

Ion-pair Formation between Iodine and Substituted Ferrocenes in Benzene Solution

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Received June 16, 1980

Some years ago, Brand and Snedden [1] reported that iodine reacted with ferrocene by a reversible redox process which, in a medium of low dielectric permittivity and at low concentrations, was adequately represented by equation (1),



where Fn denotes the ferrocene molecule and Fn^+ the ferricenium cation. They carried out various spectrophotometric measurements in benzene solution at different solute concentrations which showed that the data were consistent with the formula of the product being Fn^+I_3^- and that the equilibrium constant K_1 had the value $174 \text{ M}^{-3/2}$ at 20°C .

It was desired to find out how substituents on the ferrocene molecule affected this equilibrium and whether the ensuing changes could readily be rationalised in terms of any simple parameter.

Experimental

Solutions of iodine (AR grade) and of various substituted ferrocenes, whose purities had been checked by NMR, were prepared in benzene (AR grade). By mixing measured volumes, just before spectral analysis on a Unicam SP800 spectrophotometer, sample solutions were obtained in which the 'nominal' concentrations of the ferrocene, Fn (a) and

of I_2 (b) were known and were in the region of 10^{-3} M . By comparing the UV spectrum of the sample solution with that of the two stock solutions, it was possible to calculate the increase in absorbance at 380 nm attributable to the ion-pair, Fn^+I_3^- . The concentration, x , of the latter was calculated assuming $\epsilon = 27, 730 \text{ M}^{-1} \text{ cm}^{-1}$ and the equilibrium constant $K_1 = x/(a - x)(b - 3/2 x)^{3/2}$ was then evaluated. For each ferrocene compound, measurements were made at several concentrations to ensure consistency.

Results and Discussion

The variation produced in K_1 by substitution was quite considerable as is demonstrated in Table I, which shows that the equilibrium constant for formation of the ion-pair decreased when an electron-withdrawing substituent was present and increased when the substituent was electron-donating.

One process notionally involved in reaction (1) is the removal of an electron from the ferrocene moiety to yield the corresponding ferricenium ion. Although the nature of this process is constant, it will involve an energy change which depends on the substituent. The free energy change is given by $-n\text{FE}^\circ$, where F denotes the Faraday and E° is the standard redox potential for the ferrocene–ferricenium oxidation. Since the free energy change in reaction (1) is $-RT\ln K_1$ one might expect $\ln K_1$ to be a linear function of E° , on the assumption that the other processes involved in reaction (1) are unaffected by the substituent.

Polarographic half-wave potentials $\text{E}_{1/2}$, which differ only slightly from standard redox potentials E° , have been measured [2, 3] for a number of the compounds listed in Table I. The relation between the $\text{E}_{1/2}$ values and $\ln K_1$ is illustrated in Fig. 1, which shows a reasonable correlation. However, the behaviour of the electron-withdrawing phenyl substituent is arguably anomalous since on the one hand the first

TABLE I. Values of Equilibrium Constant K_1 and of $\text{E}_{1/2}$ for Substituted Ferrocenes.

Compound	Equilibrium Constant, K_1	$\text{E}_{1/2}/\text{V}$
Ferrocene	175 ± 3	0.34
Methylferrocene	632 ± 35	0.28
Ethylferrocene	595 ± 30	
1,1'-dimethylferrocene	3314 ± 150	0.24
1,1'-diisopropylferrocene	1482 ± 60	
Phenylferrocene	35 ± 2	0.37
1,1'-diphenylferrocene	145 ± 10	0.37
[3]ferrocenophane	1673 ± 60	0.27

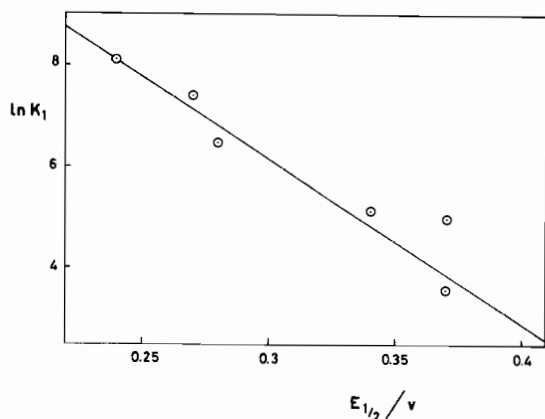


Fig. 1. Plot of $\ln K_1$ against the half-wave potential, $E_{1/2}$, for the various substituted ferrocenes.

phenyl group raises $E_{1/2}$ by 0.03 V while the second has no further effect but on the other hand, while the first phenyl group lowers K_1 by a factor of 5, the second then increases it by a factor of 4. This behaviour contrasts with that of the methyl substituent where the effect, both on $E_{1/2}$ and on K_1 , is apparently cumulative, and in the expected direction for an electron-releasing substituent.

If the point for 1,1'-diphenylferrocene is ignored then the slope of the best straight line is found to

be -32.5 , whereas $-F/RT$ would give a value of -39.6 . This disparity may in part reflect the fact that whereas the $E_{1/2}$ values were measured in the fairly polar medium of aqueous ethanol, the equilibrium constants were measured in non-polar benzene. However, it is also relevant to point out that the precision of the half-wave potentials is not considered [2] any better than ± 0.01 V.

Thus the major influence on K_1 for substituted ferrocenes is clearly the effect of the substituent on the ease of oxidation to the corresponding ferricenium ion.

Acknowledgments

The authors are very grateful to Dr. W. E. Watts of this department for supplying the ferrocene derivatives used in this study.

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