Olefin Hydrogenation with Iron Carbonyls as Catalysts

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The study of [Fe(CO)\textsubscript{5}], [Fe\textsubscript{2}(CO)\textsubscript{9}] and [Fe\textsubscript{3}(CO)\textsubscript{12}] as precursors catalytic in the reactions of hydrogenation of cyclohexene and 1-hexene was investigated. A photochemical reactor with H\textsubscript{2} flux and UV-vis continuous irradiation was used for these studies. The infrared spectra of the samples showed the formation of [Fe(CO)\textsubscript{4}(olefine)] and [HFe(CO)\textsubscript{3}(\pi-allyl)] as intermediates. The activity of [Fe\textsubscript{2}(CO)\textsubscript{9}] in the hydrogenation of cyclohexene was higher (66.6\%) than the activity of the other iron carbonyls (43.0\% [Fe(CO)\textsubscript{5}], [Fe\textsubscript{3}(CO)\textsubscript{12}]). The competition between isomerization and hydrogenation in the reaction of 1-hexene was studied. The isomerization rate was much higher than the hydrogenation rate and the polynuclear species promoted isomerization more rapidly than [Fe(CO)\textsubscript{5}]. The alkane conversions were: 60.0\% ([Fe(CO)\textsubscript{5}], [Fe\textsubscript{3}(CO)\textsubscript{12}]) and 75.4\% [Fe\textsubscript{2}(CO)\textsubscript{9}], showing that for the 1-hexene hydrogenation [Fe\textsubscript{2}(CO)\textsubscript{9}] also exhibited the highest activity.

Keywords: iron carbonyls, olefin hydrogenation, catalysis

Introduction

The utility of [Fe(CO)\textsubscript{5}] and [Fe\textsubscript{3}(CO)\textsubscript{12}] as photocatalysts in the hydrogenation of alkenes has been known since the 1970s\textsuperscript{1-4}. Many unsaturated derivatives are produced in these reactions via the loss of CO groups from the iron carbonyls, and the actual catalyst is probably a reduced carbonyl species, such as [Fe(CO)\textsubscript{x}] or [Fe(CO)\textsubscript{5}]\textsuperscript{5-10}. Surprisingly, the photocatalytic activity of the dinuclear compound [Fe\textsubscript{2}(CO)\textsubscript{9}] has never been investigated. In this paper, we report our studies on the photocatalytic activity of [Fe\textsubscript{2}(CO)\textsubscript{9}] in the hydrogenation of cyclohexene and 1-hexene. Furthermore, comparative studies of the photocatalytic activities of [Fe(CO)\textsubscript{5}] and [Fe\textsubscript{3}(CO)\textsubscript{12}] in these processes were also performed.
amounts were used for the three iron carboxyls studied in order to allow the data to be compared.

IR spectra were taken with a Perkin-Elmer 1430 spectrophotometer (ν\textsubscript{CO} region, 2200-1900 cm\textsuperscript{-1}). Samples were analyzed by capillary gas chromatography (HP5890A gas chromatograph, FID detector, 23 m x 0.25 mm, SE-30 capillary column, HP3392A integrator).

**Results and Discussion**

As previously reported\textsuperscript{10}, the activity of the catalytic precursors [Fe(CO)\textsubscript{5}], [Fe\textsubscript{2}(CO)\textsubscript{9}] and [Fe\textsubscript{3}(CO)\textsubscript{12}] in the cyclohexene hydrogenation reaction shows that [Fe\textsubscript{2}(CO)\textsubscript{9}] is the most active of the iron carboxyls while the conversion values obtained for [Fe(CO)\textsubscript{5}] and [Fe\textsubscript{3}(CO)\textsubscript{12}] are quite similar (Table 1).

Although [Fe\textsubscript{2}(CO)\textsubscript{9}] is highly insoluble in toluene, no insoluble material was seen in the reactor soon after the irradiation started (~1 min). The absence of a heterogeneous component was confirmed by a mercury test\textsuperscript{14}. The presence of an heterogeneous component would have been detected by the decrease in activity due to amalgam formation.

One possible explanation for the higher activity of [Fe\textsubscript{2}(CO)\textsubscript{9}] is that upon photochemical activation, the dinuclear species [Fe\textsubscript{2}(CO)\textsubscript{8}]\textsuperscript{15,16} is formed, together with [Fe(CO)\textsubscript{4}]. Since [Fe\textsubscript{2}(CO)\textsubscript{6}(olefin)\textsubscript{2}] derives from [Fe\textsubscript{2}(CO)\textsubscript{8}]\textsuperscript{17a,18}, this kind of intermediate might be present in the system, leading to high activity. In Scheme 1 it is suggested that the olefin dinuclear compound is part of the cycle as suggested by Wrighton and Mitchener\textsuperscript{17a}. Thus, mono and dinuclear iron species could be present in the three systems. In
the case of [Fe$_2$(CO)$_9$], the concentration of the dimeric species would be the highest, because of the photochemically induced CO dissociation fragmentation, whereas in the other cases, the dimeric species would be formed upon the condensation of two mononuclear fragments.

The IR spectrum of the solution from the cyclohexene reaction with [Fe(CO)$_5$] after 1h, shows bands which are characteristic of [Fe(CO)$_4$(olefin)] (2080, 2025, 2001, and 1960 cm$^{-1}$). The bands at 2060 and 2025 cm$^{-1}$ correspond to [Fe$_3$(CO)$_{12}$]. These bands are present in all of the reactions studied, and the formation of [Fe$_3$(CO)$_{12}$] may be due to the decomposition of the catalyst. There is a shoulder at 1945 cm$^{-1}$, suggesting the presence of [HFe(CO)$_3$(π-allyl)] (2064, 1994, and 1945 cm$^{-1}$), but the overlap with the band at 1960 cm$^{-1}$ ([Fe(CO)$_4$(olefin)]) does not allow a conclusive band assignment. As observed in the case of [Fe(CO)$_5$], the reaction with [Fe$_2$(CO)$_9$] as the catalyst also showed bands due to [Fe(CO)$_4$(olefin)] and [Fe$_3$(CO)$_{12}$]. Furthermore, in this case, a well-defined band at 1945 cm$^{-1}$ ([HFe(CO)$_3$(π-allyl)]) was observed. During the process, the intensity of this band does not change appreciably. In the case of the reaction with [Fe$_3$(CO)$_{12}$], the bands due to [Fe(CO)$_4$(olefin)] and [HFe(CO)$_3$(π-allyl)] (approx. 1945 cm$^{-1}$) appear again. In all of the iron carbonyl reactions the presence of [Fe$_2$(CO)$_6$(olefin)$_2$] could not be characterized due to the superimposition of the 2059 and 1982 bands on other bands in the spectra. All IR bands are in agreement with the data in the literature$^{5,17}$. Fig. 1 shows the IR bands for the [Fe$_2$(CO)$_9$] reaction.

Regarding the three iron carbonyls, it was observed that during the first hour of reaction, 1-hexene suffered mainly

![Figure 1. Infrared spectra in the $\nu$(CO) region of the cyclohexene hydrogenation using [Fe$_3$(CO)$_{12}$] as the catalyst.](image)

**Table 1.** Product conversions in the cyclohexene and 1-hexene hydrogenation reactions using [Fe(CO)$_5$], [Fe$_2$(CO)$_9$], and [Fe$_3$(CO)$_{12}$] as catalytic precursors.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product</th>
<th>Conversion [%]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 h</td>
<td>4 h</td>
</tr>
<tr>
<td>[Fe(CO)$_5$]</td>
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<td>15.75</td>
<td>32.10</td>
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<tr>
<td></td>
<td>hexane</td>
<td>8.41</td>
<td>34.46</td>
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<td></td>
<td>trans-2-hexene</td>
<td>75.91</td>
<td>54.08</td>
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<tr>
<td></td>
<td>cis-2-hexene</td>
<td>13.62</td>
<td>10.26</td>
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<tr>
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<td>32.11</td>
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<td>10.90</td>
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<td>9.00</td>
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<tr>
<td>[Fe$<em>3$(CO)$</em>{12}$]</td>
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<td>15.25</td>
<td>31.90</td>
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<tr>
<td></td>
<td>hexane</td>
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<tr>
<td></td>
<td>cis-2-hexene</td>
<td>15.61</td>
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</table>
isomerization and only 11% was converted to hexane. Afterwards, the hydrogenation process predominated (Table 1).

Polynuclear species require less energy to form compounds such as \([\text{Fe(CO)}_2(\text{olefin})]\), because the cleavage of the iron-iron bond demands less energy than that of the iron-CO bond\(^{15}\), which explains the lower activity of \([\text{Fe(CO)}_3]\) for isomerization. In the step where the hydrogenation reaction predominates (after 1h of reaction), similar results were found for cyclohexene. In Scheme 1, possible mechanisms are suggested for these hydrogenation and isomerization processes, based on Refs. 5 and 17. It is suggested here that the step involving the equilibrium between \([\text{Fe(CO)}_3(\text{olefin})]\) and \([\text{Fe(CO)}_3(\text{olefin})]_2\) is more important in the hydrogenation cycle, which explains why \([\text{Fe}_2(\text{CO})_9]\) is more active in hydrogenation than in isomerization reactions: when \([\text{Fe}_2(\text{CO})_9]\) is used, there is an increase in the \([\text{Fe(CO)}_3(\text{olefin})]_2\) concentration, and consequently the \([\text{Fe(CO)}_3(\text{olefin})]\) concentration increases.

The IR spectra for the 1-hexene reaction of the three iron compounds show a pattern which is analogous to that for the cyclohexene reaction. The bands characteristic of \([\text{Fe(CO)}_3(1\text{-hexene})]\), \([\text{HFe(CO)}_5(\pi\text{-allyl})]\) and \([\text{Fe}_3(\text{CO})_{12}]\) can be observed.

All attempts to identify the wine-colored compound which precipitates under vacuum at -78 °C failed. As soon as the temperature rises, the wine-colored solid compound becomes green and the IR spectrum shows only \([\text{Fe}_3(\text{CO})_{12}]\) bands.

**Conclusions**

The photochemical activation of \([\text{Fe(CO)}_3]\), \([\text{Fe}_2(\text{CO})_9]\), and \([\text{Fe}_3(\text{CO})_{12}]\) at low temperature (0 °C) and in the presence of olefins led to the formation of compounds that catalyze isomerization and hydrogenation processes.

Isomerization is faster than hydrogenation, but does not have any influence on the catalyst activity, as far as hydrogenation is concerned, which confirms that there are intermediates common to the two processes.

\([\text{Fe}_2(\text{CO})_9]\) shows the highest activity in the hydrogenation of both cyclohexene and 1-hexene. This leads to the conclusion that the dinuclear species \([\text{Fe}_2(\text{CO})_9(\text{olefin})]_2\) is important in the hydrogenation process.

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**References**