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Physical Characterization of Titanium Polyferrocene Oximes

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ABSTRACT

Characterization of titanium polyferrocene oximes is described. Soluble, short-chain products are obtained when excess base is employed. Thermal transitions occur by similar exothermic routes in air and nitrogen to about 180°C and thereafter occur by different paths. The products begin to degrade about 250°C but retain over 50% weight to 600°C. Resistivities vary from 10^5 to 10^7 ohm-cm, reaching minimal values at 100 V with the initial values pressure dependent to 500 V.

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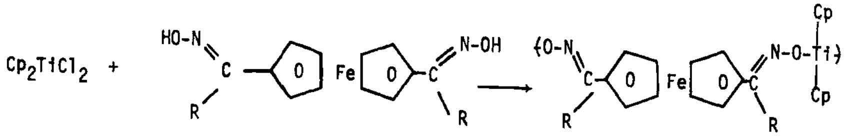
*This work was done in part with M. J. Christensen at the University of South Dakota and in part with J. A. Schroeder at Wright State University.

INTRODUCTION

While the synthesis of ferrocene dioximes has been known for about 20 years, reports of reactions involving them have been essentially nonexistent, and no polymers containing or derived from them have been reported [1-3].

We recently reported the initial synthesis of titanium polyferrocene oximes of form I [4]. Here we report the initial characterization of several of these products.



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EXPERIMENTAL

Detailed reaction and analytical procedures are described elsewhere. Briefly, dioximes were synthesizes as described by Rausch et al. [1] and Woodward et al. [3]. The polymerization apparatus is described in detail elsewhere [5] and consists of a 1-pt Kimax Emulsifying Mill jar placed on a Waring Blendor. Aqueous solutions of oxime containing added base are added to stirred organic solutions containing Cp_2TiCl_2. Polymer rapidly precipitates from the reaction system. Elemental analysis, solution techniques and results, and infrared techniques have been previously described [4]. The products were insoluble in all attempted liquids (unless noted otherwise) which prevents applications and determinations (as product molecular weight) requiring polymer solubility but does not prevent product uses and applications not requiring polymer solubilization.

Viscometry was conducted on products utilizing serial dilutions employing Cannon-Ubbelohde semimicro dilution viscometers.

Product conductivity was determined by utilizing a RCA WV-511A Picoammeter, Hewlett-Packard 6516A DC power supply, and specially designed sample assembly described elsewhere [6]. Resistance R is obtained by using Ohm's relationship by measuring amperage at applied voltages. Specific resistance p is calculated from Eq. (1), where a is the pellet area and t the pellet thickness.

$$p = R(a/t) \qquad (1)$$

Differential scanning calorimetry (DSC) was determined by employing a duPont 990 Thermal Analyser console employing a linear baseline compensator. Samples were weighed with a Mettler HT balance. Thermal gravimetric analysis (TGA) was conducted by using a duPont 951 TGA instrument. All samples were ground and run in the open.

RESULTS AND DISCUSSION

We previously reported the initial synthesis of titanium polyferrocene oximes and a number of associated synthetic reaction dependencies. Reactions are rapid, second-order overall (first order in each reactant; $k \cong 0.1$ to 10 liter/mole-sec) and general for both aliphatic and aromatic R (form I) with a reaction being more rapid for aliphatic R, presumably due to increased steric requirements of the aromatic substituents and/or decreased nucleophilicity of the oxime anion [4]. These products were insoluble in all attempted liquids. There are a number of possible ploys that might be used to obtain soluble products.

In an attempt to obtain soluble products, excess base was used which might limit product molecular weight by hydrolysis of the acid chloride or by some other mode. At quite high amounts of added base (about 1000-fold excess) the precipitated material contained materials such as $Cp_2Ti(OH)_2$ in addition to some of the desired condensation product (Table 1). The desired product was obtained, without detectable contaminents from the acid chloride, utilizing a threefold excess of base. These products were poor in the Cp_2Ti moiety as indicated by diminished infrared bands associated with the Cp_2Ti moiety indicating a preferential capping by the oxime. In fact only N—O—H end groups are found for these products. The materials are somewhat tacky after initial isolation and are soluble in such dipolar aprotic solvents as acetone, triethylphosphate, DMSO and DMF. Limiting viscosity numbers of ca. 5 ml/g are obtained which correspond to short chains of weight-average degrees of polymerizations of ca. 5.

The use of increased base decreases product yield over the equivalence systems and results in a fairly rapid degradation of the products (Table 1).

Representative thermograms appear in Figs. 1 and 2. Degradation begins by similar exothermic routes in air and nitrogen about 180° C. Many products containing ferrocene degrade readily within the 150-300° C range, eliminating the ferrocene moiety or fragments of the ferrocene moiety accounting for 30 to 80% weight losses of polymers [7, 8]. The current products lose only about 4 to 15% of their weight in this area and appear stable to 400° C (for the dibenzoyl product) and 800° C (for the diacetyl product), with some of the iron remaining

TABLE 1. Results as a Function of Time and Amount of Base[a]

Stirring time (sec)	Yield (%) With 0.67 mmole NaOH	Yield (%) With 2.0 mmole NaOH
5		8
30	47	21
60		b
120	80	12
240	86	
300		
720	94	

[a] Reaction conditions: aqueous solutions (25 ml) of 1,1'-diacetylferrocene dioxime (0.335 mmoles) with sodium hydroxide are added to stirred (20,500 rpm no load) solutions of Cp_2TiCl_2 (0.335 mmole) contained in carbon tetrachloride (25 ml) at 25°C for designated stirring time.

[b] Under same conditions but with 75 mmole NaOH the yield was 10% at 60 sec stirring time.

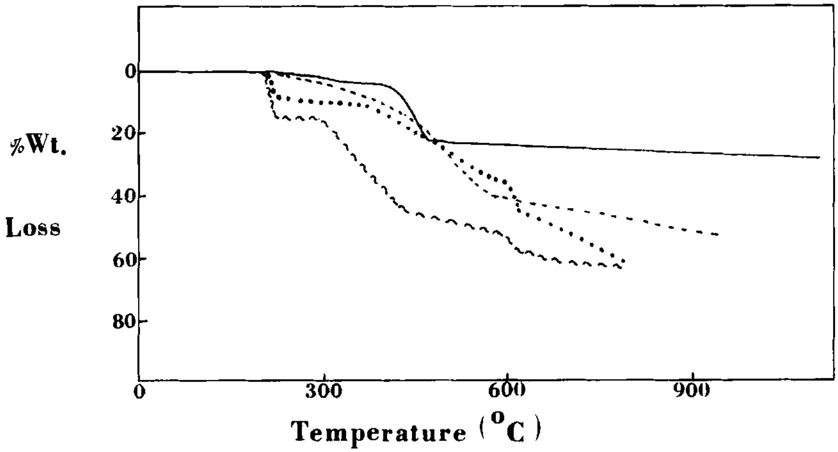

FIG. 1. TGA thermograms of titanium polyferrocene oximes derived from 1,1'-dibenzoylferrocene oxime (——) in air and (-----) in nitrogen and 1,1'-diacetylferrocene oxime (~~~~~) in air and (· · · ·) in nitrogen at 20°C/min.

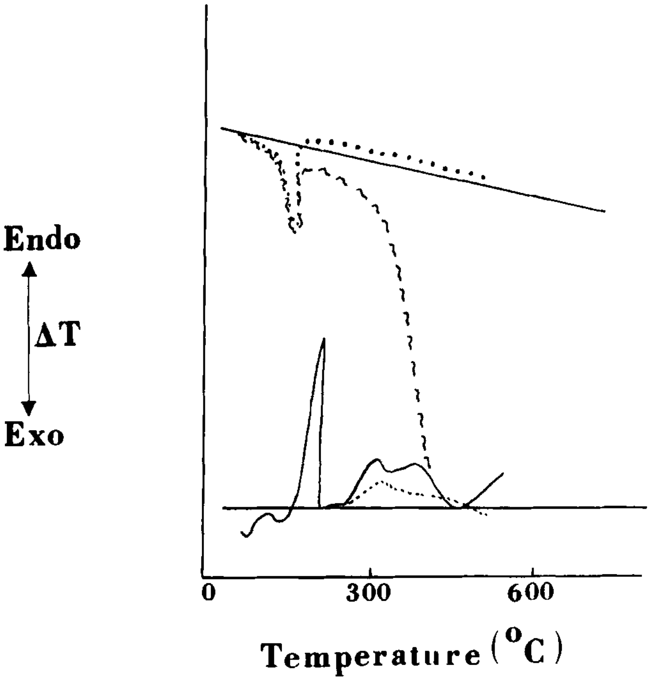

FIG. 2. DSC thermograms of titanium polyferrocene oximes at a heating rate of 20°C/min for 1.00 mg of material: 1,1-dibenzoylferrocene oxime (—) in air and (--) in nitrogen; 1,1-diacetylferrocene oxime (~ ~) in air and (· · ·) in nitrogen.

to 800°C. Corresponding titanium polyferrocene esters experience 30 to 70% weight losses in the 150 to 300°C range [9]. Many of the ferrocene products previously studied by us were derived from salts of 1,1'-dicarboxylic ferrocene acid which can eliminate carbon dioxide, thus freeing the ferrocene moiety. The present ferrocene oxime products apparently degrade by different routes. This points out the potential importance of the bonding connecting the ferrocene moiety to the remainder of the chain.

Thermal degradations vary greatly between the two products. Degradation with the diacetyl compound occurs by low energy exothermic routes above ca. 250°C in nitrogen but is largely by exothermic routes in air, indicative of oxidative degration in air. For the dibenzoyl compound, degradation above 300°C occurs in both air and nitrogen by dissimilar endothermic routes.

Visual observation using a Fisher-Johns melting point apparatus indicates an initial discoloration about 190°C which corresponds to

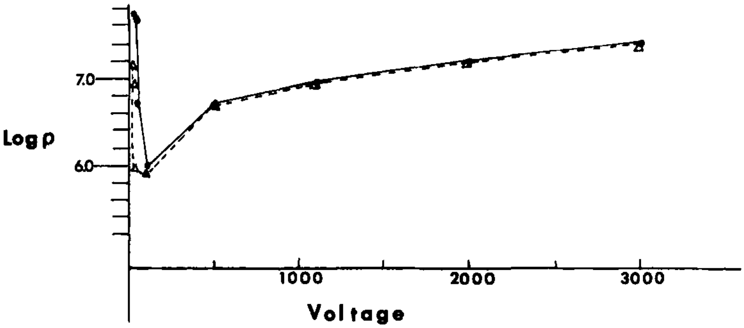

FIG. 3. Resistivity values as a function of voltage input for the product from Cp_2TiCl_2 and dibenzoylferrocene dioxime at (--) 1000 lb/in^2 and (△) 300 lb/in^2 pressure.

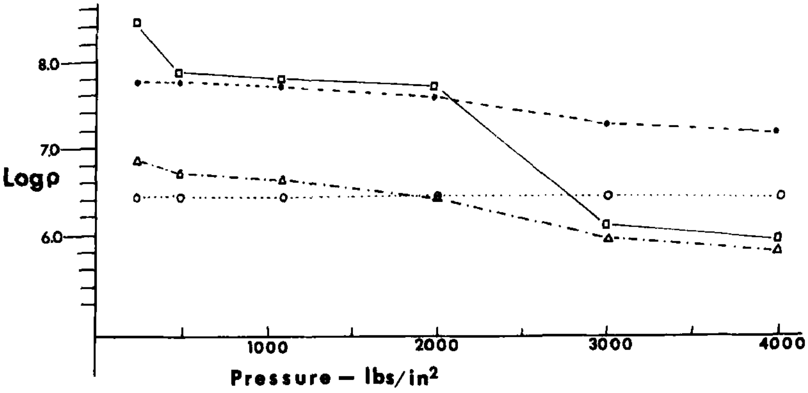

FIG. 4. Resistivity values as a function of pressure for the product from Cp_2TiCl_2 and dibenzoylferrocene dioxime: (●) 1 V; (□) 5 V; (△) 10 V; (○) 500 V input.

the exothermic regions and initial weight losses illustrated in Figs. 1 and 2.

Overall, the products exhibit poor low temperature stabilities and moderate high temperature stabilities. Stability plateaus are kinetically controlled.

Initial investigation of the gross electrical properties of a number of organometallic polymers has begun. Preliminary observations indicate that, though each family exhibits similar trends with respect to voltage and pressure variations, each family must be studied

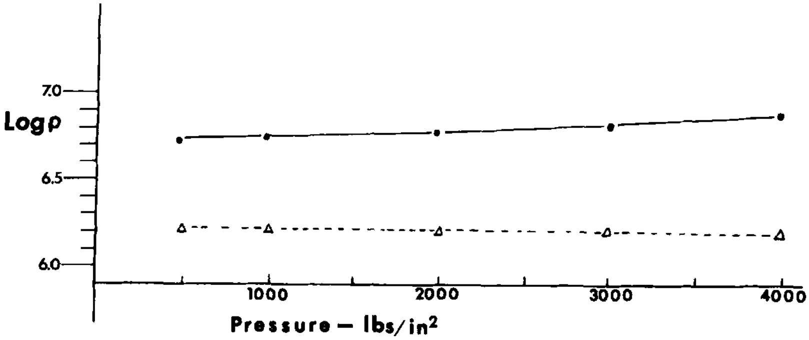

FIG. 5. Resistivity values as a function of pressure for the product from Cp_2TiCl_2 and dimethylferrocene dioxime at (●) 10 V and (△) 50 V input.

separately to establish the particular trend for that family. This has been done for the titanium polyferrocene oximes. Representative results appear in Figs. 3-5.

Resistivities vary, from ca. 10^5 to 10^7 ohm-cm, lying within the lower range for usual semiconductor use. Resistivity values are minimal at ca. 100 V input with the initial values to ca. 500 V dependent on pressure. Above 500 V, resistivity is independent of pressure as voltage is varied. The difference in resistivity between the low voltage inputs (like 1 V) and the minimum region are significant. For the product from the 1,1'-dibenzoylferrocene dioxime there is greater than a tenfold variation between the low voltage resistivities and the minimal resistivities.

For voltages less than ca. 100 V, resistivity decreases with increase in pressure, but above 100 V input resistivity is essentially constant as pressure is varied.

REFERENCES

[1] M. Rausch, M. Vogel, and H. Rosenberg, J. Org. Chem., 22, 903 (1957).

[2] M. Rosenblum and R. Woodward, J. Amer. Chem. Soc., 80, 5443 (1958).

[3] R. Woodward, M. Rosenblum, and M. Whitting, J. Amer. Chem. Soc., 74, 3458 (1952).

[4] C. Carraher and M. Christensen, Angew. Makromol. Chem., in press.

[5] C. Carraher, J. Chem. Ed., 46, 314 (1969).
[6] C. Carraher, J. Chem. Ed., 54, 476 (1977).
[7] C. Carraher, Inorg. Macromol. Revs., 1, 271 (1972).
[8] C. Carraher, Interfacial Synthesis, F. Millich and C. Carraher, Eds., Marcel Dekker, New York, 1977, Chapt. 22.
[9] C. Carraher, Chemtech., 741 (1972).

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