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

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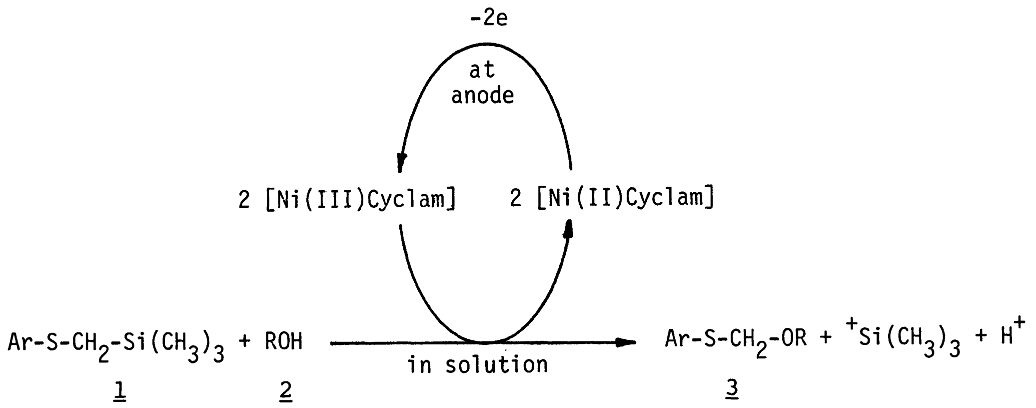
The first example of an Ni(III)-mediated indirect electrolysis was found in the oxidation of silicon compounds using an Ni(III)/(II) redox couple having a macrocyclic polyamine(cyclam) as a ligand.

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 couple[4) 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), [Ni(II)cyclam]$(ClO_4)_2$ gave a reversible cyclic voltammogram, which was not deformed by addition of 2(R = Allyl). The oxidation peak(Pa_1) was increased by addition of 1(Ar = p-Tolyl) and 2(R = 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 [Ni(II)cyclam]$(ClO_4)_2$. When 1(1 mmol) was electrolyzed by passing 2 mF at 1.0 V *vs.* SCE at a Pt anode in the presence of 2(20 mmol) and [Ni(II)cyclam]$(ClO_4)_2$ (0.3 mmol) in 0.13 M $NaClO_4/CH_3CN$(15 cm^3) in an undivided cell, 1 was completely consumed to give 3 in 33 % yield(Turnover number based on 3 formed, 2.2). Another combination of 1(Ar = Phenyl) and 2(R = Methyl) also gave a similar voltammogram and electrolytic result(Yield of the corresponding 3, 41 %; turnover number, 2.4). These facts confirm the occurrence of the indirect electrooxidation mediated by the [Ni(III)/(II)cyclam] redox couple.

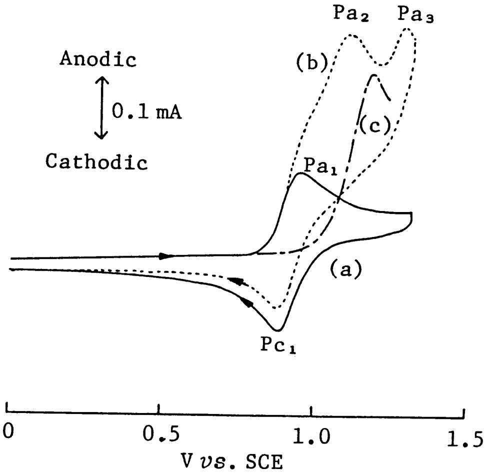


Fig. 1. Cyclic voltamograms at a glassy carbon electrode(0.28 cm^2) in 0.1 M (1 M = 1 mol dm^{-3}) $NaClO_4/CH_3CN$ at 50 mV^{-1} of scan rate.

(a) 3 mM [Ni(II)cyclam]$(ClO_4)_2$ in the presence and absence of 2(0.1 M, R = Allyl).

(b) 3 mM [Ni(II)cyclam]$(ClO_4)_2$ + 3 mM 1 (Ar = p-Tolyl) in the presence of 2 (0.1 M, R = Allyl).

(c) 3 mM 1 (Ar = p-Tolyl) in the presence of 2 (0.1 M, R = Allyl).

The [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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