

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

HERBERT NAGORSKI

*Universität Duisburg, F.B.6 Angewandte Chemie, Lotharstrasse 63, D-4100 Duisburg (West Germany)*

and MANFRED J. MIRBACH \*

*University of Petroleum and Minerals, Department of Chemistry, Dhahran 31261 (Saudi Arabia)*

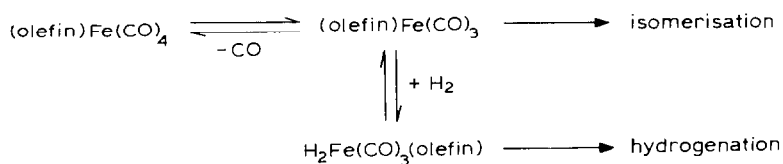
(Received February 18th, 1985)

### Summary

A high pressure IR and UV spectroscopic study of the catalysis of hydrogenation of 1-octene by  $\text{Fe}(\text{CO})_5$  under UV irradiation reveals that  $\text{Fe}(\text{CO})_5$  and  $(\text{olefin})\text{Fe}(\text{CO})_4$  are the light absorbing species. The primary photolysis product  $\text{Fe}(\text{CO})_4$  reacts with  $\text{H}_2\text{Fe}(\text{CO})_4$  to give  $\text{HFe}(\text{CO})_4$  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  $(\text{olefin})\text{Fe}(\text{CO})_4$  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  $\text{H}_2$  to form the actual hydrogenation catalyst:



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  $\text{HFe}(\text{CO})_4$  radicals [9]. These radicals are also believed to be



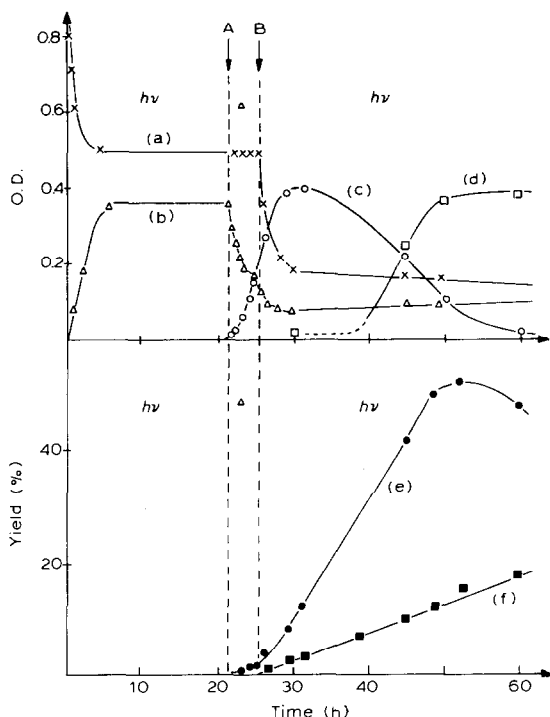


Fig. 1. Photochemical and thermal reactions of iron carbonyls in the presence of hydrogen and 1-octene as a function of reaction time. Conditions: 0.010  $M$   $\text{Fe}(\text{CO})_5$ , 50 bar  $\text{H}_2$ , 1.0  $M$  1-octene in 700 ml methylocyclohexane, 35°C, 600 W medium pressure Hg lamp, pyrex filter. A: Lamp off and addition of 1-octene; B: lamp on;  $h\nu$ : irradiation period;  $\Delta$ : dark period; plotted are relative concentrations of (a)  $\text{Fe}(\text{CO})_5$ ; (b)  $\text{H}_2\text{Fe}(\text{CO})_4$ ; (c)  $(\pi\text{-RCH=CH}_2)\text{Fe}(\text{CO})_4$ ; (d)  $(\pi\text{-R'CH=CHR'')}\text{Fe}(\text{CO})_4$ , 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  $\text{H}_2\text{Fe}(\text{CO})_4$  is present in the solution. However, the octane yield is not proportional to the  $\text{H}_2\text{Fe}(\text{CO})_4$  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.

$\text{H}_2\text{Fe}(\text{CO})_4$  (**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  $\text{Fe}(\text{CO})_5$  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  $\text{Fe}(\text{CO})_5$  yields  $\text{Fe}(\text{CO})_4$  as the primary product [12]. Photolysis

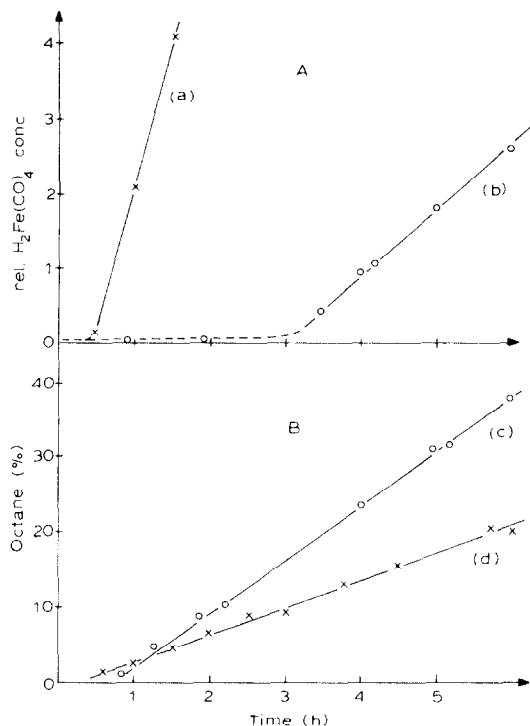
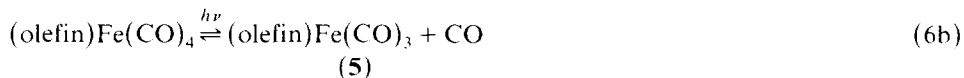
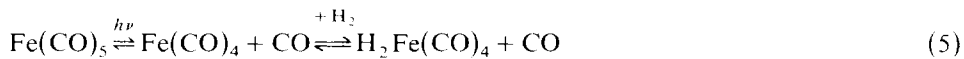


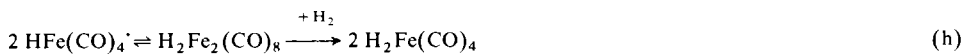
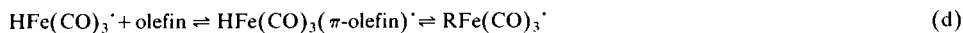
Fig. 2. (A) Formation of  $\text{H}_2\text{Fe}(\text{CO})_4$  during photolysis of  $\text{Fe}(\text{CO})_5$  at 90 bar  $\text{H}_2$  (a) and 15 bar  $\text{H}_2$  pressure (b). (B) Octane yield at 15 bar (c) and at 90 bar (d)  $\text{H}_2$  pressure in the photochemical hydrogenation of 1-octene with  $\text{Fe}(\text{CO})_5$  as the starting catalyst. Reaction conditions as in Fig. 1.

of the olefin complexes **3** and **4** results in the formation of either  $\text{Fe}(\text{CO})_4$  or  $(\text{olefin})\text{Fe}(\text{CO})_3$ , **5**. The latter species is the repeating unit of the isomerisation cycle, as was found previously [4,5].



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  $\text{H}_2$  pressure, ruling out a simple competition between the  $\text{H}_2$  and the olefin for the same catalyst. This leaves as an alternative only that  $\text{Fe}(\text{CO})_4$  and  $\text{H}_2\text{Fe}(\text{CO})_4$  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.



By analogy to the reactions of the corresponding radical anions [13], activation of the olefin via an iron tricarbonyl hydride radical and the related  $\pi$ -complex seems possible (see Scheme 1, reaction d). However, the  $\text{HFe}(\text{CO})_4 \cdot$  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  $\text{H}_2\text{Fe}(\text{CO})_4$  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  $\text{H}_2$  or may be trapped by CO, which was liberated in one of the dissociation steps.

## Experimental

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  $\text{N}_2$  carrier). The iron carbonyls were identified by their IR spectra:  $\text{Fe}(\text{CO})_5$  at 2022, 2000  $\text{cm}^{-1}$ ;  $\text{H}_2\text{Fe}(\text{CO})_4$  at 2048, 2035  $\text{cm}^{-1}$ ;  $(\text{R}'\text{CH}=\text{CHR}'')\text{Fe}(\text{CO})_4$  at 2083  $\text{cm}^{-1}$ ;  $(\text{RCH}=\text{CH}_2)\text{Fe}(\text{CO})_4$  at 2072  $\text{cm}^{-1}$ .

In a typical experiment (see Fig. 1) 600 ml of methylcyclohexane, 1 ml of  $\text{Fe}(\text{CO})_5$ , 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  $\text{H}_2$  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  $\text{Fe}(\text{CO})_5$  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  $\text{H}_2$  pressures and with added carbon monoxide.

## Acknowledgement

The authors thank Dr. Marlis F. Mirbach for stimulating discussions and the Deutsche Forschungsgemeinschaft for financial support.

## References

- 1 F. Asinger, B. Fell and G. Collin, *Chem. Ber.*, 96 (1963) 716.
- 2 F. Asinger, B. Fell and K. Schrage, *Chem. Ber.*, 98 (1965) 372, 381.
- 3 M.D. Carr, V.V. Kane and M.C. Whiting, *Proc. Chem. Soc. (London)*, (1964) 408.
- 4 M. Schroeder and M.S. Wrighton, *J. Am. Chem. Soc.*, 98 (1976) 551.
- 5 H. Fleckner, F.W. Grevels and D. Hess, *J. Am. Chem. Soc.*, 106 (1984) 2027.
- 6 R.L. Whetten, K.J. Fu and E.R. Grant, *J. Chem. Phys.*, 77 (1982) 3769.
- 7 R.L. Whetten, K.J. Fu and E.R. Grant, *J. Am. Chem. Soc.*, 104 (1982) 4270.
- 8 M.E. Miller and E.R. Grant, *J. Am. Chem. Soc.*, 106 (1984) 4635.
- 9 P.J. Krusic, *J. Am. Chem. Soc.*, 103 (1981) 2131.
- 10 P.J. Krusic, Plenary Lecture, 3rd Intern. Symp. Homog. Catal. Milano, 1982.
- 11 M.F. Mirbach, M.J. Mirbach, A. Saus and S. Schwerdt, *Chem. Ztg.*, 106 (1981) 335.
- 12 G.L. Geoffroy and M.S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979.
- 13 P.J. Krusic and J. San Fillippo, Jr., *J. Am. Chem. Soc.*, 104 (1982) 2645.