

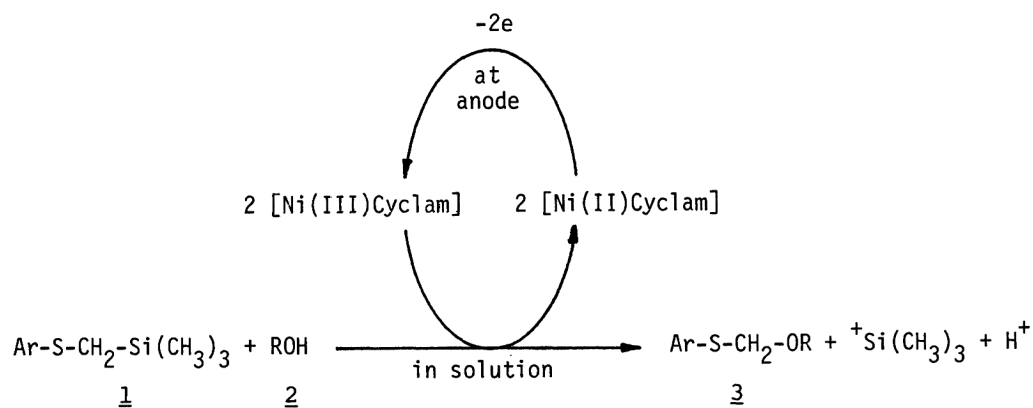
Indirect Electrooxidation Mediated by an Ni(III)/(II)
Redox Couple with a Cyclam Ligand

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The first example of an Ni(III)-mediated indirect electrolysis was found in the oxidation of silicon compounds using an Ni(III)/(II) redox couple having a macrocyclic polyamine(cyclam) as a ligand.

Macrocyclic polyamines incorporate strongly transition metal ions which sometimes are in unusual oxidation states and the resulting stable complexes are expected to be useful in a variety of fields including electrochemistry.¹⁾ However, only two examples of indirect electrolyses mediated by this type of metal complexes have been reported: Reduction of dioxygen and carbon dioxide using Co(II)/(III)²⁾ and Ni(I)/(II),³⁾ respectively. In this paper, we wish to report that the cyclam complex of an Ni(III)/(II) redox couple⁴⁾ can mediate the indirect electrooxidation of arylthiomethyltrimethylsilanes in the presence of alcohols (Scheme 1).⁵⁾ This is the first example of an Ni(III)-mediated indirect electrolysis.



Scheme 1.

As shown in Fig. 1(a), $[\text{Ni(II)cyclam}](\text{ClO}_4)_2$ gave a reversible cyclic voltammogram, which was not deformed by addition of $\underline{2}$ ($\text{R} = \text{Allyl}$). The oxidation peak (Pa_1) was increased by addition of $\underline{1}$ ($\text{Ar} = \text{p-Tolyl}$) and $\underline{2}$ ($\text{R} = \text{Allyl}$), while the reduction peak (Pc_1) was decreased (Fig. 1(b)). The peaks Pa_2 and Pa_3 could not be clearly assigned in a relation to the voltammogram (c) measured in the absence of $[\text{Ni(II)cyclam}](\text{ClO}_4)_2$. When $\underline{1}$ (1 mmol) was electrolyzed by passing 2 mF at 1.0 V *vs.* SCE at a Pt anode in the presence of $\underline{2}$ (20 mmol) and $[\text{Ni(II)cyclam}](\text{ClO}_4)_2$ (0.3 mmol) in 0.13 M $\text{NaClO}_4/\text{CH}_3\text{CN}$ (15 cm^3) in an undivided cell, $\underline{1}$ was completely consumed to give $\underline{3}$ in 33 % yield (Turnover number based on $\underline{3}$ formed, 2.2). Another combination of $\underline{1}$ ($\text{Ar} = \text{Phenyl}$) and $\underline{2}$ ($\text{R} = \text{Methyl}$) also gave a similar voltammogram and electrolytic result (Yield of the corresponding $\underline{3}$, 41 %; turnover number, 2.4). These facts confirm the occurrence of the indirect electrooxidation mediated by the $[\text{Ni(III)}]/[\text{Ni(II)cyclam}]$ redox couple.

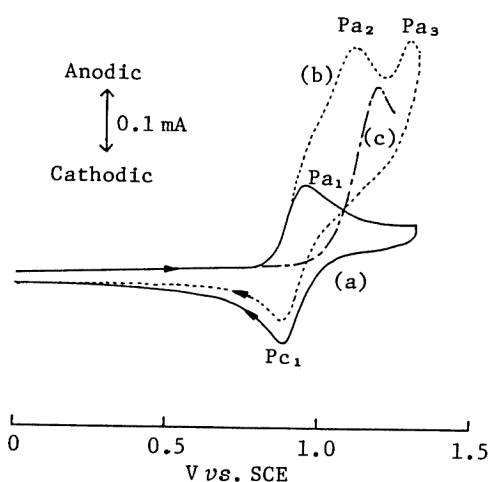


Fig. 1. Cyclic voltammograms at a glassy carbon electrode (0.28 cm^2) in 0.1 M ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) $\text{NaClO}_4/\text{CH}_3\text{CN}$ at 50 mV^{-1} of scan rate.

- (a) 3 mM $[\text{Ni(II)cyclam}](\text{ClO}_4)_2$ in the presence and absence of $\underline{2}$ (0.1 M, $\text{R} = \text{Allyl}$).
- (b) 3 mM $[\text{Ni(II)cyclam}](\text{ClO}_4)_2$ + 3 mM $\underline{1}$ ($\text{Ar} = \text{p-Tolyl}$) in the presence of $\underline{2}$ (0.1 M, $\text{R} = \text{Allyl}$).
- (c) 3 mM $\underline{1}$ ($\text{Ar} = \text{p-Tolyl}$) in the presence of $\underline{2}$ (0.1 M, $\text{R} = \text{Allyl}$).

The $[\text{Ni(II)cyclam}]$ complex used in this work can be varied by alternations of central metal and macrocyclic polyamine as legand.¹⁾ Therefore, it should be expected that extensive applications of this new class of mediatory system to a variety of indirect electrolyses will be possibly developed.

References

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(Received March 23, 1987)