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Acid-assisted catalytic oxidation of benzyl alcohol by NO_x with dioxygen

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1. Introduction

Oxidation plays a key role in laboratory synthesis and industrial manufacture in which the stoichiometric oxidants like dichromate, persulfate, permanganate and nitrite are traditionally used [1]. With the increasing concerns about environmental issues, developing new methods to use cheap and clean dioxygen as the terminal oxidant and even without the toxic heavy metal ions has been attracting more and more attention than ever [2]. Because dioxygen exists in the inactive triplet ground state, its efficient activation is crucial for its successful utility in catalytic process. In recent years, NO_x has attracted considerable attention as an efficient oxygen activator through coupling with p-benzoquinone/Pd [3], 2.2.6.6-tetramethyl-piperidyl-1-oxyl (TEMPO)/Br₂ [4], hypervalent iodine(V)/Br₂ [5], [bis(acetoxy)iodo]benzene/TEMPO [6] and TEMPO/FeCl₃ [7] in versatile oxidations. In these laboratories, we have also successfully developed a few efficient oxygen activators including 2,3-dichloro-5,6-dicyano-benzoquinone/ NO₂ for the oxidative dehydrogenation of dihydroarenes and vanadyl sulfate/NO₂ for alcohol oxidation [8,9]. In addition to the above systems for using NO_x as dioxygen activator, stoichiometric NO_x has also been applied in the oxidation of 1,4-dihydropyridines to the corresponding pyridine derivatives, and in formation of carbonyl compound from alcohols, in which NO_x was activated by certain acids to in situ generate the high active nitrosonium cation intermediate (NO^+) [10–12]. In this communication, a simple inorganic acid/NaNO₂/dioxygen system has

ABSTRACT

Efficient transformation of alcohols to the corresponding aldehydes is an important process in organic synthesis and industry. In the absence of transition metal ion, an acid-activated NO_x has been explored for the catalytic oxidation of benzyl alcohol. Under the optimal conditions, 95% yield of benzyl aldehyde could be achieved at room temperature with dioxygen as the terminal oxidant. The reaction mechanism was investigated through UV-visible spectrometry and cyclic voltammetry, and the key active species for oxidation have been assigned to the nitrosonium cation.

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been developed for catalytic oxidation of benzyl alcohol, and 95% yield of aldehyde could be achieved at room temperature.

2. Experimental

Analytical pure chemicals were used as received without further purification. Benzyl nitrite was synthesized through nitrosation of benzyl alcohol according to the literature [13].

The oxidation experiments were carried out in a 10 mL polytetrafluoroethylene autoclave. After a certain amount of acid, 2 mmol of benzyl alcohol and 2 mL of CH₂Cl₂ were added in the autoclave, 10 mol% NaNO₂ were added with stirring. Then, the autoclave was sealed immediately and charged with dioxygen (0.5 MPa), and then, the reaction mixture was stirred at 20 °C for 2 h. The products were analyzed by GC, and further confirmed by GC–MS. The isolated yield was obtained through silica gel column.

The UV–visible experiments were carried out with a Shimadzu UV-2550 spectrophotometer. The electrochemical measurements were performed with a PARSTAT 2273 potentiostat/galvanostat with Ag/AgCl electrode as reference electrode, a glassy carbon disc electrode (3 mm) as working electrode, and a platinum wire as counter electrode.

3. Results

3.1. Influence of different acids

Although NaNO₂/acid has been generally used as an efficient stoichiometric oxidant in organic synthesis [11,12], its catalytic performance is scarcely investigated. Initially, 10 mol% NaNO₂ together with 30 mol% different acids were employed to catalyze benzyl alcohol

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Table	1

Entry	Acid	Conversion	Yield (%)			
		(%)	Benzyl aldehyde	Benzyl nitrite	Other	
1	H ₃ BO ₃	2	26	74	0	
2	CH₃COOH	2	27	73	0	
3	H_3PO_4	5	28	72	0	
4	НОСОСООН	5	16	84	0	
5	H_2SO_4	84	99	0	1	
6	HClO ₄	55	96	0	4	
7 ^b	H_2SO_4	100	97 (95)	0	3	
8 ^{b,c}	H_2SO_4	100	98 (94)	0	2	

^a Reaction conditions: 2 mmol benzyl alcohol, 0.6 mmol acid, 0.2 mmol NaNO₂, 2 mL CH₂Cl₂, 0.5 MPa O₂, 20 °C, 2 h.

^b 0.8 mmol acid, isolated yield to benzyl aldehyde is in bracket.

Influence of different acids on benzyl alcohol oxidation.⁴

^c 1 h.

oxidation using dioxygen as oxidant (0.5 MPa) at 20 °C (Table 1). For the added acid, one third reacts with NaNO₂ to generate NO_x, and the remains could activate NO_x to generate the active intermediate for oxidation. When the weak/medium acids were used in reaction, the conversions were below 10% with 16–28% selectivity to benzyl aldehyde (Entries 1–4 in Table 1), and the dominant product was benzyl nitrite, suggesting that these weak/medium acids are inefficient to activate NO_x. When the strong acids like H_2SO_4 and HClO₄ were applied, 84% and 55% conversion could be achieved with 99% and 96% selectivity to benzyl aldehyde, respectively. Significantly, in the case of using 40 mol% H_2SO_4 and 10 mol% NaNO₂, 100% conversion of alcohol could be achieved with 94% isolated yield of benzyl aldehyde in 1 h, or 95% yield in 2 h. In the blank experiments, H_2SO_4 or HClO₄ alone leads to minor aldehyde formation, supporting that the presence of NaNO₂ is crucial for the efficient catalytic oxidation.

3.2. Influence of acid amount

The influence of H_2SO_4 usage is displayed in Fig. 1. When 10 or 20 mol% H_2SO_4 was used in reaction, the catalytic efficiency was apparently low, and a large amount of benzyl nitrite was formed as well as those in the weak/medium acids. When loading 30 mol% H_2SO_4 , the formation of benzyl nitrite was minimized, and 96% selectivity to benzyl aldehyde was achieved with 84% conversion. Complete conversion of benzyl alcohol could be achieved with 40 mol% H_2SO_4 , suggesting that in comparison with stoichiometric oxidation, 60% of H_2SO_4 and 90% of NaNO₂ could be saved through the catalytic process developed here.



Fig. 1. Influence of H₂SO₄ amount on benzyl alcohol oxidation.



Fig. 2. Influence of H₂SO₄ concentration on benzyl alcohol oxidation.

3.3. Influence of acid concentration

Due to the formation of water in the oxidation process, the concentration of H_2SO_4 would gradually decrease with the reaction proceeding. Thus, the influence of the initial acid concentration was investigated, and the results are presented in Fig. 2. When 25–60% H_2SO_4 was used, only 5–9% conversion could be obtained with benzyl nitrite as the major product, which is quite similar with those from the weak/medium acids. When the initial concentration of H_2SO_4 increased from 60% to 98%, the conversion could be sharply improved from 9% to 100% with the selectivity changing from 35% to 97% for aldehyde, supporting that the oxidation of benzyl alcohol is apparently acid concentration dependent.

3.4. UV-visible spectrometry and cyclic voltammetry study on the solution of NaNO₂ in H_2SO_4

In line with the catalytic efficiency, the influence of H_2SO_4 concentration on the NO⁺ formation has been directly evidenced by the UV-visible spectrometry. The maximum absorbance of the UV spectrum is below 200 nm for NaNO₂ in aqueous H_2SO_4 with concentration less than 60%, which is characteristic of HNO₂, whereas the maximum absorbance shifts to the range of 214–350 nm when NaNO₂ was dissolved into 60–98% H_2SO_4 , indicating the appearance of the NO⁺ species [14].

The redox behavior of NaNO₂ in H_2SO_4 was studied by cyclic voltammetry. In Fig. 3, graph a shows no redox signal in 20% H_2SO_4 . The oxidation signal of NO to NO⁺ occurs in 50% and 60% H_2SO_4 , however, the corresponding reduction signal of NO⁺ is invisible in 50% H_2SO_4 , and insignificant in 60% H_2SO_4 (graphs b and c). In literatures, the absence of the NO⁺ reduction signal has been attributed to the rapid hydrolysis of the NO⁺ species [15–18]. In 80% H_2SO_4 (graph d), the redox response of the NO⁺ species is evidently close to a reversible process, implicating that the hydrolysis of the NO⁺ species becomes ignorable [16,19]. Furthermore, the rising reduction current indicates the increase of the NO⁺ concentration with the increase of acid concentration.

4. Discussion

4.1. The confirmation of the active species

When sodium nitrite was added to the H_2SO_4 solution, the release of N_2O_3 was observed. Although NO_x alone can catalyze the oxidation of certain organic compounds like olefin and hydroquinone with dioxygen at room temperature, the compounds are limited to those capable of inducing the disproportionation of NO_x to generate the active NO^+ species [20,21], and NO_x alone is apparently incapable of oxidizing relatively stable substrates like benzyl alcohol. In the case of



Fig. 3. Cyclic voltammograms of NaNO2 in H2SO4 solution, mass concentration of H2SO4 solution: a, 20%; b, 50%; c, 60%; d, 80%.

 N_2O_3 as the stoichiometric oxidant, a strong acid was generally employed as catalyst to generate the active NO^+ species for alcohol oxidations [10]. In addition, the NO^+ species was even proposed as the key active species in the oxidations with stoichiometric $NaNO_2$ [11,12]. Because neither H_2SO_4 nor NO_x alone is capable of oxidizing benzyl alcohol in the present study, and the formation of the NO^+ species from H_2SO_4 and $NaNO_2$ has been detected by UV–visible and cyclic voltammogrametry at room temperature, accordingly, the NO^+ species could be assigned as the key active species in this $H_2SO_4/$ $NaNO_2$ catalyzed alcohol oxidation.

Furthermore, the proposal of the NO⁺ as the active species could well interpret the reaction data presented above. The formation of NO⁺ is closely related with the strength of the acids. In the weak/medium acids, the proton (H⁺) concentration is limited, which leads to the shortage of the NO⁺ cation in the catalytic solution and the failure of efficient oxidation (entries 1–4 in Table 1), whereas much NO⁺ species could be generated in strong acids [22], thus benzyl alcohol was selectively oxidized to benzyl aldehyde. In addition, the formation of the NO⁺ species is remarkably influenced by acid concentration. The UV– visible and cyclic voltammetric observations indicate that it seldom exists in H₂SO₄ with concentrations below 60%. In line with these, the efficient oxidation could be only observed at H₂SO₄ beyond 60%. Furthermore, the increase of acid loading is helpful to resist its dilution during reaction, thus it provides a higher conversion of substrate (Fig. 1).

4.2. Formation of benzyl aldehyde

Since benzyl nitrite was found to be the dominant product when weak/medium acid (Table 1) or diluted strong acid (Fig. 2) was used, the formation of the benzyl nitrite has been suspected to be one step in aldehyde formation in catalytic cycle as well as in stoichiometric oxidation with N_2O_3 [10]. To test this postulation, 0.5 g of benzyl nitrite was dissolved into 5 mL of CH_2Cl_2 with 0.1 mL 80% H_2SO_4 catalyst. After stirring under nitrogen protection for 0.5 h at room temperature, benzyl nitrite was completely converted, and 45% benzyl aldehyde was obtained with 55% benzyl alcohol, meanwhile, NO was released quickly, implicating that the participation of another NO⁺ cation is essential for the oxidation of benzyl nitrite to the corresponding aldehyde (the NO⁺ cation was generated through hydrolysis of benzyl nitrite). When the transformation was carried out in air, benzyl nitrite was quantitatively converted into benzyl aldehyde within 0.5 h. In contrast, the transformation

mation of benzyl nitrite to aldehyde was very slow with 50% H_2SO_4 , and hydrolysis of benzyl nitrite to benzyl alcohol dominated. These results strongly suggest that the participation of the NO^+ species is essential for the transformation of benzyl nitrite to the corresponding aldehyde.

Thus, a plausible mechanism has been proposed for this inorganic acid/NaNO₂ catalyzed alcohol oxidation (Scheme 1). In the catalytic cycle, reaction of NaNO₂ with acid under oxygen generates NO_x which can be converted to the active NO⁺ species with proton (H⁺). One NO⁺ reacts with benzyl alcohol to generate benzyl nitrite with releasing H⁺; then, oxidation of benzyl nitrite in the participation of another NO⁺ provides the aldehyde product with releasing NO. The reduced NO is reoxidized by oxygen to NO_x which finally regenerates the NO⁺ species in the presence of acid.

5. Conclusions

In summary, this work demonstrated a successful example of acidactivated NO_x as the efficient dioxygen activator for oxidizing alcohol to the corresponding aldehyde, in which the NO^+ species has been proposed as the key active species in the catalytic cycle. The mechanistic information revealed here advices that the formation of the NO^+ species



Scheme 1. Proposed catalytic cycle for benzyl alcohol oxidation by in situ generated NO⁺ species.

should be taken into account when NO_x is employed as a catalytic component under an acidic environment. Since liquid sulfuric acid is unfavorable in terms of green chemistry, the activation of NO_x with reusable solid acids is currently under investigation with oxygen as oxidant.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.catcom.2010.06.012.

References

- G. Tojo, M. Fernández, Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice, Springer, New York, 2006.
- [2] J. Piera, J.-E. Backvall, Angew. Chem. Int. Ed Engl. 47 (2008) 3506–3523.
- [3] Z.J. An, X.L. Pan, X.M. Liu, X.W. Han, X.H. Bao, J. Am. Chem. Soc. 128 (2006) 16028–16029.

- [4] R.H. Liu, X.M. Liang, C.Y. Dong, X.Q. Hu, J. Am. Chem. Soc. 126 (2004) 4112-4113.
- [5] R.H. Mu, Z.Q. Liu, Z.J. Yang, Z.G. Liu, L.M. Wu, Z.L. Liu, Adv. Synth. Catal. 347 (2005) 1333–1336.
- [6] C.I. Herrerias, T.Y. Zhang, C.J. Li, Tetrahedron Lett. 47 (2006) 13-17.
- N.W. Wang, R.H. Liu, J.P. Chen, X.M. Liang, Chem. Commun. (2005) 5322–5324.
 W. Zhang, H. Ma, L.P. Zhou, Z.Q. Sun, Z.T. Du, H. Miao, J. Xu, Molecules 13 (2008)
- 3236–3245. [9] Z.T. Du, H. Miao, H. Ma, Z.O. Sun, J.P. Ma, J. Xu, Adv. Synth. Catal. 351 (2009)
- 558–562. [10] N.C. Marziano, L. Ronchin, C. Tortato, S. Ronchin, A. Vavasori, J. Mol. Catal. A Chem.
- 205 (2005) 26-34.
- [11] M.A. Zolfigol, F. Shirini, A.G. Choghamarani, I. Mohammadpoor-Baltork, Phosphorus, Sulfur Silicon Relat, Elem. 178 (2003) 1709–1715.
- [12] M.A. Zolfigol, F. Shirini, A.G. Choghamarani, I. Mohammadpoor-Baltork, Green Chem. 4 (2002) 562–564.
- [13] W.A. Noyes, J. Am. Chem. Soc. 55 (1933) 3888-3889.
- [14] J.M.R. Deschamps, C. R. Acad. Sci. Ser. C 245 (1957) 1432-1434.
- [15] J.D. Zhang, M. Oyama, Anal. Chim. Acta 540 (2005) 299–306.
- [16] E.V. Milsom, J. Novak, M. Oyama, F. Marken, Electrochem. Commun. 9 (2007) 436-442.
- [17] G.L. Beltramo, M.T.M. Koper, Langmuir 19 (2003) 8907-8915.
- [18] T.L. Broder, D.S. Silvester, L. Aldous, C. Hardacre, R.G. Compton, J. Phys. Chem. B 111 (2007) 7778–7785.
- [19] R.W. French, A.M. Collins, F. Marken, Electroanalytical 20 (2008) 2403-2409.
- [20] E. Bosch, J.K. Kochi, J. Am. Chem. Soc. 118 (1996) 1319–1329.
- [21] E. Bosch, R. Rathore, J.K. Kochi, J. Org. Chem. 59 (1994) 2529-2536.
- [22] R.Y. Zhang, M.T. Leu, L.F. Keyser, J. Phys. Chem. 100 (1996) 339-345.