JOURNAL OF CATALYSIS **105**, 249–253 (1987)

Modified Chromium(III) Acetate Used in the Polymerization of α-Olefins

A chemically modified form of chromium acetate obtained by refluxing commercial chromium(III) acetate with a mixture of acetic anhydride and acetic acid has recently been reported in the patent literature (*1*). This new form of chromium acetate in combination with $AlEt_2Cl$ was found to show extremely high activity in the polymerization of ethylene. Other workers have since successfully used the catalyst for both the homopolymerization of propylene and the random copolymerization of ethylene and propylene (*2, 3*). However, little is known about the structure of the modified chromium acetate or the active species involved in the catalytic system.

We now report the results of a series of chemical and physical investigations on the modified chromium acetate with the view of throwing light on its structure and the role of acetic anhydride in its formation.

Preparation of samples. The modified chromium(III) acetate was prepared by three different methods:

(a) Ten grams of commercial acetate [samples from two sources, viz., (A) ex Hopkin & Williams, England, and (B) ex Yoneyama, Osaka, Japan] was refluxed with a mixture of 60 ml acetic anhydride and 40 ml glacial acetic acid for 4 h. The resulting bright green and nonsticky fine powdery product was collected on a suction filter and dried over sodium hydroxide pellets.

(b) Ten grams of chromium acetate and 100 ml of glacial acetic acid were refluxed overnight. The green product formed was collected and dried as in (a).

(c) Ten grams of chromic chloride hexahydrate (Merck) was refluxed with 100 ml of acetic acid until the evolution of HCl gas was complete. The green solution was evaporated and refluxed with fresh glacial acetic acid until the product was formed.

The products from these methods showed identical IR spectra. Undoubtedly the modified acetate can be prepared most speedily by applying the conditions stated in the patent literature which specifically made use of $Cr(CH_3COO)_3H_2O$, acetic anhydride, and acetic acid. However, we have shown that the same product may be obtained without the use of acetic anhydride, although a longer refluxing time is required. The fact that the same product is obtainable from chromic chloride hexahydrate and glacial acetic acid suggests that the starting material is not critical; any compound which can generate chromium(III) acetate *in situ* may be used as the starting material.

In contrast to the starting materials which are readily soluble in water, the product is insoluble in solvents ranging from the very polar water to the nonpolar hydrocarbons.

Elemental analysis. The chromium content was determined spectrophotometrically as outlined by Vogel (*4*). Elemental analysis of carbon and hydrogen was carried out by the Australian Mineral Development Laboratories, Australia. Complex A found: Cr, 20.6; C, 21.2; H, 3.5 (calculated for $Cr(CH_3COO)_3H_2O$: Cr, 21.1; C, 29.2; H, 4.4). Complex B found: Cr, 27.3; C, 17.5; H, 3.7 (calculated for $Cr(CH_3COO)_2OH$: Cr, 26.7; C, 12.8; H, 3.7). Product found: Cr, 21.6; C, 29.7; H, 4.0 (calculated for

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$Cr(CH_3COO)_3$: Cr, 22.7; C, 31.4; H, 3.9). While the Cr contents of the samples agree well with the calculated values, the results of the C and H are not satisfactory or reproducible, especially in the case of complexes A and B. Such a discrepancy could arise either because of inherent difficulties in the determination of C and H in metallic complexes or because the samples contain impurities.

Differential scanning calorimetry (DSC). DSC scans were recorded on a Perkin-Elmer DSC-2C instrument. The temperature scale was calibrated against water (273.15 K) and indium (429.78 K). Samples (10–15 mg) encapsulated in standard aluminum pans were scanned at a rate of 20 K/min. Figure 1 shows the thermograms of the starting chromium acetate A and B and the final product. All the three compounds have undergone irreversible thermal decomposition as confirmed by repeating the heating scans. In each case all the peaks became unobservable.

Sample A displays two broad endotherms with maxima at 373 K and 556 K. The first is probably due to the initial loss of coordinated H_2O while the second is due to decomposition. On the other hand, Sample B has two endotherms at 386 K and 472 K, followed by an exotherm at 552 K. Undoubtedly, both the starting compounds are very different structurally and chemically.

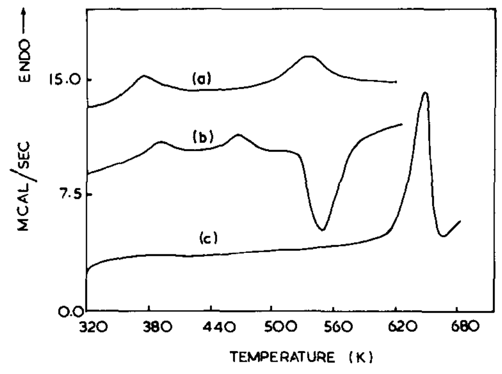


FIG. 1. DSC scans. (a) Sample A (chromium acetate from Hopkin & Williams); (b) Sample B (chromium acetate from Yoneyama); (c) modified product.

The product is thermally stable up to 570 K. It decomposes rapidly above 580 K as indicated by the sharp endotherm at 620 K. The fact that there is no endotherm around 373 K confirms the absence of any coordinated H_2O. Its exceptional thermal stability, together with its insolubility in all common solvents, suggests that it is probably polymeric in structure.

Magnetic susceptibility. The effective magnetic moment of a metal complex obeying the Curie Law is given by $\mu_{\text{eff}} = 2.84\sqrt{\chi_M T}$ B.M., where χ_M is the molar susceptibility after correcting for the diamagnetic effect of ligands. This in turn may be related to n, the number of unpaired electrons in the molecule. The spin-only formula is given by $\mu_{\text{eff}} = \sqrt{n(n+2)}$ B.M.

The bulk magnetic susceptibilities of the initial chromium acetate and the modified product were determined by the Gouy method (*5*) at 298 K. The oxidation state of both the starting chromium acetate and the product have been confirmed to be Cr(III) by ESR spectroscopy (*2, 3*).

For a monomeric Cr(III) complex in an octahedral environment, the effective magnetic moment is expected to be in the region of 3.7–3.9 B.M. (*6*), corresponding to that of a d^3 system with three unpaired electrons. The μ_{eff} of the product was found to be as low as 3.20 B.M. (with $n = 2.34$) which indicates extensive antiferromagnetic interactions among the neighboring Cr in the lattice, consistent with the nondiscrete nature of the complex.

Infrared (IR) spectroscopy. IR spectra were recorded on a Beckman Acculab 4 spectrometer. The samples were pressed into KBr pellets at about 2% w/w for the measurement. The spectra are shown in Fig. 2. Samples A and B show a broad band at 3000–3500 cm^{-1}, which indicates the presence of OH and H_2O in these two samples in accordance with their assigned empirical formulas. The absence of this peak in the spectrum of the product is consistent with the DSC results.

IR spectra of coordinated complexes

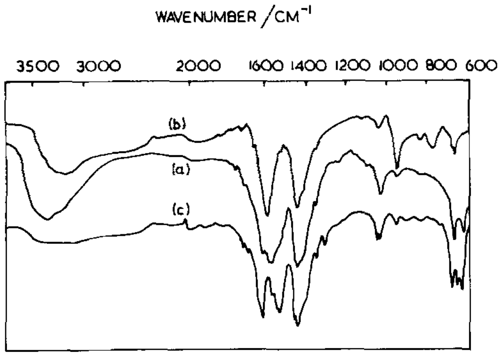


FIG. 2. Infrared spectra for (a) starting material from Hopkin & Williams (a); (b) starting material from Yoneyama (b); (c) modified product.

with acetate ligands have been extensively studied and reviewed (*7*, *8*). In general, the free acetate ion gives rise to two characteristic bands about 144 cm^{-1} apart. There is a strong antisymmetric band, $\nu_a(CO_2^-)$, at approximately 1560 cm^{-1}, and a weaker symmetric band, $\nu_s(CO_2^-)$, at approximately 1416 cm^{-1}. These bands are sensitive to the modes of coordination of the acetate group to metal ions. In the case of a unidendate complex, ν(C=O) is higher than $\nu_a(CO_2^-)$ while the ν(C—O) is lower than $\nu_s(CO_2^-)$. As a result the separation of the two ν(CO) is much larger than 200 cm^{-1}. On the other hand, in the chelating mode of coordination the opposite trend is observed; i.e., the separation is much smaller than 100 cm^{-1}. Finally, in the bridging mode, although both the ν(CO) bands may shift their positions, their separation is close to that of the free ion, in the range of 100–200 cm^{-1}.

Sample B appears to contain only bridging acetate groups on the basis of the separation between the two ν(CO) bands, being 130 cm^{-1}. In the case of Sample A, more than one type of coordinated acetate is apparent. It is certain that bridging groups are present. The peak at 1600 cm^{-1} may be attributed to the ν(C=O) band of the unidendate acetate although its ν(C—O) band is not clearly visible due to overlap. It must be pointed out that the H-O-H bending mode also gives rise to absorption around the same region. However, such absorption should be relatively very weak.

In the case of the product, the pair of peaks at 1320 and 1630 cm^{-1} (separation of 310 cm^{-1}) clearly demonstrates the presence of unidendate acetate. The peak at 1320 cm^{-1} was assigned to the ν_s(OCO) mode in preference to that at 1350 cm^{-1} (observed in all the three spectra) which has been assigned to the $\delta(CH_3)$ mode (*8*).

The peak at 1700 cm^{-1} is indicative of the presence of a small amount of free acetic acid (*7*). The two pairs of peaks at 1420 and 1540 cm^{-1} (separation 120 cm^{-1}) and 1450 and 1580 cm^{-1} (separation 130 cm^{-1}) clearly indicate the presence of two different bridging acetate groups. Alternatively, if the peaks at 1420 and 1580 cm^{-1} (separation 160 cm^{-1}) and the peaks at 1450 and 1540 cm^{-1} (separation 90 cm^{-1}) were paired, then it could be interpreted as both the bridging and chelating acetate being present. We shall discuss which combination is the more likely below.

Ethylene polymerization. One ethylene polymerization experiment was carried out to demonstrate the activity of the catalyst. 0.0235 g of the modified chromium acetate was transferred into a 250-ml reactor under nitrogen atmosphere; 79.3 ml benzene was added followed by 0.7 ml $AlEt_2Cl$ solution at a concentration of 1 mmol ml^{-1}. The mixture was degassed, then thermostated to 40°C and ethylene was introduced at a pressure of 100 kPa. The reactor was equipped with a stirrer set at 300 rpm and the polymerization was followed by recording the volume of monomer consumed. The reaction was terminated when a large amount of polymer was formed in the reactor and which prevented the stirrer from functioning properly.

Figure 3 summarizes the kinetics of the polymerization of ethylene. Using as little as 23.5 mg of the prepared product (Cr content about 5 mg), the catalyst was able to polymerize 1700 ml ethylene within 1 h. The activity of the catalyst system in-

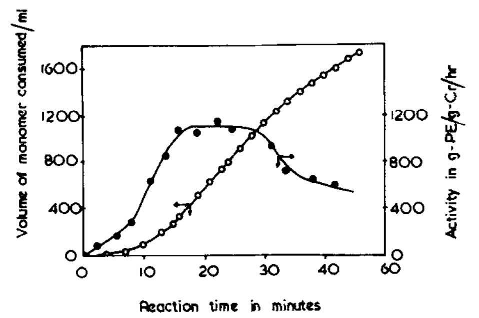


FIG. 3. Kinetics of polymerization of ethylene. Polymerization condition Al/Cr = 10. T = 40°C; monomer pressure 100 kPa.

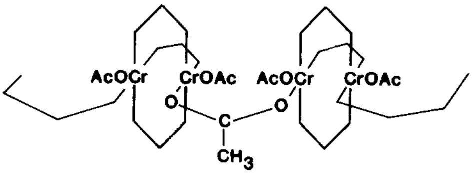
creased rapidly and reached a maximum of 1180 g polymer/g Cr/hr.

The role of acetic anhydride in the modification reaction. Comparing the empirical formulas of the starting chromium acetate A and the product suggests the loss of a water molecule during the activation process by acetic anhydride and acetic acid. The role of acetic anhydride or the acetic acid is not confined solely to dehydration. This was demonstrated by subjecting the hydrated chromium acetate to a variety of dehydration conditions. For instance, the $Cr(CH_3COO)_3H_2O$ was evacuated over P_4O_{10} in an Abderhalden drying pistol maintained at 100°C for a prolonged period of time. It was also refluxed in a variety of dehydrating solvents including 2,2-dimethoxypropane and triethyl-*ortho*-formate. In all these cases no trace of the green product could be detected. Thus the formation of the product involves structural changes in addition to dehydration.

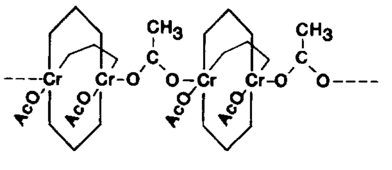
Structure of the modified chromium acetate. Structural determination by X-ray crystallography cannot be carried out due to difficulty in obtaining suitable single crystals of the modified acetate. However, based on the results of the other techniques described, a reasonable deduction of the structure of the complex can be attempted.

Elemental analysis has shown that the complex corresponds well to the empirical formula of $Cr(CH_3COO)_3$. Its insolubility in both polar and nonpolar solvents, coupled with its thermal stability, strongly suggests a polymeric structure such as **I** or **II**. Such structures containing pairs of Cr centers held closely by three bridging acetate groups would give rise to extensive antiferromagnetic interaction, as demonstrated by a remarkable drop in magnetic moment from the expected value of a monomeric Cr(III) complex.

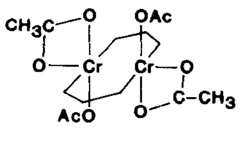
In addition, the IR spectrum agrees well with structure **I** or **II**, which contains both unidendate and bridging acetate groups. As pointed out earlier, the IR bands at 1450 and 1540 cm^{-1} may alternatively be considered as a pair to support the presence of a chelating acetate group. The only possible structure with unidendate, bridging as well as chelating acetate groups, which agrees with the empirical formula, is structure **III**. However, such a dimeric structure, with highly strained four-membered chelate rings, is not consistent with the observed



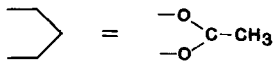
I



II



III



properties of the complex, especially its thermal stability.

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Received August 8, 1985