SHORT COMMUNICATIONS

Chronopotentiometric Oxidation of Biferrocenyl in Anhydrous Acetonitrile and in Methylene Chloride[1]

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It is well known from voltammetric studies that ferrocene as well as its substituted derivatives generally shows a reversible one electron oxidation wave in nonaqueous solvents.[3] By using chronopotentiometry at the bright platinum anode, we found that biferrocenyl which consists of two equivalent ferrocenyls shows two step waves, each corresponding to one electron oxidation.

The current reversal chronopotentiograms of biferrocenyl in both solvents are shown in Figs. 1 and 2. Results of the current reversal at the first oxidation step show the oxidation proceeds reversibly in both solvents, because the ratio of transition time τ (A)/τ (A′) equals 3/1, and $E_{0.25\ \tau(A)}$ equals approximately $E_{0.22\tau(A)}$. On the contrary, the second oxidation step seems completely irreversible in acetonitrile, since no reduction wave is shown by the current reversal at the second oxidation step (ABA′ in Fig. 1). Nevertheless the reduction wave corresponding presumably to the reduction of the oxidized product in the case of the current reversal at the first oxidation step remains unchanged. The product at the second oxidation step is more stable in methylene chloride than in acetonitrile. As is shown in Fig. 2, the reduction wave (B′) of the oxidized product at the second oxidation step appears in spite of its irreversible character. In curve ABB′A′, Fig. 2, the ratio of transition times, τ(A):τ(B):τ(B′):τ(A′), is equal to 1.0:2.5:0.3:0.9, which is approximately equal to the theoretical value[4]; 1.0:3.0:0.29:1.05.

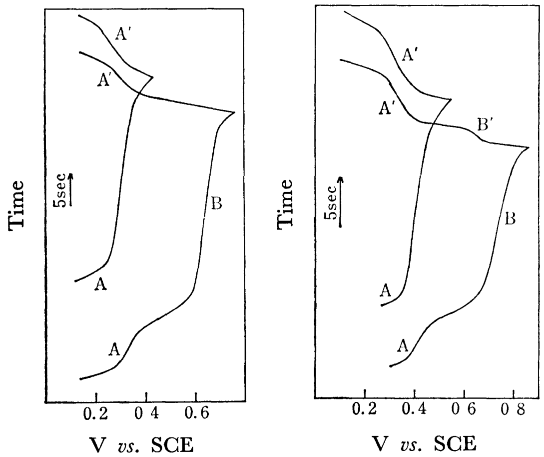

Fig. 1 Fig. 2

Figs. 1 and 2. Current reversal chronopotentiograms of biferrocenyl in acetonitrile (Fig. 1) and in methylene chloride (Fig. 2).

$$\mathrm{Fc{-}Fc} \underset{\substack{+e \\ A'}}{\overset{\substack{A \\ -e}}{\rightleftarrows}} \mathrm{Fc^{+}{-}Fc}, \qquad \mathrm{Fc^{+}{-}Fc} \underset{\substack{+e \\ B'}}{\overset{\substack{B \\ -e}}{\rightleftarrows}} \mathrm{Fc^{+}{-}Fc^{+}}.$$

Biferrocenyl: 0.406 mmol/*l* (Fig. 1); 0.144 mmol/*l* (Fig. 2). Supporting electrolyte: 0.1M–Et_4NClO_4 (Fig. 1); 0.05M–Bu_4NClO_4 (Fig. 2).

Concerning the mechanism of the electrochemical oxidation of the biferrocenyl, it seems that in analogy to the oxidation of ferrocene derivatives each ferrocenyl group in a biferrocenyl molecule is oxidized at different potentials (Table 1). Denoting (C_5H_5)Fe-(C_5H_4)– by Fc–, the following oxidation scheme can hold in both solvents.

$$\mathrm{Fc{-}Fc} - e = \mathrm{Fc^{+}{-}Fc} \quad \text{(1st wave)}$$
$$\mathrm{Fc^{+}{-}Fc} - e = \mathrm{Fc^{+}{-}Fc^{+}} \quad \text{(2nd wave)}$$

The reason for the splitting of the oxidation step can be understood by considering that for the first oxidation of one ferrocenyl group the other ferrocenyl group in a same molecule acts as an electron donating substituent group. Consequently the quarter wave potential is shifted to a more negative direction compared with that of ferrocene. Contrary to this, at the second oxidation step, the oxidized form of one ferrocenyl group acts as an electron withdrawing substituent group to the other ferrocenyl group. Thus, the characteristic potential of the second wave is shifted to the more positive potential compared with that of ferrocene. As for the second oxidation step in acetonitrile solvent, it seems that the product reacts chemically with an unoxidized biferrocenyl causing disproportionation to give Fc+–Fc, which is identical with the product at the first oxidation step.

TABLE 1. CHARACTERISTIC POTENTIALS[a] OF BIFERROCENYL AND FERROCENE (25°C)

Solvent / Compound	Acetonitrile (0.1M Et_4NClO_4)	Methlyene chloride (0.05M Bu_4ClO_4)
Biferrocenyl		
1st wave	+0.286	+0.380
2nd wave	+0.635	+0.715
Ferrocene	+0.385	+0.440

a) $E_{0.25\tau(A)}$ (1st wave) and $E_{0.42\tau(B)}$ (2nd wave); V *vs.* SCE

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