

Calorimetric Study of the Stabilities of Some α -Ferrocenyl Cations in Sulfuric Acid

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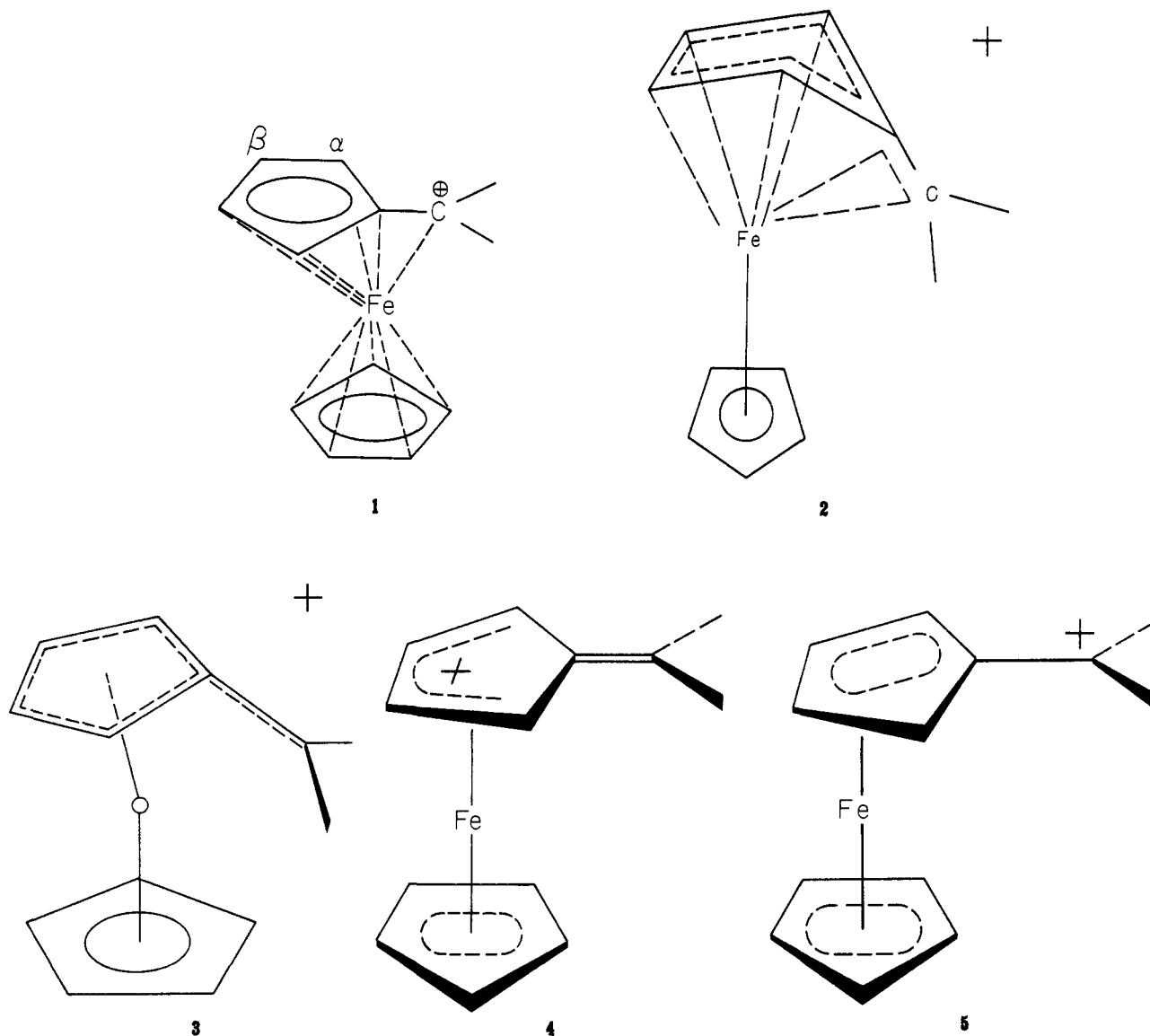
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Abstract: The relative heats of formation of a series of α -ferrocenyl carbonium ions and the relative heats of protonation of some ferrocene-substituted ketones have been measured in concentrated sulfuric acid. The well-known extraordinary stabilizing effect of an α -ferrocene group was observed, the effect being much more pronounced with the carbonium ions than with the protonated ketones. The effect of other substituents on the stability of α -ferrocenyl cations is small; a methyl group does not stabilize the carbonium ion. The substituent effects are those expected for substitution β to a charge center.

Quantitative evidence for the unusual stability of α -ferrocenyl carbonium ions¹ has been obtained by several methods. Solvolysis of metallocenylmethyl acetates proceeds at rates faster than those of triphenylmethyl acetates.² The thermodynamic stability of α -ferrocenyl carbonium ions may be several powers of ten greater than that indicated by kinetic studies.³ Torsional barriers to the racemization of optically active α -ferrocenyl carbonium ions have been observed.⁴ The NMR spectra of several α -ferrocenyl cations

indicate the delocalization of large amounts of positive charge into the ferrocene system.⁵

Several models have been developed to explain the unique stability of the carbonium ions.^{1,6} An excellent brief summary appears in a recent paper by Watts.⁷ Some of the structures are shown (1-5) and are described briefly below. Structure 1 has been advocated by Richards⁸ and contains a planar substituted ring, conjugated as in fulvene and has the Fe shifted toward the methylene group. The unsubsti-



tuted ring remains in the same position relative to the Fe. Cais¹ has proposed a structure (2) in which the substituted ring is bent to allow better overlap between Fe and ligand orbitals. Based on MO calculations, Gleiter and Seeger⁹ have proposed structure 3 in which both rings are tilted, and the methylene group is bent toward the ion. Traylor¹⁰ has suggested a structure which is a resonance hybrid of 4 and 5. A diradical species can be used to explain some recently observed reactions of the ferrocenyl cation.¹¹⁻¹³

All of these structural proposals involve extensive delocalization of positive charge into the ring. There is abundant evidence for this delocalization. Recent extended Hückel calculations¹³ support a bent structure (3) which allows interaction of the iron's filled nonbonding $3d_{z^2}$ orbital with the empty π^* orbital of the fulvene moiety. Half of the positive charge is on iron and the other half distributed evenly between the two rings. An X-ray analysis^{5b} of the ferrocenyl carbonium ion shows the exocyclic carbon deviating from the planes of the two rings to which it is bonded by $19^\circ 53'$ and $17^\circ 41'$, supporting the bent structure. ESCA measurements on this same ion are consistent with significant positive charge on the iron atoms.¹⁴ The ^{13}C NMR spectra of α -ferrocenyl carbonium ions and the corresponding alcohols have been obtained. Both chemical shifts and coupling constants are consistent with extensive charge delocalization over the ferrocene system.¹⁵ Mossbauer experiments also indicate extensive charge delocalization to Fe.¹⁶

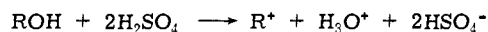
Our purpose in undertaking the work described here was not to attempt to distinguish between the various possible mechanisms of the charge delocalization into the ferrocene system but to investigate more carefully the magnitude of the stabilization. The quantitative experimental information about the relative stabilities of the ferrocenyl cations comes from pK measurements and solvolysis rates. The pK measurements assumed³ that the ferrocenyl cations followed H_{R^+} . With solvolysis data, there always exists the possibility of changes in the nature of the transition state over a series of compounds as well as complications arising from lack of knowledge of the structure of the transition state. Thus we felt that calorimetric stabilities of a series of ferrocenyl cations should be obtained. We also wanted to investigate the effect of the substituents on the stability of the remarkably stable α -ferrocenyl cations.

Experimental Section

The calorimeter and its use have been previously described.^{17,18} The strength of the sulfuric acid was determined by measuring the heat of solution of water in the acid and using the data of Giaque¹⁹ in which ΔH_s of water in H_2SO_4 is given as a function of H_2SO_4 concentration. The measured $\Delta \bar{H}_s$ for water of -7.44 ± 0.23 kcal/mol corresponds to an acid strength of 96.1% H_2SO_4 . All compounds were commercially available or prepared by standard methods.²⁰⁻²⁴ The purity of all compounds used was verified by thin-layer chromatography and ^1H NMR.

Results and Discussion

The cations were generated in 96.1% H_2SO_4 from alcohols in the reaction shown below. All structures were verified by ^1H NMR.



Consider first the cations whose relative heats of formation are contained in Table I. The extraordinary stability of the α -ferrocenyl cations is immediately apparent, a single ferrocene substituent stabilizing a cation by 9 kcal/mol more than a pair of phenyl substituents. This observation merely confirms a phenomenon detected by a variety of other experimental techniques.

Table I. Relative Heats of Formation (ΔH_{R^+}) of Some Ferrocenyl Cations, in 96.1% H_2SO_4 at 25° and Some Model Compounds

Ion precursor	$\Delta \bar{H}_{s, \text{CCl}_4}$	$\Delta H_{s, \text{acid}}$	ΔH_{R^+}
FcCH_2OH	4.99 ± 0.23	-24.6 ± 0.4	-29.6 ± 0.5
FcCHCH_3	6.23 ± 0.14	-22.3 ± 1.0	-28.6 ± 1.0
FcCHC_6H_5	4.93 ± 0.54	-24.6 ± 0.3	-29.5 ± 0.6
$\text{FcCHC}_6\text{H}_4\text{-}p\text{-CH}_3$	5.00 ± 0.45	-23.0 ± 0.6	-28.0 ± 0.7
$\text{FcC}(\text{C}_6\text{H}_5)_2$	4.87 ± 0.19	-25.1 ± 1.0	-30.0 ± 1.0
FcCHFc	4.06 ± 0.26	-47.6 ± 1.6	-51.7 ± 1.6
$(\text{C}_6\text{H}_5)_2\text{CH}$	6.54 ± 0.21	-13.9 ± 1.2	-20.5 ± 1.2
$\text{C}_6\text{H}_5\text{CHC}_6\text{H}_5\text{-}p\text{-CH}_3^a$	7.57 ± 0.12	-10.6 ± 0.7	-18.2 ± 0.7
$(\text{C}_6\text{H}_5)_3\text{C}^a$	4.83 ± 0.20	-17.5 ± 1.1	-22.3 ± 1.1

^a Data from E. M. Arnett and J. W. Larsen, "Carbonium Ions," Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1968.

Perhaps the most striking feature of the data in Table I is the substituent effect on the α -ferrocenyl cations, more specifically, the lack of a substituent effect. Replacing either one or two hydrogens in the α -ferrocenyl carbonium ion by phenyl groups has no effect on the stability of the cation. A methyl substituent may actually destabilize the cation slightly. To our knowledge, this is the first observation of a cation not stabilized by a methyl substituent. It is expected that the substituent effect on a very stable cation will be less than that on a less stable cation. One can explain these data as a limiting case of this phenomenon: a cation so stable that there is no substituent effect. However, a second ferrocenyl group stabilizes the α -ferrocenyl carbonium ion by 22 kcal/mol, an extraordinary amount. These data raise questions in our minds whether it is wise to consider the α -ferrocenyl carbonium ion as a substituted carbonium ion (methyl cation). Perhaps so much charge is delocalized into the ferrocene that an alternative description is warranted. If the methyl substituent is sufficiently removed from the center of charge so that its normally stabilizing effect will not operate, a substituent effect quite analogous to the Baker-Nathan²⁵ order is possible and can be rationalized using either steric hindrance to specific solvation,²⁶ cation size arguments,^{18,27} or any of the other many explanations for that phenomenon. The absence of stabilization by the phenyl substituent is caused in part by the fact that the phenyl ring is not in the plane of the ferrocene moiety as shown by NMR studies.⁵ This will account at least in part for the lack of stabilization by a phenyl substituent. The distinction between this example of a small phenyl substituent effect and others^{28,29} which have been observed recently should be made clear. In the other cases, the phenyl group was conjugated to both the starting material and the ion and could stabilize both by resonance. In this case, resonance stabilization only of the ion is possible, though decreased by steric factors. It should be noted that a p -methylphenyl group is somewhat less stabilizing than a phenyl group. The magnitude of this effect is striking, and we have no explanation for it, although a smaller effect in this direction might be rationalized on the same basis as a Baker-Nathan order.

The substituent effects observed here are much smaller than those reported on the pK 's of these ions in water obtained using the H_R acidity function.³ Not enough data are

Table II. Relative Heats of Protonation of Ferrocenyl Ketones and Substituted Ferrocenes in 96.1% H₂SO₄ at 25° Model Compounds

Compd	$\Delta\bar{H}_{s,CCl_4}$	$\Delta H_{s,acid}$	ΔH_{R^+}
	3.39 ± 0.19	-12.4 ± 0.61	-15.8 ± 0.6
	4.04 ± 0.18	-11.4 ± 0.54	-15.4 ± 0.6
	3.89 ± 0.25	-9.11 ± 0.14	-13.0 ± 0.3
	0.91 ± 0.01 ^a	-8.33 ± 0.23	-9.24 ± 0.23
	0.79 ± 0.01 ^a	-12.0 ± 0.2	-12.8 ± 0.2
	5.26 ± 0.25 ^a	-5.60 ± 0.21	-10.9 ± 0.3
	2.53 ± 0.16	-6.77 ± 0.37	-9.30 ± 0.40
	0.35 ± 0.02	-6.60 ± 0.15	-6.98 ± 0.15

^a Data from E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Am. Chem. Soc.*, **92**, 3977 (1970).

given in the communication to determine whether the compounds studied [FcC⁺H₂, FcC⁺HCH₃, FcC⁺HC₆H₅, and FcC⁺(C₆H₅)₂] all followed H_R precisely. In a subsequent paper,³⁰ Hill reports a plot of $\log [R^+]/[ROH]$ vs. H_R for FcC⁺(CH₃)₂ has a slope of 0.85 indicating that this compound does not follow H_R . Other workers have obtained much lower pK' 's for ferrocenyl cations using acidity function techniques.^{31,32} In the absence of more experimental detail, we cannot definitely ascribe the stability differences to problems in the use of the H_R acidity function for these ions; however, it is a strong candidate.

The data in Table II are in striking contrast to those in Table I. The ferrocenyl group does not enhance the heat of protonation of the ketones nearly as much as it enhances the relative heats of formation of the carbonium ions. This phenomenon has been observed frequently with phenyl groups and is usually explained by invoking similar resonance stabilization of the base in its protonated and unprotonated forms,^{28,29} although a leveling effect due to stabilization of the cation by oxygen has been invoked in a different system to explain this effect.^{33,34} These data indicate that the ferrocenyl group does stabilize the protonated ketone in comparison to a phenyl group. As with the previous series of ions, replacement of H by methyl does not stabilize the ferrocenyl substituted ion. The same explanation can be offered for both sets of compounds.

The heat of protonation of ferrocene itself has been measured. It has been known for some time that ferrocene protonates on iron.³⁵ It is a reasonably strong base, comparable to ketones. The presence of a *n*-butyl group on the ring sharply and surprisingly destabilizes the ion. One can invoke any of the explanations used for the large Baker-Nathan orders which have been observed in strong acids to explain this. This behavior is in sharp contrast to the effect of alkyl substitution on ring protonated ferrocene. Alkyl groups are stabilizing.³⁶

In summary, it is quite apparent that the ferrocenyl group is a uniquely stabilizing substituent for carbonium ions. It completely dominates the situation, other substitu-

ents having very small effects. This can be viewed as a limiting case of the notion that the effect of an electron-donating substituent will be proportional to electron demand. Perhaps another way of saying the same thing is that most of the charge on α -ferrocenyl cations is delocalized into the ferrocene group so that the substituent effects observed are those for substitution β to a cationic carbon, not directly on it.

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