

Preliminary communication

LOW TEMPERATURE SPECTROSCOPIC OBSERVATION OF OXYGEN-PROTONATED TROPONEIRON TRICARBONYL COMPLEXES

M.S. BROOKHART*, C.P. LEWIS,

University of North Carolina, Department of Chemistry, Chapel Hill, North Carolina 27514 (U.S.A.)

and A. EISENSTADT*

Department of Chemistry, Tel-Aviv University, Tel-Aviv (Israel)

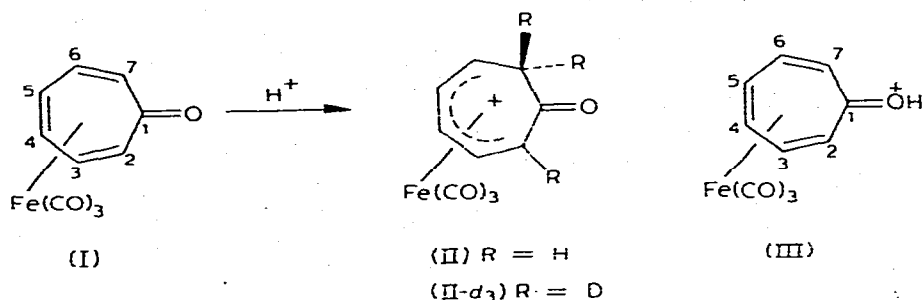
(Received August 16th, 1976)

Summary

Troponeiron tricarbonyl and 7-methyltroponeiron tricarbonyl undergo kinetically controlled oxygen protonation at low temperatures to give the corresponding hydroxytropyliumiron tricarbonyl cations, observable by ^{13}C and ^1H NMR spectroscopy. At higher temperatures, the oxygen-protonated species isomerize to yield the thermodynamically more stable carbon-protonated pentadienyliron tricarbonyl cations.

The reactions of polyolefin transition metal complexes with the simplest of electrophiles, the proton, has received considerable attention due to the fundamental nature of these reactions and the diverse patterns of reactivity observed. One of the most intriguing but complex systems examined in this regard has been the troponeiron tricarbonyl complex, I. In view of the stability of the fluxional tropyliumiron tricarbonyl cation [1] and the fact that protonation of free tropone occurs at oxygen to yield the hydroxy-tropylium cation [2], protonation of I was expected to yield the hydroxy-tropyliumiron tricarbonyl cation. However, both Eisenstadt [3] and Hunt [4] observed that protonation of I occurred not at oxygen but at carbon to yield the pentadienyl cation, II. Furthermore, work by Hunt established that protonation with trifluoroacetic acid (TFA) occurred stereoselectively *exo*; deuterium labeling experiments suggested that protonation occurred at the coordinated double bond (C(2)). In contrast, Eisenstadt reported that treatment of I with DSO_3F resulted in nonstereoselective incorporation of deuterium into *exo* and *endo* sites.

*To whom correspondence should be addressed.



Both Eisenstadt [3] and Hunt [4] noted that treatment of I with D_2SO_4 resulted in deuterium exchange and the production of the trideuterated ion II- d_3 . One attractive intermediate to account for exchange is the hydroxy-tropyliumiron tricarbonyl complex, III, (oxygen-protonated I) which is potentially fluxional and thus would allow exchange of the C(2) and C(7) sites.

Eisenstadt [5] has suggested that such O-protonated species account for the observation that protonation of 7-methyl-, 7-chloro-, and 7-phenyl-troponeiron tricarbonyl complexes, IV, in H_2SO_4 results in only the 2-substituted ions, whereas low temperature quenching experiments indicate that protonation in HSO_3F at -78°C yields both the 2- and 6-substituted isomeric complexes. That is, in H_2SO_4 at 25°C any 6-substituted derivatives formed may isomerize to the more stable 2-substituted isomers via oxygen-protonated intermediates.

In this preliminary communication we wish to report observation of the heretofore elusive oxygen-protonated troponeiron tricarbonyl complex III. Addition of an orange solution of I in CD_2Cl_2 to a mixture of TFA/ $\text{SO}_2/\text{SO}_2\text{F}_2$ (2/3/3 volume ratios) at -78°C followed by mixing yields a deep blood-red solution of a species which we attribute to the oxygen-protonated complex III. Upon warming to 0°C the blood-red solution slowly fades to light orange to give the carbon-protonated II as previously reported [3,4]. The ^1H NMR spectrum of III is summarized in Table 1 along with the spectra of I and II. Not unexpectedly, the ^1H NMR spectrum of III is quite similar to that of the unprotonated complex I. Comparing the chemical shifts of I and III, downfield shifts are observed for H(3) and H(4) (ca. 0.5 ppm) and H(6) (ca. 0.4 ppm) whereas H(2), H(5), and H(7) remain relatively unaffected. The downfield shifts observed are of the same order of magnitude as those observed for ^1H resonances of the oxygen-protonated cycloheptadieneoneiron tricarbonyl IV (generated in TFA or H_2SO_4) relative to the free complex [4]; however, there is relatively little correlation between the shifts of specific protons. In that III is a completely conjugated system, it is not surprising that ^1H shifts of IV serve as a relatively poor model. Observed coupling constants for I and III are quite similar, probably indicative of a relatively small change in the geometry of I upon protonation.

More convincing evidence of the oxygen-protonated species is derived

TABLE 1
1H NMR DATA

Species	Solvent	Temperature (°C)	Chemical shifts ^a							Coupling constants (Hz)
			H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	
I	CDCl ₃	25	3.20	6.37	6.37	2.72	6.56	5.04	$J_{A,7}$ 10.8, $J_{5,6}$ 8.0 $J_{2,3}$ 2.2, $J_{1,1}$ 1.1	
II ^b	TFA		4.85	6.53	7.40	6.54	5.10	2.34 (exo) 3.12 (endo)		
III	TFA/SO ₂ / SO ₂ F ₂ /CD ₂ Cl ₂	-45	3.04	{ 6.6-6.9(m) }		2.47	6.85	5.05	$J_{A,7}$ 11.0, $J_{5,6}$ 8.0 $J_{4,5}$ 7.2, $J_{2,3}$ 2.5 $J_{1,1}$ 1.0	
V	CDCl ₃	25	3.15	{ 6.25-6.47 }		2.68	6.25-6.47	1.48 (CH ₃)	J (CH ₃ , H _A) 1.4	
VI	TFA/SO ₂ / SO ₂ F ₂ /CD ₂ Cl ₂	-40	3.14	{ 6.70-6.94 }		2.77	6.72	1.50 (CH ₃)	J (CH ₃ , H _A) 1.4	

^aAll chemical shifts are reported in δ relative to TMS ($\delta = 0$ ppm). In TFA solution methylene-^d₂ chloride ($\delta = 5.30$ ppm) was used as an internal standard.
^bFrom ref. 4.

TABLE 2
13C NMR DATA^a

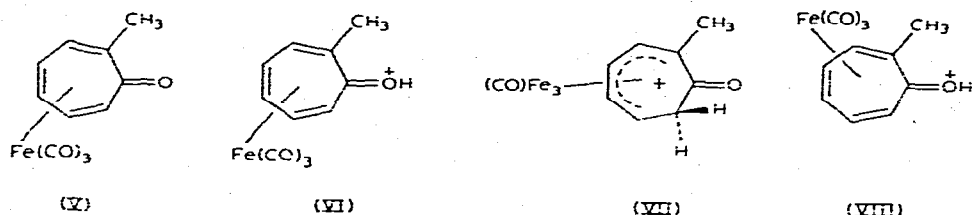
Species	Solvent	Temperature (°C)	Chemical shifts							CO's
			C(1)	C(2)/C(5)	C(3)/C(4)	C(6)	C(7)	C(8)		
I	CDCl ₃	-30	199.4	50.8 60.4	91.3 96.0	148.8	121.8	203.5 ^b 204.7 ^b 213.5 ^b		
II	TFA/SO ₂ / SO ₂ F ₂ /CD ₂ Cl ₂	-60	211 ^c	52.0(d,156) 58.9(d,156)	95.0(d,178) 99.3(d,176)	158(d,162)	121.2(d,168)	202.5 ^d 204.0 ^d 214.5 ^d		

^aChemical shifts are in ppm downfield from TMS. In parentheses is the multiplicity of the signal in the coupled spectrum together with the directly bonded J (¹³C,H) coupling constant in Hz. ^bAbove -30°C these CO resonances broaden and merge to a singlet. From linewidths at -20°C the rate constant for scrambling can be estimated as 30 sec⁻¹. ^c $\Delta G^\ddagger = 12.5$ kcal/mol. ^dLinewidth in the decoupled spectrum ca. 6 Hz, linewidth in coupled spectrum ca. 22 Hz. ^eLinewidths in both coupled and decoupled spectrum ca. 5 Hz.

from its ^{13}C NMR spectrum summarized in Table 2 along with ^{13}C chemical shifts for the neutral ketone I. Assignment of the C(6) and C(7) resonances of I and III for the carbons of the free vinyl group were made by analogy with other α,β -unsaturated ketones [6], while the C(3)/C(4) and C(2)/C(5) assignments were made by analogy with other cyclic dieneiron tricarbonyl complexes [7]. Of critical importance is assignment of the C(1) resonance, that is, distinguishing it from the three metal carbonyl resonances. For I this was done by noting that the metal carbonyl resonances are temperature dependent, as has been observed for other dieneiron tricarbonyl complexes [8]. The signals at 203.5, 204.7, and 213.5 merge to a single line at 25°C, thus establishing the 199.4 resonance as that of C(1) (See Table 2). For the protonated species III, the C(1) resonance was assigned by comparing the linewidths of the carbonyl signals in the coupled and decoupled spectra (See Table 2, footnotes *c*, *d*).

The most notable differences in the ^{13}C spectra of I and III are the substantial downfield shifts of C(1) and C(6) in III of 12 and 9 ppm, respectively. In contrast, the C(7) shift is relatively unaffected by protonation. Viewing the C(1)—C(7)—C(6) unit as an α,β -unsaturated ketone, little change for C(7) and large downfield shifts of C(1) and C(6) are expected based on data for protonated α,β -unsaturated ketones [9]. Qualitatively this pattern is observed; however, the magnitude of the C(1) and C(6) downfield shifts are smaller than those observed for α,β -unsaturated ketones, which may be due to the fact that substantially more charge delocalization can occur in the fully conjugated ion III. No good models exist for the expected change in shifts of C(2), C(3), C(4), C(5). The internal carbons of the bound diene, C(3), C(4), move downfield by ca. 4 ppm while the external C(2), C(5) carbons remain essentially unchanged. The coupled spectrum of the O-protonated species indicates that all ring carbons except C(1) have only one directly-bonded hydrogen. This fact, as well as the observed ^{13}C —H coupling constants, is in accord with the postulated structure.

The 7-methylcycloheptatrieneiron tricarbonyl complex V has also been investigated. In a manner similar to I, the blood-red oxygen protonated species VI is formed from protonation of V at -78°C in TFA/SO₂/SO₂F₂. The ^1H NMR spectra of V and VI are summarized in Table 1. Shifts and shift differences are similar to those observed for unsubstituted III and support the assignment of the blood-red species as the oxygen-protonated complex VI. Upon warming to 0°C the blood-red solution of VI fades to an orange solution which, as verified by PMR, is the previously observed carbon-protonated species VII [5]. Interestingly, during the isomerization of VI to VII, we failed to detect by NMR any evidence for the isomeric oxygen-protonated species VIII. This observation implies one of the following conditions must hold: (a) isomer VI is thermodynamically more stable than VIII, (b) the rate of iron shift to yield VIII must be slow relative to isomerization of VI to VII, or (c) any VIII formed does not accumulate and is rapidly converted to product VII.



The above results clearly demonstrate that in TFA oxygen is the site of kinetically controlled protonation of I whereas the thermodynamically most stable species is the carbon-protonated pentadienyl ion II. We are currently extending our investigation of the oxygen-protonated species to determine if such species are indeed fluxional, their possible role in the observed deuterium exchange reactions [3,4], and whether such species play a part in determining the contrasting stereochemistry of protonation in HSO_3F and TFA.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

- 1 (a) R. Pettit, *J. Amer. Chem. Soc.*, **86** (1964) 2589; (b) T.H. Whitesides and R.A. Budnik, *J. Chem. Soc. Chem. Commun.*, (1971) 1514.
- 2 H.J. Dauben and H.J. Ringold, *J. Amer. Chem. Soc.*, **73** (1951) 876.
- 3 A. Eisenstadt and S. Winstein, *Tetrahedron Lett.*, (1971) 613.
- 4 D.F. Hunt, G.C. Farrant and G.T. Rodeheaver, *J. Organometal. Chem.*, **38** (1972) 349.
- 5 A. Eisenstadt, *J. Organometal. Chem.*, **97** (1975) 443.
- 6 G.C. Levy and G.L. Nelson, *Carbon-13 Magnetic Resonance for Organic Chemists*, Wiley-Interscience, New York, 1972, p. 67.
- 7 M. Brookhart, G.W. Koszalka, G.O. Nelson, G. Scholes and R.A. Watson, *J. Amer. Chem. Soc.*, **98** (1976) 8155.
- 8 L. Kruczynski and J. Takats, *J. Amer. Chem. Soc.*, **96** (1974) 932.
- 9 G.A. Olah, Y. Halpern, Y.K. Mo and G. Liang, *J. Amer. Chem. Soc.*, **94** (1972) 3554.