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ELECTRONIC SPECTRA OF PROTONATED FERROCENES[1]

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Abstract: The electronic absorption spectra of two protonated ferrocenes have been recorded and the results require a reaccessment of the identity of the species present in weak acid.

During the course of our investigations of the protonation of ferrocenes we have observed that there is little apparent difference in color between solutions of ferrocenes in very strong acids and in common solvents. As the visible absorptions of ferrocenes are associated with the same nonbonding metal electrons that are presumed to be responsible for iron basicity and iron-hydrogen bond formation, it was thought that an examination of the electronic spectra of protonated ferrocenes might provide evidence for the electronic changes which occur upon protonation. Although this work is still proceeding, the implications of the early results are thought to justify a preliminary communication.

NMR studies of ferrocene and many of its alkyl derivatives have demonstrated that long-lived metal protonated species are formed in trifluoroboric acid, HBF_3OH[2]. The transparency of this acid over the range of wavelengths studied, 270 nm - 700 nm, made it an ideal medium for examining the spectra of two protonated ferrocenes, ferrocene and [3]-ferrocenophane, which have been throughly characterized by NMR. 10^{-3} M solutions which were prepared with rigorous exclusion of oxygen limited ferrocene oxidation to about 9% of the starting material and completely eliminated oxidation of [3]ferrocenophane over the time of the experiment.

Electronic spectra were recorded on a Cary 15 UV-visible Spectrometer and the observed absorption maxima and molar absorption coefficients are presented in Table I along with values of these compounds in ethanol. The small hypsochromic shifts of the visual absorptions are consistent with the subjective impression of color retention upon protonation. An increase in the molar absorption coefficient is observed for the visual absorption of ferrocene but not for [3]ferrocenophane. In contrast to the relatively unaffected visual absorptions, the ultraviolet absorptions of these compounds have increased greatly in intensity over their values in ethanol. In both cases, spectral cutoff occured at about 300 nm and it was not possible to observe any maxima associated with the 320 nm absorption. If such a maximum does occur, it must have a molar absorption coefficient in excess of 1000.

Watts and Barr[3] have recorded the electronic spectra of several alkylferrocenes and ferrocenophanes and have found that absorption maxima vary irregularly with substitution and bridging, but that molar absorption coefficients tend to increase with ring tilting. It is likely that the spectral changes observed in the protonated ferrocenes are a consequence of ring tilting which is known to occur upon ferrocene protonation.

Illuminati and his coworkers[4,5] have reported that changes in the electronic

TABLE I: Electronic Spectra of Ferrocene Compounds in Ethanol and Trifluoroboric Acid.

Compound	Ethanol[3]		Trifluoroboric Acid	
Ferrocene	440 (90)	325 (50)	437 (127)	300 cutoff $(>10^3)$
[3]Ferrocenophane	443 (185)	318 (85)	423 (183)	300 cutoff $(>10^3)$

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spectrum of ferrocene in benzene indicate that ferrocene undergoes a reaction with trichloroacetic acid which is reversible by addition of base. The species formed by ferrocene and the acid was characterized by an increase in the absorption intensity of the ultraviolet absorption, but the visible absorption was not greatly affected. Equilibrium constants for the ferrocene-acid reaction were calculated and it was found that alkyl substitutents favored the formation of the ferrocene-acid species. Metal protonation was dismissed on the somewhat dubious grounds that two substituents on the same ring had an additive effect on the equlibrium constant while two substituents on opposite rings had a statistical effect. This same spectral evidence was cited in a later paper[6] with the conclusion that a hydrogen bond association between the acid and the π cloud of the cyclopentadienyl ring was responsible for the spectral changes. In this paper it was stated that "(o)ccurance of any metal protonation in mildly protic media is unlikely from these data, since no spectral change is found in the visible region in which the absorption is related to the electronic structure of the metal"[6].

It is clear from the present work that the presumption that visual spectral changes must accompany metal protonation is false. In point of fact, the spectral changes reported by Illuminati for ferrocenes in dilute acid media are entirely consistent with the formation of metal protonated ferrocenes as the equilibrium species. A through investigation of the identity of the species formed in dilute acid media is now underway in our laboratory using NMR, Raman and electronic absorption spectroscopies.

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