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# ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

NaBrO<sub>3</sub>/guanidinium-based sulfonic acid: as a transition metaland strong inorganic acid-free oxidation system for alcohols and alkyl arenes

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Bromate anion as a safe, cheap, stable and easily stored oxidizing system has been utilized for the oxidation of a wide range of alcohols and alkyl arenes to the corresponding aldehydes and ketones. The reaction was performed in the presence of guanidinium-based sulfonic acid as a Brønsted acid organocatalyst in aqueous acetonitrile at room temperature. Products are isolated in high yields and catalyst could be easily recovered and recycled.

In recent years, development of many chemical transformations such as oxidation processes as cheapest routes to synthesis of useful molecules from natural materials have increasingly gained attention. The selective oxidation plays a crucial role in organic syntheses and is among the most common classes of reactions. Given that carbonyl compounds are versatile intermediates of valuable products such as pharmaceuticals, agricultural, and fine chemicals,<sup>1-6</sup> most of them are produced from the oxidation of alcohols and alkyl arenes. Recently, a large number of organic and inorganic oxidants has been conducted in this area.<sup>7-11</sup>

Sodium bromate is an important oxy-halo reagent which has employed as a useful oxidizing agent for this purpose because of its capability in multi-electron transfer.<sup>12-15</sup> In spite of the fact that sodium bromate is thermodynamically a strong oxidant, according to the literature, bromate anion itself cannot oxidize organic compounds.<sup>16</sup> The standard redox potential of the bromate ion, BrO<sub>3</sub>, is 0.61 V in alkaline aqueous solution,<sup>17</sup> 1.10 V in pH 7,18 while in aqueous acidic media, it has a potential of 1.42 V.<sup>17</sup> Because of the low standard redox potential in neutral or weak acidic media and also very low solubility in most of organic solvents, it is usually utilized in aqueous media in the presence of inorganic acids such as HBr,<sup>19</sup> H<sub>2</sub>SO<sub>4</sub>,<sup>20</sup> NaHSO<sub>3</sub><sup>21</sup> and HCI-TEMPO,<sup>22</sup> in which final isolation of the product demands quenching and neutralization steps to remove the acid from the reaction media, or expensive and toxic metal catalysts such as cerium(IV) ammonium nitrate (CAN),<sup>23,24</sup>

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tungstophosphoric acid( $H_3PW_{12}O_{40}$ ),<sup>25</sup> ruthenium(II)complex<sup>26</sup> and vanadyl alkyl phosphonate.<sup>27</sup>

Guanidines and their corresponding guanidinium salts have been known to chemists because of widespread use as strong and weak Brønsted base catalysts in useful chemical transformations, respectively.<sup>28</sup> Recently, a number of excellent reviews on guanidine organocatalysis exist because of their high charge dispersion, excellent thermal and chemical stabilities owing to their special structures.<sup>29-35</sup> Despite this wealth of functionality present in the guanidine, the synthesis of guanidinium-based Brønsted acid is reported very recently.<sup>36</sup> In continuation of our efforts to introduce new and efficient strategy for various organic transformations, 37-41 herein, we report the oxidation of a wide range of alcohols and alkyl arenes to the corresponding aldehydes and ketones using sodium bromate in the presence of guanidinium-based sulfonic acid (1,1,3,3-tetramethylguanidine sulfonic acid: TMG-SO<sub>3</sub>H) as a Brønsted acid organocatalyst in aqueous acetonitrile at room temperature (Scheme 1).



Scheme 1. Oxidation of alcohols and alkyl arenes using sodium bromate in the presence of TMG-SO<sub>3</sub>H

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Published on 11 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 11/12/2015 20:10:55

### **Results and discussion**

In our previous report, a simple procedure for the synthesis of TMG-SO<sub>3</sub>H as an acidic organocatalyst for the first time was disclosed.<sup>36</sup> The catalyst is simply prepared by dropwise addition of chlorosulfonic acid to n-hexane mixture of tetramethyl guanidine (TMG) at 0 °C (Scheme 2).



Scheme 2. Preparation of catalyst

In this work, we investigated the performance of TMG-SO<sub>3</sub>H as an organocatalyst in the oxidation process using sodium bromate as an oxidant. In a pilot experiment, benzyl alcohol was performed as a model substrate and reactions were carried out at room temperature under various conditions. As shown in Table 1, firstly the reaction was attempted using 1:0.50 molar ratio of benzyl alcohol: NaBrO3 and 10% mol of TMG-SO3H in CH<sub>3</sub>CN/H<sub>2</sub>O (2:1) as solvent at room temperature. The reaction was incomplete after 6 h, but showed the formation of benzaldehyde by TLC and GC. After workup and separation, 54% of benzaldehyde was obtained (Table 1, Entry 1). The reaction was then attempted using 1:1 ratio of benzyl alcohol: NaBrO3 at former conditions and it was incomplete after 6 h. This time, 80% of benzaldehyde was obtained (Table 1, Entry 2). Finally, for improving the rate of the reaction and producing better yield, we used 1:1.50 molar ratio of benzyl alcohol: NaBrO<sub>3</sub>. The reaction completed after 3 h and yielded 99% was obtained (Table 1, Entry 3). Also the reaction was carried out in various amount of TMG-SO<sub>3</sub>H. As indicate in Table 1, when 10% mol of TMG-SO<sub>3</sub>H was used, the reaction performed in good yield (Table 1, Entries 3-5). In order to obtain the best solvent, we have examined various solvents such as H<sub>2</sub>O, EtOAc, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, n-hexane and CH<sub>3</sub>CN/H<sub>2</sub>O (2:1). As exposed in Table 2, CH<sub>3</sub>CN/H<sub>2</sub>O (2:1) is the best solvent for this reaction in terms of yield and time. In the cases of, EtOAc, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub> and nhexane the reaction times were longer in order to produce reasonable yields (68-80) (Table 1, Entries 2-5).

**Table 1.** Optimizing the amount of NaBrO<sub>3</sub> and TMG-SO<sub>3</sub>H in the oxidation reaction (Reaction conditions: benzyl alcohol (1 mmol),  $CH_3CN/H_2O$  (3 ml), r.t.)

Entry	Substrate:NaBrO <sub>3</sub>	, TMG-SO₃H (mol%)	Time (h)	Yield (%)
1	1:0.50	10	6	54
2	1:1	10	6	80
3	1:1.50	10	3	99
4	1:1.50	5	6	78
5	1:1.50	3	6	66

View Article Online **Table 2.** Comparative study between various solvents: (Reaction conditions: benzyl alcohol (1 mmol), NaBrO3 (1.50 mmol), TMG-SO3H (10% mol), r.t.)

Entry	Solvent	Time (h)	Yield (%)
1	H <sub>2</sub> O	8	5
2	EtOAc	8	68
3	CH₃CN	8	75
4	CH <sub>2</sub> Cl <sub>2</sub>	8	72
5	n-Hexane	8	80
6	CH <sub>3</sub> CN/H <sub>2</sub> O (2:1)	3	99

Thus the reaction of benzyl alcohol with NaBrO<sub>3</sub> in 1:1.50 molar ratio in the presence of TMG-SO<sub>3</sub>H (10 mol%) in CH<sub>3</sub>CN/H<sub>2</sub>O (2:1) as solvent gave the optimum yield of the product. Subsequently reaction of different alcohols was attempted with the above optimized reaction conditions. As indicated in Table 3, secondary alcohols are converted into the corresponding ketones in good yields (Entries 7-11) and aldehydes are achieved in comparable yields from the oxidation of primary alcohols (Entries 1-6). In addition, it was observed that aldehydes did not undergo subsequent oxidation to carboxylic acids. After screening reactions of a series of alcohols and in order to further assess the ability of this reagent, the oxidation of alkyl arenes to related carbonyl compounds in the similar optimizing reaction conditions was investigated. The results of the mentioned reactions are provided in the Table 4.

One of advantages of TMG-SO<sub>3</sub>H is its ability to function as a recyclable organocatalyst. Recyclability of the TMG-SO<sub>3</sub>H was examined in the oxidation reaction of benzyl alcohol. After extracting of the product with dichloromethane, solvents were evaporated under vacuum. Then, TMG-SO<sub>3</sub>H was extracted from inorganic compounds, sodium bromide and un-reacted sodium bromate, with acetonitrile and reuses it for subsequent reactions. This procedure was performed for four repetitive cycles (Figure 1).

The results of our catalyst with respect to the yields, solvents, temperature and reaction times have been compared with previously reported catalysts in the oxidation of organic compounds. Using eco-friendly co-catalyst with minimal environmental impact in the absence of transition metals, also reasonable reaction time at room temperature are notable features of this procedure in comparison with the existing methods (Table 5).



Figure 1. Recycling of catalyst in the oxidation of benzyl alcohol

**Table 3.** Oxidation of various alcohols with NaBrO<sub>3</sub> in the presence of TMG-SO<sub>3</sub>H (Reaction conditions: organic compounds (1 mmol), NaBrO<sub>3</sub> (1.50 mmol), TMG-SO<sub>3</sub>H (10% mol), CH<sub>3</sub>CN/H<sub>2</sub>O (2:1), r.t.)

Entry	Alcohol	Product	Time (h)	Yield (%) <sup>a</sup>	Conversation (%) <sup>a</sup>
1	ОН	0	3	99(98,95,92) <sup>b</sup>	99

#### ARTICLE



<sup>a</sup>Conversion and yield determined by GC analysis.

<sup>b</sup> Isolated yields after recycling of catalyst.

**Table 4.** Oxidation of various arenes using NaBrO<sub>3</sub> in the presence of TMG-SO<sub>3</sub>H (Reaction conditions: organic compound (1 mmol), NaBrO<sub>3</sub> (1.50 mmol), TMG-SO<sub>3</sub>H (10% mol), CH<sub>3</sub>CN/H<sub>2</sub>O (2:1), r.t.)

Entry	Arene	Product	Time (h)	Yield (%) <sup>a</sup>	Conversation (%) <sup>a</sup>
1		°	20	96	96
2		o L	24	90	99
3			24	80	98
4		° –	24	88	98
5			20	99	99
6			24	90	99

<sup>a</sup>Conversion and yield determined by GC analysis.

Entry	Catalyst	Conditions	Yield (%)	Time (h)	Ref.
1	4-Benzamido-TEMPO, HCl	DCM/H <sub>2</sub> O, r.t.	99	1	22
2	CAN	CH₃CN/80 °C	81	1.5	23
3	$H_{3}PW_{12}O_{40}$	CH₃CN/H₂O, r.t.	90	3	25
4	<i>cis</i> -[Ru(2,9-Me <sub>2</sub> phen) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	H₂O, 23 °C	72	10	26
5	Guanidinium-based sulfonic acid (TMG-SO₃H)	CH₃CN/H₂O, r.t.	99	3	This work

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## Conclusions

The main aim of this research was to introduce a mild, simple and efficient novel method for oxidation of alcohols and alkyl arenes to the corresponding carbonyl compounds using NaBrO<sub>3</sub> in the presence of guanidinium-based sulfonic acid as a Brønsted acid catalyst. The advantages of this bronsted acid catalyst make it a promising candidate to be employed as a cocatalyst for performing highly efficient oxidation reactions. Further examination of the application of this co-catalyst for other oxidation processes and also other organic transformations are currently in progress.

#### Experimental

#### General

All chemicals were purchased from Aldrich or Merck companies and used without further purification. Identification and quantification were carried out on a Varian model 3600 gas chromatograph (Varian Iberica, Madrid, Spain) equipped with a split/splitless capillary injection port and flame ionization detector (FID).

#### General procedure for the oxidation of alcohols and alkyl arenes

A mixture of an organic compound (1.00 mmol), NaBrO<sub>3</sub> (0.22 g, 1.50 mmol) and TMG-SO<sub>3</sub>H (10 mol%) was added to a round bottom flask containing a magnetic stirring bar containing CH<sub>3</sub>CN/H<sub>2</sub>O (2:1) (3 mL) at room temperature, while the progress of the reaction was followed by TLC and GC. GC conversions and yields were obtained using *n*-decane as an internal standard based on the amount of organic compound employed relative to authentic standard product. After completion of the reaction, the product was extracted from the reaction mixture with dichloromethane (3×5 mL). Evaporation of the solvent gave the product with sufficient purity for most purposes.

#### Acknowledgements

This investigation was financially supported by the Iran National Elites Foundation (INEF) and the Research Council of Shahid Beheshti University.

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A new catalytic system for the oxidation of organic compounds in good to excellent yields at room temperature