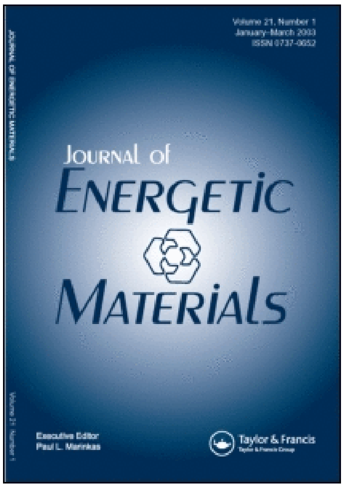

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Quantum-Chemical Studies on TATB Processes

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Quantum-Chemical Studies on TATB Processes

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Quantum chemical studies have gained paramount importance in screening of thermodynamically feasible chemical processes. The current investigation attempts to select an appropriate process for the synthesis of 1,3,5-triamino-2-,4,6-trinitro benzene (TATB), a reasonably powerful insensitive high explosive (IHE) through density functional theory (DFT) calculations. Although, 1,3,5-trichlorobenzene (TCB) and 1,3,5-trihydroxybenzene (THB) routes for synthesis of TATB have been well established, this article demonstrates the predictive capability of thermochemical computations for the identification of a viable process. Thermochemical parameters of reaction species have been obtained from DFT B3LYP/6-31G* calculations and feasibility of the process has been worked out on the basis of free energies of reactions and equilibrium constant as derived from standard enthalpy and entropy of the reaction species. The detailed computational studies have revealed that the THB route is thermodynamically feasible and the same has been supported experimentally.

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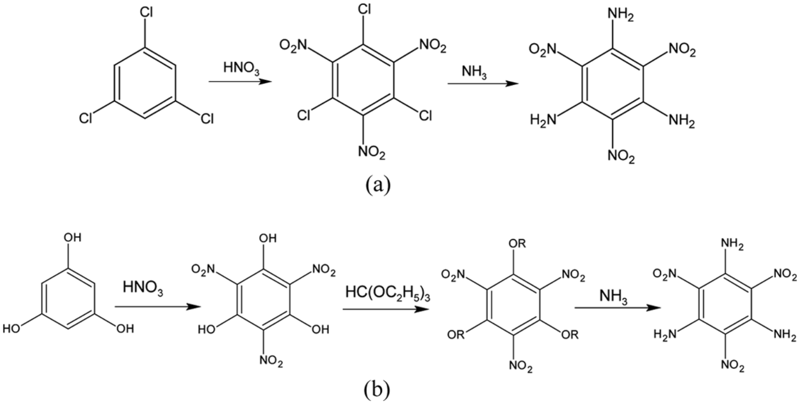
Keywords: 1,3,5-trihydroxybenzene, density functional theory, heat of reaction, insensitive high explosive, TATB

Introduction

1,3,5-Triamino-2,4,6-trinitro benzene (TATB) is a reasonably powerful insensitive high explosive (IHE), whose thermal stability and insensitivity are considerably higher than those of any other known material of comparable energy. Hence, TATB is the explosive of choice for several modern strategic warheads. A large number of synthetic routes were explored before the 1990s for the preparation of TATB based on various starting materials, viz. dinitrobenzoic acid, dichloroanisole, trinitrotoluene, and symmetric trichlorobenzene [1,2]. However, for economic purposes, TATB is being manufactured using 1,3,5-trichlorobenzene (TCB) globally, wherein nitration of TCB is followed by amination (Fig. 1(a)). The nitration of sym-TCB is exothermic and requires rather extreme conditions. Moreover, TCB is also known to be a carcinogenic material. In addition, all the chlorine in the starting material is converted to chlorinated waste. The by-products generated



(a)

(b)

Figure 1. Reaction schemes for processes 1 and 2.

during nitration are about 10% (w/w), which includes tri- and tetra-chloro-dinitrobenzenes [3]. The nitration product 1,3,5-trichloro-2,4,6-trinitrobenzenes is subjected to amination in toluene medium where ammonium chloride is generated as the by-product. Hence, it is desirable to explore a nonhazardous synthetic route free from halogenated waste and toxic substances.

Atkins et al. [4,5] reported an economic process for the preparation of TATB from 2,4,6 trinitrotoulene. In this method, hydrogen sulfide partially reduces TNT to 4-amino-2,6-dinitrotoluene (ADNT), which is then treated with nitric acid in sulfuric acid to provide pentanitroaniline (PNA) via an unexpected oxidative nitration of ADNT. Treatment of PNA with ammonia gives TATB in addition to polynitrophenol by-products. The conversion of TNT to TATB proceeds with an overall yield of 44%. Although all of the reactants are relatively inexpensive, the cost of pollution abatement ultimately prevented the industrial scale-up of this process. As a result, a new synthetic approach was developed for the synthesis of TATB, which utilizes relatively inexpensive starting materials and mild reaction conditions. This process relies on amination of nitroaromatic starting materials using a reaction method known as *vicarious nucleophilic substitution of hydrogen* [6,7]. This reaction uses surplus rocket propellant fuel, unsymmetrical dimethylhydrazine (UDMH), and ammonium picrate [8].

Recently, a new three-stage route was also explored for the synthesis of TATB that uses a non-halogen-containing starting material 1,3,5-trihydroxybenzene [9] (Fig. 1(b)). This route avoids the use of halogenated reagent. In this synthetic route, initially 1,3,5-trihydroxy benzene is nitrated to 1,3,5-trihydroxy 2,4,6-trinitrobenzene. This nitrated product is converted to 1,3,5-trialkoxy 2,4,6-trinitrobenzene by reacting with trialkyl orthoformate. Amination of 1,3,5-trialkoxy 2,4,6-trinitrobenzene is further carried out in the last stage to obtain TATB.

Among the various synthetic routes for TATB, the THB route is reported to be a possible alternative route and hence it should be further investigated for its feasibility. In recent days, quantum-chemical tools brought advantage of evaluating thermodynamic feasibility of reactions by modeling chemical processes [10]. The two principles involved in establishing conditions for performing a reaction are chemical kinetics and thermodynamics. Generally, a rate equation for a reaction is not readily available; hence, it is essential to determine the temperature envelope in which the chemical reaction will proceed at a reasonable rate. The values of the equilibrium constant, K, in this temperature range must be computed using Gibbs energy of each species participating in the reaction at the reaction conditions. However, the Gibbs energy is not usually obtained directly but is derived from thermochemical properties [11].

The thermochemical properties are usually predicted using an empirical approach, quantum mechanics, and/or a combination of both. Computational chemistry simulates chemical structure and reactions numerically, based in full or in part on the fundamental laws of physics and a vital adjunct to experimental studies. Recently, densities functional methods have been found to be attractive because they consider the effects of electron correlation and are least expensive compared to ab initio methods. The density functional theory (DFT) methods, especially the B3LYP hybrid model, not only can produce reliable geometries and energies but require less time and computer resources [12]. In this article, the B3LYP method in combination with the 6–31G* basis set has been chosen to evaluate the enthalpy of formations for reaction species by designing reasonable isodesmic reactions [13]. Isodesmic reaction processes, in which the number of each kind of formal bond is conserved, are used with application of the bond separation reaction rules.

Increasing demand for TATB imposes to explore the environmentally benign productive process. Hence, the present study has been carried out to explore the process of the THB route in comparison with the TCB route. The theoretically screened process was experimentally studied in detail and the effect of process parameters was studied to establish the environmentally benign productive process.

Experimental

Computational Methodology

All calculations were carried out with the Gaussian 03 program package [14]. The hybrid density functional B3LYP method with 6–31G* basis set was used. Molecular geometries were optimized and the optimized structures were characterized to the relative energy minimum of the potential surface by frequency calculation. Thermal corrections to the enthalpy at 298.15 K were also obtained from frequency calculation. The method of isodesmic reaction was employed successfully to calculate heat of formation (HOF) from total energies obtained by DFT calculations (Table 1). Figure 2 illustrates the isodesmic reaction for TATB. The heat and free energy of reactions of two different processes studied in the present investigation are shown in Table 2. Standard free energy of reaction was also derived from the individual component's free energy computed from quantum-chemical calculations.

Synthesis and Characterization Details

In the current manufacturing method of TATB, TCB is nitrated to 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) using a

Table 1
Thermochemical information of reaction species obtained from isodesmic approach using B3LYP/6–31 G* calculations

Reaction species	ΔH_f^o (kJ/mol)	ΔS^o (kJ/mol·K)
1,3,5-Triamino-2,4,6-trinitro benzene	−66.14	0.54
1,3,5-Trichlorobenzene	13.87	0.38
1,3,5-Trichloro-2,4,6-trinitrobenzene	135.69	0.60
1,3,5-Trihydroxybenzene	−467.26	0.36
1,3,5-Trihydroxy-2,4,6-trinitrobenzene	−537.68	0.52
1,3,5-Triethoxy-2,4,6-trinitrobenzene	−418.32	0.74
Triethyl orthoformate	−632.70	0.48

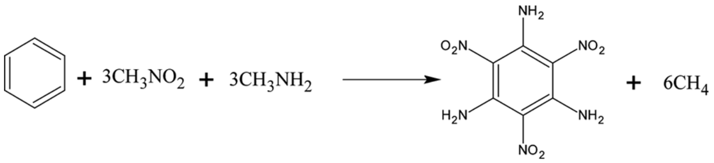


Figure 2. Isodesmic reaction scheme for TATB.

mixture of concentrated nitric acid (98%) and oleum (20%) at a temperature of 150°C for about 3 h. TCTNB is filtered, dried, and dissolved in toluene and aminated using dry ammonia gas in a pressure reactor at 125°C for 7 h. The overall yield is about 78% [2].

An alternative route involves the nitration of THB as described by Salter and Simkins [15]. The nitration process was optimized by varying reaction time and temperature. 1,3,5-Trihydroxy-2,4,6-trinitrobenzene (THTNB) was characterized by Fourier transform infrared (FT-IR) spectroscopy in KBr pellets and peaks observed were 3,684, 3,578, 3,127, 1,637, 1,584, 1,425, 1,391, 1,318, 1,254, 1,171, 911, and 695 cm^{-1}. The stoichiometric formula was confirmed by elemental analysis. DSC analysis shows that THTNB melts at 168.3°C; decomposition peaks at 170°C and the major decomposition takes place at 211°C. The impact sensitivity ($h_{50\%}$ explosion @ 2 kg) is 85 cm and friction insensitivity of THTNB was found up to 32.4 kg.

THTNB was alkylated using triethyl orthoformate as per lines of reported method [9]. 1,3,5-Triethoxy-2,4,6-trinitrobenzene

Table 2
Gas-phase heat of reaction (kJ/mol) obtained from quantum-chemical calculations

	Process 1	Process 2
Step 1	−202.15	−394.39
Step 2	−341.53	+137.64
Step 3	—	−215.59
Overall	−543.68	−471.75

(TETNB) was recrystallized from ethanol and characterized by FT-IR in KBr pellets. The peaks observed at the following wave numbers (cm^{-1}) confirm the structure: 2,293, 1,597, 1,544, 1,466, 1,332, 998, 896, 835, and 730. The peaks at δ(1.34 (t, 3H) and 4.22 (q, 2H) in proton nuclear magnetic resonance (NMR; 300 MHz, $CDCl_3$) confirms the structure. Elemental analysis confirmed the stochimetric formula. The impact sensitivity ($h_{50\%}$ explosion @ 2 kg) of TETNB was observed to be 0% explosion at 170 cm and friction insensitivity was found up to 36 kg.

Further, TETNB was aminated in toluene with gaseous ammonia at 4–5 kg/cm^2 pressure for 5 h. The yellow precipitate of TATB formed was filtered off and washed with toluene and dried in an oven. The compound was characterized by FT-IR in KBr pellets. The peak observed at the following wave numbers (cm^{-1}) confirms the structure: 3,315, 3,215, 1,608, 1,564, 1,225, 1,169, and 694. DSC of TATB shows the decomposition at 365°C, which coincides well with the TATB obtained by the TCB route. Elemental analysis confirmed the stoichiometric formula. The impact sensitivity ($h_{50\%}$ explosion @ 2 kg) and friction insensitivity of TATB were found to be 170 cm and 36 kg, respectively.

Results and Discussion

Process chemistry deals with developing and realizing an appropriate and safe process. It is essential to understand the effect of reaction parameters in order to achieve an absolute process [16]. Globally, there is continuous search for alternative environmentally benign routes for TATB, because the current TCB route is associated with thermal and health hazards. Figure 1 shows the routes for synthesis of TATB. This article compares the synthesis feasibility and thermal hazards by generating thermochemical information from quantum-chemical calculation.

Computational Evaluation for Process Feasibility

The energies of chemical bonds in a given molecule exhibit enthalpy of formation that is difficult to determine. HOFs must be obtained from calorimetry or from relatively high-level (computationally expensive) quantum-chemistry calculations [12,17]. In contrast, entropy and heat capacity are functions of molecular geometry and vibrational frequencies, which can be obtained spectroscopically or by relatively inexpensive quantum-chemical calculations. In the present scenario, computers have become more powerful, and user-friendly quantum-chemistry software is available for widening array of computational chemistry to scientists and engineers. The present study computes the standard heat of formation and entropy at a reasonable level of theory, viz. DFT B3LYP/ 6–31G*, by employing an isodesmic approach. Recently, the isodesmic approach has been demonstrated for determination of HOFs within a few kcal/mol of deviations from experimental values [18]. The present computational methodology predicts HOF in gas phase, whereas the prediction for its condensed state is not well explored from electronic structure. Isodesmic reactions have been constructed for the reaction species of both the routes and computed HOFs (Table 1).

Heat of reaction and free energy of reaction are the most important entities to evaluate the feasibility of a process and they have been derived from thermochemical data given in Table 2. Comparison of heat of reaction for the nitration step in processes 1 and 2 reveals that process 2 is more exothermic than process 1. Standard entropy change is also negative in the case of process 1 and it shows that the spontaneity of process 1 is dominated by the heat of reaction rather than the entropy contribution. Similarly, though the heat of reaction is more negative for process 1, the entropy favors process 2 for the final step of amination (step 2 in process 1 and step 3 in process 2). Overall the calculated gas-phase heat of reactions for processes 1 and 2 are −543.68 and −471.75 kJ/mol, respectively. Similarly, the computed free energy of reactions for both the processes show that process 2 is more spontaneous than process 1. The standard free energy of reaction reveals that both the processes are feasible at 298 K.

The standard enthalpy of formations and entropies for a chemical reaction are dependent on temperature to some extent. If the reaction temperature is not far away from the standard temperature (298 K), the ΔH^o and ΔS^o are assumed to be temperature independent [19]. Hence, free energy can be derived at different temperatures from ΔH^o and ΔS^o. Variation in free energies at different temperatures is shown in Fig. 3 and the free energy of reaction increases linearly with temperature for process 1, whereas there is a sharp decrease in process 2. Temperature dependency of free energy for process 1 is insignificant compared to process 2. This trend implies that process 2 may be more productive at elevated temperatures.

The equilibrium constant of the reaction depends only on the temperature and is used to determine the limit to which the reaction can proceed under the conditions of temperature, pressure, and reactant composition that appear most suitable. A plot of equilibrium constants derived from standard free energy change at various temperatures for both the processes is shown in Fig. 4. It is seen that the equilibrium constant for both the

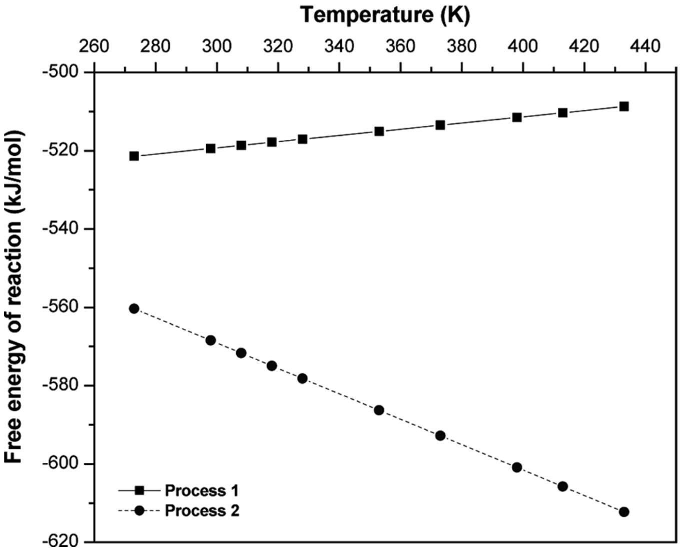


Figure 3. Plot of free energy of reaction versus temperature.

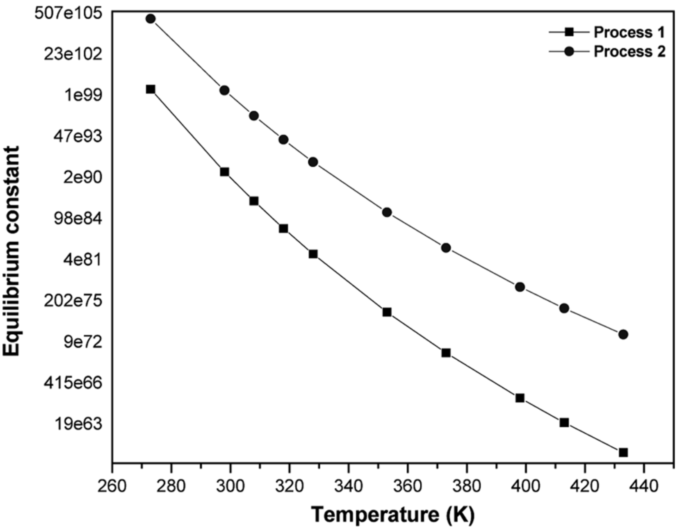


Figure 4. Plot of equilibrium constant versus temperature.

processes exponentially decreases with temperature and equilibrium conversion is significantly higher at higher temperatures for process 2 than process 1. This computational study concludes that process 2 is thermodynamically more favorable than process 1.

Experimental Evaluation

The quantum-chemical computational study reveals that process 2 is relatively better than process 1 in terms of thermodynamic feasibility. In addition, process 2 uses safe THB in contrast to the hazardous TCB in process 1; hence, laboratory experiments have been carried out to generate the process chemistry data.

Nitration involves the nitrosation of 1,3,5-trihydroxy benzene to 1,3,5-trihydroxy 2,4,6-trinitrosobenzene, which is successively oxidized to give 1,3,5-trihydroxy 2,4,6-trinitrobenzene without separation. Reaction time for the preparation of THTNB is optimized by varying nitrosation times. The plot of nitration time versus yield is shown in Fig. 5, which indicates

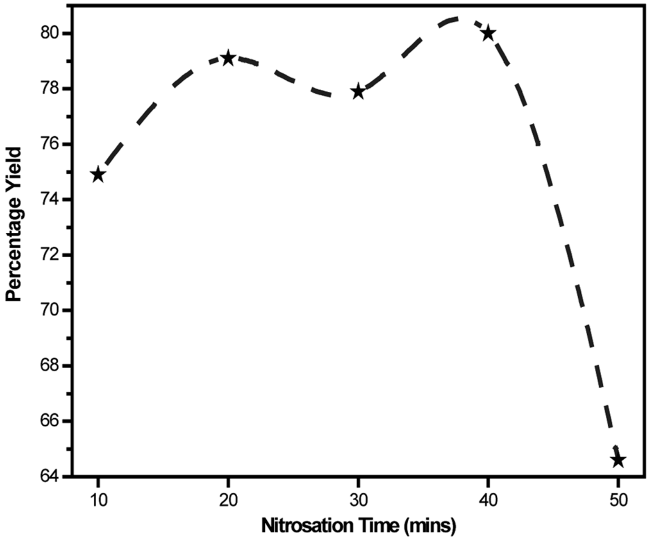


Figure 5. Plot of nitration time versus yield of THTNB.

that there is not much variation in the yield if the reaction time is varied from 20 to 40 mins. But the nitrosation beyond 40 min decreases the yield. The optimized conditions for this reaction are tabulated in Table 3. Experiments were carried out by using

Table 3
Optimal reaction parameters for process 2

Reaction steps	Temperature (°C)	Reaction time (min)	% Yield
Nitration			
N1, Nitrosation	5	40	80
A1, Ageing	15	30	
N2, Oxidation	50	30	
A2, Ageing	50	20	
Alkylation	145	165	95
Amination	25	60	98

optimized process conditions that resulted in 80% yield of 1,3,5-trihydroxy 2,4,6-trinitrobenzene. This nitration process does not require anhydrous 1,3,5-trihydroxy benzene and also avoids handling of hazardous sulphuric acid.

The yellow crystalline nitrated product obtained from the nitration reaction is alkylated using triethyl orthoformate. The yield obtained is about 95% based on THTNB (Table 3).

Amination was carried out using ammonia gas under pressure in toluene medium. Reaction conditions for the preparation of TATB from TETNB have been optimized (Table 3). A good yield of about 98% was obtained even with 1 h of amination by maintaining 5 kg/cm^2 pressure of NH_3 gas at room temperature. The particle size distribution obtained for the final product TATB at different reaction times is given in Table 4. The obtained particle size is found to be lower compared to TATB obtained by the TCB route (50 to 90 µm). A comparison of processes 1 and 2 is shown in Table 5.

Overall, process 2 establishes a ‘‘green’’ synthetic route involving less toxic starting material (THB), mild nitration conditions, and, more significantly, it allows the elimination of chlorinated species. The process has been studied in detail to optimize reaction parameters and the intermediates/products have been completely characterized. The overall yield is about 75% and the process produced the required quality of TATB without nullifying the benefits of substitutions in contrast to the current TCB route. However, the THB route

Table 4
Effect of amination reaction time on yield and particle size of TATB

Time (h)	% Yield	Particle size (µm)
5	97.6	25
5	97.4	18
3	95.6	16
1	97.7	17

Table 5
Comparison of TCB and THB routes

Particulars	TCB route	THB route
Starting material	Carcinogenic TCB	Noncarcinogenic THB
Cost of starting material	TCB is cheap	More expensive than TCB
Number of steps	Two	Three
Reaction conditions	High-temperature nitration and amination (150 and 125°C)	Mild nitration and amination (50°C and RT)
Reaction hazards	Corrosive hazards of oleum	No oleum
Thermal hazards	Possibility of runaway reaction	Mild, safer conditions
Overall yield	78%	75%
Particle size of TATB	$>50\,\mu m$	$<25\,\mu m$
Environmental aspects	Generation of chlorinated waste	No halogenated waste

involves the highly sensitive intermediate THTNB, which limits the choice for scale-up, as widely reported.

Conclusions

Although, 1,3,5 trichlorobenzene (TCB) and 1,3,5 trihydroxybenzene (THB) routes for synthesis of TATB have been well established, this study demonstrates the predictive capability of thermochemical computations for the identification of a viable process. Computational evaluation revealed that the THB route is more feasible thermodynamically. The THB route has been explored and optimal reaction parameters have been obtained to achieve a comparable yield without compromising TATB quality. Hence, the computational and experimental studies find their usefulness in identifying an environmentally benign synthetic process to prepare TATB equivalent to the current manufacturing process.

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