

Journal of Organometallic Chemistry, 415 (1991) 257–263
Elsevier Sequoia S.A., Lausanne
JOM 22008

Chemistry of coordinatively unsaturated and electron deficient carbonyl metallate ions. Gas phase reactions of $[\text{Fe}(\text{CO})_2]^{-\bullet}$ with hydrocarbons

I.K. Gregor

School of Chemistry, The University of New South Wales, Kensington, N.S.W. 2033 (Australia)

(Received April 9th, 1991)

Abstract

A study has been carried out of the gas phase reactions of the radical anion $[\text{Fe}(\text{CO})_2]^{-\bullet}$ with twenty-one C_2 – C_8 hydrocarbons, including acyclic, cyclic and isomeric alkenes, dienes, alkynes, and aromatics. Dehydrogenation and decarbonylation processes have been identified in the principal reaction channels, which were dependent on the hydrocarbon structure, while sequential ligand substitutions were observed for the reaction of C_2H_2 with $[\text{Fe}(\text{CO})_2]^{-\bullet}$ to give the terminal product ion $[(\text{C}_2\text{H}_2)_2\cdot\text{Fe}]^{-\bullet}$.

Introduction

Coordinatively unsaturated and electron-deficient carbonyl metallate ions have long been recognized as reactive intermediates in solution phase organometallic and catalytic chemistry [1–3]. The availability of recently developed experimental techniques such as Fourier transform ion cyclotron resonance (FTICR) spectroscopy now provides opportunities for new insights to be gained into the elementary ion/molecule reactions of specifically synthesized organometallic ions in the gas phase [4–6]. Such ions may be trapped for long periods (seconds) and at low pressures (10^{-9} – 10^{-7} mbar) within ICR cells to enable simultaneous and consecutive reaction channels, together with novel reaction products and intermediates, to be identified from time resolved mass spectral data and high resolution mass measurements [4,6,7–9]. As part of a continuing study of the ion/molecule chemistry of carbonyl metallate ions [10–14], results are now presented for the gas phase reactions of the 13-electron radical ion $[\text{Fe}(\text{CO})_2]^{-\bullet}$ with a representative series of hydrocarbons that includes acyclic, cyclic and isomeric alkenes, dienes, alkynes and aromatics.

Experimental

All ion/molecule experiments were performed in a Spectrospin CMS-47 FTICR spectrometer. Details of this experimental technique and instrumentation have been

described previously [5,6,8,15]. The volatile reagents were admitted to the ICR cell via a 40°C temperature regulated inlet system fitted with Balzers precision leak valves type BDV-035. The ICR cell temperature was somewhat above ambient (ca. 35°C) owing to heat from the 4 cm remotely positioned rhenium ribbon cell filament. All pressures were measured with a magnetically shielded Balzers type IMR-132 ionization gauge positioned in proximity (ca. 10 cm) to the Balzers TPU 330 turbomolecular pump. Low energy ionisation (5 eV) of $\text{Fe}(\text{CO})_x$ at a pressure of 5×10^{-8} mbar gave the ionic products $[\text{Fe}(\text{CO})_4]^-$ (100%), $[\text{Fe}(\text{CO})_3]^-$ (15%), and $[\text{Fe}(\text{CO})_2]^-$ (5%), which are consistent with other reported negative ion mass spectra [16]. As both anions and electrons are trapped in the ICR cell during negative ion experiments, electrons were ejected from the cell after the electron beam pulse (25 ms) by the application of an oscillating electric field across the trapping plates (5 ms at ca. $2 V_p$, amplitude 4.2 MHz and -2.5 V trapping voltage). Mass selected $[\text{Fe}(\text{CO})_2]^-$ ions were trapped in the cell after the application of broad band excitation pulses to eject other extraneous ions from the cell. Translational excitation of the reactant $[\text{Fe}(\text{CO})_2]^-$ ions was minimized by use of the lowest possible radio frequency fields. Neutral reactants were admitted to the ICR cell in the pressure ratio 5/1 to the metal carbonyl and to a total indicated pressure of 2.5×10^{-7} mbar. Except where otherwise indicated, reaction delays of 1 s were used to establish ionic product distributions for all ion/molecule reactions. The elemental formulae of all ionic reaction products were determined from mass measurements and ion/molecule reaction channels were deduced as a result of selective ion ejections or plots of the temporal variations of ionic product distributions ("time plots").

Accurate estimates of neutral particle densities in the ICR cell, and hence rate constant measurements, were not meaningfully obtainable because of well-established low pressure inaccuracies in ionization gauge readings particularly in high magnetic field regions, and the present absence of absolute pressure calibration instrumentation at these working pressures.

Iron pentacarbonyl was obtained from Strem Chemicals Inc. and the organic reagents were high purity commercial samples from Matheson Gases, Phillips-66, Aldrich, Fluka and B.D.H., which were admitted to the CMS-47 FTICR spectrometer after undergoing multiple freeze-pump-thaw cycles to remove non-condensables. Propene, methyl- d_3 , 99% D was obtained from Cambridge Isotope Laboratories. Where appropriate, sample purities were checked from positive ion mass spectra run on the CMS-47 instrument.

Results and discussion

The twenty-one hydrocarbons whose reactions with $[\text{Fe}(\text{CO})_2]^-$ were examined are listed in Table 1. Product distributions for the reactions between $[\text{Fe}(\text{CO})_2]^-$ and the 1-alkenes, II, III, VIII, X, XV, XVIII and XIX are given in Table 2.

Except in the case of III, the principal reaction channel led to the formation of a dehydrogenated ionic product, $[\text{C}_n\text{H}_{2n-2}\text{Fe}(\text{CO})_2]^-$; in the case of III, this species was detected along with a decarbonylated product. For the C_4 and higher alkenes the dehydrogenation reaction channel parallels that previously identified for reactions of the 13-electron ion $[\text{Cr}(\text{CO})_3]^-$ with alkenes [13]. That is, a necessary structural feature of these 1-alkenes appears to be their ability, after dehydrogena-

Table 1

[Fe(CO)₂]⁻/hydrocarbon reactants

| Hydrocarbon | | Isomer |
|-------------|--|--|
| I | C ₂ H ₂ | acetylene |
| II | C ₂ H ₄ | ethylene |
| III | C ₃ H ₆ | propene |
| IV | C ₃ H ₃ D ₃ | propene, methyl- <i>d</i> ₃ |
| V | C ₃ H ₆ | cyclopropane |
| VI | C ₄ H ₆ | 1,3-butadiene |
| VII | C ₄ H ₆ | 2-butyne |
| VIII | C ₄ H ₈ | 1-butene |
| IX | C ₄ H ₈ | <i>trans</i> -2-butene |
| X | C ₅ H ₁₀ | 1-pentene |
| XI | C ₅ H ₁₀ | <i>cis</i> -2-pentene |
| XII | C ₆ H ₆ | benzene |
| XIII | C ₆ H ₈ | 1,3-cyclohexadiene |
| XIV | C ₆ H ₁₀ | cyclohexene |
| XV | C ₆ H ₁₂ | 1-hexene |
| XVI | C ₇ H ₈ | toluene |
| XVII | C ₇ H ₁₂ | 1-methylcyclohexene |
| XVIII | C ₇ H ₁₄ | 1-heptene |
| XIX | C ₈ H ₁₆ | 1-octene |
| XX | C ₈ H ₁₆ | 2,2,4-trimethyl-1-pentene |
| XXI | C ₈ H ₁₆ | 2,2,4-trimethyl-2-pentene |

tion, to form an η^4 -conjugated double bonded complex with the metal centre via a π -allyl metal-hydrido intermediate, and this is followed by β -hydrogen abstraction and H₂-elimination as shown in Scheme 1.

Support for this rationalization is provided by the ionic product data given in Table 3 for the reactions of the isomeric C₈H₁₆ alkenes, XX and XXI with [Fe(CO)₂]⁻, which give as the predominant ionic products decarbonylated rather than dehydrogenated species because of the inability of XX and XXI for structural reasons to form η^4 -conjugated complexes with the metal centre.

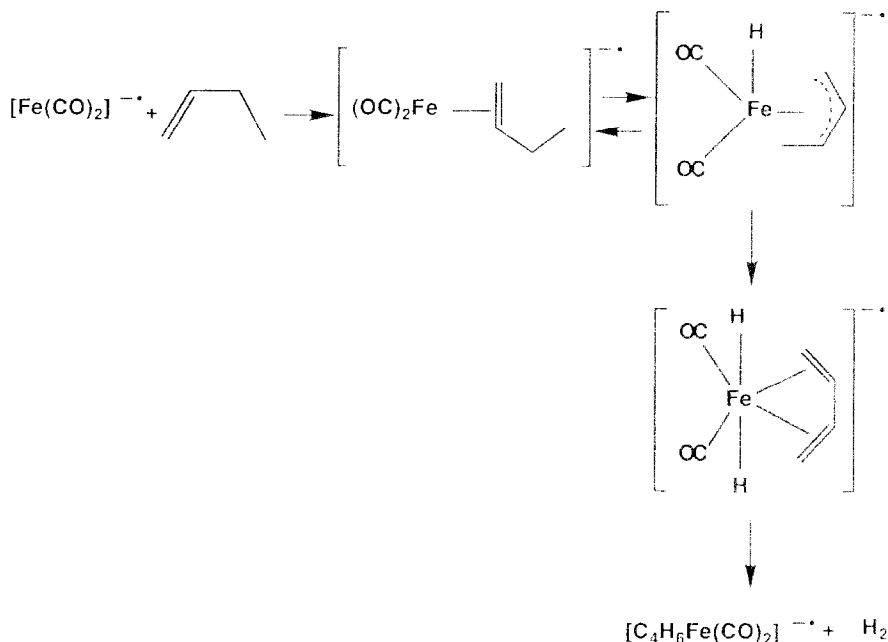
A qualitative comparison of the rates of the dehydrogenation reaction channels for the [Fe(CO)₂]⁻ reactions with the C₂ and C₅ 1-alkenes II and X, is given in

Table 2

Product distributions for reactions of [Fe(CO)₂]⁻ with 1-alkenes ^a

| Alkene | | Ionic products ^b | |
|--------|--------------------------------|--|--|
| | | [C _n H _{2n-2} Fe(CO) ₂] ⁻ | [C _n H _{2n} Fe(CO)] ⁻ |
| II | C ₂ H ₄ | 1.0 | 0 |
| III | C ₃ H ₆ | 0.29 | 0.71 |
| VIII | C ₄ H ₈ | 1.0 | 0 |
| X | C ₅ H ₁₀ | 1.0 | 0 |
| XV | C ₆ H ₁₂ | 1.0 | 0 |
| XVIII | C ₇ H ₁₄ | 1.0 | 0 |
| XIX | C ₈ H ₁₆ | 1.0 | 0 |

^a Reaction times of 1 s. ^b Based on ⁵⁶Fe.



Scheme 1.

Fig. 1. This plot shows the variation with time of product distributions for the reaction



and indicates that under the experimental conditions used complete reaction of $[\text{Fe}(\text{CO})_2]^{-}$ takes place within ca. 1 s and that the reaction rates for the two systems are similar.

Whereas the C_3 -alkene III gave only a decarbonylated reaction product with the 13-electron ion $[\text{Cr}(\text{CO})_3]^{-}$ [13], both ionic dehydrogenated and decarbonylated species were identified for the reaction of $[\text{Fe}(\text{CO})_2]^{-}$ with III, Table 2; the former product is thought to be a $[\pi\text{-allene}\cdot\text{Fe}(\text{CO})_2]^{-}$ complex. Such species were identified in previously reported flowing afterglow studies of the reactions of π -systems with the 15-electron ion $[\text{Fe}(\text{CO})_3]^{-}$ [17]. However, the complexity of the present reaction has been established from the results for the $[\text{Fe}(\text{CO})_2]^{-}$ /

Table 3

Product distributions for reactions of $[\text{Fe}(\text{CO})_2]^{-}$ with isomeric alkenes^a

| Alkene | Ionic products ^b | |
|---|---|---|
| | $[\text{C}_n\text{H}_{2n-2}\text{Fe}(\text{CO})_2]^{-}$ | $[\text{C}_n\text{H}_{2n}\text{Fe}(\text{CO})]^{-}$ |
| IX C_4H_8 , <i>trans</i> -2-butene | 1.0 | 0 |
| XI C_5H_{10} , <i>cis</i> -2-pentene | 1.0 | 0 |
| XX C_8H_{16} , 2,4,4-trimethyl-1-pentene | 0 | 1.0 |
| XXI C_8H_{16} , 2,4,4-trimethyl-2-pentene | 0.03 | 0.97 |

^a Reaction delays of 1 s. ^b Based on ^{56}Fe .

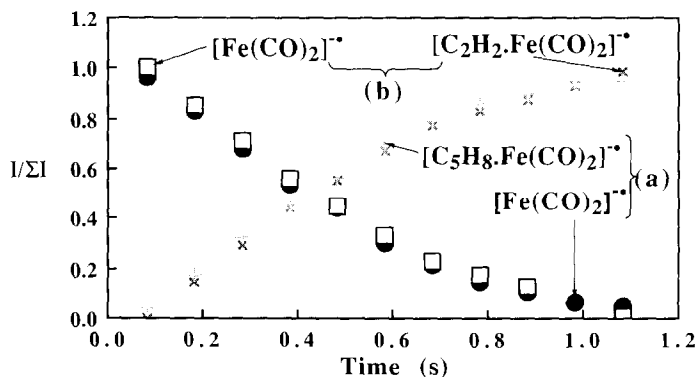


Fig. 1. Variations of ion abundances with time for the reaction of $[\text{Fe}(\text{CO})_2]^-$ with 1-pentene, X, (a) and ethylene, II, (b). $I/\Sigma I$ = ion abundance/sum of product ion abundances. ^{56}Fe considered.

$\text{CD}_3\text{CH}=\text{CH}_2$ (IV) system for which the variations of ionic product distributions with time are given in Fig. 2.

Four ionic reaction products were identified from mass measurements of the species shown in Fig. 2, namely those with m/z 155, $[(\text{CO})_2\text{Fe}\cdot\text{C}_3\text{H}_3\text{D}_3]^-$; m/z 154, $[(\text{CO})_2\text{Fe}\cdot\text{C}_3\text{H}_2\text{D}_2]^-$; m/z 138, $[(\text{CO})_2\text{Fe}\cdot\text{C}_2\text{H}_2]^-$; and the decarbonylated species m/z 129, $[(\text{CO})\text{Fe}\cdot\text{C}_3\text{H}_3\text{D}_3]$. From the measured ionic elemental compositions and the product distribution profiles, the m/z 155 and m/z 154 species appear to owe their origins to neutral losses of H_2 and HD from a common complex hydrido precursor whereas alkane elimination [12] appears to be involved in the formation of the m/z 138 ion, $[(\text{CO})_2\text{Fe}\cdot\text{C}_2\text{H}_2]^-$. This latter ion was observed previously in a (higher pressure) flowing afterglow investigation of the reaction of $[\text{Fe}(\text{CO})_3]^-$ with acetylene, the implication being that the acetylene ligand functions as a four-electron donor, thereby occupying two coordination sites on the metal [17]. In the present work the reaction of isomeric C_3H_6 cyclic alkane V with $[\text{Fe}(\text{CO})_2]^-$ gave the dehydrogenated species $[\text{C}_3\text{H}_4\cdot\text{Fe}(\text{CO})_2]^-$, m/z 152, as the

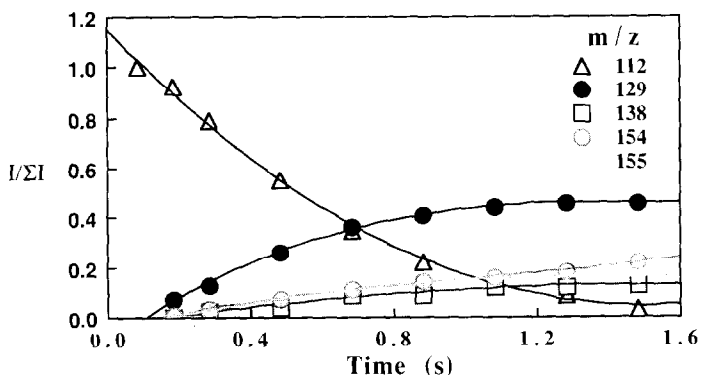


Fig. 2. Variations of ion abundances with time for the reaction of $[\text{Fe}(\text{CO})_2]^-$ with propene, methyl- d_3 (IV), with the reactant ion $[\text{Fe}(\text{CO})_2]^-$, m/z 112; and product ions $[(\text{CO})\text{Fe}\cdot\text{C}_3\text{H}_3\text{D}_3]^-$, m/z 129; $[(\text{CO})_2\text{Fe}\cdot\text{C}_2\text{H}_2]^-$, m/z 138; $[(\text{CO})_2\text{Fe}\cdot\text{C}_3\text{H}_2\text{D}_2]^-$, m/z 154; and $[(\text{CO})_2\text{Fe}\cdot\text{C}_3\text{HD}_3]^-$, m/z 155. $I/\Sigma I$ = ion abundance/sum of product ion abundances. ^{56}Fe considered.

sole ionic product. Although at this juncture a concomitant ring cleavage process leading to the formation of the C_3H_4 moiety cannot be excluded, the observation of only this single ionic reaction product makes it unlikely that the reaction proceeds via a metallocyclobutane intermediate of the type postulated for the reactions of metal-containing ions with cycloalkanes [18]. However it is significant that in a recent flowing afterglow study of C-H bond activation in acyclic and cyclic alkanes by carbonyl metallate ions, C_5 and C_6 alkanes were also shown to form [adduct- H_2] $^-$ ions in their reactions with $[Fe(CO)_2]^-$ [19].

In reactions much slower than those between $[Fe(CO)_2]^-$ and C_5 - C_8 alkanes, single ionic products were formed in the reactions between $[Fe(CO)_2]^-$ and the C_6 - C_7 cyclic hydrocarbons XII, XIII, XIV, XVI and XVII. Ligand exchange/decarbonylation reactions only were identified for the aromatic system reactions of XII and XVI with $[Fe(CO)_2]^-$ to give the 17-electron products $[\eta^6-R \cdot C_6H_5 \cdot Fe(CO)]^-$, with $R = H$ and CH_3 for XII and XVI, respectively. The hydrocarbons XIV and XVII in their reactions with $[Fe(CO)_2]^-$ gave the corresponding 17-electron dehydrogenated $[\eta^4\text{-cyclo}diene \cdot Fe(CO)_2]^-$ products, whereas XIII reacted very slowly with $[Fe(CO)_2]^-$ to give the ionic products $[C_6H_8 \cdot Fe(CO)_2]^-$, m/z 192, 62%, and $[C_6H_6 \cdot Fe(CO)]^-$, m/z 162, 38%. Both of these ions can be regarded as 17-electron species if η^4 - and η^6 -hydrocarbon metal bonding, respectively, is involved. In contrast, reaction of the acyclic diene VI with $[Fe(CO)_2]^-$ gave as the sole ionic product $[\eta^4-C_4H_6Fe(CO)]^-$.

Whereas the alkyne VII underwent a very slow reaction with $[Fe(CO)_2]^-$ to form only the decarbonylated product [adduct-CO] $^-$, sequential CO displacement was observed for the $[Fe(CO)_2]^-$ /acetylene (II) reaction the product distribution/time plot for which is shown in Fig. 3.

It is relevant here that π -bonding is favoured between acetylene and the iron atom in the decarbonylated species $[C_2H_2 \cdot Fe(CO)_2]^-$ that was identified from the flowing afterglow reaction of the 15-electron ion $Fe(CO)_3^-$ with acetylene [17], rather than hydrogen bonded or metal C-H insertion species [20]. In the reaction studied in the present work between $[Fe(CO)_2]^-$ and II, exothermic substitution of C_2H_2 for CO to give the 15- and 17-electron C_2H_2 π -bonded complexes $[C_2H_2 \cdot$

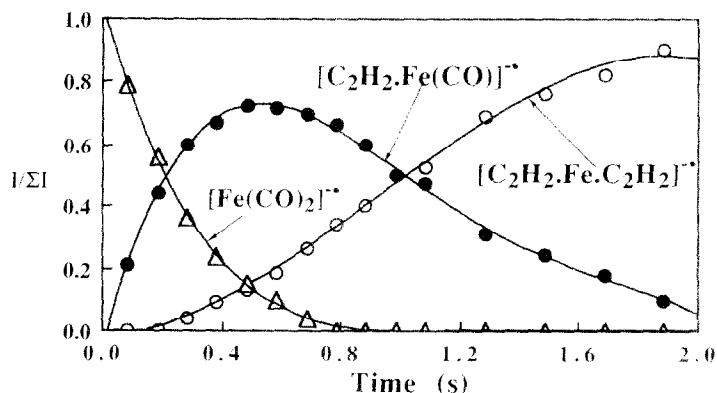


Fig. 3. Variations of ion abundances with time for the reaction of $[Fe(CO)_2]^-$ with acetylene. $I/\Sigma I$ = ion abundance/sum of product ion abundances. ^{56}Fe considered.

$\text{Fe}(\text{CO})]^{-}$ and $[(\text{C}_2\text{H}_2)_2 \cdot \text{Fe}]^{-}$ is feasible in terms of the known $[\text{CO} \cdot \text{Fe}-\text{CO}]^{-}$ bond strength of (1.0 ± 0.3) eV, the linear geometry of $[\text{Fe}(\text{CO})_2]^{-}$, and the predicted destabilization of the occupied Fe–CO π -orbitals in this ion that would be expected to occur upon reaction with II [21].

Acknowledgement

Support of this work by the Australian Research Council is acknowledged.

References

- 1 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
- 2 J.K. Kochi, Organometallic Mechanisms and Catalysis: The Role of Reactive Intermediates in Organic Processes, Academic Press, New York, 1978.
- 3 G.W. Parshall, Homogeneous Catalysis: The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes, Wiley, New York, 1980.
- 4 M.V. Buchanan (Ed.), Fourier Transform Mass Spectrometry, ACS Symposium Series 359, American Chemical Society, Washington, DC, 1987.
- 5 B.S. Freiser, in J.M. Farrar and W.H. Saunders Jr. (Eds.), Techniques for the Study of Ion–Molecule Reactions, Wiley-Interscience, New York, 1988, Ch. II, p. 61.
- 6 (a) A.G. Marshall and F.R. Verdun, Fourier Transforms in NMR, Optical and Mass Spectrometry, A User's Handbook, Elsevier, Amsterdam, 1990, Ch. 7, p. 225; (b) A.G. Marshall and P.B. Grosshans, Anal. Chem., 63 (1991) 215A.
- 7 R.R. Squires, in D.H. Russell (Ed.), Gas Phase Inorganic Chemistry, Plenum, New York, 1989, Ch. 2, p. 43.
- 8 N.M.M. Nibbering, Acc. Chem. Res., 23 (1990) 279.
- 9 R.R. Squires, Chem. Rev., 87 (1987) 623.
- 10 I.K. Gregor, Inorg. Chim. Acta, 176 (1990) 19.
- 11 I.K. Gregor, Org. Mass Spectrom., 24 (1989) 529.
- 12 I.K. Gregor, Org. Mass Spectrom., 132 (1987) 3.
- 13 I.K. Gregor, J. Organomet. Chem., 329 (1987) 201.
- 14 I.K. Gregor and M. Guilhaus, Mass Spectrom. Rev., 3 (1984) 39.
- 15 L.J. de Koning, R.H. Fokkens, F.A. Pinkse and N.M.M. Nibbering, Int. J. Mass Spectrom. Ion Proc., 77 (1987) 95.
- 16 R.N. Compton and J.A.D. Stockdale, Int. J. Mass Spectrom. Ion Phys., 22 (1976) 47.
- 17 R.N. McDonald, A.K. Chowdhury and P.L. Schell, J. Am. Chem. Soc., 106 (1984) 6096.
- 18 J. Allison, Prog. Inorg. Chem., 34 (1986) 627, and references therein.
- 19 R.N. McDonald, M.T. Jones and A.K. Chowdhury, J. Am. Chem. Soc., 113 (1991) 476.
- 20 E.S. Kline, Z.H. Kafafi, R.H. Hauge and J.L. Margrave, J. Am. Chem. Soc., 107 (1985) 7559.
- 21 P.C. Engelking and W.C. Lineberger, J. Am. Chem. Soc., 101 (1979) 5569.