Studies on green and efficient catalytic oxidation of a triazole compound

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Abstract. 1-Methyl-3,5-dinitro-1,2,4-triazole is an insensitive energetic compound that can be prepared by oxidizing the nitrate salt of 1-methylguanazole. The influence of the reaction time, reaction temperature, reactant ratio, feeding method and catalytic oxidation method on the yield were discussed. The results show that the optimum reaction conditions are as follows: mass ratio of sodium tungstate to nitrate salt to 1-methylguanazole, 4:4.4; time, 5.5h; and temperature, 65-75°C. The yield of this oxidation reaction reached 51.36%.

1. Introduction

Oxidations are important and widely used reactions. \text{H}_2\text{O}_2\text{ is a popular oxidizer because it is inexpensive, non-toxic, safe, and environmentally friendly. Many reports have been published that investigate molybdate and tungstate for catalytic wet peroxide oxidation of alcohols and alkenes}^{[1-13]}. 1-Methyl-3, 5-dinitro-1,2,4-triazole (DNMT) is an insensitive energetic compound with a low melting point. Although information on the synthesis of DNMT has been reported, no information has been made available on the optimization of the process. Price and DiStasio \textsuperscript{[14]} synthesized DNMT in two steps, but the yield was unsatisfactory, and heavy metal wastewater was obtained, which, if not effectively discarded, could cause environmental contamination. The cause of this low yield has not yet been determined. In this study, we investigate the effect of the oxidation stage on the yield in order to determine this cause. Several determining factors of the oxidation stage were studied. The highlights of this study are as follows: (a) optimizing the parameters of the process; (b) determining the optimal catalytic oxidation method and feed ratio; (c) exploring the reuse of the wastewater generated by the process.

2. Results and discussion

2.1. The catalytic oxidation system

The presence of oxalate or hydrochloric acid improved the yield to different degrees. The oxidizing ability is stronger in an acid solution. For example, sodium tungstate reacts with \text{H}_2\text{O}_2 to form peroxtungstate. In the presence of oxalate, \text{[WO(O}_2\text{)\textsubscript{2}C_2\text{O}_4]}^{2-}, a coordination complex was formed \textsuperscript{[15]}. Because of its lipophilicity, this kind of catalyst more easily passes into the oil phase, which
allows the reaction to be fully carried out. As shown in table 1, the catalytic oxidation was more efficient when p-toluene sulphonic acid (TsOH) was used as an additive. The results shown in table 2 also indicate that the highest yield was obtained when TsOH was 1.2 mmol (of sodium tungstate).

| Additives | H₂SO₄ | HCl | oxalate | TsOH | acetic acid | H₃PO₄ |
|-----------|-------|-----|---------|------|-------------|-------|
| Yield (%) | 36.82 | 42.27 | 38.64 | 50.22 | 34.09 | 30.17 |

| Dosage of TsOH (mmol) | 0.6 | 1.2 | 1.8 | 2.4 | 3.0 |
|-----------------------|----|----|----|----|----|
| Yield (%)             | 50.22 | 51.36 | 45.45 | 42.50 | 23.18 |

2.2. Properties of the catalyst for cycling studies
At the end of reaction, most of the catalyst was dissolved in mother liquors. In order to study the usable life of the catalyst, the recovered mother liquors were enriched to 10ml. Then, 25ml (35%) H₂O₂ was added, and the reaction was left to run for 5.5 h at 65°C. The results indicated that when the catalyst was used repeatedly for 5th, the yield still reached 22.7%, as shown in table 3. This illustrates the catalytic oxidation system has better catalytic activity and more effective recycling performance.

| Time       | 1st | 2nd | 3rd | 4th | 5th |
|------------|-----|-----|-----|-----|-----|
| Yield (%)  | 35.6 | 33.4 | 31.5 | 28.3 | 22.7 |

2.3. Process parameters studies

2.3.1. Reaction temperature. In order to investigate the effect of the temperature on the oxidation process, oxidation was conducted at 60, 65, 70, 75 and 80°C. The process was found to be safe below 70°C, and the yield was also larger in the temperature range of 65-70°C, as shown in figure 1.

2.3.2. Reaction time. The reaction time is critical to any organic reaction, especially when the reaction is performed in an environment with an excessive amount of acid under an elevated temperature. If the reaction time is too long, the product may be degraded, causing unnecessary waste. However, if the time is too short, full synthesis may not be accomplished. According to the data shown in figure 2, 5.5 h is the optimal amount of time.

2.3.3. Ratio of the reactant and the consumption of materials. As a mild oxidizer with weak acidity, H₂O₂ has significant advantages and does not cause impurities. However, it decomposes at high temperatures, which directly affects its utilization ratio. The results shown in figure 3 indicate that H₂O₂ values of greater or less than 25 ml were not beneficial to the yield.

The present research indicated that the mass ratio of sodium tungstate and DAMT had a significant impact on the reaction. If too little sodium tungstate was added, a low oxidizing degree resulted, reducing the yield and leading to unwanted by-products. However, too much sodium tungstate addition accelerated the decomposition of the hydrogen peroxide, which also resulted in a low oxidizing degree. Figure 4 shows the percentage of 4:4.4 is the most beneficial to the yield.
3. Experiment

3.1. General

The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker-Avance DRX 500 MHz NMR instrument with DMSO-d$_6$ solvent. The IR spectra were tested by a Perkin Elmer Spectrum 100 instrument. Elemental analyses were performed on a HERAEUS 1106 elemental analyzer (Germany). All the reagents were of analytical grade, purchased from commercial sources, and used as received. The dicyandiamide, aqueous solution of methyl hydrazine (40%), ethyl acetate, acetone, sodium bicarbonate and sodium nitrite were purchased from Nan Tong Dong Li Corporation (China).

3.2. Synthesis

1-Methyl-3, 5-dinitro-1,2,4-triazole. Nitrate salt of 1-methylguanazole, Na$_2$WO$_4$, TsOH and (35%) H$_2$O$_2$ was mixed in the mole ratio of 0.023:0.012:0.0012:0.439. The resulting mixture was heated to 65°C and stirred for 5.5 h. After repeated extraction by ethyl acetate, the extract was separated, dried with anhydrous Na$_2$SO$_4$, filtered, concentrated under reduced pressure, and dried in a vacuum to yield a light yellow solid product (2.21 g, 50.22%). mp 93-95°C. $^1$H NMR (500MHz, DMSO-d$_6$) δ: 4.4755(s, 3H, CH$_3$). $^{13}$C NMR(500MHz, DMSO-d$_6$) δ: 155.772, 153.423, 39.024. IR (KBr): 2925, 1373 (-CH$_3$), 1514, 1319 (-NO$_2$).
4. Conclusions
In this paper, the oxidation of DNMT was studied. The process parameters were optimized through single factor experiments. The results showed that the best conditions for the synthesis are to mix Nitrate salt of 1-methylguanazole, Na₂WO₄, TsOH and (35%) H₂O₂ with a molar ratio of 0.023:0.012:0.0012:0.439 for 5.5 h at a temperature between 65~70°C. Under these conditions, the yield reached up to 51.36%. In addition, the catalytic system of Na₂WO₄ and TsOH reduces the discharge of waste water and shows high cyclability.

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References
[1] Jacobson S E, Muccigrosso, D A and Mares F 1979 Oxidation of alcohols by molybdenum and tungsten peroxo complexes. *Journal of Organic Chemistry* **44** 921-924.
[2] Trost M B and Masuyama Y 1984 Chemo selectivity in molybdenum catalyzed alcohol and aldehyde oxidation. *Tetrahedron Letter* **25** 173-176.
[3] Dengel A C, Griffith W P and Parkin B C 1993 Studies on polyoxo and peroxo- metalates. Part 1. Tetrameric heteropoly peroxo-tungstates and heteropoly peroxo molybdates. *Journal of Chemical Society Dalton Transaction* **18** 2683-2688.
[4] Neumann R and Gara M 1995 The manganese-containing polyoxo metalate [WZnMn II (ZnW9O34)2]12-, as a remarkably effective catalyst for hydrogen peroxide oxidation. *Journal of American Chemical Society* **117** 5066-5074.
[5] Zhang H X, Gao J J and Meng H 2012 Removal of thiophenic sulfurs using an extractive oxidative desulfurization process with three new phosphotungstate catalysts. *Industrial & Engineering Chemistry Research* **51**(19) 6658-65.
[6] Ding Y X, Zhu W S and Li H M 2011 Catalytic Oxidative Desulfurization with a Hexatungstate/Aqueous H₂O₂/Ionic Liquid Emulsion System. *Green Chem* **13**(5) 1210-16.
[7] Wen S Z, Guo P Z and Hua M L, 2011 Oxidative desulfurization of fuel catalyzed by metal-based surfactant-type ionic liquids. *J Mol Catal A: Chem* **347** 8-14.
[8] Tang L, Luo G Q and Kang L H, 2013 A novel [Bmim] PW/HMS catalyst with high catalytic performance for the oxidative desulfurization process. *Korean J Chem Eng* **30**(2) 314-320.
[9] Huang W L, Zhu W S and Li H M 2010 Heteropolyanion-based ionic liquid for deep desulfurization of fuels in ionic liquids. *Ind Eng Chem Res* **49**(19) 8998 -9003.
[10] Leng Y, Zhao P P and Zhang M J 2012 A dicatonic ionic liquid-modified phosphotungststate hybrid catalyst for the heterogeneous oxidation of alcohols with H₂O₂. *Sci China Chem* **55**(9) 1796-1801.
[11] Isbii Y, Yamawaki K and Ura T 1988 Hydrogen peroxide oxidation catalyzed by heteropoly acids combined with cetylpyridinium chloride: epoxidation of olefins and allylalcohols, ketonization of alcohols and diols, and oxidative cleavage of 1, 2-diols and olefins. *Journal of Organic Chemistry* **53** 3587-3593.
Bortolini, O, Conte V and Furia F D 1986 Metal catalysis in oxidation by peroxides. Molybdenum and tungsten catalyzed oxidations of alcohols by diluted hydrogen peroxide under phase-transfer conditions. Journal of Organic Chemistry 51 2661-63.

Bortolini O, Campestrini S and Furia F D 1987 Metal catalysis in oxidation by peroxides anionic molybdenum picolinate N-oxido-peroxo complex: an effective oxidation of primary and secondary alcohols in nonpolar solvent. Journal of Organic Chemistry 52 5467-69.

Price W and DiStasio A R 2010 Synthesis of DNMT: A new energetic melt-pour ingredient, in 2010 insensitive munitions and energetic materials technology symposium.

Dickman M H and Pope, M T 1994 Peroxo and superoxo complexes of chromium, molybdenum and tungsten. Chemical Review 94 569-584.