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DETERMINATION OF pK_{R^+} VALUES FOR CYCLOBUTADIENEIRON TRICARBONYL-SUBSTITUTED CARBOCATIONS

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Summary

pK_{R^+} values for a series of cyclobutadieneiron tricarbonyl-substituted carbocations have been determined by a Hammett-Deno indicator acidity study utilizing trifluoroacetic acid-water solutions. The results show that these carbocations are considerably more stable than a variety of similar organic and organometallic carbocations but less stable than the corresponding ferrocene systems.

Introduction

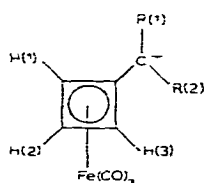
While studying the reactions of various derivatives of the cyclobutadieneiron tricarbonyl system, Pettit and coworkers [1,2] gathered solvolytic data which suggested that cyclobutadieneiron tricarbonyl-substituted carbocations were very stable. Subsequent isolation of salts of these cations confirmed their stability. In an attempt to gain quantitative information concerning the relative stability of these cations, a ^{13}C NMR study was undertaken [3]. That work sought to measure changes in charge distributions at the various carbon atoms upon conversion of the alcohol to the cation. However ^{13}C chemical shifts are known to be dependent also on other factors such as hybridization as well as anisotropic, diamagnetic, and paramagnetic effects. Measurements of pK_{R^+} values for ionization of the related alcohols should give more valuable information on the relative stabilities of this class of carbocations. Since a large amount of this type of data is available for a wide range of organic and organometallic systems, we decided to measure pK_{R^+} values for a series of cyclobutadieneiron tricarbonyl-substituted carbocations so that a direct comparison of their stabilities with those of other organometallic cations can be made.

Results and discussion

The pK_{R^+} values of the cations were determined by a Hammett-Deno indicator acidity study. In the usual method [4] electronic spectra are measured in a variety of sulfuric acid-water solutions. Because of the low concentrations of sulfuric acid required, some solubility problems were encountered; therefore, the method of Stewart [5] which utilizes trifluoroacetic acid-water solutions has been used. In order to demonstrate that the cations are generated in concentrated trifluoroacetic acid (TFA), NMR spectra were recorded in this medium (Table 1). Comparisons with spectra of the corresponding alcohols and with spectra of the alcohols dissolved in concentrated sulfuric acid or reported spectra of the isolated cation salts reveal that in all cases studied the cations are formed quantitatively when the alcohols are dissolved in concentrated TFA.

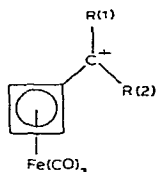
Examination of the NMR data reveals that deshielding is experienced by all protons when the alcohol is converted to the carbocation. The $RR'CHOH$ proton in secondary alcohols undergoes a relatively large (8–9 ppm) change in chemical shift, $\Delta\delta$, when the alcohol is converted to a carbocation, $RR'CH^+$, which is not highly stabilized [6]. When the carbocation is highly stabilized, $\Delta\delta$ is observed to be smaller. On conversion of ferrocenyl-substituted secondary carbinols to the stable cations, $\Delta\delta$ for the carbinyl proton is in the range 2.6–2.9 ppm [7]. The related benzenechromium tricarbonyl ($\Delta\delta = 2.13$ [8]), cyclopentadienylmanganese tricarbonyl ($\Delta\delta = 2.04$ ppm [9]), and nonacarbonyltricobalt carbon ($\Delta\delta = 1.5$ – 2.0 ppm [10]) systems show similar effects. By comparisons $\Delta\delta = 2.07$ – 2.46 ppm for the carbinyl proton in compounds Ia–Ic. While it might be tempting to relate the degree of stability to the magni-

TABLE 1
NMR SPECTRA OF CATIONS IN TFA (SPECTRA OF ALCOHOLS IN CCl_4 IN PARENTHESES)



Compound	R(1)	R(2)	Chemical shifts, δ (ppm)			
			H(2)	H(1,3)	R(1)	R(2)
Ia	H	phenyl	6.64 (4.16)	5.76, 6.31 (4.01, 4.03)	7.42 (5.08)	7.64 (7.30)
Ib	H	<i>p</i> -tolyl	6.45 (4.09)	5.68, 6.18 (3.97)	7.46 (5.00)	7.42 (7.11)
Ic	H	methyl	6.67 (4.14)	5.56, 5.98 (4.07)	6.35 (4.28)	1.91 (1.15)
Id	phenyl	phenyl	6.42 (4.37)	5.93 (4.08)	7.55 (7.30)	7.55 (7.30)
Ie	methyl	phenyl	6.46 (4.22)	5.88 (3.90, 5.10)	2.29 (1.62)	7.60 (7.35)

TABLE 2
ELECTRONIC SPECTRA OF CATIONS IN TFA



Compound	R(1)	R(2)	λ_{\max} (log ϵ)	pK_{R^+}
Ia	H	phenyl	307 (4.04), 387 (3.93)	-3.42
Ib	H	<i>p</i> -tolyl	318 (3.93), 417 (4.00)	-2.79
Id	phenyl	phenyl	325 (3.66), 3.96 (4.03), 480 (3.73)	-1.46
Ie	methyl	phenyl	304 (3.83), 382 (3.89)	-2.89
If	H	<i>p</i> -anisyl	329 (3.81), 474 (4.23)	-1.72

tude of $\Delta\delta$, some difficulties arise. Principal among these is the fact that proton chemical shifts are influenced by a number of factors other than the charge density at the carbon atom to which the proton is attached. Furthermore in cases where $\Delta\delta$ and thermodynamic values are both available, it has been observed that a smaller value of $\Delta\delta$ does not necessarily indicate a more stable cation (see Table 3). The main conclusion that can be drawn from the $\Delta\delta$ values obtained in this work is that these cations are highly stabilized by the organometallic substituent.

The electronic spectra (200–600 nm) of the alcohols dissolved in 95% ethanol and concentrated TFA have been measured. The alcohols show no distinct absorption bands at wavelengths greater than 300 nm whereas the cations (at the same concentration) generally show intense absorption bands above 300 nm (Table 2). The methyl cyclobutadienyliron tricarbonyl carbocation is an exception in that it produces only weak absorptions that are obscured by the tailing absorptions of the metal carbonyl groups. Solutions of the cations in concentrated TFA show no significant changes in absorbancy over a period of 3 hours and are observed to obey Beer's Law over a wide range of concentrations. Dilution of the acid solutions with water regenerates the alcohol.

The pK_{R^+} values (Table 2) were determined according to the method of Deno [4] using the H_R values for trifluoroacetic acid-water mixtures obtained by Stewart [5]. The slopes of the plots of $\log Q$ vs. H_R (where $Q = [R^+]/[ROH]$) were found to be approximately equal to unity (0.95–1.05) for all compounds investigated. The pK_{R^+} values reveal that these cations are very stable. Table 3 shows a comparison of the stabilities of the cyclobutadienyliron tricarbonyl-substituted carbocations with related organic and organometallic systems. As can be seen, the cations reported in this study are much more stable than the phenyl-substituted carbocations, indicating the tremendous ability of the cyclobutadienyliron tricarbonyl system to donate electron density to the electron-deficient center. Substituents on the benzene ring (cations Ia, Ib and If) also influence the stability of the cations but to a much smaller degree than in the analogous organic compounds, suggesting that the organometallic system

TABLE 3

 pK_{R^+} VALUES OF RELATED ORGANIC AND ORGANOMETALLIC CARBOCATIONS

Substituents		(I)	(II)	(III)	(IV)	(V)	(VI)
R ₁	R ₂						
H	phenyl	-3.42	-13.3 [4]	0.40 [13]	-10.4 [15]	-8.7 [9]	—
H	<i>p</i> -tolyl	-2.79	-11.6 [11]	—	-9.4 [15]	—	—
H	<i>p</i> -anisyl	-1.72	-7.9 [11]	1.37 [14]	-5.4 [15]	—	—
methyl	phenyl	-2.89	-10.4 [12]	—	—	-8.3 [9]	—
phenyl	phenyl	-1.46	-6.6 [4]	0.75 [13]	—	-6.5 [9]	-7.4 [16]

is primarily responsible for the stabilization of the cation. When compared to other organometallic systems, the organoiron systems are seen to be more effective than the others in stabilizing adjacent electron-deficient centers. The greater efficiency of ferrocene as compared to cyclobutadienyliron tricarbonyl most likely lies in the ability of the second cyclopentadienyl ligand to donate electron density whereas the metal carbonyl groups behave primarily as electron-withdrawing groups.

Experimental

The alcohols used in this work were prepared by reaction of formyl-, acetyl-, and benzoyl-cyclobutadienyliron tricarbonyl with the necessary Grignard reagents as previously described [3,17-19]. A Perkin-Elmer R-32 NMR spectrometer was used to obtain the NMR spectra and a Cary 114 Ultraviolet-Visible Spectrophotometer was used to measure the electronic spectra.

pK_{R⁺} determinations. Stock solutions of the carbinols (concentrations ca. $6 \times 10^{-2} M$) were prepared by weighing a sample of the alcohol into a 5-ml volumetric flask and diluting with degassed 95% ethanol. Solutions for spectroscopic observation of the cations were prepared by injecting 5- μ l aliquots of the ethanolic stock solution of the alcohol into a 5-ml volumetric flask containing the appropriate acid solution. This solution was then transferred to a 1-cm cell and immediately scanned from 600 to 200 nm. Repeated scanning of the solutions over time periods of greater than 30 minutes indicated little change in absorbancies. A plot of the data obtained for the methylphenylcyclobutadienyliron tricarbonyl carbinyl cation (Ie) is shown in Fig. 1. It is typical of plots generated for all systems. Correlation coefficients greater than 0.97 were obtained for all cases studied.

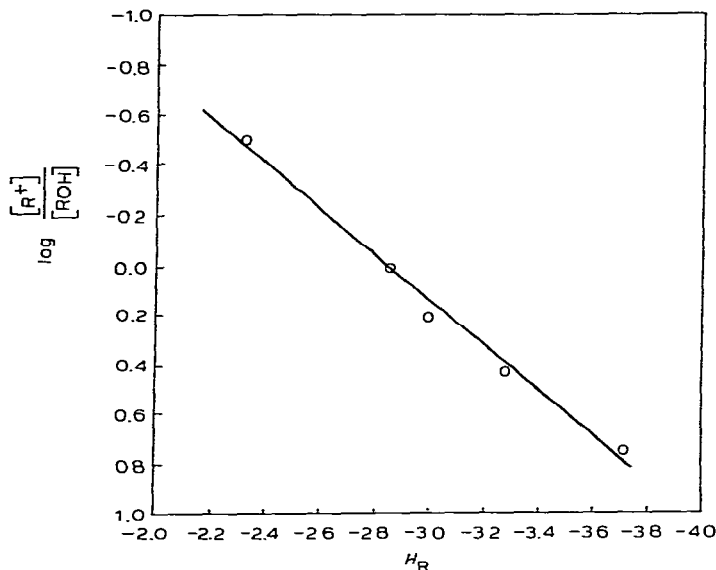


Fig. 1. A plot of $\log [R^+]/[ROH]$ vs. H_R for methylphenylcyclobutadienyliron tricarbonyl carbinol in aqueous trifluoroacetic acid solutions.

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