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Preliminary communication

The electronic structure of di-η^5-cyclopentadienyliron(II) derivatives

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Abstract

Ultraviolet photoelectron spectroscopic and cyclic voltammetric data for twenty substituted ferrocene derivatives are presented, which demonstrate (for the first time for organometallic compounds) that there is a linear correlation between the first ionization energies of the complexes in the gas phase and the electrochemical oxidation potentials in solution.

Although there is abundant evidence (both empirical and theoretical) for the existence of a linear correlation between the first ionization energies in the gas phase and the electrochemical oxidation potentials in solution for a wide range of related organic molecules [1–8], no such relationship for structurally related organometallic compounds has been convincingly established. Two systems have received limited attention: [Cr(arene)$_2$] (arene = benzene, methylbenzene, or 1,3,5-trimethylbenzene) [9] and [Fe(C$_5$R$_5$)(arene)] (R = H or Me; arene = C_6Me_6, C_6Et_6 or C_6H_3-1,3,5-(CMe_3)$_3$) [10]. Although a linear correlation was found for the former set, the usefulness of this observation is limited by the restricted number of data points (three). For the latter set, the oxidation potentials (obtained in both aqueous lithium hydroxide and *N,N*-dimethylmethanamide) did not give a linear correlation with the first ionization energy in the gas phase. We report here the results of a study upon an extensive series of di-η^5-cyclopentadienyliron(II) derivatives, including

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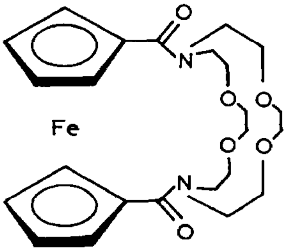
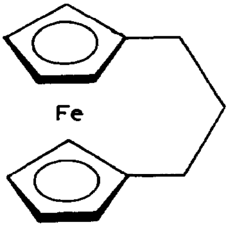
$[Fe(C_5H_5)(C_5H_4R)]$ ($R = CH_2CH_2COOH$ (**3**), COOMe (**6**), COMe (**7**), CHO (**10**), $CH{=}CH_2$ (**18**) or CHMeCOOMe (**19**)), $[Fe(C_5H_4R)_2]$ (R = Me (**2**), $CONMe_2$ (**4**), H (**5**), Cl (**8**), COOMe (**9**), COMe (**11**), COCl (**12**), CHO (**14**) or CH(OH)Me (**17**)), $[Fe(C_5H_3Cl_2)_2]$ (**13**), $[Fe(C_5R_5)_2]$ (R = Me (**1**) or Cl (**15**)) and the linked-ring compounds **16** and **20**, by gas-phase ultraviolet photoelectron spectroscopy (UVPES), mass spectrometry (MS), and cyclic voltammetry (CV; both DC and AC).



(16)



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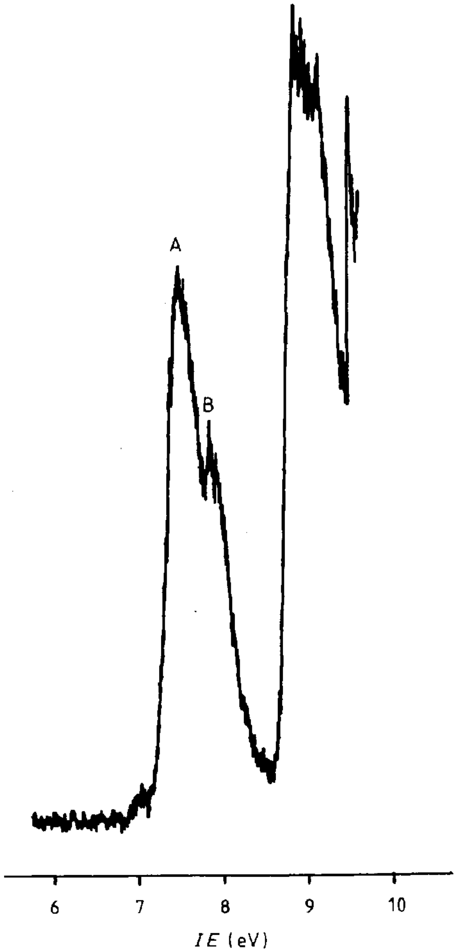

Fig. 1. The He(I) photoelectron spectrum of $[Fe(C_5H_3Cl_2)_2]$ (**13**).

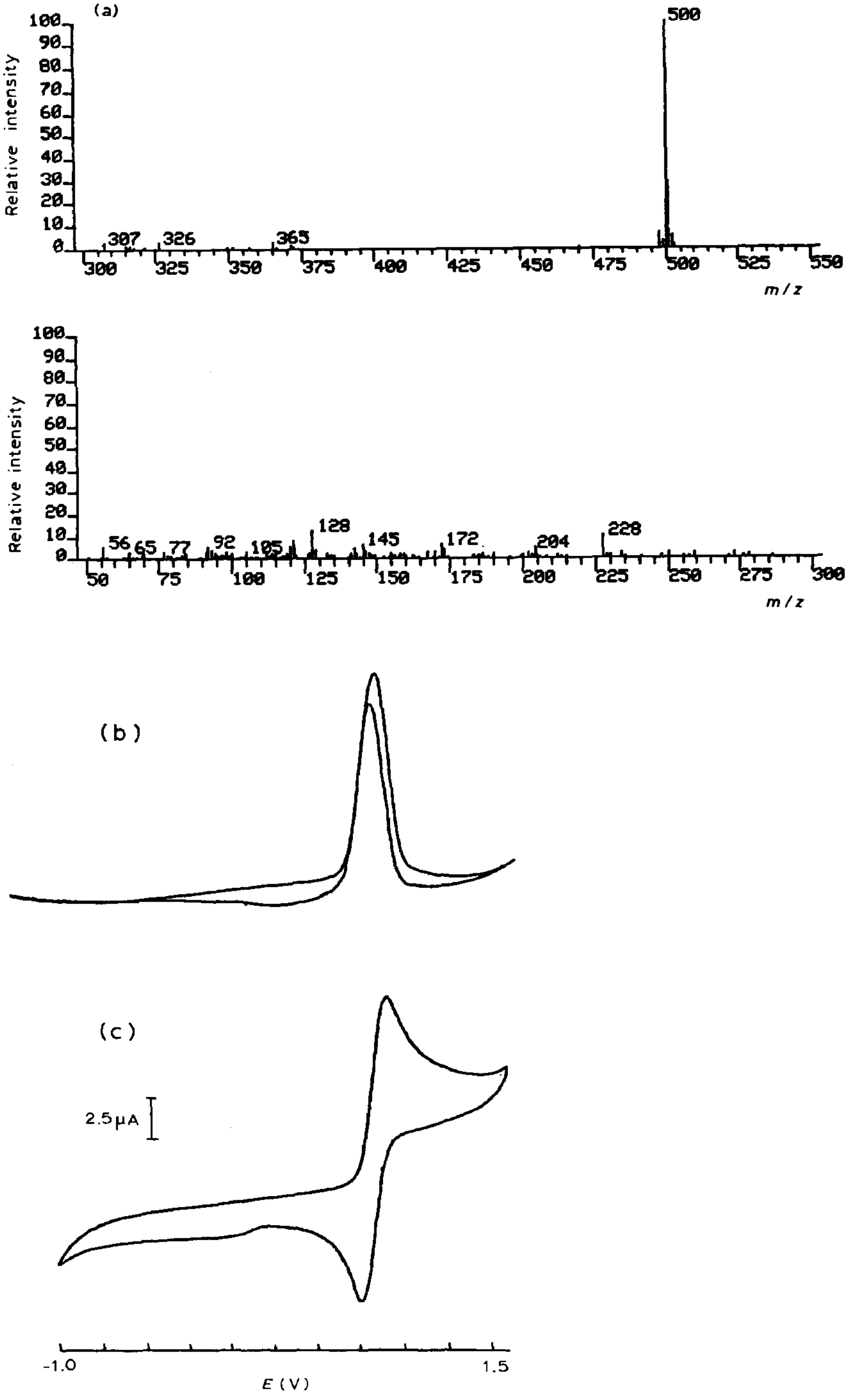

Fig. 2. (a) The EI (70 eV) mass spectrum of **16**, illustrating the quite phenomenal stability of the molecular ion. (b) The AC cyclic voltammogram (100 mV s^{-1}; 500 Hz) of **16** in CH_2Cl_2 (support electrolyte: 0.1 *M* $[NEt_4][ClO_4]$) at 20 °C. (c) The DC cyclic voltammogram (100 mV s^{-1}) of **16** in CH_2Cl_2 (support electrolyte: 0.1 *M* $[NEt_4][ClO_4]$) at 20 °C.

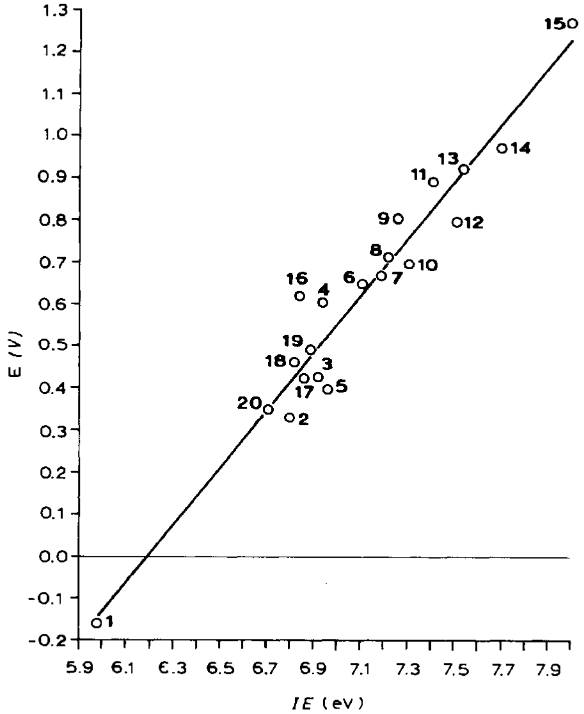

Fig. 3. The first oxidation potentials (in dichloromethane at ambient temperature, vs. SHE) for a series of substituted ferrocenes plotted as a function of their gas phase first ionization energies. The experimental data are plotted as points, and numbered as according to the compound number, as defined in the text; the line is the result of a conventional least-squares linear regression analysis of these data ($r = 0.942$, $n = 20$).

The di-η^5-cyclopentadienyliron(II) derivatives studied were prepared by simple variations of standard methods [11–13], and characterized by microanalytical data, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. The He(I) photoelectron spectra of the volatile samples were recorded, and a typical spectrum is illustrated in Fig. 1. The assignments of the two lowest energy bands (A and B) follow those generally accepted for $[Fe(C_5H_5)_2]$ (although, of course, the symmetry labels will change according to the point group to which the molecule belongs) [14,15]: under D_{5d} symmetry, band A corresponds to the HOMO (e_{2g} symmetry) and band B to the SHOMO (a_{1g} symmetry). All the samples shared a similar low ionization energy profile, except for several for which the two bands A and B merged. The mass spectra of the samples suggested that in each case the gas-phase species was indeed the monomeric molecule, and for the compound with the two cyclopentadienyl rings linked, the molecular ions showed a remarkable stability (Fig. 2a). The electrochemistry of each of the samples studied was uncomplicated (see Figs. 2b and 2c for a typical DC and AC cyclic voltammogram), and for all the samples (except **15**) for which data are summarized (in Fig. 3), the electrochemical response was chemically reversible.

Figure 3 illustrates the linear correlation observed between the gas-phase vertical first ionization energies (IE (eV)) and the solution (CH_2Cl_2) oxidation potentials (E_{ox} (V) (vs. SHE)). The linearity of the plot (which spreads over experimental data

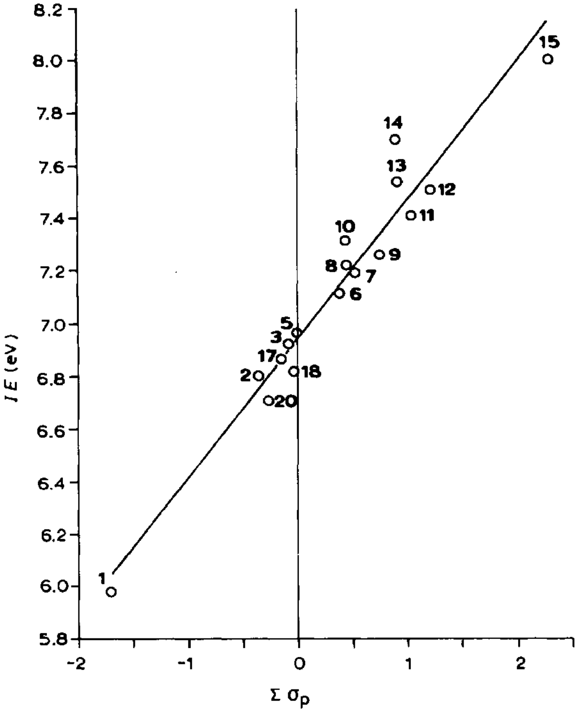

Fig. 4. The gas-phase first ionization energies for a series of substituted ferrocenes plotted as a function of the sum of Hammett σ_p parameters for the cyclopentadienyl ring substituents. The experimental data are plotted as points, and numbered as for Fig. 3; the line is the result of a conventional least-squares linear regression analysis of these data ($r = 0.946$, $n = 17$).

differing by up to 2 eV) is remarkably good, and establishes beyond reasonable doubt that the two parameters are strongly correlated (see eq. 1). Indeed, the

$$E_{ox} = 0.681 IE - 4.163 \qquad (1)$$

gradient observed is closely similar to those found for aromatic hydrocarbons in ethanenitrile (0.679 [2]) and in trifluroethanoic acid (0.71 [7]), and for [Cr(arene)$_2$] in dichloromethane (0.67 [9]). Finally, Fig. 4 depicts the plot of the gas-phase vertical ionization energies against the sum of the appropriate Hammett parameters [16], $\Sigma\sigma_p$, evaluated by assuming that the effects of the substituents were additive, regardless of their position relative to other substituents, an assumption that is upheld by the linearity of the plot. Of the various simple substituent parameters in common use, the Hammett σ_p values gave the best linear correlation, as might have been expected since they provide a measure of the combined tautomeric and polar effects.

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