



Cubane decomposition pathways – A comprehensive study

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ABSTRACT

This work focuses on the development of a detailed chemical kinetics mechanism for the decomposition of the high energy density compound cubane. Quantum mechanics based ab initio calculations have been carried out to elucidate the various chemical pathways that lead to the formation of previously known product species from cubane. Optimised structures of ground states and transition states appearing in the chemical reaction scheme were obtained by using various levels of theory. Minimum energy paths were also traced for each elementary reaction. The mechanism thus obtained, along with the computed rate parameters and thermodynamic data, was used in a flow reactor model to simulate a flow reactor experiment that was carried out previously by others. Comparison of the simulation and experimental results validated the formulated reaction mechanism and provided valuable insights into the chemical behaviour of cubane.

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1. Introduction

Strained hydrocarbons are an emerging area of research from thermodynamic and chemistry perspective on account of the enormous amount of energy that molecules of this class contain [1]. This makes them suitable for potential use as propellants (as a pure compound, or in a mixture with existing propellants) in launch vehicles or as explosives. Among strained hydrocarbons, cage compounds are highly energetic. Cubane is one such compound that has been synthesised and multiple efforts are being made to synthesise other cage structures as well. Presently, active research is in progress on synthesising and testing high energy derivatives of cubane [2]. Cubane was first synthesised in 1964 by Eaton and Cole [3]. The synthesis or even existence of such a strained compound was considered impossible till then. High energy of the cage structure in cubane can be attributed to the highly strained carbon–carbon bonds. Apart from the angle strain, the torsional strain that prevents free rotation about a single bond also contributes to the high energy. The simplest of these cages have been derived directly from the platonic solids, which are highly symmetric. Cubane's structure is such that it accommodates three 19° strains at each of the 8 vertices. This is a huge deviation from the normal 109.5° bond angle of an sp³ bond [4]. It is because of this strain that cubane has a heat of formation as

high as 148 kcal/mol [5]. Although this large bending is energetically very demanding, the hydrogen atoms on the main diagonals stabilise the cubic configuration corresponding to a local instead of the global minimum of potential energy as a function of the atomic coordinates [4].

Addition of a single methyl group decreases the heat of formation of cubane, as was indicated in the study of the decomposition pathways of cubane and methylcubane by Li and Anderson [1]. Because these compounds are highly strained, a study of their decomposition pathways helps in analysing their behaviour under pyrolysis and combustion. This information would be useful because these compounds would undergo possible pyrolysis during regenerative cooling in liquid propulsion systems, as well as during reaction in the fizz zone in solid propulsion systems. There is a high built-in strain energy that may lead to an unusual combustion process [1]. The efficient harnessing of this built-in energy can be attempted by analysing the decomposition pathways of these compounds so that the elementary reaction wherein maximum energy is released will be revealed. This shall equip us in using the reactions in a controlled manner in engineering applications. The physical and chemical properties as well as the decomposition pathway of these cage structures can be altered with functionalisation. Cubane is a solid, so it can either be used as an energetic binder or as an additive in liquid propulsion systems depending on its solubility. Cage compounds such as cubane have a realistic potential to be future fuels; however, the limited synthetic capabilities have been a hindrance and have led to restriction of their quantitative and qualitative analysis to droplet combustion experiments,

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thermogravimetric analysis, and fast pyrolysis studies among others. Hence, analysing these compounds through ab initio computation methods to get a first-hand idea of their overall behaviour during decomposition would benefit the research community.

In the present work, a theoretical study by means of ab initio calculations as implemented in Gaussian 09 [6] has been carried out to explore the various reaction pathways existing during the decomposition of cubane. Optimised molecular structures of reactants, products, and transition states in the pathways were obtained. The formulated chemical pathways were validated by comparing the computed data with that in the available literature (both computational and experimental). The heats of formation of the chemical species were calculated and reaction rate constants were determined for all the elementary reactions. Thermodynamic data for all the species under consideration in the reaction mechanism was also generated. Finally, simulations were carried out to analyse the growth and decay of various species in the cubane decomposition process using the combustion models available in Chemkin [7] for validation with the results of flow reactor experiments carried out by Li and Anderson [1].

2. Molecular modelling

The modelling of short-lived, unstable intermediates and even transition states can be carried out using quantum mechanics based molecular modelling. Density Functional Theory (DFT) [8] as implemented in Gaussian 09 [6] was used to perform all calculations and optimisations in this study. The geometries of the intermediates (from reactants to products) and transition states were optimised using B3LYP functional with 6-31++G(d,p) basis set. CBS-QB3 compound method was also used, which strikes a good balance between accuracy and computational effort [9] for the molecular sizes encountered in the present study.

Relaxed potential energy scan was carried out by means of B3LYP functional, along with 6-31+G(d) basis set, on optimised molecular structures of reactants and products for obtaining the initial guesses for transition state structures, which were then subjected to transition state optimisation calculations. Presence of a single negative frequency in the molecular vibration modes confirmed the obtained transition state to be correct for the elementary reaction under consideration as it corresponds to a saddle point on the potential energy surface. These optimised structures were then used as starting structures for CBS-QB3 calculations for faster convergence. Intrinsic reaction coordinate (IRC) calculations were done in both the forward and reverse directions for all the transition states to make sure that the transition states precisely corresponded to the envisioned reaction paths. Reactions in the condensed phase were studied by applying the polarisable continuum model (PCM) along with the integral equation formalism variant (IEFPCM) [9] to reflect the assumption that the liquid-phase reactions can be treated as occurring in a solution phase. Cyclohexane was used as the solvent in all the optimisation studies, frequency and IRC calculations except for benzene (where benzene itself was used as the solvent), because cubane or any of its isomers are not directly available as a solution medium in Gaussian 09. Cyclohexane being a ring compound containing only carbon and hydrogen atoms, similar to most of the species involved in the decomposition of cubane, is expected to closely match the exact solution phase medium. The effect of change in solution medium is found to be negligible on the calculated reaction parameters [9]. Chemkin [7] is then used for analysing the global reaction mechanism under varying conditions of temperature using the energetics of the various elementary reactions modelled through Gaussian 09. Flow reactor model that simulates continuous flowing systems has been used for comparing with the available experimental results.

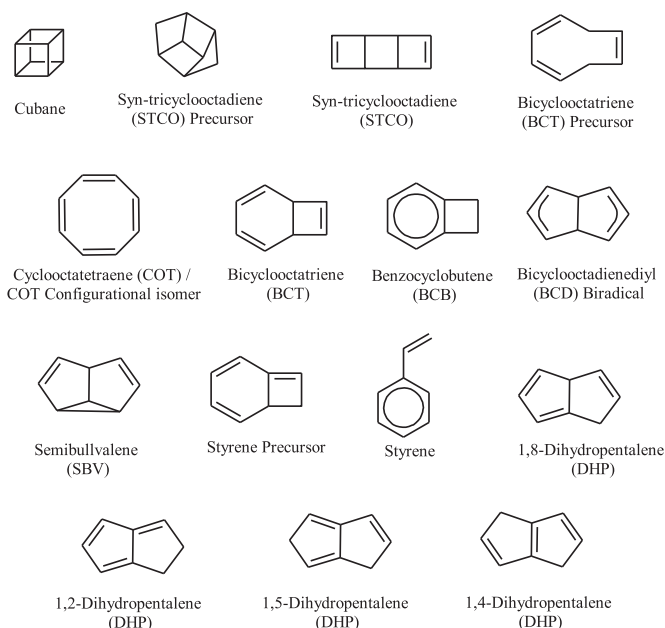


Fig. 1. C_8H_8 isomers.

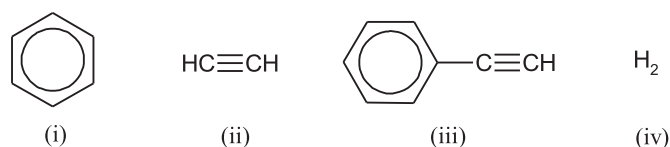


Fig. 2. C_8H_8 decomposition products.

3. Results and discussion

3.1. Reaction mechanism for the decomposition of cubane

The decomposition behaviour of cubane in both gas phase and condensed phase was studied to explain the formation of the major products shown in Figs. 1 and 2 such as cyclooctatetraene (COT), benzene, acetylene, phenylacetylene (PA), hydrogen, styrene, and dihydropentalenes (DHPs). Experimental and computational results available in the literature were used as a guideline [10]. The reactions identified in the cubane decomposition process are shown in Table 1. The rate constants for gas phase reactions were calculated at 573 K (sufficiently above the boiling point of cubane, which is 434 K), and those for condensed phase reactions were calculated at 420 K (melting point of cubane being 406 K) [2]. The pyrolysis of cubane studied by Martin et al. showed acetylene, benzene, COT, styrene, and three dihydropentalenes (DHPs) as the products [10]. This investigation also showed that the reactions are strongly pressure dependent [10]. Benzocyclobutene (BCB), phenylacetylene (PA), and hydrogen appeared as the decomposition products in the plug flow reactor study by Li and Anderson [1] and hence were considered in the present analysis. Thermochemical parameters for the reactions listed in Table 1 correspond to the CBS-QB3 calculations. Transition states corresponding to some of the key reactions are given in the Supplementary material. Gas-phase reaction mechanism is discussed in detail in the subsequent sections followed by a discussion on reactions in the condensed phase.

3.1.1. Initiation reactions

All the elementary reactions that were identified by carrying out molecular modelling calculations are listed in Table 1. The initial step in cubane decomposition is the scission of one C–C

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