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# ELECTRON SPIN RESONANCE STUDY OF RADICAL ANIONS DERIVED FROM SUBSTITUTED FERROCENES[1]

Wayne C. Danen and Charles T. West
Department of Chemistry, Kansas State University,
Manhattan, Kansas 66502

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Although electron spin resonance (esr) spectroscopy has developed over the past ten years into a powerful technique for the study of radical species by providing detailed information concerning the distribution of unpaired spin density, it has only very recently been applied to the investigation of paramagnetic species containing the ferrocenyl substituent (2-4). We presently wish to report several interesting aspects of the effect of the ferrocenyl substituent in nitrobenzene radical anions.

The esr spectrum of 1,1'-*bis*-(*p*-nitrophenyl)ferrocene radical anion obtained at room temperature is shown in Figure 1-A; hyperfine splitting constants and *g*-values for this and related radical anions are listed in Table 1. It can be noted immediately from the spectrum that the unpaired electron is located exclusively on one side of the ferrocene molecule with no apparent transannular interaction. In both 1,1'-*bis*-(*o*-nitrophenyl)- and 1,1'-*bis*-(*p*-nitrophenyl)ferrocene radical anions the lone electron resides primarily on one substituent group. Some delocalization of the unpaired electron onto the attached five-membered ring in the *para* isomer occurs but there is no interaction with the second substituent. These observations indicate that the iron atom in such ferrocenes does not allow effective electronic conjugation between the two rings.

The result obtained with 1,1'-*bis*-(*p*-nitrophenyl)ferrocene can be contrasted with the work of Harriman and Maki (5) in which intramolecular electon transfer in various symmetrical disubstituted radical anions was studied. These authors noted that the unpaired electron in the radical anion of *bis*-(*p*-nitrophenyl)methane interacts with both rings on the time scale of esr even though there cannot be direct conjugation between the two rings because of the intervening

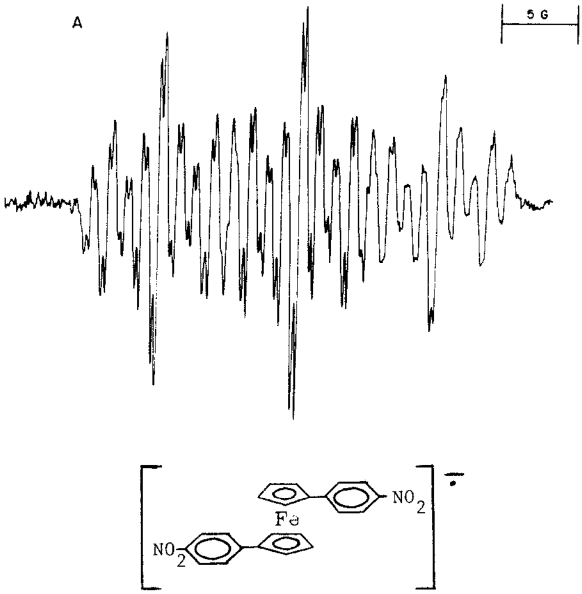


Figure 1-A

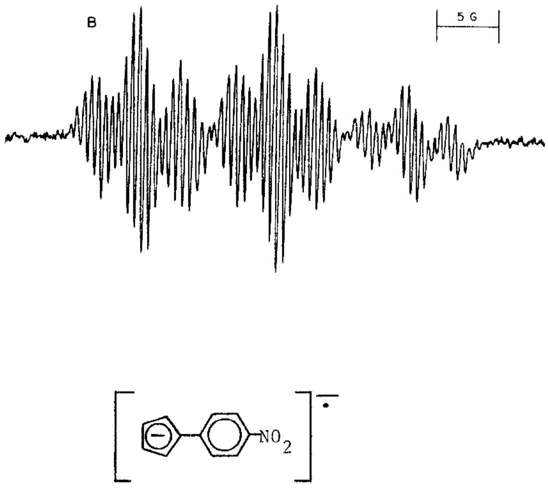


Figure 1-B

Table 1

| Compound | Five-Membered Ring (ortho) | N | Phenyl Ring[a] o | m | p | g-value |
|---|---|---|---|---|---|---|
| 1,1'-Bis-(p-nitrophenyl)ferrocene[b] | 0.31 | 9.20 | 3.26 | 1.11 | - | 2.0061 |
| 1,1'-Bis-(o-nitrophenyl)ferrocene | - | 10.09 | 2.77 | 1.16 | 3.60 | 2.0055 |
| p-Nitrophenylferrocene | 0.31 | 9.25 | 3.29 | 1.12 | - | 2.0061 |
| m-Nitrophenylferrocene | - | 9.75 | 3.32 | 1.11 | 3.92 | 2.0047 |
| p-Nitrophenylcyclopentadienyl Anion | 0.57[c] | 11.02 | 3.25 | 1.11 | - | 2.0047 |

All spectra in DMSO solution at room temperature unless otherwise indicated.
(a) Positions relative to the nitro group. (b) DMF solution; 0.31 g hfs not resolved in DMSO. (c) Overlapping lines prevent unambiguous assignment.

methylene group.

In a related study Gerson amd Martin (6) concluded that the number of methylene groups, *n*, separating the benzene rings in [n.n] paracyclophane radical anions must be $> 3$ to prevent the unpaired electron from delocalizing over both moieties while in the corresponding open-chain compounds the requirement is only that $n > 1$. Although there is essentially free rotation about the iron-ring bonds in ferrocene (7) these results suggest that the two nitrophenyl groups in such heteroannular substituted ferrocene radical anions exist, at least on the time average, in a *transoid* conformation as depicted in Figure 1-A for the *para* isomer.

It was noted that exposure of DMSO or DMF solutions of *p*-nitrophenylferrocene or 1,1'-*bis*-(*p*-nitrophenyl)ferrocene to the fluorescent lighting of the laboratory resulted in cleavage of

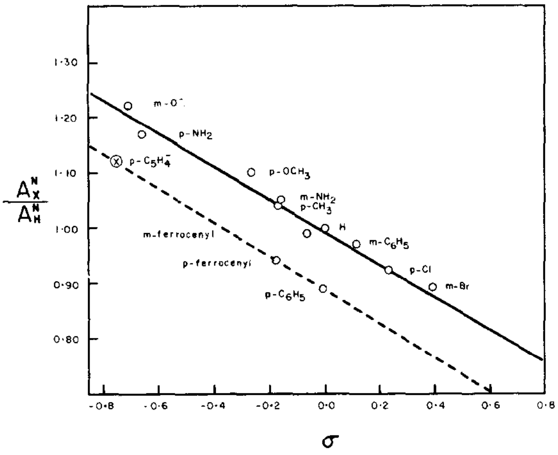
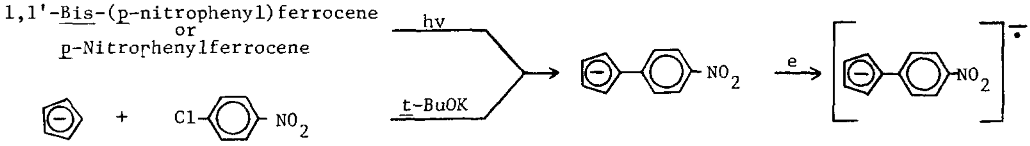


Figure 2.
Plot of $a_X^N/a_H^N$ for substituted nitrobenzene radical anions *vs* Hammett sigma constants (11).

the iron-ring bonds of the ferrocene compounds and formation of the *p*-nitrophenylcyclopentadienyl anion(8). Electroreduction of irradiated solutions of either substituted ferrocene produces the paramagnetic *p*-nitrophenylcyclopentadienyl radical dianion (Figure 1-B). This course for the photodecomposition is confirmed by observing an esr spectrum identical in hyperfine splitting and *g*-value from the reaction of cyclopentadiene and *p*-chloronitrobenzene in the presence of excess base followed by *in situ* electroreduction of the reaction solution.



Additional evidence for this mode of decomposition is obtained from the *g*-value measurements recorded in Table 1; the decrease in *g*-value from 2.0061 to 2.0047 is consistent with cleavage of the iron-ring bonds and constitutes proof that the metallocene compounds are intact prior to photolysis.

This facile photodecompostion allows an unique and interesting comparison of the ferrocene compound with the corresponding cyclopentadienide compound. Figure 2 shows a plot of $a_X^N/a_H^N$ versus Hammett sigma constants for a series of *m*- and *p*-substituted nitrobenzene radical anions. Janzen (9) has recently reviewed the subject of substituent effects on esr spectra and has shown that the spin density on nitrogen in nitrobenzene radical anions follows the Hammett equation although deviations can be expected when a substituent exerts more than a minor perturbation on the system. It can be noted that the *p*-phenyl and *p*-ferrocenyl substituents both fall somewhat below the line defined by the majority of the substituents. If it is assumed that the *p*-cyclopentadienyl anion substitutent is ill-behaved to the same extent (all three substituents are similar in being six-π-electron ring systems) the σ-value for the negatively charged *p*-cyclopentadienide substituent can be estimated as -0.79. A similar value, -0.77, is obtained from a correlation of cyclic voltammetric reduction potentials (10). This value contrasts the -0.17 value for the *p*-ferrocenyl substituent and illustrates the profound moderating effect the iron atom in ferrocene exerts on the π-electrons in the five membered ring (12).

An almost doubling in magnitude of the hyperfine splitting for the *ortho* hydrogens of the five-membered ring in going from the *p*-nitrophenylferrocene radical anion to the dissociated *p*-nitrophenyl cyclopentadienyl radical dianion can be noted. Analysis of the spectrum in Figure 1-B also reveals interaction of the unpaired electron with the *meta* hydrogens of the cyclopentadienyl ring in the radical dianion. A discussion of these interesting observations will be reserved for the detailed publication of this work.

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