Practical Olefin Aziridination with a Broad Substrate Scope

T. Siu and A.K. Yudin, J. Am. Chem. Soc. 124 (2002) 530.

Although chemical redox reagents can be highly selective, many produce toxic by-products. In contrast, electrochemical redox reactions (i.e., reactions involving electron transfer at the surface of an electrode) generate fewer by-products, and selectivity can be achieved by using an appropriate redox potential. The aim of this study was to find an alternative method for the aziridination of olefins, since the standard method requires stoichiometric amounts of toxic lead(IV) oxidants. The first approach used catalytic amounts of lead(II) acetate at a potential of +1.60 V (the redox potential of lead(II) acetate). However, it was noted that a large overpotential was required for the direct oxidation of olefins at a platinum electrode, and hence aziridination of olefins could be achieved by direct electrochemical oxidation (i.e., in the absence of lead(II) acetate). The optimum applied potential for the aziridination of cyclohexene was +1.8 V (vs. silver pseudo-reference electrode). A number of other olefins could also be aziridinated, with yields between 42 and 93 %.

Superoxide Dismutase-Based Third-Generation Biosensor for Superoxide Anion

Y. Tian, L. Mao, T. Okajima and T. Ohsaka, Anal. Chem. 74 (2002) 2428.

Although glucose determination has been the focus of most electrochemical biosensor studies, a number of other physiologically important molecules have also been studied, including superoxide. In this study, selective detection of superoxide was realized through its highly-specific reaction with superoxide dismutase (SOD). The enzyme electrode used for this reaction consisted of a self-assembled layer of cysteine on the surface of a gold electrode, with the SOD immobilized on the cysteine layer. The cysteine layer also acts as a mediator for electron transfer reactions between SOD and the electrode. These electron transfer reactions allow both catalytic oxidation and reduction of superoxide by SOD. The performance of the SOD-based biosensor was therefore assessed under both anodic and cathodic conditions (applied potentials of +300 mV and -200 mV (vs. Ag/AgCl), respectively). The response of the biosensor was proportional to the rate of generation of superoxide over the range of 13 - 130 nM/min, with good sensitivity and a detection limit of a few nM. The stability of the electrode and the lack of interference from other physiologically important molecules were also promising.

Electrochemical Immunoassay Moving into the Fast Lane

N.J. Ronkainen-Matsuno, J.H. Thomas, H.B. Halsall and W.R. Heineman, Trends Anal. Chem. 21 (2002) 213.

The evolution of electrochemical immunoassays has resulted in significant improvements in assay times and detection limits. This review provides an excellent account of the important milestones in the development of this analytical method. Various electrochemical approaches for detecting analytes of interest are clearly described. The authors go into fundamental details of areas such as sandwich immunoassay and the development of paramagnetic beads. Other aspects described are the developments in reaction chambers, use of polystyrene cuvettes, hematocrit tubes and microcapillaries, non-specific absorption and micro total analysis systems with a special emphasis on the application of paramagnetic microbeads as antibody support surface.

Microbeads provide a way to separate the surface on which the primary antibody is immobilized from the reaction chamber, and this makes the system versatile. The ability to disperse throughout a solution due to their small size decreases the diffusional distances of reagents to the bead surface and results in a shorter assay time. Agitating the beads in solution further minimizes the slow diffusional processes. These and other attributes of this application have led to the extension of electrochemical immunoassay into automated microfluidic systems. Sandwich immunoassay with electrochemical detection has evolved from a process requiring several hours to give assay times less than 30 min. The work in this application continues.

Characterization and Reactions of Previously Elusive 17-Electron Cations: Electrochemical Oxidations of $(C_6H_6)Cr(CO)_3$ and $(C_5H_5)Co(CO)_2$ in the Presence of $[B(C_6F_5)_4]^-$

N. Camire, A. Nafady and W.E. Geiger, J. Am. Chem. Soc. 124 (2002) 7260

Previous attempts to study 17-electron radicals of "half-sandwich" complexes such as $(C_6H_6)Cr(CO)_3$ [**1**] and $(C_5H_5)Co(CO)_2$ [**2**] using electrochemical oxidation have been hindered by their reactivity with weak nucleophiles present in the solution, including the anions of the supporting electrolyte. In this study, the 17-electron radicals of **1** and **2** were stabilized by the presence of $[B(C_6F_5)_4]^-$, which is significantly less nucleophilic than conventional supporting electroyte anions such as ClO_4^- and PF_6^-. $\mathbf{1}^+$ was found to be stable in solution for at least one hour in the presence of $[B(C_6F_5)_4]^-$, whereas it decomposed rapidly in the presence of PF_6^-. Previous studies of **2** by cyclic voltammetry showed an irreversible oxidation; that is, $\mathbf{2}^+$ was unstable on the time scale of the cyclic voltammetry

experiment. In the presence of $[B(C_6F_5)_4]^-$, **2** showed a reversible oxidation by cyclic voltammograms at concentrations less than 0.3 mM. However, as the concentration increased, the wave broadened and resolved into two couples. On the basis of digital simulation using DigiSim®, it was proposed that the second wave was due to oxidation of the metal-metal dimer $[(C_5H_5)_2Co_2(CO)_4]^+$, which is formed by reaction of **2** and $\mathbf{2}^+$.

Unusual Response in Mediated Biosensors with an Oxidase / Peroxidase Bienzyme System

R. Matsumoto, M. Michizuki, K. Keno and T. Ikeda, Anal. Chem. 74 (2002) 3297.

One problem inherent in the design of enzyme sensors based on the mediated electron transfer of oxidase enzymes is the competition between mediated oxidation and reoxidation by oxygen. This study reports the unusual current response of an oxidase/peroxidase bienzyme sensor for glucose that was based on the detection of hydrogen peroxide (by mediated electron transfer reactions of the peroxidase) that was generated by reaction of glucose and oxygen with glucose oxidase. At low glucose concentrations (0.5 mM), the current-time transient (measured using a CV-50W) showed the expected sigmoidal response. However, at higher concentrations (5 mM), a peak-shape current transient was observed. In addition, the relationship between the steady-state current response and the glucose concentration was linear only at low concentrations, and the calibration curve was peak-shaped at higher concentrations. This was attributed to depletion of oxygen in the enzyme layer at higher concentrations, which, combined with presence of the electron transfer mediator for the peroxidase reaction, decreased the hydrogen peroxide concentration in this layer. This proposal was supported by the digital simulation of the current-time transients. On the basis of these results, it was proposed that a linear response would be obtained by decreasing the amount of glucose oxidase in the sensor, and this was found to be the case.

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