

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. H₂O₂ 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 [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 H₂O₂ to form peroxotungstate. In the presence of oxalate, [WO(O₂)₂C₂O₄]²⁻, a coordination complex was formed [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).

Table 1. Effect of acidic additives to the yield

Additives	H ₂ SO ₄	HCl	oxalate	TsOH	acetic acid	H ₃ PO ₄
Yield (%)	36.82	42.27	38.64	50.22	34.09	30.17

Table 2. Effect of TsOH dosage to the yield

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.

Table 3. Effect of repeated use of the catalyst to the yield

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.

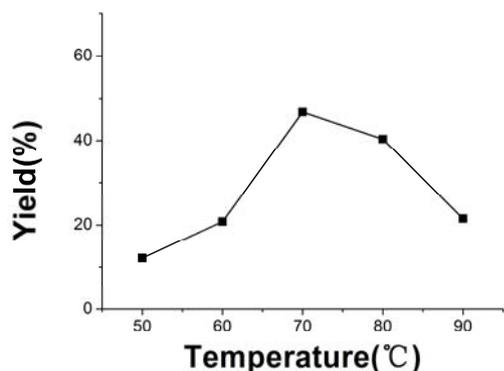


Figure 1. Temperature of the reaction.

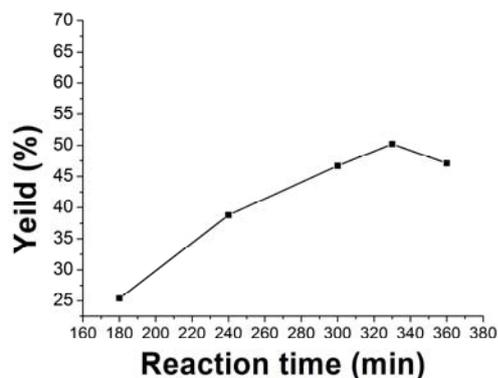


Figure 2. Time of the reaction.

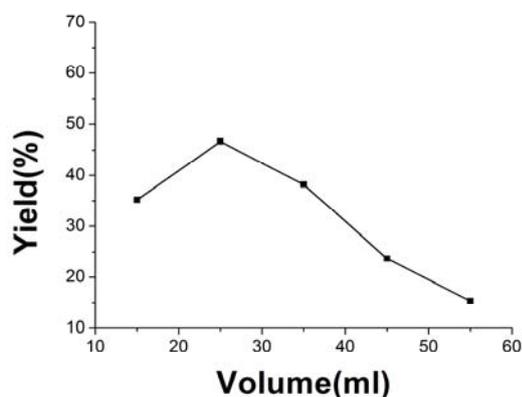


Figure 3. Dosage of H₂O₂.

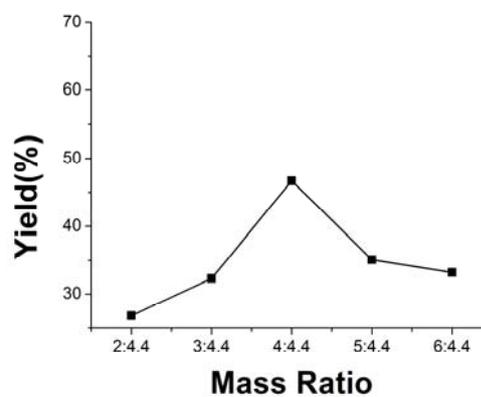


Figure 4. Sodium tungstate : DAMT.

3. Experiment

3.1. General

The ¹H and ¹³C NMR spectra were recorded on a Bruker-Avance DRX 500 MHz NMR instrument with DMSO-d₆ 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, Na₂WO₄, TsOH and (35%) H₂O₂ 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 Na₂SO₄, 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. ¹H NMR (500MHz, DMSO-d₆) δ: 4.4755(s, 3H, CH₃). ¹³C NMR(500MHz, DMSO-d₆) δ: 155.772, 153.423, 39.024. IR (KBr): 2925, 1373 (-CH₃), 1514, 1319(-NO₂).

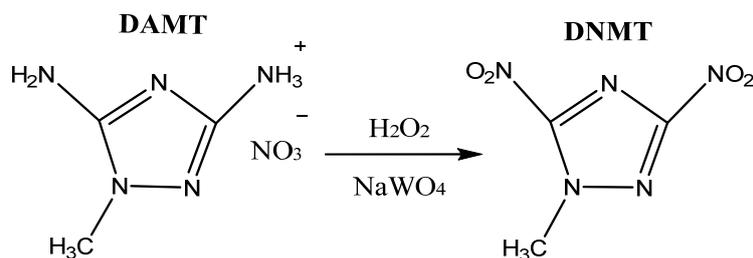


Figure 5. Preparation of DNMT.

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.

Acknowledgments

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