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Abstract

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TRANSANNULAR ELECTRONIC EFFECTS

IN THE FERROCENYL NUCLEUS

DISSOCIATION CONSTANTS

OF SUBSTITUTED FERROCENECARBOXYLIC ACIDS

The existence of a transannular influence of substituents in the ferrocene molecule was established in early studies on the reactivity of ferrocene derivatives. However, the electronic nature of this influence remained unclear.

In the present work, the transmission of electronic effects in the ferrocene molecule has been studied quantitatively using as an example a reaction series—the dissociation of ferrocenecarboxylic acids in which the substituent and the reaction center are located in different rings (^{1}).

Table 1

Dissociation constants of several heteroannular substituted ferrocenecarboxylic acids
$X—C_5H_4FeC_5H_4COOH$ *

No.	$-X$	$K \cdot 10^7$	pK 50% C_2H_5OH	$pK^{(3)}$ 50% C_2H_5OH	$pK^{(2)}$ 68% CH_3OH	σ_i
1	C_3H_7	4.5	6.35	–	–	–
2	C_4H_9	4.7	6.33	–	6.50	–
3	C_2H_5	5.0	6.30	6.34	6.43	−0.05
4	$CH_2C_6H_5$	5.5	6.26	6.25	–	+0.04
5	H	8.1	6.09	6.11	6.29	0
6	OCH_3	8.5	6.07	–	–	+0.31*
7	Cl	12.6	5.90	–	–	+0.47*
8	Br	12.6	5.90	–	–	+0.44*
9	$COOCH_3$	16.5	5.81	–	6.08	+0.30
10	COC_2H_5	21.4	5.67	–	–	–
11	COC_3H_7	21.9	5.66	–	5.95	–

No.	$-X$	$K \cdot 10^7$	pK 50% C_2H_5OH	$pK^{(3)}$ 50% C_2H_5OH	$pK^{(2)}$ 68% CH_3OH	σ_i
12	COC_6H_5	23.4	5.63	5.90	–	–
13	$COCH_3$	25.7	5.59	5.76	5.91	+0.28
14	CN	36.0	5.45	–	5.82	+0.56*

* For benzoic acid under the same conditions $pK = 5.69$; the values of σ_i marked with an asterisk are taken from the work of O. Exner (^{10}). The remaining values of σ_i are taken from the review by V. Palm (^{6}).

Table 1 gives the apparent dissociation constants of the acids, determined potentiometrically in 50% ethanol; from these data it is evident that the alkyl substituents studied lower the dissociation constant of ferrocenecarboxylic acid to approximately the same extent, while all the other substituents increase it.

Earlier, Nik. A. Nesmeyanov and O. A. Reutov (^{2}) and a number of other authors (^{3}), who determined the dissociation constants of ferrocenecarboxylic acid and of individual substituted ferrocenecarboxylic acids, arrived at the same qualitative conclusions.

A complicating circumstance in the study of such compounds is that in solution rotation is possible, or at least substantial oscillations of the rings (^{4}) about the axis passing through their centers, which can bring the substituent and the reaction center to such distances at which direct interaction between them is possible. Therefore, first-

before speaking of the electronic effects of substituents, it is necessary to make sure that there is no substantial direct interaction between the substituent and the reaction center.

A preliminary study of the formal oxidation-reduction potentials of a series of heteroannular disubstituted ferrocenes (5) and, in particular, of some substituted ferrocenecarboxylic acids showed that the potentials of these compounds are additive quantities and that, consequently, in solutions there is no substantial interaction between groups located in different rings. A study was also made of the IR spectra of the acids obtained by us; it showed that intramolecular hydrogen bonds are absent in them. Thus, as a first approximation, it may be assumed that the changes in the apparent dissociation constants of the ferrocenecarboxylic acids studied are mainly due to the electronic effects of the substituents.

Fig. 1. Dependence of $\lg K$ for dissociation of ferrocenecarboxylic acids on the values of σ_i.

Turning to the correlation analysis of the data obtained, we first select, from the set of substituents studied, those whose influence on the reaction center will be mainly inductive: these are alkyl groups, benzyl, hydrogen, and the

Fig. 1. Dependence of $\lg K$ for dissociation of ferrocenecarboxylic acids on the values of σ_i

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carbomethoxy group. In the plot of the dependence of $\lg K$ on i (Fig. 1), a straight line passes through these points; the acetyl and CN groups also fall on it ($\rho_i = 1.385,\ r = 0.936^*,\ n = 6$). Points corresponding to the methoxy group and halogens deviate noticeably from the straight line. The influence of these substituents is composed of an inductive effect and a conjugation effect. From the magnitude of the deviation, the values of σ_c were estimated, characterizing the conjugation of these substituents with the aromatic five-membered ring and with the reaction center in the ferrocene molecule. In Table 2 the values found are compared with the values of σ_c^0 for the same substituents, obtained from the oxidation-reduction potentials of the corresponding monosubstituted ferrocenes, and with the values of σ_c^0 for the same substituents in the phenyl nucleus (6).

Table 2

Values of σ_c for substituents –X from different reaction series

–X	$X—C_6H_4COOH$	$X—C_5H_4FeC_5H_5 \rightleftarrows XC_5H_4Fe^+C_5H_5$	$X—C_5H_4FeC_5H_4COOH$
$–OCH_3$	–0.41	–0.34	–0.30
–Cl	–0.20	–0.26	–0.34
–Br	–0.19	–0.28	–0.31

From the data in Table 2 it is seen that the $+C$-effect of the methoxy group gradually decreases on going from the phenyl nucleus to the ferrocenyl nucleus with the reaction center being the iron atom (a strongly electron-deficient reaction center), and further to the ferrocenyl nucleus with a comparatively weak electron-deficient reaction center–the carboxyl group. In the latter case, the contribution of the $+C$-effect of the methoxy group differs little from the influence of the same group from the meta position of the phenyl nucleus. Indeed, it turned out that the methoxy group lies on the common straight line with the other substituents in the correlation of $\lg K$ with the values of σ_m^0 ($r = 0.952,\ n = 6$). Thus, judging from these data, there is no direct polar conjugation between the substituents and the reaction center located in different rings of the ferrocene molecule.

From the data in Table 2 it is also evident that the values of σ_c for chlorine and bromine as substituents in ferrocenecarboxylic acids are substantially greater

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[*] The accuracy of the determinations of the apparent dissociation constants makes such correlation coefficients quite acceptable.

than the values of σ_c^0 for the same substituents in the phenyl nucleus and greater than the values of σ_c^0 obtained for these substituents on the basis of the oxidation-reduction potentials of haloferrocenes. Moreover, these values are practically equal to the values of σ_c^+, which characterize the $+C$-effect of halides in the para position of the phenyl nucleus with respect to very strongly electron-unsaturated reaction centers. It is clear that the carboxyl group as a reaction center, even under favorable conditions in the para position of the phenyl nucleus, cannot induce such a strong $+C$-effect of halides. In addition, the values of σ_c^0 for halides as substituents, obtained from measurements of oxidation-reduction potentials, where the strong electron-unsaturated reaction center—the iron atom—acts as the reaction center, although higher than the values of σ_c^0 for halides in the phenyl nucleus, are nevertheless somewhat lower than the values of σ_c obtained in the present work. Probably, the decrease in the electron-acceptor properties of halides is caused not by an increase in their $+C$-effect, although this effect is included in the determined values of σ_c, but by certain other features of their interaction with the ferrocenyl nucleus. It should be noted that the specific reactivity of halides in haloferrocenes has been noted repeatedly ([7]).

From all that has been said it follows that, with the exception of halides, the influence of most of the substituents studied on the dissociation constants of heteroannular ferrocenecarboxylic acids is inductive in character. The ferrocenyl nucleus acts as an obstacle to the transmission of conjugation from the substituent to the reaction center.

In the work of Cram et al. ([8]), using reactions of (2,2)- and (3,3)-paracyclophanes as examples, it was shown that the transannular influence of substituents even on strongly electron-deficient reaction centers is, to a first approximation, also inductive. The reason is that the interaction of $2p\pi$-orbitals of rings with one another, and also with the $4s$- and $3d$-orbitals of the metal in three-dimensional bicyclic aromatic systems with parallel rings—paracyclophanes, ferrocene, and dibenzobromine—is of σ-character ([19]), and, consequently, the transfer of electronic effects from one ring to another must be inductive in nature and reflect the ability of π-electrons to transmit the electronic influence of substituents in a direction perpendicular to the plane of the ring.

In contrast to other groups that impede conjugation between the substituent and the reaction center, for example the CH_2 group, the ferrocenyl nucleus does not weaken the inductive influence of substituents. The value $\rho_i = 1.385$, which characterizes the ability of the ferrocenyl nucleus to transmit the inductive influence of substituents from one ring to the other, is close to the value of ρ_i for para-substituted benzoic acids (1.464 in 50% ethanol) ([11]). Consequently, the inductive conductivity of the ferrocenyl and benzene nuclei is very similar in magnitude.

Experimental Part

Ferrocenecarboxylic acid and heteroannularly substituted ferrocenecarboxylic acids were obtained as described by us earlier (^{1}). 1,1′-Carbomethoxyferrocenecarboxylic acid was obtained by the method proposed by N. A. Nesmeyanov and O. A. Reutov (^{2}).

Measurement of the pH of the acid solutions was carried out on an AK acidimeter (Delba) with a glass electrode. A saturated calomel electrode served as the reference electrode. Titration was carried out in a nitrogen atmosphere at a temperature of $25 \pm 0.1^{\circ}$. A weighed portion of acid, $2.5 \cdot 10^{-4}$ M, was dissolved in 50 ml of 50% (by volume) ethanol and titrated with an alcoholic solution of sodium hydroxide. Titration was carried out for three degrees of neutralization. The pK values were calculated by the known formula $^{(11)}$; K_w for 50% ethanol was taken to be $1.585 \cdot 10^{-15}$ $^{(12)}$. The acid dissociation constants are given in Table 1*.

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* The data of Table 1 are averages of three measurements. The differences between individual pK values do not exceed 0.02 pK unit for each acid.

Note: Figure translations are in progress. See original paper for figures.

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