2^{\ominus}$. Second, Pearson's theory deals mainly with polarization and ionic terms. For the present systems additional terms such as mass transport and solution may also be important.

The thermal characteristics of the polythioethers were studied utilizing DSC and TGA along with visual observations. The products generally turned brown to black in the temperature range of 300 to 550°C. They then lightened in color, becoming white to cream by 650 to 800°C. They remained light in color to 1100°C (the highest temperature utilized). Similar behavior is observed for the analogous polyesters [12].

Table 2 exhibits weight loss data as a function of atmosphere and reactant. Figures 1 to 3 contain representative thermograms. Heat change values are listed in Table 3. Several points of interest are evident. First, the products initially begin to degrade around 50°C; thus they exhibit a poor low temperature thermal stability with respect to weight retention. This weight loss is generally accompanied by the production of a "thiol-like" odor. Additionally, initial thermal degradation (to the 150 to 250°C range) often appears to be identical in air and nitrogen, indicating an internal type of degradation by a nonoxidative mode. The products generally exhibit moderately good weight retentions at higher temperatures, several retaining 80% of their weight at 800°C.

There appear to be no general trends with respect to weight retention as a function of atmosphere, metal, or thiol. The analogous Group IVB polyesters exhibited trends such that weight retention followed the order nitrogen > air and Hf > Zr > Ti for a given carboxylate moiety [12].

Other work with Group IVB products indicates that the products of extensive heating in air are generally largely the metal oxides, MO_2. This should be considered when evaluating the TGA data. The first column of Table 2 contains the % MO_2 that would result if the

TABLE 2. Weight Losses as a Function of Polythioether Composition

Reactants (% theory if MO_2)	Temperature (°C) for a given % weight loss							
	In air				In nitrogen			
	10%	20%	30%	50%	10%	20%	30%	50%
1,6-Hexanedithiol with								
(23) Cp_2TiCl_2	190	330	420	1160	220	350	700	[c]
(33) Cp_2ZrCl_2	120	250	420	[a]	130	260	950	[d]
(46) Cp_2HfCl_2	270	800	[b]		320	900	[e]	
1,2-Ethanedithiol with								
(31) Cp_2TiCl_2	170	430	970		170	630	900	[h]
(40) Cp_2ZrCl_2	260	500	[g]	[f]	300	850	[i]	
(53) Cp_2HfCl_2	200	820	1180		300	1040		
1,3-Propanedithiol with								
(29) Cp_2TiCl_2	160	420	960	[j]	180	630	1100	[l]
(38) Cp_2ZrCl_2	200	400	[k]		200	390	600	[m]
EMPAT								
(20) Cp_2TiCl_2	150	170	180	270	160	180	190	310
(27) Cp_2ZrCl_2	340	640	1100		340	770	1120	[o]
(39) Cp_2HfCl_2	270	320	360	[n]	270	330	400	[p]

[a] 40% wt loss at 1100°C.
[b] 27% wt loss at 1040°C.
[c] 47% wt loss at 1000°C.
[d] 32% wt loss at 1100°C.
[e] 25% wt loss at 1040°C.
[f] 35% wt loss at 1100°C.
[g] 26% wt loss at 930°C.
[h] 31% wt loss at 930°C.
[i] 23% wt loss at 930°C.
[j] 35% wt loss at 1100°C.
[k] 28% wt loss at 1040°C.
[l] 31% wt loss at 1130°C.
[m] 35% wt loss at 900°C.
[n] 47% wt loss at 900°C.
[o] 32% wt loss at 1080°C.
[p] 43% wt loss at 780°C.

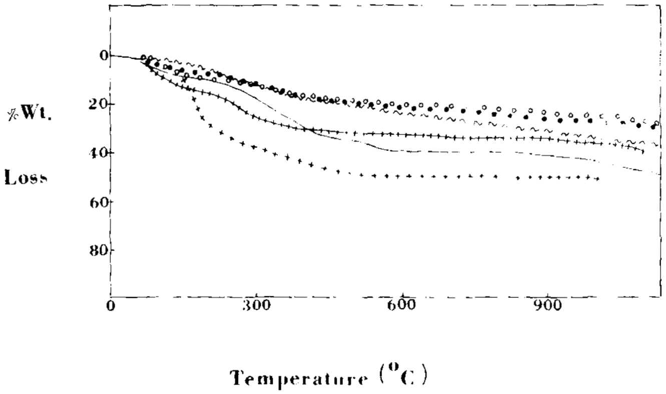


FIG. 1. TGA thermograms for the condensation products of Cp_2TiCl_2 with 1,6-hexanedithiol (—); Cp_2ZrCl_2 with 1,6-hexanedithiol (——); Cp_2HfCl_2 with 1,6-hexanedithiol (····); Cp_2TiCl_2 with 1,2-ethanedithiol (++++); Cp_2ZrCl_2 with 1,2-ethanedithiol (○○○○○); and Cp_2HfCl_2 with 1,2-ethanedithiol (~~~) in air at a heating rate of 30°C/min and a gas flow rate of 0.2 L/min.

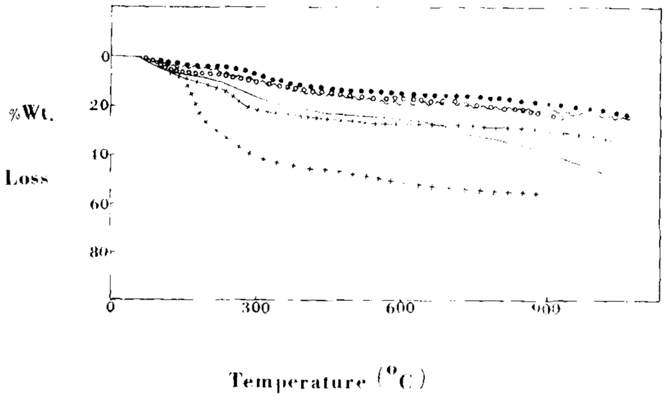


FIG. 2. TGA thermograms for the condensation products as listed in Fig. 1 in nitrogen.

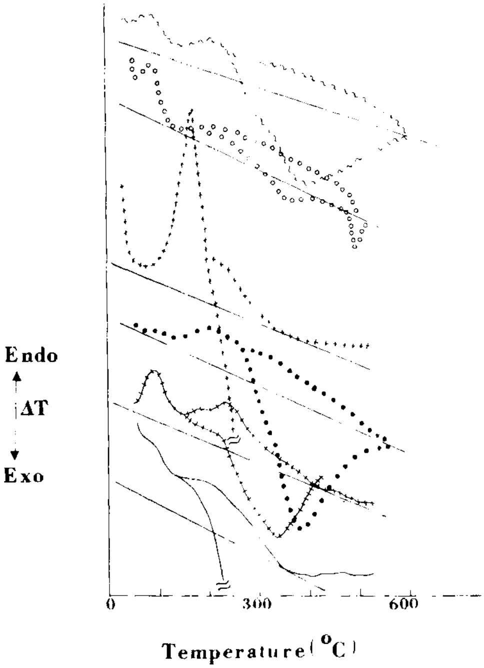


FIG. 3. DSC thermograms for the condensation products as listed in Fig. 1 in air (lower portion) and nitrogen (upper portion) for 1.00 ± 0.01 mg samples with the straight line being ΔT = 0.

degradation product were all MO_2. The products all retain more than this weight, many containing significantly even more at 1100° C. Thus the degradative products still contain considerable organic material after heating.

The observed "stability plateaus" are normal for many organometallic products and are probably a consequence of the heterogeneity of bond energies present in the polymer backbone.

Degradation occurring in air (after the 150 to 250° C range) is exothermic whereas degradation occurring in nitrogen is endothermic. The occurrence of exothermic degradations in air is often found for metal-containing products and is indicative of cross-linking or oxidation reactions [13]. Since the DSC and TGA thermograms are dissimilar in air and nitrogen, degradation is probably occurring via an oxidative route. The products remained solid over the temperature ranges studied. Thus degradation in air and nitrogen presumably occurs by a solid-state pathway. Transitions occurring in the 30 to 100° C range are endothermic and small (often around 0.02 cal/g) and often tail into higher temperature range transitions.

TABLE 3. Heat Changes in Air and Nitrogen as a Function of Reactants[a]

	ΔH (cal/g) atmosphere	
Reactants	Air	N_2
Cp_2TiCl_2 with		
1,6-Hexanedithiol	0.60	-0.057
1,2-Ethanedithiol	0.47; 0.060	-0.13
EMPAT	0.50; 0.090	-0.15
1,3-Propanedithiol	0.75	-0.040
Cp_2ZrCl_2 with		
1,6-Hexanedithiol	0.24	-0.094
1,2-Ethanedithiol	0.013; 0.0081	-0.010
EMPAT	0.052	-0.038
1,3-Propanedithiol	0.090	-0.063
Cp_2HfCl_2 with		
1,6-Hexanedithiol	0.089; -0.022	-0.064
1,2-Ethanedithiol	0.080; -0.018	-0.080
EMPTA	0.095; -0.056	-0.10

[a] Convention utilized: Exothermic values are reported as positive values whereas endothermic values are reported as negative values.

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