SONOCHEMICAL SYNTHESIS OF KETONE - ALDEHYDE OXIMES

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Abstract

In recent days the various techniques have been used in synthesis of organic, inorganic compounds which are harmless to environment under the name Green chemistry. Ultrasound irradiation is one of these widely used techniques in chemistry and elsewhere. This short communication reports the comparative study of synthesis of oxime using ultrasonic irradiation and traditional chemical method. Oximes are used as intermediates in the organic synthesis of anilide, also selective protection and de-protection of carbonyl group during synthesis to prefer conversion of desired functional group in to targeted product. Yield and kinetics of oxime preparation by routine chemical method and ultrasonic irradiation method are compared in this report. Yields by ultrasound technique are found to be higher as compared to the yield by routine synthetic method. Even the time required for completion of reactions by ultrasonic irradiation method was found to be less than that of by traditional chemical method. Moreover the exclusion of organic solvent as reaction medium was achieved.

Keyword: Oxime, Ultrasound technique, Analysis

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INTRODUCTION

In this short report, we try to communicate effective use of ultrasound technique to synthesise oximes. Oximes are normally in use as intermediate compound during anilide synthesis, protection and de-protection of carbonyl group for selective synthesis, to check the purity of carbonyl compounds; it also can be used as insecticide and pesticide. Ultrasound irradiation enables many chemical reactions to proceed, because ultrasound can produce temperature as high as that on the surface of the Sun; and pressure as great as that at the bottom of the ocean by the acoustic cavitation mechanism. Cavitation means the formation, the growth, and the impulsive collapse of bubble. During cavitation bubble collapse gives intense local heat (of the order of $\geq 5000^0C$), and pressures (of about 1000 atmospheres) and heating and cooling rates above 1010 K/s (1, 2). The reaction carried under ultrasonic irradiations has higher rate of reaction as it provides activation energy in a short time also the selectivity of reactions pertaining to the functional groups can be altered (3-5). Many organic reactions are done in a short time by ultrasonic irradiation. As reported by Srinivasan et al, the heck reaction is completed in a very short time (1.5-3 h) at ambient temperature (30°C) using ultrasonic technique (6).

Apart from this organic synthesis related application, the ultrasound technique is in use in various fields like homogenisation of fluids and cell disruption in biochemistry, to assist in mechanical operations like drilling, grinding, cutting, welding along with the mechanical testing of a hard material, and also for cleaning and drilling in dentistry (7, 8).

An Oxime is an organic compound containing the >C=NOH functional group.

Oximes are the derivatives of aldehyde and ketone (Scheme 1) and are highly crystalline. Therefore trasformation of an organic compound into oxime is a very efficient method for characterisation and purification of carbonyl compound. Oximes are not only useful for protection, purification, and characterization of carbonyl compound but also they can serve as intermediate for conversion of carbonyl compounds into nitro compounds, nitriles and amides (9, 10).

ULTRASOUND IN OXIME SYNTHESIS: A number of criteria like toxicity, cost of starting material, reagent and solvent usage, energy requirement, yield and time required for the completion of reaction are to be considered to set reaction conditions for a chemical transformation. In green chemistry, during organic synthesis it is aimed to form product in short time, with high yield, minimum possible utilization of energy and without use of toxic chemicals.
Organic synthesis by routine method requires more time for the completion of the reaction and vigorous reaction conditions like high pressure, temperature, use of catalyst, toxic organic solvent still yield are comparatively low, which ultimately increases the cost of reaction and leaves adverse effect on environment. As alternative routes of synthesis, Mostafa Karimkoshteh reports use of Fe$_3$O$_4$ nanoparticles as catalyst during solvent free synthesis of oximes from carbonyl compounds (12). It is reported that the magnetic nanoparticles can be used effectively for synthesis of oxime in short period under clean reaction conditions, easy work-up procedure, along with suppression of any side product. Another unconventional approach for synthesis of oximes is put by Lakhinath Saikia and the co-authors in terms of grindstone chemistry. They have proved the effective use of Bi$_2$O$_3$ as catalyst to run the reaction in churned form of the reactants in order to follow ecofriendly synthesis (13). Use of ultrasonic irradiation in organic synthesis gives product of the reaction in very short time with higher yield compare to routine synthetic method, also it do not require high temperature, pressure and can be carried out even without using catalyst and using less toxic solvent too (14). Hence these are green method of preparation of organic compounds.

**Experimental**

**Materials:** All the chemicals used in the oxime preparations are procured from Merck Chemicals India Ltd Purity: 99.9% AR Grade. The synthesis was carried out pertaining to the following conditions:

**Molar Ratio:** Basis: 1 gm of Benzophenone

- Benzophenone (5.4mM), Acetophenone (8.3 mM), 4-Chlorobenzaldehyde (7.3mM)

**Temperature:**

- i) for chemical method 58$^{0}$C
- ii) for ultrasonic method 25$^{0}$C

**Synthesis of Oxime:**

In traditional way, preparation of oximes is carried out by refluxing carbonyl compounds with hydroxylamine hydrochloride solution and ethyl alcohol as solvent (Scheme 1), it takes around 50-60 minutes for the completion of reaction, the yield of product ranges around 70-75%.

**Scheme 1: Proposed reaction:**

Preparation of same oximes was attempted using ultrasonic irradiation. For this no reaction medium was required; hence ethanol was absent and the reaction was carried out using sonicator (Scheme 2). The proposed reactions for synthesis of oxime with starting material Benzophenone (1), Acetophenone (2), 4-Chloro benzaldehyde (3) by ultrasonic irradiation are as follows,
RESULTS AND DISCUSSION

It is found that the product by ultrasound technique was formed in less time (10-20 min), with yield ranging from 75 to 85% which were high as compared to traditional one. The reduction in time required is obvious as the cavitation increases the local temperature and pressure enormously. The conversion takes place rapidly; the elevated temperature further favours the conversion of aldehyde and ketones to oximes at high pressures. Though the rate of conversion is increasing the yield is not found to be increasing considerably. This might be due to the limited reactivity of carbonyl groups.

As shown in the table -1, in benzophenone, presence of two phenyl groups increases the electron density considerably at carbonyl group to affect the conversion adversely. That is why the %yield for benzophenone as starting material is the least amongst three of the reactants under study.

The -CH₃ group in Acetophenone neither support nor interferes the conversion rate as its electron donating capacity is less as compare to phenyl group.

In 4-chlorobenzaldehyde, due to electron withdrawing effect of chlorine, reactivity of carbonyl group is greater as compare to the group in other two reactants under study.

Time required for the completion of the reactions by ultrasonic irradiation was less as compared to chemical method. Yield were also compared, it was found that yields of oxime prepared by ultrasonic irradiation method were high as those of the chemical method.
**Table 1:** Comparative Results for Oxime preparation by Chemical and Ultrasonic Method.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of Compound</th>
<th>Chemical method</th>
<th>Ultrasound method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melting / Boiling point °C</td>
<td>Yield %</td>
<td>Rf Value</td>
</tr>
<tr>
<td>1</td>
<td>Benzophenone oxime</td>
<td>141</td>
<td>76.40</td>
</tr>
<tr>
<td>2</td>
<td>Acetophenone oxime</td>
<td>60</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>4-Chloro benzaldehyde oxime</td>
<td>107</td>
<td>79</td>
</tr>
</tbody>
</table>

**TLC:** TLC (Thin layer chromatographic) plates were run using suitable mobile phase and same chromatographic conditions for the identification of the product formed by routine chemical synthetic method and ultrasonic method. Products formed by both the methods are found to appear at same Rf value. Hence Oximes formed by both the method are identical is confirmed.

**Fig a:** TLC plates showing Benzophenone (1), oximes A (prepared by chemical method) and A-1 (prepared by ultrasonic method)
**Fig b:** TLC plates showing Acetophenone (2), oximes B (prepared by chemical method) and B-1 (prepared by ultrasonic method)

**Fig c:** TLC plates showing 4-chlorobezaldehyde (3), oximes C (prepared by chemical method) and C-1 (prepared by ultrasonic method)

**Infrared Data:**

To confirm the formation of oximes by both the methods of preparation, the products obtained were subjected for Infrared spectral analysis. The instrument used for the analysis was Bruker FTIR with ATR in the region 4000-200 cm\(^{-1}\).

The IR spectral values obtained for oximes prepared using three different starting materials are tabulated as follow.

**Table 2: C=N stretching frequencies of oximes (cm\(^{-1}\)) formed by chemical and ultrasonic method**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of Compound</th>
<th>Results</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chemical method</td>
<td>Ultrasound method</td>
</tr>
<tr>
<td>1</td>
<td>Benzophenone oxime</td>
<td>1676</td>
<td>1660</td>
</tr>
<tr>
<td>2</td>
<td>Acetophenone oxime</td>
<td>1644</td>
<td>1629</td>
</tr>
<tr>
<td>3</td>
<td>4-Chloro benzaldehyde oxime</td>
<td>1627</td>
<td>1639</td>
</tr>
</tbody>
</table>

Oximes have three characteristic bands in the infrared spectrum, at wavenumbers 3600 (O-H), 1665 (C=N) and 945 (N-O) (15). Oxime of benzophenone formed by chemical method (A) shows C=N stretching frequencies at 1676.33 cm\(^{-1}\) and that of formed by ultrasonic irradiation (A-1) shows C=N stretching frequency at 1660.10 cm\(^{-1}\) which are within the standard range of 1650 – 1700 cm\(^{-1}\).

The IR spectra for all the three oximes prepared by both chemical method and ultrasonic irradiation method are given below,
**Fig d :** IR Spectra for Oxime of Benzophenone(A) formed by chemical method

![IR Spectra for Oxime of Benzophenone(A)](image)

**Fig e :** IR Spectra for Oxime of Benzophenone(A-1) formed by ultrasonic method

![IR Spectra for Oxime of Benzophenone(A-1)](image)

**Fig f :** IR Spectra for Oxime of Acetophenone (B) formed by chemical method

![IR Spectra for Oxime of Acetophenone (B)](image)

**Fig g :** IR Spectra for Oxime of Acetophenone(B-1) formed by ultrasonic method

![IR Spectra for Oxime of Acetophenone(B-1)](image)
CONCLUSION

The oximes can be synthesised by using ultrasound technique. The ultrasonic irradiation method for the synthesis of organic compound is more efficient method as compare to routine organic synthesis as it limits the use of toxic, volatile and carcinogenic organic solvent. Reaction can be carried out at ambient temperature, which ultimately saves energy and achieves economy. Chemical method is time consuming with low rate of reaction however the ultrasonic irradiation method is having high rate of reaction. Hence it can be stated that ultrasound technique is in favour of green synthesis of oximes starting with benzophenone, acetoophenone and 4-chlorobenzaldehyde. However the substituent at carbonyl group of starting material has pronounced effect on its conversion rate to the oxime.
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