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The production of NO from the reaction of Fe(III) Schiff base complexes and nitrite ions in acetonitrile

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Abstract

The Fe(III) Schiff base complexes: FesalenNO$_2$, FesalenCl, [Fesalen]$_2$O$^+$BF$_4^-$ and FeacacenCl have been treated with the nitrite reagents: PPNNO$_2$, AgNO$_2$ and NaNO$_2$ in acetonitrile. Only FesalenNO$_3$ and FesalenCl produced NO with all of the reagents according to the equation: $2\mathrm{Fesalen}^+ + 3\mathrm{NO}_2^- = 2\mathrm{NO} + (\mathrm{Fesalen})_2\mathrm{O} + \mathrm{NO}_3^-$. No evidence of Fe(III) nitrite complex formation was found. FeacacenCl did not react under these conditions and the Fe(III,IV) compound, [Fesalen]$_2$O$^+$BF$_4$, produced NO$_2$(g). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nitrite; Nitric oxide; Iron Schiff base complexes; Acetonitrile

1. Introduction

There is considerable interest in the nitrite complexes of Fe(III) [1,2], especially those of the iron(III) porphyrins. Several of these have been prepared and their structure and chemical nature examined [3–5]. In solution they slowly disproportionate to produce the nitrosyl and nitrate complexes [6]. The porphyrin nitrite complexes have an active oxygen atom which is able to oxidize a number of different species [7,8], including O$_2$ to produce O$_3$ [9].

Early attempts to prepare the Fe(III) Schiff base nitrite, FesalenNO$_2$,[1] were carried out by reacting (Fesalen)$_2$O in dichloromethane with N$_2$O$_3$, the anhydride of nitrous acid, using a vacuum line at low temperature [10]. A black solid resulted which had an indefinite analysis, but spectral properties indicated that it was a mixture of the nitrate, nitrite and μ-oxo compound. Attempts to prepare a pure nitrite complex by this method were unsuccessful. A related reaction involved (Fesalen)$_2$O in dichloromethane solution being treated with NO followed by O$_2$. The black solid product from the reaction gave upon recrystallization the nitrate, FesalenNO$_3$ [11]. The latter compound had been prepared earlier by reacting (Fesalen)$_2$O in solution with dilute nitric acid [12].

An attempt to prepare FesalenNO$_2$ using a simple replacement reaction was carried out by mixing acetonitrile solutions of PPNNO$_2$ and the nitrate, FesalenNO$_3$. Surprisingly, NO was rapidly generated at room temperature with no apparent formation of the nitrite or nitrosyl complexes. This report considers this reaction in more detail. For comparison, reactions with PPNNO$_2$ and the Fe(III)chloro complex of the Schiff base, acacen, and the Fe(III, IV) complex, [Fesalen]$_2$O$^+$BF$_4^-$ were carried out. Nitrite salts other than PPNNO$_2$ were also used.

2. Experimental

2.1. Chemicals

Literature procedures were used to prepare FesalenNO$_3$ [12], FesalenCl [13], [Fesalen]$_2$O$^+$BF$_4^-$ [14] and Fe(acacen)Cl [15]. PPNNO$_2$, AgNO$_2$, and NaNO$_2$ were obtained as reagent grade materials and used as

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[1] salen, *N*,*N*′-ethylenebis(salicylideneimine) 2-anion; acacen, N,N′-ethylene-bis(acetyl-acetonylideneimine) 2-anion; PPNNO$_2$, bis-(triphenylphoshoranylidene)- ammonium nitrite.

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obtained from the manufacturer, except $PPNNO_2$ was dried at 100°C for 24 h prior to use. NO gas from Matheson Gas Products was passed through a KOH column prior to use. Chromatography grade acetonitrile from newly opened bottles was used.

2.2. Vacuum line reactions

A total of 0.50 mmol each of the solid Fe(III) complex and nitrite reagent along with a magnetic stirring bar were placed into a dry reaction tube and the atmosphere removed. The tube was cooled to liquid nitrogen temperature and 50 ml of acetonitrile was added by vacuum distillation. The acetonitrile was deoxygenated prior to distillation by three cycles of freezing and thawing on the vacuum line. The solution was allowed to warm to room temperature and stirred. The pressure became constant after about 3 h.

A sample of the gas was collected in a 10 cm IR gas cell attached to the vacuum system and the IR spectrum measured on a Nicolet Model 5DX spectrophotometer. A NO calibration curve (absorbance at 1875.2 cm^{-1} vs. the NO pressure, P_{NO}) was established for the gas cell using pure NO gas.

2.3. Ion chromatography

Nitrate and nitrite analyses were obtained using a Dionex Series 2003i ion chromatograph equipped with an HPIC-CS5 analytical column, a visible detector and a Model 4270 integrator. The indirect photometric detection method of Hayakawa et al. [16] was used with determinations made at a detection wavelength of 330 nm. The eluant was 1.5 mM $Na_2[Cu(edta)]$, pH 6.5, and a flow rate of 0.5 ml min^{-1}. The injection volume was 25 µl. Nitrate and nitrite ions produced negative peaks with retention times of 4.0 and 5.1 min, respectively.

2.4. UV–Vis spectra

Solution spectra were taken using a B&L Spectronic 2000 Spectrophotometer and a 1.0 cm quartz cell.

3. Results and discussion

When $FesalenNO_3$ was treated with $PPNNO_2$ in equimolar amounts (0.5 mmol/50 ml) in acetonitrile on the vacuum line, NO was liberated and the color of the solution changed from purple to brown. The reagents were mixed in equimolar amounts since it was anticipated that only the simple replacement of the nitrate by nitrite would take place. It took about three hours for the reaction to reach an equilibrium gas pressure as the reaction mixture warmed from liquid nitrogen temperature to room temperature. No unusual species were observed as the temperature slowly increased. If the reagents were mixed at room temperature they reacted immediately. Only the spectrum of NO was observed in the IR gas cell [17]. Since the equilibrium gas pressure might be due to both P_{NO} and solvent vapor pressure, the amount of NO was determined from the gas IR spectrum using a calibration curve. From the volume of the vacuum system, P_{NO}, and the temperature, the moles of NO produced were calculated.

Table 1 gives the results of the reactions of the Fe Schiff base complexes in the vacuum system with several nitrite reagents in equimolar amounts. In these reactions if the equation is assumed to be:

$$2\mathrm{Fesalen}^+ + 3\mathrm{NO_2}^- = 2\mathrm{NO} + (\mathrm{Fesalen})_2\mathrm{O} + \mathrm{NO_3}^- \quad (1)$$

then the nitrite reagent is the limiting reagent and the yields were calculated by multiplying the quantity of NO produced by three halves and dividing by the amount of nitrite reagent originally present (0.50 mmol). The reactions of $FesalenNO_3$ with $PPNNO_2$, $NaNO_2$ and $AgNO_2$ and that of FesalenCl with $PPNNO_2$ gave essentially quantitative results. The presence of water in the reaction medium reduces the yield, probably resulting from the conversion, by hydrolysis, of some of the Fe(III) complex to the $(Fesalen)_2O$. The slightly less than 100% yields are likely due to the presence of trace amounts of moisture in the reaction mixtures.

The possibility existed wherein the $Fesalen^+$ species might react with trace water

$$3\mathrm{H_2O} + 2\mathrm{Fesalen}^+ = (\mathrm{Fesalen})_2\mathrm{O} + 2\mathrm{H_3O}^+$$

$$3\mathrm{H_3O}^+ + \mathrm{NO_2}^- = 2\mathrm{NO} + \mathrm{NO_3}^- + \mathrm{H_2O} \quad (2)$$

in the mixture to produce H_3O^+ which might then react with NO_2^- to generate NO. Hydrolysis of the Fe complex did not result in NO formation.

Table 1
Reactions of Fe complexes with nitrite reagents on the vacuum line in 50 ml of acetonitrile with a 10 mM concentration of each reactant

Fe Complex	Nitrite reagent	NO produced?	Yield [a] (%)
$FesalenNO_3$	$PPNNO_2$	yes	97
$FesalenNO_3$	$NaNO_2$	yes	90
$FesalenNO_3$	$AgNO_2$	yes	95
FesalenCl	$PPNNO_2$	yes	98
$FesalenNO_3$	$PPNNO_2$ + 1 ml H_2O	yes	63
FeacacenCl	$PPNNO_2$	no	
FeacacenCl	$AgNO_2$	no	
$[Fesalen]_2O + BF_4^-$	$PPNNO_2$	no, NO_2 produced	

[a] See text for calculation.

The solution from the reaction of FesalenCl and $PPNNO_2$ was evaporated to dryness on the vacuum line. The solid residue was treated with 50 ml of water and an aliquot of the solution removed, filtered through a 30 μm syringe filter and injected into the ion chromatograph. The nitrite peak was absent and the nitrate peak was present. The IR spectra of the solid residues from the reactions with 90% or greater yields were measured and all showed a band at 830 cm^{-1} indicative of the presence of $(Fesalen)_2O$.

All results indicate that the reaction is that shown in Eq. (1) which is similar to the reaction of nitrite ions with strong acid shown in Eq. (2). The Fe(III) complex in Eq. (1) serves as a Lewis acid in its interaction with the nitrite ion promoting the disproportionation of the nitrite to NO and nitrate. As mentioned the Fe(III) porphyrin nitrite complexes slowly decompose to the porphyrin nitrate and nitrosyl complexes. It appears that the Fe(III)salen group in acetonitrile has no great tendency to form the nitrosyl complex. FesalenNO is made in benzene by reacting Fe(II)salen with an excess of NO [18] and seems to be much more reactive with O_2 than the iron porphyrin nitrosyls.

FeacacenCl does not react with $PPNNO_2$ or $AgNO_2$ in acetonitrile to generate NO. The reaction with $AgNO_2$ does form AgCl, but no NO. Attempts to isolate pure $FeacacenNO_2$ were unsuccessful. The lack of a reaction with Fe(III)acacen compared with Fe(III)salen may be the result of the difference between the structures of the coordination spheres of the two complexes. The salen complexes have more distortion in their coordination spheres than do the acacen ones [15]. Reaction (1) appears at this time to be a unique property of the Fe(III)salen complexes.

The Fe(III,IV)salen, $[Fesalen]_2O^+BF_4^-$, complex readily oxidized the nitrite ion to produce NO_2 and $[Fesalen]_2O$. On the vacuum system the brown NO_2 gas was found in the IR gas cell with no NO being present.

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