Electrochemical Generation and Stability of Butadiene(tricarbonyl)iron Anion in the Presence of Electrophiles and under CO Pressure[1]

Nabil El Murr* and John D. Payne

Institut de Recherches sur la Catalyse, CNRS, 2, avenue Albert Einstein, 69626 Villeurbanne Cédex, France

In tetrahydrofuran at −20 °C cyclic voltammetry of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ shows two one-electron reduction steps whereas at room temperature only the first is observed; electrolysis leads to the generation of the corresponding anion, in which one of the C–C double bonds is no longer co-ordinated to the iron atom, this anion reacting with H^+ or halides leading to the π-allyl complexes, and under CO pressure, the butadiene ligand is deco-ordinated with formation of $[Fe_2(CO)_8]^{2-}$.

The change in reactivity of a diene on co-ordination to a transition metal, and the high stability of the $[Fe(CO)_3(\eta^4\text{-diene})]$ unit, have provoked a wide interest in the reactions of molecules of this type with protons,[2,3] Friedel–Crafts reagents,[4] carbanions,[5] the trityl cation,[6] *etc.* However, the electrochemistry of these species has received much less attention. We now report some electrosynthetic reactions of the simplest homologue, $[Fe(CO)_3(\eta\text{-}C_4H_6)]$, with H^+ and CO.

The electrochemical behaviour of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ was first studied by Dessy *et al.*,[7] who noted that, on reduction, passage of 1.3 Faraday/mol was required, but that the system was destroyed. More recently it has been reported that in the gas phase, $[Fe(CO)_3(\eta\text{-diene})]$ compounds readily accept electrons to yield anions which decompose by CO and diene elimination.[8] Finally, Krusic *et al.* treated $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ in tetrahydrofuran–hexamethylphosphoramide (THF–HMPA) at −80 °C with finely dispersed Na–K alloy to give the formally 17-electron complex $[Fe(CO)_3(\eta^2\text{-}C_4H_6)]^-$ where only one of the butadiene double bonds is co-ordinated.[9] Analogous behaviour was observed by us for the heterodiene compound $[Fe(CO)_3(\eta^4\text{-bda})]$, bda = benzylideneacetone.[10] Two monoelectronic reduction processes accompanied by liberation of the carbonyl group of the bda give respectively 17- and 18-electron species.

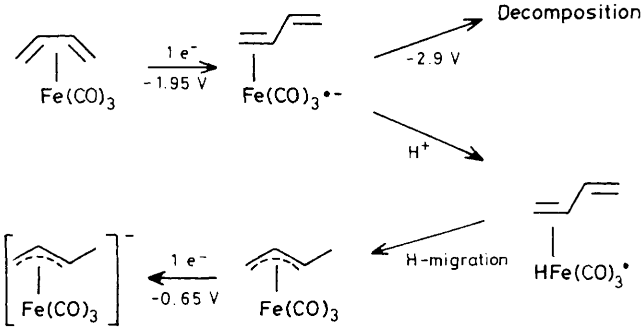
At room temperature in THF solution with 0.3 M $[Bu_4N][PF_6]$ as supporting electrolyte, polarography at a dropping mercury electrode showed that $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ (4 mM) undergoes one reduction process in the 0 to −2.8 V region with $E_{\frac{1}{2}} = -1.95$ V relative to saturated calomel electrode (s.c.e.). Cyclic voltammetry on C and Pt electrodes showed that the reduction was irreversible at scan rates of up to 200 mV s^{-1}, and revealed in the return scan a new anodic peak at −0.6 V. Cyclic runs indicated this to be a reversible couple with $\Delta E = 80$ mV. The oxidation of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ at +1.3 V was observed by cyclic voltammetry; it was also irreversible and slightly larger than the reduction wave.

By analogy with the $[Fe(CO)_3(\eta\text{-dba})]$ system, it might be expected that $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ would also show two monoelectronic reduction waves. It is known that on cooling an electrolytic solution the discharge of the electrolyte support is displaced to a more cathodic potential.[11] Thus, in THF at −20 °C, cyclic voltammetry showed a second reduction wave at −2.9 V, approximately two-thirds the size of the first wave. No anodic waves were observed in the return scan.

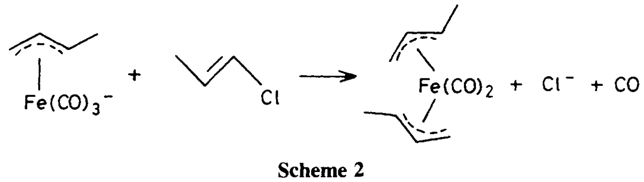
When 5—10% of water was added to a THF solution of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ at room temperature, the reduction wave increased slightly in size, as did the product wave at −0.65 V, suggesting the participation of H^+ in the reaction. Accordingly, addition of a slight excess of phenol caused a further increase in the heights of these two waves. Controlled potential electrolysis of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ in the presence of phenol at −2.1 V required 2 Faraday/mol, and was accompanied by a colour change from pale yellow to orange. A cyclic voltammogram of the electrolysed solution showed a reversible oxidation system at $E_{\frac{1}{2}} = -0.65$ V, with a peak height half that of the original $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ reduction. An i.r. spectrum of the product in THF solution revealed two strong CO absorptions at 1930 and 1834 cm^{-1}, characteristic of complexes of the type $[Fe(CO)_3(\eta^3\text{-allyl})]^-$.[12] The initial reduction product, $[Fe(CO)_3(\eta^2\text{-}C_4H_6)]^-$, demonstrated by Krusic,[9] is attacked by a proton, presumably at the metal. Hydrogen migration to the non-co-ordinated double bond of the butadiene forms the 1-methylallyl(tricarbonyl)iron radical which is itself reducible at this potential to the corresponding anion in an overall *ECE* reaction (Scheme 1).

Products of the type $[Fe(CO)_3(\eta^3\text{-allyl})]^-$ have previously been prepared electrochemically from $[Fe(CO)_3(\eta^3\text{-allyl})X]$ (X = Br, Cl, or I) *via* two successive one-electron reductions.[12] The second reduction which is reversible occurs at −0.7 V *vs.* s.c.e., confirming that any $[Fe(CO)_3(\eta^3\text{-}C_3H_4Me)]$ formed would be immediately reduced at the electrode to the corresponding anion. A comparison of the cyclic voltammetric peak heights suggests that the formation of $[Fe(CO)_3(\eta\text{-}C_3H_4Me)]^-$ from $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ in the presence of phenol is virtually quantitative.

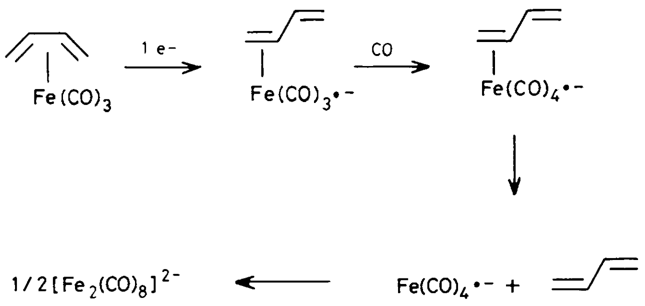
The identity of the product has been confirmed by its chemical reactivity. Addition of an excess of *trans*-1-chlorobut-2-ene to a freshly prepared THF solution of $[Fe(CO)_3(\eta\text{-}C_3H_4Me)]^-$ caused a colour change from orange to dark red. Column chromatography of the products on Kieselguhr, with n-hexane as eluant, allowed the recovery of a small amount of starting material and an orange liquid



Scheme 1



Scheme 2



Scheme 3

identified as $[Fe(CO)_2(\eta^3\text{-}C_3H_4Me)_2]$ by its characteristic i.r. (ν_{CO} 1997 and 1952 cm^{-1}), and ^{1}H n.m.r. spectra.[13] The equivalence of the two methylallyl groups suggests that they are both in the *syn*-form (Scheme 2).

Protonation of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ in which double bonds are co-ordinated to the metal leads to 1-methylallyl groups in the *anti*-form.[2,3] Thus, rotation about the C(2)–C(3) bond in the intermediate $[Fe(CO)_3(\eta^2\text{-}C_4H_6)]^-$ provides a synthetic route to the other series of *syn*-1-methylallyl iron complexes.

Controlled potential electrolysis of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$ was performed at −2.1 V *vs.* s.c.e under 4 bars of CO pressure under anhydrous conditions. After passage of one elctron per molecule of $[Fe(CO)_3(\eta\text{-}C_4H_6)]$, cyclic voltammetry showed that no starting material remained, and revealed a new irreversible anodic wave at + 0.1 V. The i.r. spectrum of the solution showed CO bands at 1905 and 1860 cm^{-1} and an absorption at 1775 cm^{-1} due to free butadiene. These observations are consistent with the formation of $[Fe_2(CO)_8]^{2-}$.[14] Attack of the initial reduction product by CO gives the species $[Fe(CO)_4(\eta^2\text{-}C_4H_8)]^-$, which has only a short lifetime at room temperature. Loss of butadiene is followed by dimerisation to the observed product (Scheme 3). The same unstable intermediate can be produced by reduction of complexes of the type $[Fe(CO)_4(\eta^2\text{-alkene})]$.

Received, 22nd October 1984; Com. 1494

References

1 Electrochemistry under gas pressure: for previous paper see J. D. Payne and N. El Murr, *J. Chem. Soc., Chem. Commun.*, 1984, 1137.
2 G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 1964, 836.
3 T. H. Whitesides and R. W. Arhast, *J. Am. Chem. Soc.*, 1971, **93**, 5296.
4 E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Commun.*, 1969, 1124.
5 M. F. Semmelhack and J. W. Herndon, *Organometallics*, 1983, **2**, 363.
6 E. O. Fischer and R. D. Fischer, *Angew. Chem.*, 1960, **72**, 919.
7 R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, 1966, **88**, 471.
8 M. R. Blake, J. L. Garnett, I. K. Gregor, and S. G. Wild, *J. Chem. Soc., Chem. Commun.*, 1979, 496.
9 P. J. Krusic and J. San Filippo, Jr., *J. Am. Chem. Soc.*, 1982, **104**, 2645.
10 N. El Murr, M. Riveccie and P. Dixneuf, *J. Chem. Soc., Chem. Commun*, 1978, 552.
11 R. P. Van Duyne and C. N. Reilley, *Anal. Chem.*, 1972, **44**, 142.
12 S. P. Gubin and L. I. Denisovich, *J. Organomet. Chem.*, 1968, **15**, 471.
13 A. N. Nesmeyanov and I. I. Kritskaya, *J. Organomet. Chem.*, 1968, **14**, 387.
14 N. El Murr and A. Chaloyard, *Inorg. Chem.*, 1982, **21**, 2206.