

REDUCTION OF ALKYL HALIDES BY ELECTROGENERATED COBALT(I) SALEN AND NICKEL(I) SALEN: REACTIONS OF ALKYL RADICALS WITH NO AND O₂

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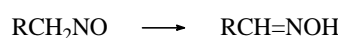
Formation of Oximes and Nitriles via the Reaction of Nitric Oxide with Alkyl Radicals Arising from Photolysis of Electrogenerated Alkylcobalt(III) Salen Species

Previous work in our laboratory has indicated that solution-phase NO can react with electrogenerated alkyl radicals to afford nitrogen-containing adducts (1). In this paper, we will discuss the oxidative addition of electrogenerated cobalt(I) salen to three different substrates—namely, 1-iodooctane, 1-iododecane, and (2-bromoethyl)benzene—to form an alkylcobalt(III) salen intermediate. Light causes the latter species to dissociate homolytically to produce an alkyl radical and cobalt(II) salen. In the presence of dissolved NO, the resulting alkyl radical reacts to yield an oxime and a nitrile as major products.

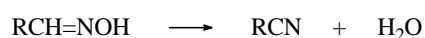
In terms of a mechanism, we propose that the alkyl radical initially undergoes coupling with NO to give a nitroso compound:



Once formed, the nitroso species rearranges immediately to give the oxime



and the oxime can lose water to form the corresponding nitrile:



Combined yields of the oxime and nitrile appear to be greater than 70%. An aldehyde is obtained in small yield from each of the three alkyl halides; in addition, in the case of 1-iodooctane, small amounts of hexadecane and dioctyl ether are observed.

Formation of Aldehydes via the Reaction of Dioxygen with Alkyl Radicals Arising from Nickel(I) Salen-Catalyzed Reduction of Alkyl Halides

It has been demonstrated earlier (2) that nickel(II) salen can be reversibly converted to nickel(I) salen and that, when nickel(I) salen is electrogenerated in the presence of a bromo- or iodoalkane, a rapid catalyst-substrate reaction occurs to form alkyl radicals which lead to the production of dimers, alkanes, and olefins. In the present research, we have discovered that addition of an alkyl monobromide (such as 1-bromohexane, 1-bromooctane, 1-bromononane, or 1-bromo-3-phenylpropane) to a solution containing electrogenerated nickel(I) salen,

followed by subsequent exposure of the reaction mixture to either air or dioxygen, results in the formation of an aldehyde. A number of variables have been examined to determine the conditions that favor the production of an aldehyde: (a) time of exposure of the reaction mixture to air or dioxygen; (b) relative concentrations of nickel(I) salen, alkyl bromide, and dioxygen; and (c) effect of light.

Table 1 lists some product distributions for the reduction of 1-bromooctane by nickel(I) salen in solutions that were stirred for different lengths of time while being simultaneously exposed to air and to ultraviolet-visible radiation from a xenon arc lamp. For these experiments, an excess of the substrate was present; therefore, after the substrate was injected into the solution containing electrogenerated nickel(I) salen, further controlled-potential electrolysis of nickel(II) salen was employed to form fresh nickel(I) salen to complete reduction of the substrate. Results from these and other experiments indicate that, although some aldehyde is formed even in a cell from which all light is excluded, the formation of aldehyde is markedly enhanced by light. Not surprisingly, the yield of aldehyde is increased if the reaction mixture is bubbled with pure dioxygen instead of air. In addition, as seen in Table 1, the yield of aldehyde appears to increase as the stirring time is lengthened.

It is interesting to compare our findings concerning the formation of an aldehyde via the nickel(I) salen-alkyl bromide-dioxygen reaction with the classic scheme that is involved in aldehyde production by the photodecomposition of alkylcobalt(III) species in the presence of dioxygen (3,4).

Table 1. Product Distributions Obtained as a Function of Stirring Time from the Reaction of 4 mM 1-Bromooctane with 2 mM Nickel(I) Salen in Dimethylformamide Containing 0.10 M Tetramethylammonium Tetrafluoroborate Exposed to Dioxygen and to Ultraviolet-Visible Radiation from a Xenon Arc Lamp

Stirring Time (minutes)	Product Distribution (%)				
	1	2	3	4	5
30	49	27	7	1	2
30	44	36	6	1	2
70	44	46	5	1	2
70	47	43	5	1	2
70	45	41	5	1	2

1 = hexadecane; 2 = octanal (caprylaldehyde); 3 = octane; 4 = 1-octene; 5 = 1-octanol

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