

CATALYTIC ISOMERISATION OF ALKENES BY Fe(CO)₄

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Abstract—Photolysis of alkene solutions of iron dodecacarbonyl at wavelengths greater than 500 nm causes dissociation into Fe(CO)₄. With ethylene and propene the latter forms (alkene)Fe(CO)₄ complexes. With higher alkenes it promotes isomerisation of terminal to internal alkenes. This isomerisation is non-sequential.

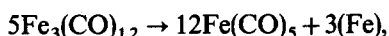
Preliminary observations on the isomerisation of *n*-octenes by photolysed Fe₃(CO)₁₂ have been published,¹ and the full details of this are presented here, together with evidence that Fe(CO)₄ is the catalytic agent. The participation of Fe(CO)₄ has been suggested in other reactions,² produced from Fe₃(CO)₁₂ thermally or by IR irradiation of Fe(CO)₅, and the existence of discrete Fe(CO)₄ has been demonstrated in frozen gas matrices³ and in a polymer matrix.⁴

RESULTS AND DISCUSSION

Formation of Fe(CO)₄

The electronic spectrum of iron dodecacarbonyl has a maximum at 450 nm overlapping the tail of strong absorption in the UV region. There is a more pronounced maximum at 605 nm, and the radiation used was filtered to ensure absorption in this region only. At 373 K the thermal decomposition of Fe₃(CO)₁₂ to Fe(CO)₅ in hexane solution is appreciable but at 293 K formation of Fe(CO)₅ was immeasurable in the dark.

Irradiation of solutions of Fe₃(CO)₁₂ at 293 K under nitrogen produces Fe(CO)₅ in 96% yield according to the equation



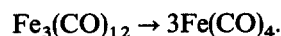
where (Fe) represents iron bound in the uncharacterised precipitate. Similar results were obtained under argon and hydrogen atmo-

spheres. Replacement of the nitrogen by carbon monoxide, however, led to all the iron being converted to Fe(CO)₅:



and no initial precipitate was formed, although of course Fe(CO)₅ itself decomposes slowly giving a brown precipitate.

These results suggested that the photodissociation was simply



Reaction with ethylene

Irradiation of iron dodecacarbonyl solutions in the presence of ethylene gave a solution having a complex IR spectrum in the metal-carbonyl stretching region (Table 1). Bands due to Fe(CO)₅ and (C₂H₄)Fe(CO)₄ were detected, and the PMR spectrum⁵ confirmed the presence of (C₂H₄)Fe(CO)₄. The presence of other species was suspected because of variations in relative peak heights and half-widths, and of small shifts in the position of maxima in IR spectra obtained from different experiments. These variations did not appear to be produced by differences in concentration, temperature or length of irradiation. Small differences resulted from the use of non-purified hydrocarbon solvents, and large ones from the use of halogenated solvents, or unfiltered radiation.

The solutions were stable at 195 K in the dark, but decomposed to Fe₃(CO)₁₂ in sunlight. They were moderately sensitive to oxygen, but not at all to hydrogen, carbon monoxide, propene or propyne. Addition of cyclopentadiene appeared to displace some ethylene.

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Table 1. IR spectra in the metal-carbonyl region (in *n*-heptane, except where stated)

Species	Maxima (cm ⁻¹)				
Fe ₃ (CO) ₁₂	2046(s)	2024(s)			
Fe(CO) ₅		2024(s)		2001(s)	1964(vw)
Fe(CO) ₅ in CCl ₄		2028(s)		1999(s)	
(C ₂ H ₄)Fe(CO) ₄ ¹⁶	2088(s)	2013(sh)	2007(s)		1986(s)
C ₂ H ₄ + Fe ₃ (CO) ₁₂ + <i>hν</i>	2086(w)	2023(s)	2008(s)	2001(s)	1984(s)
C ₃ H ₆ + Fe ₃ (CO) ₁₂ + <i>hν</i>	2083(vw)	2024(s)		2001(s)	1982(s)
C ₅ H ₆ + Fe ₃ (CO) ₁₂ + <i>hν</i>	2089(w)	2047(s)	2024(s)	2001(s)	1982(s)
					1974(s)

Reaction with propene

Solutions similar to, but much less stable than, those obtained with ethylene were obtained with propene.

The PMR spectrum of C₃H₆Fe(CO)₄ was obtained in CFCl₃ at 203 K and at temperatures up to 243 K showed no appreciable change, but thereafter the rate of decomposition of the complex increased and was rapid at 273 K.

The measured parameters of the spectrum are compared with literature values⁶ for propene itself in Table 2. The value of zero given to *J*₂₃, *J*₂₄ and *J*₃₄ is only approximate, there being considerable peak broadening in the spectrum, probably due to suspended particles of iron produced by decomposition of the complex. However, double irradiation experiments confirmed the values obtained, and showed no signs of *J*₂₃, *J*₂₄ or *J*₃₄ coupling.

As expected the chemical shifts of protons attached to carbon atoms interacting directly with the metal are shifted to higher field. The methylene protons have a similar chemical shift to those in the ethylene complex, but the relative values of the shifts of the protons *cis* and *trans* to the lone proton are reversed with respect to the free propene, assuming that the protons have been correctly assigned (on the basis of the *trans* coupling being greater than the *cis*). The chemical shift of the methyl protons remains effectively the same.

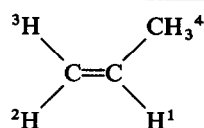
A discussion of the significance of the value of *J*₂₃ in terms of the bonding in the complex would not be helpful in view of the uncertainty in the value of *J*₂₃, and the doubts which have been expressed about the validity of correlations between coupling constants and bond angles. The reduction of coupling constants in going from the free propene to the complex is paralleled in other π-alkene complexes of iron tetracarbonyl such as (H₂C=CHCOOCH₃)Fe(CO)₄.⁷

Isomerisation of alkenes

The preceding experiments demonstrate that Fe(CO)₄ is formed by dissociation of Fe₃(CO)₁₂ resulting from absorption of light at 605 nm, and that it forms complexes with ethylene and propene. It seemed likely that it might catalyse the isomerisation of alkenes, as has since been reported to occur when alkenes were treated with various iron carbonyl species.⁸ This photochemical route seemed to be a particularly clean way of preparing (alkene)Fe(CO)₄ species, since they would not absorb light of such wavelengths. Using hex-1-ene under the conditions

Table 2. Chemical shifts and coupling constants for propene and propeneiron tetracarbonyl

Proton	Chemical shift (δ value)	
	Propene ⁶	Complex
1	5.767	3.35
2	4.883	2.65
3	4.968	2.41
4	1.713	1.73
	Coupling constants (Hz)	
<i>J</i> ₁₂	10.02	7.5
<i>J</i> ₁₃	16.81	12.5
<i>J</i> ₁₄	6.40	6.0
<i>J</i> ₂₃	2.08	0.0
<i>J</i> ₂₄	-1.33	0.0
<i>J</i> ₃₄	-1.75	0.0



Chemical shift (δ value)

Table 3. Isomerisation of oct-1-ene in light petroleum at 293 K; product ratios, relative to *trans*-oct-3-ene = 100

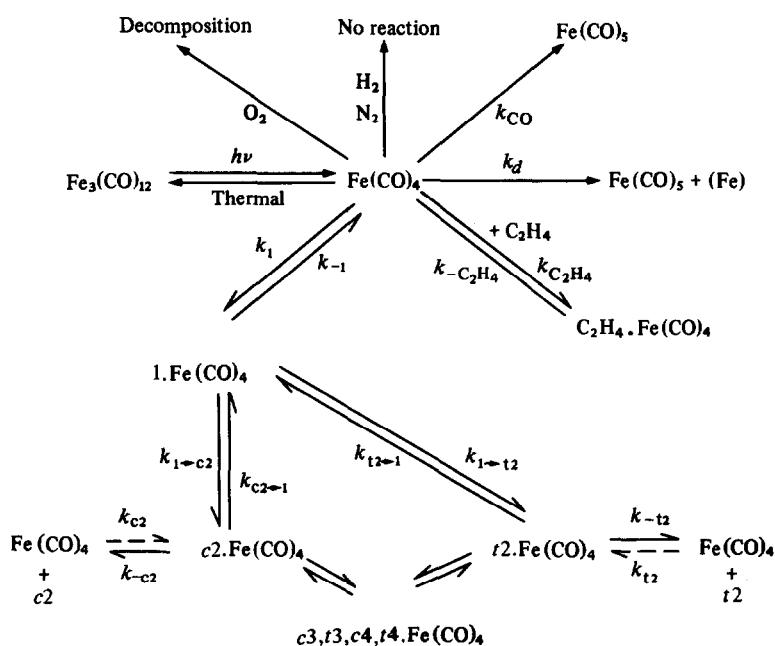
Time (s)	<i>trans</i> -4 (t4)	<i>cis</i> -4 (c4)	<i>trans</i> -3 (t3)	<i>cis</i> -3 (c3)	<i>trans</i> -2 (t2)	<i>cis</i> -2 (c2)	% isomerisation
90	58.3	7.8	100	19.5	93.7	23.7	4.1
180	56.2	8.2	100	16.4	103.0	21.7	10.4
270	61.7	7.2	100	16.7	102.9	23.5	10.3
360	66.5	5.2	100	15.5	98.8	22.5	13.5
450	52.2	5.4	100	14.2	88.3	23.3	19.3
540	59.2	7.2	100	15.2	95.4	24.5	22.4
630	59.7	6.2	100	13.3	94.2	21.8	28.4
720	58.0	10.1	100	14.7	99.9	24.6	27.7
(<i>equil.</i>) ¹	82	15	100	17	104	27	—
(<i>calc.</i>) [*]	59	7	100	19	97	23	—

* By least-square extrapolation.

described above it was shown that extensive isomerisation occurred, giving up to 96% of internal hexenes; that the presence of alkene inhibited the disproportionation reaction (no immediate precipitate); that carbon monoxide inhibited the isomerisation; and that no reaction takes place in the absence of light. Using oct-1-ene it was found that no reduction to octane occurred.⁹ When the mixtures obtained after varying degrees of reaction were analysed ("method B")¹⁰ and the ratios of the

products to *trans*-oct-3-ene (chosen arbitrarily) were extrapolated to zero conversion,²² the initial product-mixture from oct-1-ene was shown already to contain substantial amounts of the oct-3-enes and oct-4-enes. Indeed, its composition did not differ greatly from that of an equilibrium mixture of the *n*-octenes.¹²

It is quite possible that the equilibrium coefficients for the six internal octenes as Fe(CO)₄ complexes are very similar to those for the octenes themselves, and



(1 = oct-1-ene etc.)

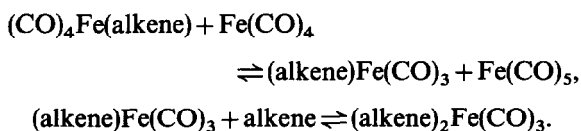
$k_{\text{CO}} > k_{\text{C}_2\text{H}_4} > k_1 > k_d > k_{t2}, k_{c2}, k_{\text{H}_2}, k_{\text{N}_2}$

$k_{1 \rightarrow c2}$ etc. $>$ k_{-c2} etc.

Scheme 1.

that (oct-1-ene)Fe(CO)₄ rapidly converts to this equilibrium mixture, before the much slower equilibration between these alkenes and their complexes makes significant progress. Alternatively, the rate of dissociation of the complexes may be slower than that of the isomerisation processes but not much slower than the slowest of these, perhaps $k_{13 \rightarrow c4}$. In that case the kinetic product mixture will be distorted from the hypothetical equilibrium mixture. The marked delay in the precipitation of iron (or iron sub-carbonyl species) when hex-1-ene is present suggests that the complexing rate of a terminal alkene, k_1 , compares favourably with that of disproportionation, k_d , and this was confirmed when oct-1-ene and Fe₃(CO)₁₂ were irradiated in a *ca* 700:1 molar ratio, when at least 270 mol of oct-1-ene were isomerised per mol of Fe₃(CO)₁₂. However, the similar isomerisation of *cis*- and *trans*-oct-4-enes could not be examined in detail, because the disproportionation process in this case proved to be relatively too fast. Evidently complexing rates for disubstituted alkenes are much lower than for terminal alkenes and the Fe(CO)₄ complexes much less stable.

We may summarise the behaviour of Fe(CO)₄ in the scheme shown; its properties are reminiscent of those of a reactive intermediate of moderate stability, like CCl₂, and could in principle be explored quantitatively, using visible-light photolysis of Fe₃(CO)₁₂ as a cleaner source of this species than, e.g. thermolysis of Fe₂(CO)₉. This would require more rigorous exclusion of unwanted reactants (oxygen, impurities in solvents etc.) than was attempted here. Our work has no bearing on the mechanism of the isomerisation reaction. It has been suggested¹³ that it occurs via an intermediate of the type (CO)₃Fe(alkene)₂ and our results are consistent with this view, providing the intermediate can be generated by some such process as the following:



EXPERIMENTAL

In pilot experiments using commercial solvents unexpected peaks were obtained in the metal-carbonyl stretching region of the IR spectra. These were due to alkene impurities in the hydrocarbons (*n*-heptane, iso-octane, methylcyclohexane and cyclopentane) complexing the Fe(CO)₄ formed during irradiation. They were eliminated by carefully purifying the solvents (stirring for 1 week with acid

potassium permanganate solution, separating, drying and filtering through two silica gel columns).

Iron dodecacarbonyl was prepared both from iron pentacarbonyl¹⁴ and di-iron nonacarbonyl.¹⁵

General procedure

Solutions of iron dodecacarbonyl were prepared by stirring the solid in the solvent and filtering under nitrogen and with as much protection from daylight as possible. The concentration of the solutions was calculated from the absorbance of the 605 nm absorption in the VIS (using a Unicam SP800 spectrophotometer; molar absorption coefficient of Fe₃(CO)₁₂ = 2505 m² mol⁻¹). 25–50 cm³ portions of the solutions in glass tubes fitted with gas inlet and outlet were immersed in a cooling bath maintained at 283–293 K by circulating the coolant through ice. The coolant contained sodium dichromate (4 g dm⁻³), a 1 cm thickness of which was sufficient to absorb all radiation of shorter wavelength than 500 nm. Light was provided by a 2 kW xenon arc lamp. The products were examined by IR spectroscopy in 1 mm solution cells (NaCl) on a Perkin-Elmer 257 over the range 4000–650 cm⁻¹. Concentrations of Fe(CO)₅ were determined from the optical densities of the two major peaks by comparison with a calibration graph. Vapour phase chromatograms were run on a Perkin-Elmer F11 using a 2 m long $\frac{1}{8}$ " diameter stainless steel column packed with 25% M. & B. Embaphase silicone oil on 60–80 mesh Diatoport-S at 298 K using a flame ionisation detector, except for the analysis of octene mixtures, where method B of ref. 10 was used.

Thermal stability of Fe₃(CO)₁₂

A solution of Fe₃(CO)₁₂ in *n*-heptane was protected from the light and heated to 373 K in a stream of nitrogen. The issuing gas was passed through a trap at 195 K. Several samples were collected in succession and all contained Fe(CO)₅ (IR).

In a related experiment at 293 K a little Fe(CO)₅ was obtained initially (presumably from prior decomposition) but, thereafter, none. Thus decomposition of Fe₃(CO)₁₂ is appreciable at 373 K but not at 293 K.

Photolysis of Fe₃(CO)₁₂ under nitrogen

A solution of Fe₃(CO)₁₂ (5.67×10^{-5} mol) in *n*-heptane was irradiated at 293 K for 75 min in a slow stream of N₂. The amount of Fe(CO)₅ carried forward in the gas stream (8.20×10^{-8} mol) was

negligible compared to that remaining in solution (1.30×10^{-4} mol). The intense green of the $\text{Fe}_3(\text{CO})_{12}$ had given way to the pale straw-colour of $\text{Fe}(\text{CO})_5$, and a black precipitate had formed (5.1 mg). On the basis of carbonyl groups the yield of $\text{Fe}(\text{CO})_5$ was 96%. The precipitate had a broad absorption at 2000 cm^{-1} and contained 57% iron (determined by dissolution in conc. HCl, reduction with SnCl_2 , and titration against standard potassium dichromate). Qualitatively similar results were obtained under argon and hydrogen.

Photolysis of $\text{Fe}_3(\text{CO})_{12}$ under carbon monoxide

A solution of $\text{Fe}_3(\text{CO})_{12}$ (2.20×10^{-5} mol) in *n*-heptane was irradiated for 30 min in a slow stream of CO. A clear pale-yellow solution of $\text{Fe}(\text{CO})_5$ was obtained (6.44×10^{-5} mol; 98% of the iron used) but no precipitate.

Photolysis of $\text{Fe}_3(\text{CO})_{12}$ under ethylene

Passage of a slow stream of C_2H_4 through a solution of $\text{Fe}_3(\text{CO})_{12}$ in *n*-heptane during irradiation gave a pale yellow solution, and no precipitate. The solution appeared to contain $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_4$ (IR, Table 1). It slowly decomposed, depositing a brown precipitate, but in sunlight some $\text{Fe}_3(\text{CO})_{12}$ (IR, UV-VIS) was reformed. At low temperature in the dark the solution was stable for at least 2–3 weeks.

PMR spectrum of $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_4$

The IR spectra of solutions obtained from the irradiation of $\text{Fe}_3(\text{CO})_{12}$ with C_2H_4 in *n*-heptane and in CFCl_3 were different. However, when the two solutions were diluted each with an equal volume of the other solvent (i.e. *n*-heptane with CFCl_3 ; CFCl_3 with *n*-heptane) the resulting solutions had identical spectra. This suggests that the differences in the spectra are a solvent effect and that the species present are in fact the same. Solutions in CCl_4 paralleled the behaviour of those in CFCl_3 . The slow decomposition of the complex, on the other hand, is probably different in the two types of solvents, since in hydrocarbons a brown precipitate is formed, whereas in the chlorinated solvents it is white.

$\text{Fe}_3(\text{CO})_{12}$ (0.379 g) was stirred with CFCl_3 in a current of C_2H_4 and irradiated for 80 min. The solution was concentrated by vacuum evaporation of the solvent at 195 K and separated from solid matter by allowing it to evaporate in vacuum at 293 K and condensing the evaporate. The PMR spectrum (100 M.c. Varian HA100 NMR spectrometer) of the solution was compared with one

of C_2H_4 in CFCl_3 . There was an additional sharp singlet at δ 2.31 (relative to TMS), attributed to the complex.⁵

Reactions of $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_4$

A solution of the complex in *n*-heptane was prepared as before. After bubbling H_2 , CO, propene and propyne through separate portions of the solution no change was found in the IR spectrum of the metal-carbonyl region. Bubbling oxygen through reduced the intensity of the spectrum.

Reactions of $\text{Fe}(\text{CO})_4$ with cyclopentadiene

A solution of $\text{Fe}_3(\text{CO})_{12}$ in *n*-heptane was irradiated for 5 min in the presence of C_5H_6 . The solution became colourless and had a characteristic spectrum (Table 1). After 24 h a brown precipitate had formed.

Reaction of $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_4$ with cyclopentadiene

A solution of the ethylene complex was prepared in the usual way. C_5H_6 was added. The IR spectrum of the solution (2087, 2047, 2007, 2001, 1982, 1975 cm^{-1}) had the appearance of a mixture of the ethylene and cyclopentadiene complexes. After 24 h a brown coating had appeared on the tube, and after 48 h the IR spectrum of the solution had reverted almost completely to that of the ethylene complex, but was less intense.

Photolysis of $\text{Fe}_3(\text{CO})_{12}$ under propene

This was effected in the same way as for ethylene. A mixture of $\text{Fe}(\text{CO})_5$ with the $(\text{CH}_3\text{CHCH}_2)\text{Fe}(\text{CO})_4$ complex was obtained, and the propene complex identified by its PMR spectrum as described above. The propene complex was much less stable than the ethylene analogue, but could be kept satisfactorily at 195 K in the dark. It did not react with H_2 .

Isomerisation of 1-hexene

A solution of $\text{Fe}_3(\text{CO})_{12}$ (7.97×10^{-5} mol), 1-hexene (1 cm^3) and *n*-octane (1 cm^3) in *n*-heptane (50 cm^3) was irradiated for 35 min. A heavy precipitate was produced and the solution was pale yellow.

The trap contained $\text{Fe}(\text{CO})_5$ (2.55×10^{-7} mol). After standing, the characteristic green of $\text{Fe}_3(\text{CO})_{12}$ returned (VIS showed 6.79×10^{-6} mol), and the solution also contained $\text{Fe}(\text{CO})_5$ (1.97×10^{-4} mol). After 16 h the concentration of $\text{Fe}_3(\text{CO})_{12}$ had increased to 1.06×10^{-5} mol. The ratio of internal

hexenes to 1-hexene was 41:1 (VPC). The IR spectrum indicated a trace of some compound other than $\text{Fe}(\text{CO})_5$, presumably a hexene complex.

A solution of $\text{Fe}_3(\text{CO})_{12}$ was divided into three 25 cm^3 portions (3.89×10^{-5} mol in each) and 1 cm^3 1-hexene was added to each. The first was kept dark, and no reaction occurred. The second was irradiated under N_2 and gave $\text{Fe}(\text{CO})_5$ (1.06×10^{-4} mol; IR peak ratios and the presence of an additional small peak indicated some undecomposed hexene complex). The ratio of internal hexenes to 1-hexene was 1.44 to 1. The third solution was irradiated under CO. No isomerisation occurred, but a little alkene complex appeared to be present in the $\text{Fe}(\text{CO})_5$ (1.15×10^{-4} mol).

Isomerisation of oct-1-ene

The $\text{Fe}(\text{CO})_4$ was produced in these experiments by light from a tungsten-iodine lamp (3400 K) filtered through a Kodak No. 8 yellow filter, and the solvent was light petroleum. 25 cm^3 of $\text{Fe}_3(\text{CO})_{12}$ solution (2 mg dm^{-3}) and 80 mg of oct-1-ene were irradiated. 30 mg of octene isomerised, i.e. 274 mol of oct-1-ene per mol $\text{Fe}_3(\text{CO})_{12}$. In a similar experiment, the product ratios of the internal octenes were measured by VPC at 90 s intervals throughout the irradiation (Table 3). In further experiments, *cis*-oct-4-ene isomerised less than 1% after 24 min and *trans*-oct-4-ene about 2% in 23 min.

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