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Short Communication

Comparative material study and synthesis of 4-(4-nitrophenyl)oxazol-2-amine via sonochemical and thermal method

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ABSTRACT

The present paper deals with the synthesis of aminooxazole derivatives via thermal and ultrasonic methods using deep eutectic solvent as medium. It was observed that ultrasound-assisted method gave 90% yield in just 8 min as against 3.5 h required to get 69% yield by thermal method. One of the compounds 4-(4-nitrophenyl)-1,3-oxazol-2-amine synthesized by both methods were subjected to material characterization study via XRD, TGA and SEM analysis. It was observed that use of ultrasound not only increased the rate of reaction but also improved the quality of product obtained. The crystallinity of the product from ultrasound method was 21.12% whereas thermal method fetched only 8.33% crystallinity thereby improving crystallinity by almost 60%. In addition, sonochemical synthesis also saved more than 70% energy as depicted by energy calculations.

1. Introduction

Sonochemical energy delivery has been used as an excellent alternative to thermal energy in promoting organic reactions, especially those requiring harsh conditions. The use of ultrasound has also been known to improve the rates of reaction and yields thereby saving tremendous amount of energy required for synthesis [1]. The origin of this energy lies in the cavitation phenomenon that involves sequential formation, growth and collapse of several millions of microscopic vapor bubbles (voids) in the liquid [2,3]. These fast implosions generate extremely high pressures of about 1000 atm and temperatures of 5000 °C within the cavity thereby sustaining heating and cooling rates above 10 billion °C per second. Such extreme and localized hot spots act as micro reactor wherein sound energy is transformed into useful form of chemical energy [4–6].

This cavitationally induced phenomenon is known to activate reactant molecules entering into it and thereby converting them into reactive intermediates. In addition, such a phenomenon occurs more easily in solvents with low vapor pressure [7,8]. In this context, we had applied the effective combination of deep eutectic solvents and ultrasound, for the first time, in synthesis of novel oxazole derivatives [9]. Therein, we have explained the effectiveness of this combination in improving reaction parameters and conserving the energy. It is well known that ultrasound technique not only improves the rates and yields of reaction but also affects properties of material like crystallite size, percentage crystallinity and morphology of product crystals [10]. We now apply this strategy for the synthesis of amino oxazole derivatives and also perform material characteristics study of 4-(4-nitrophenyl)-1,3-oxazol-2-amine.

The oxazole moiety was chosen for conducting property studies due to the significant applications like versatile biological activities [11,12], application as important precursors in organic transformations [13,14], fluorescent whitening agents [15] and scintillating compounds [16]. Moreover, the advantages of using deep eutectic solvents, as reaction media, are several owing to their obvious green characteristics like bio-degradability, non-toxicity, non-volatility and recyclable nature [17]. Due to these beneficial features, they have been applied in several organic transformations [18–22] and also for electrochemical applications [23].

The product materials derived from sonochemical method (US) and thermal method (NUS) were compared for various characteristics such as crystallinity, thermal decomposition and morphology of crystals via X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscope (SEM) respectively. In

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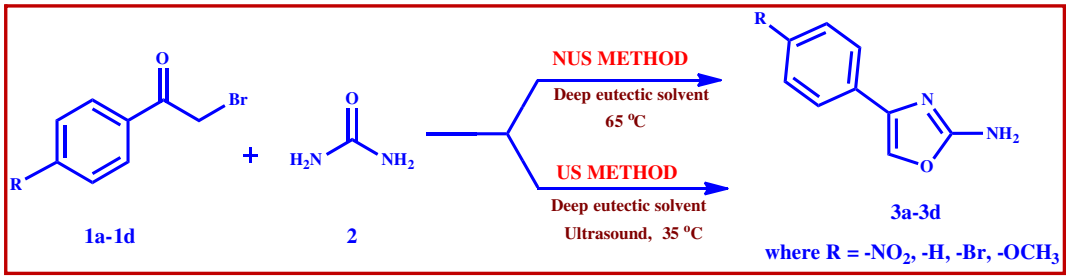


Scheme 1. Thermal and ultrasound assisted synthesis of oxazole derivatives **3a–d** using deep eutectic solvent as reaction medium.

addition, the energy efficiency of sonochemical method is also described.

2. Materials and methods

2.1. Materials

All the solvents and chemicals were procured from S D fine chemicals (India) and were used without further purification. The reactions were monitored by TLC using 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized with UV light.

Key intermediate 2-bromo-1-(4-methoxyphenyl) ethanone, 2-bromo-1-(4-nitrophenyl)ethanone, 2-bromo-1-(4-bromophenyl)ethanone was prepared by bromination of their respective acetophenone derivative with *N*-bromosuccinimide (NBS) in accordance with the reported reference [24]. The deep eutectic solvent used in the present work was easily prepared from choline chloride (1 eq) and urea (2 eq) at 80 °C by a previously reported method [25] with 100% atom economy. The resulting viscous liquid with freezing point of 12 °C [17], was used directly without any purification.

2.2. Reaction scheme

The reaction scheme of phenacyl bromide derivatives and urea in deep eutectic medium is shown in Scheme 1.

2.3. Ultrasound set-up

Ultrasound for sonochemical synthesis is generated with the help of ultrasonic instrument set-up (horn type). The specification and details of the set-up, processing parameters used during the experiments are:

Make: ACE, USA.
Operating frequency: 22 kHz.
Rated output power: 750 W.
Diameter of stainless steel tip of horn: 1.3×10^{-2} m.
Surface area of ultrasound irradiating face: 1.32×10^{-4} m^2.
Intensity: 3.4×10^5 W/m^2.

2.4. Synthesis of oxazole derivative **3** by thermal heating in DES medium (NUS method)

A mixture of phenacyl bromide derivative **1a–d** (1.0 eq) and urea **2** (1.0 eq) was added to the deep eutectic solvent (7.0 g) with stirring. The reaction mixture was stirred at (65 ± 2 °C). The reaction was monitored by thin layer chromatography (TLC). The phenacyl bromide derivative was almost completely consumed after certain time (as given in Table 1). The reaction mass was extracted using dichloromethane (DCM). The DCM layer was subjected to evaporation under reduced vacuum to obtain the final product **3a–d**.

2.5. Synthesis of oxazole derivative **3a** by ultrasound method in DES medium (US method)

A mixture of phenacyl bromide derivative **1a–d** (1.0 eq) and urea **2** (1.0 eq) was added to the deep eutectic solvent (7.0 g) and the mixture was stirred initially for the mixing of substrates. The reaction mixture was then placed under sonication using an ultrasonic horn (ACE horn, 22 kHz frequency) at 40% amplitude for required time with a 5 s ON and 5 s OFF cycle from time $t = 0$ h. The temperature of the process was maintained at 35 ± 2 °C by means of supply of water to the jacketed reactor, used for the synthesis. The reaction was monitored by thin layer chromatography (TLC). The complete consumption of reactant was observed after certain time (as stated in Table 1). The reaction mass was extracted using dichloromethane (DCM). The DCM layer was subjected to evaporation under reduced vacuum to obtain the final product **3**. The reaction time was estimated by repeating the same reaction three times.

The deep eutectic solvent could be easily isolated after extraction of product as mentioned in procedure owing to its immiscibility in DCM. The recovered DES was further used for the next run wherein the reaction between 2-bromo-1-(4-nitrophenyl)ethanone and urea was considered as a standard reaction.

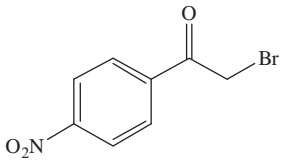
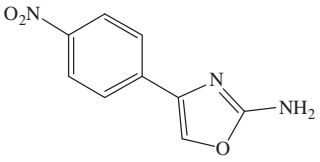
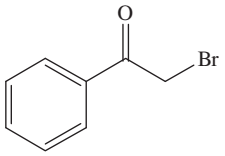
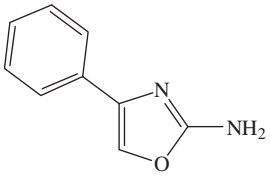
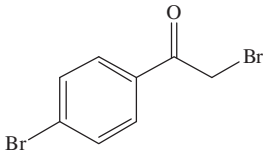
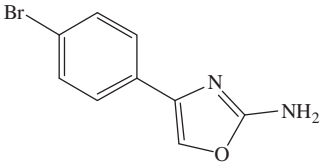
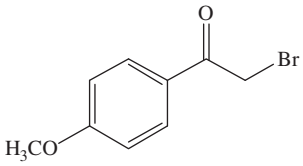
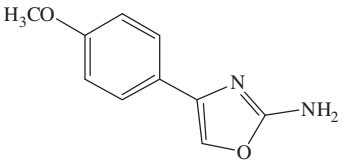
2.6. Characterization and spectral data

4-(4-Nitrophenyl)-1,3-oxazol-2-amine (**3**): m.p. = 186 °C (lit. m.p. = 190 °C [26]); (νmax/cm^{-1} 3400 (N–H), 3128 (Ar. C–H), 1667 (C=N), 1567 (C=C), 1493 (C=C), 1447 (C=C), 1068 (C–O); ^{1}H NMR(300 MHz; $CDCl_3$; Me_4Si) δ = 8.25–8.20 (2H, m, CH), 8.19–8.17 (1H, s, CH), 7.90–7.84 (2H, m, CH), 7.00–6.90 (2H, bs, NH_2); ^{13}C NMR(300 MHz; $CDCl_3$; Me_4Si) δ = 161.9, 145.9, 137.5, 130.8, 130.4, 125.4, 124.0; EIMS m/z = 206.2, $C_9H_7N_3O_3$, calculated m/z: 205.1.

3. Characterization and material study

The oxazole derivative was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy and mass spectrometry. ^{1}H NMR and ^{13}C NMR spectrums were recorded on Varian 300 MHz mercury plus spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectral data were obtained with micromass-Q-Tof (YA105) spectrometer. In order to study the properties of materials, the oxazole samples synthesized by both methods were initially subjected to X-ray diffraction (XRD) on a Rigaku Mini-Flex X-ray Diffractometer. The XRD patterns were

Table 1
Synthesis of oxazole derivatives from phenacyl bromide derivatives with urea by thermal and ultrasound methods.

Entry[a]	Acyl bromide	Product	Reaction time		Yield (%)		Melting point (°C)	
			NUS[b] (h)	US[c] (min)	NUS[b] (h)	US[c] (min)	Literature	Observed
3a			3.5	8	69	90	190 [26]	186
3b			4.5	12	63	88	140 [26]	138
3c			4	13	53	82	185–186 [27]	182
3d			5	20	51	79	180 [26]	188

[a] All reactions were carried out with derivative of phenacyl bromide (1 eq), urea 2 (1 eq), DES (7.0 g).
[b] Isolated yields of oxazoles by thermal method (NUS), reaction temperature = 65 ± 2 °C.
[c] Isolated yields of oxazoles by ultrasonic method (US) at room temperature (35 ± 2 °C).

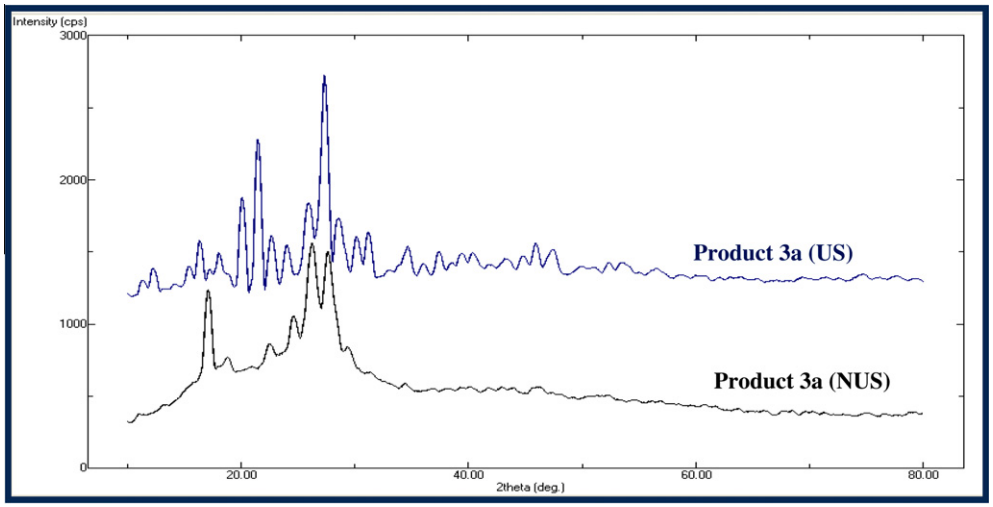


Fig. 1. XRD pattern of the product **3a** obtained by thermal (NUS) and ultrasound method (US).

recorded at angles between 2° and 80°, with a scan rate of 2°/min. The crystallite sizes were obtained using the Debye–Scherrer equation. The thermal studies of these samples were conducted by thermo-gravimetric analysis (TGA) done with the help of TA Instruments (SDT R600v8.2 Build 100), USA at heating rate of 10°/min. The Scanning Electron Microscopy was performed on a JOEL JSM 680LA 15 kV SEM by deposition of platinum on sample powder thereby giving a prediction about the surface characteristics of samples.

4. Results and discussions

4.1. Synthesis of oxazole derivatives by thermal (NUS) and ultrasound (US) method

Keeping in mind the parameters derived in our earlier report [9], we considered extending it towards the synthesis of substituted aminooxazole derivatives. The method showed good tolerance towards both electron donating and withdrawing

Table 2
Crystallinity measurements, percentage yield and energy data for synthesis of 4-(4-nitrophenyl)-1,3-oxazol-2-amine synthesizd by thermal (NUS) and ultrasound method (US).

Method	Reaction time	Crystallinity (%) Average	Crystallite size, *d* (nm) Average	Yield (%) Average	Energy utilized (kJ/g)
Thermal (NUS)	3.5 h	8.33	15.865	69	6.46
Ultrasonic (US)	8 min	21.12	51.414	90	0.52

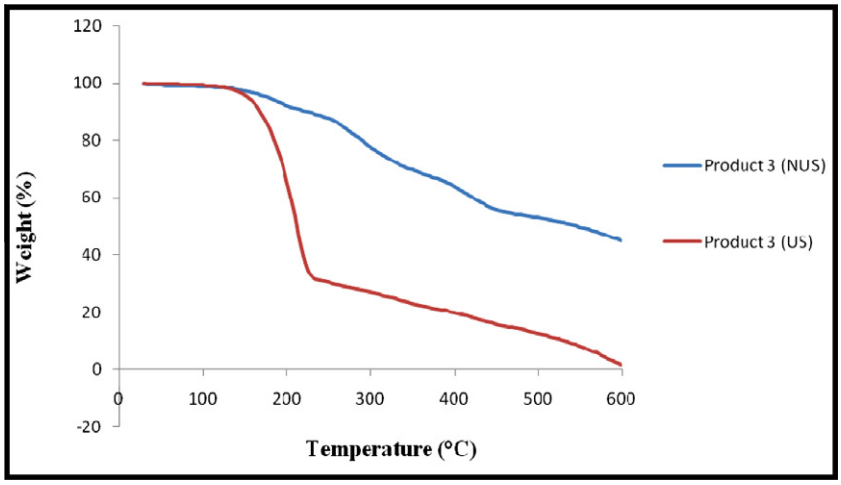


Fig. 2. Thermogravimetric analysis of product **3a** synthesized by thermal (NUS) and ultrasound (US) method.

substituents. The thermal method took a longer time and gave product with moderate yields. However, it was interesting to know that ultrasound method led to complete consumption of reactant within just 8–20 min in good yields (Table 1). The impact of acoustic energy was evident in reduction of the processing time and increasing yield of the reaction mass. This is due to the rapid micromixing that results in faster reaction.

4.2. Prediction of X-ray diffraction (XRD) data

X-ray diffraction analysis represents a versatile technique for characterization of various crystalline forms or phases in powder and solid samples. It also assists in deriving the percentage crystallinity and crystallite size of samples.

From the XRD patterns (Fig. 1), calculating percentage crystallinity and crystallite size are possible. The amorphous phase fraction of the sample may be determined by taking the ratio of the amorphous area of the X-ray diffractogram to the total exposed area (amorphous and crystalline). The area covered by the amorphous region means that the area of the diffractogram not contained by any sharp diffraction peaks. A method for estimation of amorphous phase fraction from XRD patterns have been developed by Pandit and workers [28,29].The results summarizing the% crystallinity and crystallite size of material for compound **3a** are depicted in Table 2.

It can be seen from Fig. 1 that the peaks at different crystal planes of NUS synthesized oxazole derivatives matches exactly with that of US synthesized oxazole derivatives which shows that there is no difference in the two synthesized products. Broadening peaks, for both samples, in the XRD pattern also clearly shows that there may be formation of very small nanocrystals. The crystallinity of all the samples is still considerable because of the inherent characteristics of the sonically assisted process. It was found that US synthesized oxazole shows more crystallinity (21.12%) than NUS synthesized oxazole (8.33%). The reasons for obtaining such results are due to the useful environments created by ultrasound during sonication that facilitates faster reaction, allowing crystal to form properly. The possible reasoning behind increase in the crystallinity of US sample than NUS sample have been explained in our earlier work [10].

4.3. Thermogravimetric analysis (TGA)

The oxazole product **3a** derived from both methods were subjected for study of its thermal stability under nitrogen atmosphere via thermogravimetric analysis (TGA). It can be observed from Fig. 2 that product **3a** obtained from NUS method decomposed slowly over a range of temperature. However, the phase transformation was very sharp and rapid in case of product derived from US method, which is consistent with its observed higher crystallinity. The reason behind slow decomposition may be because of higher amorphous phase content. Higher the percentage of amorphous phase content in any organic derivative, lower is the decomposition rate. It is due to the better micro or molecular level mixing which enhances the formation of clear crystal structure.

4.4. Scanning electron microscope (SEM) analysis

The scanning electron microscope images were taken for product **3** synthesized by both thermal and ultrasound method. The magnification at 1000× clearly shows sharper rod-like natured crystals of the product derived by US method (Fig. $3B_1$) as compared to thermal method (Fig. $3A_1$) that gave clustered aggregate which were amorphous in nature. This aspect became clearer on further magnification (Fig. $3A_2$ and $3B_2$). It is clearly seen that lesser or no agglomeration and sharply defined structures are observed in the case of the US synthesized sample. The use of ultrasound as an intensification tool has had its influence in the

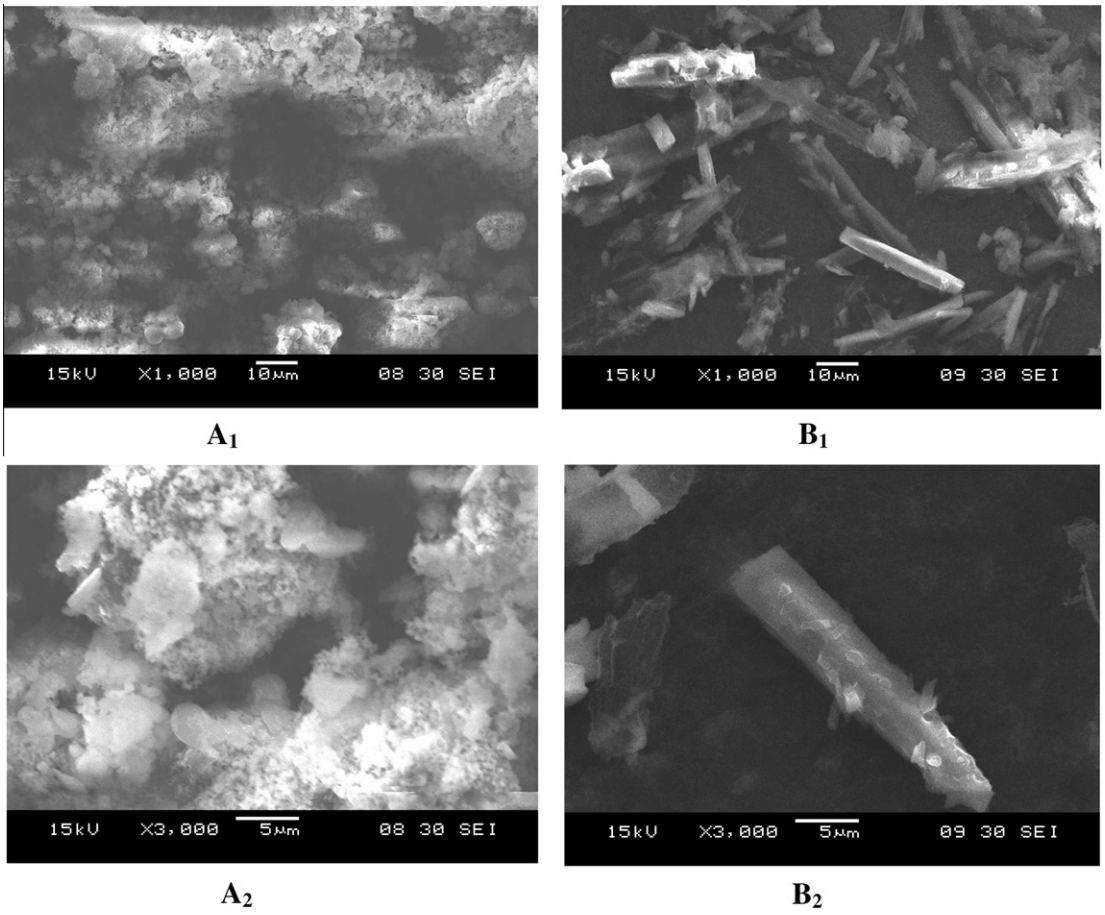


Fig. 3. SEM micrograph of product **3a** at: 1000×: (A_1) thermal method (NUS) and (B_1) ultrasound method (US). 3000×: (A_2) thermal method (NUS) and (B_2) ultrasound method (US).

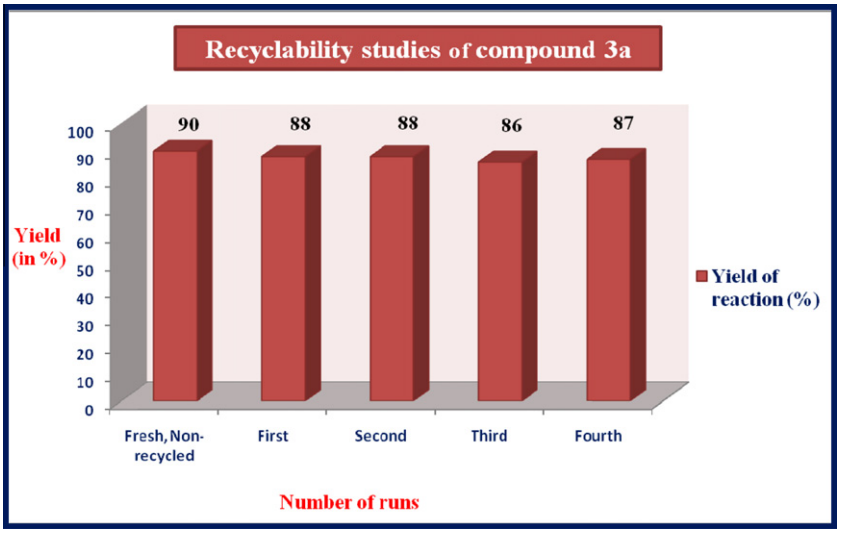
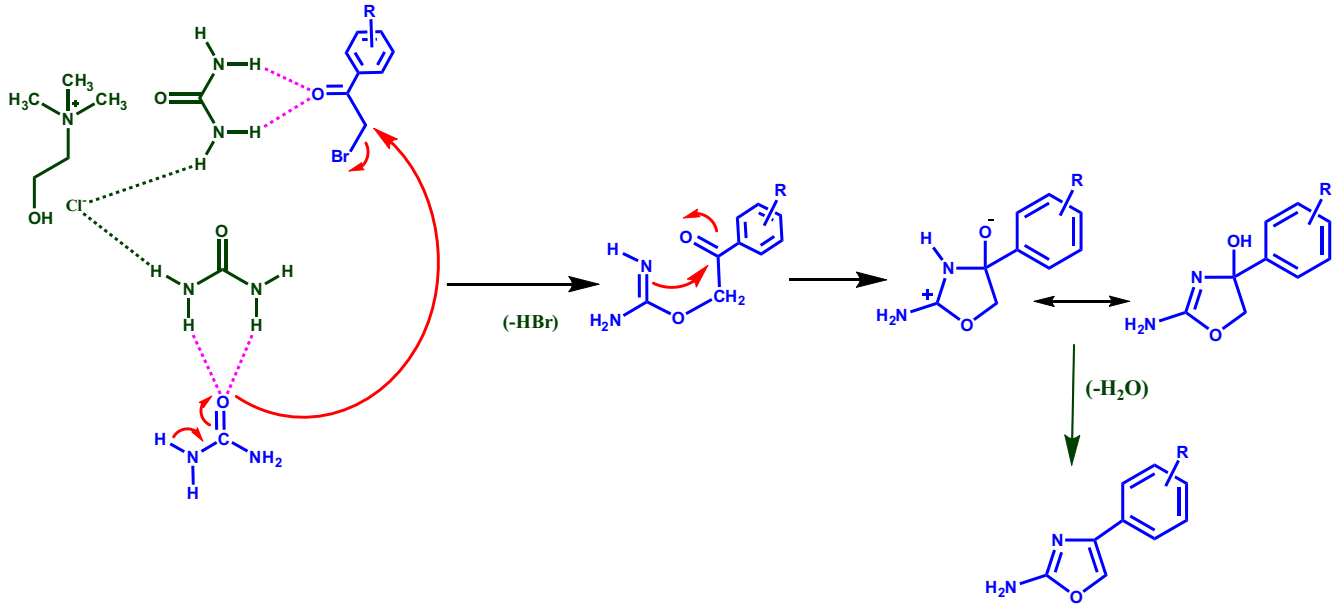


Fig. 4. Recyclability studies in synthesis of amino oxazole derivative (**3a**) from 2-bromo-1-(4-nitrophenyl)ethanone and urea.

reaction step by considerably changing crystals at the synthesis stage itself. This not only helps in improving its effect on material properties by reducing the overall reaction time, improving product quality but also aids in decreasing the difference in the types of crystal shapes formed and bringing more uniformity.

4.5. Recyclability of deep eutectic solvent

The deep eutectic solvent medium derived from choline chloride and urea was recycled and re-used up to five consecutive runs. Reaction of 2-bromo-1-(4-nitrophenyl)ethanone with urea was



Scheme 2. Plausible mechanism for synthesis of oxazole derivatives.

selected as the model reaction. A slight darkening of the eutectic mixture was observed after recycling, however, no significant decrease in yields of products was obtained as shown in Fig. 4. This indicates the fact that ultrasound does not hold any negative impact on the eutectic mixture thereby highlighting the significance of using DES as reaction medium in sonochemical approach.

4.6. Efficacy of energy utilization

Appendix A show the comparison of the energy based performance of the two types of synthesis methods, conventional (NUS) and sonochemical (US) used for synthesizing aminooxazole derivative. The energy utilized for the synthesis of oxazole material is the total energy supplied (kJ) per unit weight of the material processed/obtained (g). It is already explained in Section 4.1 that reaction time to synthesize oxazole was 8 min for US method and 3.5 h for NUS method. Total energy required per unit weight of the material processed to synthesize oxazole is 0.523 (kJ/gm) for US method and 6.46 (kJ/gm) for NUS method. Thus, US method proved to be energy efficient which saved more than 70% of energy utilized by NUS method and also a reduction in the reaction duration.

4.7. Mechanism of reaction

A suitable mechanism is proposed that illustrates the role of DES in oxazole synthesis (Scheme 2). This mechanism is in sync with our earlier predicted mechanism [9]. The ability of urea component in DES [21] to catalyze reactions is well known and hence has been applied in our case too wherein the urea component can stabilize the oxygen atom of carbonyl group thereby promoting attack of amide on acyl bromide and consequent cyclization. The sonochemical energy might help in creating highly reactive species that assists in faster cyclization and dehydration steps considering previous reports using ultrasound and ionic liquids [1].

5. Conclusions

We successfully extended the ultrasound assisted methodology in deep eutectic solvent towards the synthesis of aminooxazole derivatives. The results were compared with the thermal method wherein it was observed that use of ultrasound improved the yield and rates of reaction. The ultrasonic irradiation also gave better crystallinity of product (improvement by 60%) as observed by XRD studies. This fact was confirmed by SEM images which showed better rod-shaped crystals in comparison to clustered aggregates obtained by thermal method. Moreover, the energy calculation data indicated more than 70% saving in energy during synthesis. In conclusion, the method was green, rapid, energy-efficient and gave better properties of product.

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Appendix A

A.1. Energy calculations

Following sample calculation is done on the basis of data taken from Table 1 for the synthesis of compound 3a.

A.1.1. Energy delivered during sonication

- Energy delivered during sonication = Energy required to synthesize Oxazole material.
- Electrical energy delivered during sonication using horn for 8 min (indicated by the power meter) = 14.45 kJ.
- Efficiency of Horn taken for the calculation = 30% (estimated independently using calorimetric studies).
- Actual energy delivered by horn during sonication = Energy delivered during sonication using horn in 8 min × Efficiency of Horn = 14.45 × 30/100 = 4.33 kJ.
- Quantity of material processed = Quantity of 2-bromo-1-phenylethanone + Quantity of urea + Quantity of DES =1 (g) + 0.24 (g) + 7 (g) = 8.24 (g).

- Net energy supplied for processing of material using sonochemical method = Actual energy delivered by horn during sonication/Total reaction mass processed = 4.33 (kJ)/8.24 (g)

$$= 0.525\ (\mathrm{kJ/g}) \qquad (A)$$

A.1.2. Energy delivered during conventional method

- Voltage input in overhead stirrer (Model REMI Motors RQ-129/D Rajendra Electrical Industries Ltd., Vasai, India.
- Current measured using digital multimeter (KUSAM-MECO Model 2718, Kusam Electrical Industries Ltd., Mumbai, India) = 37 mA = 37×10^{-3} A.
- Power input in magnetic stirrer = Voltage input × Current measured = 230 (V) × 37×10^{-3} (A) = 8.51 W (J/s).
- Efficiency of magnetic stirrer taken for the calculation = 40% (estimated independently using calorimetric studies).
- Actual power input in overhead stirrer = Power input in magnetic stirrer (W) × 40/100 =8.51 (W) × 40/100 = 3.404 W (J/s).
- Time required for completion of reaction = 3.5 h (12,600 s).
- Energy delivered during conventional method for stirring = Power input in magnetic stirrer × Time required for completion of reaction = 3.404 J/s × 3.5 h × 3600 s/h = 42890 J = 42.89 kJ.
- Quantity of material processed = Quantity of 2-bromo-1-phenylethanone + Quantity of urea + Quantity of DES = 1 (g) + 0.24 (g) + 7 (g) = 8.24 (g).
- Energy supplied for heating reaction mixture to 65 °C from room temperature (35 °C)

$$\begin{aligned} &= \mathrm{Mass} \times C_p \times \Delta T \\ &= 8.24 \times 1 \times (65 - 35) \quad (C_p \approx 1) \\ &= 247.2\ \mathrm{cal} \\ &= 1034\ \mathrm{Joules} \qquad (1\ \mathrm{cal} = 4.184\ \mathrm{Joules}) \end{aligned}$$

- Total energy supplied for heating reaction mixture to 65 °C from room temperature (35 °C)

$$\begin{aligned} &= \text{Energy supplied for heating reaction mixture to } 65\ ^\circ\mathrm{C} \\ &\quad \text{from room temperature } (35\ ^\circ\mathrm{C}) \times 3.5\ \mathrm{h} \times (1/30)\ \mathrm{h} \\ &\quad \times (30\ \text{min are required for cooling}) \\ &= 1034\ \mathrm{Joules} \times 10 \\ &= 10,340\ \mathrm{Joules} = 10.34\ \mathrm{kJ} \end{aligned}$$

- Net energy delivered during conventional method = Energy delivered during conventional method for stirring + Total energy supplied for heating reaction mixture to 65 °C from room temperature (35 °C) = 42.89 + 10.34 = 53.23 kJ
- Net energy supplied for processing of material using conventional method = Net energy delivered during conventional method/Quantity of material processed = 53.23 (kJ)/8.24 (g)

$$= 6.46\ (\mathrm{kJ/g}) \qquad (B)$$

A.1.3. Percentage of energy saved (%)

- Net energy saved = (Net energy supplied for processing of material using conventional method (B)) − (Net energy supplied for processing of material using sonochemical method (A))/(Net energy supplied for processing of material using conventional method (B)) × 100 = (6.46 − 0.52)/8.24 × 100 = 72.08%

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