ALKYLATION OF [2,2′-([2,2′-BIPYRIDINE]-6,6′-DIYL)BIS-[PHENOLATO]-N,N′,O,O′]NICKEL(II)

Danielle M. Goken and Dennis G. Peters

Department of Chemistry, Indiana University,
Bloomington, Indiana 47405 (U.S.A.)

In our laboratory recent work, focusing on the use of nickel(II) salen and cobalt(II) salen to reduce various environmentally hazardous alkyl halides, has indicated that the salen ligand is chemically modified during the course of these reductions.[1] Such modifications ultimately destroy the catalyst and cause all catalytic activity to cease. In an effort to better understand what factors contribute to the overall stability of electrochemical catalysts, we extended our studies to include [2,2′-([2,2′-bipyridine]-6,6′-diyl)bis[phenolato]-N,N′,O,O′]nickel(II), because of its increased chemical stability relative to its nickel(II) salen analogue.

Various spectroscopic and electrochemical techniques have been utilized to examine this system. These results demonstrate that [2,2′-([2,2′-bipyridine]-6,6′-diyl)bis-[phenolato]-N,N′,O,O′]nickel(II) is a poor catalyst.[2,3] However, when this system was examined by means of controlled-potential electrolysis, we made some interesting observations.

Figures 1 and 2 show high-performance liquid chromatograms for solutions containing the catalyst before and after bulk reduction with 30 equivalents of 1-iodooctane, respectively. At the end of an electrolysis, none of the original [2,2′-([2,2′-bipyridine]-6,6′-diyl)bis-[phenolato]-N,N′,O,O′]nickel(II) remains in solution, but several small peaks with long retention times are observed. This indicates that the catalyst has been converted into a variety of new species. Additionally, product distributions, voltammetry, ultraviolet–visible spectrophotometry, ^{1}H NMR spectroscopy, and mass spectrometry suggest that the [2,2′-([2,2′-bipyridine]-6,6′-diyl)bis[phenolato]-N,N′,O,O′]nickel(II) is alkylated multiple times during the reduction of a simple alkyl halide and, consequently, all catalytic activity is lost.

We have attempted to prevent this modification by adding a proton donor, 1,1,1,3,3,3-hexafluoro-2-propanol or acetic acid, to the electrolysis solution. Addition of a proton donor or hydrogen atom donor has been shown to improve turnover in other electrolyses.[4,5] Other attempts aimed at the prevention of catalyst modification will also be described.

Previous studies with nickel(II) salen and cobalt(II) salen only provided circumstantial evidence for modification of the catalysts.[1] We believe that the increase in aromaticity of the ligand is responsible for the dramatic amount of modification found in the [2,2′-([2,2′-bipyridine]-6,6′-diyl)bis[phenolato]-N,N′,O,O′]nickel(II) system compared to that of nickel(II) salen. Analogous examinations of other catalytic systems will be described.

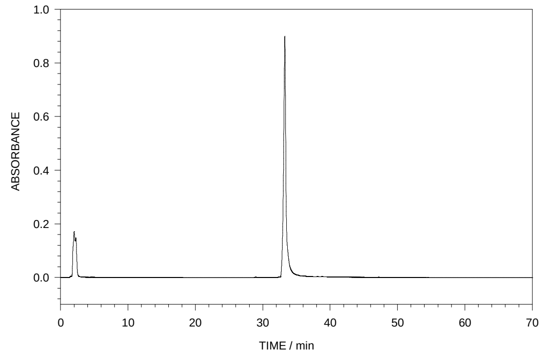

Figure 1. High-performance liquid chromatogram of a solution of 1.00 mM [2,2′-([2,2′-bipyridine]-6,6′-diyl)bis-[phenolato]-N,N′,O,O′]nickel(II) in dimethylformamide containing 0.1 M tetramethylammonium tetrafluoroborate recorded prior to electrolysis.

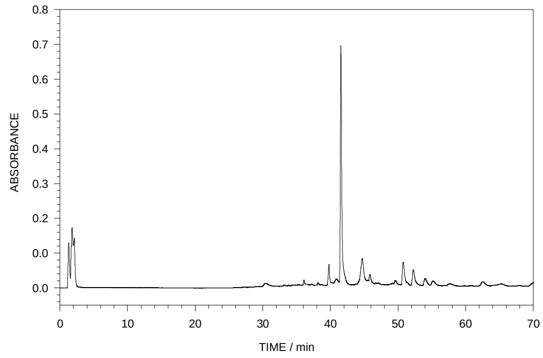

Figure 2. High-performance liquid chromatogram of a solution of 1.00 mM [2,2′-([2,2′-bipyridine]-6,6′-diyl)bis-[phenolato]-N,N′,O,O′]nickel(II) in dimethylformamide containing 0.1 M tetramethylammonium tetrafluoroborate recorded after bulk reduction of 30 equivalents of 1-iodooctane.

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2. J. Y. Becker, J. B. Kerr, D. Pletcher, and R. Rosas, *J. Electroanal. Chem.*, **1981**, *117*, 87.
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