Electrochemical investigation into the electron transfer mechanism of a diiron hexacarbonyl complex bearing a bridging naphthalene moiety

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A B S T R A C T

Electrochemical investigations and chemical reduction of the diiron hexacarbonyl complex bearing a 1,8-naphthalene moiety bridging linkage into which a ferrocenyl group was deliberately incorporated were performed. The complex exhibited two reduction and two oxidation processes in dichloromethane. Our results revealed that the first reduction could be assigned to an ECE (Electrochemical, Chemical and Electrochemical) mechanism with the second potential inversed. When the monoanion generated in the first reduction underwent, in part, the ECE mechanism, the rest of the monoanion continued to accept the second electron without involving a coupled chemical reaction, so called EE (Electrochemical and Electrochemical) mechanism. The two mechanisms co-existed in the electron transfer and compete with each other. By both increasing scanning rate and lowering temperature, the coupled reaction in the ECE mechanism could be effectively suppressed whereas the second reduction is highly irreversible. The coupled chemical reaction following the EE process might lead to the same dianion as that produced in the ECE processes. Although chemical reduction and re-oxidation were unsuccessful of confirming the transformation between the two dianions, DFT calculations did support this proposed chemical reaction.

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1. Introduction

Diiron carbonyl complexes of the core, "Fe$_2$(CO)$_x$" (x = 4-6), have attracted a great deal of attention due to their resemblance to the diiron subunit of [FeFe]-hydrogenase (Fig. 1), a metalloenzyme catalysing rapidly and reversibly hydrogen evolution and oxidation with preference to catalysing hydrogen evolution [1,2]. Since either hydrogen evolution or oxidation involves transfer of two-electron per molecule, therefore, understanding the electron transfer mechanism of those diiron mimics has been an important issue in the mimicking chemistry of the enzyme. The electrochemical investigations into a wide range of diiron mimics have greatly advanced our understanding of the mechanism [3–11]. It is certain that the diiron core have the capacity of accepting two electrons. The simplest situation is that two electrons are injected successively with potential separation over 500 mV. But the unique structure of the diiron complicates the process of the electron transfer. After accepting the first electron, one of the four Fe–S bonds may de-coordinate to form an isomer without deconstructing the entire motif [12–14]. The reaction rate of the isomerisation, the coupled chemical reaction, and the thermodynamic stability of the mono-anion dictate largely how the transfer of the second electron transfer proceeds. Particularly, the isomerised product may be more electron-deficient than its parent complex due to the de-coordination of one iron-thiolate bond from the one-electron-reduced bimetallic core (the monoanion).

When the coupled reaction is extremely fast, an ECE mechanism with potential inversion is adopted. In this mechanism, the potential of the second reduction is not more negative than the first one [6–8,11,15–17]. A typical example is 1,2-benzenedithiolate system and its derivatives in which the bridging motif is 1,2-benzenedithiolate [5,16–18]. Depending on the electronic nature of the bridging linkage, the monoanion without isomerisation may be stable enough to be detected by cyclic voltammetry. But in this case, the second potential could be as close as dozens mV to the first potential [9,11]. If the bridging ligands are electron-withdrawing or a large conjugating bridging moieties such as naphthalene [19,20] and biphenyl moieties [21], The diiron complexes show two successive processes in their electron

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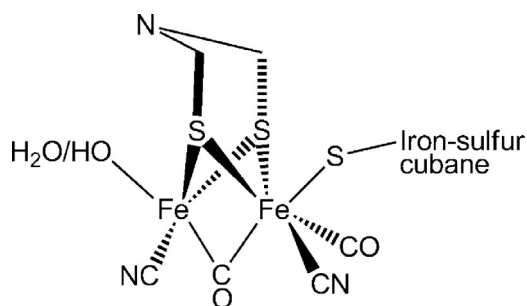(X. Liu).

Fig. 1. The diiron core of the subunit of [FeFe]-hydrogenase.

transfer. But whether the two processes are perfectly two successive one-electron ones is questionable despite that they are often assigned so. But our investigations into the mechanisms of electron transfer of diiron carbonyl complexes [9,10,22] implied that the mechanism of electron transfer may not be as simple as being thought and prompted us to further explore the electrochemistry of the system bearing naphthalene moiety as a bridging linkage to gain some insight.

Herein, we report the electrochemical, chemical and theoretical investigations into the diiron mimic (**1**) derived from 1,8-naphthalenedithiolate derivative bearing a ferrocenyl group. The ferrocenyl group is deliberately incorporated into the molecule to calibrate the electron number involved in the electron transfer as we reported before [10]. Our investigations allowed us concluding that there are two pathways for electron transfer in the system. The ECE mechanism with potential inversion competes with the other pathway, two successive one-electron processes, that is, the EE mechanism. Particularly, theoretical calculations revealed that the dianion formed in the latter pathway undergoes isomerisation into the dianion generated from the ECE process.

2. Experimental and DFT calculations

2.1. Materials and instruments

All organic solvents were pre-treated and freshly distilled under Ar atmosphere prior to use. Synthetic manipulations were performed using Schlenk technique when necessary. FTIR spectra were recorded on an Agilent 640 spectrometer. Elemental analyses were preformed on Elementar Vario MICRO. ^1H and ^{13}C NMR spectra were recorded on Varian 400MR in $CDCl_3$. Electrochemistry was performed on AUTOLAB with a self-designed gas-tighten three-electrode system in which a vitreous carbon disk ($\Phi = 1$ mm) was used as a working electrode, a carbon strip as counter electrode, and Ag/AgCl (inner reference solution: 0.45 mol L^{-1} [$NBut_4$]$BF_4 + 0.05$ mol L^{-1} [$NBut_4$]Cl in dichloromethane) against which the potential of ferrocenium/ferrocene couple is 0.55 V in 0.5 mol L^{-1} [$NBut_4$]BF_4 in dichloromethane. Further details for electrochemical experimental details can be found elsewhere

[9,10]. All potentials reported in this work were quoted against ferrocenium/ferrocene couple. All chemicals were purchased locally and used as received unless otherwise stated. $Fe_3(CO)_{12}$ was prepared from $Fe(CO)_5$ using the procedure described in the literatures [23,24].

2.2. Synthesis

2.2.1. 1,8-S_2-2CHOC$_{10}$H$_5$ (L)

$POCl_3$ (1.2 mL, 12.9 mmol, 1.75 eq.) was added dropwise to a stirred solution of naphthalene 1,8-disulfide (1.4 g, 7.4 mmol) in dry DMF (7 mL) at $0\,°C$ under a argon atmosphere. The resulting dark red solution was allowed to warm to room temperature, stirred overnight under nitrogen, and quenched with water to give an orange solid. The residue was extracted by dichloromethane (30 mL × 3). The organic phase was washed three times with brine and dried over Na_2SO_4, filtered, and dry-loaded onto silica gel. Purification by flash column chromatography (elution: dichloromethane/petroleum ether = 3/2, v/v) provided compound 1,8-S_2-2CHOC$_{10}$H$_5$ (0.80 g, 50%). M.p. 169-171 °C, ^1H NMR ($CDCl_3$, 400 MHz): δ 10.08 (1H, CHO, s), 7.70 (1H, naphthalene, s), 7.49 (4H, naphthalene, m). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 187.93, 130.61, 129.07, 122.16, 120.72, 117.07; IR (KBr) ν /cm^{-1}: 1641.7, 1584.9, 1519.8, 1431.8.

2.2.2. [Fe$_2$(CO)$_6$(1,8-S_2-2CHOC$_{10}$H$_5$)]

$Fe_3(CO)_{12}$ (0.331 g, 0.66 mmol) and 1,8-S_2-2CHOC$_{10}$H$_5$ (145 mg, 0.67 mmol) were dissolved in toluene (25 mL). The mixture was refluxed for 1.5 h under argon atmosphere before the removal of the solvent under reduced pressure. Purification by column chromatography (elution: dichloromethane/petroleum ether = 3/2, v/v) yielded complex [Fe$_2$(CO)$_6$(1,8-S_2-2CHOC$_{10}$H$_5$)] as red powder (178 mg, 60%). IR (dichloromethane, cm^{-1}): ν (CO), 2078.4, 2043.6, 2004.4 cm^{-1}, (KBr): 1690.6 (νCHO,w), 1614.4 (w), 1601.4 (w), 1589.9 (w), 1576.0 (w), 1570.0 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 11.29 (1H, s, CHO), 8.23 (1H, d, = 6.8 Hz, Ph), 7.95 (3H, d, = 5.2 Hz, Ph), 7.44 (1H, t, = 7.6 Hz, Ph). ^{13}C NMR ($CDCl_3$, 400 MHz): 207.27, 191.40, 133.86, 132.41, 131.47, 127.81, 127.23, 123.97. Microanalysis ($C_{17}H_6Fe_2O_7S_2$, MW = 498.05): cal. (found) (wt%), C, 41.00 (40.33), H, 1.21 (1.37).

2.2.3. [Fe$_2$(CO)$_6$(1,8-S_2-2CH$_2$OHC$_{10}$H$_5$)]

To a solution of [Fe$_2$(CO)$_6$(1,8-S_2-2CHOC$_{10}$H$_5$)] (148 mg, 0.30 mmol) in dried THF (30 mL) under ice-salt bath was added $NaBH_4$ (11.5 mg, 0.30 mmol) in small portions. The reaction was monitored by TLC until the starting material was consumed within 2 h. The mixtures was filtered and purified by column chromatography (elution: dichloromethane) to give the product as a red solid (100 mg, 67%). IR (dichloromethane, cm^{-1}): ν (CO), 2075.4, 2040, 2000 cm^{-1}, (KBr): 3437.6, 1627.0 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.26 (1H, d, = 8.4 Hz, Ph), 8.00 (2H, m, Ph), 7.74 (1H, d, = 8.4 Hz, Ph), 7.39 (1H, t, = 7.8 Hz, Ph), 5.32 (2H, d, = 6.4 Hz, CH_2), 2.15 (1H, t, = 6.2 Hz, OH). ^{13}C NMR ($CDCl_3$, 400 MHz):
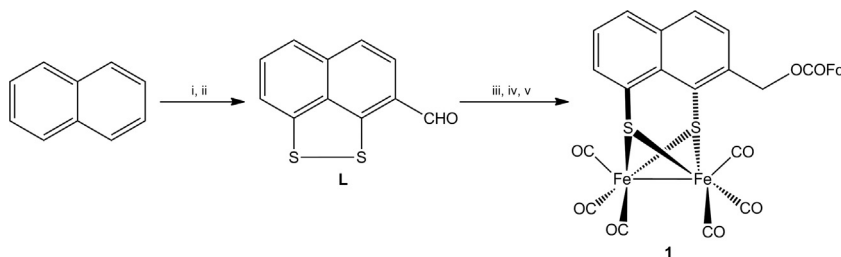
Scheme 1. Synthesis of diiron complex **1** (i n-BuLi/hexane, S$_8$, THF; ii POCl$_3$, DMF; iii Fe$_3$(CO)$_{12}$, Toluene,110 °C, iv NaBH$_4$, THF, 0 °C, v FcCOCl, NEt$_3$, THF, Fc = ferrocenyl group).