

HYDROXYLAMINE DECOMPOSITION IN THE PRESENCE OF IRON STUDIED BY CALORIMETRY, ONLINE MID-IR AND UV-VIS SPECTROSCOPY

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Introduction

Although studied for decades, the propensity of hydroxylamine to decompose into gas and liquid products in the presence of transition metals remains poorly understood. Recent explosions at two chemical plants manufacturing hydroxylamine solution, in which transition metal impurities have been suggested as a contributing factor, revived research on this industrially relevant compound^{1,2}.

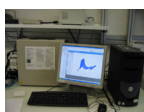
Since no mechanism, products or intermediates have been identified without controversy, we propose to investigate this decomposition with different 3d metals and determine a satisfactory mechanism. This poster presents preliminary results about hydroxylamine reactivity in the presence of iron(III) and iron(II).

Instrumentation

The reaction has been studied by calorimetry, gas production, MID-IR and UV-VIS spectroscopy.



The pressure proof small reaction calorimeter (CRCv4)³ was used to measure calorimetric, pressure and IR signals.



IR data was collected *in-situ* with an ATR probe connected to a *ReactIR 4000* spectrometer (*Mettler Toledo*).



UV-VIS spectra were measured in cells using a *Cary 50* spectrophotometer (*Varian Inc*). All measurements were made at isothermal conditions.

Materials and Methods

Hydroxylamine solution 50% in water and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ high purity were acquired from *Fluka*. High grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was purchased from *Fluka* and *Riedel-de Haën*.

The reaction order of hydroxylamine and iron has been studied at industrially relevant concentrations using UV-VIS spectroscopy to follow changes in the iron spectrum.

The hydroxylamine concentration was varied between 3 mol/L and 1 mmol/L (5000 times to no excess). Three different concentrations of iron were also used (0.0002 – 0.0044 mol/L). All measurements have been done at 25°C, pH 1 and constant ionic strength (0.1 mol/L).

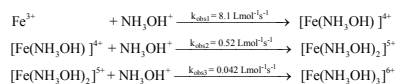
Any decomposition of hydroxylamine was recorded by calorimetry, gas production and IR spectroscopy using highly concentrated solutions.

Mechanisms and associated parameters were determined by fitting of kinetic models to the collected data⁴.

Results

Complexation reaction (acidic conditions)

At pH 1 and for a fixed iron(III) concentration, three complexation steps were observed.



The behaviour of iron(II) appears similar but slower.

For a fixed hydroxylamine concentration, iron(III) has a negative reaction order. We have yet to interpret this result.

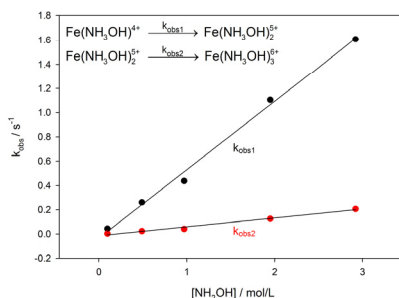


Figure 1 : Second and third complexation steps
[Fe³⁺] = 1 mmol/L

Decomposition reaction (acidic conditions)

No significant gas production, heat production or change in the IR hydroxylamine spectrum could be detected.

This suggests that no decomposition (oxidation or reduction) occurs under such conditions.

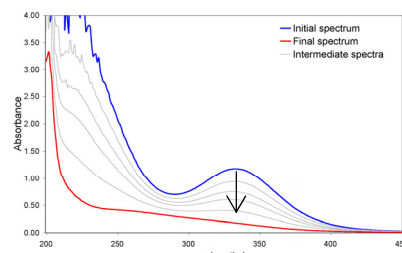


Figure 2 : UV-VIS Spectrum of iron(III)
[NH₂OH] = 1 mol/L, [Fe³⁺] = 1 mmol/L

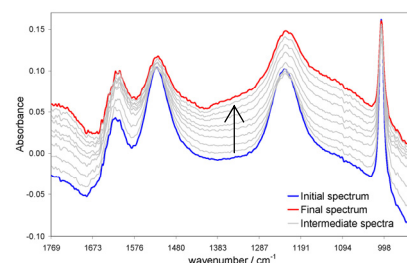


Figure 3 : IR Spectrum of hydroxylamine
[NH₂OH] = 2 mol/L, [Fe³⁺] = 0.75 mol/L

Conclusions and perspectives

It is suspected that under strongly acidic conditions binding to iron occurs via O rather than N. This could explain why there is no hydroxylamine decomposition. This is supported by the lack of reactivity of NH_4^+ with iron under the same conditions.

These results suggest that metal impurities pose little risk at low pH.

Study of the reaction at higher temperature and alkaline pH is now being undertaken. Preliminary investigations at higher pH showed significant decomposition and associated heat and gas production. This indicates that a different mechanism will apply.

References

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3. Visentin, F.; Gianoli, S. I. et al. *Organic Process Research & Development* 2004, 8(5), 725.
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