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AUTOMATED THERMAL DEGRADATION STUDIES ON SOLID σ-ORGANOTRANSITION METAL COMPLEXES: DIMETHYL-TITANOCENE, -ZIRCONOCENE AND -HAFNOCENE

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Summary

The volatile products resulting from the solid-state thermal decomposition of the dimethylmetallocenes $Cp_2M(CH_3)_2$ (M = Ti, Zr, Hf) have been characterized by gas chromatography—mass spectrometry. Analogous studies utilizing $Cp_2Ti(CD_3)_2$ have provided evidence for the various degradative pathways involved in these thermolysis processes.

Introduction

Ever since the original synthesis of dimethyltitanocene, $Cp_2Ti(CH_3)_2$, in 1956 by Piper and Wilkinson [1], it has been known that this remarkable organotitanium compound decomposes rapidly and spontaneously on heating, apparently in an autocatalytic manner. Clauss and Bestian [2] subsequently prepared dimethyltitanocene in higher yield, but noted that this substance decomposed rapidly in light and even slowly in the dark at room temperature. During the course of some recent photolysis studies on dimethyltitanocene [3], we have likewise observed that freshly prepared samples of this material on occasion decompose autocatalytically, even when stored under argon in the absence of light and at low temperatures.

In order to investigate the nature of this degradation process and to determine the products of decomposition, we have undertaken a detailed thermoanalytical study of pure $Cp_2Ti(CH_3)_2$ and its deuterated analog, $Cp_2Ti(CD_3)_2$. The thermal degradation of several other σ-bonded organotitanium compounds have recently been reported [4—6], but thermolysis studies on $Cp_2Ti(CH_3)_2$ have been limited to solution studies, in which methane was apparently the sole organic product [7].

We have also carried out similar studies on the zirconium and hafnium analogs $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$ whose thermal degradation processes do not appear to include the autocatalytic decomposition mode and are thus more straightforward.

Two novel and complementary thermal degradation techniques have been employed in this study, enabling the reactions to be continually monitored with respect to the evolved volatile products, and these species to be subsequently identified by gas chromatographic and mass spectral analysis.

Experimental

Starting materials

All reactions were carried out under an anhydrous, oxygen-free argon atmosphere, using Schlenk-type glassware and techniques. Pentane and ethyl ether were refluxed over and distilled from $LiAlH_4$. $Cp_2Ti(CH_3)_2$ was prepared by a modification of a literature procedure [2]. Two equivalents of CH_3Li in ethyl ether solution were added dropwise with stirring to one equivalent of Cp_2TiCl_2 in ethyl ether solution at −78°C. After the addition, the reaction mixture was allowed to warm to ca. −20°C over a period of 30 min, and the solvent was then evaporated at this temperature. The residue was extracted with a minimum amount of pentane and the extracts were filtered over a frit. On cooling the filtrate to −78°C, large orange crystals of $Cp_2Ti(CH_3)_2$ separated. These were subsequently dried in vacuo; yield 80—85%. $Cp_2Ti(CD_3)_2$ was prepared in an analogous manner from Cp_2TiCl_2 and CD_3Li. The latter reagent was readily prepared from CD_3Br and lithium metal in ethyl ether solution. The CD_3Br (99.5% purity) was obtained from Stohler Isotope Chemicals Co. Since both $Cp_2Ti(CH_3)_2$ and $Cp_2Ti(CD_3)_2$ are very light-sensitive and thermally unstable, they were either used immediately or stored under argon at −78°C in the dark. $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$ were prepared according to a literature procedure described earlier by one of us [8].

Thermal analysis

Two complementary controlled thermal degradation and pyrolysis techniques were employed, the instrumentation and procedures being as follows:

The MP 3 Thermal Chromatograph (Spex Industries, Methuchen, N.J.) is a pyrolysis unit which combines evolved gas analysis and gas chromatographic analysis. The sample (ca. 5 mg) was placed in a quartz tube (1/4 inch o.d.) through which helium gas was continually passed. A ceramic furnace surrounds the horizontally placed sample tube; the furnace has available programmable heating rates from 4° to 40° per min. Evolved gases from sample decompositions were swept in the helium stream through both flame ionization and thermal conductivity detectors, giving profiles of detector response to total evolved gases as a function of temperature. Volatiles were then trapped automatically and after the thermal process was complete, the total trapped gas mixture was swept onto an internal gas chromatographic column as a narrow band and the components separated, thermal conductivity and flame ionization detection again being employed. This procedure enabled a full thermal history of a sample with temperature to be obtained with respect to evolved volatiles, and is thus complementary to thermal gravimetric analysis in the information obtained.

The Pyroprobe 100 (Chemical Data Systems, Oxford, Pa.) was used alternatively in the identification of evolved volatiles in the gas chromatographic—mass spectral mode. The method was developed to eliminate the need for trapping individual component peaks from the Thermal Chromatograph prior to mass spectral analysis. The procedure involved the solid sample (ca. 5 mg) being placed in a small quartz tube, open at each end, and placed in turn within the coil of the pyrolysis probe inserted into the injection port of a gas chromatograph—mass spectrometer system. While this probe is customarily employed for solid sample pyrolysis by rapid heating of the coil, in this case the heated injection port of the gas chromatograph was used to supply heat for the thermal decomposition of the sample. The temperature was set 10—15° higher than that determined for the first sharp decomposition maximum as determined by the MP 3 system. Under these conditions, decomposition occurred within a few seconds and all evolved volatiles were swept onto the gas chromatographic column with minimal band spreading. The effectiveness of the method for handling a sample showing such a rapid decomposition as $Cp_2Ti(CH_3)_2$ was shown by the fact that identical chromatograms were obtained with both the probe method and the thermal chromatograph.

Gas chromatography

In both the Thermal Chromatograph and GC/MS systems, columns employed were 1/8 inch o.d. stainless steel packed with Porapak P or Q (Waters Associates, Milford, Mass.) or Chromosorb 102 (Johns Manville, Denver, Colo.) porous polymer substrates. A Perkin—Elmer 990 gas chromatograph was employed in the GC/MS study.

Mass spectrometry

A Hitachi—Perkin—Elmer RMU 6L single-focusing mass spectrometer operating at ionizing voltages of 80 eV or 16.5 eV was employed, interfaced to the gas chromatograph with a Watson—Biemann separator.

Results and discussion

Gas evolution profiles were recorded on the Thermal Chromatograph, the sample temperature being programmed from ambient temperature to ca. 650°C at 40° per minute. Five mg samples were heated in a flowing helium gas stream, flame ionization detection being employed for detection to gain maximal sensitivity. Figure 1 shows the profiles for the three dimethylmetallocenes.

In the case of $Cp_2Ti(CH_3)_2$ (a), very rapid and extensive gas evolution was noted between 120° and 125°C, consistent with the autocatalytic behavior previously noted, the sample changing from orange to black. The major evolution of volatiles for the complete decomposition of $Cp_2Ti(CH_3)_2$ occurs in this narrow range, as is evident from the attenuation change of more than 1000 shown in Fig. 1. Subsequent slow thermal decomposition of the residue was noted to about 550°C, the shape of the profile being reproducible from sample to sample. The zirconium and hafnium analogs $Cp_2Zr(CH_3)_2$ (b) and $Cp_2Hf(CH_2)_2$ (c) show substantially different degradation, the autocatalytic decomposition being absent, although a major breakdown does occur in each case with a maximum in the 155—165°C region. The amount of volatiles evolved in this early peak

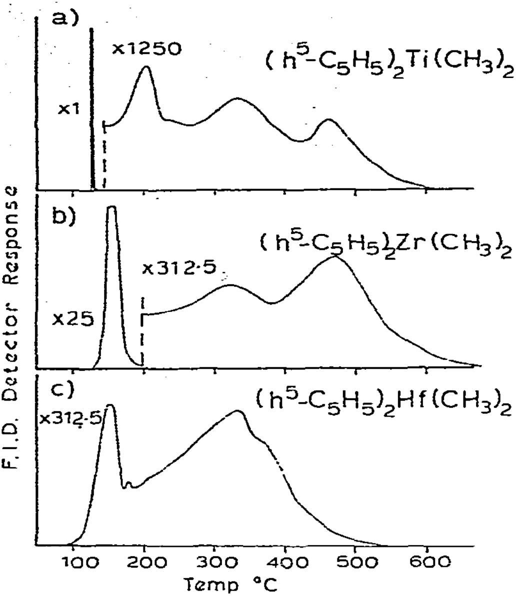

Fig. 1. Gas evolution profiles for dimethylmetallocenes, obtained on the MP 3 Thermal Chromatograph. Five mg samples, temperature programmed at 40° per minute, flame ionization detection, sensitivities as noted.

from the zirconium compound is much less than in the case of the titanium analog; for the hafnium compound the relative amount of volatiles evolved in this region is even smaller. Similar subsequent slow thermal degradation of the compounds is again evident up to ca. 600°C. For the latter compounds, the total volatiles produced in the early rapid and later gradual degradation processes are in the approximate ratios (measured as areas) of 5 to 1 for $Cp_2Zr(CH_3)_2$ and 1 to 5 for $Cp_2Hf(CH_3)_2$. This is in contrast to the ratio of 25 to 1 for $Cp_2Ti(CH_3)_2$.

Although there is clearly a substantial difference in the degradation of $Cp_2Ti(CH_3)_2$ from that of its zirconium and hafnium analogs, since all show a rapid low-temperature degradation, this region could be readily analyzed by the Pyroprobe GC/MS technique already described. Injection port temperatures were set at 145°C for $Cp_2Ti(CH_3)_2$ and at 180—195°C for $Cp_2Zr(CH_3)_2$ and $CpHf(CH_3)_2$. Volatiles were evolved over a period of a few seconds and were identified after GC separation by mass spectral fragmentation patterns and by GC retention data comparisons with standards. As noted previously, gas chromatograms produced in this fashion showed identical component peaks to those obtained on the thermal chromatograph.

The thermal decomposition products of $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$ are relatively simple and are explicable by direct fragmentation of the molecules. In each case, the early decomposition produces only methane and cyclopentadiene in the approximate ratios of 1 to 4 for both $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$. There is also evidence for the formation of very small amounts of methylcyclopentadiene from both thermolyses (in each case less than 0.1% relative to cyclopentadiene). Retention times on two independent columns agree with methylcyclopentadiene as the reference compound, although the level and gas chromatographic resolution is too low for positive mass spectral confirmation. In the thermolyses of all three dimethylmetallocenes, chromatography on the Thermal Chromatograph indicates that the only identifiable volatile species to be produced between ca. 200° and 600°C was cyclopentadiene, which was shown to be evolved continuously over this range.

As might be predicted by the markedly different behavior of $Cp_2Ti(CH_3)_2$, the thermal decomposition of this compound was notably more complicated, giving rise to a variety of different products which were identified and quantitated. Gas chromatography—mass spectrometry was performed on the degradation products from both $Cp_2Ti(CH_3)_2$ and $Cp_2Ti(CD_3)_2$, and the data is summarized in Table 1, all products being produced in the initial very rapid autocatalytic decomposition step. For the deuterated compound, mass spectra for the gaseous products were obtained at a low ionization energy (ca. 16.5 eV). This minimized fragmentation of the molecular ions, allowing relative ratios of isotopic species to be determined. Thus a pure sample of CD_3H run at 16.5 eV gave ion ratios for *m/e* 19:18:17:16 of 10:1:0:0 in comparison with 10:4:5:1 obtained at 80 eV.

In order to confirm that no hydrogen—deuterium exchange occurred within the gas chromatographic column itself or in the heated interface to the mass spectrometer, a pure (99% deuterated) sample of CD_4 was gas chromatographed and shown to produce a mass spectrum (at 16.5 eV) completely consistent with the specified D/H ratio (*m/e* 20:19 ratio of 97:3). No evidence of deuterium hydrogen exchange was observed and an identical spectrum resulted from introduction of the CD_4 sample through the conventional gas inlet system of the mass spectrometer. Additional evidence against H—D exchange within the mass spectrometer source to form CD_3H was also gained by observation of an identical *m/e* ratio at 20:19 for a CD_4 spectrum obtained at 80 eV.

The following conclusions can be drawn from the data in Table 1. The formation of both CD_3H and CD_4 (3 : 1 ratio) in the thermolysis of $Cp_2Ti(CD_3)_2$ suggests that methane, the major product, is formed by abstraction of a hydrogen atom both from the cyclopentadienyl rings and from the sceond methyl substituent. Similar results and conclusions have recently been reported by Bockel, Teuben and De Liefde Meijer [6] concerning the thermal decomposition of solid Cp_2TiPh_2 and various deuterated analogs. The presence of an additional minor peak at *m/e* 18 in the spectrum of methane produced in this process could possibly arise from further reaction of a transient carbenoid complex such as

TABLE 1

THERMAL DECOMPOSITION PRODUCTS FROM $Cp_2Ti(CH_3)_2$ AND $Cp_2Ti(CD_3)_2$

Compound evolved	Relative proportion	Deuteration of products from $Cp_2Ti(CD_3)_2$
Methane	60	CD_3H/CD_4 3:1
Ethylene	10	C_2H_4 exclusively
Ethane	1	$C_2D_2H_4$, with traces of C_2DH_5 and C_2H_6
Cyclopentadiene	30	C_5H_6 exclusively
Methylcyclopentadiene	3	$C_5H_5CD_3$ exclusively

$Cp_2Ti{=}CH_2$ [9], although it could also be due to fragmentation of the CD_4 (*m/e* 20) or CD_3H (*m/e* 19) produced, as discussed above.

In contrast to the results of Boekel et al. [6], who obtained RH as the only volatile product in essentially quantitative yield in the thermolysis of Cp_2TiR_2 (R = Ph, CH_2Ph), we have detected at least four other organic products in the thermal decompositions of $Cp_2Ti(CH_3)_2$ and $Cp_2Ti(CD_3)_2$. Cyclopentadiene was the second major volatile compound produced, and the absence of any deuterated cyclopentadienes (mass peaks > *m/e* 66) in the thermolysis of $Cp_2Ti(CD_3)_2$ indicates that the cyclopentadienyl rings do not abstract hydrogen atoms from the methyl ligands.

Ethylene was isolated and identified as approximately 10% of the total volatiles evolved in the degradation of $Cp_2Ti(CH_3)_2$. Most remarkably, the mass spectra of the ethylene formed from the thermolysis of $Cp_2Ti(CD_3)_2$ shows it to be solely C_2H_4 (*m/e* 28), and peaks due to deuterated ethylenes are completely absent. Thus, the ethylene evolved in the thermal decomposition of $Cp_2Ti(CH_3)_2$ must be derived exclusively from thermal degradation of the cyclopentadienyl ligands. Although ethylene was not reported in the thermal decompositions of Cp_2TiPh_2 or $Cp_2Ti(CH_2Ph)_2$, Boekel et al. did note the total destruction of the Cp_2Ti moiety in their studies, and hydrogen abstraction by a methyl substituent in the thermolysis process could conceivably lead to further breakdown of the cyclopentadienyl ring.

Although it is produced as only a very minor product, ethane is also formed in the thermal degradation of $Cp_2Ti(CH_3)_2$ and $Cp_2Ti(CD_3)_2$. Studies using the latter deuterated analog indicated that ethane of *m/e* 32, coresponding to $C_2D_2H_4$, was the major product, together with lesser amounts of C_2DH_5 (*m/e* 31) and C_2H_6 (*m/e* 30). These products likewise indicate a complex degradative pathway, in this case involving both the methyl and cyclopentadienyl substituents. It is noteworthy that the thermolysis of $Cp_2Ti(CD_3)_2$ produced no C_2D_6 (*m/e* 36), which might be expected to be formed if coupling of methyl free radicals from homolytic cleavage of the methyl—titanium σ-bond were a straightforward process, as implied by Razuvaev et al. [7] in their solution studies involving $Cp_2Ti(CH_3)_2$.

Finally, methylcyclopentadiene was also found to be a minor but reproducible product from the thermolysis of $Cp_2Ti(CH_3)_2$, as well as from the zirconium and hafnium analogs mentioned above. The formation of methylcyclopentadiene of *m/e* 83 ($C_6D_3H_5$) in the thermal degradation of $Cp_2Ti(CD_3)_2$ indicates that the product is produced by a simple combination of both methyl and cyclopentadienyl substituents in the thermolysis process.

While a number of the products obtained in the present study and in that of Boekel et al. [6] on the thermal decompositions of Cp_2TiR_2 systems are explicable in terms of homolytic cleavage of carbon—titanium σ-bonds and the formation of organic radicals, it seems questionable if "free" radicals are actually formed in these solid-state thermal decompositions. On the other hand, intermediate species possessing radical-like character, possibly of the type suggested by Waters et al. [5], remain a distinct possibility. Additional studies are planned to elucidate these thermal degradative pathways more fully. Furthermore, the thermoanalytical techniques described in this paper should prove generally applicable to the thermolyses of a wide variety of organometallic compounds, metal chelates, etc., and such studies are currently in progress.

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References

1 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
2 K. Clauss and H. Bestian, Liebigs Ann. Chem., 654 (1962) 8.
3 H. Alt and M.D. Rausch, J. Amer. Chem. Soc., 96 (1974) 5936.
4 H. Bürger and H.J. Neese, J. Organometal. Chem., 21 (1970) 381.
5 J.A. Waters, V.V. Vickory and G.A. Mortimer, J. Organometal. Chem., 33 (1971) 41.
6 C.P. Boekel, J.H. Teuben and H.J. De Liefde Meijer, J. Organometal. Chem., 81 (1974) 371.
7 G.A. Razuvaev, V.N. Latyaeva and L.I. Vyshinskaya, Dokl. Akad. Nauk SSSR, 159 (1964) 383.
8 E. Samuel and M.D. Rausch, J. Amer. Chem. Soc., 95 (1973) 6263.
9 F.S. D'yachkovskii and N.E. Khrushch, Zhur. Obshch. Khim., 41 (1971) 1779.