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Screening Schiff-base Complexes for Activity in Dehalogenation of Chloroform

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Abstract

The metal-chelate assisted dehalogenation of chloroform was studied using bis(salicylaldimine)-nickel(II) compounds of the type $(5\text{-}ZC_6H_3\text{-}2\text{-}0\text{-}1\text{-}CH{=}NR)_2Ni$ in the presence of $(CH_3)_2NCH_2CH_2N(CH_3)_2$. The nickel compounds were screened for activity in terms of percent chlorine converted to chloride ion following a 6 h reflux period. The conversion was insensitive to the nature of Z, but sensitive to the nature of R (=H, alkyl, and substituted phenyl). Chloride conversion was related to the electronic effects of substituents on substituted phenyls that affected two competing effects in the transition state: (1) increase in electron density on the coordinated nitrogen to enhance the basicity and ease of proton removal from chloroform *vs.* (2) reduction in the formal charge of nickel that would reduce the tendency of chlorine from chloroform to be coordinated. Effects of other structural changes are considered.

Introduction

Olszewski and Martin [1] noted an anomalous amine exchange reaction occurred in methanol–chloroform solutions of an amine (ethylenediamine) and a Schiff-base complex [bis(N-n-butylsalicylidineiminato)nickel(II)]. The product was a violet solid, (ethylenediamine)nickel(II) chloride, which clearly was the result of dehalogenation of chloroform.

Subsequently, the kinetics of dehalogenation were studied in 50% (v/v) chloroform–methanol using the same metal-chelate compound, but a different diamine, N,N,N′,N′-tetramethylethylenediamine [2]. This diamine could not undergo amine exchange with Schiff-base, so that one potential reaction was eliminated. The kinetic study indicated that dehalogenation followed pseudo-first order kinetics over the temperature range 63–75 °C. In addition, a rate expression was formulated (eqn. (1)):

$$\text{Rate} = k_\psi[\text{diamine}]_T = (k_1 + k_2[\text{complex}])[\text{diamine}] \quad (1)$$

Specifically, the pseudo-first order rate constant showed a dependence upon the concentration of added complex, and the rate expression dictates two processes: a slower amine-assisted one, and a more rapid metal–chelate-assisted process [2, 3].

Subsequently, Nahar and Mukhedkar [4, 5] retained most features of the kinetic system, and varied the central metal ion. Under these conditions, the pseudo-first order rate constant for dehalogenation varied with the divalent metal, *i.e.* $Zn < Cu < Ni < Pd > Pt$. Also specifically, these workers [5] found a correlation between the activation energy and the electronegativity of the divalent metal (using values of Allred and Rochow, [6]).

The previous paper in the series [7] compared the dehalogenation of three chlorinated hydrocarbons (chloroform, dichloromethane, and methylchloroform) in the presence and absence of bis(salicylaldimine)metal(II) compounds.

The present study considers altering electronic properties of the aromatic ring on or near the coordinated nitrogen in bis(salicylaldimine)nickel(II) complexes and the effect on dehalogenation. The subject is of interest because of the potential importance of these complexes as models for dehalogenation by organisms and because of the potential utility of coordination entities in dehalogenating halocarbons that have become environmental contaminants. A rapid, reliable screening test to measure metal-chelate assisted dehalogenation is described.

Experimental

Synthesis of metal-chelate compounds

Unless otherwise noted, the melting points of the compounds were in agreement with those previously described [1]. Melting points and analytical data for additional compounds tested are in a table stored with the editors and also available from the authors.

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Screening studies

The following general procedure was used to screen for dehalogenation. A 10 ml solution of 50% (v/v) chloroform–methanol containing tetramethylethylenediamine (Aldrich, 5×10^{-4} mol) and metal-chelate compound (2.5×10^{-5} mol) was refluxed for 6 h. The solution was rapidly cooled and divided into two 5 ml portions. Each portion was extracted three times with 15 ml of water, then the combined aqueous extracts were titrated with standardized 0.05000 M $AgNO_3$ using potassium dichromate indicator. Under these conditions, each milliliter of titrant corresponded to 10% conversion of organic chloride to tris(diamine)nickel(II) chloride. Results are presented in Table I.

TABLE I. Chloroform Dehalogenation Screening Tests with Compounds of the Type $(ZC_6H_3\text{-}2\text{-}O\text{-}1\text{-}CH{=}NR)_2Ni$ in the presence of $(CH_3)_2NCH_2CH_2N(CH_3)_2$[a]

Z	R	Cl^- Produced 10^4 mol
3-Cl	H	1.22 ± 0.04
3-Cl	H	1.29 ± 0.13
H	C_6H_5	1.17 ± 0.02[b]
H	C_4H_9	1.14 ± 0.12
H	$2\text{-}ClC_6H_4$	1.76 ± 0.02[b]
H	$4\text{-}CH_3OC_6H_4$	1.60 ± 0.21
H	$2\text{-}C_2H_5C_6H_4$	1.28 ± 0.20
H	$C_6H_5CH_2$	1.12 ± 0.06[b]
H	$CH_2CH_2N(CH_3)_2$	1.39 ± 0.01
H	$2,4\text{-}Cl_2C_6H_3$	1.20 ± 0.07[b]
H	$(CH_2CH_2)_{1/2}$	1.78 ± 0.03
–	–	0.40 ± 0.003[c]

[a] See text for concentrations. [b] Insoluble material remaining at end of run. [c] Control run; no metal chelate compound present.

Results and Discussion

The results of dehalogenation of chloroform in the presence of (salicylaldimine)nickel(II) complexes and tetramethylethylenediamine are presented in Table I, but certain limitations should be kept in mind when reviewing the data. One limitation is the titration of chloride ion which inevitably occurs in the presence of an amine. These are less than optimum conditions, owing to the competition of amine and problems of extraction, but fair precision was obtained with the best relative standard error of less than 1% and an average relative standard error of 6% for all runs.

A second limitation is solubility. Some metal complexes did not dissolve initially, but did during the course of the reaction. In four instances, however, some precipitate remained at the end of the six-hour reaction period (*cf.* Table I). Six hours appeared to be an optimum time to achieve a fair conversion during a convenient length of time and not have the results seriously altered by the length of time required to reach constant reflux temperature.

The data available in Table I indicate several interesting points concerning the effect of the metal-chelate compound on dehalogenation that may serve as a guide to the design of other more effective molecules.

The favorable electronic effects involve those constituents that through resonance or inductive effects increase the electron density on the coordinated nitrogen. This results in a strengthened N–Ni bond, and it should increase the electron density on nitrogen and thus the basicity should also increase. As a result of the last effect, the rate of dehalogenation should also increase if the previously described transition state is correct [2]. Here it is invisioned that chloroform is coordinated to the central nickel(II) and that the hydrogen is attracted to the nitrogen and that the key step is the removal of a proton owing to the attraction to nitrogen. Thus changes in substituents that are electron donors (OCH_3, R) should enhance the production of chloride through increases in the electron density of the nitrogen. The same effect might be anticipated for electron-withdrawing groups, e.g. *o*-Cl–. The limited data indicate the argument has some validity. For example, enhancements of dehalogenation are observed for the 4-methoxy- and 2-chloro-phenyl derivatives.

Problems of interpretation arise, however, because conflicting results can be anticipated from consideration of the electronic effects. For example, electron-donating substituents can produce an unfavorable effect by reducing a formal charge on nickel and ostensibly reducing the tendency for chloroform to be coordinated. Also, ortho substituents can produce conflicting results favorably in terms of electron donation, either through resonance or inductive effects; or unfavorably through steric effects or a combination of steric-electronic effects. For example, ethyl substituents in the *ortho* positions should enhance dehalogenation, which it did, though not by the amount anticipated.

Logically, a 2-methylaniline derivative should have been tried, but the compound is a suspected carcinogen. The 2-ethyl aniline derivative was used instead, and the enhancement of dehalogenation over the unsubstituted was minimal, possibly because of conflicting effects.

Other structural features may be considered briefly. Substitution on the salicyladehyde ring did not appear to produce a profound effect on the dehalogenation yield, which seemingly differ little from those of the N-butyl or N-phenyl compounds. In contrast, a greater dehalogenation enhancement was observed using a mixed-chelate system which contained a N-β-dimethylaminoethyl moiety. By comparison, the N-butyl, N-phenyl, and N-benzyl derivatives did not differ in dehalogenating ability. Finally, a quadridentate ligand was used, [Table I, $R = (CH_2CH_2)_{1/2}$] and this nickel(II)–chelate compound produced the maximum chloride release.

Though structural features can alter the chloride release to varying extents, (up to a 50% enhancement, relative to the N-butyl derivative), the central metal can have a more significant effect. Quadridentate ligand complexes were compared, and the nickel(II) compound ($R = CH_2$, Table I) was used as the standard to compare effects of different metals. The yield ratios were calculated as 1.0 (Ni complex), 0.86 (Cu complex), and 0.47 (Zn complex), which is consistent with the trend noted by Nahr and Mukhedar [4] for dehalogenation rates of similar reaction mixtures but using bis(N-n-butylsalicylaldimine)metal(II). The difference between their trend and the one reported here is for zinc. For their system at 60 °C, the relative rates were 1.0 (Ni complex), 0.88 (Cu complex), and 0.76 (Zn complex). Presumably, the platinum(II) derivative should be more effective in assisting dehalogenation. Though the enhancement was about 8%, according to Nahar and Mukhedar [4], the increase would hardly justify the additional cost.

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