

NICKEL(SALEN) CATALYSED CHLORINATION OF SATURATED
HYDROCARBONS BY SODIUM HYPOCHLORITE

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Summary: in the presence of nickel(salen) as the catalyst, basic (pH 11) aqueous solutions of sodium hypochlorite chlorinate saturated hydrocarbons under very mild conditions.

During the last decade, an impressive number of papers addressing the catalytic functionalization of both unsaturated and saturated hydrocarbons by soluble metalloporphyrins have been published.^{1,2} Most of this work dealt with the substrate oxygenation, but other reactions have also been investigated. Particularly, the catalytic incorporation of non-oxygen functions (Cl, Br, I, N₃) in weakly reactive unactivated alkanes has been achieved, with manganese porphyrins as catalysts, in the presence of sodium hypochlorite or of both chloride (or bromide, iodide or azide) ions and iodosylarenes.^{3,4} These studies are of interest not only for synthetic purposes, but also because they could in principle provide useful information about the activity of some enzymes, particularly chloroperoxidase, a heme-containing chlorinating enzyme.⁵ However, metalloporphyrins resulted, so far, rather poor catalysts for these non-oxygen functionalizations and, despite extensive efforts,^{3,6} the competitive substrate oxygenation usually remained the main reaction.

We have now found that, in the presence of sodium hypochlorite, the simple substitution of the manganese porphyrin for nickel²⁺(salen)^{6,7} completely reverses the reaction course affording very high selectivities for chlorination versus oxygenation.

The reactions were run in a biphasic water/dichloromethane system: in a typical experiment 2 mmol of alkane, 0.05 mmol of Ni²⁺(salen), and 0.075 mmol of hexadecyltrimethylammonium bromide in 5 mL of dichloromethane were vigorously stirred, at room temperature, with 9 mL of 0.9 M solution of sodium hypochlorite whose pH had been previously adjusted to 11 by addition of 10% hydrochloric acid. After a reaction time ranging from 0.5 to 3 hours, the aqueous and the organic layers were separated and the latter was analysed by g.l.c., with an internal standard. Some significant results are summarised in Table 1: for comparison purposes, the best literature data about metalloporphyrins catalyzed chlorination are also

included. It is worth noting that, for the sodium hypochlorite/ $\text{Ni}^{2+}(\text{salen})$ system, the chlorination versus oxygenation selectivities ($R\text{-X}/R\text{-O}$ values of Table 1) were actually even higher than those reported in the Table, because substantial amounts of polychlorinated products were often detected by g.l.c.-m.s. analysis. Only trace (<0.5%) amounts, if any, of chlorinated products were detected when adamantane or ethylbenzene were allowed to react in the absence of the nickel catalyst.

Identical results were obtained under aerobic or anaerobic conditions and both the rate and the yield of the reaction were unaffected by the addition of a donor ligand such as 4-terbutylpyridine. On the other hand, the reaction efficiency was pH dependent and the best yields were obtained at an initial pH of 11: both higher and lower values resulted in poorer yields. However, the pH was not constant during the reaction course but diminished from 11 to ca. 7.5.

The catalyst was destroyed under the reaction conditions: a fine black precipitate of nickel peroxide usually formed, within few minutes, upon the addition of the hypochlorite solution; at the same time, g.l.c. analyses showed that the reaction rate greatly decreased. At the end of the runs, no $\text{Ni}^{2+}(\text{salen})$ survived in the reaction mixture.

With aromatic hydrocarbons (toluene, ethylbenzene) as substrates, benzyl chlorides formed in reasonable yields while no evidence for chlorination of the aromatic nuclei was obtained. Among aliphatic C-H bonds, a marked preference for the functionalization of tertiary versus secondary C-H was observed in the chlorination of adamantane (C_3/C_2 ratio 8.5 after statistical correction). Primary C-H bonds turned out to be poorly reactive and only traces of 1-phenyl-2-chloroethane could be detected in the ethylbenzene chlorination, 1-phenyl-1-chloroethane being by far the major product. In some cases (cyclohexane, ethylbenzene), ketones were detected as the only monooxygenated products, thus suggesting that they arose by hydrolysis of gem-dichloroderivatives rather than by oxidation of an intermediate alcohol.

Although more informations are needed to identify the chlorination mechanism, the reaction of $\text{Ni}^{2+}(\text{salen})$ with sodium hypochlorite^{7,8} (or of strictly related complexes with iodosylbenzene⁹) to afford high valent nickel-oxo species makes quite likely that these species are involved in the chlorination reaction, possibly through a mechanism similar to that proposed for metalloporphyrates.^{2,4} This view is also supported by the high value of the C_3/C_2 ratio, close to those observed with metalloporphyrates.^{2,3} However, a radical chain mechanism, initiated by the metal and propagated by $\text{Cl}\cdot$ or $\text{ClO}\cdot$, can not, at present, be excluded.^{7b,10}

Table 1. Chlorination of saturated hydrocarbons catalysed by metal complexes.*

Substrate	Catalyst	Time, min	Substrate conversion, %	Products	Yields, % ^b	R-X/R-O ^c
Adamantane	none	80	<5	1-chloroadamantane	<0.5	-
"	Ni(salen)	80	86	1-chloroadamantane 2-chloroadamantane adamantan-1-ol adamantan-2-ol	34 12 1.2 0.2	33
"	Mn(TPP)Cl	180	^d	1-chloroadamantane 2-chloroadamantane adamantan-1-ol adamantan-2-ol adamantan-2-one	11.2 ^e 6.1 ^e 12.3 ^e 1.6 ^e 1.8 ^e	1.1
Cyclohexane	Ni(salen)	120	77	cyclohexyl chloride cyclohexanone	51 5	10
"	Mn(oFPP)Cl	120	60	cyclohexyl chloride cyclohexanol cyclohexanone	15 ^f 4 ^f 5 ^f	1.7
Toluene	Ni(salen)	120	69	benzylchloride	42	-
Ethylbenzene	none	30	<5	-	-	-
"	Ni(salen)	30	79	1-phenyl-1-chloroethane acetophenone	56 6	9.3

*Unless otherwise stated, the results are from this work and the reaction conditions were as described in the text. Abbreviations used: Mn(TPP)Cl, manganese (tetraphenylporphinato) chloride; Mn(oFPP)Cl, manganese tetrakis(o-fluorophenyl)porphinato chloride. ^bYields (based on starting hydrocarbon) were determined by g.l.c. using n-dodecane (n-tetradecane for adamantane) as an internal standard. ^cMoles of chlorinated products/moles of oxygenated products. ^dNot determined (the substrate was in excess with respect to the oxidant). ^eData from ref. 3g (chlorinating agent: iodosylbenzene and chloride ion; yields based on the iodosylbenzene). ^fData from ref. 3b (chlorinating agent: aqueous sodium hypochlorite).

These nickel catalysed chlorinations could result of some interest from the synthetic point of view, because they proceed under extremely mild reaction conditions and without using chlorine: further work is now in progress to explore this point.

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