

ELECTRODES REVERSIBLE TO DERIVATIVES OF THE FERRICINIUM CATION

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The creation of an electrode reversible with respect to the ferricinium cation [1] has permitted an investigation of its thermodynamic stability in aqueous solutions [2], its hydrolytic decomposition [3] and complex formation [4, 5], a determination of the heat of hydration [6, 7], and an answer to a number of other problems. The influence of various substituents in the ferricinium cation on the properties enumerated above can be studied successfully when electrodes reversible with respect to the corresponding ferricinium derivatives are available.

This communication presents data on the electrodes that we developed, reversible with respect to the tert-butylferricinium and benzylferricinium cations, and the properties that a redox system (ferrocene derivative-ferricinium derivative) should possess for the realization of an electrode reversible to the ferricinium derivative. Tertiary butyl butyl-ferrocene was synthesized according to the direct alkylation of ferrocene with isobutylene in the presence of the molecular compound of orthophosphoric acid with boron fluoride [8, 9]. The alkylation was conducted in an autoclave with a mixing device, in n-heptane solution, at an equimolar ratio of the reagents, 60°C, and duration of reaction 5 h. At the end of the reaction the solvent was distilled off, and the alkylate was fractionated twice in a stream of nitrogen at a residual pressure of 5 mm Hg. In this case up to 60% monotert-butylferrocene was isolated, the physicochemical constants of which corresponded to the literature data [10]. The purity of the synthesized tert-butylferrocene was > 92% (Fig. 1).

The proton magnetic resonance spectrum of tert-butylferrocene consists of the peak of the methyl protons with chemical shift 1.18 δ and the system of lines typical of the cyclopentadienyl protons of monotert-butylferrocene, consisting chiefly of two signals 4.03 δ and 3.94 δ . The ratio of the areas of the CH_3 peak to the summary area of the signals of the cyclopentadienyl protons is equal to 1.09, which indicates a negligible admixture of ditert-butylferrocene. The other signals noticeable (at high amplification) in the spectrum are apparatus interference and satellites of C^{13} of the basic signal of monotert-butylferrocene.

Most of the known alkyl-substituted ferrocenes are liquids at 25° and 1 atm [8]; they practically do not dissolve water and are themselves practically insoluble in water. The indicated property permits us to assert that in emulsions of an alkyl derivative of ferrocene in an aqueous salt solution at equilibrium of the process of dissolution and not too high a degree of dispersion of the phase of the alkyl derivative,* the value of the chemical potential of the alkyl derivative is a function of the pressure and temperature and does not depend on the salt composition of the aqueous phase. If the aqueous solution contains a salt of a ferricinium derivative in sufficient concentration ($\geq 10^{-5}$ M) and does not contain other buffer redox systems, then the emulsification of the corresponding alkyl derivative of ferrocene in this solution leads to the formation of a stable potential on a platinum electrode lowered into the solution, when the following conditions are fulfilled:

1. A high rate of exchange of electrons between the oxidized and reduced forms in solution.

* The average size of the drops should be sufficiently large that the excess free energy of the surface layer can be neglected.

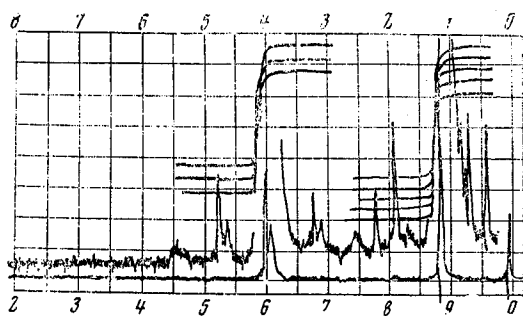


Fig. 1

Fig. 1. NMR spectrum of tert-butylferrocene (Perkin-Elmer P-12 instrument, working portion 60 MHz, $t = 34^\circ\text{C}$, solvent CCl_4 , internal standard hexamethyldisiloxane).

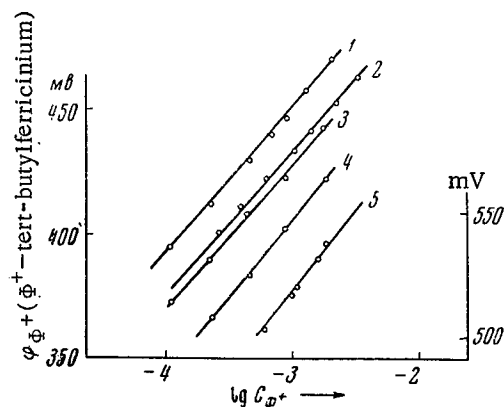


Fig. 2

Fig. 2. Dependence of the potential of tributylferricinium and benzylferricinium electrodes on the concentration of the corresponding cations. Salt background: 1) 1 N KCl, 0.01 N HCl; 2) 1.01 N HCl; 3) 1 N NaClO_4 , 0.01 N HClO_4 ; 4) 1.01 N HClO_4 ; 5) 1 N KCl, 0.01 N HCl.

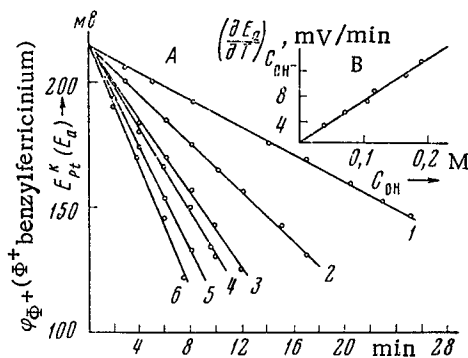
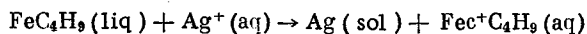


Fig. 3. A) Dependence of the emf of the galvanic cell on the time at various concentrations of OH^- : 1) 10^{-2} M; 2) $7.4 \cdot 10^{-2}$; 3) $1.1 \cdot 10^{-1}$; 4) $1.2 \cdot 10^{-1}$; 5) $1.6 \cdot 10^{-1}$; 6) $1.74 \cdot 10^{-1}$ M. B) Dependence of $(\partial E_a / \partial t)_{C_{\text{OH}^-}}$ on the OH^- concentration.

2. A sufficiently high rate of saturation of the aqueous phase with the reduced form. The latter increases in proportion to S/V (S is the surface of separation of the phases; V is the volume of the aqueous phase), i.e., the degree of dispersion.

The ferrocene-ferricinium cation system belongs to one of the most rapid systems [9]. We should expect that the derivative systems will also retain this property. Whether the first and second conditions are fulfilled can be verified according to the rate at which the heterogeneous oxidation of the emulsified alkyl derivative of ferrocene by an aqueous solution of an oxidizing agent (AgClO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$) takes place. An electrode reversible with respect to the tert-butylferricinium cation was prepared in the following way. A known amount of silver perchlorate was added to an aqueous acid solution with emulsified tert-butylferrocene. The tert-butylferrocene was taken in excess. After equilibrium of the heterogeneous reaction



had been reached, the solution was filtered off, and the unreacted silver ion quantitatively precipitated by the introduction of HCl or KCl. Tert-

butylferrocene in amounts of 0.3 g per 50 ml of solution was added to the acid solution obtained, and the mixture emulsified by shaking. Platinum electrodes (grid and smooth) in such a system possessed a stable and reproducible value of the potential. Figure 2 presents the dependence of the potential of a platinum electrode, measured against a saturated calomel electrode and recalculated to a hydrogen electrode in various salt solutions as a function of the logarithm of the tert-butylferricinium concentration ($\log C_{\Phi^+}$). As can be seen, the functions are linear, and the derivative $\partial E / \partial \log C_{\Phi^+} = 59 \text{ mV} \mp 2$, which corresponds to $2.3 \text{ RT}/F$. Constancy of the composition and concentration of the salt background ensures constancy of the activity coefficient of the tert-butylferricinium cation and diffusion potential and, consequently, a reversible tert-butylferricinium electrode under the indicated conditions should possess the potentials described by the equation:

$$\varphi_{\Phi^+} = \psi_{\Phi^+}^0(P, T) + \frac{RT}{F} 2.3 \lg C_{\Phi^+}. \quad (1)$$

The experimental functions satisfy this equation. The electrode reaction can be expressed by the equation:

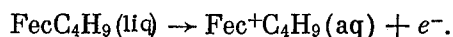


TABLE 1

	Composition of solution			
	1 N KCl 0,00 N HCl	1,01 N HCl	1 N NaClO ₄ 0,01 N HClO ₄	1,01 N HClO ₄
$\varphi_{\Phi^+}^0$, mV	627	609	603	581
$\psi_{\text{Fec}^+}^0$, mV	637	605	618	560

The values of $\varphi_{\Phi^+}^0$ are cited in Table 1. By comparing the values of $\varphi_{\Phi^+}^0$ with the standard potentials of the ferrocenium electrode [1], it can be noted that their mutual arrangement is the same, lower in perchlorate solutions than in chloride solutions. However, when the alkali metal ion in the salt background is replaced by a hydrogen ion, $\Delta\varphi_{\Phi^+}^0$ is appreciably lower than for the corresponding $\Delta\varphi_{\text{Fec}^+}^0$. The explanation for this should be sought in the electron donor properties of the C₄H₉ group and its large volume. Both these factors lower the

strength of perchlorate and chloride associates with respect to the substituted ring. The products of alkaline decomposition of tert-butylferricinium, containing iron (tert-butylferrocene, Fe³⁺), are formed in the same ratios as for the ferricinium cation [3]. This indicates that the reaction mechanism is the same. We used a tert-butylferricinium electrode to study the hydrolytic decomposition of tert-butylferricinium. The experiments were conducted at 25° in the following way. Tert-butylferrocene was added to an aqueous acid solution with the composition 1 N KCl, 0.01 N HCl, $1.7 \cdot 10^{-3}$ N Fec⁺C₄H₉Cl⁻ and emulsified by shaking. The system obtained was poured into a measuring cell, containing platinum [2], glass, and calomel electrodes, the readings of which were measured. Then a known volume of an aqueous solution of NaOH was added to the cell, and the mixture was mixed with a stream of argon. The time of mixing was noted, and then the emf of the galvanic couples tert-butylferricinium-calomel (a) and glass-calomel (b) electrodes was measured over a period of time. The amount of added alkali was always sufficiently great that the emf of the couple (b) did not depend on the time.

Figure 3 presents the dependences of the emf of the couple (a) on the time at various values of C_{OH⁻}. As can be seen from the figure, the functions are linear, i.e., $(\partial E_a / \partial t)_{C_{OH^-}} = \text{const}$. The values of $(\partial E_a / \partial t)_{C_{OH^-}}$, in turn, are linear functions of C_{OH⁻} (Fig. 3A), and when C_{OH⁻} = 0 $(\partial E_a / \partial t)_{C_{OH^-}} = 0$.

Considering that the tert-butylferrocene-tert-butylferricinium system is a rapid redox system, while no other rapid systems are manifested during the reaction (all the inorganic iron is deposited in the form of the hydroxide), it may be considered that for any moment of time expression (1) is correct for the potential of the platinum electrode. In this case, differentiating Eq. (1) with respect to the time, we obtain:

$$\left(\frac{\partial E_a}{\partial t}\right)_{C_{OH^-}} = \frac{RT}{F} \frac{1}{C_{\Phi^+}} \frac{dC_{\Phi^+}}{dt} \quad (2)$$

From (2) it is evident that $(\partial E_a / \partial t)_{C_{OH^-}}$ can be constant with time only when the following equation is fulfilled:

$$-dC_{\Phi^+}/dt = K' C_{\Phi^+}, \quad (3)$$

i.e., when the decomposition reaction is first order with respect to the tert-butylferricinium cation. Substituting (3) into (2), we obtain

$$-\left(\frac{\partial E_a}{\partial t}\right)_{C_{OH^-}} = \frac{RT}{F} K'. \quad (4)$$

Since the quantity $(\partial E_a / \partial t)_{C_{OH^-}}$ is proportional to C_{OH⁻} (Fig. 3), then

$$K' = K C_{OH^-} \quad (5)$$

and, consequently, the kinetic equation of the reaction takes the form

$$-dC_{\Phi^+}/dt = K C_{\Phi^+} C_{OH^-}. \quad (6)$$

For one molar KCl at 25°, $K = 4.5 \cdot 10^{-2}$ liter/mole · sec, which is appreciably less than the rate constant ($7 \cdot 10^{-1}$ liter/mole · sec) of the hydrolytic decomposition of the ferricinium cation under the same conditions [3].

Since the solubility of most ferrocene derivatives in aqueous solutions is extremely low (for ferrocene $\sim 3.8 \cdot 10^{-5}$ M), the basic difficulty in the preparation of an electrode reversible with respect to the corresponding stable derivatives of ferricinium is the reaction of sufficient buffer capacity with respect to the reduced form in the space near the electrode. For crystalline substituted ferrocenes, a substantial increase in the latter can be achieved by

applying the finely divided substance under the surface of a platinum plate. Thus, analogously to the ferricinium electrode [1], we prepared an electrode reversible with respect to the benzylferricinium cation. For this purpose finely divided benzylferrocene,* produced by salting out with water from acetic acid solution, was smeared onto a platinum plate, and then placed in an aqueous solution of 1 N KCl, 0.01 N HCl, and $\sim 1.7 \cdot 10^{-3}$ N $\text{Fec}^+\text{CH}_2\text{C}_6\text{H}_5$. The potential of the platinum plate in the solution was reproducible and stable. Figure 2 presents the dependence of the potential of a benzylferricinium electrode (with respect to a standard hydrogen electrode) on the logarithm of the benzylferricinium concentration. As can be seen from the figure, the dependence is linear, while the derivative of the potential has a value of 59 mV, which corresponds to the theoretical value for a reversible benzylferricinium electrode within the limits of accuracy of our measurements. The benzylferricinium solution was prepared analogously to the tert-butylferricinium solution.

Thus, it was shown in the work that both for liquid and for crystalline derivatives of ferrocenes, the preparation of electrodes reversible with respect to the oxidized forms of these compounds, working in aqueous solutions, is theoretically possible. The electrodes can be successfully applied to the study of the kinetics of the hydrolytic decomposition of ferricinium derivatives in alkaline solutions.

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