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The Characteristic of the Interaction of Substituted Ferrocenes with Tetracyanoethylene

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It is well known that metallocenes are able to form charge-transfer complexes with some appropriate acceptors, in which either the π-cyclopentadienyl rings or the metal act as an electron donor to a π-acceptor. Rosenblum [1, 2] has investigated the structure of the charge-transfer complex between ferrocene and tetracyanoethylene (TCNE) and has demonstrated that it must be formulated in the classical benzenoid structure.

While the complexation of TCNE with a large variety of donors has been examined [3], the study of its interaction with ferrocenes is limited to the parent compound. Therefore, it is of interest (also in relation to our previous work in the field [4]) to investigate the stability of the charge transfer complexes originated from the interaction of a series of substituted ferrocenes with TCNE.

Results and Discussion

Although the iron group metallocenes are regarded as aromatic substances of exceptionally high reactivity [5], the relatively low ionization potentials of these substances may make the neutral charge-transfer state unstable with respect to the radical ions resulting from complete electron transfer [6, 7], even with acceptor components of moderate electron affinity. For example, N,N,N′,N′-tetramethyl-*p*-phenylenediamine has been observed to give a series of complexes with electron acceptors [8], which range from the covalent molecular complexes commonly described as charge-transfer complexes to compounds resulting from complete electron transfer, which are best described as salts. The course of this reaction is influenced by the dielectric constant of the solvent, since molecular complexes are favored in low dielectric media while electron transfer is favored in high dielectric media [9].

Although the complexes between ferrocenes and TCNE cannot be detected in moderately polar solvents, their presence in cyclohexane is evidenced by the characteristic broad absorption in the region of 800–1200 nm [10]. The formation of the ferricenium cation and of the tetracyanoethylene anion radical was excluded from the absence of their characteristic absorptions in the 600 and 400 nm region.

TABLE I. Association Constants (K) for the 1:1 Complexes of TCNE with Substituted Ferrocenes in Cyclohexane at 25 °C.

Compound	K	$E_{1/4}$ mV	λ_{max} nm
Ferrocene	40	341	900, 1075
Phenylferrocene	35	366	950
Ethylferrocene	65	281	1000, 1150
1,1′-Diethylferrocene	70	224	1100, 1275
1,3-Diethylferrocene	90	225	1170, 1260
Iodoferrocene	25	482	850
Acetylferrocene	15	587	710
Benzene	14.5[a]	–	382
Pentamethylbenzene	200[a]	–	500
Hexamethylbenzene	285[b]	–	533

[a] From Ref. 1. [b] From Ref. 3.

The association constants, which are collected in Table I, were determined by the application of the Benesi–Hildebrand equation [11] (see Experimental). For testing the reliability of these association constants, the K values of benzene, pentamethylbenzene and hexamethylbenzene complexes with TCNE were evaluated under the same experimental conditions and found to be in good agreement with the literature data.

The association constants of Table I immediately show a qualitative correlation with the polar effects of the substituentes. With respect to ferrocene, alkyl substituents show an increase of the equilibrium constants, in agreement with the higher π-electron donation for the Cp rings. On the other hand, the electron withdrawing substituents produce a decrease in the association constants. In addition the association constants were found to correlate linearly with the chronopotentiometric redox potentials, $E_{1/4}$, (see Table I) determined in acetonitrile [12, 13], which refer mainly to the electronic density on iron.

The single equilibrium constants do not allow an unambiguous formulation of the complex structure, *i.e.* whether the π donor site is represented by the iron or the cyclopentadienyl rings.

However, the trend in the stability constants of the series ferrocene, ethylferrocene, 1,1′-diethylferrocene and 1,3-diethylferrocene appears to be quite conclusive in this respect. The equilibrium constants of ferrocene (K = 40), ethylferrocene (K = 65) and 1,1′-diethylferrocene (K = 70) increase in a way which shows an additivity effect of the substituents. Also the redox potentials of the substrates change in accordance with the well known additivity of the polar effects of the substituents; accordingly, the

$E_{1/4}$ of 1,3-diethylferrocene and of 1,1′-diethylferrocene are nearly identical. However the donor properties of the two compounds, as revealed by the charge-transfer association constants, appear to be quite different, since the K value of 1,3-diethylferrocene ($K = 90$) is acutely higher than that of 1,1′-diethylferrocene. This clearly reveals that stabilization of the ferrocene–TCNE complexes is accomplished through the interaction of a filled π-orbital, and excludes the alternative structure which attributes the donor role to the non-binding electrons largely localized on the metal atom.

Another point of interest is the comparison of the stability constants of ferrocenes with those of benzenoid substrates (Table I). The K value of ferrocene is higher than that of benzene, in agreement with the higher electron density on the Cp rings. However, the introduction of methyl groups increases more rapidly the association constants of the polymethylbenzenes than those of ferrocenes. This is probably due to a 'saturation' effect connected with the high electron density of the Cp rings of ferrocenes.

Experimental

Materials

The ferrocene derivatives were prepared according to the methods reported in the literature [5]. The cyclohexane used as solvent in the reactions was dried by refluxing over CaH_2, distilling and saturing with dry nitrogen. All other reagents were commercial products which were recrystallized or sublimed to a constant melting point. The commercially available tetracyanoethylene was crystallized and sublimed several times up to a field invariant molar susceptibility of -57×10^{-6} c.g.s.

Spectrophotometric Measurements

The visible and ultraviolet spectra, as well as the absorptivity measurements for the evaluation of the association constants, were recorded with Beckmann model DK and DU spectrophotometers.

The association constants for complex formation were determined by the application of the Benesi–Hildebrand equation. For a 1:1 complex, a dimensionless constant, K, is defined by the expression

$$\frac{[\mathrm{TCNE}]\, l}{\log(I_0/I)} = \frac{1}{K\epsilon[\mathrm{B}]} + \frac{1}{\epsilon}$$

where $\log I_0/I$ is the optical density, l is the path length and ϵ is the molar absorptivity of the complex and [TCNE] is the stoichiometric molar concentration of tetracyanoethylene. By plotting the term on the left against $1/[\mathrm{B}]$, a straight line is obtained with an intercept equal to $1/\epsilon$ and a slope of $1/K\epsilon$. It must be observed that the accuracy of the values of K is not very high since low values of K and ϵ increase the slope of the plot and lead to a relatively greater error in the determination of $1/\epsilon$. The error in K may be estimated in the order of 15%.

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