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# Synthesis and Structural Characterization of Titanium Polyoximes

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# Synthesis and Structural Characterization of Titanium Polyoximes

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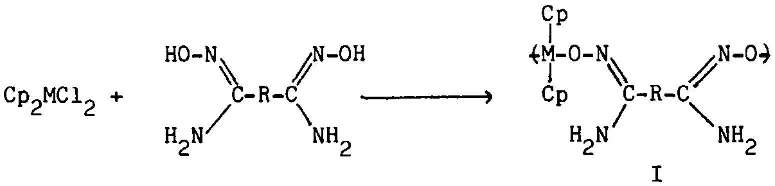
## ABSTRACT

The synthesis and structural characterization of titanium polyoximes derived from bis(cyclopentadienyl)titanium dichloride is described. Dioximes were selected for study based on geometrical dissymmetry, potential biological activity and the potential for extended conjugation through the resulting polyoxime chain. Product yield and chain length appears dependent on the electronic character of the oxime. Product chain length also appears dependent on polymer solubility. Structural characterization using elemental analyses, infrared spectroscopy, light scattering photometry, control reactions and coupled thermogravimetric-mass spectroscopy is described.

## INTRODUCTION

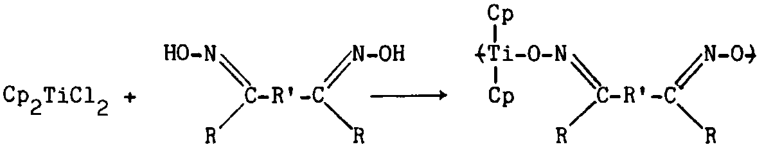
The synthesis and characterization of organometallic polymers is an ongoing portion of our research program. Recently we reported the synthesis of titanium and zirconium polyamidoximes of form I [1,2].



I

While reaction is known to almost exclusively occur only at the oxime sites, reaction at the amine sites does occur when excess $Cp_2MX_2$ is employed leading to branched and crosslinked products. Group IVB containing polymers have generally shown poor solubilities in both extent and range. Even small amounts of crosslinking could permit this generally poor solubility to become complete insolubility.

Here we report the synthesis of titanium polyoximes of form II. The use of dioximes allows the use of the oxime functional group yet eliminates the formation of branched and crosslinked products.



II

## EXPERIMENTAL

The following chemicals were used as received without further purification: bis(cyclopentadienyl)titanium dichloride (Strem Chemicals, Inc., Davers, Mass.), menadione (Vitamin $K_3$; United States Biochemical Corp., Cleveland, Ohio), Progesterone ($\Delta^1$-pregnan-3,20-dione; U.S.B.C.), Androstadiendione ($\Delta^{1,4}$-androstadien-3,17-dione, U.S.B.C.), 3,20-Pregnanedione (Eastern Chemicals), Phenindione (2-phenyl-1,3-indanone; Pfaltz-Bauer, Inc., Stamford, Conn.), 1,4-cyclohexanedione (Aldrich Chemical Company, Milwaukee, Wis.), p-benzoquinone dioxime (Aldrich), and hydroxylamine hydrochloride (Fisher Scientific Company, Fairlawn, N.J.).

The oximes were synthesized as described in reference 3. The resulting solids were washed with 1:1 ethanol-water after the product was recovered by suction filtration. The product was then recrystallized twice from 1:1 ethanol-water.

*2-Methyl-1, 4-naphthoquinone dioxime (menadioxime, Vitamin $K_3$ dioxime)*,: the yellow solid [4] was obtained in 49% yield; m.p. = 164-167°C, (lit. 166-168°C; IR (KBr) 3260 cm$^{-1}$ (O-H), 1620 cm$^{-1}$ (C=N), 980 cm$^{1}$ (N-O).

*$\Delta^1$-Pregnan-3,20-dioxime (progesterone dioxime)*,: the white solid [5] was obtained in 86% yield; m.p. = 248-252°C, (lit. 247-256°C; IR (KBr) 3280 cm$^{-1}$ (O-H), 1640 cm$^{-1}$ (C=N, 915-980 cm$^{-1}$ (N-O).

*$\Delta^{1,4}$-Androstadien-3,17-dioxime (androstadiendioxime)*: the white solid[ 6 ] was obtained in 90% yield; m.p. = 232-235°C, (lit. 229-230°C); IR (KBr) 3260 cm$^{-1}$ (O-H), 1660 cm$^{-1}$ (C=N), 870-980 cm$^{-1}$ (N-O).

*3,20-Pregnanedioxime (pregnanedioxime)*: the white solid [7] was obtained in 72% yield; m.p. = 174-176°C (lit. 260°C); IR (KBr) 3300 cm$^{-1}$ (O-H, 1695 cm$^{-1}$(C=N), 900-1010 cm$^{-1}$ (N-O),

Anal. Calcd. for $C_{21}H_{34}O_2N_2$: C, 73.0; H, 9.9; O, 9.3%

Found: C, 76.2; H,10.1; O, 9.2%

*1,4-Cyclohexanedione dioxime*: the white crystalline solid [8] was obtained in 70% yield; m.p. = 189-192°C, (lit. 188°C), IR (KBr) 3200 cm$^{-1}$ (O-H), 1660 cm$^{-1}$ (C=N), 925-1000 cm$^{-1}$ (N-O.

*2-Phenyl-1,3-indanone dioxime (phenindioxime)*: the white solid [9] was obtained in 68% yield; m.p. = 198-200°C, (lit. 193-196°C); IR (KBr) 3200 cm$^{-1}$ (O-H), 1650 cm$^{-1}$ (C=N), 957, 1045 cm$^{-1}$ (N-O).

Reaction sequences were similar to those described elsewhere [10,11]. Briefly the $Cp_2TiCl_2$ contained in an organic (for interfacial polycondensations) or aqueous (for aqueous solution polycondensations) liquid is added to rapidly stirred aqueous solutions containing neutralized dioxime. The polyoxime precipitates from the reaction solution and is recovered using suction filtration. The product is washed repeatedly with water and chloroform. The reaction assembly is described elsewhere [12].

Infrared spectra were obtained using KBr pellets employing a Perkin-Elmer 457 Grating Spectrophotometer. Light scattering photometry was conducted employing a Brice-Phoenix BP-3000 Universal Light Scattering Photometer. Refractive index increments were determined using a Bausch and Lomb Abbe Refractometer Model #3-L.

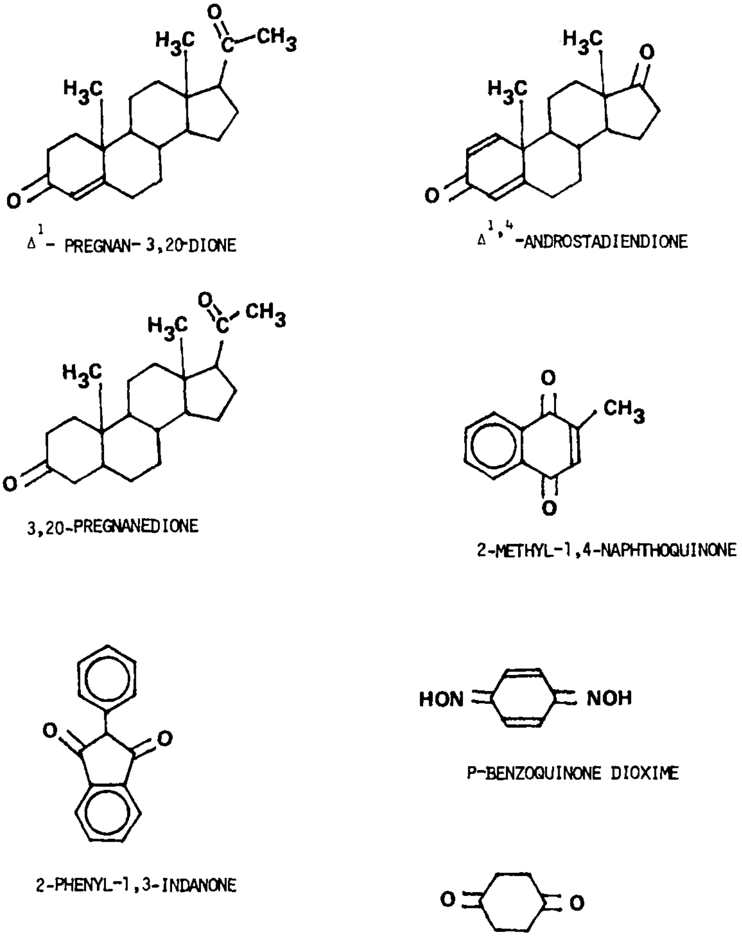
Mass spectral data was obtained using a Model 21-491 DuPont Mass Spectrometer which was coupled through a jet separator to a DuPont 951 Thermogravimetric Analyzer controlled through a DuPont 990 Thermal Analyzer console. The TG-MS assembly was interfaced with a Hewlett-Packard 2116C computer. The assembly is described in detail elsewhere [13].

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Elemental analyses for the metals were performed by thermal degradation of the samples to $TiO_2$.

## RESULTS AND DISCUSSION

A number of dioximes could have been utilized since they are readily synthesized from corresponding diones. The utilized dioximes were chosen based on geometrical dissymmetry (to discourage crystalline formation enhancing product solubility), potential biological activity (a number of these compounds are currently undergoing biological study) and the potential for extended conjugation through the polymer chain (electrical characterization is currently occurring). Dioximes can be considered as weak acids with Lewis acid-base reaction characteristics similar to carboxylic acids, such as forming salts on addition of sodium hydroxide. The diones and dioximes utilized in this study are pictured in Figure 1.

Bis(cyclopentadienyl)titanium dichloride contains two readily identifiable chromophores: the red Ti-Cl chromophore and the



$\Delta^{1}$ - PREGNAN-3,20-DIONE

$\Delta^{1,4}$-ANDROSTADIENDIONE

3,20-PREGNANEDIONE

2-METHYL-1,4-NAPHTHOQUINONE

2-PHENYL-1,3-INDANONE

P-BENZOQUINONE DIOXIME

1,4-CYCLOHEXANEDIONE

FIGURE 1. Diones and dioximes utilized to synthesize titanium polyoximes.

yellow Ti-Cp chromophore [14]. Carraher and co-workers [10] have noted that in all polymer families synthesized involving the titanium metallocene studied (except the titanium polyester-ethers where the Lewis base coloration mask any color change) that the initial color of $Cp_2TiCl_2$ in organic solvents is deep red, which gives way to a yellow color upon polycondensation.

The interfacial polymerization procedure was as described earlier. It was noted that the deep red color of $Cp_2TiCl_2$ (dissolved in chloroform) faded after 10-15 seconds of reaction (stirring) to leave a yellow color for the remaining time of reaction. This indicates the loss of the chlorine atoms from the metallocene moiety, leaving the Ti-Cp chromophore as the only color site, hence, the yellow color of the reaction mixture. (The red Ti-Cl is the dominant chromophore [14]). This color change was observed for all reactions studied utilizing the interfacial polymerization process, except for the reactions run using p-benzoquinone dioxime as the Lewis base. p-Benzoquinone dioxime is a deep brown color (dissolved in a basic aqueous solution) and thus masks any color change due to the $Cp_2TiCl_2$ monomer that may occur during reaction.

Polymerization was also performed utilizing the aqueous solution method (also described earlier). As the color of $Cp_2TiCl_2$ dissolved in water is yellow (rather than red when dissolved in chloroform), no color changes were observed during the polymerization reaction. Polyoximes synthesized using the aqueous solution technique gave lower yields and otherwise similar thermal and solubility results as compared to the same polyoximes synthesized employing the interfacial method.

Percentage yield and molecular weight as a function of dioxime is given in Table 1. Table 2 contains a listing of trends as a function of various parameters. There appears to

TABLE 1.

Results as a function of dioxime.

| Dioxime (Product Identification Number) | Yield(%)[a] | %Ti Found | %Ti Theory | Solubility[b] (% by weight) | dn/dc[c] | $\bar{M}_w$[c] | $\overline{DP}$ |
|---|---|---|---|---|---|---|---|
| $\Delta^1$-Pregnane-3,20-dione(1) | 40 | 8.9 | 9.2 | 0.60 | -0.217 | $3.0\times10^5$ | 590 |
| 3,20-Pregnanedione(2) | 12 | | | 0.067 | -2.9 | $9.7\times10^3$ | 19 |
| $\Delta^{1,4}$-Androstadiendione(3) | 35 | 10.0 | 9.8 | 0.13 | -1.9 | $2.0\times10^4$ | 41 |
| 2-Methyl-1,4-Naphthoquinone(4) | 35 | 12.3 | 12.7 | 0.27 | -1.1 | $9.1\times10^4$ | 240 |
| 2-Phenyl-1,3-Indanone(5) | 62 | 10.9 | 11.2 | 0.21 | -0.66 | $1.6\times10^5$ | 370 |
| p-Benzoquinone(6) | 64 | 14.6 | 15.2 | 0.11 | -1.9 | $2.1\times10^4$ | 67 |
| 1,4-Cyclohexanedione(7) | 28 | 14.7 | 15.0 | 0.20 | -1.2 | $7.8\times10^3$ | 25 |

[a] Reaction conditions: 1.0 mmole $Cp_2TiCl_2$ in 25.0 ml chloroform added to a rapidly stirred (23,000 rpm no load) solution containing 1.0 mmole dioxime and 2.0 mmole NaOH in 25.0 ml water.

[b] Solubility of product in 1-methylimidazole at 25°C.

[c] Determined in 1-methylimidazole at 25°C.

TABLE 2

Trends as a Function of Various Parameters (Using the Numerical Designations Given in Table 1)

| | |
|---|---|
| Yield (decreasing) | 6 > 5 > 1 > 3 ≈ 3 > 7 > 2 |
| Chain Length (decreasing) | 1 > 5 > 4 > 6 > 3 > 7 > 2 |
| Steric (increasing) | 6 ≈ 7 > 4 ≈ 3 > 1 ≈ 2 > 5 |
| Nucleophilicity of Oxime (decreasing) | 6 ≈ 4 > 3 > 1 > 5 > 7 ≈ 2 |
| Product Solubility (decreasing; in 1-methylimidazole) | 1 > 4 > 5 ≈ 7 > 3 ≈ 6 > 2 |
| Size (decreasing) | 1 ≈ 2 > 3 > 5 ≈ 4 > 7 ≈ 6 |

be a general correlation between product average chain length and product yield and the factor of nucleophilicity of the oxime emphasizing a reasonable correlation where both yield and chain length growth are favored by a more nucleophilic oxime. There also exists an even better fit of chain length with polyoxime solubility. This also is reasonable if product insolubility is in fact an important factor in determining polyoxime chain length. (It must be noted that the solubility trend is for 1-methylimidazole and not the polymerization system.)

Elemental analyses for nitrogen and hydrogen were generally consistent with expected (calculated) values. Values found for carbon were typically 30-40% lower than expected. (Elemental analyses of products of $Cp_2TiCl_2$ and $\Delta^{1,4}$-androstadiendioxime, %C=71.0 calc., 39.8 found; %H-7.0 calc., 5.6 found; %N-5.7 calc., 4.5 found; 2-methyl-1,4-naphthoquinone dioxime, %C-66.7 calc., 44.8 found; %H-4.8 calc., 3.8 found; %N-7.4 calc., 4.8 found; 2-phenyl-1,3-indanone-70.1% calc., 57% found; %H-4.7 calc., 4.2 found; %N-6.5 calc., 8.3 found; b-benzoquinone diocime-%C=61.2 calc., 42.2 found; %H-4.5 calc., 4.0 found; %N-8.9 calc., 9.9 found). Other workers have also found poor elemental analysis results to be typical of Group IVB metallocene containing polymers. It is thought that this behavior is due, at least in part, to the moderate to good high (>1000°C) temperature stability of the thermal degradation residue of the polymers. Elemental analyses for titanium were in agreement with expected values based on form II (Table 1).

Infrared spectral bands characteristic of the cyclopentadienyl, Cp, moiety from the metallocene typically occur at 1440, 1010, and 830 $cm^{-1}$ [15]. The presence of the Cp moiety in the IR spectra of most of the polyoximes cannot be unambiguously identified as some of the dioxime monomers have bands at about 1440, 1010, and/or 830 $cm^{-1}$, which mask the major contributions from the Cp moiety.

All of the polyoxime products exhibited bands characteristic of the dioxime monomer used. For instance, IR spectra of the condensation product of 2-methyl-1,4-naphthoquinone dioxime and $Cp_2TiCl_2$ shows bands at 1430 and 1010 $cm^{-1}$ characteristic of the Cp moiety. The region at about 830 $cm^{-1}$ which is also characteristic of the Cp moiety is masked by a medium to strong band at 820 $cm^{-1}$ derived from the dioxime itself. A strong broad band is observed in both dioxime monomer and polyoxime product at about 3600 to 3100 $cm^{-1}$. This was believed to be due to the presence of O-H stretching [15] in the dioxime. This assignment appears to be incorrect as the strong band from 3600 to 3100 $cm^{1}$ appears in the IR spectra of the polyoxime. A salt of the dioxime monomer was made [5]. Inspection of the resulting IR spectra showed the strong broad peak to be present. The following are bands present in the polyoxime product; Bands at about 2980 to 2900 $cm^{-1}$ which are attributed to the presence of aliphatic C-H (stretching) groups; Bands at about 1630 to 1600 $cm^{-1}$ are characteristic of C=N stretching; Bands at about 1020 to 950 $cm^{-1}$ are characteristic of N-O stretching; Bands at 820, 770, and 700 $cm^{-1}$

are characteristic of the presence of disubstituted benzene moieties; Other bands present in both monomer and polymer appear at 1385, 1350, 1315, 1270, 1240, and 895 cm$^{-1}$. A new non-assigned band appears at 495 cm$^{-1}$ in the polyoxime product. Thus, the presence of components from each reactant is indicated by the infrared spectrum of the product.

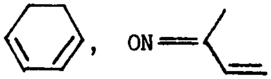
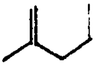
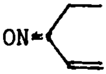
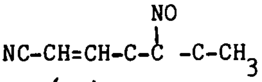
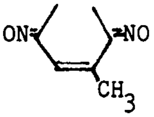
Two polyoxime products were studied using coupled thermogravimetric-mass spectroscopy, TG-MS. Briefly, as the TG temperature increases, volatile components resulting from sample degradation are carried, employing helium gas, into the MS, resulting in a mass spectrum characteristic of the evolved fragments. Mass spectrum were recorded for each 8C° increment of temperature from ambient to about 900°C.

The product from 2-methyl-1,4-naphthoquinone dioxime exhibits a weight loss beginning at 40°C with an almost constant rate of weight loss to 230°C resulting in a total weight loss of about 10% of the sample weight. This is followed by a more rapid weight loss (about 6%) from 230°C to 285°C. From 285°C to 900°C the weight loss (about 27%) was almost constant. The degradation occurring at about 230°C to 285°C gave volatile products which yielded 23 major mass-to-charge, m/e, peaks all present in the scan at 250°C (Table 3; Normalized intensity > 1; normalized to mass 28 (nitrogen) = 100.0%) The masses at 66, 65, 39, 40, 38, 62, 31, and 37 amu and the respective intensities of these mass peaks is consistent with the standard [16] mass spectra of the Cp moiety.

Mass peaks characteristic of the Cp moiety reach a maximum at 250°C, then decrease ending by 500°C. Thus, masses characteristic of the Cp moiety are the major components of the initial thermal degradation occurring from about 100°C to 500°C. These mass peaks then decrease as temperature continues to increase, and larger mass fragments indicative of the dioxime moiety appear.

# TABLE 3

TG-MS Data from the Polycondensation Product of 2-Methyl-1,4-naphthoquinone dioxime and $Cp_2TiCl_2$.

| Mass Peak (m/e) | Possible Assignments | Normalized Intensity at ($^oC$) | | | |
|---|---|---|---|---|---|
| | | 127.3 | 181.0 | 250.0 | 472.3 |
| 20 | | 1.501 | | | |
| 26 | HC = CH | | | 1.355 | |
| 29 | | 1.280 | | | |
| 31 | (Cp) | | | 2.576 | |
| 38 | (Cp) | | | 1.914 | |
| 39 | (Cp) | | 1.908 | 8.289 | |
| 40 | (Cp) | | 4.297 | 10.156 | |
| 41 | $CH_3$-C-$CH_2$ | | | | 2.952 |
| 43 | O-N=CH | 1.721 | | | 1.611 |
| 50 | HC-C=C-CH | | | 1.269 | |
| 51 | HC=C-CH=CH | | | 1.838 | |
| 52 | HC=CH-CH=CH | | | 1.374 | |
| 55 | ON=C-CH | | | | 4.232 |
| 56 | O-N=C-$CH_2$ | | | | 1.524 |
| 57 | O-N=CH-$CH_2$ | 1,228 | | | |
| 61 | HC=C-C=CH=CH | | | 1.374 | |
| 63 | HC=CH-CH-C-C | | 1.339 | 3.685 | |
| 65 | (Cp) | 1.186 | | 10.894 | 1.028 |
| 66 | (Cp) | 2.760 | 4.769 | 22.689 | |
| 67 | | | | 1.137 | 1.994 |
| 68 | O-N=C-HC-CH | | | | 2.186 |
| 69 | O-N=C-C-$CH_3$ | | | | 1.341 |
| 77 | ONC-C-CH-CH-C | | | | 1.071 |
| 79 | | | | | 2.552 |
| 80 |  | | | 3.335 | |
| 81 |  | | | | 2.386 |
| 91 | | | | | 2.404 |
| 94 |  | | | | 2.186 |
| 95 | | | | | 1.620 |
| 105 | | | | | 2.334 |
| 107 | | | | | 1.193 |
| 117 | | | | | 1.742 |
| 121 |  $NC\text{-}CH{=}CH\text{-}C\text{-}\overset{NO}{C}\text{-}C\text{-}CH_3$ | | | | 1.959 |
| 131 |  | | | | 1.054 |

The absence of significant (normalized intensities > 1) masses at 47 (Ti), 79 ($TiO_2$), 112 (CpTi), and 170-180 ($Cp_2Ti$) indicates titanium containing, volatile species are not present, which is consistent with the metal remaining within the residue.

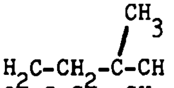
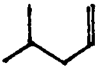
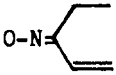
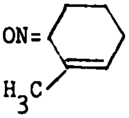
The polyoxime derived from $\Delta^1$-pregnone-3,20-dioxime exhibits a constant weight loss of about 10% over the temperature range of ambient to 265°C. A comparatively rapid degradation occurs from 265°C to 310°C resulting in a weight loss of 11%. Weight loss is again almost constant to 470°C (≈10%) and is followed by another more rapid degradation of 8% to 525°C. Weight loss from 525°C to 900°C is again almost constant reulting in a total weight loss of 56%. The relative ion intensity reached a maximum at about 260°C within the temperature range of ambient to 265°C. The MS scan at 160°C showed only three fragments with normalized intensities greater than one. All these are indicative of the presence of the Cp moiety (Table 4; e/m = 66, 65, 40) indicating that as in the case of the previously described polyoxime the Cp moiety is the initial species released during thermal degradation.

The degradation from 265°C to 310°C yielded 19 major mass peaks all present in the scan at 278°C (Table 4). Again, masses at 66, 65, 39, 40, 38, 62, 31, and 37 were present, indicating a major source of degradation products in this range was the Cp moiety. Masses at 80, 63, 44, 41, 32, and 29 are also present, and can be tentatively assigned to fragments of the steroid moiety (Table 4).

During the third range of degradation (470°C-585°C), masses indicative of the Cp moiety have all but disappeared. Larger fragments (81, 91, 105, 117, 121, 131) have appeared and can be tentatively assigned to larger fragments of the progesterone dioxime moiety (Table 4).

TABLE 4

TG-MS Data from the Polycondensation Product of a Δ-pregnane-3,20-dione dioxime with $Cp_2TiCl_2$

| Mass Peak (m/e) | Possible Assignment | Normalized Intensity at (°C) 158.3 | 278.0 | 342.3 | 472.7 |
|---|---|---|---|---|---|
| 27 | $H_2C-CH$ | | 1.847 | | 2.160 |
| 29 | Cp | | 1.339 | | |
| 37 | | | 1.129 | | |
| 38 | Cp | | 1.549 | | |
| 39 | | | 5.758 | | |
| 40 | Cp | 1.808 | 9.250 | 2.456 | |
| 41 | HC=NO, $H_2C-CH_2-CH$ | 4.122 | 3.202 | 2.952 | |
| 43 | | | | | 1.611 |
| 55 | $H_2C-CH_2-C-CH_3$ | | | | 4.232 |
| 56 |  , $ONC-CH_2$ | | | 1.524 | |
| 63 | | | 1.129 | | |
| 65 | Cp | 1.648 | 6.852 | | 1.028 |
| 66 | Cp | 4.276 | 14.221 | 1.577 | |
| 67 | $H_2C-CH_2-C-CH-CH_2$ | | | 1.994 | |
| 68 |  $H_2C-CH_2-\overset{CH_3}{C}-CH$ | | | | 2.186 |
| 69 | $ON-C-CH_2-CH$ | | | | 1.341 |
| 77 | $ON-C-CH_2-CH$ | | | | 1.071 |
| 79 | $HC-C-CH_2-CH_2-CH-CH$ | | | 1.193 | 2.552 |
| 80 | | | 1.146 | | |
| 81 |  , $ON=C-CH=C-CH_2$ | | | | 2.386 |
| 91 | | | | | 2.404 |
| 94 |  | | | | 2.186 |
| 95 | | | | | 1.620 |
| 105 | | | | | 2.334 |
| 107 | | | | | 1.193 |
| 117 | | | | | 1.742 |
| 121 |  | | | | 1.959 |
| 131 | | | | | 1.054 |

Again, no mass peaks indicative of titanium containing fragments (47, 79, 170-180) are present, consistent with the metal remaining within the residue.

An interesting mass peak of 343 amu was observed at a temperature of about 550°C. The molecular weight of the $\Delta^1$-pregnan-3,20-dioxime moiety is 344.5 amu. Thus, the peak observed is consistent with the dioxime moiety stripped of its two acidic hydrogens, as it would exist in the polyoxime backbone.

Reactions were attempted excluding either monomer, dioxime or $Cp_2TiCl_2$ with all other reaction conditions held constant. The reactions resulted in clear solutions as compared to the gelatinous or foamy material formed when both monomers are present.

In summation, the evidence presented within this section is consistent with the formation of polyoximes of the form II. Control reactions indicate that the product is the result of both monomers being present. TG-MS data show the presence of the Cp moiety from the metallocene in the product and is consistent with the presence of the dioxime moiety. Elemental analyses for

the presence of the dioxime moiety. Elemental analyses for

hydrogen, nitrogen, and titanium are consistent with expected values for products of the form II. IR data show the presence of the dioxime moiety in the respective polyoxime product and for many compounds, also the presence of the $Cp_2M$ moiety.

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