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**RESEARCH INTO KINETICS OF ELECTRON EXCHANGE REACTIONS IN THE SYSTEM SYM. OCTAMETHYLFERROCENE/SYM. OCTAMETHYLFERRICINIUM HEXAFLUOROPHOSPHATE****N.Z. Ibrahimova, G.M. Jafarov, D.B. Tagiyev, I.U. Lyatifov**

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**Abstract:** *The constant of electron exchange rate ( $k_{ex}$ ) in the system of sym. octamethylferrocene/sym. octamethylferricinium hexafluorophosphate  $[(CH_3)_4C_5H]_2Fe/(CH_3)_4C_5H]_2Fe^+PF_6^-$  (hereinafter are denoted as  $Me_8Fc^{+/0}$ ) was determined by method of  $^1H$  NMR line broadening. The appearance of eight methyl groups in each reagent of the redox-system of  $Me_8Fc^{+/0}$  increases the constant of exchange rate approximately 4.8 times, in comparison with the unsubstituted ferrocene-ferricinium system  $[(C_5H_5)_2Fe/(C_5H_5)_2Fe^+PF_6^-]$  ( $Fc^{+/0}$ ). The increase of exchange rate in series of  $Fc^{+/0} \rightarrow Me_6Fc^{+/0} \rightarrow Me_8Fc^{+/0} \rightarrow Me_{10}Fc^{+/0}$ , though it corresponds to the electron donor property of the methyl group, is interpreted by us as the result of reduction of reorganization energy of solvent molecule (acetone) by increasing the reagent volumes of the redox couples of  $Me_nFc^{+/0}$  ( $n = 6, 8, 10$ ).*

**Keywords:** *sym. octamethylferrocene, cation of sym. octamethylferricinium, chemical shift, electron exchange*

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### Introduction

Over the past 10–15 years an emphasis of a great number of research works has been laid on the study into kinetics and mechanism of electron exchange in the system of ferrocene-ferricinium and their alkyl derivatives [1–3]. The main reason of an emphasis on these objects is due to the necessity of replacement of unstable in a number of solvents ferrocene-ferricinium reference electrode ( $Fc^{+/0}$ ) by more promising, from the point of IUPAC standards, systems - highly substituted alkyl derivatives of ferrocene [2, 3]. In spite of numerous experimental and theoretical studies of electron exchange in the homogeneous and electrochemical heterogeneous systems [1–8],

no mechanism of its proceeding has completely been clarified [3, 7]. This work is a continuation of our previous researches [7, 8] revealing that the electron exchange process in the system of  $Me_6Fc^{+/0}$  is determined not by the electron conjugation of the reactants in the transition state and the dynamics of the solvent molecules but by the energy of the reorganization of the solvent molecules around reactants. We consider that the study of electron exchange in redox couples whose components are representatives of two complete homologous series (ferrocene and cation of ferricinium) can provide us with even greater clarity about the mechanism of this process.

### Results and discussion

*$^1H$  NMR study into sym. octamethylferrocene and paramagnetic cation of sym. octamethylferricinium.*

$^1\text{H}$  NMR spectra of diamagnetic sym. octamethylferrocene and paramagnetic sym. octamethylferricinium hexafluorophosphate are obtained in deuterioacetone at 25°C. The values of chemical shifts ( $\nu$ ) and half-widths of resonance lines ( $W$ ) are given in Table 1.

**Table 1.** The observed chemical shifts in  $^1\text{H}$  NMR spectra of sym.  $\text{Me}_8\text{Fc}$  and sym.  $\text{Me}_8\text{Fc}^+\text{PF}_6^-$  in deuterioacetone ( $\nu$  in Hz, on tetramethylsilane; in square brackets are presented the half-widths of resonance lines ( $W$ ) in Hz)\*

sym. $\text{Me}_8\text{Fc}$ (diamagnetic complex)		sym. $\text{Me}_8\text{Fc}^+\text{PF}_6^-$ (paramagnetic complex)	
$\nu_{\text{D}}$ ; H(Cp) [ $W_{\text{D}}$ ]	$\nu_{\text{D}}$ ; H( $\text{CH}_3$ ) [ $W_{\text{D}}$ ]	$\nu_{\text{P}}$ ; H(Cp) [ $W_{\text{P}}$ ]	$\nu_{\text{P}}$ ; H( $\text{CH}_3$ ) [ $W_{\text{P}}$ ]
957 [ $\approx 1$ Hz]	516 [ $\approx 1$ Hz] 498 [ $\approx 1$ Hz]	8430 [2060 Hz]	-8640 [405 Hz] -11310 [405 Hz]

\* – spectrometer Bruker-300 MHz,  $t = 25$  °C,

The spectrum of cation of sym.  $\text{Me}_8\text{Fc}^+$  differs from the spectrum of appropriate diamagnetic complex – sym.  $\text{Me}_8\text{Fc}$  mainly in two aspects: a) large range of proton chemical shifts and b) great width of resonance lines (Table 1).

We have calculated isotropic shifts ( $\Delta\nu$ ) of protons of methyl groups [ $\Delta\nu(\text{H}_{\text{Me}})$ ] and cyclopentadienyl ring [ $\Delta\nu(\text{H}_{\text{ring}})$ ] necessary for

$$\nu_{\text{D}}(\text{H}_{\text{Me}})_{\text{ave.}} = (516 + 498) : 2 = 507 \text{ Hz}$$

$$\nu_{\text{P}}(\text{H}_{\text{Me}})_{\text{ave.}} = [-8640 + (-11310)] : 2 = -9975 \text{ Hz}$$

$$\Delta\nu(\text{H}_{\text{Me}})_{\text{ave.}} = |\nu_{\text{D}} - \nu_{\text{P}}| = |[507 - (-9975)]| = 10482 \text{ Hz}$$

$\nu_{\text{D}}(\text{H}_{\text{Me}})_{\text{ave.}}$  – average value of the chemical shift of protons of methyl groups of diamagnetic reagent in Hz;

$\nu_{\text{P}}(\text{H}_{\text{Me}})_{\text{ave.}}$  – average value of the chemical shift of protons of methyl groups of paramagnetic reagent in Hz;

$\Delta\nu(\text{H}_{\text{Me}})_{\text{ave.}}$  – average value of the isotropic shift of protons of methyl groups in Hz.

### $^1\text{H}$ NMR study of electron exchange in the system of sym. $\text{Me}_8\text{Fc}^{+/0}$ .

$^1\text{H}$  NMR research of the redox-system of sym.  $\text{Me}_8\text{Fc}^{+/0}$  in deuterioacetone, first of all, made it possible to establish that this system is chemically stable in the solution: shift ( $\nu_{\text{DP}} - \nu_{\text{D}}$ ) of resonance line frequency of protons of diamagnetic component in an invariable molar fraction of the cation salt ( $f_{\text{P}}$ ) and various total concentrations ( $C_{\text{total}}$ ) remained constant.

Further, on the basis of calculated isotropic shifts ( $\Delta\nu$ ), half-widths of the resonance lines ( $W_{\text{D}}$  and  $W_{\text{P}}$ ) and molar fraction of paramagnetic salt in the mixture ( $f_{\text{P}}$ ), according to the formula (1), the constant of exchange rate ( $k_{\text{ex}}$ ) in the system of sym.  $\text{Me}_8\text{Fc}^{+/0}$  [7] was calculated:

$$k_{\text{ex}} = \frac{4 \pi f_{\text{D}} f_{\text{P}} (\Delta\nu)^2}{(W_{\text{DP}} - f_{\text{D}}W_{\text{D}} - f_{\text{P}}W_{\text{P}})C_{\text{total}}} \quad (1)$$

where  $W_{DP}$  – half-widths of the resonance line of the diamagnetic component in the presence of paramagnetic salt (220 Hz);

$f_P$  – molar fraction of paramagnetic salt in the mixture calculated from expression

$$f_P = \frac{C_{OMFc^+}}{C_{OMFc^+} + C_{OMFc}} = \frac{C_{OMFc^+}}{C_{total}} \quad (OMFc = Me_8Fc) \quad (1)$$

The study of concentration dependence of the rate constant made it possible to establish that the kinetic equation of electron

exchange reaction is expressed by Equation 2, and the reaction order is equal to two:

$$\text{exchange rate} = k[Me_8Fc] \cdot [Me_8Fc^+] \quad (\text{mol/l}\cdot\text{sec.}) \quad (2)$$

The constant value of electron exchange rate in the system of sym. octamethylferrocene/cation of sym. octamethylferricinium [ $k_{ex}(Me_8Fc^{+/0}) = 2.2 \cdot 10^7$  l/mol·sec] is

approximately 4.8 times more than exchange rate constant in the system  $Fc^{+/0}$  [9], previously offered as a reference electrode:

$$k_{ex}(Me_8Fc^{+/0}) = 2.2 \cdot 10^7 \approx k_{ex}(Fc^{+/0}) \cdot 4.8 \approx (4.6 \cdot 10^6) \cdot 4.8 \quad (\text{l/mol}\cdot\text{sec.}) \quad (3)$$

On this basis we can conclude that the system of sym.  $Me_8Fc^{+/0}$  offered as the reversible reference electrode satisfies the condition of reversibility – the most important requirement presented for the reference electrodes by IUPAC [6].

1,2,4,1',2',4'-hexamethylferrocene/cation of 1,2,4,1',2',4'-hexamethylferricinium [7] and decamethylferrocene/cation of decamethylferricinium [9] are given in Table 2. The value of rate constant in the system of sym.  $Me_8Fc^{+/0}$  confirms the results obtained in the work [7] – the exchange rate increases together with the rise in the methyl groups number in the composition of reagents of the redox couple (Table 2).

The constant values of electron exchange rate in the system of sym. octamethylferrocene/cation sym. octamethylferricinium, along with the reference data on the systems of ferrocene/cation of ferricinium [9],

**Table 2.** The constants of electron exchange rate in the systems of  $Fc^{+/0}$ ,  $Me_6Fc^{+/0}$ , sym.  $Me_8Fc^{+/0}$  and  $Me_{10}Fc^{+/0}$  in deuterioacetone at 25°C

System	$Fc^{+/0}$	$Me_6Fc^{+/0}$	$Me_8Fc^{+/0}$	$Me_{10}Fc^{+/0}$
$k_{ex}$ (l·mol <sup>-1</sup> ·sec <sup>-1</sup> )	$4.6 \cdot 10^6$ [9]*	$1.5 \cdot 10^7$ **	$2.2 \cdot 10^7$	$2.4 \cdot 10^7$ [9]

\* – in square brackets [ ], the references are presented

\*\* – corrected values  $k_{ex}$  in system of sym.  $Me_6Fc^{0/+}$  (see Experimental part)

The observed increase in the electron exchange rate in a series of the redox couple of  $Fc^{+/0} \rightarrow Me_6Fc^{+/0} \rightarrow Me_8Fc^{+/0} \rightarrow Me_{10}Fc^{+/0}$  (Table 2) basically corresponds to the electron-donor property of methyl substituent. Really, by taking into consideration this property, it can be assumed that under the impact of the increasing number of methyl groups, the effective positive charge on the iron atom must consistently decrease by causing spatial expansion of  $e_{2g}$  orbitals. The expansion of  $e_{2g}$

orbitals, in its turn, should lead to an increase in the degree of  $e_{2g}-e_{2g}$  overlapping in collision complex (if, in collision complex, the reagents are “side by side”), and consequently to an increase in the rate of electron exchange.

However, if we take into consideration that in the methyl homologues of ferrocene and the cation of ferricinium, methyl groups are in-plane of the cyclopentadienyl ring, it is obvious that methylation of ring will be accompanied by a significant (not less than 3–4 Å) increase in

the distance between atoms of iron molecules and cations in the collision complex leading to noticeable reduction of overlap of  $e_{2g}$  orbitals in comparison with the overlapping in the unsubstituted ferrocene-ferricinium complex of collision. As a consequence, electron exchange rate in the redox couple of methyl homologues of ferrocene and ferricinium, for steric reasons must be decreased in comparison with the system of  $Fc^{+/0}$ . But, in the experiment [7, 9 and Table 2 of the work], the opposite is observed.

Therefore, the increase of electron exchange rate in the reviewed systems should be retraced in changes of other factors that may affect the exchange rate.

The role of the factors capable of affecting the electron exchange rate has been reviewed in the theory of electron transfer of R.A. Marcus

[10]. In previous work [7], it has been noted that, from four factors affecting the value of free activation energy, in the systems of  $Me_nFc^{+/0}$  and in the exchange conditions selected by us, the impact of three factors (by ionic strength of solution, Coulombic forces of interaction between reagents and energy expended on changes in the collision complex) can be disregarded. Therefore, free activation energy ( $\Delta G_{ex}^\ddagger$ ) is defined only by the reorganization energy value of solvents ( $\Delta G_{SR}^\ddagger$ ), so  $\Delta G_{ex}^\ddagger \approx \Delta G_{SR}^\ddagger$  should be accepted.

The values of reorganization energy of acetone for the systems of  $Fc^{+/0}$  and sym.  $Me_8Fc^{+/0}$  calculated by the improved Marcus formula (Xiang-Yuan Li's formula [11] (4)) are respectively 11.22 and 9.35 (kJ/mol):

$$\Delta G_{SR}^\ddagger = \left( \frac{N_A e^2}{16\pi\epsilon_0} \right) \left[ \left( \frac{1}{2r_1} \right) + \left( \frac{1}{2r_2} \right) - \left( \frac{1}{\sigma} \right) \right] \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \frac{\epsilon_s - \epsilon_{op}}{\epsilon_{op}(\epsilon_s - 1)} \quad (4)$$

where  $\sigma$  – the sum of effective radii of reagents  $r_1$  and  $r_2$ ,

$e$  – electron charge;

$\epsilon_0$  – vacuum permittivity (it is used in the International System of Units);

$\epsilon_{op}$  – optical dielectric permittivity of solvent permeability;

$\epsilon_s$  – static dielectric solvent permeability.

In the presented calculations of reorganization energy, the radius for each of components of couple of sym.  $Me_8Fc^{+/0}$  has been taken equal to the radius accepted for reactants of the couples of  $Me_{10}Fc^{+/0}$ . Probably, if it was possible to take into account some asymmetry of van der Waals surface for the couples of  $Me_8Fc^{+/0}$  in the reorganization energy formula (4) (i.e., actually to take into consideration the difference of their radius from the radius of the couple  $Me_{10}Fc^{+/0}$ ), then the reorganization energy (9.35 kJ/mol) would have some what

increased value and more appropriate to the real physical picture.

However, despite this degree of approximation, the general conclusion arising from the observed tendency of change  $\Delta G_{SR}^\ddagger$  is that the exchange rate constant consistently rises with the increase in substitution degree of hydrogen atoms of  $C_5$ -ring by methyl groups and the reason is the decrease of acetone molecule reorganization energy with an increase in volumes of reactants in the couples of  $Me_nFc^{+/0}$  ( $n = 6, 8, 10$ ), in comparison with the couple of  $Fc^{+/0}$ .

## Experimental part

The reactants containing the redox couple of sym.  $Me_8Fc^{+/0}$  were synthesized by methods indicated in the works [12, 13]. For NMR research, methylferrocenes were twice sublimated, and hexafluorophosphate salts

were twice recrystallized from acetone solution.

$^1H$  NMR spectra were obtained in deuteroacetone by means of spectrometer Bruker-300 MHz with the internal standard

(tetramethylsilane) at a temperature of 25°C. The total concentration of reagents in the systems studied by us varied within 0.030–0.45 M, but molar fraction of paramagnetic salt  $f_P$  was 0.01–0.350.

The errors in values of exchange rate constants computed on the basis of uncertainties of half-widths of resonance lines are about 10%. The difficulties of defining half-widths of resonance lines of spectra of the electron exchange process in the systems of

sym.  $\text{Me}_6\text{Fc}^{+/0}$  and sym.  $\text{Me}_8\text{Fc}^{+/0}$  are caused

$$f_P = \frac{v_{\text{DP}} - v_{\text{D}}}{\Delta v}$$

where  $v_{\text{DP}}$  – average values of chemical shifts of protons of the diamagnetic component

by overlapping absorption bands belonging to protons of Me groups with the different numbers of vicinal Me groups. The repeated, more thorough analysis of the overlapping bands in the spectrum of the system of sym.  $\text{Me}_6\text{Fc}^{+/0}$  led to a small correction of initial value  $k_{\text{ex}}=1.67 \cdot 10^7$  [7]. The corrected value  $k_{\text{ex}}$  for the system of sym.  $\text{Me}_6\text{Fc}^{+/0}$  is equal to  $1.5 \cdot 10^7$ .

Molar fractions were also calculated on the basis of the values of  $v_{\text{DP}}$  relatively to  $v_{\text{D}}$  and  $v_{\text{P}}$ , according to the formula:

in the mixture with appropriate paramagnetic salt in Hz (–743.1 Hz), wherein  $f_P$  was 0.119.

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### **SİM. OKTAMETİLFERROSEN/SİM. OKTAMETİLFERRİSİNİUM-HEKSAFLÜORFOSFAT SİSTEMİNDƏ ELEKTRON MÜBADİLƏ REAKSİYASININ KİNETİKASININ TƏDQIQI**

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*Sim. oktametilferrosen/sim. oktametilferrisinium-heksaflüorfosfat*  $[(CH_3)_4C_5H]_2Fe/(CH_3)_4C_5H]_2Fe^+ PF_6^-$  (və ya  $Me_8Fc^{+/0}$ ) sistemində baş verən elektron mübadilə reaksiyasının sürət sabiti ( $k_{ex}$ )  $^1H$  NMR rezonans zolaqlarının genişlənməsi üsulu ilə müəyyən edilmişdir.  $Me_8Fc^{+/0}$  sisteminin hər bir reagentində 8 ədəd metil qrupunun yaranması bu sistemin sürət sabitinin ferrosen/ferrisinium  $[(C_5H_5)_2Fe/(C_5H_5)_2Fe^+ PF_6^-]$  ( $Fc^{+/0}$ ) sisteminə nəzərən təxminən 4.8 dəfə artmasına səbəb olur.  $Fc^{+/0} \rightarrow Me_6Fc^{+/0} \rightarrow Me_8Fc^{+/0} \rightarrow Me_{10}Fc^{+/0}$  sırası üzrə mübadilə reaksiyasının sürətinin artması metil qrupunun elektronodonor xassəsinə uyğun olsa da, bu hadisə  $Me_nFc^{+/0}$  ( $n = 6, 8, 10$ ) redoks-cütlərində reagentlərin həcmnin artması nəticəsində aseton molekullarının reorqanizasiya enerjisinin azalması ilə izah olunmuşdur.

**Açar sözlər:** sim. oktametilferrosen, oktametilferrisinium kationu, kimyəvi sürüşmə, elektron mübadilə

### **ИЗУЧЕНИЕ КИНЕТИКИ РЕАКЦИИ ЭЛЕКТРОННОГО ОБМЕНА В СИСТЕМЕ СİM. OKTAMETİLFERROSEN/HEKSAFLÜORFOSFAT SİM. OKTAMETİLFERRİSİNİUM**

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Константа скорости электронного обмена ( $k_{ex}$ ) в системе сим. октаметилферроцен/гексафторфосфат сим. октаметилферициния  $[(CH_3)_4C_5H]_2Fe/(CH_3)_4C_5H]_2Fe^+ PF_6^-$  (далее обозначаются как  $Me_8Fc^{+/0}$ ) определена методом уширения  $^1H$  ЯМР линий. Появление восьми метильных групп в каждом реагенте редокс-системы  $Me_8Fc^{+/0}$  увеличивает константу скорости обмена примерно в 4.8 раза, по сравнению с незамещенной ферроцен-ферициниевой системой  $[(C_5H_5)_2Fe/(C_5H_5)_2Fe^+ PF_6^-]$  ( $Fc^{+/0}$ ). Увеличение скорости обмена в ряду  $Fc^{+/0} \rightarrow Me_6Fc^{+/0} \rightarrow Me_8Fc^{+/0} \rightarrow Me_{10}Fc^{+/0}$  хотя и соответствует электронодонорному свойству метильной группы, однако интерпретируется нами как результат уменьшения энергии реорганизации молекул растворителя (ацетона) с увеличением объемов реагентов редокс-пар  $Me_nFc^{+/0}$  ( $n = 6, 8, 10$ ).

**Ключевые слова:** сим. октаметилферроцен, катион сим. октаметилферициния, химический сдвиг, электронный обмен.