PHYSICAL CHEMISTRY

E. E. WEINSTEIN, Yu. F. KOPELEV

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. E. WEINSTEIN, Yu. F. KOPELEV

X-RAY SPECTROSCOPIC STUDY OF SOME POLYFERROCENES

(Presented by Academician A. P. Vinogradov, December 25, 1962)

In recent years several works have been published devoted to the study of the physicochemical properties of polyferrocenes ($^{1-4}$). In these works the optico-magnetic and magnetic characteristics of these compounds were studied, and a number of assumptions were made concerning the connection of these properties with the electronic structure of the molecules. New information on the distribution of electron density in polyferrocene molecules can be obtained by studying the x-ray absorption spectra of iron in these compounds. With the aid of the methods developed in works ($^{5-11}$), it is possible to determine the effective charges concentrated on the iron atom and on the ligands. The results of analogous calculations for monomeric ferrocene molecules were published earlier (^{11,12}). It seemed of interest to study by the same method the influence of polymerization on the character of charge distribution between the metal and the ligands in various polymer molecules.

In the present work an attempt is made to solve this question experimentally.

Five polyferrocenes, synthesized in the Laboratory of High-Molecular Compounds of INEOS, Academy of Sciences of the USSR, headed by Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak, and kindly placed at our disposal by S. L. Sosin, to whom the authors express their gratitude,* were investigated.

Some properties of these polymers and their numbering, used below, are given in Table 1.

Table 1

Substance	Molecular weight	Melting temperature, °C
Polyferrocene (I)	–	300–360
Polybutylferrocene (II)	4450	200–240
Polydibutylferrocene (III)	3900	190–240
Polyamylferrocene (IV)	7300	175–205
Polydiisopropylferrocene (V)	~800	~200°

Fig. 1 and Fig. 2: absorption curves

Figure 1: Fig. 1 and Fig. 2: absorption curves

Under the same conditions, the Fe K-absorption spectra in ferrocene and ferricinium were again obtained. The x-ray K-absorption spectra of iron in the substances studied were obtained on a spectrograph with focusing by reflection from the planes (1340) of a quartz crystal bent along a circle of radius 500 mm. The resolving power of the instrument in the region of the iron K-edge was $\sim$ 13500 (width of the distortion curve $\sim$ 0.53 eV). The absorbers were briquetted from finely ground powder of the substance under study (with allowance for a surface density in iron of 5 mg/cm^2) and were isolated from the spectrograph chamber by thin layers of cellophane in order to protect the absorbent

* After the present work had been carried out, Yu. S. Karimov and I. F. Shchegolev (^{13}) showed that the anomalous properties of the polyferrocene samples investigated in (^{2,4}) and placed at our disposal are due to the presence in them of small amounts of paramagnetic or ferromagnetic impurities. This circumstance, however, should not have a noticeable influence on the structure of the x-ray absorption spectrum of the principal substance.

from sublimation in vacuum. The spectra were recorded photographically. The exposure time was chosen so that the maximum level of photographic density on the radiographs did not exceed 0.7.

The absorption spectra, obtained with allowance for the densitometric characteristic of the film, were corrected for instrumental distortions by the method of steps (^{14}), and were then represented as curves of the dependence of the absorption coefficient (μx) on energy. The absorption curves obtained in this way are shown in Figs. 1 and 2 by thick solid lines. The iron absorption spectra in the polyferrocenes designated by the symbols I, II, III, and IV proved to be practically identical.

The method for calculating the spectra has already been described by us earlier (^{11}). However, in analyzing the experimental curves obtained in the present work, in addition to the usual calculation procedure, we also used a method recently developed by us (^{15}) for processing the data in order to estimate directly the ratio η/n^* from the shape of the spectra, even before resolving them into components corresponding

Fig. 1

Fig. 1. Iron K-edge absorption in $Fe(C_5H_5)_2Cl$ and $Fe(C_5H_5)_2$. The thick solid line is the experimental curve after correction for instrumental distortion according to (^{13}). The thin solid lines are successive selective absorption bands and the true edge; the dashed line is the total theoretical absorption curve from the hydrogen-like series of absorption bands and the true edge; the dotted line is

the absorption band associated with the transition of K-electrons to the lowest unoccupied molecular levels of the system.

Fig. 2

Fig. 2. Iron K-edge absorption in polyferrocenes (numbering of substances as in Table 1). The designations are the same as in Fig. 1.

to successive bands of selective absorption and to the true edge. This method is based on measuring the area bounded by the absorption curve in the region of the principal edge and comparing this value with the value of the absorption coefficient in the region of continuous absorption. In the method, the reduction of the function

$$\varphi(n) = \sum_{j=0}^{\infty} \frac{(n+j)^2 - 1}{(n+j)^5},$$

whose values in

$$\eta$$

in the range of change in n of interest to us were tabulated by us. The accuracy with which the value η/n can be estimated by the latter method proved quite satisfactory. It was checked on the spectrum of ferrocene, for which the value $\eta/n = 0.81$ was obtained instead of 0.87, determined previously ([11]). In this way, even before decomposition of the spectra, it was possible to show that, under the condition $n = \text{const}$, the magnitude of the effective charge on the Fe atom in the molecules studied decreases slightly in the series

$$\mathrm{Fe(C_5H_5)_2} \; - \; \mathrm{Fe(C_5H_5)_2Cl}\,(I, II, III, IV) \; - \; V.$$

Table 2

Substance	η	n	Γ, eV	η'
$\mathrm{Fe(C_5H_5)_2}$	1.75	0.75	2.2	10.4
$\mathrm{Fe(C_5H_5)_2Cl}$	1.7	0.7	2.2	8.8
I, II, III, IV	1.6	0.6	2.2	10.4
V	1.5	0.5	2.2	11.2

More accurate data on the magnitudes of the effective charges on the metal and on the ligands in ferrocene and polyferrocenes can be obtained in the course of a more detailed analysis of the structure of the iron K-absorption spectra in these

---

* η is the effective charge of the K-ionized atom in the molecule, and n is the effective principal quantum number of the final level of the K-electron transition.

Fig. 3. Dependence of the width of selective absorption bands in the X-ray iron K-spectra of metallocenes on the magnitude of the charge on the pentadienyl rings. 1—from work (^{11}); 2—according to the data of the present work; a—for the Fe spectrum in polyisopropylferrocene (V), b—for all the remaining polyferrocenes studied in the work (I—IV).

Figure 2: Fig. 3. Dependence of the width of selective absorption bands in the X-ray iron K-spectra of metallocenes on the magnitude of the charge on the pentadienyl rings. 1—from work (^{11}); 2—according to the data of the present work; a—for the Fe spectrum in polyisopropylferrocene (V), b—for all the remaining polyferrocenes studied in the work (I—IV).

molecules. The values we obtained for the charges and other spectral parameters (Γ and n) are given in Table 2. Here η' is the effective charge concentrated on the central atom of the molecule.

In the preceding work (^{11}) it was shown that in the metal K-absorption spectra of monomeric metallocene molecules the value Γ, which characterizes the half-width of the successive selective-absorption bands, increases linearly as the charge concentrated on the pentadienyl rings in these molecules, η'', increases (Fig. 3, curve 1). The same dependence can also be found by comparing the values of Γ obtained in the present work for ferrocene and ferricinium (Fig. 3, straight line 2). Owing to the fact that in the latter case it was possible to take more rigorously into account the magnitude of the instrumental broadening, straight line 2, as was to be expected, proved parallel to 1 and shifted toward smaller values of the width.

Fig. 3. Dependence of the width of selective absorption bands in the X-ray iron K-spectra of metallocenes on the magnitude of the charge on the pentadienyl rings. 1—from work (^{11}); 2—according to the data of the present work; a—for the Fe spectrum in polyisopropylferrocene (V), b—for all the remaining polyferrocenes studied in the work (I—IV).

Noteworthy is the fact that the dependence between Γ and η'' for monomeric metallocenes is violated on going to polyferrocenes, for which the experimentally obtained value of Γ is appreciably larger than the value that would be expected. It is not excluded, however, that this is a consequence of the excess charge on the pentadienyl rings in these compounds, which leads to additional broadening of the corresponding emission bands.

As the estimate shows (Fig. 3), the effective charges concentrated on the rings in molecules of types (I—IV) and V, in this case, should have increased to values on the order of 0.37 e and 0.47 e, respectively, and should have proved to be all the more significant the smaller the magnitude of the positive charge on the metal atom in the polymer molecule.

Institute of Inorganic Chemistry
Siberian Branch

Academy of Sciences of the USSR

Received
10 XII 1962

CITED LITERATURE

1. V. V. Korshak, S. L. Sosin, V. P. Alekseeva, DAN, **132**, 360 (1960).
2. A. N. Nesmeyanov, V. V. Korshak, et al., DAN, **137**, 1370 (1961).
3. V. V. Korshak, S. L. Sosin, V. P. Alekseeva, Vysokomolek. soed., **3**, 1332 (1961).
4. A. N. Nesmeyanov, A. M. Rubinshtein et al., DAN, **138**, 125 (1961).
5. E. E. Vainshtein, K. I. Narbutt, Izv. AN SSSR, OKhN, **1945**, no. 1, 71.
6. E. E. Vainshtein, R. L. Barinskii, K. I. Narbutt, DAN, **77**, 1003 (1951).
7. E. E. Vainshtein, R. L. Barinskii, K. I. Narbutt, ZhETF, **23**, 593 (1952).
8. E. E. Vainshtein, R. L. Barinskii, K. I. Narbutt, DAN, **79**, 225 (1951).
9. R. L. Barinskii, E. E. Vainshtein, K. I. Narbutt, DAN, **82**, 355 (1952).
10. E. G. Nadzhakov, R. L. Barinskii, DAN, **129**, 1279 (1959).
11. E. E. Vainshtein, Yu. F. Kopelev, Zhurn. strukturn. khim., **3**, 448 (1962).
12. E. E. Vainshtein, Yu. F. Kopelev, B. I. Kotlyar, DAN, **137**, 1117 (1961).
13. Yu. S. Karimov, I. F. Shchegolev, DAN, **146**, 1370 (1962).
14. I. Ya. Nikiforov, Izv. AN SSSR, ser. fiz., **21**, 1362 (1957).
15. Yu. F. Kopelev, E. E. Vainshtein, Izv. SO AN SSSR, ser. khim., No. 2(6), (1963).

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