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Mössbauer Spectroscopy Applied to the Study of a Homogeneous Ziegler-Type Hydrogenation Catalyst

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Mössbauer spectra obtained using solid glassy toluene matrices have shown that high-spin Fe(II) is formed upon reaction of ferric acetylacetonate with triethylaluminum at −83°C. Upon warming to room temperature, a further reaction occurs to yield an active homogeneous hydrogenation catalyst discovered earlier by others. No metallic iron particles, even as small as 17 Å, could be detected by Mössbauer spectroscopy in solutions of the active catalyst.

INTRODUCTION

In recent years, the hydrogenation, isomerization and polymerization of unsaturated compounds have been studied under mild conditions using homogeneous catalysts prepared by the reaction of transition metal salts, usually acetylacetonates, with organo-aluminum compounds (*1–7*). Both components are dissolved in a suitable organic solvent, inert under the conditions of the reaction.

Because of the instability of the catalyst solutions in the presence of oxygen or water, the molecular complexes responsible for the catalytic activity of the solutions have not been isolated. Further, very little direct evidence is available as to the structure of the catalytic complexes. The work reported here was carried out in order to investigate the catalyst resulting from the reaction of ferric acetylacetonate [$Fe(acac)_3$] with triethylaluminium ($AlEt_3$).

In particular, it was hoped to find evidence concerning the possible presence in such catalytic systems of very small metallic particles that cannot be detected by X-ray diffraction.

EXPERIMENTAL

(*A*) *Hydrogenation Procedure*

$Fe(acac)_3$ powder (2.0×10^{-4} moles) was placed in a Fischer–Porter bottle equipped with a magnetic stirring bar. The bottle was alternately evacuated and filled with N_2 gas. The bottle was flushed with H_2 and the $Fe(acac)_3$ was dissolved in 5 cc of benzene. 2.0×10^{-2} moles of 1-hexene (purified by passing through a column of pure alumina) was added by syringe, followed by the addition of 1.2×10^{-3} moles of $AlEt_3$ (dropwise with stirring). A constant H_2 pressure of 50 psi was applied. The reaction was allowed to proceed at room temperature. After 2 hr, the bottle was depressurized, and a sample was extracted by syringe and analyzed chromatographically.

Both the benzene and 1-hexene were deoxygenated with bubbling N_2 just before use. The H_2 was purified with a "Deoxo" purifier and a column of activated Linde 4A molecular sieve.

(*B*) *Procedure for Obtaining X-ray Diffraction Patterns*

A special liquid sample cell was constructed of high-purity aluminum metal. A 1 mm thick aluminum window was attached to the cell body with epoxy. Samples

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of toluene were injected into the cell with a hypodermic syringe. A small piece of mica was affixed to the outer surface of the aluminum window to serve as a standard for calibration of the angular scale. The cell was mounted vertically in the cold-finger of a variable temperature liquid nitrogen-cooled dewar. The cold-finger was plunged into a bath of liquid nitrogen to solidify the toluene sample. Then, the liquid-nitrogen chamber was filled in order to maintain the sample temperature at the required value.

(*C*) *Preparation of Samples for Infrared Study*

The catalyst solution was prepared as follows. Two serum bottles were capped with rubber septa. One contained a magnetic stirring bar and the other contained 0.457 g (1.34×10^{-3} moles) of Fe(acac)$_3$. The serum bottles were filled with nitrogen gas using a hypodermic needle assembly, alternately evacuating and filling with nitrogen. Six cc of benzene were transferred to the bottle containing the Fe(acac)$_3$ by syringe. Five cc of the benzene were transferred to the bottle containing the magnetic stirring bar. Into the latter was transferred 0.918 cc (6.72×10^{-3} moles) of AlEt$_3$ from another stoppered serum bottle. Five cc of the Fe(acac)$_3$ solution were added dropwise with stirring to the AlEt$_3$ solution. Other samples for infrared analysis were prepared similarly with the same concentration as that of the Fe(acac)$_3$ in the catalyst solution (0.112 M).

The samples were transferred by syringe to a liquid sample cell flushed with dry nitrogen gas. The cell windows were KBr and the cell thickness was 0.114 mm. The reference cell was filled with pure benzene. Solutions of aluminum acetylacetonates were prepared by reacting, in benzene, the stoichiometric amounts of AlEt$_3$ and acetylacetone (2,4-pentanedione).

(*D*) *Preparation of Samples for Mössbauer Study*

The catalyst sample was prepared in a sample cell that fitted into the cold-finger of a liquid nitrogen-cooled dewar attached to the Mössbauer spectrometer. The body of the cell was a pure aluminum cylinder ½ in. long and ½ in. in diameter. The windows were 1 mil thick pure aluminum foil. Short pieces of hypodermic needle served as inlet and outlet ports. The cell contained a tiny Pyrex-coated magnetic stirring bar. After flushing with nitrogen gas, the cell was just half filled with a toluene solution of AlEt$_3$. The cell was placed in a dry ice–acetone bath and a toluene solution of Fe(acac)$_3$ was added dropwise with stirring, just filling the cell. The inlet and outlet ports were sealed with Teflon plugs. The cold-finger was then plunged quickly into a bath of liquid nitrogen to solidify the sample, and the liquid nitrogen chamber was filled to maintain the sample temperature at 77 K. The concentration of iron in the solution was 0.112 M and the Al/Fe molar ratio was 6/1.

(*E*) *Chemicals*

The benzene and toluene were reagent grade and were distilled over sodium metal under nitrogen atmosphere. They were stored in stoppered flasks under a nitrogen atmosphere. The Fe(acac)$_3$ was obtained from Research Organic/Inorganic Chemical Corp. Inc. The AlEt$_3$ was obtained from Texas Alkyls, Inc. The tank N$_2$ gas was purified by passing through activated Linde 4A molecular sieve and a heated BTS catalyst.

(*F*) *Spectrometers*

The X-ray patterns were obtained using a Pickett X-ray Bi-Planar Diffractometer. The diffractometer was equipped with a variable-temperature liquid nitrogen-cooled dewar. A Cu$K\alpha$ X-ray source was used.

The infrared spectra were obtained using a Perkin-Elmer 457 Double-Beam Grating Infrared Spectrometer. The spectrometer automatically records spectra from 250 to 4000 cm^{-1}

The Mössbauer spectra were obtained using a constant velocity-type spectrometer described elsewhere (*8*). The spectrometer was equipped with a liquid nitrogen-cooled dewar evacuated by a 2-in.

oil diffusion pump. The source was ^{57}Co diffused into chromium. The spectra were least-squares analyzed using a computer, assuming that the lines were Lorentzian in shape. All isomer shifts are reported relative to a room temperature sodium nitroprusside standard absorber and refer to the absorber at 77 K and the source at room temperature.

RESULTS AND DISCUSSION

The Hydrogenation of 1-Hexene

In order to be sure that the solutions studied here possessed the catalytic activity reported by other investigators, the hydrogenation of 1-hexene was carried out. A benzene solution of the $Fe(acac)_3$–$AlEt_3$ catalyst was employed with a 1-hexene to iron atom molar ratio of 10^2. The hydrogenation was allowed to proceed for 2 hr at room temperature and with a constant hydrogen pressure of 50 psi. The conversion of 1-hexene to hexane was 100%.

Infrared Analysis of the Catalyst Solution

The infrared spectra of benzene solutions of the following systems were obtained: (1) $Fe(acac)_3$; (2) $Al(acac)_3$; (3) $AlEt_3$; (4) $AlEt_2(acac)$; (5) $6AlEt_3 + Fe(acac)_3$. A comparison of the spectra showed that the spectrum of the catalyst solution (spectrum 5) was nearly identical to the superposition of spectra (3) and (4). The bands at 1271 and 428 cm^{-1} in spectrum (1) were shifted to 1289 and 472 cm^{-1}, respectively, in spectrum (5). These bands occurred at 1287 and 486 cm^{-1}, respectively, in spectrum (2).

The band at 1271 cm^{-1} was assigned to a sum of C–C and C–CH_3 stretching modes of the acetylacetonate ligands complexed with the Fe(III) atom in $Fe(acac)_3$ (*9*). The band at 428 cm^{-1} was assigned to a mode localized in the stretching vibration of the Fe–O bond. The bands at 1287 and 486 cm^{-1} in the spectrum of $Al(acac)_3$ have been assigned to the corresponding vibrational modes of this molecule. The fact that the bands appear at 1289 and 472 cm^{-1} in the spectrum of the catalyst solution clearly indicates that the acetylacetonate ligands are transferred from the iron to the aluminum atoms in the reaction of $Fe(acac)_3$ with $AlFe_3$.

The C–H stretching vibrations for the ethyl ligand in $Fe(C_2H_5)_2$ $(dipyridine)_2$ were assigned to bands at 3000 and 2800 cm^{-1} (*10*). If ethyl ligands were coordinated to the iron atom of the catalyst solution, bands of similar frequencies would be expected. Unfortunately, the region of the spectrum between 2700 and 3000 cm^{-1} is obscured in the case of the catalyst solution by the C–H stretching vibrations of the ethyl ligands bound to the aluminum atoms. Thus, the existence of iron-ethyl bonds in the catalyst solution cannot be determined by infrared analysis.

The Fe–H stretching vibrations for the hydride ligand of FeH_2 $(P(C_2H_5)(C_6H_5)_2)_3 \cdot N_2$ occur at 1950–1960 cm^{-1} and 1855–1863 cm^{-1} (*11*). In the spectrum of the catalyst solution, no bands could be detected in this region. However, this does not indicate the absence of the iron hydride species, since there are cases in which the existence of Fe–H bonds can be shown by other methods when no corresponding infrared absorption bands can be found (*12*).

Mössbauer Analysis of the Catalyst Solution

Mössbauer spectroscopy has frequently proven to be a very useful tool in the elucidation of the structure of chemical compounds. This is especially true in the case of iron compounds, since the Mössbauer resonance of ^{57}Fe is readily observable. Moreover, considerable effort has been made to systematize the Mössbauer parameters of iron-organic compounds (*13*, *14*).

For these reasons, Mössbauer spectroscopy was used to investigate the structure of the catalyst prepared by the reaction of $Fe(acac)_3$ and $AlEt_3$. For all practical purposes, Mössbauer spectra can only be obtained if the sample being analyzed is a solid. Thus, it was necessary to solidify the catalyst solutions before obtaining their Mössbauer spectra. It was decided to use toluene, a glass-forming liquid, as the solvent for the catalyst solutions. The toluene solutions were solidified by rapid quenching to 77 K in order to minimize the distortion or precipitation of the catalytic molecular complexes during the solidification process.

Before obtaining any Mössbauer spectra, a sample of pure toluene was examined by X-ray diffraction to confirm the fact that rapid quenching to 77 K does result in a glassy rather than a crystalline toluene matrix. An aluminum sample holder, similar to that used in obtaining Mössbauer spectra, was used to contain the toluene. When the toluene was quenched to 77 K, no X-ray diffraction peaks could be detected at the highest resolution of the spectrometer, indicating that the toluene had solidified without crystallizing. This was further confirmed by the appearance of diffraction peaks due to crystalline toluene when the temperature of the sample was raised to 123 K, a few degrees above the glass transition temperature of the toluene *(15)*. When the sample was cooled slowly from the liquid state to below the melting point, very sharp diffraction peaks corresponding to those of crystalline toluene were observed *(16)*.

For purposes of comparison with the Mössbauer spectra of catalyst solutions, spectra of Fe(acac)$_3$ were obtained. These spectra, and all others reported here, were obtained at a sample temperature of 77 K. The spectrum of crystalline Fe(acac)$_3$ consisted of a single broad line (Fig. 1a). That of a benzene solution of the compound, rapidly quenched to 77 K, was identical to that of the crystalline solid (except for having a larger linewidth). That the benzene solution spectrum closely resembles the crystalline spectrum was reported by J. W. G. Wignall *(17)*. He suggested that the Fe(acac)$_3$ crystallizes separately when the solution is frozen, giving rise to the spectrum characteristic of the crystalline material. The Mössbauer parameters of these two spectra are given in Table 1.

When Wignall dissolved the Fe(acac)$_3$ in EPA, a glass-forming solvent, hyperfine lines were observed (at 4.2 K and for dilute solutions). This indicates that the relaxa-

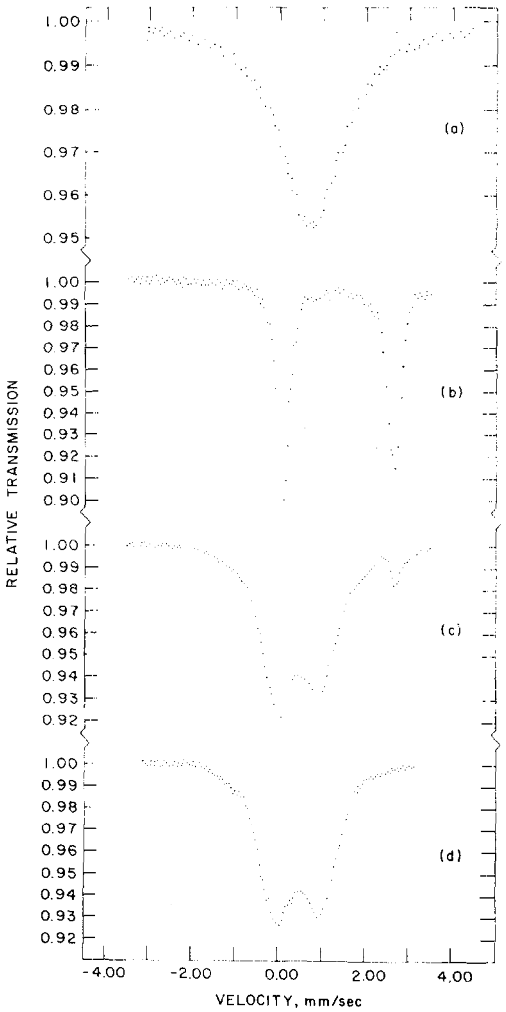


FIG. 1. Mössbauer spectra: (a) crystalline Fe(acac)$_3$; (b) catalyst solution prepared at −83°C and quenched to 77 K; (c) catalyst solution prepared at −83°C, warmed to 10°C without stirring and quenched to 77 K; (d) catalyst solution prepared at −83°C, warmed to room temperature with stirring, and quenched to 77 K.

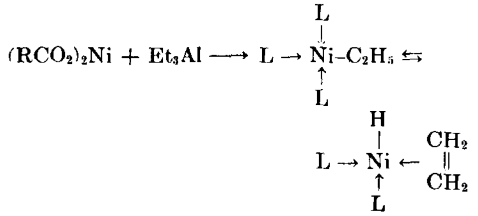
TABLE 1

PARAMETERS OF Fe(acac)$_3$ MÖSSBAUER SPECTRA

Sample	Isomer shift (mm/sec)	Half-width (mm/sec)
(1) Crystallized Fe(acac)$_3$	0.74 ± 0.01	1.74 ± 0.01
(2) 0.156 *M* Fe(acac)$_3$ in benzene	0.73 ± 0.01	2.56 ± 0.01

tion of the electronic spins is slower for more dilute solutions. He reported that, as the concentration of Fe(acac)$_3$ was increased, the hyperfine lines broadened due to the spin–spin relaxation mechanism. Similar results are to be expected with other glass-forming solvents. In particular, when we examined a 0.156 *M* solution of Fe(acac)$_3$ in toluene that had been rapidly quenched to 77 K, an extremely broad absorption band was seen. However, no hyperfine structure was resolved. This indicates that, while the crystallization of the compound was prevented, the electronic relaxation time was too short to allow the hyperfine structure to be resolved at this concentration and temperature.

In a recent investigation (*6*), S. J. Lapporte examined the NMR spectra of concentrated toluene solutions of the homogeneous catalyst prepared from the reaction of nickel 2-ethylhexanoate and triethylaluminum. The catalyst was prepared at −78°C and spectra were obtained at −60°C (without further warming) and 24°C. Signals in the −60°C spectrum were interpreted to indicate the presence of both π-bonded ethylene and metal–hydrogen bonds. These signals irreversibly disappeared when the sample was warmed to 24°C. In view of this and other evidence, Lapporte suggested that the nickel (II) in the nickel 2-ethylhexanoate is reduced to nickel (0), probably via unstable ethylnickel and nickel hydride species [see Eq. (1)].



$$(RCO_2)_2Ni + Et_3Al \longrightarrow L \rightarrow \overset{\overset{L}{|}}{\underset{\underset{L}{\uparrow}}{Ni}}\text{–}C_2H_5 \rightleftarrows L \rightarrow \overset{\overset{H}{|}}{\underset{\underset{L}{\uparrow}}{Ni}} \leftarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \quad (1)$$

where L = solvent, $CH_2 \times CH_2$, or RCO_2AlEt_2.

The NMR evidence for the existence of unstable intermediates in the solutions of the nickel catalyst suggested the use of Mössbauer spectroscopy to search for the presence of similar unstable intermediates in toluene solutions of the Fe(acac)$_3$–AlEt$_3$ catalyst. The paramagnetic Fe(III) atom would, of course, prohibit the use of NMR spectroscopy in this case.

The Mössbauer spectrum of the catalyst solution prepared, with stirring, at −83°C and rapidly quenched to 77 K consisted of two narrow lines with a quadrupole splitting (Δ) = 2.56 mm/sec and an isomer shift (δ) = 1.37 mm/sec (Fig. 1b). When this solution was warmed to 10°C, without stirring, and quenched again to 77 K, the Mössbauer spectrum consisted of a new doublet with much smaller quadrupole splitting and isomer shift (Δ = 0.99 mm/sec, δ = 0.57 mm/sec). Also, the doublet seen in the first spectrum was still present, although with very much reduced intensity (Fig. 1c). When the solution was warmed to room temperature, stirred, and quenched to 77 K, only the doublet with the smaller quadrupole splitting and isomer shift remained (Fig. 1d). The Mössbauer parameters of this catalyst solution were, to within experimental error, identical to those of catalyst solutions prepared externally, transferred to the Mössbauer sample cell by syringe, and quenched to 77 K.

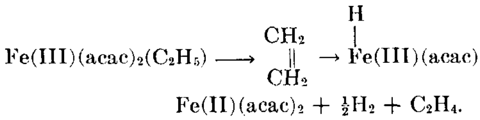
The Mössbauer parameters corresponding to the catalyst solution prepared at −83°C and quenched without warming indicate unambiguously that the solution contains a high-spin Fe(II) species. There are no indications of the presence of iron atoms in any other valence or spin state. The Mössbauer spectrum of ferrous acetylacetonate has not been reported. However, a possible explanation for the spectrum of the catalyst solution is that, at this temperature, the reaction of Fe(acac)$_3$ with AlEt$_3$ is limited to a one-electron reduction process. This may occur via a ligand-exchange step followed by a series of steps leading to reduction of the iron and the production of hydrogen and ethylene. For example,

$$Fe(III)(acac)_3 + Al(C_2H_5)_3 \rightarrow Fe(III)(acac)_2(C_2H_5) + Al(acac)(C_2H_5)_2 \quad (2)$$

$$2Fe(III)(acac)_2(C_2H_5) \rightarrow 2Fe(II)(acac)_2 + H_2 + 2C_2H_4[\text{or } + C_2H_6 + C_2H_4]. \quad (3)$$

The reaction expressed by Eq. (3) may

proceed by the formation of unstable iron-hybride and π-bonded ethylene species, as in the case of the nickel catalyst studied by Lapporte:



$$\mathrm{Fe(III)(acac)_2(C_2H_5)} \longrightarrow \overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{\|}} \rightarrow \overset{\mathrm{H}}{\overset{|}{\mathrm{Fe(III)}}}\mathrm{(acac)_2} \rightarrow \mathrm{Fe(II)(acac)_2} + \tfrac{1}{2}\mathrm{H_2} + \mathrm{C_2H_4}. \quad (4)$$

When the temperature is raised, the system reacts further to give species in solution capable of catalyzing the room temperature hydrogenation and polymerization of olefins. This is indicated by the Mössbauer spectra of the catalyst solution heated to room temperature and again quenched to 77 K. The question naturally arises as to the nature of the iron species present in these room-temperature solutions. It is generally assumed that the active catalyst solutions contain zero-valent transition-metal atoms, formed by the complete reduction of the transition-metal salts by the organo-aluminum compounds. The infrared spectra reported here indicate that, in the room temperature catalyst solution, the acetylacetonate ligands have all been transferred from the iron to the aluminum atoms. This information, coupled with the Mössbauer evidence of an initial one-electron reduction of Fe(III) to Fe(II) followed by a further reaction between the Fe(II) and $\mathrm{AlEt_3}$, strongly supports this assumption.

It should be noted, however, that the Mössbauer spectra of the catalyst solutions do not contain the 6-line hyperfine pattern characteristic of metallic iron. As shown recently by Khammouma (*18*), the presence of metallic iron particles, even as small as 17 Å, would give rise to the 6-line spectrum, even at room temperature.

It would be hoped that the parameters of the Mössbauer spectrum of the room-temperature catalyst solution would give some indication of the nature of the iron species contained therein. In fact, the Mössbauer parameters of organo-iron compounds are not strong functions of the structure of these compounds. In the absence of any other structural information concerning the iron-containing catalytic species, it is inadvisable to try to draw further conclusions from the Mössbauer spectra at the present time.

CONCLUSIONS

Toluene, the simplest glass-forming liquid, has been successfully used to create a solid, glassy matrix in which highly reactive, dissolved catalytic complexes can be examined by Mössbauer spectroscopy. X-ray analysis of samples of rapidly cooled toluene confirmed their glassy structure by the observation of slow crystallization of the toluene a few degrees above the glass transition point. A comparison of the Mössbauer spectra of benzene and toluene solutions of ferric acetylacetonate indicated that the toluene solutions did not crystallize with rapid cooling to 77 K.

Mössbauer spectroscopy has shown that the reaction of ferric acetylacetonate with triethylaluminum at −83°C results in a one-electron reduction of the iron to high-spin Fe(II). Warming of the catalyst solution to room temperature results in a further reaction. Infrared evidence indicates that the acetylacetonate ligands are transferred from the iron to the aluminum atoms in the room-temperature solution. The iron atoms in the room-temperature solution exhibit Mössbauer parameters that, along with other structural information, aid in the characterization of the molecular complexes responsible for the activity of the catalytic solutions.

While further work is clearly necessary to specify further what the catalyst is, Mössbauer spectroscopy tells us unequivocally what it is not: the catalyst does not contain detectable quantities of metallic iron particles, as such particles even as small as 17 Å—and therefore undetectable by X-ray diffraction—would exhibit the characteristic 6-line spectrum of metallic iron, as shown by Khammouma (*18*). No indication of such spectra was obtained in this work.

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