

ALKYLATION OF NICKEL SALEN DURING CONTROLLED-POTENTIAL ELECTROLYSES IN THE PRESENCE OF ALKYL HALIDES

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Recent work in our laboratory (1), involving the catalytic reduction of alkyl halides with electrogenerated [2,2'-(2,2'-bipyridine)-6,6'-diyl]bis[phenolato]-*N,N',O,O'*nickel(I), revealed that up to four alkyl moieties are incorporated into the ligand of the catalyst during an electrolysis. Unfortunately, owing to the numerous sites where alkyl group substitution can occur, it proved impossible to ascertain the locations of the various alkyl moieties on the ligand.

As part of ongoing work (2–4), this paper deals with the catalytic reduction of 1-bromooctane, 1-iodooctane, and 1-iodobutane by electrogenerated nickel(I) salen:

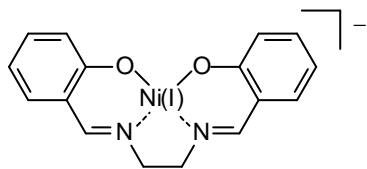


Table 1 is a compilation of product distributions for controlled-potential electrolyses at -1.10 V (5) of 1 mM solutions of nickel(II) salen in dimethylformamide (DMF) containing 0.10 M tetraethylammonium tetrafluoroborate (TEABF₄) and either 10 mM 1-iodooctane or 1-bromooctane.

Table 1. Product Distributions for Electrolyses at -1.10 V of DMF Solutions Containing 0.10 M TEABF₄, 1 mM Nickel(II) Salen, and 10 mM Alkyl Halide

RX	Product Distribution (%)					Total
	1	2	3	4	5	
RI ^a	9	2	1	1	66	79
RI ^a	13	3	0	1	65	82
RBr ^b	12	2	0	0	60	74
RBr ^b	12	2	0	1	69	84

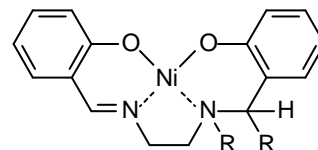
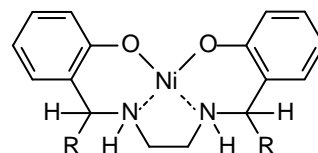
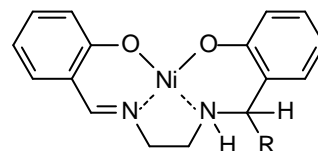
^a 1-iodooctane; ^b 1-bromooctane.

1 = octane; **2** = 1-octene; **3** = 1-octanal; **4** = unreacted RX; **5** = hexadecane.

Little or none of the original alkyl halide is detected after the electrolysis; however, the material balance (total recovery) is still well below 100%. Such behavior is not without precedent. For example, with the system mentioned above (1) that involves the use of [2,2'-(2,2'-bipyridine)-6,6'-diyl]bis[phenolato]-*N,N',O,O'*nickel(I), the attempted mediated reduction of 30 mM 1-iodooctane in the presence of 1 mM catalyst results in a material balance (total recovery) of only 58%—and almost 90% of

this recovered material is unreduced alkyl iodide. Thus, we conclude that (a) one or more alkyl groups derived from the unrecovered starting material are incorporated into the ligand of the original nickel complex and (b) the modified complex has little or no ability to catalyze the reduction of the alkyl halide.

With respect to the catalytic reduction of 1-iodooctane by electrogenerated nickel(I) salen, we have obtained evidence for multiple alkylation of the imino (C=N) bonds of the salen ligand during the catalytic process. After a controlled-potential electrolysis, various alkylated nickel salen species have been separated by means of HPLC, fractions containing individual species have been collected and examined with the aid of ESI-MS, and NMR (COSY, NOESY, and TOCSY) spectroscopy has been employed to establish the pattern of alkyl-group substitution. For the catalytic reduction of 1-iodooctane, the following modified nickel salen species (where R = C₈H₁₅) have been identified:



Analogous species have been found after the catalytic reduction of 1-iodobutane by electrogenerated nickel(I) salen.

To account for the alkylated nickel salen species, we propose that reduction of nickel(II) salen could produce a species, Ni(II)L^{•-} (with ligand radical-anion character), which couples with alkyl radicals to form Ni(II)LR⁻ or which attacks RX to give Ni(II)LR. In turn, Ni(II)LR⁻ can react with RX again to yield Ni(II)LR₂, or Ni(II)LR can be reduced to Ni(II)LR^{•-} which interacts with another RX to afford Ni(II)LR₂.

- Goken, D. M.; Peters, D. G.; Karty, J. A.; Reilly, J. P. *J. Electroanal. Chem.* **2004**, *564*, 123–132.
- Fang, D. M.; Peters, D. G.; Mubarak, M. S. *J. Electrochem. Soc.* **2001**, *148*, E464–E467.
- Guyon, A. L.; Klein, L. J.; Goken, D. M.; Peters, D. G. *J. Electroanal. Chem.* **2002**, *526*, 134–138.
- Dahm, C. E.; Peters, D. G. *J. Electroanal. Chem.* **1996**, *406*, 119–129.
- This potential is with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with DMF saturated with both solid cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V vs. SCE at 25°C.