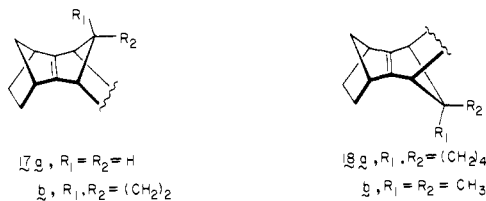


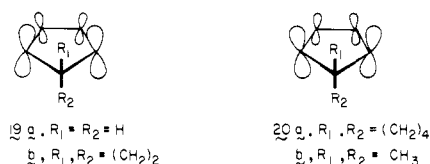
Without doubt, the carbon shielding effects operating in **12** are reversed relative to those in **8**!

The ^{13}C spectral data parallel exactly the differing stereoselectivities of dienophile capture exhibited by **8** and **12**. Thus, while **8** undergoes below-plane bonding to electron-deficient olefins with formation of adducts of type **17b**,^{15a} **12** engages in Diels-Alder



chemistry from its exo surface to give **18a**.^{15,25} The *gem*-dimethyl derivative **1** ($R_1 = R_2 = \text{CH}_3$) behaves comparably to **12**, but no technique has yet been found to distinguish between these substituents (^{13}C shifts: 23.55 and 22.92 ppm).

In isodicyclopentadiene, the influence of the norbornane σ -electron network is to cause disrotatory tilting within the subjacent π_s diene orbital toward the methano bridge (see **19**) with resultant



minimization of closed-shell antibonding interaction on the endo surface during dienophile approach.⁸ However, various theoretical calculations reveal this tilting to be critically dependent upon all σ orbital energies.²⁶ In fact, simple replacement of hydrogen atoms by alkyl groups at R_1 and R_2 (with $R_1 = R_2$) is adequate to reverse the mode of disrotation as in **20**. The exception is the spirocyclopropane **8**, where the high level of spiroconjugation²⁷ that develops as the result of strong π interaction with the symmetric Walsh orbitals of the three-membered ring²⁸ causes π_s once again to become tilted as in **19b**.¹⁵ Consequently, in the ground state of those dienes whose π -electron character is of type **19**, R_2 should experience greater shielding than R_1 . The reverse should be true in **20**, as observed experimentally. It follows that [4 + 2] cycloaddition occurs preferentially from the *less shielded* face of these dienes in order to profit from lower secondary antibonding influences along this pathway.

While ^{13}C shieldings are dominated chiefly by local paramagnetic electron currents,²⁹ local diamagnetic effects make the more important contribution to ^2H chemical shifts.³⁰ These differences may account for the spectral parameters of **2-4**.³¹

Registry No. 1 ($R, R_2 = \text{H}$), 6675-72-5; **2**, 81897-83-8; **3**, 81897-84-9; **4**, 81897-85-0; **5a**, 81969-70-2; **5b**, 81897-86-1; **6a**, 81897-87-2; **6b**, 81967-92-2; **7a**, 81897-88-3; **7b**, 81967-93-3; **8**, 81897-89-4; **9a**, 81897-90-7; **9b**, 81897-91-8; **9c**, 81967-94-4; **10**, 81897-92-9; **11**, 81967-95-5; **12**, 81897-93-0; **13**, 81897-94-1; **14**, 81897-95-2; **15**, 81897-96-3; **16**, 81897-97-4.

(25) Exceptions to this behavior are sometimes encountered with those dienophiles, e.g., dimethyl acetylenedicarboxylate and *N*-methyltriazaolinedione, that possess a second π bond or nonbonded electron pairs orthogonal to that π bond which constitutes the seat of reaction. The consequences of these secondary electronic perturbations will be discussed elsewhere.

(26) Gleiter, R.; Böhm, M. C., private communication.

(27) Staley, S. W.; Howard, A. E.; Harmony, M. D.; Mathur, S. N.; Kattija-Ari, M.; Choe, J.-L.; Lind, G. *J. Am. Chem. Soc.* **1980**, *102*, 3639 and references cited therein.

(28) Gleiter, R.; Heilbronner, E.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 1029.

(29) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1980; Chapter 2.

(30) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; Chapter 2-2.

(31) We are indebted to the National Cancer Institute (Grant CA-12115) for their generous financial support of this program.

Electrochemical Preparation of a Prussian Blue Analogue: Iron-Ruthenium Cyanide

Kingo Itaya,* Tatsuaki Ataka, and Shinobu Toshima

Research Institute of Electrical Communication
and Department of Applied Chemistry

Faculty of Engineering

Tohoku University, Sendai 980, Japan

Received December 23, 1981

Recent reports by Neff et al. have shown a method of preparation of Prussian blue (PB) on platinum and gold electrodes based on a chemical method.^{1,2} We disclosed very recently an electrochemical method of synthesis for the preparation of thin films of PB³ and have discussed the electron-transfer reactions and the possibilities for application in electrochromic displays.^{3,4} The crucial point for the preparation of PB films in both the chemical and the electrochemical methods is that a ferric ferricyanide mixture obtained by mixing solutions of ferric ion, Fe^{3+} , and of ferricyanide ion, $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$, is a clear solution where no precipitate is formed for several hours. Other mixing combinations lead immediately to heavy precipitates (gels) that have been called Prussian blue, Turnbull's blue, and Prussian white (Everitt's salt), depending on the valency values of the iron ions used.^{5,6} Recently, Siperko and Kuwana obtained a copper hexacyanoferrate film on a glassy carbon electrode based on dissolution of copper layers on the substrate.⁷

We disclose here a method for the preparation of thin films of ferric ruthenocyanide, $\text{Fe}_4^{3+}[\text{Ru}^{\text{II}}(\text{CN})_6]_3$, by means of an electrochemical reduction method and discuss the spectroelectrochemical results. Precipitation reactions for ruthenocyanide ion, $\text{Ru}^{\text{II}}(\text{CN})_6^{4-}$, and ruthenicyanide ion, $\text{Ru}^{\text{III}}(\text{CN})_6^{3-}$, are quite similar to those of ferric and ferrocyanide ions.^{8,9} Both ferricyanide and ruthenicyanide yield red-brown solutions, but no precipitates, with ferric ion.⁹ This result strongly encouraged us to extend the method employed in our previous paper^{3,4} for the preparation of films of iron ruthenocyanide mixed-valency complexes.

The ruthenicyanide solutions used here were prepared by adding lead peroxide, PbO_2 , to a solution of 1 mM $\text{K}_4\text{Ru}(\text{CN})_6$, obtained from the Soekawa Chemical Co., in 0.01 M H_2SO_4 . A fresh solution of reagent grade $\text{Fe}_2(\text{SO}_4)_3$ (1 mM) and $\text{K}_3\text{Ru}(\text{CN})_6$ (1 mM) was prepared by mixing solutions of each. The electrodes, SnO_2 , Pt, or glassy carbon, immersed in the above solution, were cathodically polarized under galvanostatic conditions by using a current density of about $20 \mu\text{A}/\text{cm}^2$. A large platinum foil was used as a counterelectrode. The purple due to the formation of ruthenium purple (RP), $\text{Fe}_4^{3+}[\text{Ru}^{\text{II}}(\text{CN})_6]_3$,^{5,10} can be seen right from the beginning of the electrolysis. This behavior is basically the same as observed in the preparation of PB reported previously. However, the current efficiency for the deposition of RP was far below the value of 100% obtained in the case of PB.

Figure 1 shows cyclic voltammograms of an RP-modified Pt electrode in 0.5 M K_2SO_4 adjusted to pH 4.0 with sulfuric acid. The amount of RP ($3 \text{ mC}/\text{cm}^2$) was estimated from a coulometric curve measured during the potential scan from 0.6 to -0.2 V vs. SCE (saturated calomel electrode). The peak potentials of the reductive and oxidative waves are 0.22 and 0.25 V vs. SCE, which are slightly dependent on the scan rate. Although the peak currents are directly proportional to the scan rate up to 50 mV/s, distortion of the wave is observed at higher scan rates. It is an

* Research Institute of Electrical Communication.

(1) Neff, V. D. *J. Electrochem. Soc.* **1978**, *125*, 886.

(2) Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* **1981**, *85*, 1225.

(3) Itaya, K.; Shibayama, K.; Akahoshi, H.; Toshima, S. *J. Appl. Phys.* **1982**, *53*, 804.

(4) Itaya, K.; Ataka, T.; Toshima, S., submitted for publication.

(5) Ludi, A.; Güdel, H. U. *Struct. Bonding (Berlin)* **1973**, *14*, 1.

(6) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(7) Siperko, L. M.; Kuwana, T., submitted for publication.

(8) Gmelin, "Handbuch der anorganischen Chemie"; 8th ed.; System Verlag Chemie G.m.b.H.: Berlin, 1932; No. 59, Part B, pp 643-652.

(9) DeFord, D. D.; Davidson, A. W. *J. Am. Chem. Soc.* **1951**, *73*, 1469.

(10) Robin, M. B. *Inorg. Chem.* **1962**, *1*, 337.

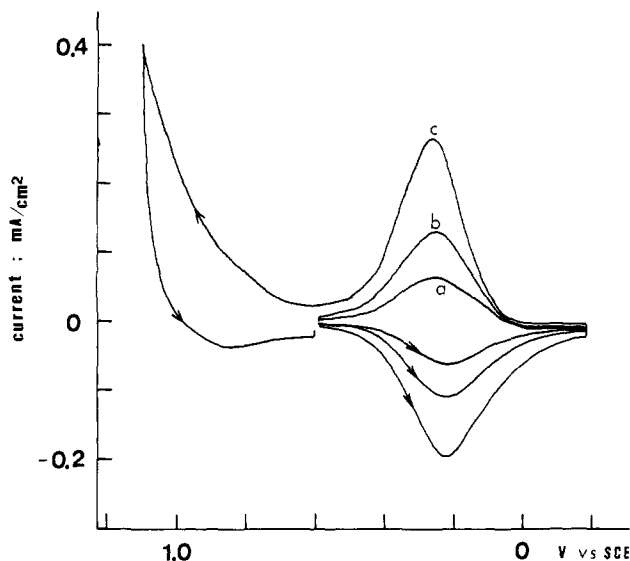
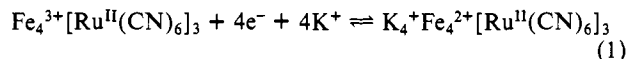


Figure 1. Cyclic voltammograms of an iron-ruthenium cyanide modified Pt electrode with 3 mC/cm² as the total charge consumed in the reduction in a solution of 0.5 M K₂SO₄ (pH 4.0). The scan rates of the electrode potential were (a) 5 mV/s, (b) 10 mV/s, and (c) 20 mV/s.

important result that the peak potentials obtained here are nearly equal to those observed in the reduction of PB.¹⁻⁴ This indicates that the Coulombic interactions as well as the electron-exchange interactions in the RP crystal are almost the same as those in PB with respect to the high-spin iron ions. The electron-transfer mechanism in RP crystal can be formulated as follows by assuming the formula Fe₄³⁺[Ru^{II}(CN)₆]₃.⁵



As is observed at the PB electrode,^{2,4} not only K⁺ ions but also NH₄⁺, Rb⁺, and Cs⁺ ions can be expected to transport through the crystal of RP because of its open lattice with a cell constant of 10.3 Å.⁵

It has been previously reported that the oxidation of PB occurs at about 0.9 V vs. SCE, yielding Berlin green.²⁻⁴ However, no distinct oxidation wave is observed for RP, as shown in Figure 1. A shoulder observed at 0.8 V might be due to the oxidation of the ruthenium ions in the crystal. It is noteworthy that a fairly large background current commencing at about 1.0 V is observed in the anodic scan of electrode potential. We believe that this large background current involves oxygen evolution. It is well known that the mixed oxide of ruthenium electrodes exhibit the lowest overpotential for oxygen evolution.¹¹ If the anodic background as shown in Figure 1 is due to oxygen evolution, the electrode prepared here should be one of the best catalysts for oxygen evolution. The electrochemistry of the RP electrode has been examined in a 1.0 M KCl solution (pH 4.0). Again, a large anodic background current commenced at 0.8 V. In this case, chlorine evolution might have occurred. Exactly the same results were obtained at RP-modified SnO₂ and glassy carbon electrodes.

Figure 2 shows the absorption spectrum of the film at a SnO₂ electrode obtained in situ in a 1.0 M KCl solution (pH 4.0). The spectrum observed at 0.6 V can be attributable to the intervalence charge-transfer band in Fe₄³⁺[Ru^{II}(CN)₆]₃, i.e., Fe³⁺...N-C...Ru^{II} → Fe²⁺...N-C...Ru^{III}.^{5,6} Robin reported a similar spectrum with a colloidal form of RP prepared by adding a stoichiometric amount of Fe³⁺ to a Ru(CN)₆⁴⁻ solution.¹⁰

The spectrum observed at -0.2 V shows no band in the visible region. The purple is completely bleached out during the potential scan from 0.6 to -0.2 V. Continuous cyclic scans of the potential between 0.6 and -0.2 V resulted in no degradation of the wave up to 10⁵ cycles.

(11) Yeo, R. S.; Orehtsky, J.; Visscher, W.; Srinivasan, S. *J. Electrochem. Soc.* **1981**, *128*, 1900.

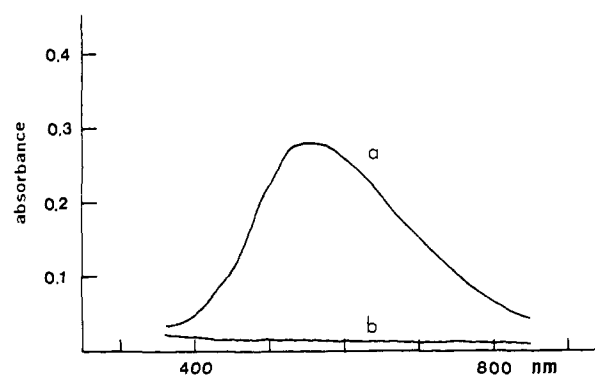


Figure 2. Absorption spectra obtained on a SnO₂ electrode with 3.1 mC/cm² of the iron-ruthenium cyanide at two different electrode potentials in 1.0 M KCl (pH 4.0): (a) at 0.6 V vs SCE; (b) at -0.2 V vs SCE.

Numerous applications to catalysis and electrochromism can readily be imagined from the results discussed above.

Acknowledgment. We appreciate the receipt of the preprint of ref 7 from Dr. T. Kuwana prior to publication. Helpful suggestions by Dr. R. M. De La Rue of Glasgow University are gratefully acknowledged.

Registry No. Fe₄³⁺[Ru^{II}(CN)₆]₃, 41898-61-7.

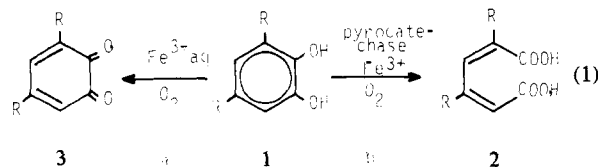
Ferric Nitritriacetate: An Active-Center Analogue of Pyrocatechase

Michael G. Weller* and Ulrich Weser

Physiologisch Chemisches Institut der Universität Tübingen
Anorganische Biochemie, 7400 Tübingen, West Germany

Received November 6, 1981

Pyrocatechase (catechol 1,2-dioxygenase, EC 1.13.11.1),¹ a nonheme iron(III) dioxygenase, catalyzes the intradiol ring cleavage of catechol **1** by dioxygen; both atoms of the O₂ are incorporated into the product, *cis,cis*-muconic acid (**2**) (eq 1b, R = H). The substrate catechol is known to be initially bound



to iron² and oxidized subsequently via a yet unknown mechanism. Recent comprehensive reviews on ferric dioxygenases are available.^{3,4}

However, with 3,5-di-*tert*-butylcatechol—chosen for the stability of its oxidation products—it was demonstrated that oxidation in the presence of Fe(III) ions selectively leads to the quinone **3**⁵ (eq 1a, R = *t*-Bu). Hitherto, only a mixture of 3,5-di-*tert*-butylcatechol with Fe²⁺, bpy, and pyridine in THF gave some muconic acid besides the quinone as the main product.⁶ Catechol

(1) Hayaishi, O.; Katagiri, M.; Rothberg, S. *J. Am. Chem. Soc.* **1955**, *77*, 5450-5451. Hayaishi, O.; Nozaki, M.; Abbott, M. T. "The Enzymes"; Boyer, P. D., Ed.; Academic Press; New York, 1975; Vol. XII, pp 119-189. Nozaki, M.; Ishimura, J. "Microbial Iron Metabolism"; Neilands, J. B., Ed.; Academic Press; New York, 1975; pp 417-444.

(2) Fujisawa, H.; Hiromi, K.; Uyeda, M.; Okuno, S.; Nozaki, M.; Hayaishi, O. *J. Biol. Chem.* **1972**, *247*, 4422-4428.

(3) Nozaki, M. *Top. Curr. Chem.* **1979**, *78*, 145-186.

(4) Que, L., Jr. *Struct. Bonding (Berlin)* **1980**, *40*, 39-72.

(5) Grinstead, R. R. *Biochemistry* **1964**, *3*, 1308-1314. Mentasti, E.; Pelizzetti, E.; Saini, G. *J. Chem. Soc., Dalton Trans.* **1973**, 2909-2914.