Tetrahedron Letters No.22, pp. 2381-2387, 1966. Pergamon Press Ltd.
Printed in Great Britain.

ELECTRONIC PROPERTIES OF THE FERROCENYL AS A SUBSTITUENT

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(Received 29 March 1966)

Since Tart's first papers (1) enabled the partition of the effects responsible for the σ-value, the evaluation of the latter became the method (2) allowing to determine the electronic effects of various atomic groups substituting the benzene ring in metha- or para-position.

In our previous papers the ferrocenyl was demonstrated to be relatively strong electron donating substituent. In this paper the σ-evaluation was performed in order to study electronic effects on which the total electron donation of the ferrocenyl depends.

Dissociation constants of substituted benzoic acids and metha- and para-substituted ferrocenylbenzoic acids were determined by means of acid-base potentiometric titration in 70% dioxane. The same method permitted us to determine the dissociation constants of various substituted phenols and para-ferrocenylphenol in 50% ethanol, as well as the K_b of para- and metha-substituted ferrocenylanilines in 80% ethanol (4). Earlier we have obtained (5) the formal redox potentials of the substituted ferrocenes in which the CH_2-group stands between the nucleus and substituent, and these values were now used to estimate the inductive effect of the ferrocenyl as a substituent. To estimate the ferrocenyl electrophilic reactivity the protolysis of diferrocenylmercury was studied in $HClO_4$-90% dioxan medium (6). The usual least square technique (7) was applied to the data obtained; σ-values characterizing the ferrocenyl as a substituent in the different positions of the benzene ring for the vaious reaction series are listed in Table 1.

The Hammet σ_p is -0,18 for the ferrocenyl as a substituent in the benzene ring. On the Hammet σ_p scale (8) this value stands between σ_p of methyl /-0,170/ and of methoxyl /-0,268/ groups. Hence ferrocenyl is somewhat stronger electron donating substituent than methyl when characterized according to its total electronic effect in the benzene ring para-position. The same result is obtained, for example, by comparison of the corresponding substituted ferrocenes redox potentials with the first redox potential of diferroce-

Table 1

Reaction Series	The Ferrocenyl σ-Values*			
	ρ	n	r	σ-Values** for $R = C_5H_5FeC_5H_4-$
$R-C_6H_4COOH$ Dissociation in 70% Dioxan at 25.0°C	1.60	7	0.993	$\sigma_p = -0.18$ $\sigma_m = -0.15$ $(\sigma) = -0.28$
$R-C_6H_4OH$ Dissociation in 50% Ethanol at 25.0°C	2.50	5	0.999	$\sigma_p = -0.05$
$R-C_6H_4\overset{+}{N}H_3$ Dissociation in 80% Ethanol at 25.0°C	3.53	7	0.991	$\sigma_p = -0.03$ $\sigma_m = 0.00$
$R-CH_2C_5H_4FeC_5H_5$ Redox Potentials in 75%CH_3COOH 0.066N $HClO_4$ at 25.0°C	-0.30	6	0.994	$(\sigma_i) = -0.12$ $\sigma_i = -0.08$
R_2Hg Protolysis in 90% Dioxan at 25.0°C	3.78	12	0.995	$\frac{(\sigma + \sigma^+)}{2} = -0.64$ $(\sigma^+) = -1.0$*** $\sigma_p^+ = -0.65$

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* The given σ-values accuracy of ±10% is usual for such measurments.

** The values in brackets are calculated from $lgK_{RY}/K_{C_6H_5Y} = \rho XC_6H_4Y(\sigma)$, where Y is reaction center, X - substituent and $R = C_5H_5FeC_5H_4-$. According to our data /Y = COOH/ the $(\sigma)/\sigma_p$ ratic equals 1.55. Similiar quantity may be obtained from the values cited elsewhere: $(\sigma^+) = -1.09$ (13) and $\sigma_p^+ = -0.71$ (14). The factor 1.55 shows the extent to which the total electronic effect of the ferrocenyl nucleus considered as substituent disappears when the benzene ring is introduced between the substituent and the reaction center. We used this factor to calculate σ_i and σ_p^+ values from our experimental data.

*** It will be noted that the σ^+-value found from the protolysis of the diferrocenylmercury is in close agreement whth that obtained by Arnett and Buschick (13) from the protonation of the diferrocenylketone.

nyl (5).

Unlike phenyl the ferrocenyl is a comparatively strong electron donating substituent not only in para- but also in the metha-position, $\sigma_m = -0.15$. This fact alone could prooves that ferrocenyl has a large positive inductive effect the metha-activity of a substituent being predominantly inductive. Accordingly the ferrocenyl inductive aromatic parameter σ_i found in our paper is equal to -0.08, i.e. its absolute value is one of the greatest determined for electron donating substituents (8). The definite inductive electron donating behaviour of the ferrocenyl substituent may be induced by some excessive negative charge in the five-membered aromatic ring. In this sense our results confirm the ferrocene molecule MO calculation performed by Shustorovich and Dyatkina (9). These authors have shown the ferrocene five-membered rings have an effective negative charge of about 0.35 electron.

When the ferrocenyl substitutes the para-position of benzene ring a positive inductive effect adds to the positive conjugation effect resulting from the conjugation of ferrocenyl with the benzene ring and with the carboxyl group as a reaction center.

To estimate this effect quantitatively the obtained σ_p, σ_m and σ_i values were used to calculate the ferrocenyl σ_R value which was found to be -0.11. A comparison of the ferrocenyl σ_R with σ_R of other substituents prooves but a weak ferrocenyl (as well as phenyl, $\sigma_R = -0.10$) conjugation with the benzene ring and with the carboxyl group the latter being relatively weak electron withdrawing reaction center.[*]

Ferrocenyl σ_p - values were also received from the reaction series whose reaction centers were groups with unseparated electron pairs. The received values (as well as these of other substituents possessing +R - effect (10)) are significantly lower than Hammet's σ_p values probably owing to the "saturation" effect.

The electronic influence of the ferrocenyl is significantly increased by interaction with strong electron withdrawing reaction centers. The ferrocenyl electrophilic aromatic parameter σ_p^+ may be compared with that of methoxyl (-0.778) being for greater than that methyl (-0.311) (8). Accordingly, the total ferrocenyl influence on the electrophilic reactions may be compared with that of methoxy-group. This is in good agreement with the data concerning the ferrocene electrophilic reactivity (11).

The ferrocenyl contribution to the total electron donation effect significantly increases when the former interacts with the strong electron donation reaction centers the σ_R^+

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[*] The σ_R-values characterizing the ferrocenyl group conjugation are obtained from the following relations: (15)

$$\sigma_p = 1.13\,\sigma_i + \sigma_R\,; \qquad \sigma_p^+ - \sigma_i = \sigma_R^+;$$

$$\sigma_m = \sigma_i + 0.5\,\sigma_R; \qquad \sigma_R^+ = -\,0.57;$$

$$\sigma_R = -0.11 \qquad \sigma_R^+ - \sigma_R = \Delta\sigma_R^+;$$

$$\Delta\sigma_R^+ = -0.46;$$

value being equal to -0.57. The value is much higher that of phenyl (-0.28) thus demonstrating the significantly stronger polarizability of the ferrocenyl electrons as compared with that of phenyl. The ferrocenyl $\Delta\sigma_R^+$ -value is almost three times higher than that of phenyl (-0.46 and -0.18 respectively) which is in agreement with the data of Hill (12) who found that the ferrocenyl ability to stabilize an α-cationic center is much greater than that of phenyl and is comparable with that of triphenylmethyl group. In this respect however, (i.e. as for as to the polarizability induced by the effect of the strong electron attracting groups is concerned) the ferrocenyl is much weaker than the groups possessing an unseparated electron pair, e.g. CH_3O– and $-NH_2$ whose σ_R^+'s are equal to -1.03 and -1.4 respectively (8).

The ferrocenyl +R - effect increase due to the interaction with the strong electron attracting reaction centers may probably be attributed to the fact that in the transition state the back-donation increases directed from the iron to the ligand - a cationoid five-membered ring.

To sum up, the ferrocenyl electronic influence on the neighbouring atomic groups is determined by the strong +I-effect in addition to the +R-effect whose value significantly depends on the reaction center nature.

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