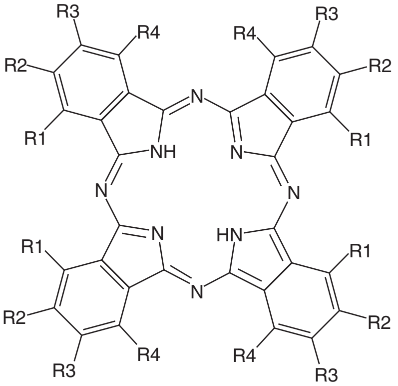
Electron-Donating or -Withdrawing Nature of Substituents Revealed by the Electrochemistry of Metal-Free Phthalocyanines

R. Li, X. Zhang, P. Zhu, D.K.P. Ng, N. Kobayashi and J. Jiang, Inorg. Chem. 45 (2006) 2327.



One of the most common applications of cyclic voltammetry is to examine the effects of different substituents (e.g., alkyl groups, phosphines, etc.) on the redox potentials of organic molecules and transition-metal-based coordination compounds. The authors of this article used the BASi CV-50W to investigate the electronic effects of a number of functional groups (including alkyl, alkoxy and phenyloxy groups) coordinated at positions R1 - R4 of metal-free phthalocyanines. All compounds showed two quasi-reversible one-electron oxidations and up to four quasi-reversible one-electron reductions. For some derivatives, the first oxidation and first reduction were shifted by the same amount relative to the unsubstituted molecule, so there was no change in the HOMO-LUMO gap. For other derivatives, the first oxidation and first reduction were shifted by different amounts, leading to significant variations in the HOMO-LUMO gap. These variations in the frontier orbitals were similar to those found from the electronic absorption spectra and from molecular orbital calculations.

Efficient Electronic Communication between Two Identical Ferrocene Centers in a Hydrogen-Bonded Dimer

H. Sun, J. Steeb and A.E. Kaifer, J. Am. Chem. Soc. 128 (2006) 2820.

Intra-molecular communication between two redox-active sites is currently a topic of considerable interest. Such communication typically requires linkage structures such as unsaturated functional groups or metal-metal bridges. In this study, a ferrocene derivative (i.e., electrochemically active) containing a quadruple hydrogen bonding motif was synthesized and its electrochemical properties were examined by cyclic voltammetry using a BASi 100B/W. Two reversible oxidations with similar peak currents separated by 390 mV were observed in methylene chloride. Acetonitrile was then added, and the peak current of the more positive oxidation decreased as the proportion of acetonitrile increased, until only the first oxidation was observed in 100% acetonitrile. This behavior is consistent with formation of a dimer in methylene chloride, with extensive electronic communication between the identical redox centers. Since the dimerization is achieved solely by hydrogen bonding, the addition of acetonitrile provides competition for the hydrogen bonds, thereby destabilizing the dimer. Separation of the peak potentials (and hence the extent of electronic communication) is comparable with that observed in some molecules (e.g., biferrocene) with covalent bonding between the redox centers.

Amperometric Assay for Aldose Activity: Antibody-Catalyzed Ferrocenylamine Formation

A. Sagi, J. Rishpon and D. Shabat, Anal. Chem. 78 (2006) 1459.

The aldol reaction is an important C-C bond formation reaction, and hence there is a need for catalysts to achieve it. In this article, it was shown that the conversion of a new ferrocene-aldol derivative (substrate) to ferrocenylamine (product) via a retro-aldol reaction could be used as screening assay for potential aldol catalysts. The redox properties of these two ferrocene derivatives were determined by cyclic voltammetry using a BASi CV-50W, and it was found that the oxidation potential of the product was about 150 mV lower than that of the substrate. Hence, by holding the working electrode at an appropriate potential (-30 mV vs. Ag/AgCl), concentration of the ferrocenylamine product could be selectively measured in the presence of the substrate. This amperometric assay was demonstrated using aldolase antibody 38C2 as the aldol catalyst, and the Michaelis-Menten constants determined by this method were in agreement with those reported for 38C2 with similar substrates.

An Adaptable Spectroelectrochemical Titrator: The Midpoint Reduction Potential of the Iron-Sulfur Centers in Lysine 2,3-Aminomutase

G.T. Hinckley and P.A. Frey, Anal. Biochem. 349 (2005) 103.

This article describes development of a spectroelectrochemical cell for use with a number of different spectroscopic methods. The novel feature of this cell was a detachable spectroscopic cell; that is, the electrolysis takes place in one compartment, and the electrolyzed sample is then transferred to another compartment, which can then be removed and analyzed in the appropriate spectrometer. Two experiments were reported to demonstrate use of this cell, both of which used a BASi epsilon™ electrochemical analyzer to electrolyze the sample prior to spectroscopic analysis. The first experiment measured the midpoint reduction potential of methyl viologen based on UV/vis spectroscopy, and the second used EPR to measure the midpoint reduction potential of the [4Fe-4S] active group in 2,3-aminomutase.

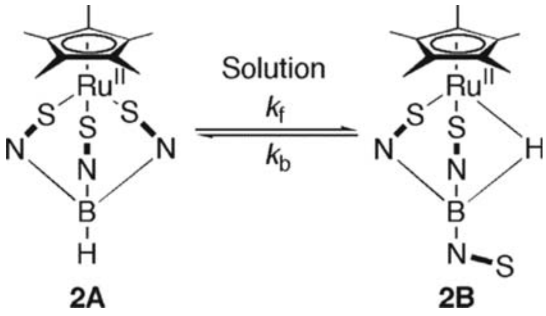
Continuous On-Line Monitoring of Extracellular Ascorbate Depletion in the Rat Striatum Induced by Global Ischemia with Carbon Nanotube-Modified Glassy Carbon Electrode Integrated into a Thin-Layer Radial Flow Cell

M. Zhang, K. Liu, K. Gong, L. Su, Y. Chen and L. Mao, Anal Chem. 77 (2005) 6234.

Ascorbate is frequently regarded as an interferant when analyzing physiological samples using electrochemical detection, since it is ubiquitous and easily oxidized. However, in this article, depletion of ascorbate was used to monitor physiological processes in the brain, particularly those involving reactive oxygen species. Since many neurochemically active molecules (e.g., catecholamines and their metabolites) are also readily oxidized, appropriate selectivity was required in order to determine ascorbate. This selectivity was achieved using single-walled carbon nanotube (SWNT)-modified glassy carbon electrodes which oxidized ascorbate at -50 mV (vs. Ag/AgCl), compared with +200 - +400 mV required for the oxidation of catecholamines and their metabolites. These electrodes also showed little fouling due to adsorption, providing good stability and reproducibility. This method was used for detection of ascorbate in rat brain with BASi microdialysis equipment for *in vivo* sampling using an on-line BASi flow cell and a BASi 100B/W for controlling applied potential and measuring current response.

Redox-Dependent Isomerization of Organometallic Ru^{II}/Ru^{III} Compounds Containing the Hydrotris(methimazolyl)borate Ligand: An Electrochemical Square Scheme Mechanism

S.L. Kuan, W.K. Leong, L.Y. Goh, and R.D. Webster, Organometallics 24 (2005) 4639.



This article details another example of a molecule that exists in two isomers, both redox-active. Therefore, there are four molecular species and their inter-conversion can be represented using the well-known "square scheme." In this example, a cyclopentadienyl ruthenium (Cp*Ru) complex with a tridentate ligand containing three sulfur binding sites was characterized by cyclic voltammetry. In the Ru(III) oxidation state, the dominant isomer (> 99%) had the tridentate ligand coordinated using all three sulfur groups (A), whereas the dominant isomer for Ru(II) (> 95%) had one of the sulfur groups displaced by an agostic B-H-Ru interaction (B). The isomerization kinetics were studied using both variable temperature and variable scan rate cyclic voltammetry experiments, and quantified using the BASi cyclic voltammetry simulation software DigiSim®. The rate of isomerizations were such that the kinetics could be studied using moderate scan rates (up to 50 V s^{-1}), and the inter-conversion of the Ru(II) isomers was also evident using variable temperature NMR.

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The War of the Soups and the Sparks: The Discovery of Neurotransmitters and the Dispute Over How Nerves Communicate By Elliot S. Valenstein, 256 pp, ISBN 0-231-13588-2, Columbia University Press, October 2005

This book was very widely reviewed in 2005. I was unable to resist it and was not at all disappointed. It is a wonderful perspective on a scientific challenge of signal transmission from neuron to neuron. Does it happen electrically? Or does it happen chemically? Is the synapse an electrical component or a chemical component?

At least as important as the science is the human story. The three primary actors in this play are Otto Loewi (1873-1961), Henry Dale (1875-1968) and Walter Cannon (1871-1945). There also is a large cast of other characters who played a role in moving the science forward and, in a few cases, backwards by intractable stubbornness. It is a fascinating tale and hard to imagine that anyone active in neuroscience would not want to read it.

For those of us who grew up in the industrialized, heavily funded science of 1960s higher education, it is quite interesting to read of the far smaller and informal struggles of academic research as the 19th century evolved into the 20th. A most fascinating aspect of this tale is how it is interwoven with corresponding colonial wars, World War I, anti-Semitism, World War II and all sorts of trouble that impacted research funding, priorities and even where one was allowed to live and do research without fear for one's life. When you think about it, this is still true today for a good 80% of humanity. (Peter T. Kissinger).

Churchill and America By Martin Gilbert, 503 pp, ISBN 0743259920, Free Press, October 2005

I am a confessed "Churchillophile," having a library of works by him and about him. (You know something about me when you learn that my ideal companions for a men's night out dinner would be Winston Churchill, Michael Faraday, Teddy Roosevelt, George Patton, Don Rumsfeld and Benjamin Franklin.) Today we would be celebrating the 300th anniversary of Franklin's birth, and all but Faraday would enjoy a cigar and a very stiff drink. I recommend this book because I can, but also because it relates so well to the volume reviewed above. Churchill (1874-1965) was a contemporary of the three protagonists in the above volume. His times were their times, and it is not possible to fully understand the advances of science without a broader connection to the period in which it was pursued.

Martin Gilbert has published many volumes on Churchill, each with a different theme. This one concentrates on his interactions with our side of the Atlantic, including travel logs of his various visits, beginning with a trip to New York in November of 1895 and a side excursion to Cuba (he was a lieutenant) where he was shot at without result and filed newspaper reports. It is interesting that today we have blogs from active military, an evolution from what even then was not forbidden communication. Interestingly, Churchill got paid for these dispatches and kept himself solvent (often barely) by writing for pay during his entire professional life. This volume gives reference to many contemporaries on both sides of the Atlantic and sets the stage for the special relationship Churchill believed existed among "English-speaking peoples" wherever they may be.

I am fascinated by human conflict, including the 30-year battle to achieve daylight saving time here in Indiana. When reading about Churchill, Loewi, Dale and Cannon I am quick to conclude that all the conflict we have today about global warming, the war on terror, elections in Italy and employment policies in France are variations on the same theme – power and control. Our species just thoroughly enjoys casting derision on those with whom we share DNA. We live in a world full of turmoil, but so did Churchill and it is fun to read all about it. (Peter T. Kissinger)

The Cutter Incident: How America's First Polio Vaccine Led to the Growing Vaccine Crisis
By Paul A. Offit, M.D., 256 pp, ISBN 0300108648, Yale University Press, September 2005

Harvey Wiley taught chemistry at Purdue University, rode a high-wheeler bicycle, started an Army company at Purdue and was a major player in the Pur[du]e Food and Drug Act of 1906. This book is a reminder of the troubles that occurred with a huge clinical trial on a Polio vaccine in 1955 and resulted in expansion of the legal concept of liability without negligence, which evolved further to virtually wipe out vaccine production in the USA. That cancer then invaded everything from asbestos law suits to playground equipment to gun manufacturing, and more directly to adverse events with all pharmaceuticals. Stretching even further, we are now at the point where everything is someone else's fault and nothing is our own fault or responsibility.

The problem here (as with asbestos) evolved from very primitive understanding of what was important in vaccine production, what needed to be controlled, how it should be controlled and then how it should be measured. We are still not quite there even today with the complexities of producing "biologicals" for commercial use, but we are much further along. We see good commercial evidence now of vaccines beginning to come back to the front burner of more pharmaceutical companies. I found this book to be a good reminder of my youth as well as a thought-provoking history of the first biotechnology products (vaccines) and the desperate times for parents when Polio was a common reality. (Peter T. Kissinger)

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