



A Mild Method to Synthesize TATB by Amination of 1,3,5-Trialkoxy-2,4,6-Trinitrobenzene under Phase Transfer Catalysis Conditions

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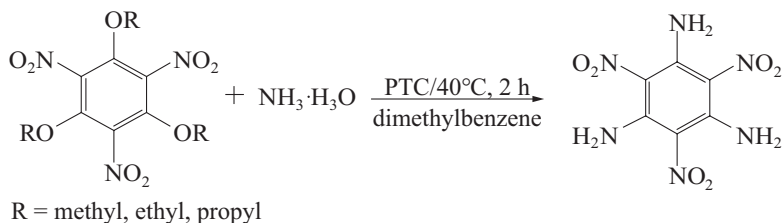
Abstract: Nucleophilic amination, as a vital step in the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) using 1,3,5-trialkoxo-2,4,6-trinitrobenzene (TORTNB) and aqueous ammonia as the starting materials and catalyzed by phase transfer catalysis (PTCs) under mild conditions is described. Various phase transfer catalysts, such as crown ethers, tertiary amines, quaternary ammonium salts, poly ethers and cyclodextrin, and various experimental parameters, such as no. of equivalents of PTC, mole ratio of ammonium hydroxide to the starting material, reaction time, reaction temperature and cycle times of the organic phase were investigated. The crown ethers, especially 18-crown-6, show good catalytic activity and re-usability for the amination of 1,3,5-triethoxy-2,4,6-trinitrobenzene giving a yield of 96.52%. This makes for a safe process and suitable for scale-up, because the reactions are carried out under atmospheric conditions. The material synthesised by the new system was characterized by DSC, SEM and LPS.

Keywords: TATB, phase transfer catalysis, atmospheric amination reaction

1 Introduction

1,3,5-Triamino-2,4,6-trinitrobenzene, commonly known as TATB, is an attractive insensitive high explosive (IHE) as it satisfies the safety requirements at high temperatures and is resistant to accidental initiation and explosion [1]. In addition, it readily forms eutectics with other explosives such as 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) [2-7], 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) [8, 9].

An important step in the synthesis of TATB is the nucleophilic amination reaction which can be carried out under various conditions. The conventional industrial amination method, which prepares TATB by amination of 1,3,5-trichloro-2,4,6-trinitrobenzene, is carried out in a two-phase gas-liquid system under high pressure conditions [10-15]. In these cases, the pressure vessel is indispensable so that the risk coefficient in large-scale industrial production is high and the equipment is expensive. In addition, the amination reaction can also be carried out by adopting solid ammonium compounds as aminating agent under atmospheric conditions [16, 17]. However these too have some shortcomings, such as long reaction times, high reaction temperatures *etc.* Huang *et al.* [18] discussed the synthesis of TATB using aqueous ammonia as the aminating agent in ethanol, giving a high yield. Due to the low solubility of 1,3,5-trialkoxo-2,4,6-trinitrobenzenes (named as TORTNBs) in ethanol, requiring large amounts of ethanol, it is not suitable for industrial production of TATB. In view of these implications, we have explored an efficient and low-cost method to access TATB involving nucleophilic amination, using aqueous ammonia as the aminating agent, of TORTNBs under PTC conditions (Scheme 1).



Scheme 1. Synthesis of TATB under PTC conditions

Phase Transfer Catalysis (PTC), is widely used to promote reaction between two mutually insoluble phases, to give high conversion and selectivity under very mild reaction conditions, and is effective for the reaction we envisaged. Compared with other methods, phase transfer catalysis has long been recognized as a versatile methodology for organic synthesis in both industrial and academic laboratories, is a simple reaction procedure, using safe, inexpensive, environmentally friendly reagents, and affords ease of scale-up and high-pressure-reactor-free conditions [19-23].

PTCs are of several types and they have different catalytic effects for the same reaction. Therefore, it is necessary to find the best PTC for promoting the nucleophilic attack of ammonia. In this paper, we describe our efforts to screen for an appropriate PTC for the synthesis of TATB by using ammonium hydroxide as the aminating agent under mild conditions. In this respect, 18-crown-6 shows

superior catalytic activity, the temperature is mild, the reaction time is shorter, no pressure equipment is required and the solvent can be used repeatedly.

2 Materials and Methods

2.1 Materials

The TORTNBs were synthesized from 1,3,5-trihydroxybenzene in our lab (the methods were reported by Bellamy *et al.* [24]), and the other chemicals were purchased from commercial sources and used without further purification. The products are known compounds and were identified by comparison with authentic samples using HPLC.

2.2 Characterization

The melting points were obtained with a WRS-1B Digital Melting Apparatus. The IR spectra were recorded on a Nexus 870 FT-IR spectrometer and expressed in cm^{-1} . ^1H NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer. The DSC experiments for TATB were performed with a METTLER DSC1 in a nitrogen atmosphere at a flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$ and a heating rate of $20 \text{ K}\cdot\text{min}^{-1}$, from $50 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$. Scanning electron microscopic (SEM) images were obtained with a Hitachi TM-5000 microscope operated at an acceleration voltage of 30 kV. Particle sizes of TATB were analyzed using a Malvern MAM5004 Laser Mastersizer, United Kingdom.

2.3 Preparation of 1,3,5-trihydroxy-2,4,6-trinitrobenzene (TNPG) by nitration of 1,3,5-trihydroxybenzene [24]

To a solution of anhydrous 1,3,5-trihydroxybenzene (5.52 g, 20 mmol) in 98% sulphuric acid (20 mL) was added a mixture of fuming nitric acid (5.305 g, 84.2 mmol) and 98% sulphuric acid (1.8 mL), whilst maintaining the temperature below $0 \text{ }^\circ\text{C}$. The reaction mixture was stirred for 1 h and then poured onto ice (100 g) with stirring. The resultant yellow precipitate was filtered off immediately, washed with cold 3 M HCl ($2 \times 20 \text{ mL}$) and dried to yield 1,3,5-trihydroxy-2,4,6-trinitrobenzene (4.96 g, 95%). Melting point: $166.2\text{--}167 \text{ }^\circ\text{C}$. IR (KBr, cm^{-1}): ν 3647(w), 3580(w), 3119(w), 1629(s), 1517(m), 1469(m), 1315(s), 1203(m), 1169(m), 916(w), 791(w), 634(w). ^1H NMR (500 MHz, acetone- d_6 , TMS): δ 3.5 ppm (bs, 3H, OH). ^{13}C NMR (125 MHz, DMSO, TMS): δ 122.0, 152.5 ppm.

2.4 Preparation of 1,3,5-trimethoxy-2,4,6-trinitrobenzene (TMTNB) by methylation of TNPG [24]

To a solution of anhydrous 1,3,5-trihydroxy-2,4,6-trinitrobenzene (4.96 g, 19 mmol) in dimethylbenzene (50 mL) was added trimethyl orthoformate (28 mL) at 100 °C. An azeotropic mixture of methanol and methyl formate was distilled off. The reaction mixture was then heated at 125 °C for a further 1 h, during which time further distillate was collected. After cooling, the reaction mixture was washed with cold 5% aqueous sodium carbonate solution (2 × 20 mL). Removal of the dimethylbenzene yielded 1,3,5-trimethoxy-2,4,6-trinitrobenzene (5.01 g, 87%). Melting point: 73.4-74 °C. IR (KBr, cm⁻¹): ν 3460(w), 2960(w), 2881(w), 1593(s), 1542(s), 1350(s), 1197(m), 1126(s), 1103(s), 941(m), 887(m), 717(m), 663(w), 634(w). ¹H NMR (500 MHz, DMSO-d₆, TMS): δ 4.1 ppm (s, 9H, OCH₃). ¹³C NMR (125 MHz, acetone-d₆, TMS): δ 64.0, 135.5, 147.3 ppm.

2.5 Preparation of 1,3,5-triethoxy-2,4,6-trinitrobenzene (TETNB) by ethylation of TNPG [24]

The method was same as in 2.4, except that the alkylating reagent was triethyl orthoformate. This compound was obtained as pale yellow crystals. Melting point: 115.9-116.7 °C. IR (KBr, cm⁻¹): ν 3433(w), 3134(w), 1635(s), 1585(m), 1425(m), 1321(s), 1211(m), 1178(m), 916(w), 703(w). ¹H NMR (500 MHz, CDCl₃, TMS): δ 1.2 (t, 9H, CH₃), 4.2 ppm (m, 6H, CH₂). ¹³C NMR (125 MHz, CDCl₃, TMS): δ 15.6, 74.7, 136.6, 146.7 ppm.

2.6 Preparation of 1,3,5-tripropoxy-2,4,6-trinitrobenzene (TPTNB) by propylation of TNPG [24]

The method was same as in 2.4, except that the alkylating reagent was tripropyl orthoformate. This compound was obtained as white crystals. Melting point: 104.5-105 °C. IR (KBr, cm⁻¹): ν 2976(m), 2941(w), 2883(w), 1589(m), 1534(s), 1471(m), 1444(m), 1345(s), 1279(w), 1122(s), 1048(m), 930(m), 889(m), 840(m), 757(m), 648(m). ¹H NMR (500 MHz, DMSO-d₆, TMS): δ 0.8 (t, 3H), 1.6 (m, 2H), 4.1 ppm (t, 2H). ¹³C NMR (125 MHz, DMSO, TMS): δ 9.8, 22.8, 79.4, 135.4, 146.7 ppm.

2.7 General procedure for the synthesis of TATB catalyzed by PTCs

1,3,5-Trimethoxy-2,4,6-trinitrobenzene (or 1,3,5-triethoxy-2,4,6-trinitrobenzene or 1,3,5-tripropoxy-2,4,6-trinitrobenzene) (6.0 mmol) and the PTC (0.03 mmol) were dissolved in dimethylbenzene (15 mL). The mixture was then heated to 40 °C with vigorous stirring. As the same time, 25% (w/w) aqueous ammonia

(12 mL) was added dropwise to the mixture during 2 h and a yellow solid was obtained. The product was filtered off, washed with acetone, ethanol, and water and then air dried to give TATB. Melting point: 378.84 °C. IR (KBr, cm^{-1}): ν 3312(w), 3212(w), 1602(m), 1440(m), 1221(s), 1158(s), 783(m), 679(m). ^1H NMR (500 MHz, DMSO-d_6 , TMS): δ 3.3 ppm (s, 6, NH_2).

2.8 The synthesis of TATB in a pressure vessel (the conventional method)

The method for the synthesis of TATB from 1,3,5-triethoxy-2,4,6-trinitrobenzene in a pressure vessel (a liquid-gas two-phase system) has been reported [24].

2.9 The synthesis of TATB in ethanol

The method for the synthesis of TATB from 1,3,5-triethoxy-2,4,6-trinitrobenzene in ethanol (a liquid-liquid single-phase system) has been reported [18]. To a solution of 1,3,5-triethoxy-2,4,6-trinitrobenzene in ethanol was added 25% (w/w) aqueous ammonia dropwise at 40 °C. The reaction mixture was stirred for 2 h and a yellow solid was obtained. The product was filtered off, washed with acetone, ethanol, and water and then air dried to give TATB.

3 Results and Discussion

3.1 Synthesis

When the solution of TETNB alone in dimethylbenzene was heated at 40 °C and was stirred vigorously whilst aqueous ammonia was added to the solution during 2 h, only 6.5% of TATB was recovered (Table 1, entry 1). The addition of 18-crown-6 produced a dramatic rate acceleration and TATB was isolated in 96.52% yield after 2 h (Table 1, entry 2). Aminations catalyzed by various types of catalyst were carried out and the results are shown in Table 1. The results showed that all of the PTCs except β -CD can promote this reaction, especially 18-crown-6 (entries 2-10). The reaction rates for the different PTCs increased in the following order: crown ethers > tertiary amines > quaternary ammonium salts > polyethers > cyclodextrin (CD).

Table 1. Screening for an appropriate PTC for the synthesis of TATB from TETNB^a

Entry	Catalyst ^b	Yield [%]	Purity [%]
1	–	6.50	–
2	18-crown-6	96.52	98.8
3	15-crown-5	94.95	98.6
4	PEG400	26.29	98.2
5	β -CD	trace	–
6	CTAB	73.84	98.4
7	TBAC	42.44	98.3
8	TEBA	19.44	98.2
9	TBAB	27.84	98.3
10	Py	78.73	98.5

^a Reaction conditions: n(TETNB)/n(aqueous ammonia) = 1:6, TETNB/dimethylbenzene (6.0 mmol/15 mL), 40 °C, 2 h.

^b The catalyst amount was 1% molar ratio to TETNB.

The effect of the molar ratio of TETNB to aqueous ammonia (n(TETNB)/n(aqueous ammonia)) was investigated and the results are summarized in Table 2. It was observed that the yields were improved significantly as the amount of aqueous ammonia was increased up to a mole ratio of aqueous ammonia to TETNB of 6. The yield then increased more slowly with increasing molar ratio. The reason for this may be that aqueous ammonia also plays a role in providing a basic environment for the reaction.

Variation of the yield with time is shown in Figure 1. Almost no product was observed before 20 min. Later, the yield of TATB increased and the reaction rate gradually decreased with time. The cause for this phenomenon may be due to water being insoluble in dimethylbenzene and a combination of catalyst and ammonia is needed for a period of time.

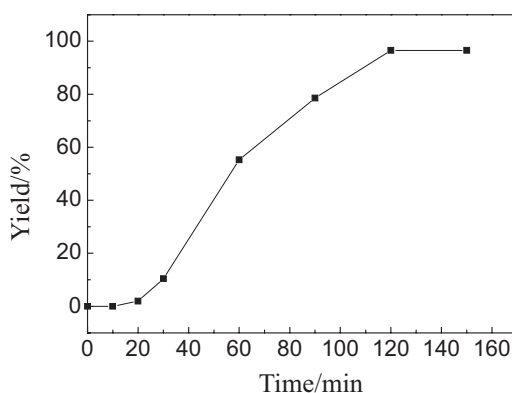
In addition, the effect of reaction temperature on amination was explored and the results are shown in Table 3. When the reaction temperature was 20 °C, only 72.17% yield was obtained in 120 min and the yield increased as the reaction temperature was increased from 20 °C to 40 °C. Continuing to increase the reaction temperature had an adverse effect on the yield. The reason for this may be that a higher temperature reduces the solubility of ammonia in water.

Figure 2 shows the effect of the catalyst amount on the amination. The yield of TATB increased dramatically with the adding of the catalyst. Beyond 0.2 mol% the effect became less and less as the dosage of catalyst was increased.

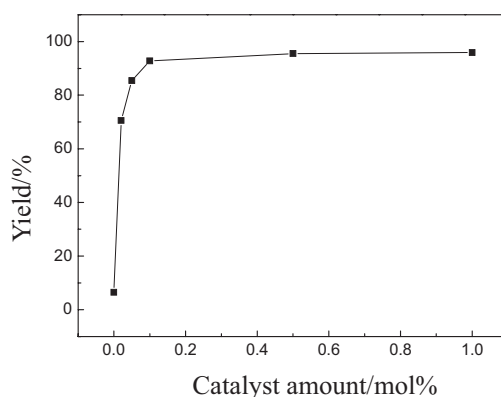
Table 2. Effect of molar ratio on the amination^a

Entry	n(TETNB)/n(aqueous ammonia)	Yield [%]	Purity [%]
1	1:3	46.50	98.3
2	1:4	76.52	98.5
3	1:5	90.75	98.6
4	1:6	96.52	98.8
5	1:7	96.55	98.8
6	1:8	96.60	98.7

^a Reaction conditions: 18-crown-6 (0.03 mmol), TETNB/dimethylbenzene (6.0 mmol/15 mL), 40 °C, 2 h.

**Figure 1.** The effect of reaction time on the amination yield^a

^a Reaction conditions: n(TETNB)/n(aqueous ammonia) = 1:6, 18-crown-6 (0.03 mmol), 40 °C TETNB/dimethylbenzene (6.0 mmol/15 mL).

**Figure 2.** Effect of catalyst amount on the amination yield^a

^a Reaction conditions: n(TETNB)/n(aqueous ammonia) = 1:6, TETNB/dimethylbenzene (6.0 mmol/15 mL), 40 °C, 2 h.

Table 3. Effect of reaction temperature on the amination yield^a

Entry	Temperature [°C]	Yield [%]	Purity [%]
1	20	72.17	98.4
2	30	84.15	98.7
3	40	96.52	98.5
4	50	96.25	98.4
5	60	94.69	98.2
6	80	90.60	98.3

^a Reaction conditions: n(TETNB)/n(aqueous ammonia) = 1:6, 18-crown-6 (0.03 mmol), TETNB/dimethylbenzene (6.0 mmol/15 mL), 2 h.

The recycling performance of the filtrate consisting of solvent, catalyst and aqueous ammonia of low concentration was investigated by the amination of TETNB with deficiencies of aqueous ammonia under the identical conditions (Table 4). The filtrate could be reused directly in the next reaction. A marginal decrease in yield and purity of TATB was observed when the filtrate was used during five cycles, which could be attributed to a cumulative effect of by-products so that TATB crystallized with more impurities.

Finally the reaction was compared with different substrates (Table 5). It was observed that TMTNB, TETNB and TPTNB were all viable substrates, and they afforded good to excellent yields under the previously optimized reaction conditions. It should be pointed out that the size of the leaving group has an effect on the reactivity of the substrate. The yield became excellent by increasing the size of the leaving group.

Thus, we chose the following reaction conditions as an optimum for all subsequent aminations: 2.070 g of TETNB, 0.008 g 18-crown-6, and 12 mL aqueous ammonia in dimethylbenzene (15 mL) at 40 °C for 2 h in air.

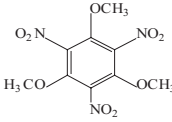
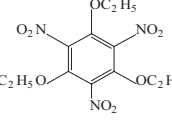
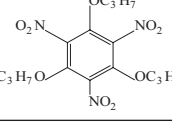
Table 4. Reuse of filtrate in the amination of TETNB

Entry	Run	Yield [%]	Purity [%]
1	Fresh ^a	96.52	98.5
2	1 st run ^b	96.25	98.2
3	2 nd run ^b	96.15	98.1
4	3 rd run ^b	96.08	98.0
5	4 th run ^b	95.83	98.0
6	5 th run ^b	94.84	97.3

^a Reaction conditions: n(TETNB)/n(aqueous ammonia) = 1:6, 18-crown-6 (0.03 mmol), TETNB/dimethylbenzene (6.0 mmol/15 mL), 40 °C, 2 h.

^b Reaction conditions: n(TETNB)/n(aqueous ammonia) = 1:3, TETNB (6.0 mmol), 40 °C, 2 h.

Table 5. Synthesis of TATB from various substrates ^a

Entry	Substrate	Yield [%]	Purity [%]
1		92.17	98.6
2		96.52	98.7
3		99.48	98.7

^a Reaction conditions: n(TETNB)/n(aqueous ammonia) = 1:6, 18-crown-6 (0.03 mmol), TETNB/dimethylbenzene (6.0 mmol/15 mL), 40 °C, 2 h.

3.2 Characterization

The scanning electron micrograph (SEM) obtained for the TATB synthesised under the conditions of the new system (entry 2, Table 1) is shown in Figure 3. Compared with the product produced by the conventional method (the synthesis of TATB in a pressure vessel) (Figure 4), the material we prepared was granulated rather than flakes, and the particle distribution appeared more uniform. This conclusion was also confirmed by the particle distribution curve (Figures 5 and 6). This is because PTC as the surfactant is advantageous for reducing the aggregation between particles.

The thermal behaviour, as measured by DSC, of the TATB synthesized by the new, two-phase liquid-liquid system with PTC, was comparable to that of TATB synthesized by the single-phase liquid-liquid system and by the two-phase liquid-gas system (Figure 7). The DSC thermograms of TATB from the different systems showed that the TATB synthesized by the new system exhibits a large decomposition exotherm at 378.84 °C, although it was lower than that of the TATB from the two-phase liquid-gas system. It was also slightly higher than the TATB synthesized in ethanol (377.46 °C).

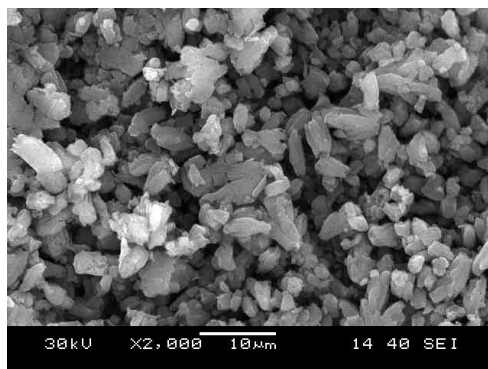


Figure 3. SEM of TATB synthesised under the PTC conditions in air

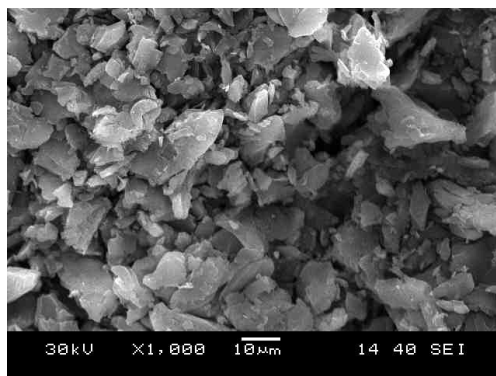


Figure 4. SEM of TATB synthesised under the pressure conditions

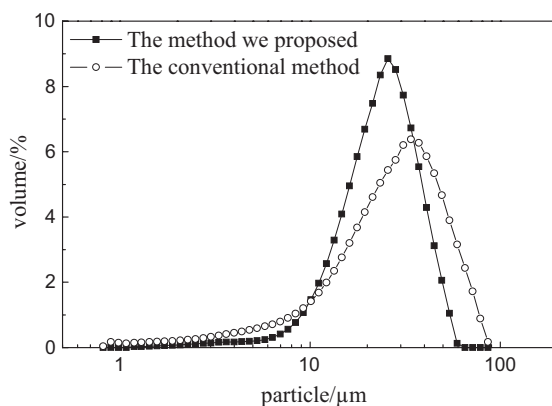


Figure 5. The particle distribution curves method on TATB particles (μm) prepared by two methods

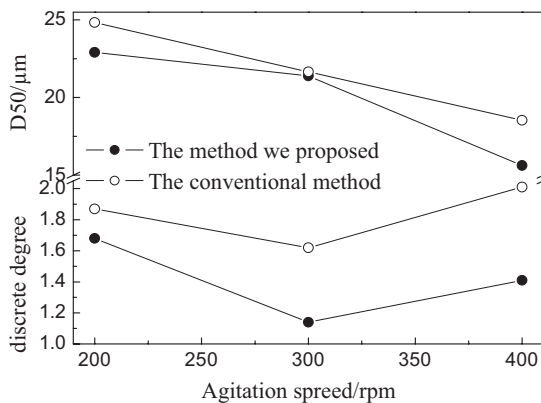


Figure 6. Influence of the preparation on the particle size of TATB

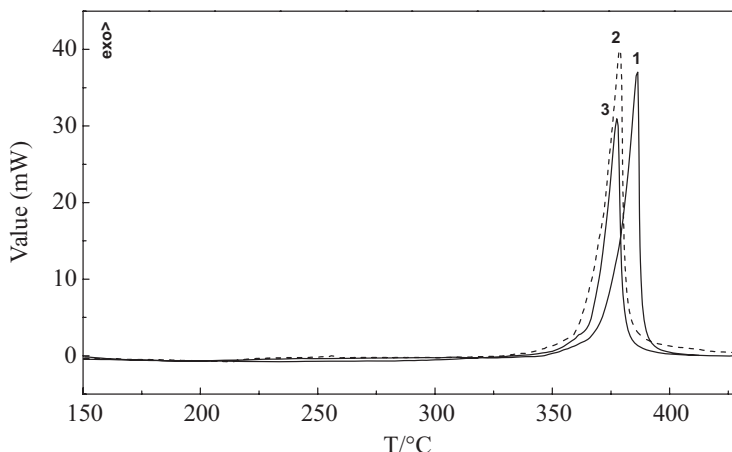


Figure 7. DSC thermograms of TATB synthesised in different systems.
1: TATB from two-phase of liquid-gas (peak: 388.12 °C);
2: TATB from two-phase of liquid-liquid with PTC (peak: 378.84 °C);
3: TATB from single-phase of liquid-liquid (peak: 377.46 °C)

4 Conclusions

In conclusion, we have successfully developed a new efficient process for synthesizing TATB in a liquid-liquid two-phase system under PTC conditions (using aqueous ammonia and 18-crown-6 in dimethylbenzene), in 96.52% yield. The material obtained by this method has good purity (98%), an exothermic

decomposition temperature of 378 °C and a narrow particle size distribution, which belongs to China GJB II class TATB.

Thus, we believe that this reaction will find considerable application in industrial production due to its simple experimental operation and mild reaction conditions, to replace the use of a pressure reactor which is dangerous and expensive. Further investigations on the mechanism of the reaction are underway in our laboratories, and will be reported in the future. In addition, the combination of 18-crown-6 and aqueous ammonia seems to be a useful aminating system. Therefore, the amination of other alkoxy-nitro-aromatic compounds using this mild reaction system should be further studied.

Symbols and Abbreviations

CTAB $\text{De}_{16}\text{Me}_3\text{N}^+\text{Br}^-$

TBAC $\text{Bu}_4\text{N}^+\text{Cl}^-$

TEBA $\text{BnEt}_3\text{N}^+\text{Cl}^-$

TBAB $\text{Bu}_4\text{N}^+\text{HSO}_4^-$

Py pyridine

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