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A RADICAL MECHANISM FOR THE PHOTOCHEMICAL IRON PENTACARBONYL CATALYZED HYDROGENATION OF OCTENES

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Summary

A high pressure IR and UV spectroscopic study of the catalysis of hydrogenation of 1-octene by $Fe(CO)_5$ under UV irradiation reveals that $Fe(CO)_5$ and $(olefin)Fe(CO)_4$ are the light absorbing species. The primary photolysis product $Fe(CO)_4$ reacts with $H_2Fe(CO)_4$ to give $HFe(CO)_4$ radicals, which are suggested to be the active hydrogenation promoters.

Introduction

When iron pentacarbonyl is irradiated in the presence of an olefin, the olefin undergoes a double bond migration [1-3], probably via an olefin iron tricarbonyl species as the repeating unit in the catalytic cycle [4,5]. In the presence of molecular hydrogen the olefin is also hydrogenated [4,6-8]. The complex (olefin)Fe(CO)₄ was proposed as the common catalyst precursor for hydrogenation and isomerisation [4]. It was believed to lose a CO ligand to give a coordinatively unsaturated complex which could either catalyse the isomerisation or react with H₂ to form the actual hydrogenation catalyst:

$$(olefin)Fe(CO)_{4} \xrightarrow{-CO} (olefin)Fe(CO)_{3} \xrightarrow{} isomerisation$$

$$|| + H_{2}$$

$$H_{2}Fe(CO)_{3}(olefin) \xrightarrow{} hydrogenation$$

This hydrogenation mechanism has never been challenged, although it is known from ESR experiments that photolysis of iron pentacarbonyl under high pressure of hydrogen yields $HFe(CO)_4$ radicals [9]. These radicals are also believed to be

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important in the photocatalytic hydroformylation of olefins [10]. Unfortunately, the detection of $H_2Fe(CO)_4$ or of $HFe(CO)_4$ radials under the hydrogenation conditions does not prove that either of the two species is the active catalyst or even that they are involved in the catalytic cycle. Additional proof is necessary.

Using on-line UV and IR spectroscopy [11] we have carried out a study of the photoreactive species in the photocatalytic hydrogenation of 1-octene using $Fe(CO)_s$ as the precatalyst. The results provide evidence that the reaction probably proceeds via a radical mechanism.

Results and discussion

A 0.01 *M* solution of $Fe(CO)_5$ in methylcyclohexane was irradiated through a Pyrex filter with a medium pressure Hg lamp at 35°C and 50 bar H₂ in the absence of an olefin. During irradiation the iron pentacarbonyl 1 was converted into iron tetracarbonyl hydride 2, until a photostationary state was reached. In a control experiment it was shown that 2 reacts in a thermal reaction with the CO, liberated in the first step, to regenerate $Fe(CO)_5$. Minor amounts of polynuclear iron carbonyls (< 5%) are also formed.

$$Fe(CO)_{5} + H_{2} \stackrel{h\nu}{\rightleftharpoons} H_{2}Fe(CO)_{4} + CO \xrightarrow{\text{slow}} \text{polynuclear species}$$
(2)
(1) (2)

After 21 h the light was turned off and the 1-octene (1 M) was added in the dark. The concentration of the hydride 2 immediately decreased and olefiniron tetracarbonyl was formed, the concentration of the Fe(CO)₅ remaining constant. This indicates that the hydrogen of 2 is replaced by an olefin ligand (eq. 3).

$$H_{2}Fe(CO)_{4} + RCH = CH_{2} \xrightarrow{\Delta}_{h\nu} (\pi - RCH = CH_{2})Fe(CO)_{4} + H_{2}$$
(3)
(2) (3)

After 5 h of dark reaction the UV lamp was restarted and the irradiation continued, now in the presence of octene. This led to a further decrease in the concentrations of 1 and 2 and to an increase in the concentration of the olefin complex 3, as represented by eqs. 3 and 4:

$$Fe(CO)_{5} + RCH = CH_{2} \xrightarrow{n\nu} 3 + CO$$
(4)

Upon prolonged irradiation the concentration of the terminal olefin complex 3 passes through a maximum, since it is slowly converted into the corresponding complex of the internal olefin 4, reflecting the double bond migration of the olefin.

$$(\pi - \text{RCH} = \text{CH}_2) \text{Fe}(\text{CO})_4 \stackrel{h\nu}{\rightleftharpoons} (\pi - \text{R'CH} = \text{CHR''}) \text{Fe}(\text{CO})_4$$
(5)
(3) (4)

Figure 1b shows, that the olefin isomerises rapidly during the second irradiation period. The minor amounts of internal olefins formed during the preceding dark period can be attributed to some thermal catalytic activity of the traces of polynuclear carbonyls present in the solution.

At 50 bar hydrogen pressure hydrogenation is observed only, when the solution is irradiated. The octane yield increases linearly with the irradiation time, indicating that the product formation is of zero order with respect to the octene concentration.



Fig. 1. Photochemical and thermal reactions of iron carbonyls in the presence of hydrogen and 1-octene as a function of reaction time. Conditions: 0.010 *M* Fe(CO)₅, 50 bar H₂, 1.0 *M* 1-octene in 700 ml methylcyclohexane, 35°C, 600 W medium pressure Hg lamp, pyrex filter. A: Lamp off and addition of 1-octene; B: lamp on: $h\nu$: irradiation period; Δ : dark period; plotted are relative concentrations of (a) Fe(CO)₅; (b) H₂Fe(CO)₄; (c) (π -RCH=CH₂)Fe(CO)₄; (d) (π -R'CH=CHR")Fe(CO)₄, and the product yields of (e) internal octenes; (f) octane.

This behaviour is typical of a photochemical reaction in which absorption of a new photon is required for each product molecule. In contrast, the isomerisation exhibits kinetics typical of a thermal reaction, indicating that the isomerisation proceeds through many catalytic cycles after the photochemical initiation (see Fig. 1b).

Control experiments show that the octene is hydrogenated only when $H_2Fe(CO)_4$ is present in the solution. However, the octane yield is not proportional to the $H_2Fe(CO)_4$ concentration (Fig. 2). The formation of the hydride **2** is accelerated by increasing the hydrogen pressure and is much faster at 90 bar than at 15 bar, but the hydrogenation rate is lower at 90 bar than at 15 bar.

 H_2 Fe(CO)₄ (2) can always be detected during the hydrogenation, but its concentration is so low that it absorbs only a negligible fraction of the incoming light. Since 2 is also not a thermally active catalyst (compare Fig. 1), it can be ruled out as the catalytically active or even as the photoreactive species in the photochemical hydrogenation.

Analysis of the UV and IR spectra indicated that $Fe(CO)_5$ is the main light-absorbing species during the early stages of the reaction. Later, when it is converted into the olefin complexes 3 and 4, these species absorb most of the light.

The photolysis of $Fe(CO)_5$ yields $Fe(CO)_4$ as the primary product [12]. Photolysis



Fig. 2. (A) Formation of $H_2Fe(CO)_4$ during photolysis of $Fe(CO)_5$ at 90 bar H_2 (a) and 15 bar H_2 pressure (b). (B) Octane yield at 15 bar (c) and at 90 bar (d) H_2 pressure in the photochemical hydrogenation of 1-octene with $Fe(CO)_5$ as the starting catalyst. Reaction conditions as in Fig. 1.

of the olefin complexes 3 and 4 results in the formation of either $Fe(CO)_4$ or (olefin)Fe(CO)₃, 5. The latter species is the repeating unit of the isomerisation cycle, as was found previously [4.5].

$$\operatorname{Fe}(\operatorname{CO})_{5} \stackrel{h_{P}}{\rightleftharpoons} \operatorname{Fe}(\operatorname{CO})_{4} + \operatorname{CO} \stackrel{+\operatorname{H}_{2}}{\rightleftharpoons} \operatorname{Fe}(\operatorname{CO})_{4} + \operatorname{CO}$$
(5)

$$(olefin)Fe(CO)_4 \stackrel{h\nu}{\rightleftharpoons} Fe(CO)_4 + olefin$$
 (6a)

$$(olefin)Fe(CO)_4 \stackrel{h\nu}{\rightleftharpoons} (olefin)Fe(CO)_3 + CO$$
(6b)
(5)

However, the unsaturated olefin complex 5 can be excluded as the active hydrogenation catalyst, since hydrogenation and isomerisation follow different kinetics. Also, the rate of hydrogenation is not proportional to the H₂ pressure, ruling out a simple competition between the H₂ and the olefin for the same catalyst. This leaves as an alternative only that $Fe(CO)_4$ and $H_2Fe(CO)_4$ are both involved in the decisive steps of the catalytic cycle. From what is known about the chemistry of these two species [9], we conclude that a radical mechanism, as summarized in Scheme 1, is responsible for the photochemical hydrogenation. A similar mechanism was proposed for the iron carbonyl photocatalyzed hydroformylation of olefins [10].

SCHEME 1. Possible mechanism for the photocatalyzed hydrogenation of olefins with iron carbonyl catalysts.

$$Fe(CO)_5 \rightleftharpoons Fe(CO)_4 + CO$$
 (a)

 $Fe(CO)_4 + H_2 \rightleftharpoons H_2 Fe(CO)_4$ (b)

$$HFe(CO)_4 \approx HFe(CO)_3 + CO$$
 (c)

$$HFe(CO)_{3} + olefin \rightleftharpoons HFe(CO)_{3}(\pi - olefin) \rightleftharpoons RFe(CO)_{3} \qquad (d)$$

$$HFe(CO)_{4} + olefin RFe(CO)_{4} \stackrel{\leftarrow}{\underset{+CO}{\leftarrow}} RFe(CO)_{3}$$
(e)

$$RFe(CO)_4 + H_2Fe(CO)_4 \rightarrow RH + 2 HFe(CO)_4$$
(f)

$$RFe(CO)_3 + H_2 \rightarrow RH + HFe(CO)_3$$
(g)

<u>+</u> Р

$$2 \operatorname{HFe}(\operatorname{CO})_4 \rightleftharpoons \operatorname{H}_2\operatorname{Fe}_2(\operatorname{CO})_8 \xrightarrow{} 2 \operatorname{H}_2\operatorname{Fe}(\operatorname{CO})_4 \tag{h}$$

By analogy to the reactions of the corresponding radical anions [13], activation of the olefin via an iron tricarbonyl hydride radical and the related π -complex seems possible (see Scheme 1, reaction d). However, the HFe(CO)₄ could also add to the olefin without prior CO dissociation, as indicated in reaction e of Scheme 1. The alkyliron tricarbonyl radical may react with another molecule of H₂Fe(CO)₄ to give the alkane and a new iron carbonyl hydride radical.

This mechanism suggests that the hydrogenation goes through more than one catalytic cycle before a new photon is required. A quantum yield > 1 was in fact observed at low hydrogen pressures [4]. At high pressures, however, some intermediates react with H_2 or may be trapped by CO, which was liberated in one of the dissociation steps.

Experimental

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The experiments were performed in a 1 l autoclave equipped with a 700 W medium pressure Hg lamp. The autoclave was connected to a high pressure circulating system, which allowed on-line IR and UV spectroscopic investigation of the reaction mixture as described in ref. 11. The organic products were analyzed by GC (200 m Ucon LB 550 X glass capillary column at 40°C with 2.0 bar N₂ carrier). The iron carbonyls were identified by their IR spectra: Fe(CO)₅ at 2022, 2000 cm⁻¹; $H_2Fe(CO)_4$ at 2048, 2035 cm⁻¹; (R'CH=CHR")Fe(CO)₄ at 2083 cm⁻¹; (RCH=CH₂)Fe(CO)₄ at 2072 cm⁻¹.

In a typical experiment (see Fig. 1) 600 ml of methylcyclohexane, 1 ml of $Fe(CO)_5$, and 10 ml of n-decane, as internal GC standard, were added to the autoclave, and 80 ml 1-octene was placed in a high pressure reservoir. The system was flushed twice with 20 bar H₂ and then pressurized with hydrogen to 50 bar. The solution was agitated with a vertical magnetic stirrer and pumped through the high pressure UV and IR cells. Then the irradiation was started. After 21 h the lamp was turned off and the octene was added from the reservoir, yielding a solution which was 0.010 M in Fe(CO)₅ and 1.0 M in 1-octene. After 5 h dark reaction the irradiation was restarted. The solution was monitored spectroscopically and samples for external GC analysis were removed at appropriate times. Similar experiments were carried out at various H₂ pressures and with added carbon monoxide.

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