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ELECTROLYTIC OXIDATION OF FERROCENE IN THE PRESENCE OF TRACE AMOUNTS OF DISSOLVED OXYGEN

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Ferricinium ion formed by the electrolytic oxidation of ferrocene in polar aprotic solvents is very sensitive to the presence of trace amounts of dissolved oxygen. By the use of current reversal chronopotentiometry and cyclic voltammetry, it was shown that a part of ferricinium ion rapidly decomposes according to unknown chemical processes.

It is well known that ferrocene (dicyclopentadienyl iron (II)) is reversibly oxidized to ferricinium ion in several polar aprotic solvents. Therefore, the redox potential of this couple is often used as a relative standard for the comparison of other redox couples in different solvents.1)

On the other hand, there are reports of a rather instable characteristic of ferricinium ion in solution. For example, when ferrocene is oxidized chemically by lead dioxide in a polar aprotic solvent, a blue color of the solution due to the ferricinium ion fades rapidly in few minutes and the solution turns pale yellow. Moreover, organic chemists report the reactivity of several organic solvents towards ferricinium ion due to a nucleophilic character of solvents.2)

In order to solve the above mentioned contradiction concerning the stability of ferricinium ion, the present authors intended to investigate precisely the stability of ferricinium ion by using several electroanalytical methods.

As current reversal chronopotentiometry is one of the most sensitive methods of detecting the presence of chemical reactions coupled to an electrode reaction, the transition time ratio τ_{ox} / τ_{RED} was investigated in several polar aprotic solvents as shown in Table 1. The transition time ratio deviates clearly from the anticipated value for the ideal reversible case (3 : 1) in acetonitrile and in N,N-dimethylformamide. After several attempts to find out the reason for this deviation from the theoretical value, we focused our attention on the presence of dissolved oxygen. Though the redox potential of oxygen is about one volt more negative than that of ferrocene/ferricinium redox couple, it must be very reactive towards electrolytically formed ferricinium ion. Therefore, contrary to the usual experimental condition of a deaerated solution, the chronopotentiometric behavior of ferrocene was studied in an oxygen saturated solution. As shown in Fig. 1, the transition time for the oxidation step increases in the presence of dissolved oxygen, whereas the transition time for the reverse reduction wave decreases with the increase in the concentration of oxygen, and moreover a new reduction wave appears at about +0.15 V. On the contrary, a chronopotentiogram under completely deaerated conditions using repeated freeze-pump thaw cycle showed typical reversible characteristic. The same peculiarity is shown with cyclic voltammetry in an oxygen saturated solution (Fig. 2, curve A). A cyclic voltammogram does not show a reverse reduction wave, and a new wave appears at about 0 V after the second cycle. The redox potential of the unknown species approximately coincides with that of inorganic iron (ferric/ferrous ion couple). In order to confirm this postulation, we are continuing spectroscopic study of the electrolyzed solution of ferrocene.

Table 1. Transition Time Ratio of Current Reversal Chronopotentiometry of Ferrocene (Ferrocene; 1 mM, TBAP; 0.1 M)

Solvent	Transition time(sec)		Ratio	Current density(A/cm^2)
	τ_{OX}	τ_{RED}	τ_{OX}/τ_{RED}	
Acetonitrile	19.7	4.2	4.7	69.3
N,N-Dimethylformamide	15.9	4.2	3.8	24.75
Dimethylsulfoxide	9.3	3.1	3.0	24.75

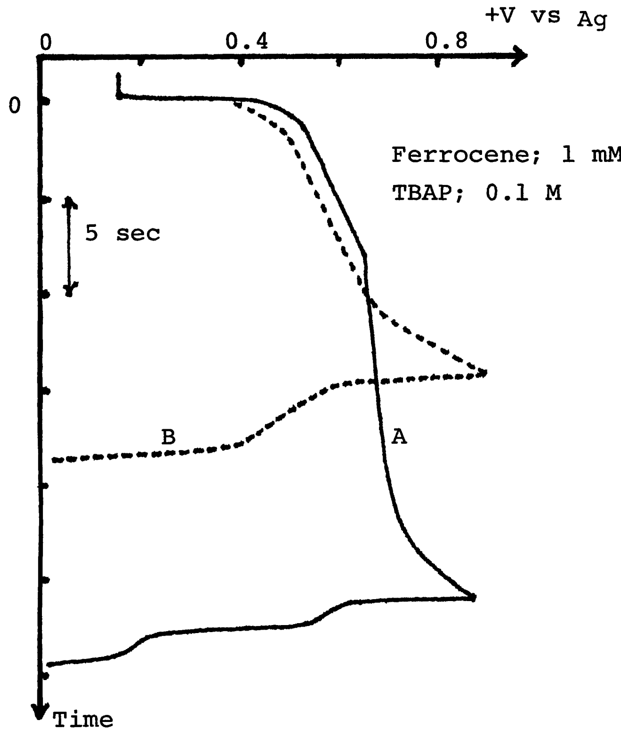

Fig. 1 Chronopotentiogram of Ferrocene in Dimethylsulfoxide

A; oxygen saturated

B; completely deaerated

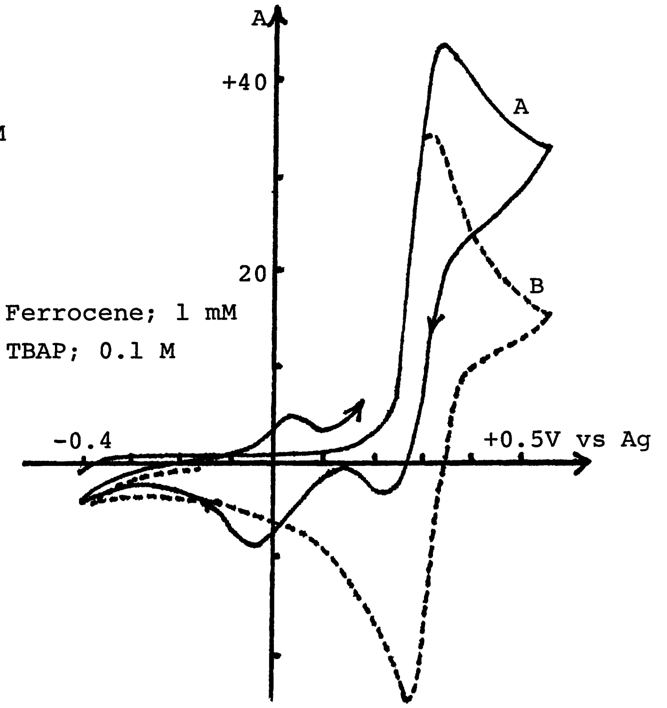

Fig. 2 Cyclic Voltammogram of Ferrocene in Dimethylsulfoxide

A; oxygen saturated

B; completely deaerated

References

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