



Short Communication

Ni(NO₃)₂·6H₂O/I₂/water: A new, mild and efficient system for the selective oxidation of alcohols into aldehydes and ketones under sonic condition

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ABSTRACT

A new, simple, efficient and rapid method for the oxidation of alcohols into respective aldehydes and ketones by Ni(NO₃)₂·6H₂O/I₂/water system under ultrasonic irradiation is reported. The process is mild and inexpensive; the yields are high and the reactions go to completion within 2–7 min.

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1. Introduction

First report on the use of ultrasound in organic syntheses was presented by Richards and Loomis in the year 1927 [1]. Compared to traditional methods, sonic reactions are more convenient and high yielding and hence, a large number of organic reactions have been reported in the literature [2–7]. Organic reactions not only get accelerated, the number of steps involved can also be reduced, and cruder reagents can be used under sonic conditions. These effects of ultrasound are achieved due to the phenomenon of acoustic cavitation [8] and the primary chemical reactions are due to the transient state of high temperatures and pressures [9].

Oxidation of alcohols into corresponding carbonyl compounds is an important transformation in organic synthesis [10–13]. In particular, the controlled oxidation of primary alcohols to aldehydes, without forming over-oxidized product is really a challenging task. Traditionally, this reaction is carried out by using various inorganic oxidants. In recent years, efforts have also been made to develop more valuable catalytic oxidizing processes including homogenous catalysts as well as heterogeneous catalysts [14,15] such as transition metal salts [16], oxygen-containing oxidants [17] including oxygenated organic solvents [18–20]. Recently, we have oxidized a series of benzyl alcohols into respective benzaldehydes by FeCl₃/HNO₃ under sonic condition in high yields [21]. We, in this paper, present another simple, efficient and rapid oxidation

of primary alcohols to aldehydes and secondary alcohols into ketones by a Ni(NO₃)₂·6H₂O/iodine/water system under ultrasonic condition. The process is mild and inexpensive; the yields are high and the reactions go to completion within 2–7 min as shown in Schemes 1–3.

2. Experimental section

2.1. Materials and instruments

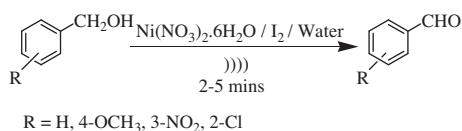
Anisyl alcohol, 3-nitrobenzyl alcohol, 2-chlorobenzyl alcohol and furfuryl alcohol were prepared by the reduction of respective aldehydes. All the other reagents used were commercially available. The products were characterized by IR and GC–mass spectral analysis. All the reactions were studied using SIDILU Indian make sonic bath working at 35 kHz (constant frequency) at 25 °C; and followed by SHIMADZU GC–MS QP 5050A instrument equipped with a 30 m long and 0.32 mm dia BP-5 column with the column temperature programme 80–15–250 °C.

2.2. Oxidation of alcohols under ultrasonic condition: a general procedure

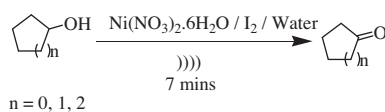
A mixture of alcohol (10 mmol), Ni(NO₃)₂·6H₂O (2.908 g, 10 mmol), I₂ (1.3 g, 10 mmol) and water (2 mL) were sonicated in a sonic bath working at 35 kHz (constant frequency) maintained at 25 °C by circulating water. After completion of the reaction (Table 5, monitored on TLC), the product was taken into diethyl

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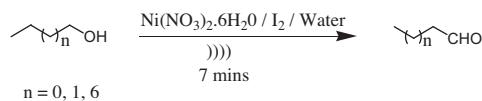
E-mail address: m_af_pasha@gmail.com (M.A. Pasha).



Scheme 1.



Scheme 2.



Scheme 3.

Table 1

A comparative study on the oxidation of benzyl alcohol (10 mmol) to benzaldehyde by different metal nitrates (10 mmol) without solvent.

Entry	Metal nitrates	Time (min)		Yield (%) ^a Benzaldehyde ^b
		At 25 °C))))	
1	Fe(NO ₃) ₃ ·9H ₂ O	240–300	180–240	10
2	Ni(NO ₃) ₂ ·6H ₂ O	240–300	180–240	20
3	Cu(NO ₃) ₂ ·5H ₂ O	240–300	180–240	ND
4	Ba(NO ₃) ₂	240–300	180–240	ND
5	NaNO ₃	240–300	180–240	ND

ND: not detected.

^a Isolated yields.

^b Characterized by IR and by comparison with authentic sample on TLC.

ether (10 mL), the organic matter was washed with sat. NaHCO₃ (2.5 mL), water (5 mL) and then dried over anhydrous Na₂SO₄. The organic layer was evaporated in a fume hood to get almost pure aldehyde. The crude was then subjected to silica gel column chromatography to get the pure product. All the products were characterized by IR, GC–mass spectral analysis; and the physical

Table 2

A comparative study on the oxidation of benzyl alcohol (10 mmol) into benzaldehyde by Ni(NO₃)₂ (10 mmol) in different solvents under normal and sonic condition.

Entry	Solvent ^a	Time (min)		Yield (%) ^b Benzaldehyde ^c
		At 25 °C))))	
1	No solvent	120–180	60–80	5 ^d
2	Water	60–80	20–40	30
3	Water (distilled)	60–80	20–40	30
4	Deionized water	60–80	20–40	30
5	Ether	60–80	20–40	20 ^d
6	Ethanol	60–80	20–40	ND
7	Acetone	60–80	20–40	ND
8	Acetonitrile	60–80	20–40	10 ^d
9	Xylene	60–80	20–40	5 ^d
10	Hexane	60–80	20–40	25
11	THF	60–80	20–40	20

^a 5 mL.

^b Isolated yields.

^c Characterized by IR and by comparison with authentic sample on TLC.

^d GC, ND: not detected.

properties were compared with the properties of authentic samples.

3. Results and discussion

Metal nitrates are known to oxidize alcohols [22]. Laura et al. [23] used various metal nitrates and bromides for the selective sulfoxidation reaction and showed that Fe(NO₃)₃·9H₂O–FeBr₃ was the most effective system. On the same lines we used various metal nitrates in order to develop a new catalytic system for the oxidation of alcohols into respective aldehydes and ketones. Benzyl alcohol was selected as a standard and the oxidation of benzyl alcohol, we found that, Ni(NO₃)₂ or ferric nitrate give only a trace amount of benzaldehyde after several hours at 25 °C, without any solvent. Among the two, Ni(NO₃)₂ gave some promising results as can be seen from the data presented in Table 1. Reaction of benzyl alcohol was then studied with Ni(NO₃)₂ in different solvents, the results of this study are presented in Table 2. It can be seen from Table 2 that, in water the yield of benzaldehyde is only 30% which is again not appreciable. Since, iodine is a good oxidizing agent, which is non-hazardous and readily available, we used iodine along with Ni(NO₃)₂ to get the desired product in 95% yield in water as a solvent. In order to standardize the conditions, the reactions were carried out under various conditions and the results of all these studies are presented in Tables 3–5. From Tables 1–5 it is clear that, oxidation of benzyl alcohol using Ni(NO₃)₂/I₂/water system under the influence of ultrasound at 35 kHz is efficient and gives high yield of the product in short duration (Table 3, entry 5).

From Tables 1 and 2 it is clear that, Ni(NO₃)₂ alone and Ni(NO₃)₂ in solvent do not have much effect on the oxidation. Table 3 indicates that, equimolar amounts of Ni(NO₃)₂/I₂ are essential for the reaction to give high yields of the desired products in water without any side products (entry 5). The data given in Table 4 indicates that, for 10 mmol of the reactants and reagents, a minimum of 2 mL of water is required for the reaction (entry 10). It is also clear from Table 5 that, only Ni(NO₃)₂/water or only I₂/water does not give the expected products; Ni(NO₃)₂/I₂/water system is essential to convert primary alcohols into aldehydes and secondary alcohols into respective ketones and under sonic condition the reactions goes to completion within 7 min (entry 3).

In order to find the generality of the use of Ni(NO₃)₂/I₂/water system for the oxidation of alcohols, different substituted aromatic alcohols, primary and secondary aliphatic alcohols were selected and the oxidation was carried out under sonic condition. The results of this study are presented in Table 6. It can be seen that, alcohols give respective aldehydes and ketones in very high yields without any side products.

4. Mechanism

A plausible mechanism for the oxidation of alcohols into aldehydes and ketones which is on par with the mechanism proposed by Mohammad [24] is envisaged in Scheme 4. Iodine present in the organic layer of the above mentioned biphasic system may activate the alcohol in the first step; subsequent loss of HI may give intermediate **A**. Ni(NO₃)₂ present in the aqueous layer may react with HI to give HNO₃, the *in situ* generated HNO₃ may then react with **A** to give the intermediate **B**. Under the influence of ultrasound a molecule of nitrous acid may get eliminated from **B** in the subsequent step to give the desired carbonyl compound **C**. As a molecule of HI, HOI and a molecule of HNO₂ have to be removed from the intermediates **A** and **B** in the steps 2, 3 and 4, we feel, the steps 2, 3 and 4 are influenced by ultrasound (Scheme 4).

Table 3A comparative study on the oxidation of benzyl alcohol to benzaldehyde with different amounts of $\text{Ni}(\text{NO}_3)_2$ and iodine in water (2 mL) under sonic condition.

Entry	Ratio (eq)			Time (min)	Yield (%) ^{a,b}	
	Benzyl alcohol	$\text{Ni}(\text{NO}_3)_2$	I_2		Benzaldehyde	Benzoic acid
1	1	1	0.2	17	25	ND
2	1	1	0.4	17	35	ND
3	1	1	0.6	10	60	ND
4	1	1	0.8	5	75	ND
5	1	1	1	2	95	ND
6	1	0.2	1	8	30	70
7	1	0.4	1	8	35	70
8	1	0.6	1	10	50	45
9	1	0.8	1	10	75	20

^a Isolated yields; after silica gel column chromatography.^b Characterized by IR and by comparison with authentic samples on TLC. ND: not detected.**Table 4**A comparative study on the oxidation of benzyl alcohol (10 mmol) to benzaldehyde with $\text{Ni}(\text{NO}_3)_2$ (10 mmol) and iodine (10 mmol) in different volumes of water.

Entry	Water (mL)	Time (min)	Yield (%) ^{a,b}	
			Benzaldehyde	Benzoic acid
1	0.5	15	15	ND
2	1	15	25	ND
3	1.5	15	70	ND
4	2	15	95	ND
5	2	12.5	95	ND
6	2	10	95	ND
7	2	7.5	95	ND
8	2	5	95	ND
9	2	2.5	95	ND
10	2	2	95	ND
11	2.5	2	95	ND
12	2.5	4	95	ND
13	5	2	95	ND
14	10	2	90	ND

^a Isolated yields; after silica gel column chromatography.^b Characterized by IR and by comparison with authentic samples on TLC. ND: not detected.**Table 5**

A comparative study on the oxidation of benzyl alcohol (10 mmol) to benzaldehyde in the presence of different reagent systems at 25 °C and under sonic condition (35 KHz).

Entry	Reagent system	Time (min)		Product ^a	Yield (%) ^b
		25 °C))))		
1	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{water}$	60–80	20–40	Benzaldehyde	30 ^c
2	I_2/water	20–40	3–10	Benzoic Acid	95
3	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{I}_2/\text{water}$	80	2–7	Benzaldehyde	95

^a Characterized by IR and GC–mass spectral analysis and by comparison with authentic samples on TLC.^b Isolated yields.^c After silica gel column chromatography.

According to the proposed mechanism, HNO_3 which may form during the course of the reaction participates in the oxidation. To examine this, the reaction of alcohols with different amounts of the reagent/s viz., con. HNO_3 (with and without iodine), in water and in acetone as solvents was studied and the results of this study are presented in Table 7.

It can be seen from Table 7 that, benzyl alcohol with $\text{HNO}_3/\text{I}_2/\text{water}$ system gives benzaldehyde in 75% yield along with benzoic acid 25% (entry 3); and cyclohexanol gives cyclohexanone in 90% yield (entry 4). As benzaldehyde was formed along with an appreciable amount of benzoic acid, we feel that, use of $\text{Ni}(\text{NO}_3)_2/\text{I}_2/\text{water}$ system is more useful for the conversion of alcohols into

Table 6Oxidation of alcohols to corresponding aldehydes and ketones by $\text{Ni}(\text{NO}_3)_2/\text{I}_2/\text{water}$ under sonic condition (35 kHz constant frequency at 25 °C).

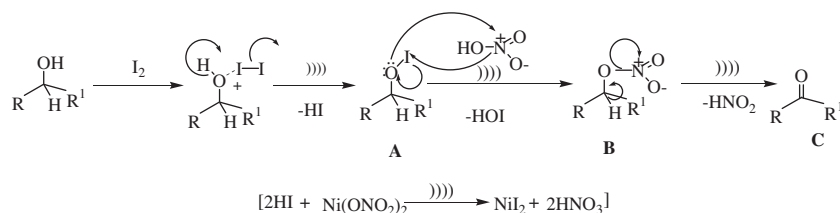
Entry	Substrate	Time (min)	Product ^a	Yield (%) ^b
1	Benzyl alcohol	2	Benzaldehyde	95
2	Anisyl alcohol	2	Anisaldehyde	90
3	3-Nitrobenzyl alcohol	3	3-Nitrobenzaldehyde	85
4	2-Chlorobenzyl alcohol	5	2-Chlorobenzaldehyde	83
5	Furfuryl alcohol	2	Furfuraldehyde	90
6	Cyclohexanol	2	Cyclohexanone	93
7	Cyclopentanol	2	Cyclopentanone	92
8	Cycloheptanol	2	Cycloheptanone	90
9	<i>n</i> -Butanol	7	<i>n</i> -Butanal	75
10	<i>n</i> -Pentanol	7	<i>n</i> -Pentanal	85
11	<i>n</i> -Decanol	7	<i>n</i> -Decanal	85

^a Characterized by IR and GC–mass spectral analysis and by comparison of physical constants of authentic samples.^b Isolated yields after silica gel column chromatography.

respective aldehydes and ketones than $\text{HNO}_3/\text{I}_2/\text{water}$ system under sonic condition.

4.1. Effect of ultrasound on the reaction

Ultrasound enhances the chemical reactions through the generation and subsequent destruction of cavitation bubbles in liquid media. Ultrasound provides an unusual mechanism for generating high-energy chemistry due to the immense temperature, pressure and the extraordinary heating rates generated by the cavitation bubble collapse. In some cases, it can increase the chemical rate by nearly million-folds [25]. The present reaction involves a two phase system: the liquid phase (reagents in solvents viz., iodine in organic layer and $\text{Ni}(\text{NO}_3)_2$ in water), and the gas phase (dissolved gases in the liquids and gases on the inner-surface of the vessel). When ultrasonic waves propagate through such a medium by a series of compression and rarefaction cycles, the rarefaction cycle exceeds the attractive forces of the molecules of the liquids and 'cavitation bubbles' will form. These cavitation bubbles grow by a process called 'rectified diffusion' which means small amounts of gas from the medium goes into the cavity (cavitation bubble) during its expansion phase, and the gas is not fully expelled during compression. The creation of the so-called hot spots in the reaction mixture produces intense local temperatures and high pressures inside the cavitation bubble and at the interfaces. The collapse can be symmetrical or can occur near the surface of the vessel resulting in an inrush of liquid predominantly from the side of the cavitation bubble remote from the surface because the surface provides resistance from one side leading to generation of powerful liquid jets, setting the molecules into rapid motion due to the energy imparted to them, hence effective collisions take place,



Scheme 4.

Table 7

Sonochemical oxidation of alcohols (10 mmol) by con. HNO_3 (2.5 mmol)^a under different conditions.^{bc}

Entry	Reagent system	Substrate (10 mmol)	Time (min)	Product ^{d,e}	Yield (%) ^f
1	$\text{HNO}_3/\text{water}$	Benzyl alcohol	5	Benzaldehyde	5 ^g
2	$\text{HNO}_3/\text{water}$	Cyclohexanol	5	Benzoic acid	80
3	$\text{HNO}_3/\text{I}_2/\text{water}$	Benzyl alcohol	5	Cyclohexanone	85
4	$\text{HNO}_3/\text{I}_2/\text{water}$	Benzyl alcohol	5	Benzaldehyde	75
5	$\text{HNO}_3/\text{I}_2/\text{water}$	Benzyl alcohol	5	Benzoic acid	25
6	$\text{HNO}_3/\text{I}_2/\text{water}$	Cyclohexanol	5	Cyclohexanone	90
7	$\text{HNO}_3/\text{acetone}$	Benzyl alcohol	5	Benzaldehyde	ND
8	$\text{HNO}_3/\text{I}_2/\text{water}$	Benzyl alcohol	5	Benzoic acid	95
9	$\text{HNO}_3/\text{acetone}$	Cyclohexanol	5	Cyclohexanone	50
10	$\text{HNO}_3/\text{I}_2/\text{acetone}$	Benzyl alcohol	5	Benzaldehyde	ND
11	$\text{HNO}_3/\text{I}_2/\text{acetone}$	Benzyl alcohol	5	Benzoic acid	ND
12	$\text{HNO}_3/\text{I}_2/\text{acetone}$	Cyclohexanol	5	Cyclohexanone	70

^a With 10 mmol HNO_3 benzoic acid is formed instantaneously.^b Iodine-10 mmol.^c Solvent-2 mL.^{d,e} Characterized by IR and GC-mass spectral analysis and by comparison with authentic samples.^f Isolated yields after silica gel column chromatography.^g By GC; ND: not detected.

thereby enhances the reaction rate of the reaction [21,26–28]. Further, in heterogeneous liquid-liquid systems, the cavitation is possible in both the phases and the tiny droplets of these layers get distributed into each other forming an emulsion. As the tiny droplets of the substrate molecules get equally distributed in the aqueous layer and vice-versa, the rate of the oxidation reaction gets enhanced because of the maximum exposure due to the large surface area [27].

There are four important steps in the mechanism of formation of aldehydes and ketones from respective alcohols by $\text{Ni}(\text{NO}_3)_2/\text{I}_2/\text{water}$. In the first step of the reaction, the alcohol gets activated by iodine in the organic layer. In the next step a molecule of HI gets eliminated from the activated alcohol to give intermediate **A** under sonication. In a parallel reaction the water soluble HI reacts with $\text{Ni}(\text{NO}_3)_2$ in the aqueous layer to give HNO_3 . The intermediate **A** then reacts with the *in situ* generated HNO_3 to give the nitrate **B**, and a molecule of HOI may get released during this conversion. In the final step, **B** loses a molecule of HNO_2 to give the respective carbonyl compound as shown in Scheme 4. As the release of HI, HOI, HNO_3 and HNO_2 from the respective species is an important part of the present reaction, and requires sufficient energy; from the data given in Tables 1–5, it is clear that, these reactions are possible more efficiently under sonic condition than under silent condition. Of the various parameters influencing the sonochemical reactivity of the present reaction; the energy and the temperature of the solvent plays a vital role, and water has the maximum I_{max} and T_{max} values [27]. The rate of the reaction is thus very fast in water and the products are formed in very high yields as shown in the Tables 4 and 6. It is also clear from the Table 4 that, the amount of water used as a solvent has no effect on the rate and yields (entries 10–14), hence, mixing effect is not the only reason for the enhancement in the rates of the reaction. It is the cleavage of the bonds and formation of the intermediates, the products and the by-products which are influenced greatly by the ultrasound

through the formation and collapse (both symmetrical as well as unsymmetrical) of ‘cavitation bubbles’ in the form of micro jets and the shockwaves in the organic as well as aqueous layers.

5. Conclusion

In conclusion, a mild, simple and an easy approach to the oxidation of alcohols into respective aldehydes and ketones using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{I}_2/\text{water}$ system under sonic condition is developed. The reaction is facile, involves simple workup, uses readily available and inexpensive chemicals and gives high yield of the products in short duration. As the over oxidation products viz., benzoic acids are not formed from primary alcohols, this procedure could be a useful alternative to the currently available methods.

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