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Abstract

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OXIDATION-REDUCTION POTENTIALS OF HETEROANNULAR DISUBSTITUTED FERROCENES

In previous communications (1,2) we described the determination of the formal oxidation-reduction potentials of a series of monosubstituted ferrocenes and, by means of correlation analysis of the data obtained, showed (3) that the influence of substituents in the oxidation reaction of monosubstituted ferrocenes consists only of the inductive interaction between the substituent and the reaction center and of conjugation between the substituent and the five-membered aromatic ring, transmitted to the reaction center in the form of inductive polarization of the iron–ring bond. Effects similar to the effect of direct polar conjugation between the substituent and the reaction center and to the effect of conjugation between the substituted aromatic nucleus and the reaction center, observed in other reaction series, do not influence the reactivity of the iron atom in the oxidation reaction of monosubstituted ferrocenes; moreover, the substituents exert no spatial influence on the reaction center in this reaction.

In the present work the formal oxidation-reduction potentials of a series of heteroannular disubstituted ferrocenes have been determined. The measurements were carried out by the same method and under the same conditions (1) as in the determination of the potentials of monosubstituted ferrocenes; the results are given in Table 1. Under these conditions some heteroannular-

Table 1

Formal oxidation-reduction potentials of heteroannular disubstituted ferrocenes and the quantities $\lg K_{X,Y}/K_H$, $\Sigma\sigma_n^0$ (4), and $\Sigma\sigma_i$, used for correlations

$X-C_5H_4FeC_5H_4-Y$		$E_{f_0}^*$	$\lg K_{X,Y}^{**}/K_H$	$\Sigma\sigma_n^{0\,***}$	$\Sigma\sigma_i$
$-X$	$-Y$				
$-C_2H_5$	$-C_2H_5$	−0,150	1,607	−0,30	−0,10
−H	−H	−0,245	0,000	0,00	0,00
$-C_6H_5$	−Br	−0,357	−1,912	0,41	0,40
$-CH_2OH$	$-CH_2OH$	−0,386	–	–	–
$-OCOCH_3$	$-OCOCH_3$	−0,387	–	–	–
$-C_2H_5$	$-CONH_2$	−0,422	–	–	–
n-C_4H_9	−COOH	−0,451	–	–	–
n-C_3H_7	−COOH	−0,453	–	–	–
$-C_2H_5$	−COOH	−0,455	−3,553	0,31	0,25

$X-C_5H_4FeC_5H_4-Y$	$X-C_5H_4FeC_5H_4-Y$	$E^*_{f_0}$	$\lg K^{**}_{X,Y}/K_H$	$\Sigma\sigma^{0\,***}_n$	$\Sigma\sigma_i$
−J	−Cl	−0, 529	−4, 805	0, 54	0, 86
−Cl	−Cl	−0, 554	−5, 228	0, 54	0, 94
$-OCH_3$	−COOH	−0, 410	−2, 792	0, 30	0, 55

* The concentration of hydrochloric acid in the solvent is 0.066 M. The values of E_{f_0} given are averages of at least three measurements; the mean deviation does not exceed 0.002 V.

** Calculated by the formula:

$$\lg K_{X,Y}/K_H = \frac{E^{-X,-Y}_{f_0} - E^{-H}_{f_0}}{0.0591}.$$

*** The value of σ^0_n for the $-C_2H_5$ group was taken equal to the value of σ^0_n for the $-CH_3$ group.

disubstituted ferrocenes with electron-acceptor substituents: 1,1′-ferrocenedicarboxylic acid and its dimethyl ester, dinitrile of 1,1′-ferrocenedicarboxylic acid, 1,1′-diacetylferrocene and its dioxime, 1,1′-dibenzoylferrocene, and also 1,1′-nitroethylferrocene.

On the basis of the results obtained by us earlier (3), it could be assumed that in heteroannular disubstituted ferrocenes the total influence of two substituents on the reactivity of the iron atom would be an additive quantity if the nature of the influence of each substituent remains the same as in the corresponding monosubstituted ferrocenes. If, however, an additional interaction arises between the substituents, then the total influence of the two substituents will not be additive.

Table 2

Comparison of experimentally found and calculated oxidation-reduction potentials of heteroannular disubstituted ferrocenes

$X-C_5H_4FeC_5H_4-Y$	E_{exp}	E^*_{calc}	ΔE	$\Delta E/E_{exp}$, %	
−X	−Y				
$-C_2H_5$	C_2H_5	−0.150	−0.153	0.003	2.0
$-C_2H_5$	−Br	−0.357	−0.364	0.007	2.0
$-CH_2OH$	$-CH_2OH$	−0.386	−0.378	−0.013	3.4
$-OCOCH_3$	$-OCOCH_3$	−0.387	−0.403	0.016	4.1
$-C_2H_5$	$-CONH_2$	−0.422	−0.438	0.016	3.8
n-C_4H_9	−COOH	−0.451	−0.455	0.004	0.9

$X—C_5H_4FeC_5H_4$	E_{exp} Y	E^*_{calc}	ΔE	$\Delta E/E_{exp}$, %	
n-C_3H_7	–COOH	–0.453	–0.455	0.002	0.4
$–C_2H_5$	–COOH	–0.455	–0.453	–0.002	0.4
–J	–Cl	–0.529	–0.547	0.018	3.4
–Cl	–Cl	–0.554	–0.571	0.017	3.0
$–OCH_3$	–COOH	–0.410	–0.420	0.010	2.5

* It should be borne in mind that the error in the value of E_{calc} may reach 10 mV, i.e., from 2 to 5%.

To elucidate the nature of the interaction of substituents with the reaction center in the reversible oxidation reaction of heteroannular disubstituted ferrocenes, the present work uses the values of oxidation-reduction potentials. Table 2 gives the measured oxidation-reduction potentials E_{exp} and the potentials E_{calc}, calculated from the relation $E_{\text{calc}} = E_\phi + \Delta E_X + \Delta E_Y$, where E_ϕ is the oxidation-reduction potential of ferrocene, ΔE_X is the difference in potentials between ferrocene with substituent X and ferrocene, and ΔE_Y is the difference in potentials between ferrocene with substituent Y and ferrocene. Table 2 also gives the deviations of the experimentally found values of the potentials from the calculated ones, $\Delta E = E_{\text{calc}} - E_{\text{exp}}$, and the ratio of ΔE, in percent, to E_{exp}.

As is evident from the data of Table 2, in most cases there is satisfactory agreement between the values of the oxidation-reduction potentials measured and calculated in this way. Consequently, the influence of substituents located in different rings of the ferrocene nucleus on the reactivity of the iron atom in the reversible oxidation reaction of disubstituted ferrocenes is additive.

This conclusion is fully confirmed by the results of the correlation analysis. Figure 1 presents the dependence of $\lg K_{X,Y}/K_H$ on the values of $\sum \sigma_n^0$ for a series of heteroannular disubstituted ferrocenes, $\rho_0 = -8.01$; $r = 1.00$. Earlier (3) we showed that the reactivity of monosubstituted ferrocenes in the oxidation reaction is well described by the equa-

···by the equation $\lg K_X/K_H = \rho_0 \sigma_n^0$ ($\rho_0 = -8.81$). Fig. 2 represents the result of a joint correlation of $\lg K_X/K_H$ of mono- and disubstituted ferrocenes with the values $\sum \sigma_n^0$ for the corresponding substituents, $\rho_0 = -8.43$; $r = 1.01$. As can be seen, in all three cases the values of ρ_0 are practically equal. The reactivity of mono- and heteroannular disubstituted ferrocenes in the reversible-oxidation reaction is well described by the equation $\lg K_X/K_H = \rho_0 \sum \sigma_n^0$. The influence of substituents located in different rings of the ferrocene nucleus on the reactivity of the iron atom obeys the same additivity rules as the influence of substituents in phenyl nuclei symmetrically bonded to a common reaction center (^{5}).

The nature of the interaction of each substituent with the reaction center in the reversible-oxidation reaction of heteroannular disubstituted ferrocenes remains the same as in monosubstituted ferrocenes. This is clearly seen from the dependence, presented in Fig. 3, of $\lg K_{X,Y}/K_H$ on the values $\sum \sigma_i$ for the corresponding substituents; on the straight line connecting the substituents whose influence is inductive lie the points corresponding to 1,1′-diethylferrocene and 1,1′-alkylferrocenecarboxylic acids. From the deviation from

Fig. 1. Dependence between $\lg K_{X,Y}/K_H$ for the reversible-oxidation reaction of $X—C_5H_4FeC_5H_4—Y$ compounds and the values $\sum \delta_n^0$ for the corresponding substituents

Fig. 2. Dependence between $\lg K_X/K_H$ and $\lg K_{X,Y}/K_H$ for the reversible-oxidation reaction of $C_5H_5FeC_5H_4—X$ and $X—C_5H_4FeC_5H_4—Y$ compounds and the values σ_n^0 and $\sum \sigma_n^0$ for the corresponding substituents

Fig. 1

Fig. 2

[Figure 3]

Fig. 3. Relationship between $\lg K_X/K_H$ and $\lg K_{X,Y}/K_H$ for the reversible oxidation reactions of $C_5H_5FeC_5H_4—X$ and $X—C_5H_4FeC_5H_4—Y$ compounds and the values of σ_i and $\sum \sigma_i$ for the corresponding substituents

From the points of this line corresponding to 1,1′-bromoethylferrocene and 1,1′-dichloroferrocene, the values of σ_c^0 for chlorine and bromine as substituents in these compounds were estimated (−0.27 and −0.29, respectively); they are equal to the corresponding values obtained for monosubstituted ferrocenes (^{3}). Consequently, the presence of a substituent in the other ring does not exert any substantial influence on the magnitude and character of the interaction of the first substituent with the reaction center in the reversible oxidation reaction of heteroannular disubstituted ferrocenes.

These results, in our view, convincingly show that in solutions there is no substantial direct interaction between substituents located in different rings of the ferrocene nucleus.

In the present work we used ferrocene derivatives synthesized by K. I. Grandberg, V. N. Drozd, Yu. A. Ustynyuk, and L. P. Yur’ eva. The authors express their gratitude to them for kindly providing the preparations.

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