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Preliminary communication

Electronic effects in dienetricarbonyliron derivatives
II. On the electron donor capacity

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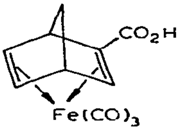
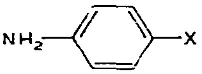
Little is known about the electronic character of metal carbonyl complexing groups. Some information is available from Mahler and Pettit's study of the dienetricarbonyliron system[1,2]. In systems where the group is far removed from the center undergoing reaction, but for which there is still interaction through a π-system, the dienetricarbonyliron system appears to act as an electron donor. Thus, while *trans,trans*-sorbic acid and bicycloheptadiene carboxylic acid exhibit pK_a values of 7.00 and 7.00, respectively, the corresponding complexed systems, I and II, show pK_a values of 7.25 and 7.50, respectively. The electron-donating character is further demonstrated by the ability of 1-phenylbutadienetricarbonyliron to undergo Friedel–Crafts acylation in the *para* position.

(I)



(II)

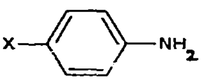
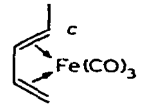


(III)

In an effort to evaluate the relative magnitude and character of the electronic property of this system, the pK_a measurements of a series of *para*-substituted anilines III were carried out. These systems were chosen for study owing to their sensitivity to *para* substituents[3] and their ready availability. Since the anilines were not completely soluble in water, apparent pK_a's were determined in aqueous ethanol (50/50, water/95% ethanol) by titration with hydrochloric acid. Calculations of the pK_a were carried out as exemplified by Albert and Serjeant[4] except no activity corrections were made. (The average deviation within any titration varied from 0.03 to 0.09 pH units.) The data are presented in Table 1.

TABLE 1

APPARENT pK_a VALUES[a] OF *para*-SUBSTITUTED ANILINES

X in 	apparent pK_a	Lit. (corrected to 28.5°[6])
$-OCH_3$[b]	5.01	
$-CH_3$[b]	4.72	4.69 (ref. 7)
$-H$[b]	4.22	4.21 (ref. 7), 4.20 (ref. 8), 3.99 (ref. 9)
$-Ph$[b]	3.91	
 [c]	3.90	
 [c]	3.81	
$-Cl$[b]	3.52	
$-Br$[b]	3.38	3.03 (ref. 9)

[a] Determined in a mixture of water/95% ethanol (50/50, v/v). [b] Purified commercial samples; using these samples, a plot of pK_a *vs.* σ_p gave a straight line. [c] Landesberg *et al.*[5] synthesised new compounds which gave satisfactory elemental analyses and spectra consistent with the proposed structures.

By comparison to groups with known electronic properties, it can be seen that both the diene and the dienetricarbonyliron group are electron withdrawing with respect to hydrogen. However, the Fe(CO)$_3$ group reduces the electron withdrawal of the simple diene; the overall effect, when comparing only the two systems, is one of electron donation. With the latter in mind, these findings are in agreement with those of Mahler and Pettit[1,2]. The electron-donor capacity is similar to that of phenyl. However, the mechanism through which the interaction takes place is not entirely clear at this time. We hope that further studies in progress will allow a comprehensive evaluation of these electronic effects.

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