

Exploring unimolecular dissociation kinetics of ethyl dibromide through electronic structure calculations

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ARTICLE INFO

Article history:

Received 5 December 2017

In final form 15 March 2018

Available online 17 March 2018

Keywords:

Rate constant

Troe's formalism

Ethyl dibromide

Fall off curve

ABSTRACT

Pathway for dissociation of multihalogenated alkyls is observed to be competitive between molecular and atomic elimination products. Factors such as molecular structure, temperature and pressure are known to influence the same. Hence present work is focussed to explore mechanism and kinetics of atomic (Br) and molecular (HBr and Br₂) elimination upon pyrolysis of 1,1- and 1,2-ethyl dibromide (EDB). For this purpose, electronic structure calculations were performed at DFT and CCSD(T) level of theory. In addition to concerted mechanism, an alternate energetically efficient isomerisation pathway has been exploited for molecular elimination. Energy calculations are further complimented by detailed kinetic investigation, over wide range of temperature and pressure, using suitable models like Canonical Transition State Theory, Statistical Adiabatic Channel Model and Troe's formalism. Our calculations suggest high branching ratio for dehydrohalogenation reaction, from both isomers of EDB. Fall off curve depicts good agreement between theoretically estimated and experimentally reported values.

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1. Introduction

Multihalogenated alkyls find profound use in variety of industrial applications, because of its inherent physical and chemical stability [1–5]. Due to the intrinsic stability, these compounds do not undergo decomposition in troposphere and slowly diffuse into stratospheric region of atmosphere, wherein there are known to damage the ozone layer [6]. Upon interacting with thermal or optical fields, these compounds are known to undergo decomposition thereby generating atomic or molecular fragments via competitive reaction pathways. Products formed primarily depends upon the structure of parent molecule. However studies have revealed that external factors like temperature and pressure also influence the generation of product. For instance, Szwarc et al. [7] observed that the thermal decomposition of benzyl bromide results in selective generation of atomic fragment (Br). On other hand, Kim et al. [8] reported that pyrolysis ClCH₂CH₂CH₂Br (over temperature range from 613 to 653 K and static pressure) results in molecular elimination of HBr. In sharp contrast to this, Tsang et al. [9] performed a single-pulse shock tube experiment (in pressure and temperature range from 1444 to 3572 Torr and 830 to 1000 K respectively) to

explore unimolecular decomposition of 3-bromopropene and reported atomic elimination of Br as a predominant channel.

From the above data, dependence of dissociation pathways (atomic or molecular) on molecular structure, temperature and pressure is clearly evitable. In present work, we have performed computationally expensive electronic structure calculations coupled with detailed theoretical kinetic analysis to identify the predominant elimination channel that is activated upon thermal decomposition of ethyl dibromide (EDB). With specific reference to the current molecule of interest, it must be noted here that EDB exist in two isomeric form, *i.e.* geminal (1,1-EDB) and vicinal (1,2-EDB). Both of these isomers are extensively used as additive in gasoline, flame retardants, refrigerants, solvents, propellants, etc [10,11]. Moreover, studies have revealed that EDB is the most abundant of all short-lived brominated compound in tropical troposphere and lower stratosphere [12]. Despite of atmospheric abundance and wide spread application of EDB, there are only limited number of reports which are focussed to explore mechanism and dissociation kinetics of EDB. For example, Lee and co-workers [13] suggested that HBr and Br₂ elimination occurs via formation of 4-centered transition structure from vicinal dihalide. More recently, Kalume et al. [14] studied the pyrolysis of 1,1-EDB, in the condensed phase. They proposed, concerted mechanism for decomposition of 1,1-EDB. In addition to this, they have investigated an alternative molecular elimination channel *i.e.* via formation of

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iso-halon as an intermediate species. It is pertinent to note here that iso-halon structures are characterized by halogen-halogen bond. Authors suggested that such isomerization pathway of molecular elimination are operable only in case of geminal halides.

In addition to above studies, Good et al. [15] performed gas-phase pyrolysis of 1,1- and 1,2-EDB, using cyclohexene as a bath gas, and recorded the global dissociation rate constant as 1.43×10^{-3} (at 686 K) and $4.9 \times 10^{-5} \text{ s}^{-1}$ (at 688.5 K) respectively. Though, the above authors reported an experimentally measured values of rate constant of EDB, however best to our knowledge, there is no theoretical work available which validates the finding of Good et al. [15]. Hence, present work is focussed to explore the energetics of all possible dissociation pathways, *i.e.* atomic (Br) and molecular (HBr and Br₂) elimination, upon thermal decomposition of 1,1- and 1,2-EDB. In addition to this, we have performed a detailed theoretical kinetic analysis, over a wide range of temperature and pressure, for each of these elimination channels, using suitable kinetic model. For instance, high pressure limiting rate constants, for atomic and molecular elimination channels, were calculated using Statistical Adiabatic Channel Model (SACM) [16,17] and Canonical Transition State Theory (CTST) [18,19] respectively. On other hand, Troe's formalism [20] was employed to derive low pressure limiting rate constant for generation of atomic and molecular fragments. Results reported in current study will help to identify the mechanism of dehalogenation processes which will act as sink in removal of these compounds from the biosphere.

2. Methodology

The electronic structure calculations reported in present work were performed using Gaussian 09 program package [21], at DFT level of theory, in conjunction with appropriate functional (B3LYP) and basis set [*i.e.* 6-311++G(3df,3pd) and aug-cc-pVTZ], using default spin option [14,22–26]. In addition to this, calculations are also performed using combination of basis set *i.e.* 6-311++G(3df,3pd), for C and H, and aug-cc-pVTZ (for Br). This basis set is abbreviated as hybrid basis set throughout the manuscript. Above methods are known to predict the structural parameters that are in close agreement with those measurement experimentally [27]. We have also calculated the harmonic vibration frequencies for zero point energy correction, and to ensure that stationary points are the true minima or transition state (TS). True minima were characterized by all positive frequencies, on other hand, presence of one imaginary frequency, along the desired reaction coordinates, provided the confirmation of TS. In addition to this, Intrinsic Reaction Coordinate (IRC) scans were performed to ensure smooth connectivity between reactant and intermediate/product via TS [28,29]. To obtain more reliable relative energies between selected stationary points, structures obtained at above level of theories were subjected to energy refinement at a higher level of single reference method [*i.e.* CCSD(T)] [14,30,31].

3. Results and discussion

3.1. Dissociation pathways of 1,1- and 1,2-EDB

The structural parameters and harmonic vibrational frequencies of 1,1-EDB obtained using aforesaid quantum chemical models are shown in Fig. 1a and Table S1 (Supporting information) respectively. For the sake of simplicity, only averaged bond length and angles obtained at different level of theories are reported. Table S1 also includes mode assignments estimated from animation of normal modes. However, due to some modes being strongly coupled, these assignment should be considered only approximate.

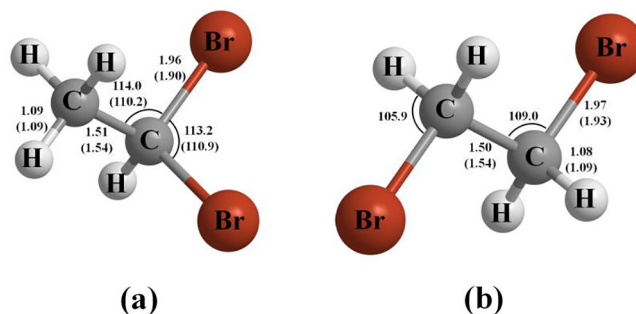
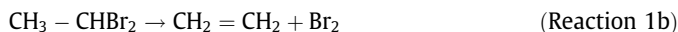


Fig. 1. Structure of (a) 1,1-EDB and (b) 1,2-EDB optimized at DFT level of theory. Averaged bond length and angles, obtained at different level of theories, are reported in Å and degrees. Numbers in parenthesis are structure parameters obtained experimentally [Ref. [27]].

It must also be noted here that, there is no general consensus existing for scaling factor of frequencies obtained using DFT with hybrid basis set. [32]. Hence, the unscaled vibrational frequencies has been used in further calculations.

Thermal decomposition of 1,1-EDB can result in generation of atomic (Br) and molecular fragments (HBr and Br₂) via following reaction channels



Different reaction pathways (mechanism) shall be operable for generation of above mentioned fragments. Herein, we have made an attempt to identify the energetics of all possible reaction pathways responsible for atomic or molecular elimination (see Fig. 2 and Table 1). From Fig. 2, it can be seen that multiple reaction pathways are responsible for molecular elimination (HBr and Br₂). The HBr elimination can occur via formation of 3-centered or 4-centered transition structure. A 3-centered transition structure results in generation of carbene, while 4-centered transition structure results in generation of more stable product *i.e.* alkene. Our calculations suggest that formation of 4-centered transition structure is energetically favourable by 45.64 kcal mol⁻¹ (including zero point energy correction) than 3-centered transition structure. It must also be noted here that present work estimates the energy requirement for HBr elimination via 4 centered TS as 57.76 kcal mol⁻¹ which is in close agreement with experimental and theoretical work of other research groups. For example, Lee et al. [13] and Kalume et al. [14] estimated the energy requirement for HBr elimination from 1,1-EDB via 4-centered TS to be 55.61 kcal mol⁻¹ and 56.16 kcal mol⁻¹ respectively, while Good et al. [15] measured the activation barrier for decomposition of 1,1-EDB as 50.52 ± 0.6 kcal mol⁻¹. On other hand, the elimination of Br₂ proceeds via formation of 3-centered transition structure. Our calculation predicts an asynchronous elimination pathway for generation of Br₂. In addition to the above reaction pathways, we had located an alternate isomerization channel for molecular elimination *i.e.* via formation of iso-halon as an intermediate species. This isomeric elimination channel proceeds via two steps [14,33,34] *i.e.* formation of iso-halon from 1,1-EDB followed by elimination of HBr or Br₂. The former step had an energy barrier of 66.31 kcal mol⁻¹, while latter step was estimated to require an energy 63.04 and 90.83 kcal mol⁻¹ for HBr and Br₂ elimination respectively. Based on energy consideration, our calculation predicts dominance for 4-centered transition structure for generation of HBr, while isomerization route is favoured for generation Br₂.

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