

# CATALYTIC REDUCTION OF ALKYL HALIDES WITH ELECTROGENERATED NICKEL(I) SALEN: FORMATION OF ALDEHYDES AND KETONES

Parichatr Vanalabhpatana and Dennis G. Peters

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

It has been demonstrated earlier<sup>1,2</sup> that nickel(II) salen can be reversibly converted to nickel(I) salen and that, when nickel(I) salen is electrogenerated in the presence of an alkyl monohalide, a rapid catalytic reaction occurs to form alkyl radicals which lead to the production of three main products (a dimer, an alkane, and an alkene). In the present research, we have discovered that addition of a primary alkyl monohalide to a solution containing pre-electrogenerated nickel(I) salen, followed by exposure of the reaction mixture to either air or dioxygen, generates an aldehyde as one of the products. Production of an aldehyde via this nickel(I) salen-alkyl monohalide-dioxygen reaction can be contrasted with that obtained by the classical photodecomposition of an alkylcobalt(III) intermediate in the presence of dioxygen.<sup>3,4</sup> Optimization of our new procedure will provide another method for synthesizing aldehydes, which are useful starting materials and reagents in the polymer, food, and drug industries.

A number of variables have been investigated to determine favorable conditions for the formation of aldehydes: (a) relative concentrations of nickel(I) salen, alkyl monohalide, and dioxygen; (b) nature of alkyl monohalides (bromo- and iodoalkanes); (c) effect of light; and (d) effect of water.

To mimic conditions for the formation of aldehydes via the classic photodecomposition of alkylcobalt(III) species, ultraviolet-visible light from a 150-watt xenon arc lamp has been employed to irradiate an electrolyzed solution containing nickel(I) salen and an alkyl halide. Production of an aldehyde is remarkably enhanced by light, although results from other experiments demonstrate that some aldehyde is formed even if all light is excluded.

Another significant key for generating an aldehyde is that water must be added to the nickel(II) salen solution. Table 1 lists product distributions for ether extracts from the reaction of nickel(I) salen and a primary alkyl monohalide as a function of water concentration. Up to 74% of an aldehyde, based on the original amount of alkyl monohalide, has been obtained. Furthermore, from studies with H<sub>2</sub><sup>18</sup>O, we have discovered that <sup>18</sup>O is incorporated into the aldehyde.

As shown in Table 2, various primary alkyl monohalides were subjected to the experimental procedure, described

earlier, to generate the corresponding aldehyde. Note that experimental factors (especially the amount of added water) were optimized for the production of 1-octanal from the reaction of 2 mM 1-bromooctane with 2 mM nickel(I) salen. Preliminary work with a secondary alkyl monohalide has revealed that, besides a dimer, an alkane, and alkenes (which are classical radical-derived species in such an experiment), a ketone is formed.

To provide more information about the formation of aldehydes, results of studies with isotopically labeled reagents such D<sub>2</sub>O and 1-bromo-1,1-dideuterioalkanes, as well as further investigations with secondary alkyl monohalides, will be described.

Table 1. Product Distributions from the Reaction between 1-Bromooctane and 2 mM Nickel(I) Salen in Dimethylformamide Containing 0.10 M Tetramethylammonium Tetrafluoroborate with Ultraviolet-Visible Light and Added Water

Substrate (mM)	H <sub>2</sub> O (M)	Product Distribution (%)				
		1	2	3	4	Total
4	0.75	42	5	1	33	81
2	1.00	25	4	1	51	81
1	1.25	9	4	2	65	80
0.5	2.00	2	2	1	74	79

1 = hexadecane; 2 = octane; 3 = 1-octene; 4 = 1-octanal

Table 2. Product Distributions from the Reaction of 2 mM Alkyl Monohalide and 2 mM Nickel(I) Salen in Dimethylformamide Containing 0.10 M Tetramethylammonium Tetrafluoroborate with Ultraviolet-Visible Light and 1 M Water

Substrate	Product Distribution (%)				
	1	2	3	4	Total
1-bromopentane	22	3	trace	58	83
1-bromoheptane	27	5	1	50	83
1-bromodecane	34	4	1	30	69
1-bromo-3-phenylpropane	49	5	1	27	82
1-iodooctane	46	5	1	25	77
1-iododecane	51	9	1	16	77

1 = dimer; 2 = alkane; 3 = 1-alkene; 4 = aldehyde

1. Gosden, C.; Healy, K. P.; Pletcher, D. *J. Chem. Soc. Dalton Trans.* **1978**, 972-976.
2. Dahm, C. E.; Peters, D. G. *Anal. Chem.* **1994**, *66*, 3117-3123.
3. Hogenkamp, H. P. C. *Biochem.* **1966**, *5*, 417-422.
4. Hayashi, T.; Okazaki, K.; Urakawa, N.; Shimakoshi, H.; Sessler, J. L.; Vogel, E.; Hisaeda, Y. *Organometallics* **2001**, *20*, 3074-3078.