Russian Chemical Bulletin, International Edition, Vol. 50, No. 1, pp. 157—158, January, 2001

Kinetics of $\eta^6\to\eta^5$ isomerization of (η^6-fluorenyl)(η^5-cyclopentadienyl)iron

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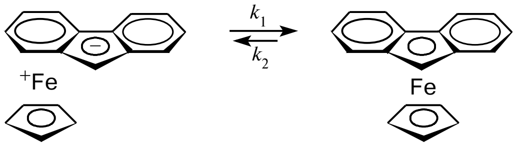
The kinetics of the reversible isomerization of the zwitterionic complex [(η^6-$C_{13}H_9$)Fe(η^5-C_5H_5)] (**1**) into dibenzoferrocene (**2**) was studied by electronic spectroscopy in the temperature range from 70 to 103 °C. The activation parameters of the reaction **1** → **2** were determined, E_a = 22.5 kcal mol^{-1}.

Key words: fluorenyl complexes of transition metals, metallotropic tautomerism, kinetics, electronic spectroscopy.

Redox activation of organometallic compounds is finding increasing use, which is a characteristic trend in modern organometallic chemistry. In this connection, comparative investigation of model reactions of complexes of transition metals with the 18-electron (18e) and odd-electron (17e and 19e) configurations is an urgent problem. From this viewpoint, inter-ring haptotropic rearrangements of transition metal complexes with condensed arenes are of great interest. However, these reactions of both 18-electron complexes[1] and 19-electron compounds[2—5] have not been adequately investigated in the quantitative sense. The aim of the present work was to study the kinetics of the $\eta^6 \rightleftharpoons \eta^5$ rearrangement of the zwitterionic complex [(η^6-$C_{13}H_9$)Fe(η^5-C_5H_5)] (**1**) into dibenzoferrocene (**2**) (Scheme 1).

Scheme 1



The rearrangement (1)[6] and an analogous rearrangement for complexes **1** and **2** with 19-electron configurations ($\mathbf{1}^{\cdot-} \rightleftharpoons \mathbf{2}^{\cdot-}$),[2] which we have found previously, were prerequisites for this study.

The kinetics of the $\eta^6\to\eta^5$ rearrangement **1** → **2** (see Scheme 1) was studied by electronic spectroscopy in the temperature range of 70—103 °C (at 70, 86.5, 96, and 103 °C) in *m*-xylene. The kinetics of the process and the equilibrium state of the system were examined by the decrease in the concentration of compound **1** monitored spectrophotometrically at 600 nm. The absorption bands of compound **2** at 380 and 530 nm (the shoulder at 420 nm) are rather diffuse, which hinders studies of the kinetics of the rearrangement **1** → **2** by the increase in the concentration of compound **2**.

The kinetic data were processed using the equation of the first-order reversible reaction

$$\ln[(D_{\text{equil}} - D_0)/(D_{\text{equil}} - D_x)] = (k_1 + 2k_2)(t_x - t_0),$$

where D_{equil}, D_0, and D_x are the absorbancies of compound **1** at 600 nm in the equilibrium state, at the initial moment t_0, and at the moment t_x, respectively. The coefficient 2 of k_2 accounts for the fact that the $\eta^5\to\eta^6$ migration of the organometallic group is doubly degenerate. Complex **1** occurred as a racemic mixture of enantiomers (separation of **1** into enantiomers was not the aim of this work). The plot of $\ln k_1$ *vs* $1/T$ for the rearrangement **1** $\rightleftharpoons$ **2** is linear (Fig. 1, the coefficient of regression $R = -0.984$).

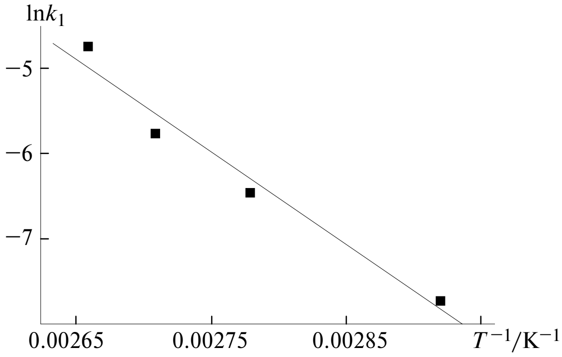


Fig. 1. Plot of the constant of the isomerization **1** → **2** *vs* the reciprocal of the temperature.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 151—152, January, 2001.

Table 1. Rate constants and equilibrium constants for the isomerization **1** → **2** in *m*-xylene

T/K	$k_{1\to2}\cdot10^{-4}$/s^{-1}	K_{equil}
343	4.44	6.42
359.5	15.53	9.88
369	31.0	9.12
376	84.48	12.57

The kinetic parameters for the isomerization **1** $\rightleftharpoons$ **2** are given in Table 1. It can be seen from the values K_{equil} = [**2**]/[**1**] that η^5-isomer **2** prevails in all cases, which confirms the experimental data obtained by us previously.[6] The value K_{equil} decreases as the temperature decreases. The activation parameters of the isomerization **1** → **2** are given below.

E_a	$\Delta H^{\#}$	log$A$	$\Delta S^{\#}$/e.u.
kcal mol^{-1}			
22.5	21.8	10.96	−10

The errors of the determination of E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$ were ~10%.

In the equilibrium state, complex **2** prevails in the system due to the contribution of the entropy component because the process **1** → **2** is characterized by the positive value ΔS = +18.9 e.u. (ΔH = 5.2 kcal mol^{-1}). The ΔS and ΔH values of the isomerization **1** → **2** were determined from the temperature profile of the equilibrium constants by the equation $\Delta H - T\Delta S = -RT\ln K_{\text{equil}}$. Therefore, η^6-isomer **1** is more favorable as judged from the enthalpy, whereas η^5-isomer **2** is more favorable as judged from the entropy. Compound **2** prevails in the equilibrium state because the entropy component is larger in magnitude than the enthalpy component throughout the temperature range under study (ΔG = 5.2 kcal mol^{-1} − $T\cdot$18.9 e.u. < 0). We believe that isomers **1** and **2** can be solvated due to the existence of short-lived associates formed by interactions between the π-electron systems of the complexes and *m*-xylene, whereas the increase in the entropy on going from **1** to **2** is associated with the higher ability of complex **1** to undergo solvation.[7,8] This rearrangement in solvents more polar than benzene, *m*-xylene, or heptane, for example, in THF or dimethoxyethane, resulted in virtually complete decomposition of complexes **1** and **2**.

The predominance of η^5-isomer **2** in the thermodynamical equilibrium **1** $\rightleftharpoons$ **2** suggests the higher thermodynamical stability of isomer **2**. This assumption has been made previously.[2,9] The inter-ring isomerization of 18-electron complexes proceeds under much more drastic conditions than an analogous process with 19-electron radical-anionic complexes $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$, which we have studied previously by cyclic voltammetry.[2] This is due to the fact that the antibonding LUMOs in complexes $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ are half-occupied and the activation barrier is low because the iron—π-ligand bond is more antibonding in character. In the equilibrium $\mathbf{1}^{\cdot-} \rightleftharpoons \mathbf{2}^{\cdot-}$, η^6-isomer $\mathbf{1}^{\cdot-}$ prevails, whereas, as was demonstrated above, η^5-isomer **2** prevails in the equilibrium **1** $\rightleftharpoons$ **2**. An increase in the portion of the η^5-isomer on going from 19-electron inter-ring haptotropic equilibria $\mathbf{1}^{\cdot-} \rightleftharpoons \mathbf{2}^{\cdot-}$ of transition metal fluorenyl complexes to the corresponding 18-electron equilibria **1** $\rightleftharpoons$ **2** has been found previously in the case of analogous fluorenyl complexes of manganese.[4]

Experimental

Complex **1** was synthesized by a procedure reported previously.[10] *m*-Xylene was distilled over sodium under argon. The electronic spectra were measured on a Specord 40 M spectrometer at room temperature. Solutions of complex **1** were prepared with different concentrations varying from $3.39\cdot10^{-3}$ to $4.05\cdot10^{-3}$ mol L^{-1}. Heating was performed under an atmosphere of purified argon. Each portion of the solution under examination was rapidly cooled to 20 °C and then transferred under argon to a standard cell with a tightly fitted cap. The cell was mounted in the spectrometer.

We thank A. N. Krylov for help in spectral studies.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-33060).

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Received April 6, 2000;
in revised form September 18, 2000