Electrochemistry

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The electrochemical control of oxidation and reduction processes in organic and inorganic systems is an area of extensive research in both academia and industry. Electrochemical techniques are extremely useful in generating interesting species in unusual oxidation states, or for producing reactive intermediates (as, for example in the reductive dimerization of vinyl cyanide in the Monsanto manufacture of Nylon 66), but provide little intrinsic structural information. To overcome this limitation, spectroscopic methods have frequently been used in conjunction with electrochemical methods in order to monitor the progress of a reaction and to obtain more detailed structural and mechanistic information. The in situ alliance of electrochemistry/spectroscopy is particularly valuable in situations where the species undergoing the redox process would not survive the transfer from an electrochemical to a spectroscopic cell, or in situations where it is essential that the spectroscopic analysis occur concurrently to the electrochemical generation, such as in kinetic studies. The focus of this research is developing and utilising spectroscopic techniques (including EPR, UV-VIS, FTIR and NMR) to study processes involving electron transfer, primarily in organic systems.

In situ Electrochemical-NMR Spectroscopy

NMR spectroscopy has the capacity for the structural identification of solution-phase species. However, despite widespread interest in both NMR spectroscopy and voltammetry, the compatibility problems that exist between the two procedures have made it extremely difficult to achieve an in situ combination, with few published attempts. The principal difficulty is the requirement that a metal electrode be located within the magnet of a NMR spectrometer, with the current flowing simultaneously to spectral acquisition. Recently, we have constructed a three-electrode, two-compartment cylindrical electrochemical cell for in situ operation in a 500 MHz 1H NMR spectrometer. The cell was designed around a standard 10 mm sample tube holder and is lowered into position within the magnet by height adjustable aluminum rods that support the wires connecting the potentiostat to the working, auxiliary and reference electrodes. The electrochemical cell functions under diffusion-controlled conditions in non spinning mode and is able to operate under variable temperature and oxygen-free regimes. The working electrode consists of a 10 nm thick gold film deposited onto the surface of a 7.49 mm OD diameter glass NMR tube that is located directly within the radio-frequency (RF) coils of the NMR probe. The NMR spectra were collected simultaneously to the current flowing during the electrolysis with typical NMR linewidths being approximately 2 Hz. The highly symmetrical nature of the cell design meant that probe tuning and gradient shimming changed minimally between each experiment, which allowed standard shim sets to be saved and recalled for later use, thereby greatly reducing the time taken for tuning processes. Insertion and removal of the cell from within the magnet is achieved within a few seconds, which combined with the rapid shimming process, makes the cell suitable for routine operation. The cell was used to study the in situ reduction of 9-bromoanthracene, 9-chloroanthracene and 4-bromobenzophenone in deuterated acetonitrile with tetrabutylammonium hexafluorophosphate as the supporting electrolyte.
The Redox Chemistry of α-Tocopherol (Vitamin E)

α-Tocopherol (α-TOH) is the most naturally abundant, extensively methylated, and biologically active of the four (α, β, γ and δ) structurally related phenolic compounds that are labelled vitamin E. α-TOH is thought to play an important role as an antioxidant in mammalian tissues by inhibiting the free radical chain autoxidation of polyunsaturated fatty acid esters (LH) in two principal steps. First, α-TOH reacts with an oxidised site on a lipid cell wall (LOO•) to yield a molecule of lipid hydroperoxide (LOOH) and the tocopheroxyl radical (α-TO•). Second, the α-TO• radical reacts with another LOO• radical so that overall one α-TOH molecule is able to inhibit two LOO• sites. To date, the important biological chemistry of vitamin E is thought to involve only the neutral compound (α-TOH) and phenoxyl radical (α-TO•).

However, electrochemical and spectroelectrochemical experiments performed in our laboratory have demonstrated the existence of several other forms of vitamin E that are linked through proton and electron transfers; the monocation radical (α-TOH+•), the dication (α-TOH2+) and the phenoxonium cation (α-TO+). Surprisingly, the phenoxonium cation was found to be very stable in dry organic solvents and readily undergoes a chemically reversible two-electron/one-proton (ECE) process with the neutral phenolic starting material. The interesting possibility that α-TO+ has biological significance is currently under investigation.

Electrochemistry and EPR Spectroscopy of Transition Metal Compounds Containing Bridging Thiolate Ligands

Various bi- and tri-metallic transition metal compounds with sulfur-containing ligands have been investigated using electrochemistry to probe the degree of electron delocalisation between the metal centres. Electrochemistry and EPR spectroscopy have been used to identify reversible homolytic S-S bond formation/cleavage in a pentamethylcyclopentadienyl ruthenium(III) thiolate-thioether system. (With L Y Goh, [National U Singapore])

http://rsc.anu.edu.au/research/webster.php