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# The oxidation of alcohols to aldehydes and ketones with *N*-bromosuccinimide in polyethylene glycol: an experimental and theoretical study

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Oxidation of aliphatic and aromatic alcohols has been studied by using *N*-bromosuccinimide (NBS) as oxidant and polyethylene glycol (PEG) as reaction medium under mild reaction conditions. Temperature and solvent effect are studied. Theoretical study is also done with the Gaussian 98 suite of program and the calculation results are in good accordance with the experimental outcome. This system offers a very clean, convenient, environmentally benign method for the oxidation of alcohols. Copyright © 2008 John Wiley & Sons, Ltd.

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## INTRODUCTION

Carbonyl compounds constitute an important group in organic chemistry, because carbonyl groups are present as an essential constituent of pharmaceutical, dyes, fragrances, industrially important chemicals, and natural products.<sup>[1,2]</sup> Oxidation of alcohols to carbonyl compounds is among the most important functional group transformations available to the synthetic chemists.<sup>[3-7]</sup> Although, numerous methods have been developed, there are still some limitations. Amongst them, stoichiometric oxidants such as manganese dioxide,<sup>[8,9]</sup> chromium(VI)-based oxidants,<sup>[10–13]</sup> hypervalent lodine,<sup>[14–19]</sup> activated dimethyl sulfoxides,  $^{\left[ 20-25\right] }$  etc. in the organic solvents (DMSO, CH\_2Cl\_2, and acetone) were the most commonly used. Though these methods are being used in various types of organic syntheses, there are also some drawbacks. As for the heavy metal oxidants, apart from being expensive, form toxic wastes, whereas hypervalent iodine, oxidants such as o-iodoxybenzoic acid (IBX) are explosive on impact or on heating to more than 200 °C. The activated dimethyl sulfoxide gives rise to awfully smelling dimethyl sulfide. Another most conventional industrial oxidant,<sup>[26]</sup> nitric acid, though cheap, unavoidably forms various nitrogen oxides. There are also aerobic oxidation methods that use copper,<sup>[27–30]</sup> palladium,<sup>[31,32]</sup> and ruthenium compounds.<sup>[33-36]</sup> Some of these methods are limited to benzylic alcohols and also require two equivalents of the catalyst per equivalent of the alcohol <sup>[27-29]</sup> or the presence of a base and additives like di-(t-butyl azodihydrazine).<sup>[30]</sup> Additionally, other heterogeneous catalyst systems reported include Ru/CeO<sub>2</sub><sup>[37]</sup> [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> on activated carbon,<sup>[38]</sup> tetrapropyl ammonium perruthenate (TPAP)/MCM-41,<sup>[39]</sup> Ru-hydroxyapatite,<sup>[40]</sup> Ru-hydrotalcite,<sup>[41]</sup> Pd-hydrotalcite.<sup>[42]</sup> Nevertheless, most of these systems are effective for only activated and benzylic alcohols. There are a variety of method reported in literature,

however, even the most commonly used catalytic oxidations have some limitations such as pH of the medium, hazardous reagents, and solvents, formation of side products, etc.<sup>[43-47]</sup> Furthermore, most of these methods are carried out at very low concentration levels, which may involve challenging product and catalyst separation steps. Therefore, oxidation of alcohols with common oxidant is now considered most desirable especially in large-scale synthesis.

*N*-bromosuccinimide (NBS), a cheap and convenient reagent, has recently received considerable attention as catalyst not only for bromination, but also for various other organic transformations.<sup>[48–59]</sup> NBS reacts differently with many organic compounds, depending upon the nature of the reactant and reaction conditions in solution. Recently, it is used in a variety of oxidation reactions under various conditions, including the oxidation of alcohols.<sup>[60–64]</sup> However, these alcohol oxidation reactions are usually carried out using either anhydrous solvents or in acidic/basic media at varied temperatures.<sup>[60–62]</sup> Moreover, the selectivities observed were also not encouraging in some cases.<sup>[65–69]</sup> Thus there is still demand for clean, safe, and efficient procedures for the oxidation of various alcohols.

Green chemistry is becoming a central issue in both academic and industrial research in the 21st century.<sup>[70–74]</sup> The recent increased awareness of the detrimental effects of organic solvents in the environment has led to rapid growth in the research on alternative reaction media. Media considered include: (a) the use of supercritical fluids <sup>[75]</sup> that have the

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advantage of facile solvent removal and easy recyclability but require high pressure; (b) fluorous based systems [76-79] that have the advantage of being highly hydrophobic but expensive and for which the solvents are probably innocuous but have the disadvantage of being volatile; (c) more recently, environmentally benign solvents such as ionic liquids,<sup>[80-83]</sup> water,<sup>[84-86]</sup> and polyethylene glycol (PEG).<sup>[87–91]</sup> Ionic liquids have a particularly useful set of properties, being nonvolatile and virtually insoluble in water and alkanes but readily dissolving many transition metal catalysts, at the same time, they are very expensive. While the use of water as solvent is probably a desirable approach, this is often not possible due to the hydrophobic nature of the reactants and the sensitivity of many catalysts to aqueous conditions. PEG and its monomethyl ethers are inexpensive, thermally stable, recoverable, and nontoxic media for phase transfer catalysts.<sup>[92,93]</sup> PEG is also a biologically acceptable polymer, which has been used extensively in drug delivery and in bioconjugates as tool for diagnostics. Important as it is, PEG has hitherto not been widely used as a solvent medium but has been used as a support for various transformations.<sup>[94-98]</sup> We herein report PEG 400 as the reaction medium for the oxidation of alcohols to the corresponding carbonyl compounds using NBS as oxidant. The methodology is clean, convenient, environmentally benign and the yield is excellent.

### **EXPERIMENTAL SECTION**

#### Materials

All the oxidants and substrates used were commercially available and analytical grade. The substrates were used directly without further purification.

# General experimental procedure for the oxidation of alcohols

NBS (0.178 g, 1 mmol) was added to a stirred solution of alcohol in PEG 400 (2 g) and the mixture was heated to the reaction temperature (60 °C) with continuous stirring. At the end of the reaction, the reaction mixture was diluted with water, extracted with ethyl ether, and then the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to dryness in vacuo to give the crude product. The identity of the products was confirmed by <sup>1</sup>H NMR and by comparison with authentic samples Scheme 1.

## **CALCULATION METHODS**

All the electronic structure calculations were performed by means of the Gaussian 98 program packages.<sup>[99]</sup> All structures were optimized by density functional theory (DFT) methods,



Scheme 1. Oxidation of alcohols under optimized conditions

using Becke's three-parameter (B3) <sup>[100,101]</sup> exchange functional along with the Lee–Yang–Parr (LYP) <sup>[102]</sup> nonlocal correlation functional (B3LYP).<sup>[103–105]</sup> The standard split-valence double- $\xi$ basis set with polarization functions on heavy atoms, 6-31G<sup>\*</sup>, was adopted. Solvation energies of the reactants and products as well as the free energies of all the reactions were considered using the polarizable continuum model (PCM) with the permittivities of 36.64, 8.93, 4.90, and 2.38 for CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and C<sub>7</sub>H<sub>8</sub>, respectively. This approach has proven to provide a reasonably good description of polarization effect of the solvent.

#### **RESULTS AND DISCUSSION**

The oxidation of a variety of activated and non-activated alcohols was carried out by heating the reaction mixture of substrate (1 mmol) and NBS (1 mmol) in PEG 400 (2 g) at 60  $^\circ$ C. Under these conditions, most alcohols studied were smoothly converted to the corresponding carbonyl compounds in excellent yields and these results are presented in Table 1. Benzylic primary alcohols (Table 1, entries 1-4) gave excellent yields of the corresponding aldehydes in short reaction times without any noticeable overoxidation to the carboxylic acids. Meanwhile, presence of benzene ring adjacent to the -OH group in the alcohol appears to enhance the conversion. For example, benzyl alcohols (Table 1, entries 1–4),  $\alpha$ -methyl benzyl alcohol (Table 1, entry 5), and benzhydrol (Table 1, entry 6) were found to be very reactive and required shorter reaction time for the oxidation. Furthermore, aromatic substituted alcohols (Table 1, entries 1-6) were found to be more reactive than alicyclic alcohols (Table 1, entries 8-9). The calculation at the B3LYP/6-31g\* level by means of DFT method shows that the C—H (the hydrogen on the carbon atom bearing the —OH group) bond energy of cyclohexanol was 27.87 and 33.32 kcal/mol larger than that of benzyl alcohol and  $\alpha$ -methyl benzyl alcohol, respectively. This strongly indicates that the substitute of hydrogen (on the carbon atom bearing the --OH group) by bromine is more easily for benzyl alcohol and  $\alpha$ -methyl benzyl alcohol compared with cyclohexanol. Therefore, the calculation result is a good answer to the question: why aromatic substituted alcohols are more reactive than alicyclic alcohols. In addition, it is noteworthy to mention that neither oxidation nor addition was observed in the carbon-carbon double bond of cinnamyl alcohol (Table 1, entry 7), keeping intact the functional group.

Competitive reactions were also done with a series of *para*-substituted benzyl alcohol derivatives in order to evaluate the influence of electronic factors on the reaction. From the results (Table 1, entries 1–3) we can see: electron-releasing substituents on benzyl alcohol enhance the reaction rate. Theoretical study of the substituent effect was also carried out by DFT method to compare with the experimental outcomes, and the calculation results (Table 5, entries 1–3) show that the free energies for the oxidation of benzyl alcohols with electron-releasing substituents is smaller than those with electron-withdrawing substituents. This indicates that electron-releasing substituents on benzyl alcohol could enhance the reaction rate. The experiments and the calculations are compatible with each other very well.

To check the efficiency and at the same time evaluate the scope of this procedure, the oxidation of primary aliphatic alcohols was also examined. It was surprising to find that for

Table 1. Oxidation of alcohols to carbonyl compounds					
Entry	Substrate	Product	Time (h)	Yield (%) <sup>a</sup>	
1	ОН	CHO	1.0	94	
2	Н3СО	Н3СО СНО	1.0	98	
3	O2N OH	O <sub>2</sub> N CHO	2.0	92	
4	ОН	CHO O	2.0	99	
5	CH3	CH3	2.0	95	
6	ОН		2.0	98	
7	ОП	СНО	4.0	57	
8	ОН	0	6.0	83	
9 <sup>a</sup> Yield was o	OH OH determined by GC.		8.0	87	



All the yields were determined by GC-MS

Scheme 2. Oxidation of primary aliphatic alcohols

2-phenylethanol (1), besides phenylacetaldehyde (1a, 1%), and unreacted 2-phenylethanol (1, 78%), the substitution products 2-bromoethyl benzene (1b, 9%), and 4-bromo-benzeneethanol (1c, 12%) were also obtained; however, for n-octanol (2), affording the overoxidated product octanoic acid (2a, 2%) and substituted product 1-bromo-octane (2b, 15%), instead of the expected octanal (Scheme 2). It is known that NBS oxidation of organic compound is complicated by parallel bromine oxidation, accordingly, these results indicate that this methodology fails in the case of primary aliphatic alcohols, but it is very efficient for primary and secondary aromatic alcohols as well as alicyclic alcohols. Previous study also shows that both primary and secondary aromatic alcohols having the -OH group on the carbon adjacent to the aromatic nucleus are oxidized by N-bromoacetamide (NBA) or NBS to aldehydes and ketones in good yields, however, aliphatic primary alcohols as well as aromatic alcohols in which the hydroxyl group is not so located, for example, 2-phenylethanol, 3-phenyl-1-propanol, cinnamyl alcohol, benzylisopropylcarbinol C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHOHCH(CH<sub>3</sub>)<sub>2</sub>, and (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>CHOH, dibenzylcarbinol, give the corresponding carbonyl compounds in yields below 1%.[106]

#### Optimizing the reaction conditions

With a view to evaluate the molar ratio of substrate to NBS, the oxidation of benzyl alcohol to benzaldehyde was examined. In the absence of NBS, no reaction was found, and with the increase of the amount of NBS, the reactivity of the reaction increase, but when NBS was increased to more than 1.0 equivalent, there's no increase in the yield of benzaldehyde. That is to say, 1.0 equivalent of NBS is enough for the oxidation and there is no need to increase the amount of NBS.

# Experimental and theoretical study of the temperature effect

In order to evaluate the efficiency of the reaction, the oxidation of benzyl alcohol at different temperature was carried out and the results were collected in Table 2. From the results we can conclude that with the increase in the temperature, the yield of the reaction increased, but it began to decrease when the temperature was increased to higher, 60 °C was selected as the reaction temperature in the following reaction.



Figure 1. The free energies (kcal/mol) of the oxidation of benzyl alcohol at different temperature

Theoretical work was also done in order to test the effect of temperature on the reaction. The free energies for the oxidation of benzyl alcohol to benzaldehyde were calculated at different temperature (25, 40, 60, 80, and 100 °C, respectively) at the B3LYP/6-31g<sup>\*</sup> level, and the results are collected in Fig. 1. From the results we can conclude: with the increase in the temperature,

Table 2. Effect of the temperature <sup>a</sup>						
		Temperature	Time	Yield		
Entry	Substrate	(°C)	(h)	(%) <sup>b</sup>		
1	Benzyl alcohol	r. t.	2.0	69		
2	Benzyl alcohol	40	1.0	64		
3	Benzyl alcohol	60	1.0	94		
4	Benzyl alcohol	80	1.0	89		
5	Benzyl alcohol	100	1.0	75		
<sup>a</sup> Reaction conditions: substrate (1 mmol), NBS (1 mmol), PEG 400 2 g. <sup>b</sup> Yield was determined by GC.						

Table 3. Effect of the various solvents <sup>a</sup>					
Entry	Substrate	Solvent	Time (h)	Yield (%) <sup>b</sup>	
1	Benzyl alcohol	PEG 400	1.0	94 <sup>c</sup>	
2	Benzyl alcohol	CH₃CN	1.0	80	
3	Benzyl alcohol	$CH_2CI_2$	1.0	77 <sup>d</sup>	
4	Benzyl alcohol	CHCl₃	1.0	65	
5	Benzyl alcohol	$C_7H_8$	1.0	37	
<sup>a</sup> Reaction conditions: substrate (1 mmol), NBS (1 mmol), solvent (3 ml) at 60 °C. <sup>b</sup> Yield was determined by GC. <sup>c</sup> PEG 400 2 g. <sup>d</sup> Reaction at refluxing temperature.					

the free energies of the reaction decrease, that is to say, the reaction occurs more easily at higher temperature, however, our experimental results show that the yield of the reaction decreases when the temperature is increased to higher than 60  $^\circ$ C. The



Table 4 (Continued)					
Table 4. (Continued)					
	$CH_3CN$	$CH_2CI_2$	$CHCl_3$	$C_7H_8$	
ОН	-10.73	-8.84	-7.16	-4.25	
ОН	-6.43	-5.32	-4.32	-2.58	
ОН	-6.43	-5.31	-4.31	-2.58	
СНО	-7.51	-6.24	-5.10	-3.07	
Н3СО СНО	-8.53	-7.09	-5.78	-3.48	
O <sub>2</sub> N CHO	-10.54	-8.84	-7.29	-4.41	
CHO O	-8.90	-7.45	-6.12	-3.72	
CH3	-6.74	-5.59	-4.55	-2.73	
	-9.17	-7.58	-6.15	-3.66	
СНО	-10.00	-8.30	-6.77	-4.07	
0	-5.45	-4.58	-3.78	-2.32	
	-5.37	-4.52	-3.73	-2.30	

Table 5. The free energies (kcal/mol) of all the reactions in different solvents					
Entry	Substrate	CH <sub>3</sub> CN	$CH_2CI_2$	CHCl <sub>3</sub>	C <sub>7</sub> H <sub>8</sub>
1	ОН	-45.49	-44.67	-43.94	-42.50
2	Н,СО	-59.71	-46.33	-45.54	-44.23
3	O <sub>2</sub> N OH	-41.79	-41.03	-40.36	-39.00
4	ОН	-46.66	-45.96	-45.27	-43.80
5	CH3	-46.60	-46.12	-45.61	-43.98
6	OH	-48.08	-47.59	-46.86	-45.17
7	ОН	-46.57	-44.33	-43.84	-43.81
8	ОН	-44.04	-43.18	-42.38	-40.60
9	OH	-46.15	-45.37	-45.06	-44.01

Table 6. The dipole moment of NBS in different solvents						
Solvent $\mu$ (D)	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	C <sub>7</sub> H <sub>8</sub>		
	3.65	3.54	3.43	3.22		

exact reason for the divarication between experimental results and theoretical outcomes is not clear at this moment, but we think it maybe for the reason that the properties of PEG are related to temperature, for example, PEG is stable at normal temperature but when the temperature is increased to 120 °C or higher, oxidation reaction with air could occur. Therefore, higher temperature than 60 °C is not suitable for the reaction.

#### Experimental and theoretical study of the solvent effect

Solvent is an important factor in organic reaction, it has some effects on the chemical equilibrium, rate as well as the mechanism of the chemical reaction. To evaluate the efficiency of this method, we also carried out the oxidation of benzyl alcohol to benzaldehyde in other different organic solvents besides PEG 400, and these results are shown in Table 3. Although among the various common solvents studied, acetonitrile was found to be more suitable, but in general, PEG 400 was the best one and required shortest reaction time.

Theoretical study of the solvent effect of four different organic solvents on both reactants and products are carried out using the PCM also at the B3LYP/6-31g<sup>\*</sup> level, and the results are collected in Tables 4 and 5. For PEG is a polymer, it is difficult to calculate its interaction with chemical compounds by the Gaussian 98 suite of program with the PCM. Therefore, the theoretical explanation for PEG's effect on the reactions can only be done based on the tendency obtained from the calculated results of the selected solvents other than directly with calculations.

The calculated results (Table 4) indicate that with the increase in solvent polarity, the interactions between solvent and reactants as well as solvent and products increase, which means that increasing the polarity of solvent could stabilize the reactants as well as products. As for PEG 400, its polarity is the highest among all the solvents selected, thus inducing from the results in Table 4, it could stabilize the reactants and products even more.

As can be seen from the calculated free energies of all the reactions in four different solvents (Table 5): with the increase in

solvent polarity, the free energies of all the reactions decrease, which indicates that the reaction occurs more easily in polar solvent than in apolar one from thermodynamic point of view. This is very well in accordance with the solvation energy results in Table 4. Consequently, in the reaction, polar solvent (PEG) is preferred.

It is assumed that the remarkable enhanced reaction rates could possibly be explained by the enhancement of the reactivity of NBS as a result of increased polarization of the N-Br bond in the more polar PEG medium.<sup>[107,108]</sup> To support this idea, Srinivasan et al.<sup>[108]</sup> recorded the <sup>13</sup>C NMR spectrum of NBS in IL ([bbim]BF<sub>4</sub>), DMF, CH<sub>3</sub>CN, and CCl<sub>4</sub>, respectively. The increased polarization of the carbonyl group of NBS from the non-polar CCl<sub>4</sub> to the polar solvent IL ([bbim]BF<sub>4</sub>) supports the above hypothesis. Meanwhile, the dipole moment of NBS in the four selected solvents (CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and C<sub>7</sub>H<sub>8</sub>) was also calculated with the DFT method and the results were collected in Table 6, the results indicate that the dipole moment of NBS in solvent increases with the increase in solvent polarity, which means an enhanced polarization of N-Br bond in polar solvent. PEG is a more polar solvent than CH<sub>3</sub>CN, hence it may increase the polarization of N-Br bond even more and therefore the reactivity of NBS for the alcohol oxidation under our optimized conditions.

The mechanism of the oxidation has not been clearly established, although two interpretations have been advanced.<sup>[109]</sup> One involves the formation of hypobromite species **1** and the other proceeds through bromine substitution of an hydrogen on the carbon atom bearing the —OH group, as shown in Scheme 3:

It has been suggested that the primary or secondary alcohol forms a hypobromite species **1** <sup>[110]</sup> which readily loses hydrogen bromide to form the carbonyl product. Meanwhile, there are also several lines of evidence in support of the B. For example, the oxidative cleavage of ethyl benzyl ether, which cannot form a hypobromite, is effected readily by NBS to form benzaldehyde.<sup>[111]</sup> Moreover, the rupture of the C—H bond and the formation of a C—C1 bond are illustrated by the conversion of benzaldehyde to benzoyl chloride using *N*-chloro succinimide.<sup>[112]</sup>

Which mechanism is more possible in the reaction? With this in mind, we calculated the free energy of the reaction for the formation of both 1 and 2 (Scheme 3). The oxidation of benzyl alcohol was selected as model and the results show that the free energy of path A and B in Scheme 3 is 1.18 and -30.80 kcal/mol,



Scheme 3. Two possible reaction mechanisms

respectively. This means that path B is a more reliable mechanism in the reaction. Furthermore, succinimide **3** is also detected in the reaction mixture by GC-MS analysis.

#### CONCLUSIONS

PEG offers a convenient, efficient, inexpentsive, non-ionic liquid, and eco-friendly reaction medium for the oxidation of a variety of activated and non-activated alcohols with NBS as oxidant. The use of NBS as oxidant makes this protocol more advantageous than previously reported methods. Meanwhile, using PEG as solvent makes it environmental friendly than organic solvents commonly used. Furthermore, the simplicity of the system, selective oxidation of alcohol in the presence of C–C double bond, simple reaction conditions and excellent yields of the products make it a facile, ideal, and attractive synthetic tool for the oxidation of alcohols to the corresponding carbonyl compounds. Moreover, the experimental results of the reaction were proved by DFT calculations with the Gaussian 98 suite of program.

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