



A simple and efficient approach for preparation of hydroxylamine sulfate from the acid-catalyzed hydrolysis reaction of cyclohexanone oxime



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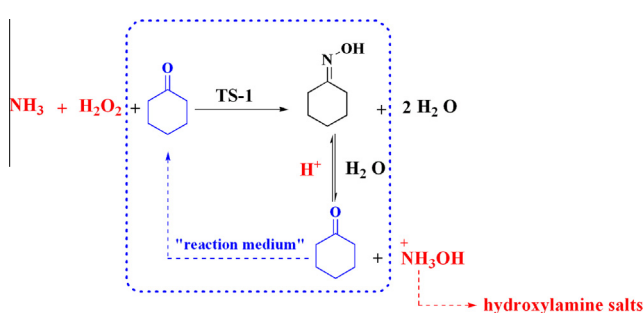
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HIGHLIGHTS

- A simple and efficient method for preparation of hydroxylamine sulfate was developed.
- The excellent selectivity of hydroxylamine sulfate and cyclohexanone was obtained.
- Hydrolysis of cyclohexanone oxime and ammoximation of cyclohexanone was integrated.
- This work serves as a direction for preparation of other hydroxylamine salts.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and efficient approach for preparation of hydroxylamine sulfate from the hydrolysis reaction of cyclohexanone oxime in the presence of sulfuric acid has been developed in this work. The effects of the molar ratio of cyclohexanone oxime to sulfuric acid, the concentration of reactants, the reaction temperature, the reaction time and the extraction solvents on the hydrolysis reaction were investigated. The results indicated the conversion of cyclohexanone oxime was over 30% with excellent selectivity of cyclohexanone and hydroxylamine sulfate under the optimal reaction conditions. Furthermore, the enthalpy change, entropy change, Gibbs free energy change and thermodynamic equilibrium constant of the hydrolysis reaction were determined in present work. This reaction is an endothermic reaction and higher temperature is favorable for the synthesis of hydroxylamine sulfate. This new preparation method is simple, rapid, efficient and economical. Maybe this work can serve as a direction for preparation of other hydroxylamine salts by such hydrolysis reaction.

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1. Introduction

It is generally known that hydroxylamine and its salts are important intermediates for the production of ϵ -caprolactam, and also widely used in the fields of pharmaceutical [1–3], pesticide [4,5], rubber [6], dye [7], military [8,9] and nuclear industries [10]. The traditional methods for the preparation of hydroxylamine

salts include the Raschig process [11], electrolysis method [12], catalytic hydrogenation of nitric oxide [13–15], catalytic hydrogenation of nitrates [16–18], the hydrolysis of nitro alkane [19], and so on. These processes have various disadvantages such as cumbersome preparation processes, excess yields of byproducts ammonium sulfate, high production cost, heavy pollution and difficulties in after-treatment and catalyst recovery. Therefore, a green, simple and environmentally friendly method has important implications for the preparation of hydroxylamine salts.

The hydrolysis of oximes [20–23], the reverse process for oximation reaction of ketones, is proposed to overcome above-mentioned

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these drawbacks. Compared with the current commercial processes, this process can be carried out under mild conditions, does not use environmentally undesirable or expensive catalysts, and almost no other by-products formed. Nevertheless, the hydrolysis of oximes is profoundly affected by thermodynamic equilibrium and the yield of hydroxylamine salts is unsatisfied. The removal of ketones from the hydrolysis reaction system is a most direct and efficient way to break the equilibrium. From this viewpoint, coupling the hydrolysis of oximes with reactive distillation [20] or membrane separation [22,23] are proposed for removing ketones and the reaction equilibrium could convert to the product side. But these approaches also have the disadvantages of high energy use and high cost for membrane components, respectively. Moreover, the ketones are not fully utilized or given a reasonable usage.

With the developments of ammoximation [24–27] over TS-1 zeolite, continuous production of hydroxylamine salts by coupling the hydrolysis of ketoximes and ammoximation reaction is considered to be a very promising and green method (see Scheme 1). In this way, the route can be described as the indirect preparation of hydroxylamine salts from ammonia and hydrogen peroxide in the presence of acids. The cyclohexanone is used as a “reaction medium” in the whole process. Therefore, a suitable method for separation and recycling of cyclohexanone becomes very important on some level. The reactive extraction [28,29] that is successfully applied in the field of biomedicine and chemistry can solve the problem effectively. The extraction solvents were introduced to extract the product cyclohexanone and the cyclohexanone in the extractive phase can be returned to the ammoximation part with simple phase separation. Furthermore, the study of hydrolysis reactive-extraction in this work has the instructive significance for the follow-up work of continuous reactive-extraction.

An integration process for preparation of hydroxylamine sulfate (HAS) from the hydrolysis reaction of ketoximes and ammoximation of ketones was developed in present work. This method has advantages of mild reaction condition, short reaction time, simple operation and excellent selectivity. Furthermore, cyclohexanone can be recycled in this process, which is satisfied with the requirement of green chemistry. This work can serve as a direction for preparation of other hydroxylamine salts by such hydrolysis reaction, and has good application prospects in industry.

2. Experiment

2.1. Apparatus and reagents

High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-20AT equipped with a Hypersil BDS-C18 (5 μ m, 4.6 mm \times 250 mm) column; Gas chromatograph was performed on a Shimadzu GC-2010 plus instrument with an RTX-5 capillary column (30 m \times 0.25 mmID \times 0.25 μ m) and a flame ionization

detector (FID). Gas chromatography-mass spectrometry (GC-MS) was run on a Shimadzu GCMS-QP2010 PLUS. All chemicals were analytical grade and the standard solutions were pre-prepared for analytical use. The cyclohexanone oxime (CHO) was purchased from Sinopec Baling Branch Company. The reagents were used in the hydrolysis reaction and product analysis as follows: 1.0–5.0 mol/L of sulfuric acids solution that was prepared by from the concentrated sulfuric acid (98%). potassium permanganate (0.1 mol/L) standard solution and ammonium ferric sulfate (25%) solution were self-prepared. Ethyl acetate, dichloromethane, *n*-hexane, cyclohexane, benzene, toluene and phosphoric acid (60%) were commercially available. The HPLC mobile phase was composed by methanol and water (65:35, v/v) and the standard solutions of CHO were prepared in the ranges 40–160 μ g/mL.

2.2. Typical experimental procedure

The hydrolysis reaction was carried out in a 250 ml round-bottom flask immersed in a water bath under atmospheric pressure. A mixture of CHO and dilute sulfuric acid solution was stirred at a set temperature. After reaction finished, a portion of the reaction solution was extracted with ethyl acetate to remove cyclohexanone and CHO for the determination of HAS. Another part of reaction solution was treated with sodium hydroxide to neutralize the sulfate acid for the determination of CHO. The quantitative analysis of CHO was performed on a Shimadzu LC-20AT HPLC using an external standard method, with the detection wavelength of 210 nm and the mobile phase flow rate of 0.8 mL/min. The cyclohexanone was analyzed using a Shimadzu GC-2010 plus and chlorobenzene was used as internal standard. HAS was determined by redox titration [30]. Accordingly, the conversion of CHO and the selectivity to HAS and cyclohexanone were calculated according to the following equation (where n_i stands for the number of moles of component i):

$$\text{Conversion of CHO} = (n_{\text{CHO added}} - n_{\text{CHO unreacted}}) / n_{\text{CHO added}} \times 100\%$$

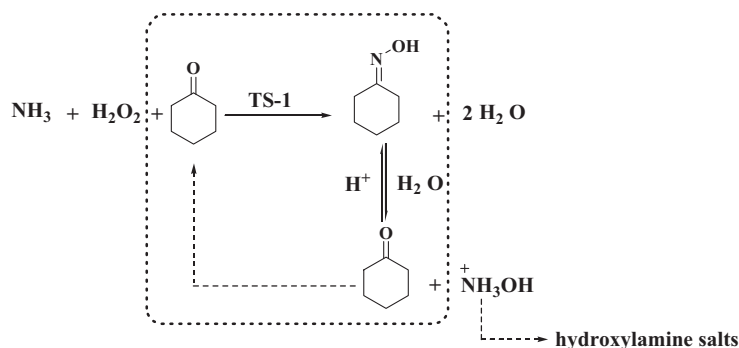
$$\text{Selectivity of HAS} = 2 \times n_{\text{HAS}} / (n_{\text{CHO added}} - n_{\text{CHO unreacted}}) \times 100\%$$

$$\text{Selectivity of cyclohexanone} = n_{\text{cyclohexanone}} / (n_{\text{CHO added}} - n_{\text{CHO unreacted}}) \times 100\%$$

3. Results and discussion

3.1. Effects of the molar ratio of sulfuric acid to CHO on the hydrolysis reaction of CHO

The sulfuric acid acts not only as the catalyst in the hydrolysis reaction of CHO, but also as a important component in the salt formation of HAS. To investigate the effect of the molar ratio of



Scheme 1. Integration process for production of hydroxylamine salts from the hydrolysis of cyclohexanone oxime and ammoximation of cyclohexanone.

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