Computational studies on the thermal decomposition and isomerization of CHBr₂O radical

Evangelos Drougas, Agnie M. Kosmas *

Department of Chemistry, University of Ioannina, Dourouti, 45110 Ioannina, Greece

Received 17 June 2004; accepted 27 October 2004

Abstract

The unimolecular decomposition study of dibromomethoxy radical, CHBr₂O, and its isomeric hydroxy dibromomethyl radical, CBr₂OH, is carried out using ab initio electronic molecular structure methods. Three kinds of reaction pathways are examined, C–H and C–Br bond scissions, intramolecular three-center HBr elimination and isomerization. Based on the ab initio results, energy-specific rate coefficients \( k(E) \) and thermal rate constants \( k(T, P) \) are evaluated using RRKM theory and master equation numerical analysis. Relevance to existing experimental evidence is discussed.

© 2004 Elsevier B.V. All rights reserved.

1. Introduction

The haloalkoxy radicals, formed in the reactions of haloalkylperoxy radicals with NO, have been suggested to play a significant role in Atmospheric Chemistry, due to their involvement in the degradation mechanisms of other organic compounds [1, 2]. Thus, several extensive experimental and theoretical investigations have been devoted to their reactivity which involves unimolecular dissociation or reaction with O₂ [3–23].

The computational studies of fluorinated and chlorinated alkoxy radicals [3–5, 9–17] have shown the particular strength of the C–F bond and the relative ease of the C–Cl bond scission pathway, although the three-center HCl elimination pathway has been found to play a competitive role in the latter case. The theoretical work on brominated alkoxy radicals and the energetics of the possible dissociation channels is more limited [22, 23]. In the present work we consider the thermal decomposition of CHBr₂O and its isomeric CBr₂OH species. The dibromomethoxy radical, CHBr₂O, is an intermediate formed in the atmospheric oxidation of CH₂Br₂ and its reactivity has been investigated by Orlando et al. [20]. The following reaction channels determine its atmospheric fate:

\[
\begin{align*}
\text{CHBr}_2\text{O} + \text{O}_2 & \rightarrow \text{Br}_2\text{CO} + \text{HO}_2 & (\text{R1}) \\
\text{CHBr}_2\text{O} + \text{M} & \rightarrow \text{CHBrO} + \text{Br} + \text{M} & (\text{R2}) \\
\text{CHBr}_2\text{O} + \text{M} & \rightarrow \text{BrCO} + \text{HBr} + \text{M} & (\text{R3})
\end{align*}
\]

The experimental study has shown that elimination of one Br atom, channel (R2), is the dominant fate of CHBr₂O. Indeed, under atmospheric conditions the Br atom removal has been estimated to be about 20 times faster than the reaction with O₂ [20], while HBr elimination, channel (R3), is shown to be negligible. The lower limit of the rate coefficient for channel (R2) has been estimated to be about \( 4 \times 10^6 \text{ s}^{-1} \) at 296 K and 700 Torr total pressure [20]. In view of these experimental findings, the theoretical study of the reactivity of CHBr₂O and its isomeric CBr₂OH presents a lot of interest and will produce a quantitative picture of the...

* Corresponding author. Tel.: +302651098441; fax: +302651098798. E-mail address: amylna@cc.uoi.gr (A.M. Kosmas).
energy barriers involved in the dissociation mechanism of CHBr$_2$O.

The following reaction channels are considered in the computations:

\[
\text{CHBr}_2\text{O} \rightarrow \text{Br} + \text{CHBrO} \quad (1)
\]
\[
\rightarrow \text{H} + \text{CBr}_2\text{O} \quad (2)
\]
\[
\rightarrow \text{HBr} + \text{CBrO} \quad (3)
\]
\[
\rightarrow \text{CBr}_2\text{OH} \quad (4)
\]
\[
\text{CBr}_2\text{OH} \rightarrow \text{CBrO} + \text{HBr} \quad (5)
\]
\[
\rightarrow \text{CBr}_2\text{O} + \text{H} \quad (6)
\]
\[
\rightarrow \text{CBrO} + \text{Br} \quad (7)
\]
\[
\rightarrow \text{CHBr}_2\text{O} \quad (8)
\]

Reactions (1), (2) and (6), (7) represent the C–Br, C–H and O–H bond scission channels while reactions (3) and (5) are the HBr elimination channels. Channels (4) and (8) represent the isomerization pathways. The investigation includes the characterization of the most important stationary points on the potential energy surface for the unimolecular decomposition of CHBr$_2$O and CBr$_2$OH radicals and the calculation of energy specific rate coefficients for channels (1)–(8), using the ab initio results. Thermal rate constants $k(T,P)$ for the most interesting decomposition pathways are evaluated and the fall-off behaviour is examined.

The reliability of the ab initio calculations is checked against the quantum mechanical investigation of the dissociation scheme for analogous chlorinated and fluorinated species [3–5,9–17] and the calculated structures of carbonyl bromide, Br$_2$CO, and carbonyl bromide radical, BrCO, products in channels (2), (6) and (3), (5), determined at very high levels of quantum theory [24]. The kinetic results are compared to the existing experimental evidence [20].

2. Computational details

2.1. Quantum mechanical calculations

The geometries of reactants, products, and stationary points have been fully optimized at the UB3LYP/6-31G(d,p) and UMP2(full)/6-31G(d,p) levels of theory. Harmonic vibrational frequencies have been calculated at the same levels to characterize the stationary structures and transition states were identified by one imaginary frequency as first order saddle points. Problems have been encountered in the optimization of the transition state configurations for HBr elimination, channels (3) and (5). Optimized geometries were obtained at the UB3LYP/6-31G(d,p) level but no convergence could be achieved at the UMP2(full)/6-31G(d,p) level. Any stretching of the C–Br and C–H bonds and reduction of the BrCH bond angle invariably led to TS1 or TS2. These difficulties most probably originate from the peculiar structure of the BrCO product in channel (3), which presents a long Br–C distance and requires elongation of the second Br–C bond as well, during the course of the reaction.

Similar problems in the determination of the transition state geometry leading to hydrogen halide elimination have also been reported in other analogous systems. For instance, in the study of CH$_2$ClO and CHCl$_2$O decompositions by Wang et al. [9] and Hou et al. [10], the determination of the transition state geometries for HCl elimination has been also problematic. In fact, solution for the former system has been established in a later report while for the latter system, it has been achieved only at the semiempirical AM1 level. Wu and Carr [17] have located the transition state for HCl elimination in CH$_2$ClO, at the MP2/6-31G(d,p) level but not at the MP2/6-31(d) level. Also, Zachariah et al. [5] have determined the HF elimination transition state in the CHF$_2$O system at the MP2/6-31G level while no structure could be found at the Hartree-Fock level. There is however, full analogy between the geometries calculated for HBr elimination for the present system at the UB3LYP/6-31G(d,p) level and the corresponding configurations determined for the analogous fluorinated and chlorinated species, regardless of the level of theory this has been accomplished. This consistency enhances our confidence in the reliability of the optimized structures.

To refine the energetics G2MP2 [25] calculations were carried out at the UMP2(full)/6-31G(d,p) optimized geometries. For the two HBr elimination transition states, the UB3LYP/6-31G(d,p) optimized geometries have been used as initial geometries for the G2MP2 energy calculations. The G2MP2 method which is a modified version of G2 [26] using MP2 instead of MP4 for the basis set extension corrections, is considered to reasonably approximate the full G2 method at a substantially reduced computational cost and it is sufficiently suitable for a large system like the present one which involves the two very heavy Br atoms. The theory levels employed for the optimization of the stationary points and the refinement of the energetics may be considered as adequate. Most important, they are of similar accuracy as the theory levels used in the decomposition studies of other haloalkoxy radicals, thus, providing a common ground for comparison of the barriers involved in the corresponding decomposition pathways.

All quantum mechanical calculations have been carried out using the Gaussian 98 series of programs [27].

Eleven new structures were investigated in total, two isomeric energy minima, seven transition state configurations, labeled in order of increasing energy barrier for each radical and the two product species, CBr$_2$O and BrCO. No symmetry constrains have been imposed in the optimization procedure. The spin contamination calculated for the CH$_3$BrO radical ($\mathcal{S}^2$) = 0.761, is only...
slightly larger than the expected value of $\langle S^z \rangle = 0.75$ for doublet states. For the various transition states determined, $\langle S^z \rangle$ has been found to range from 0.766 for the Br elimination TS1 to 0.874 for the H elimination TS2, indicating significant contamination as in the CH$_2$ClO system [17]. However, the consistency with the monochlorinated system and the experimental evidence suggest that spin contamination may not significantly affect the mechanism of the reaction. The interesting product species in channels (2), (3) and (5), (6), carbonyl bromide, Br$_2$CO, and carbonyl bromide radical, BrCO, have been also investigated and compared with the detailed examination of carbonyl halides by Dixon et al. [24].

The optimized geometries and geometrical parameters for the two minima, CHBr$_2$O, CBr$_2$OH and the transition states investigated, are shown in Fig. 1 while the total electronic energies and energy differences at the UMP2/6-311G(d,p) (calculated in the course of the G2MP2 procedure) and the G2MP2 levels of theory are summarized in Table 1. The relative energy profile at the G2MP2 level is depicted in Fig. 2. Table 2 lists the harmonic frequencies and the moments of inertia of the two isomeric energy minima and the transition state configurations.

### 2.2. Kinetic calculations

Based on the ab initio data, energy-specific rate constants, $k(E)$, for the various unimolecular pathways are evaluated using RRKM theory [28–30]

$$k(E) = \int_{E_0}^{E} \rho_{TSi}(E_+) dE_+ / h\rho_M(E),$$

(9)

where $\rho_{TSi}(E_+)$ is the density of states for the active degrees of freedom of the transition state TSi involved in the reaction step $i$ and $\rho_M(E)$ is the density of states available to the reactant minimum M at an energy $E$. The explicit $J$-dependence of the $k(J,E)$ RRKM expression has usually a small influence on the final results [15] and it has been omitted, assuming at a first approximation, similar rotational constants for the equilibrium and the transition state structures.

Thermal rate constants and fall-off curves are computed at various temperatures and pressures through the numerical solution [31] of the master equation [32].

![Fig. 1. Optimized structures at the UMP2(full)/6-311G(d,p) level for stationary points of various decomposition and isomerization channels of CH$_2$BrO. TS3 and TS5 geometries are at the B3LYP/6-31G(d,p) level of theory. Numbers indicate bond distances in Å.](image-url)
which gives the unimolecular rate constant, \( k_{\text{uni}} \), at any temperature and pressure

\[
-k_{\text{uni}} g(E) = \omega \int_0^\infty \left( P(E, E') g(E') - P(E', E) g(E) \right) dE' - k(E) g(E),
\]

(10)

\( k(E) \) is the microscopic reaction rate coefficient, \( g(E) \) denotes the population of molecules with energy \( E \), \( P(E, E') \) is the probability of energy transferred per collision and \( \omega \) is the collision frequency. The kinetic calculations were performed numerically by employing the UNIMOL suite of programs [31] with an energy grain size of 0.05 kcal mol\(^{-1}\) and an energy transfer functional form described by the biased random walk model. The detailed calculation method and basic theory employed are given in detail by Gilbert et al. [31].

The Lennard–Jones potential parameters (i.e., well depth and collision diameter \( \sigma \)) for CHBr\(_2\)O+N\(_2\) are not available in the literature. Thus, suitably adjusted parameters for the present system had to be estimated in analogy with the values employed for other halogenated analogs \([4,5,9–17,22,23]\). The estimated data \( \varepsilon = 212 \) K, \( \sigma = 4.84 \) Å have been introduced in the fall-off calculations. Finally, since two equivalent Br atoms may be removed, the degeneracy factor of 2 has been used for channel (1).

### Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>UMP2/6-311G(d,p)</th>
<th>( \Delta E^a )</th>
<th>G2MP2</th>
<th>( \Delta E^b )</th>
<th>ZPE(^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHBr(_2)O</td>
<td>-5258.562172</td>
<td>0.0</td>
<td>-5258.820918</td>
<td>0.0</td>
<td>11.8</td>
</tr>
<tr>
<td>CBr(_2)OH</td>
<td>-5258.588178</td>
<td>-16.1</td>
<td>-5258.842352</td>
<td>-13.4</td>
<td>12.0</td>
</tr>
<tr>
<td>TS1</td>
<td>-5258.543902</td>
<td>7.4</td>
<td>-5258.816281</td>
<td>2.9</td>
<td>7.7</td>
</tr>
<tr>
<td>TS2</td>
<td>-5258.528824</td>
<td>15.8</td>
<td>-5258.801201</td>
<td>12.4</td>
<td>6.7</td>
</tr>
<tr>
<td>TS3</td>
<td>-5258.524354</td>
<td>20.3</td>
<td>-5258.796731</td>
<td>15.2</td>
<td>8.4</td>
</tr>
<tr>
<td>TS4</td>
<td>-5258.517480</td>
<td>24.9</td>
<td>-5258.781733</td>
<td>24.6</td>
<td>8.7</td>
</tr>
<tr>
<td>TS5</td>
<td>-5258.540580</td>
<td>9.0</td>
<td>-5258.800641</td>
<td>12.7</td>
<td>8.8</td>
</tr>
<tr>
<td>TS6</td>
<td>-5258.520661</td>
<td>20.7</td>
<td>-5258.792853</td>
<td>17.6</td>
<td>6.5</td>
</tr>
<tr>
<td>TS7</td>
<td>-5258.506332</td>
<td>29.7</td>
<td>-5258.778322</td>
<td>26.7</td>
<td>6.5</td>
</tr>
<tr>
<td>Br + CHBrO</td>
<td>-5258.608738</td>
<td>-29.6</td>
<td>-5258.854732</td>
<td>-21.2</td>
<td>11.4</td>
</tr>
<tr>
<td>H + CBr(_2)O</td>
<td>-5258.562516</td>
<td>-6.2</td>
<td>-5258.815017</td>
<td>3.7</td>
<td>5.8</td>
</tr>
<tr>
<td>CBr(_2)OH + HBr</td>
<td>-5258.618438</td>
<td>-40.2</td>
<td>-5258.867427</td>
<td>-29.2</td>
<td>6.9</td>
</tr>
<tr>
<td>BrCOH + Br</td>
<td>-5258.525533</td>
<td>22.3</td>
<td>-5258.680409</td>
<td>25.5</td>
<td>11.1</td>
</tr>
</tbody>
</table>

\(^a\) Energy differences corresponding to UMP2/6-311G(d,p) results including ZPE corrections.

\(^b\) Energy differences corresponding to G2MP2 values (ZPE corrections included).

\(^c\) The zero-point-energy corrections correspond to HF harmonic frequencies scaled by 0.89, as included in the G2MP2 results.

### Table 2

<table>
<thead>
<tr>
<th>Harmonic frequencies (cm(^{-1})) and moments of inertia (amu (\AA)^2) at the UMP2(full)/6-31G(d,p) level of theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harmonic frequencies</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>CHBr(_2)O</td>
</tr>
<tr>
<td>CBr(_2)OH</td>
</tr>
<tr>
<td>TS1</td>
</tr>
<tr>
<td>TS2</td>
</tr>
<tr>
<td>TS3(^a)</td>
</tr>
<tr>
<td>TS4</td>
</tr>
<tr>
<td>TS5(^a)</td>
</tr>
<tr>
<td>TS6</td>
</tr>
<tr>
<td>TS7</td>
</tr>
</tbody>
</table>

\(^a\) These results correspond to B3LYP/6-31G(d,p) level of theory.
3. Reaction pathways

3.1. Bond scission processes

The ground states of CHBr₂O and CBr₂OH radicals may decompose via C–Br, C–H or O–H bond scissions according to channels (1), (2) and (6), (7) through well-defined transition states, denoted hereafter as TS1, TS2 and TS6, TS7.

Channel (1) represents the cleavage of one C–Br bond in CHBr₂O through TS1 with the products, monobrominated formaldehyde CHBrO + Br located at 21.2 kcal mol⁻¹ below reactant at the G2MP2 level. Inclusion of Br spin-orbit coupling correction (3.6 kcal mol⁻¹) [33] will lower the products but the reaction scheme will remain essentially unaltered. The associated energy barrier is found to be quite low at 2.9 kcal mol⁻¹ above the reactant at the G2MP2 level making this pathway the most thermodynamically feasible dissociation channel (Fig. 2). The comparison with similar systems is interesting. The energy barrier for Br elimination in monobrominated methoxy radical, CH₂BrO, is found to be the same, 2.6 kcal mol⁻¹ [23], while in CH₂ClO [17] and CHF₂O, CHCl₂O [10] the corresponding Cl and F elimination barriers have been calculated as 10.5, 29.5 and 22.2 kcal mol⁻¹, respectively, at similar theory levels, demonstrating the decreasing strength of the C-halogen bond from F to Br and the weakening of the C–Cl bond upon successive chlorination.

The C–Br bond cleavage in CBr₂OH takes place through the transition state configuration TS7, placed quite high, at 40.2 kcal mol⁻¹ above reactant at the G2MP2 level and located very late in the reaction pathway, being almost product like. The late location along the reaction path and the smaller absolute value of the imaginary frequency of 458i cm⁻¹ indicate a loose transition state structure, very much like the dissociation products, CBrOH + Br, placed at 39.0 kcal mol⁻¹ above the reactant CBr₂OH at the G2MP2 level.

The cleavage of the C–H bond, channel (2), leads to atomic hydrogen and dibrominated formaldehyde or carbonyl halide products, H + CBr₂O, located at 3.7 kcal mol⁻¹ above CHBr₂O at the G2MP2 level. These are the only decomposition products that are less stable than the reactant, due to the breaking of the strong C–H bond. The associated energy barrier, 12.4 kcal mol⁻¹, is substantially higher than for Br-atom removal, making this depletion route much less probable and contrary to the CF₂HO system where the H removal is more feasible. Indeed, in CHF₂O the H elimination barrier has been calculated as 18.4 kcal mol⁻¹ [5], or 14.7 kcal mol⁻¹ [10] and in CHCl₂O as 14.2 kcal mol⁻¹ [10]. In CBr₂OH, the same dissociation products, H + CBr₂O, at 17.1 kcal mol⁻¹ above reactant are formed through a high energy barrier at 31.1 kcal mol⁻¹ at the G2MP2 level.

3.2. Three-center elimination processes

Reaction pathways (3) and (5) correspond to the three-center elimination of HBr. In CHBr₂O this elimination takes place through the transition state configuration TS3 possessing an imaginary frequency of 1417i cm⁻¹ and leading to CBrO + HBr at 29.2 kcal mol⁻¹ below reactant at the G2MP2 level. Indeed, these are the most stable dissociation products. TS3 presents a three-member ring geometry and is formed from the simultaneous stretching of both breaking bonds. The barrier height for HBr elimination is rather high, 15.2 kcal mol⁻¹, much higher than the critical energy for Br atom removal and even higher than the C–H bond scission process. The comparison of TS3 with the corresponding transition state configurations in similar systems is also profitable. In all cases studied, CH₂BrO [23], CH₂ClO [17], CHF₂O [5,10] and CHCl₂O [10], triangular geometries have been obtained with the main characteristic being the substantial decrease in XCH bond angle. The corresponding barriers, 11.5, 8.0, 37.5 (33.9) and 7.9 kcal mol⁻¹, respectively, at similar theory levels, demonstrate that competition of the HX elimination pathway is only significant in the case of the chlorinated analogs. The HBr + BrCO products in the dissociation of CBr₂OH are formed via an 1, 2 elimination involving the square-type TS5 transition state configuration, located at 12.7 kcal mol⁻¹. Similar square-type geometries have been obtained in both the CF₂OH [5,10] and CCl₂OH [10] decompositions.

The structures of product carbonyl halide, Br₂CO and carbonyl halide radical, BrCO, have been found in good agreement with the results of Dixon et al. [24] who have investigated these species using high levels of ab initio molecular orbital theory with additional improvements including core/valence correlation corrections, scalar relativistic effects and spin-orbit coupling. Their most interesting result has been the structure of BrCO which contrary to CICO, is predicted to be a loose complex with a very long Br–C bond length of 3.299 Å at the CCSD(T)/VDZ level and 3.094 Å at the CCSD(T)/augVTZ level and a BrCO bond angle of 180°. The present MP2 optimization of BrCO, does predict the loose bonding character of BrCO radical and has produced a Br–C distance of 3.151 Å and a BrCO angle of 179.9°. The binding energy of BrCO including spin-orbit coupling is quite low, 0.3 kcal mol⁻¹ [24], and thus, the Br atom is readily removed. In Br₂CO the Br–C bond distance is found to be 1.961 Å, in good agreement with the value 1.909 Å found by Dixon et al. [24] at the MP2/VTZ level.

3.3. Isomerization process

The most important rearrangement pathway proceeds through TS4 and leads to the formation of
CBr₂OH, more stable than CHBr₂O by 13.4 kcal mol⁻¹ at the G2MP2 level. However, the associated isomerization barrier is the highest, 24.6 kcal mol⁻¹, making this channel the least probable reaction pathway. The energy profile in Fig. 2 indicates that CBr₂OH is considerably more stable than CHBr₂O and furthermore, that the dissociation of CBr₂OH involves much higher critical energies than the decomposition of CHBr₂O. Indeed, the CBr₂OH radical appears particularly stable while CHBr₂O readily dissociates releasing a bromine atom.

4. Reaction kinetics

4.1. Microscopic rate constants

Using the ab initio calculated harmonic frequencies, moments of inertia and barrier heights we have carried out RRKM calculations [28–30] to determine the rotationally averaged energy-specific microcanonical rate constants, \( k(E) \), for the CHBr₂O, CBr₂OH unimolecular decomposition and isomerization channels (1)–(8).

The RRKM part of the UNIMOL package [23] has been used to carry out these calculations.

Fig. 3 shows the energy-specific rate constants, \( k(E) \), as a function of the total energy \( E \). Channel (1), the C–Br bond scission in CHBr₂O, that possesses the lowest critical energy for reaction, exhibits the largest \( k(E) \) below 40 kcal mol⁻¹ and dominates the decomposition process at the low energy region. The other channels follow according to the order of the critical energy values. As the energy rises further various crossings occur due to the lower frequencies in the transition states. Channel (2) which leads to H atom removal prevails at the high energy region and exceeds the most important C–Br bond scission since the low frequencies of TS2 assume the lowest values. The HBr elimination, channel (3), is placed lower and finally, the isomerization channel (4) with the highest critical energy remains negligible throughout the entire energy region. In CBr₂OH radical the \( k(E) \) decomposition rates are generally much smaller at the lower energy region since the corresponding critical energies are much higher than in CHBr₂O. Indeed, as already mentioned, the CBr₂OH radical is considera-

![Fig. 3. Energy specific rate constants \( k(E) \) vs \( E \).](image1)

![Fig. 4. Thermal rate coefficients for processes (1)–(4) at 1 atm of pressure and fall-off curves for processes (1)–(3), with N₂ as the bath gas at 298 K.](image2)
The average downward energy transferred per collision, \(\langle \Delta E_{\text{down}} \rangle\), and the collision efficiency \(\beta\).

### 4.2. Thermal rate constants

The UNIMOL package was further employed to calculate thermal rate constants \(k(T)\) and fall-off curves. The \(k(T)\) Arrhenius expressions at 1 atm of pressure and the \(k(T,P)\) fall-off curves at \(T = 298\ \text{K}\) for the CHBr\(_2\)O thermal decomposition are given in Fig. 4.

The Arrhenius expressions \(k(T)\) for reactions (1)–(4) in the temperature range 200–500 K and 1 atm of pressure, have been obtained by least square fitting of individually calculated rate constant values and are given by the following equations in \(s^{-1}\):

\[
k_1(T) = 2.1 \times 10^{10} \exp(-1325/T),
\]

(11)

\[
k_2(T) = 7.2 \times 10^8 \exp(-4526/T),
\]

(12)

\[
k_3(T) = 2.6 \times 10^{11} \exp(-5709/T),
\]

(13)

\[
k_4(T) = 6.8 \times 10^{13} \exp(-13833/T).
\]

(14)

Fig. 4 also includes the fall-off data for the most significant decomposition channels (1)–(3) at 298 K. Channel (4) falls out of range. The rate constant of the prevailing C–Br bond scission channel, \(k_1(T,P)\), approaches the high-pressure limit around \(10^6\ \text{Torr}\) and it is consistent with the lower limit estimate, \(4 \times 10^6\ \text{s}^{-1}\) at 298 K and 700 Torr total pressure [20]. In the neighbourhood of atmospheric pressures within the lower stratospheric region it is readily seen that the rates of all three channels are well within the fall-off region. Finally, in Table 3 we have calculated collected rate constant values for the Br elimination channel in the region of important temperatures and pressures. The asymptotic values of \(k\) at the low and high pressure limits are also given in Table 3 along with the variation of the average downward energy transferred per collision, \(\langle \Delta E_{\text{down}} \rangle\) (\(\text{cm}^{-1}\)) and the collision efficiency \(\beta\).

### 5. Summary

The most important stationary points on the potential energy surface for the thermal decomposition and isomerization channels of CHBr\(_2\)O and CBr\(_2\)OH radicals are investigated using quantum mechanical methods with the initial optimization of reactants, products and transition states carried out at the UB3LYP/6-31G(d,p) and UMP2(full)/6-31G(d,p) levels of theory. The energetics has been examined using the G2MP2 methodology and the most probable decomposition pathway is the C–Br bond breaking channel.

Energy specific rate constants \(k(E)\), thermal rate constants \(k(T)\) for 1 atm of pressure and fall-off curves \(k(T,P)\) at 298 K are evaluated using RRKM theory and master equation numerical solution. The kinetic result for the Br-atom removal is consistent with the experimental evidence [20].

### References