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## Abstract

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# OXIDATION-REDUCTION PROPERTIES OF COMPOUNDS WITH TWO FERROCENYL GROUPS

Earlier ([1]) we showed that most monosubstituted ferrocenes are well titrated potentiometrically with potassium dichromate in a mixture of acetic and hydrochloric acids, which made it possible to determine their formal oxidation-reduction potentials. It was established that the potentials vary substantially depending on the substituents.

In the present work we investigated the influence of one ferrocenyl nucleus on the oxidation-reduction properties of another nucleus, when these nuclei are connected with each other directly (diferrocenyl) or through groups of different conductivity ($-Hg-$, $-CH_2-$, $-CH_2-CH_2-$, $-CH_2-O-CH_2-$, $CH_2-\overset{+}{N}(CH_3)_2-CH_2-$). In general form, the oxidation of two linked ferrocenyl nuclei may be represented by the scheme:

$$Fc-Y-Fc \underset{E_{f0}}{\rightleftarrows} Fc^+-Y-Fc+1\bar{e},$$

$$Fc^+-Y-Fc \underset{E'_{f0}}{\rightleftarrows} Fc^+-Y-Fc^++1\bar{e}.$$

where $-Y-$ is the linking group, and $E'_{f0}$ and $E''_{f0}$ are the first and second oxidation-reduction potentials, respectively. Comparison of the magnitude of $E'_{f0}$ with $E_{f0}$ of the corresponding monosubstituted ferrocenes ([1]) makes it possible to estimate the ability of the group $-Y-$ to transmit the electron-donor influence of one ferrocenyl nucleus to the other. From comparison of the magnitude of $E''_{f0}$ with $E'_{f0}$ and $E_{f0}$, one can form an idea of how the group $-Y-$ transmits the electron-acceptor influence of the group $-C_5H_4Fe^+C_5H_5$.

The effect of the difference between the values of $E'_{f0}$ and $E_{f0}$ on the shape of the titration curves was first studied on model mixtures consisting of equimolecular amounts of ferrocene and some mono-derivative of it; the results are given in Fig. 1. It was found that if the difference in the values of $E_{f0}$ is greater than 200 mV (curve $I$), two jumps appear on the curve, corresponding to the separate oxidation of both components of the mixture. At a difference of 150

Fig. 1. Typical curves of the joint titration of equimolecular amounts of ferrocene ($E_{f_0} = -0.245$ V) and its monosubstituted derivatives: I –methyl ester of ferrocenemonocarboxylic acid ($E_{f_0} = -0.511$ V); II – m-nitrophenylferrocene ($E_{f_0} = -0.358$ V); III –methoxyferrocene ($E_{f_0} = 0.166$ V).

Figure 1: Fig. 1. Typical curves of the joint titration of equimolecular amounts of ferrocene ($E_{f_0} = -0.245$ V) and its monosubstituted derivatives: I –methyl ester of ferrocenemonocarboxylic acid ($E_{f_0} = -0.511$ V); II – m-nitrophenylferrocene ($E_{f_0} = -0.358$ V); III –methoxyferrocene ($E_{f_0} = 0.166$ V).

mV between the values of $E_{f0}$, the curve has only an inflection at the point equivalent to 100% oxidation of ferrocene (curve $II$); if this difference is less than 100 mV (curve $III$), both substances are titrated as one, with a common potential jump. It is characteristic that the presence of the second substance has no substantial influence on the value of the oxidation-reduction potential $E_{f0}$ of the first. This makes it possible to determine $E_{f0}$ by a graphical method. The oxidation of compounds with two ferrocenyl groups was carried out with potassium dichromate under conditions analogous to those used by us ([1]) in the oxidation of monosubstituted ferrocenes. The oxidation-reduction potentials were determined by the graphical method (see Table 1).

Diferrocenyl could be oxidized under these conditions only at one iron atom (Fig. 2). The curve is somewhat asymmetric with respect to the point corresponding to 50% oxidation at one iron atom ($E_i' = 24$ mV, $E_i'' = 30$ mV ([2])). Comparison of the first oxidation-reduction po-

potential of diferrocenyl (−0.189 V) and ferrocene (−0.245 V) shows that, upon interaction of two ferrocenyl nuclei, owing to their electron-donor properties ([3]), the electron density in the nucleus being oxidized increases in comparison with unsubstituted ferrocene, judging from the change in electron density on the iron atom at the moment of reaction. It is known ([4]) that the interaction of two phenyl nuclei in diphenyl leads to depletion of the electrons of the reacting nucleus. In terms of electron-donor properties ([3,5]), ferrocenyl as a substituent on the basis of the first oxidation-reduction potential of diferrocenyl (−0.189 V) can be compared with methyl ($E_{f_0} = 0.198$ V) and methoxyl ($E_{f_0} = -0.166$ V) groups.

**Fig. 1.** Typical curves of the joint titration of equimolecular amounts of ferrocene ($E_{f_0} = -0.245$ V) and its monosubstituted derivatives:
**I** –methyl ester of ferrocenemonocarboxylic acid ($E_{f_0} = -0.511$ V); **II** –*m*-nitrophenylferrocene ($E_{f_0} = -0.358$ V); **III** –methoxyferrocene ($E_{f_0} = 0.166$ V).

**Fig. 2.** Titration curve of diferrocenyl. The total amount of iron in the compound is taken as 200%.

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Figure 2: Fig. 2. Titration curve of diferrocenyl. The total amount of iron in the compound is taken as 200%.

Oxidation of diferrocenylmercury (Fig. 3, curve 1) is an example of a one-electron, two-stage oxidation with a considerable difference in potentials (350 mV) between the first and second stages. The first oxidation-reduction potential of diferrocenylmercury (−0.283 V) practically coincides with the potential of monochloromercuryferrocene (−0.278 V). If, however, one compares the first oxidation-reduction potentials of diferrocenyl and diferrocenylmercury, it becomes clear that the introduction of mercury between two ferrocenyl nuclei decreases the oxidation-reduction potential by 100 mV, i.e., the mercury atom does not transmit the electron-donor influence of one ferrocenyl nucleus to the other. Moreover, it turns out that mercury interacts with the ferrocenyl nuclei in such a way as to lower the electron density on the iron atoms at the moment of reaction. The second stage of oxidation is characterized by a very low oxidation-reduction potential (−0.655 V), one of the lowest measured under these conditions. Thus the electron-acceptor influence of the positively charged ferricinium ion is readily transmitted through the mercury atom to the unoxidized ferrocene nucleus.

Upon oxidation of diferrocenylmethane and all the other compounds

(diferrocenylethane, bis-ferrocenylmethyl ether, bromide of bis-(ferrocenylmethyl)-dimethylammonium) we were dealing with one-electron two-stage oxidation with a difference in potentials between the stages of about 100 mV (Fig. 3, curve *II*). Comparison of the first redox potential of diferrocenylmethane (0.189 V) with the potential of methylferrocene (0.198 V) shows that replacement of one hydrogen atom in the methyl group of methylferrocene by such a strong electron-donating substituent as ferrocenyl leads to practically no change in the potential, i.e., as in the case of mercury, one methylene unit almost does not transmit the electron-donating influence of the ferrocenyl group. Conversely, if a positive charge arises on one of the ferrocenyl nuclei, then its influence is manifested to a considerable extent also on the second nucleus, judging by the magnitude of the second redox potential of diferrocenylmethane. Moreover, this influence is transmitted through two methylene units (diferrocenylethane) and even through three atoms

**Table 1**

Redox potentials of compounds with two ferrocenyl groups
$C_5H_5FeC_5H_4—Y—C_5H_4FeC_5H_5$
(in volts relative to the N.C.E.)*

| –Y– | $E'_{f_0}$ | $E''_{f_0}$ | M.p., °C |
|---|---|---|---|
| –Hg– | –0.283 | –0.655 | 233–234 |
| $-CH_2-$** | –0.189 | –0.308 | 143–144 |
| $-CH_2-CH_2-$ | –0.214 | –0.282 | 200–201.5 |
| $-CH_2-O-$ | –0.266 | –0.325 | 130–131 |
| $-CH_2-CH_2-CH_2-$ | –0.447 | –0.511 | 214–215.5 (with decomp.) |
| – $N^+(CH_3)_2CH_2$ | –0.189 | – | 228–230 (with decomp.) |
| –/ – Diferrocenyl | | | |

* The mean deviation from the values given for $E_{f_0}$ is $±$0.005 V.
** Diferrocenylmethane was obtained by reduction of diferrocenyl ketone by Clemmensen' s method.

$$(CH_2—O—CH_2;\ —CH_3—N^+(CH_3)_2—CH_2—),$$

although more weakly.

We also investigated the influence of certain substituents attached to the ferrocenylmethyl group on the values of the redox potentials; the results are given in Table 2. In this case, too, the same dependence is observed: electron-accepting substituents, through a methylene unit, exert a much greater influence on the reaction center—the iron atom—than do electron-donating ones. The influence of these substituents is, evidently, inductive in nature. This is seen from the dependence, shown in Fig. 4, of $\lg K/K_0$ on the Taft inductive constants of the substituents $\sigma^*$ ([6]) ($K_0$ is the equilibrium constant for the oxidation of methylferrocene; the correlation coefficient ([7]) is 0.935).

**Table 2**

Redox potentials of certain monosubstituted ferrocenes $C_5H_5FeC_5H_4CH_2X$

| –X | $E_{f_0}$, V relative to N.C.E.* | $\sigma^*_{CH_2X}$ | lg $K$ |
|---|---|---|---|
| $-CH_3$ | –0.199 | –0.100 | 0.000 |
| $-CH_2CH_3$ | –0.201 | – | – |
| –H | –0.198 | 0.000 | 0.000 |
| –COOH | –0.272 | +1.05 | 1.252 |
| $-NHCOC_6H_5$ | –0.302 | – | – |
| $-OCH_2C_6H_5$ | –0.302 | – | – |
| $-OCH_3$ | –0.302 | +0.520 | 1.760 |
| –OH | –0.309 | +0.555 | 1.878 |

Fig. 3. Titration curves: I—diferrocenylmercury, II—diferrocenylmethane. The total amount of iron in the compound is taken as 200%.

Figure 3: Fig. 3. Titration curves: I—diferrocenylmercury, II—diferrocenylmethane. The total amount of iron in the compound is taken as 200%.

Fig. 4. Dependence of lg K/K0 on Taft $\sigma^*$ for compounds in which ferrocenyl is linked with the substituent through a CH2 group ($\rho = -2.156$).

Figure 4: Fig. 4. Dependence of lg K/K0 on Taft $\sigma^*$ for compounds in which ferrocenyl is linked with the substituent through a CH2 group ($\rho = -2.156$).

| –X | $E_{f_0}$, V relative to N.C.E.* | $\sigma^*_{CH_2X}$ | lg $K$ |
|---|---|---|---|
| $-N^+(CH_3)_2H$ | −0.443 | +1.90 | 4.179 |
| $-N^+(CH_3)_2C_2H_5$ | −0.479 | +1.90 | 4.754 |

* The mean deviation from the values given for $E_{f_0}$ is $±$0.003 V.

Thus, it is found that the same conducting systems are not equally capable of transmitting the electron-donating and electron-accepting influences of a substituent. It is not yet clear whether this situation is general for any conducting systems or specific to the systems investigated in this work.

The results obtained by us are consistent with the information available in the literature, at least with respect to the methylene unit. It is known ([8]) that introduction of the group $-CH_2-$between the substituent –X and the react-

with one center reduces the influence of the first on the last by approximately 2.8 times if –X–is an electron-acceptor substituent. When, however, in the methyl group one hydrogen atom is replaced by some electron-donor substituent, its induction effect changes little (9). Norman et al. (10) apparently observed the same phenomenon in a quantitative study of the nitration of toluenes containing electron-donor and electron-acceptor substituents in the methyl group.

**Fig. 3.** Titration curves: *I*—diferrocenylmercury, *II*—diferrocenylmethane. The total amount of iron in the compound is taken as 200%.

**Fig. 4.** Dependence of $\lg K/K_0$ on Taft $\sigma^*$ for compounds in which ferrocenyl is linked with the substituent through a $CH_2$ group ($\rho = -2.156$).

## Experimental Part

All measurements were carried out by the procedure described in (1); the concentration of hydrochloric acid was always 0.066 mole per liter.* To increase the solubility of the diferrocenyls, 10% benzene (grade “for cryoscopy” ) was added to the solvent instead of water; preliminary experiments on ferrocene showed that this does not affect the value of the oxidation–reduction potential and does

not change the shape of the titration curve. The end point of the titration was determined by constructing a plot of the dependence of $\Delta E/\Delta V$ on $V$; agreement with the calculated amount of oxidant was within 0.2 ml. The weighed portions of diferrocenyls, depending on solubility, were from 25 to 40 mg.

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* In the preceding communication, through our fault, a misprint was made. The concentration of hydrochloric acid in the solvent was likewise 0.066 mole per liter.

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