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FORMAL OXIDATION-REDUCTION POTENTIALS OF MONOSUBSTITUTED FERROCENES

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To characterize ferrocene as an aromatic system, the study of the influence of substituents on the reactivity of the ferrocene nucleus is of substantial importance. Systematic investigations of this kind are still lacking. There are only isolated qualitative observations (1) showing that electron-donor substituents increase the activity of the ferrocene nucleus in electrophilic substitution reactions of the hydrogens of the cyclopentadienyl rings and facilitate oxidation to the ferricinium cation, whereas electron-acceptor substituents, on the contrary, hinder both electrophilic substitution reactions of hydrogens and oxidation to the cation.

In the present work we determined the formal oxidation-reduction potentials of a series of monosubstituted ferrocenes by the method of potentiometric titration with potassium dichromate in a mixture of acetic and hydrochloric acids, and obtained relative quantitative data on the influence of substituents on the oxidation of the ferrocene nucleus to the ferricinium cation.

Experimental Part

The formal oxidation-reduction potentials of monosubstituted ferrocenes were determined by a procedure analogous to that used by Mason and Rosenblum (2) for determining the formal oxidation-reduction potentials of arylferrocenes. Measurements were carried out on a PPTV potentiometer of the R375 type with an M-122 null galvanometer, relative to the normal calomel electrode (N.C.E.), connected with the titrated solution by an agar-agar bridge with a saturated potassium chloride solution. Before determinations, smooth platinum electrodes were treated for 10–15 min with boiling conc. HNO_3 and then washed with distilled water. As solvent, a mixture of 98% CH_3COOH (75% by volume) and aqueous hydrochloric acid (25% by volume) was used. The concentration of hydrochloric acid in the solvent was always 0.033 mole per liter. All measurements were carried out in a nitrogen atmosphere at a temperature of $25 \pm 0.1°$. For each titration, the value of E_{f_0} was calculated for five points every 0.2 ml on both sides of the value E_{f_0}. The mean deviation of the values of E_{f_0} did not exceed 0.001 V. Table 1 gives the values of E_{f_0}, averages of three titrations; reproducibility was 0.003 V.

Discussion of Results

The majority of the monosubstituted ferrocenes studied by us, on potentiometric oxidation, obey the Nernst equation well and give typical oxidation-reduction curves. The good electrochemical reversibility of the systems

$$C_5H_5FeC_5H_4X \rightleftarrows C_5H_5FeC_5H_4X$$

noted earlier as well (2, 3), made it possible for us to determine the formal oxidation-reduction potentials of monosubstituted ferrocenes, which are given in Table 1.

It is evident from Table 1 that the oxidation-reduction potentials of ferrocene derivatives change appreciably depending on the substituent. Substi-

Table 1

Formal oxidation-reduction potentials of monosubstituted ferrocenes[1] $C_5H_5FeC_5H_4X$

No.	X	E_f^0, V vs. S.C.E.	$\lg K/K_0$[2]	σ_n[3]	M.p., °C	B.p., °C / mm Hg	n_D^{20}
1	$-OCH_3$	−0.166	+1.286	−0.268	39–40	–	–
2	$-CH_3$	−0.198	+0.795	−0.170	34–35	–	–
3	$-C_3H_7$-*iso*	−0.198	+0.795	−0.151	–	111–112 / 6	1.5894
4	$-C_2H_5$	−0.199	+0.788	−0.151	–	109–110 / 6	1.6012
5	$-C_3H_7$	−0.201	–	–	–	106–108 / 3	1.5880
6	$-CH_2CH_2CH{=}CH_2$	−0.211	–	–	–	128–130 / 1	1.2022
7	$-H$[4]	−0.245	0.000	0.000	173–174	–	–
8	$-CH_2COOH$	−0.272	–	–	149–151	–	–

No.	X	E_f^0, V vs. S.C.E.	lg K/K_0[2]	σ_n[3]	M.p., °C	B.p., °C / mm Hg	n_D^{20}
9	–HgCl	−0.278	–	–	192–194 with decomp.	–	–
10	–CH=CH_2	−0.280	–	–	48–49	–	–
11	–$CHOHCH_3$	−0.283	–	–	78–79	–	–
12	–C_6H_5[4]	−0.284	−0.660	−0.01	110–110.5	–	–
13	–$CH_2CH_2N(CH_3)_2$	−0.296	–	–	–	98.5–100.5 / 0.3	1.5812
14	–$CH_2NHCOC_6H_5$	−0.302	–	–	154–155	–	–
15	–$CH_2OCH_2C_6H_5$	−0.302	–	–	88–89	–	–
16	–CH_2OH	−0.309	–	–	80–81	–	–
17	–$OCOCH_3$	−0.324	−1.337	0.31	64–65	–	–
18	–$C_6H_4N{=}N'\cdot C_6H_5$-*m*	−0.329	–	–	109–111	–	–
19	–$C_6H_4NH_2$-*m*	−0.336	–	–	111–112	–	–
20	–$OCOC_6H_5$	−0.336	–	–	108–109	–	–
21	–$C_6H_4NH_2$-*p*	−0.341	–	–	158–159.5	–	–
22	–$C_6H_4NO_2$-*m*	−0.358	–	–	83–84	–	–
23	–J	−0.384	−2.352	0.18	44–45	–	–
24	–$C_6H_4NO_2$-*p*[4]	−0.390	−2.453	0.265[5]	169–170	–	–

No.	X	E_f^0, V vs. S.C.E.	$\lg K/K_0$ [2]	σ_n [3]	M.p., °C	B.p., °C / mm Hg	n_D^{20}
25	$-\mathrm{Cl}$	−0.408	−2.758	0.227	59–60	–	–
26	$-\mathrm{Br}$	−0.410	−2.792	0.232	30–31	–	–
27	$-\mathrm{CH_2N(CH_3)_2}$	−0.445	–	–	–	125–128 / 4	1.5885
28	$-\mathrm{CONH_2}$	−0.484	–	–	168–169	–	–
29	$-\mathrm{COOH}$	−0.499	−4.297	0.45	216–220 with decomp.	–	–
30	$-\mathrm{COOCH_3}$	−0.511	−4.501	0.45[6]	70–71	–	–
31	$-\mathrm{NH_3Cl}$	−0.560	–	–	112–113	–	–

[1] The formulas of the compounds are given without taking into account changes occurring in the reaction medium.

[2] Calculated from the formula

$$\frac{E_0^X - E_0^H}{0.0591} = \lg K/K_0$$

[3] Only the primary values of σ_n obtained from the dissociation constants of the corresponding *p*-substituted benzoic acids were used ([11]).

[4] The potentials of these compounds differ somewhat from the potentials obtained in the work of Meise and Rosenblum ([9]). However, the difference between the potentials of ferrocenyl and phenylferrocene and of ferrocene and *p*-nitrophenylferrocene remains constant within the limits of experimental error.

[5] The value of σ_n was taken from ref. ([10]).

[6] The value of σ_n for the $-\mathrm{COOC_2H_5}$ group was used ([11]).

Substituents that lower the oxidation-reduction potential of substituted ferrocene in comparison with the potential of ferrocene should be classed as electron-accepting; conversely, substituents that raise the oxidation-reduction potential are electron-donating. The conventional boundary between electron-donating and electron-accepting substituents in the ferrocene nucleus is different from that between the same substituents in the benzene ring ([4]).

This is due to the higher electron-donating properties of the ferrocenyl radical than of phenyl (^{5}). A comparison of the values

of the oxidation-reduction potentials of ferrocene derivatives shows that in the ferrocene series such groups as $-CH_2COOH$, $-HgCl$, $-CH_2OH$, $-OCOCH_3$ prove to be weak electron-acceptor substituents. It should therefore be expected that these groups will somewhat hinder electrophilic substitution of the hydrogen atoms of ferrocene, in contrast to the benzene series. Halides, with respect to ferrocenyl, are already clearly pronounced electron-acceptor substituents. Only the methoxy group and alkyl radicals possess electron-donor properties with respect to ferrocenyl. Only for these ferrocene derivatives should one expect electrophilic substitution of the ring hydrogen atoms to be easier than in ferrocene. The earlier study by A. N. Nesmeyanov and co-workers (^{6}, ^{7}) of the reactions of ethyl- and 1,1′-dimethylferrocene confirms this conclusion. The influence of the substituent when it is removed from the ferrocene nucleus by one or two methylene links is weakened, just as occurs in the benzene series (^{8}) (see Table 1, compounds Nos. 31, 27, and 13, and compounds Nos. 28 and 8).

We attempted to apply to the potentials obtained the rule of linear dependence between changes in free energies (^{9}). The differences of the logarithms of the equilibrium constants for the reactions of substituted and unsubstituted ferrocenes, calculated from the corresponding potentials, we tried to correlate with Taft' s constants σ^* and σ^0 (^{10}) and Hammett' s σ_m and σ_n (^{11}). As was to be expected, the differences of the logarithms of the equilibrium constants obtained do not correlate with Taft's σ^* constants, since the oxidation-reduction potential of a substituted ferrocene, in addition to the inductive effect of the substituent expressed by Taft' s σ^* values, is substantially influenced also by other effects. Lack of correlation is also observed in the case of Taft' s σ^0 and Hammett' s σ_m.

With Hammett' s σ_n constants, the differences of the logarithms of the equilibrium constants of substituted and unsubstituted ferrocenes correlate (correlation coefficient (^{12}) 0.942), but not very well. On detailed examination of the resulting set of points, we found that ferrocenes with the substituents $-OCH_3$, $-OCOCH_3$, $-CH_3$, $-C_2H_5$, *iso*-C_3H_7 lie almost exactly on one straight line with $\rho = -4.23$, on which ferrocene is also located (correlation coefficient 0.985). Another straight line with $\rho = -7.94^*$ is given by ferrocenes with the substituents

$$-C_6H_5,\ -C_6H_4NO_2\text{-}n,\ -COOH,\ -COOCH_3,\ -J,\ -Cl,\ -Br$$

(correlation coefficient 0.982). We suppose that such a distribution of points over two straight lines is not accidental, despite the fact that a change in the value of ρ for one and the same reaction series under the same strictly maintained conditions is unusual.

Recently, to explain the remarkable stability of the α-ferrocenylcarbonium cation (^{13}, ^{14}), a well-founded suggestion has been put forward concerning the possibility of direct through-space interaction of the α-cationic center with the electrons of the iron atom (probably by the mechanism of a field effect). We suppose that not only the α-cationic center, but also any dipolar substituents, interact with the iron atom by the mechanism of a field effect. It is known (^{15}) that the field effect constitutes a certain part of Hammett’ s σ_n values. But in the series of benzene derivatives it has not yet been possible to separate the influence of the field effect and the inductive effect.

could be explained, since both the substituent and the reaction center lie in the same plane—the plane of the benzene ring—and all three types of interaction of the substituent with the reaction center (inductive, conjugation, and field effects) take place in one plane, at almost the same distance, this distance rarely being less than 5 Å.

In the case of ferrocene derivatives, however, where the iron atom serves as the reaction center, the substituent interacts with it by the mechanism of the conjugation effect and the inductive effect, as usual, through the ring, whereas by the mechanism of the field effect the interaction with the reaction center occurs through space, bypassing the ring (the distance does not exceed 3.7 Å). Thus, the field effect of the substituent will have a much greater influence on the reactivity of the iron atom in ferrocene than, for example, the field effect of the same substituent in *p*-substituted benzoic acid. Therefore, when correlating the obtained differences in the logarithms of the equilibrium constants with the Hammett constants σ_n, if the above-mentioned distribution into two straight lines is accepted, it is found that some substituents (line *A*, Fig. 1) interact with the iron atom by the mechanism of the inductive effect, the conjugation effect, and perhaps also by the mechanism of the field effect, but only to the extent to which this effect is reflected in the Hammett σ_n values, whereas other substituents (line *B*, Fig. 1), in addition to the interaction indicated above, interact with the iron atom by the mechanism of the field effect much more strongly than is reflected in the Hammett σ_n values. This assumption is consistent with the information available in the literature (9) that hydrogen and alkyl substituents are not capable of interacting with the reaction center by the mechanism of the field effect. Interaction by the mechanism of the field effect

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* We have recalculated the data of Mason and Rosenblum (^{2}) by the formula

$$\frac{E_0^{\mathrm{Ar}} - E_0}{0.0591} = \lg K/K_0,$$

where E_0 is the oxidation-reduction potential of ferrocene, and not of phenylferrocene. The resulting values of $\lg K/K_0$ correlate well (correlation coefficient 0.995) with the constants σ_n for the substituents $-\mathrm{C_6H_4X}$ ($X = -\mathrm{OCH_3}$, $-\mathrm{H}$, $-\mathrm{Cl}$, $-\mathrm{Br}$, $-\mathrm{NO_2}$) (^{16}), $\rho = -7.62$.

Fig. 1. Dependence between $\lg K/K_0$ for the oxidation of ferrocene derivatives and the Hammett σ_n values

Figure 1: Fig. 1. Dependence between $\lg K/K_0$ for the oxidation of ferrocene derivatives and the Hammett σ_n values

occurs over a shorter distance, which leads to an increase in the absolute value of ρ.

Fig. 1. Dependence between $\lg K/K_0$ for the oxidation of ferrocene derivatives and the Hammett σ_n values.

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