

INTERDEPENDENCE OF ACID-BASE AND OXIDATION-REDUCTION PROPERTIES IN A SERIES OF SUBSTITUTED FERROCENES

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Investigations of the acid-base properties of disubstituted ferrocenes, in which one of the substituents is an acid [1] or basic [2] group, have made it possible to evaluate the effect of the substituent on the acid (basic) properties of the second substituent, located either in the same ring, or in another ring. There are no analogous data in the literature for substituted ferrocenes, which, evidently to a considerable degree, is the result of methodological difficulties in the preparation of solutions of the pure oxidized forms of these compounds. These difficulties arise as a result of the low chemical stability of the latter, both with respect to hydrolytic decomposition reactions [3], to the action of strong oxidizers [4], and to complex-formers for trivalent iron [5], and with respect to the impossibility of separating out pure salts of the compounds in the oxidized form [6]. Broader investigations, devoted to determination of the oxidation potentials of mono- and disubstituted ferrocenes [7, 8], have established the presence of a simple relationship (as a rule, additive) between the oxidation potentials of heteroannular (substitutions in different rings) of di- and monosubstituted ferrocenes. For the oxidation potentials, determined in the same medium under the same conditions,

$$E_{X-Y} = E_{\text{Fec}} + \Delta E_X + \Delta E_Y, \quad (1)$$

where E_{X-Y} is the formal oxidational potential of a heteroannular disubstituted ferrocene with the substituents X and Y. E_{Fec} is the formal oxidation potential of the ferrocene. ΔE_X and ΔE_Y are, respectively, the differences of the formal potentials of the ferrocenes with the substituents X, Y, and of the ferrocene.

In the present article we shall show that the acid-base properties of substituted ferrocenes are connected with the oxidation-reduction properties, and that the rule of additivity imposes certain additional requirements on the acid-base properties of heteroannular disubstituted ferrocenes.

We write the equation of the acid-base oxidation for two disubstituted ferrocenes, having the same acid group $Y = \text{BH}^+$ ($-\text{COOH}$ or $-\text{CH}_2\text{N}(\text{CH}_3)_2\text{H}^+$, etc.) and which differ by different substituents, X_1 , X_2 (one of which can be hydrogen), and for two corresponding substituted ferrocenes (the substituents either in one ring or in several):



We designate the position of the protolytic equilibrium by pK , which, for example, for reaction (I) is equal to

$$\text{pK}_1 = -\lg K_1 = \frac{1}{2.3RT} \Delta\Phi^0 = \frac{1}{2.3RT} (\mu_{X_1\text{FecB}}^0 + \mu_{\text{H}^+}^0 - \mu_{X_1\text{FecY}}^0). \quad (2)$$

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The difference $pK_1 - pK_3$ characterizes the effect of the substituents X_1, X_2 on the acid properties of the substituent Y in a substituted ferrocene. We write an analogous expression for the ferrocene derivatives $pK_2 - pK_4$. We introduce the quantity ΔpK_{Fec+} , which indicates to what degree in the ferrocene series the acid group Y is more sensitive to the effect of the substituent, in comparison to the corresponding ferricene series:

$$\Delta pK_{Fec+}^{Fec+} = (pK_1 - pK_3) - (pK_2 - pK_4). \quad (3)$$

We substitute equations of type (2) into the identity (3):

$$\Delta pK_{Fec+}^{Fec+} = \frac{1}{2.3 RT} (\mu_{X_1 FecB}^0 - \mu_{X_1 FecY}^0 - \mu_{X_2 FecB}^0 + \mu_{X_2 FecY}^0 - \mu_{X_1 FecB}^0 + \mu_{X_1 FecY}^0 + \mu_{X_2 FecB}^0 - \mu_{X_2 FecY}^0). \quad (4)$$

We note that, in Eq. (4), the participants in the reactions (I)-(IV) form four oxidation-reduction pairs



The normal oxidation potential of one pair (for example, (V)) is equal to

$$\varphi_{X_1-Y}^0 = \frac{1}{F} (\mu_{X_1 Fec+Y}^0 - \mu_{X_1 Fec1}^0) \quad (5)$$

(F is the Faraday number).

In expression (4), it is possible to group the chemical potentials into oxidation-reduction pairs and, substituting for them equations of type (5), to express pK_{Fec+} in terms of the normal oxidation potentials of the pairs (V)-(VIII).

Thus, for any given substituted ferrocenes, there is obtained the following relationship, connecting the protolytic properties with the oxidation-reduction properties

$$\Delta pK_{Fec+}^{Fec+} = pK_1 + pK_4 - pK_2 - pK_3 = \frac{F}{2.3 RT} (\varphi_{X_1-Y}^0 - \varphi_{X_1-B}^0 - \varphi_{X_2-Y}^0 + \varphi_{X_2-B}^0). \quad (6)$$

The rule of additivity [1], with sufficient accuracy, is valid for many disubstituted ferrocenes, but imposes additional requirements on the relationship (6). The normal oxidational potential is connected with the formal oxidational potential, using, in Eq. (1), the following relationship:

$$E = \varphi^0 + \varphi_d - \varphi_{cal}. \quad (7)$$

Here φ_d is the diffusion potential; φ_{cal} is the potential of a calomel electrode.

Substituting equations of type (7) into Eq. (1), we obtain

$$\varphi_{X-Y}^0 = \varphi_X^0 + \varphi_Y^0 - \varphi_{Fec}^0. \quad (8)$$

Here $\varphi_{X-Y}^0, \varphi_X^0, \varphi_Y^0, \varphi_{Fec}^0$ are the normal oxidation potentials of a heteroannular disubstituted ferrocene, with the substituents X, Y of monosubstituted ferrocenes with the substituents X, Y , and of ferrocene, respectively.

Substituting equations of type (8) into expression (6), we obtain

$$\Delta pK_{Fec+}^{Fec+} = \frac{F}{2.3 RT} (\varphi_{X_1}^0 + \varphi_Y^0 - \varphi_{Fec}^0 - \varphi_{X_1}^0 - \varphi_B^0 + \varphi_{Fec}^0 - \varphi_{X_2}^0 - \varphi_Y^0 + \varphi_{Fec}^0 + \varphi_{X_2}^0 + \varphi_B^0 - \varphi_{Fec}^0), \quad (9)$$

TABLE 1

	$\text{FecCH}_2\text{N}(\text{CH}_3)_2\text{H}^+$	FecCOOH	$\text{C}_2\text{H}_5\text{FecCOOH}$
pK , red	9.84 ± 0.04	4.20 ± 0.06	4.7 ± 0.1
pK oxid.	7.15 ± 0.05	1.35 ± 0.1	2.0 ± 0.4
Φ^0 , mV, protonized forms	581 ± 1	641 ± 2	538 ± 4
Φ^0 , mV, basic forms	423 ± 2		
	$425 \pm 7^*$	$473 \pm 10^*$	$429 \pm 16^*$

*Values. calculated using Eq. (11).

since the oxidizing potential of each compound in expression (9) enters an even number of times with opposing signs, then

$$\Delta pK_{\text{Fec}}^{\text{Fec}^+} = 0.$$

Consequently, the rule of additivity leads us to the relationship

$$pK_1 + pK_4 - pK_2 - pK_3 = 0, \quad (10)$$

that is, it requires the equality of the damping coefficient of the ferrocene and the ferricene groups [9].

It is easy to note that Eq. (6) can be obtained by the summation of the two equalities

$$pK_1 - pK_2 = \frac{F}{2.3RT} (\Phi_{\text{X}_1-\text{Y}}^0 - \Phi_{\text{X}_1-\text{B}}^0), \quad (11)$$

$$pK_4 - pK_3 = \frac{F}{2.3RT} (\Phi_{\text{X}_2-\text{B}}^0 - \Phi_{\text{X}_2-\text{Y}}^0), \quad (12)$$

whose validity follows from Eqs. (2) and (5). It follows from Eqs. (11) and (12) that, for calculation of one of the parameters of the compound (for example, the normal potential of a disubstituted ferrocene with the substituents X and B), it is sufficient to know the acidity constants of the oxidized and the reduced form of this compound, and the oxidation potential of the protonized form.

To illustrate the validity of relationships (11) and (12), as well as the validity of the additivity rule (Eq. 10), the authors, using an aqueous solution of 1 N KCl, measured the acid dissociation constants of the following acids: $\text{FecCH}_2\text{N}(\text{CH}_3)_2\text{H}^+$, $\text{Fec}^+\text{CH}_2\text{N}(\text{CH}_3)_2\text{H}^+$, FecCOOH , Fec^+COOH , $\text{C}_2\text{H}_5\text{FecCOOH}$, $\text{C}_2\text{H}_5\text{Fec}^+\text{COOH}$, as well as the oxidation of the corresponding pairs. Table 1 gives the acid constants of the acid dissolution of the above compounds, and the normal potentials and the values of the oxidation potentials, calculated using Eq. (11).

The oxidation potentials for the ferrocene carboxy acid anions could not be determined experimentally, as a result of the rapid hydrolytic decomposition reactions of the oxidized forms. The dissociation constants of the reduced forms were determined by the method of potentiometric acid-base titration [10]. Carrying out the latter was rendered difficult by the small solubility of the ferrocene carbonic acids ($2 \cdot 10^{-4}$ mole/liter) and of the ethylferrocene carbonic acids ($4 \cdot 10^{-4}$ mole/liter) in acid solutions, and of $\text{FecCH}_2\text{N}(\text{CH}_3)_2$ ($\approx 1 \cdot 10^{-3}$ mole/liter) in alkaline solutions.

However, observing a number of precautions, there were successfully obtained considerably supersaturated solutions, which increased the accuracy of the determination of the dissociation constants up to the limits, shown in Table 1. The dissociation constants of the oxidized forms were determined by the method of the oxidizing potential [11]. To this end, a study was made of the dependence of the electromotive force of the galvanic element



on the acidity of the solution (on the pH). The ratio C_1/C_2 was maintained constant.

As is evident from the data of Table 1, the additivity rule, in many ferrocene carbonic acids, is satisfied within the limits of the experimental error, while the relationships (11) and (12), for an amino derivative of ferrocene, as was to be expected, are strictly satisfied.

Thus, in a number of heteroannular disubstituted ferrocene carbonic acids and heteroannular disubstituted amines of the $\text{XFecCH}_2\text{N}(\text{CH}_3)_2$ series, with unknown dissociation constants of the reduced-oxidized forms in aqueous solutions, it is possible to calculate the corresponding oxidized forms (reduced forms), since the additivity rule, as shown above, is satisfied with sufficient rigor.

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