Electrochemistry in liquid sulfur dioxide. 4. Electrochemical production of highly oxidized forms of ferrocene, decamethylferrocene and iron bis(tris(1-pyrazolyl)borate)

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the zero-point levels of the two spin states. The quadrupole splitting is composed of the sum of $\Delta E_{\text{val}}$ and $\Delta E_{\text{lat}}$; the subscript "val" refers to the contribution from the charge distribution of the aspherical "3d-valence" electron and the subscript "lat" from the charge distribution of the neighboring ions in the crystalline lattice. If the component of $\Delta E_{\text{lat}}$ in the $^4\text{A}$ state is assumed to be the same as that in the $^2\text{T}$ state in this calculation, the parameters are obtained as shown in Table III. Figures 11 and 12 show the plots of the experimental data of the quadrupole splitting together with the theoretical curves that are obtained by using the best parameters listed in Table III. These values evaluated from the TQS by the least-squares method are reliable rather than those from the temperature dependence of the effective magnetic moment, because we have neglected the distortion of the crystal field in the process of calculating the theoretical temperature dependence of the effective magnetic moment. However, not much significance is attached to this value, because there is a fair latitude in the choice of $C$; that is, $C$ is defined to be constant in this calculation in spite of the fact that $C$ may be in general dependent on temperature.

The ligand field parameters and crossover parameters for the rapid electronic relaxation of the spin-crossover system calculated in this study are similar to those for the slow electronic relaxation. The rates of $^2\text{T} \Rightarrow ^4\text{A}$ spin interconversion take place as fast as $10^{-7}$ s, although these electron transfer accompanied by changes in spin multiplicity, therefore, are spin-forbidden transitions ($\Delta S = 2$). The electron transfer must proceed through the ligand orbitals, and the interaction of an iron atom with lattice vibrations will play an important role. Furthermore, it is important that $\pi$-conjugation is involved in the chemical structure and the ligand is stereochemically flexible.

Conclusion

The Mössbauer absorption spectra for the spin-crossover iron(III) complexes showed the rapid electronic relaxation phenomena between $^4\text{A}$ and $^2\text{T}$ states. It is notable that the behavior of $[\text{Fe(acen)}(\text{lut})_2](\text{BPh}_4)$ is different from that of the other complexes in the electronic relaxation time in spite of its similar thermodynamic data. The introduction of a methyl group in the 2-position of pyridine results in steric hindrance, leading to the inhibition of the ligand molecule motion, and changes the electron density at the iron atom. The steric hindrance affects the coupling between the spin transition and lattice vibration and thus may cause the different electronic relaxation time according to the stereochemical structure of each complex.

Registry No. $[\text{Fe(acen)}(\text{dpp})](\text{BPh}_4)$, 83555-99-1; $[\text{Fe(acen)}-(\text{pic})_2](\text{BPh}_4)$, 62660-72-4; $[\text{Fe(acen)}(\text{lut})_2](\text{BPh}_4)$, 86507-81-5.

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Electrochemistry in Liquid Sulfur Dioxide. 4. Electrochemical Production of Highly Oxidized Forms of Ferrocene, Decamethylferrocene, and Iron Bis(tris(1-pyrazolyl)borate)$^1$

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Received November 17, 1982

The electrochemistry of $\text{Fe(C}_5\text{H}_5\text{)_2}^*$, $\text{Fe(C}_5\text{Me}_5\text{)_2}^*$, and $\text{Fe(HB(pz)_2)}^*$ ($\text{pz} = \text{pyrazolyl}$) in liquid SO$_2$ was investigated. All three species show one oxidation wave and one reduction wave corresponding to production of the $2^+$ and neutral forms, respectively. While $\text{Fe(C}_5\text{H}_5\text{)_2}^*$ is stable in SO$_2$, the $2^+$ form reacts to block the electrode surface. For $\text{Fe(C}_5\text{Me}_5\text{)_2}^*$ and $\text{Fe(HB(pz)_2)}^*$ both the $1^+$ and $2^+$ forms are stable on the coulometric time scale. The neutral forms react with the solvent to generate the $1^+$ forms. Electrochemical data and visible absorption spectra, for $\text{Fe(C}_5\text{Me}_5\text{)_2}^{2+}$ and $\text{Fe(HB(pz)_2)}^{2+}$, and magnetic susceptibility results, for $\text{Fe(C}_5\text{Me}_5\text{)_2}^{2+}$, are reported.

Introduction

In a previous paper we showed that liquid SO$_2$ is a useful solvent for the generation and study of highly oxidized transition-metal complexes. In this paper we report the first observation of the two-electron-oxidation product of ferrocene, $\text{Fe(C}_5\text{H}_5\text{)_2}^{2+}$ (1), electrochemically generated in SO$_2$. In addition, stable solvate salts of the permethylated analogues, $\text{Fe(C}_5\text{Me}_5\text{)_2}^{2+}$ (2), and the related pyrazolyl borate complex, $\text{Fe(HB(pz)_2)}^{2+}$ (3) have been obtained and characterized. While electrochemical oxidation of $\text{Fe(C}_5\text{Me}_5\text{)_2}^*$ to the $2^+$ form in AlCl$_3$/1-butylpyridinium chloride melts has been reported previously, under similar conditions $\text{Fe(C}_5\text{H}_5\text{)_2}^*$ was oxidized in a multiple-electron irreversible process. The $2^+$ form of $\text{Fe(HB(pz)_2)}^*$ has not been previously reported. Our electrochemical studies suggest a closer relation (at least electronically) of the HB(pz)$_2$ ligand with the C$_5$Me$_5$ ligand rather than the previously proposed analogy with the unsubstituted C$_5$H$_5$ ligand.$^4$

Experimental Section

Electrochemical studies were performed in conventional single- and three-compartment cells by using previously reported procedures.$^{1,2}$

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Figure 1. Cyclic voltammograms at a Pt-disk electrode (0.024 cm²) in liquid SO₂ (−40 °C; scan rate 200 mV s⁻¹; 0.1 M (TBA)PF₆): (a) Fe(C₅H₅)²⁺, 7.5 mM; (b) Fe(C₅Me₅)²⁺, 10.2 mM; (c) Fe(HB(pz)₂)²⁺, 9.2 mM. Scan rates employed were from 50 to 500 mV/s. All potentials are reported against a Ag quasi-reference electrode (AgRE) of a type previously described. The magnetic susceptibility measurement, by the Evans method, was made on a Nicolet NT200 superconducting instrument. The shape factor for the superconducting field arrangement was substituted for that of an ordinary magnetic field arrangement used in the original equation developed by Evans.

Spectrophotometric measurements on a Cary Model 14 spectrophotometer were made with use of a vacuum-jacketed quartz cell (1-cm path length) of a design described elsewhere. The solution temperature was ca. −20 °C.

Tetra-n-butylammonium hexafluorophosphate (TBA)PF₆ and Fe(HB(pz)₂)²⁺ were prepared as previously described. Ferrocene (Alfa) and decamethylferrocene (Strem) were used as received. Fe(C₅Me₅)²⁺PF₆⁻ was prepared by I₂ (0.5 equiv) oxidation of Fe(C₅Me₅)₂ in acetone followed by the addition of a slight excess of NH₄PF₆. NH₄ was removed by filtration, and water was added. The green precipitate of Fe(C₅Me₅)²⁺PF₆⁻ was filtered, washed with water followed by dimethoxyethane and ether, and finally dried in vacuo. A solution of the product was tested for residual I⁻ by the addition of Ag⁺(aq), with a white precipitate of AgI indicating the need for additional recrystallization (acetone/ether).

Fe(HB(pz)₂)²⁺PF₆⁻ was prepared by an analogous procedure; however, 1.5 equiv of I₂ was required for complete oxidation, and multiple recrystallizations (acetone/ether) were needed to remove completely all traces of I⁻.

Results

Fe(C₅H₅)²⁺. The cyclic voltammogram (CV) of an electroregenerated 7.5 mM SO₂ solution (−40 °C) of Fe(C₅H₅)²⁺ at a Pt-disk electrode is shown in Figure 1a. The reduction wave with a cathodic peak potential (Epc) of 0.08 V corresponds to the Nernstian, one-electron, electrochemically reversible reduction to Fe(C₅H₅)₂. The difference between the anodic and cathodic peak potentials (ΔE = Epa - Epc) of 48 mV corresponds closely to that expected (44 mV) for a Nernstian couple at −40 °C. The oxidation wave (Epa = 1.79 V) shown in Figure 1a corresponds to a one-electron oxidation of Fe(C₅H₅)²⁺ to Fe(C₅H₅)³⁺. However, only on the first scan is a reasonably clear wave observed. The effect of repetitive scanning is shown in Figure 2. Fe(C₅H₅)³⁺ must be unstable.

Scan rates employed were from 50 to 500 mV/s. All potentials are reported against a Ag quasi-reference electrode (AgRE) of a type previously described. However, since some variability of this electrode was encountered, an internal reference of Fe(bpy)³⁺²⁻ (E⁰' = 0.74 V

Figure 2. Scans 1–14 of a repetitive-scan cyclic voltammogram of Fe(C₅H₅)²⁺ in liquid SO₂ (−40 °C; scan rate 200 mV s⁻¹; 0.1 M (TBA)PF₆) vs. AgRE for the 2+/3+ couple in SO₂⁻ used to confirm all potentials.
Table I. Summary of Voltammetric Parameters for the Oxidation and Reduction of Fe(C,H)\textsubscript{2}\textsuperscript{+}, Fe(C,Me\textsubscript{5})\textsuperscript{+}, and Fe(HB(pz)\textsubscript{4})\textsuperscript{+} in Liquid Sulfur Dioxide\textsuperscript{a}

<table>
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<th>diagnostic parameter</th>
<th>Fe(C,H)\textsubscript{2}\textsuperscript{+}</th>
<th>Fe(C,Me\textsubscript{5})\textsuperscript{+}</th>
<th>Fe(HB(pz)\textsubscript{4})\textsuperscript{+}</th>
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<tr>
<td></td>
<td>redn wave</td>
<td>oxidn wave</td>
<td>redn wave</td>
</tr>
<tr>
<td>(E_{pa}) or (E_{pc}), V vs. AgRE</td>
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<td>1.79</td>
<td>(-0.27)</td>
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<td>(\Delta E_{pa}), mV</td>
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<td>100</td>
<td>(~50)</td>
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<tr>
<td>(i_{pa}(0.1\text{V})/i_{pa}(0.1\text{V}))</td>
<td>1</td>
<td>0.8</td>
<td>(~1)</td>
</tr>
<tr>
<td>(i_{pa}(0.1\text{V})/i_{pa}(0.1\text{V}))</td>
<td>47</td>
<td>36</td>
<td>(~17)</td>
</tr>
<tr>
<td>diffusion coeff, cm\textsuperscript{2} s\textsuperscript{-1}</td>
<td>(8.9 \times 10^{-6})</td>
<td>(9.8 \times 10^{-6})</td>
<td>(6.1 \times 10^{-6})</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 0.1 M (TBA)PF\textsubscript{6}; \(T = -40\) °C; Pt working electrode area 0.023 cm\textsuperscript{2}. \(b\) \(T = -30\) °C; Pt working electrode area 0.017 cm\textsuperscript{2}. \(c\) From reduction wave. \(d\) From oxidation wave.

Figure 3. Absorption spectra in liquid SO\textsubscript{2} at ca. -20 °C of (--) Fe(HB(pz)\textsubscript{4})\textsuperscript{2+} (\(\tau_{max} \geq 10^{-6}\) \(\mu\)s) and (--) Fe(C,Me\textsubscript{5})\textsuperscript{2+} (\(\tau_{max} \approx 2 \times 10^{-6}\) \(\mu\)s).

The decomposition product must produce a film on the electrode surface that partially blocks the electrode reactions at potentials of the 1+/2+ wave. Decomposition of the 2+ form is apparent even on the first scan, since for the 1+/2+ couple the anodic peak current, \(i_{pa}\), for the oxidation wave is only 80% of the cathodic peak current, \(i_{pc}\), for the 1+/0 reduction wave. The electrode surface could be partially regenerated by pulsing into the cathodic background. Similar behavior was observed when a glassy-carbon electrode was used. Essentially identical waves were observed, when neutral Fe(C,H)\textsubscript{2} was the starting material. The cyclic voltammetric results are summarized in Table 1.

Fe(C,Me\textsubscript{5})\textsuperscript{2+}. The CV of a 10.2 mM SO\textsubscript{2} solution of Fe(C,Me\textsubscript{5})\textsuperscript{2+} at a Pt-disk electrode is shown in Figure 1b. The oxidation wave at \(E_{pa}\) = 1.34 V is analogous to the oxidation wave of Fe(C,H)\textsubscript{2}\textsuperscript{+}, but the process now corresponds to a Nernstian, one-electron, electrochemically reversible process without any decomposition or film formation on the electrode surface.

Figure 4. Cyclic voltammogram of 6.4 mM Fe(C,Me\textsubscript{5})\textsuperscript{2+} at slower scan rate (20 mV s\textsuperscript{-1}) and increased temperature (-30 °C) (* = Fe(C,Me\textsubscript{5})\textsuperscript{4+/3+} couple).

N\textsubscript{2} as shown by cyclic voltammetry after refilling the cell. Unfortunately, separation of the dication from the supporting electrolyte could not be achieved; solvents (MeCN, CH\textsubscript{2}Cl\textsubscript{2}, THF, dimethoxyethane) that might be used to extract the supporting electrolyte or solvent impurities decomposed the complex.

The reduction wave for Fe(C,Me\textsubscript{5})\textsuperscript{2+} (\(E_{pc} = -0.37\) V) shown in Figure 1b corresponds to the formation of neutral Fe(C,Me\textsubscript{5})\textsubscript{2}. However, the wave is at the edge of the cathodic background for SO\textsubscript{2} reduction at Pt so that both the SO\textsubscript{2} and the Fe(C,Me\textsubscript{5})\textsuperscript{2+} reductions contribute to the current. Similarly, the return oxidation wave for Fe(C,Me\textsubscript{5})\textsubscript{2} also overlaps with the return oxidation wave for the reduced SO\textsubscript{2}. The reduction of SO\textsubscript{2} is quasi-reversible at a Pt electrode under these conditions. Resolution of the two processes can be achieved by increasing the temperature and decreasing the scan rate to the point where the solvent reduction is nearly reversible. Such a scan is shown in Figure 4, and the Fe(C,Me\textsubscript{5})\textsuperscript{4+/3+} couple can now be clearly resolved at a potential more positive than that of the solvent background process. Because the potential of the Fe(C,Me\textsubscript{5})\textsuperscript{4+/3+} couple is very near that for the SO\textsubscript{2} reduction process, the concentration of SO\textsubscript{2} is large and the bulk reduced SO\textsubscript{2} undergoes an irreversible coupling reaction.\(^{10}\) Oxidation of neutral Fe(C,Me\textsubscript{5})\textsubscript{2} by SO\textsubscript{2} (neat) should occur. Indeed a 4.4 mM solution of Fe(C,Me\textsubscript{5})\textsubscript{2} in SO\textsubscript{2} gives a CV essentially identical with that of the 1+ form. Only small residual currents positive of the 1+/0 couple were found, and CPC at 1 V gave a green solution of Fe(C,Me\textsubscript{5})\textsuperscript{4+/3+} with an \(n_{\text{app}}\) of only 0.24. The irreversible reactions of the reduced solvent on a coulometric time scale are indicated by the fact that the primary solvent reduction products are no longer present to be reoxidized at the electrode after electrolysis. These reaction products interfere with the oxidation of the Fe(C,Me\textsubscript{5})\textsuperscript{2+}, probably via reaction with Fe(C,Me\textsubscript{5})\textsuperscript{2+} to film the electrode, since attempted CPC at potentials sufficient to

generate the 2+ form gave initial high currents that fell rapidly to nearly zero values in seconds. This contrasts to the clean CPC oxidation found when a solution of fresh Fe(C₅Me₅)⁺⁺⁺ was oxidized.

Fe(HB(pz)₃)⁺⁺⁺. The cyclic voltammogram of a 9.2 mM solution of Fe(HB(pz)₃)⁺⁺⁺ at a Pt-disk electrode is shown in Figure 1c. The oxidation wave for Fe(HB(pz)₃)⁺⁺⁺ at 1.68 V shown in Figure 1c corresponds to a Nernstian, one-electron, reversibly process (ΔEₚ = 48 mV). However, some bulk-oxidation of neutral Fe(HB(pz)₃)₂⁺ by SO₂ occurs, since CPC oxidation of a 4.1 mM solution of Fe(HB(pz)₃)⁺⁺⁺ at 1 V and 40 °C produced a solution of the 1⁺ form and yielded nₒᵤₚ value of only 0.56. Partial oxidation by SO₂ is predicted on the basis of the potential and concentrations. As with Fe(C₅Me₅)²⁺, the oxidation of Fe(HB(pz)₃)⁺⁺⁺ by SO₂ produces products that prevent controlled-potential coulometric production of the 2⁺ form from solutions prepared from the neutral species.

The oxidation wave for Fe(HB(pz)₃)⁺⁺⁺ at Eₒ = 1.68 V shown in Figure 1c corresponds to a Nernstian, one-electron, process. CPC of the above 9.2 mM Fe(HB(pz)₃)⁺⁺⁺ solution at 2 V gave nₒᵤₚ = 0.99. A CV of the resulting solution is shown in Figure 5. Although the waves are close to the potentials expected from the 1⁺ solutions, their shapes and intensities are not those for simple diffusion-controlled processes. Instead, the shape of the first reduction wave and return oxidation wave is characteristic of a surface-confined process; ΔEₚ is nearly zero and the peak half-widths are about 100 mV (close to the 0 and 70 mV values expected for a surface-confined species at -40 °C). The nature of the surface species is not known, although the similarity of the redox potentials to those of the solution species suggest a closely related structure. If the surface reduction wave at 1.64 V involves one electron per center and each center has a diameter of 2 nm, a coverage of ca. 120 monolayers is calculated from the area under the wave.

Interestingly, no reduction of solution species (i.e., the 2⁺ form) occurs until the potential of the 1⁺/0 couple is reached, where a diffusional solution wave is observed. Surprisingly, a large Pt-gauze electrode does not seem to be similarly filmed, since the 2⁺ form is reduced back to the original Fe(HB(pz)₃)⁺⁺⁺ in a CPC experiment at the expected potentials (nₒᵤₚ = 0.97 at 1 V). The CV of the reduced solution showed poorly defined broad waves. By pulsing into the cathodic background, we could obtain a CV resembling that of the original Fe(HB(pz)₃)⁺⁺⁺ solution, but with broader waves. Thus, Fe(HB(pz)₃)⁺⁺⁺ is stable on the CPC time scale (4 h) at -40 °C but must slowly lead to the formation of a film or layer on the electrode.

The absorption spectrum of the 2⁺ form is shown in Figure 3. Only a lower limit for the maximum extinction coefficient (~10⁶) in the range of wavelengths could be obtained because of extensive decomposition of the complex to the 1⁺ form at the temperature of the cell (-20 °C). Isolation of the 2⁺ form was not possible even as a mixture with the supporting electrolyte. A dark red product containing mostly the 1⁺ form was always obtained. Unfortunately, the magnetic susceptibility of the 2⁺ form could not be measured, because the complex reacts with the C₆H₆ used as a reference standard.

Discussion

The standard potentials and other data for the couples are listed in Table I. The effect of the electron-donating methyl groups in the Fe(C₅R₅)₂ pair is evident both in the negative shift of the peak potentials of the 0/1⁺ and 1⁺/2⁺ couples and the increased stability of the 2⁺ form upon methyl substitution. This effect has previously been observed for the 0/1⁺ couple in the Fe(C₅Me₅)₂⁺ as well as the Cr, Co, and Ni metalloenes. Fe(C₂H₅)₂⁺ has not been previously observed. Oxidation of Fe(C₂H₅)₂⁺ in AlCl₃/1-butylpyridinium chloride melts under the same conditions where Fe(C₅Me₅)₂⁺ was observed gave only a multiple-electron irreversible wave.

The similarities in the electronic and coordination properties of the HB(pz)₃ and C₂H₅ ligand have been noted, as has an increased thermal and chemical stability of HB(pz)₃ complexes over analogous C₂H₅ complexes. Similarly, C₅Me₅ complexes are more stable than the C₂H₅ analogues. This suggests that the HB(pz)₃ ligand is more closely related to the C₅Me₅ ligand than to the C₂H₅ ligand. Consistent with this, the

Adjacent Methyl to Remote Methyl Isomerization of (4-Methylimidazole)pentaamminecobalt(III)1

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Received August 7, 1982

Isomers of (4-methylimidazole)pentaamminecobalt(III) have been isolated as chloride salts with the methyl group of the imidazole directed away from the five NH3 ligands (remote = R) and near the NH3 ligands (adjacent = Ad). Isomers have been assigned by a separate X-ray diffraction study. Isomers have been characterized by 1H NMR spectra showing shifts (ppm) relative to the free ligand (L) as follows: 4-CH3 Ad = 2.22, R = 2.33, L = 2.27; 5-C5H5 Ad = 7.08, R = 7.78, L = 7.65; C5-H Ad = 6.73 (C5-H), L = 6.77. In Tris or pyridinium buffers two paths are found for the isomerization of Ad to R. One path (k1 = (5.83 ± 2.18) × 104 s−1) is attributed to the isomerization of the parent 4-methylimidazole species Ad. A second path, first order in [OD−], is attributed to the imidazolato form Ad-H.

The activation parameters for the Ad to R path are

- k1 = 3.19 ± 0.07 M−1 s−1
- ΔHH° = 32.4 ± 4.1 kcal/mol
- ΔS* = 16.8 ± 11.7 eu

A mechanism is presented, suggesting a largely dissociative transition state. Comparisons are made to the linkage isomerization of (NH3)2CoX4+ coordinated to ONO− and N2 of the 5-methyltetrazolato ligand. While the isomerization of the 5-methyltetrazolato ligand is faster by 105 relative to that for 4-methylimidazole, the anion forms favor the 4-methylimidazolato isomerization by a factor of 400 vs. the 5-methyltetrazolato case. The difference is attributed to different basicity of the lone electron pairs of these ligands. The pKa's of (NH3)2CoX4+ have been found at 25.0 °C and μ = 0.10 and are as follows (X, pKα): imidazole, 9.99; 2-methylimidazole, 10.67; 4-methylimidazole (Ad), 10.46; 4-methylimidazole (R), 10.70. The acid dissociation constants of R and Ad were studied as a function of temperature, yielding values of ΔHH°, ΔS* as follows: (Ad) 17.7 ± 0.5 kcal/mol, 11.2 ± 1.6 eu; (R) 15.4 ± 0.6 kcal/mol, 2.5 ± 1.8 eu. The values of ΔHH° are within a kilocalorie of imidazole's pyrrole pKa (17.6 kcal/mol) while the values of ΔS* are more favored by charge dispersal for Ad and R by about 18 to 10 eu, respectively.

Introduction

Ellis and Purcell recently reported the preparation of (5-methyltetrazolato)pentaamminecobalt(III) by the addition of N3− across the triple bond of (acetonitrilato)pentaamminecobalt(III) as shown in Scheme I.

A slow isomerization ensues from N3 to N2 coordination as would be anticipated for removing the strain associated with the adjacent methyl group's interaction with cis-NH3 ligands. A 3.0-kcal strain energy has been calculated from association constants of imidazole and 4,5-dimethylimidazole for Fe(CN)32+, where ligand repulsions ought to be of similar magnitude. Linkage isomerization reactions between donor atoms of the same kind are much more rare than those between different atoms as in NCS−, NO2−, CN−, etc., where electronegativity and structural factors provide a driving force for...