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THE STABILITY AND ELECTRONIC STRUCTURE OF DIPHENYLCOBALTICINIUMMETHYL CARBONIUM ION

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Summary

The cobalticinium group, because of its strongly electron-withdrawing inductive, field and resonance effects greatly decreases the stability of a carbonium ion in the α-position of a side chain. The stability constant of $C_5H_5Co^+C_5H_4$-$(C_6H_5)_2C^+$, (I) has been determined spectrophotometrically in 80—96% sulfuric acid: pK_R —15.3 ± 0.3. The relative stabilities for $R(C_6H_5)_2C^+$ are: cobalticinium, 1; H, 10^2; phenyl, 5×10^8; ferrocenyl 10^{16}. Compound I, however, shows a lower sensitivity to changes in solvent acidity than would be predicted by the H_R scale.

Proton and ^{13}C NMR spectra of I in $ClSO_3H/D_2SO_4$ indicate delocalization of the positive charge onto the phenyl groups comparable to that of $(C_6H_5)_2CH^+$ and $(C_6H_5)_3C^+$ and delocalization to a much lesser extent onto the cobalticinium group.

Introduction

The stability of α-metallocenyl carbonium ions has been the subject of extensive investigations [1—8] and has been the subject of a recent review [9]. The α-ferrocenylmethyl carbonium ion has a stability constant, pK_R 1.49 ± 0.08, at least a factor of 10^{20} greater than that of the benzyl carbonium ion, which has been too unstable for accurate measurements. Replacement of the α-hydrogens by phenyl groups has produced only a slight increase in the stability [8]. Thus most of the positive charge is delocalized onto the ferrocenyl system.

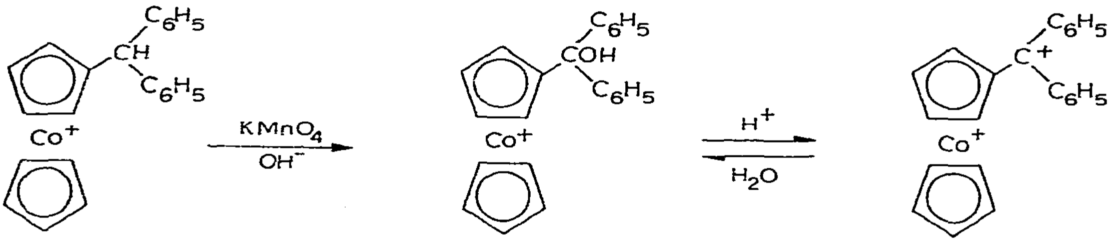
Similarly great stabilities have been observed for the ruthenocenyl group [8] and to a lesser extent for the α-cyclopentadienyltricarbonylmagnanese group [10]. Of particular interest has been the question of direct interaction between the metal atom and the vacant orbital on the α-carbon. The most recent investigations in this controversial area have shown little evidence for direct participation of the metal atom but strong evidence that the positive charge is delocalized over the entire metallocene group [4—7]. The ferrocenyl group, however, shows little ability to delocalize an adjacent negative charge.

In contrast to the ferrocenyl group, the cobalticinium group greatly enhances the stability of carbanions in the α-position and interacts strongly with other substituents bearing a lone pair of electrons [11,12]. Benzhydryl cobalticinium salts are approximately 10^{11} more acidic than triphenylmethane [11]. The enhanced acidity appears to arise both from electron-withdrawing field and inductive effects and also from electron-withdrawing resonance effects.

It was therefore of interest to prepare an α-cobalticinium-carbonium ion and compare its stability with its ferrocenyl and phenyl analogs. Since several of the recent investigations on α-ferrocenyl carbonium ions have used proton and ^{13}C chemical shifts as the basis for assigning structures and determining charge distribution [4—7], the NMR spectra of the cobalticinium species should also prove useful as a case in which delocalization of the positive charge should be much less pronounced.

Results and discussion

Diphenylcobalticinium carbinol, (II), is readily prepared by oxidation of benzhydrylcobalticinium ion, (III), with alkaline potassium permanganate (see Experimental).



(III) (II) (I)

The PF_6^- salt of the carbinol, II, is a stable yellow crystalline salt with properties similar to those of other cobalticinium salts. When dissolved in 96% H_2SO_4, a bright red color is observed, indicative of the presence of the carbonium ion, I.

Solutions of I in 96% sulfuric acid are stable for only a few hours, possibly because the small amount of II present in equilibrium with I can undergo sulfonation. Solutions of I in $ClSO_3H$, however, are stable indefinitely, and II can be recovered by careful dilution of the solutions with cold water. The phenyl rings of I must therefore be sufficiently deactivated not to undergo sulfonation.

Solutions approximately 10^{-4} M in II were prepared in 80—96% H_2SO_4 (see Experimental) and the absorption measured in the region 225—550 nm. The concentration of I could be determined from the absorption at 464 nm (ε

17000). Compound II absorbs only weakly ($\epsilon < 250$) at 464 nm. Log[II]/[I] was plotted versus the Hammett acidity function [13] H_o and the H_R scale proposed by Deno [14] in measuring the acidities of arylmethylcarbonium ions. A slope of +1.00 would indicate that compound II showed the same sensitivity toward acid as the Hammett indicators, which are aryl amines and arylazo compounds or as the series of aryl carbinols used by Deno. The plot of log [II]/[I] versus H_o was linear with a slope of 1.5 with [I] = [II] at H_o —7.53 (83.9% H_2SO_4). The plot versus H_R was linear with a slope of 0.74 with [I] = [II] at H_R —15.2. Neither acidity function gives a slope of 1.00. Compound II is more sensitive to variations in acidity than the Hammett indicators, but less sensitive than Deno's arylcarbinols.

Arnett and Bushick [15] have discussed the reasons for difference in behavior between carbonium ions and ammonium ions in solution as follows: Two factors enter into the formation of ammonium ions in solution, the ability of the solvent to protonate the amine and the ability of the solvent to solvate the ammonium ion by accepting hydrogen bonds. Increasing the solvent acidity promotes protonation but retards solvation. Carbonium ions, however, are not strongly solvated, but are more stable in more strongly ionizing solvents. Thus, increasing the acidity promotes formation of the carbonium ion and also increases its stability. Quantitatively, these effects can be shown as follows:

$$H_R = -\log\left[\frac{a_{H^+} f_{ROH}}{a_{H_2O} f_{R^+}}\right]$$

$$H_o = -\log\left[\frac{a_{H^+} f_B}{f_{BH^+}}\right]$$

where f denotes the activity coefficients of the carbonium ion R^+, the ammonium ion BH^+, the carbinol ROH, and the amine B. Since f_{ROH} and f_B vary similarly with increasing acidity [15]

$$H_R - H_o - \log a_{H_2O} = -\log\left[\frac{f_{BH^+}}{f_{R^+}}\right]$$

But f_{R^+} decreases more rapidly with increasing acidity than f_{BH^+}, so that the right side of the equation rapidly becomes more negative as the acidity increases [15].

The ionization of II to form I deviates from H_R because II already bears a positive charge and is not strongly solvated. The activity coefficient for II should vary with acidity in a manner similar to carbonium ions, while I should be even more sensitive, since it is doubly charged. The ratio of the activity coefficients f_{ROH}/f_{R^+} therefore varies more with acidity than the H_o scale, but less than the H_R scale.

In this paper we are concerned primarily with comparisons of stability relative to other carbonium ions, so the H_R scale will be used. The relative stabilities for I, $(C_6H_5)_2CH^+$, $(C_6H_5)_3C^+$ and several α-ferrocenyl carbonium ions are given in Table 1.

Compound I is clearly a very reactive carbonium ion; 10^{16} less stable than its

TABLE 1

STABILITY OF CARBONIUM IONS IN AQUEOUS SULFURIC ACID

Compound	pK_R	Relative stability	Literature ref.
$Fe[C_5H_4(CH_3)CH^+]_2$	too unstable to measure		8
$C_{10}H_9Co^+(C_6H_5)_2C^+$	−15.2	1	This work
$(C_6H_5)_2CH^+$	−13.3	10^2	14
$H_3N^+CH_2C_5H_4FeC_5H_4(CH_3)CH^+$	−9.2	10^6	8
$(C_6H_5)_3C^+$	−6.63	5×10^8	14
$C_{10}H_9FeCH_2^+$	−1.49	5.1×10^{13}	8
$C_{10}H_9Fe(CH_3)CH^+$	−0.64	4×10^{14}	8
$C_{10}H_9Fe(C_6H_5)CH^+$	+0.4	5×10^{15}	8
$C_{10}H_9Fe(C_6H_5)_2C^+$	+0.75	10^6	17

ferrocenyl analog, 5×10^8 less stable than the phenyl analog and 10^2 less stable than the hydrogen analog. The presence of the positive charge on II greatly retards formation of a second positive charge. Cerichelli et al., [8] have reported that $C_5H_4CH_2NH_3^+FeC_5H_5CH^+CH_3$ is 4×10^8 less stable than $C_5H_5FeC_5H_4CH^+CH_3$ and that the bis-carbonium ion $(C_5H_4CH^+CH_3)_2Fe$ is not formed even in very strongly acidic solutions. Since $CH_2NH_3^+$ has little direct resonance with the cyclopentadienyl ring and is too far away to exert a significant inductive effect, the reduction of stability must arise almost exclusively from a field effect. Since the preferred conformation for this compound is for the two substituents to be as far from each other as possible, the NH_3^+ group is approximately twice as far from the carbonium ion center as is the cobalt atom in II. Since the field effect diminishes as the inverse-square of the distance between the charge and the carbonium center, the reduction of the stability of II by a factor of 10^{16} as compared to the neutral ferrocene analog is not unreasonable.

The reduction of stability of 5×10^8 relative to the phenyl analog is smaller than the factor of 10^{11} for enhancement of acidity for the formation of a carbanion from $C_{10}H_9Co^+(C_6H_5)_2CH$ versus $(C_6H_5)_3CH$. In the latter case, resonance effects also strongly favor removal of the proton.

A qualitative estimate of the importance of resonance i.e. the delocalization

TABLE 2

PROTON NMR SPECTRA OF SUBSTITUTED COBALTICINIUM SALTS AND THEIR PHENYL AND FERROCENYL ANALOGS. CHEMICAL SHIFTS, δ ppm

Compound	Unsubstituted ring	Substituted ring		Phenyl ring			Literature ref.
		C(2)	C(3)	o,	m,	p	
I	6.07	6.36	6.55	7.92—8.01			This work
II	5.45	5.63	5.73	7.08			This work
III	5.20	5.36	5.46	6.80			This work
$C_5H_5Co^+C_5H_4CO_2H$	6.04	6.09	6.33				This work
$C_5H_5Co^+C_5H_4NO_2$	6.23	6.17	6.80				This work
$C_5H_5FeC_5H_4(C_6H_5)CHOH$	3.95	3.95	3.95				8
$C_5H_5Fe(C_5H_4(C_6H_5)CH^+$	4.90	4.90	5.53				8
$(C_6H_5)_2CH^+$				8.46	7.98	8.58	18
$(C_6H_5)_3C^+$				7.69	7.87	8.14	18

TABLE 3

C^{13} NMR OF SUBSTITUTED COBALTICINIUM SALTS AND THEIR PHENYL AND FERROCENYL ANALOGS, CHEMICAL SHIFTS, δ ppm TMS

Compound	Unsubstituted ring	Substituted ring			Phenyl rings				α-carbon	Literature ref.
		C(1)	C(2)	C(3)	C(1)	C(2)	C(3)	C(4)		
I	89.03	95.59	92.96	94.82	141.61	142.61	131.95	147.84	208.62	This work
II	85.62		84.24	84.24	146.15	128.14	127.22	128.43	117.94	This work
III	86.26		85.35	84.97	143.34	129.28	128.12	129.72	50.49	This work
$C_{10}H_9NH_3^+Co^+$	87.37	98.70	83.64	80.77						This work
$C_{10}H_9CO_2^-Co^+$	85.89	96.10	86.41	86.41						This work
$C_{10}H_9Fe(C_6H_5)CHOH$	68.5	94.1	66.1 67.4	68.0	143.5	126.3	128.2	127.4	72.1	5
$C_{10}H_9Fe(C_6H_5)CH^+$	82.6	101.2	79.5 81.8	92.8 93.7	133.7	130.2	130.2	133.4	121.5	5
$(C_6H_5)_3C^+$					140.2	143.6	131.4	143.6	211.8 212.7	22, 23 21
$(C_6H_5)_2CH^+$									200.2	21

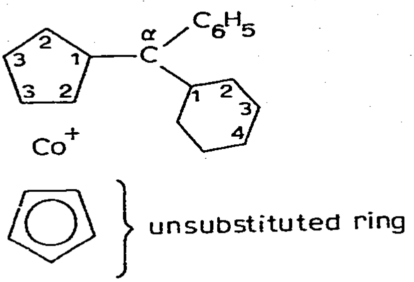


Fig. 1. Numbering system for compounds I—V.

of the positive charge onto the cobalticinium group in the stabilization of I can be gained from the proton and ^{13}C NMR spectra of I, II, III and ferrocenyl analogs, $C_{10}H_9Fe(C_6H_5)CHOH$, (IV), and $C_{10}H_9Fe(C_6H_5)CH^+$ (V), $(C_6H_5)_3C^+$, $(C_6H_5)_2CH^+$, and other analogs shown in Tables 2—3. Chemical shifts for hydrogen and carbon (Fig. 1) have been assigned as described previously [5—6,18—19]. In general, electron-withdrawing substituents cause C(3) to appear downfield from C(2) and electron-donating substituents cause C(3) to appear upfield.

Removal of the hydroxyl group of II to form I produces downfield shifts of δ 0.73 and 0.82 ppm for the 2 and 3 positions whereas for the nearest ferrocenyl analog, $C_{10}H_9FeCH^+C_6H_5$, the corresponding shifts are δ 0.95 and 1.58 ppm. The chemical shifts for I lie slightly downfield from those of cobalticinium carboxylic acid and slightly upfield from those of the nitro derivative. Although it is difficult to gain quantitative information by comparing chemical shifts measured in different solvents, it seems clear that the carbonium center interacts much more strongly with the ferrocenyl rings than with the cobalticinium and that the resonance of the carbonium ion with the rings of I is comparable to that of a carboxyl or a nitro group. The signal for the phenyl rings of I is approximately in the same region as that observed for $(C_6H_5)_3C^+$.

The ^{13}C NMR spectra of compounds I—V and their analogs are reported in Table 3. Compound V was chosen as an analog rather than $C_{10}H_9Fe(C_6H_5)_2C^+$ because the latter compound decomposes rapidly in solution [17]. The chemical shifts for C(2) and C(3) of the cobalticinium salts were assigned by analogy with the corresponding ferrocene derivatives [5,18—20]. In passing from II to I, the downfield shifts for C(2), C(3) and the unsubstituted ring are δ 8.72, 10.58 and 3.41 ppm, whereas in passing from IV to V the corresponding shifts are δ 13.4 and 14.4; 14.8 and 15.7 and 14.1 ppm. Two values are given for C(2) and C(3) because the asymmetry of the side chain causes C(2), C(5) and C(3), C(4) to have slightly different chemical shifts. The downfield shifts for I, although much smaller than for the ferrocene analog are larger than for other cobalticinium salts substituted with more weakly electron-withdrawing groups such as CO_2^- and NH_3^+. The chemical shifts for the carbons of the phenyl groups lie in the region expected for typical aryl carbonium ions, very close to the corresponding values for $(C_6H_5)_3C^+$ with the exception that C(4) in I is shifted δ 4.2 ppm further downfield. In passing from IV to V, downfield shifts for the phenyl ring of only δ 3—6 ppm are observed. The chemical shift of the α-carbon of I, 208.64 is between the shifts for $(C_6H_5)_2CH^+$ and $(C_6H_5)_3C^+$; whereas the shift for V is only δ 121.5, over 87 ppm further upfield.

If no delocalization of the positive charge onto the cobalticinium group by resonance took place, the chemical shift of the α-carbon should be further downfield than for $(C_6H_5)_3C^+$, since the cobalticinium group exerts electron-withdrawing field and inductive effects and the cobalticinium group should also offer greater steric hindrance than a phenyl group to coplanarity of the other two phenyl groups with the α-carbon. However, the extent of positive charge delocalization by the cobalticinium group is clearly less than that for either phenyl or ferrocenyl.

In α-ferrocenyl carbonium ions, the ferrocenyl group bears most of the positive charge and further substitution on the α-carbon has only a small effect on the stability (see Table 1); whereas, in I the phenyl groups bear most of the positive charge.

While further investigations on the nature of the great stability of α-ferrocenyl carbonium ions are still taking place, it is clear that the cobalticinium group does not show this stability and can be characterized best as a strongly electron-withdrawing aromatic group capable of supplying electron density only to the most demanding substituents, and then only to a limited degree.

Experimental

Proton NMR spectra were recorded on a Varian A-60A Nuclear Magnetic Resonance Spectrometer. Tetramethylammonium ion was used as an internal standard δ 3.13 ppm for the solutions in $ClSO_3H$. ^{13}C NMR were recorded at 20 MHz on a Varian CFT-20 Fourier Transform nuclear magnetic resonance spectrometer. UV spectra were recorded on a Cary 15 Ultraviolet Spectrophotometer.

Synthesis of diphenylcobalticinium carbinol (II)

Benzyhydrylcobalticinium haxafluorophosphate (III), 2.0 g (0.004 mol), potassium permanganate, 0.7 g (0.004 mol) and sodium hydroxide 0.2 g (0.005 mol) were dissolved in water and heated on a steam bath with occasional stirring for 4 h. The precipitate of MnO_2 was filtered out and washed repeatedly with water, then with acetone. The acetone solution was evaporated and the residue dissolved in water and combined with the aqueous filtrate. The carbinol, II was precipitated by dropwise addition of an aqueous solution of $NaPF_6$. The crude product was recrystallized from methanol, yield 1.7 g (82%), m.p. 195—196°C. IR ν_{max} 3540, 3100, 1595, 1490, 1448, 1415, 1390, 1335, 1230, 1215, 1170, 1060, 1030, 1010, 900—800, 760, 712, 705 and 675 cm^{-1}. The NMR and UV spectra are given in Tables 2, 3 and 4. Found: C, 53.35; H, 4.07; F, 22.15. $C_{23}H_{20}CoF_6OP$ calcd.: C, 53.50; H, 3.91; F, 22.08(%).

Measurement of the stability constant for I

Compound I was shown to follow Beer's law in 96% H_2SO_4. Solutions containing 10^{-3} *M* I were prepared in 96% H_2SO_4. Four 1 g portions were diluted with 9.0 g of sulfuric acid solutions in the range 75—96%. The resulting solutions contained a mixture of I and II with a total concentration of 10^{-4} *M*. The absorption spectrum was scanned over the region 550—225 nm immediately.

The solution in 96% H_2SO_4 was scanned first and then again after the other solutions has been completed. The total time elapsed was approximately 20 min. The loss of absorbance between the second scan and the first was less than 2% of the total absorbance. Weighed portions of the acid solutions were titrated with standard NaOH solution to determine the exact concentration of the acid. The concentration of I present in each solution could be determined from the absorption at 464 nm and the concentration of II calculated as the difference between the total concentration and the concentration of I. Plots of log [II/I] versus H_0 and H_R were prepared using the composite data from several series of solutions of different acid concentrations.

Acknowledgements

Synthesis of II was performed at the University of Dijon. The ^{13}C NMR spectra were measured at Rutgers University. The equilibrium measurements were performed at Rider College.

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