Matrix-isolated infrared absorption spectrum of CH₂BrOO radical

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1. Introduction

Alkylperoxy radicals, ROO, are important intermediates in the oxidation of alkanes in the atmosphere [1]. Halogenated alkyl peroxo radicals have received attention due to the importance of chlorine (Cl) and bromine (Br) atoms in the degradation of stratospheric ozone [2–5]. For instance, bromomethylperoxy radical (CH₂BrOO) can be generated via reaction CH₂Br + O₂ in the atmosphere (especially in the marine boundary layer), while the CH₂Br radicals are formed via abstraction of a hydrogen atom from CH₂Br by OH or Cl [6,7]. The UV absorption spectrum of gaseous CH₂BrOO has been studied, revealing a broad and structureless feature at 240 nm [2,4,8]. The rate coefficient [4] of its self-reaction of CH₃Br by OH or Cl [6,7].

2. Experimental section

The assignment was made to CH₂Br radicals as a radical precursor; residence time for the radicals in the hyperthermal nozzle is approximately 100 μs. The CH₂Br₃I precursor (97% purity) was purchased from Aldrich. The dosing nozzle for CH₂Br (97% purity) was purchased from Aldrich. The dosing nozzle for CH₂BrO radicals, CH₂BrOO can be generated in the Ar matrix via reaction (1):

CH₂Br + O₂ → CH₂BrOO

(1)

In this work CH₂Br radicals were generated via thermal decomposition of CH₂Br₃I (reaction (2)).

CH₂BrI + Δ (heat, about 900—1000 °C) → CH₂Br + I

(2)

In the paper, we have used a different method to generate CH₂BrOO radicals, specifically via the reaction CH₂Br + O₂ when the reactants in tandem supersonic nozzles are deposited in a 10 K Ar matrix. Here we report the infrared absorption spectrum of the CH₂BrOO radical in an Ar matrix. Fundamental vibrational frequencies and infrared intensities were calculated using scalar-relativistic coupled-cluster methods. The experimental frequencies and intensities are compared to computational results as well as the results obtained by Huang and Lee in the gas phase.

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The bromomethylperoxy radical, CH₂BrOO, has been generated in cryogenic matrices. Six fundamental bands for CH₂BrOO have been observed in an argon matrix at 5 K. The experimental frequencies (cm⁻¹) are: v₄ = 1274.9, v₅ = 1229.4, v₆ = 1086.7, v₇ = 961.8, v₈ = 879.9, and v₁₀ = 515.4, two of which are detected for the first time. Ab initio calculations have been performed employing coupled-cluster methods. The experimental frequencies are shown to be in good agreement with the computation as well as the four bands (v₄, v₅, v₇, and v₈) observed by Huang and Lee in the gas phase.

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with respect to each other and were approximately 2.5 cm away from the cryogenic CsI sample window. Behind the pulsed valve for the hyperthermal nozzle was the gas mixture of CH$_2$BrI and Ar (CH$_2$BrI:Ar/C$_2$5/1:200) in a 1.2 L stagnation reservoir with 1.1 atm stagnation pressure. The gas mixture for the O$_2$ nozzle was made at approximately 0.8 atm stagnation pressure in a 4 L flask with the O$_2$:Ar ratio at about 1:4. The pressure drop in each reservoir was measured using a capacitance manometer to determine the gas flow rate. The dosing rate for each nozzle was about 0.4 mmol per minute. The O$_2$ (Research grade: 99.999%) and Ar (Ultra High Purity: 99.999%) gases were purchased from Airgas. The CsI sample window was kept at 10 K during dosing (dosing time is usually a couple of hours); once the radicals were trapped in the matrix, the temperature was lowered to about 5 K and the IR spectrum of the sample was measured. Matrix spectra were recorded using a Nicolet 6700 Fourier transform infrared spectrometer equipped with a mercury/cadmium/telluride (MCT-A) detector and a Deuterated Triglycine Sulfate (DTGS) detector. The spectral resolutions of the two detectors are 0.5 and 1 cm$^{-1}$. The cryostat is equipped with a pair of CsI side windows to accommodate the FTIR beam.

3. Ab initio calculations

Employing the CFOUR program package [12], the fundamental frequencies and infrared intensities of CH$_2$BrOO have been computed at the coupled-cluster singles and doubles (CCSD) augmented [13] with a perturbative treatment of triple excitations (CCSD(T)) level [14]. The spin-free exact two-component theory in its one-electron variant (SFX2C-1e) has been used [15,16] to provide a cost-effective treatment of scalar-relativistic effects. Harmonic frequencies and intensities have been calculated using atomic-natural-orbital (ANO) basis sets of triple-zeta quality (ANO1) specifically contracted for the SFX2C-1e scheme [17–19].

Fig. 1. Energy as a function of the torsional angle computed at SFX2C-1e-CCSD(T)/ANO0 level. Other geometrical parameters have been optimized for each torsional angle.

Fig. 2. The equilibrium structure of CH$_2$BrOO (syn-CH$_2$BrOO conformer) with C$_1$ symmetry computed at the SFX2C-1e-CCSD(T)/ANO1 level.

Fig. 3. IR spectra of CH$_2$BrOO in the 490–990 cm$^{-1}$ region. The black trace (bottom) is the spectrum of CH$_2$BrI at room temperature. The blue trace (middle) is the spectrum of CH$_2$BrI pyrolysis only at around 900 °C with no added O$_2$. The pink (top) trace is the spectrum of CH$_2$BrI pyrolysis at around 1000 °C with O$_2$ added. As described in the text, CH$_2$Br and O$_2$ react in the 10 K Ar matrix producing CH$_2$BrOO. The peaks marked by a green bullet (*) are assigned to CH$_2$BrOO. The peaks marked by DB(T) are assigned to BrCH$_2$CH$_2$Br (1,2-dibromoethane) with trans conformation. The peaks marked by DB(G) are assigned to BrCH$_2$CH$_2$Br (1,2-dibromoethane) with gauche conformation. And the peaks marked by P are assigned to the precursor CH$_2$BrI. The peaks marked by (?) are unknown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
The anharmonic corrections to frequencies and intensities have been obtained from second-order perturbation theory [20] using linear, quadratic, and cubic force fields as well as the semi-diagonal elements of the quartic force fields computed with the corresponding double-zeta ANO (ANO0) basis sets. Thirty-four core electrons (the 1s electrons of C and O, as well as the 1s, 2s, 2p, 3s, 3p, 3d electrons of Br) have been kept frozen in all the CC calculations presented here. The geometry optimization and the computations of force fields have been greatly facilitated by the availability of the analytic gradients for the SFX2C-1e scheme [21,22] and for the CCSD(T) method [23,24] in the CFOUR program package.

4. Results

Our computational results have confirmed that the equilibrium structure of CH$_2$BrOO is the syn-CH$_2$BrOO conformer and has $C_s$ symmetry with 12 vibrational modes, all of which are infrared active. The anti-CH$_2$BrOO conformer (with the BrOO dihedral angle equal to 180°) lies around 0.8 kcal/mol higher in energy, as shown in Fig. 1. Consequently, in an Ar matrix at 5 K, only the syn-CH$_2$BrOO conformer can be observed. Fig. 2 shows the equilibrium structure of CH$_2$BrOO (syn-CH$_2$BrOO conformer) obtained at the SFX2C-1e-CCSD(T)/ANO1 level. Two of the twelve modes are high frequency C–H vibrations with vibrational frequencies of about 3000 cm$^{-1}$. The difference between the vibrational frequencies of the two isotopologues CH$_2^{79}$BrOO and CH$_2^{81}$BrOO is less than 1 cm$^{-1}$ for all the modes (for example, the frequency for the Br–C stretching mode in CH$_2^{81}$BrOO is 0.8 cm$^{-1}$ smaller than that in CH$_2^{79}$BrOO) and thus is insignificant for the present study. This is in line with the finding by Huang and Lee. Intuitively this can be attributed to the fact that the substitution of $^{79}$Br with $^{81}$Br does not significantly change the reduced mass of the Br–C diatomic fragment and thus does not affect the Br–C stretching frequency much. In the following we focus our discussion on CH$_2^{79}$BrOO.

The IR spectra of CH$_2$BrOO in the 490–990 cm$^{-1}$ region are shown in Fig. 3. The black trace (bottom) is the spectrum resulting from precursor CH$_2$Br only at room temperature. The blue trace (middle) shows peaks from the pyrolysis product CH$_2$Br as well as the precursor. Some secondary pyrolysis products are also observed including CH$_2$Br–CH$_2$Br (marked as DB), CH$_3$Br, CH$_2$CH$_2$ and CH$_2$Br$_2$. For 1,2-dibromoethane (or DB), there are two conformers, trans (T) and gauche (G). The assignment for the gauche conformer is tentative due to some intensity discrepancies between the literature [26] and our experiment. For example, in the literature [26] a strong band was observed at 836 cm$^{-1}$ for the gauche conformer, but in our spectrum, the band near 836 cm$^{-1}$ is relatively weak. Possible explanation is that in the literature the spectrum was collected at room temperature liquid phase, while our spectrum is measured in 5 K Ar matrix. The differences in the experimental conditions may cause changes in band intensities. However, more studies are needed to better understand this issue. The pink (top) trace in Fig. 3 is the spectrum of CH$_2$Br pyrolysis only at around 900°C with no added O$_2$. As described in the text, CH$_2$Br and O$_2$ react in the 10 K Ar matrix producing CH$_2$BrOO. The peaks marked by a green bullet (•) are assigned to CH$_2$BrOO. The peaks marked by DB(T) are assigned to BrCH$_2$CH$_2$Br (1,2-dibromoethane) with trans conformation. And the peaks marked by (?) are unknown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The IR spectra of CH$_2$BrOO in the 990–1290 cm$^{-1}$ region are shown in Fig. 4. The black trace (bottom) is the spectrum resulting from precursor CH$_2$Br only at room temperature. The blue trace (middle) shows peaks from the pyrolysis product CH$_2$Br as well as the precursor. Some secondary pyrolysis products are also observed including CH$_2$Br–CH$_2$Br (marked as DB), CH$_3$Br, CH$_2$CH$_2$ and CH$_2$Br$_2$. For 1,2-dibromoethane (or DB), there are two conformers, trans (T) and gauche (G). The assignment for the gauche conformer is tentative due to some intensity discrepancies between the literature [26] and our experiment. For example, in the literature [26] a strong band was observed at 836 cm$^{-1}$ for the gauche conformer, but in our spectrum, the band near 836 cm$^{-1}$ is relatively weak. Possible explanation is that in the literature the spectrum was collected at room temperature liquid phase, while our spectrum is measured in 5 K Ar matrix. The differences in the experimental conditions may cause changes in band intensities. However, more studies are needed to better understand this issue. The pink (top) trace in Fig. 3 is the spectrum of CH$_2$Br pyrolysis with O$_2$ added. As described earlier, CH$_2$Br and O$_2$ react in the 10 K Ar matrix to produce CH$_2$BrOO. The peaks marked by a green bullet (•) are assigned to the title peroxy radical (CH$_2$BrOO). Again CH$_2$Br–CH$_2$Br (marked as DB), CH$_3$Br, CH$_2$CH$_2$ and CH$_2$Br$_2$ are observed as secondary pyrolysis products.

The IR spectra of CH$_2$BrOO in the 990–1290 cm$^{-1}$ region are shown in Fig. 4. The black trace (bottom) is the spectrum resulting from precursor CH$_2$Br only at room temperature. The blue trace (middle) shows peaks from the pyrolysis product CH$_2$Br as well as the precursor. Some secondary pyrolysis products are also observed including CH$_2$Br–CH$_2$Br (marked as DB), CH$_3$Br, CH$_2$CH$_2$ and CH$_2$Br$_2$.
including CH₂Br-CH₂Br (marked as DB), CH₂Br, CH₂CH₂ and CH₂Br₂. The pink (top) trace in Fig. 4 is the spectrum of CH₂Br₂ pyrolysis with O₂ added. The peaks marked by a green bullet (●) are assigned to the title peroxy radical (CH₂BrOO). Again CH₂Br-CH₂Br (or DB), CH₂Br, CH₂CH₂ and CH₂Br₂ are observed as secondary pyrolysis products.

Table 1 lists the matrix IR bands of CH₂BrOO along with our calculated band positions and intensities. Six fundamental vibrational modes (v₄, v₅, v₆, v₇, v₈, and v₁₀) are observed. All experimental frequencies are in reasonable agreement with our calculations. For the four bands (v₄, v₅, v₇, and v₈) previously observed by Huang and Lee, our experimental results compare favorably with the previous report as well as our computational results (all within 5 cm⁻¹). The two new bands that we observed, v₅ and v₁₀, are in good agreement with our calculations. Since the band intensity for v₁₀ is small, it is marked as tentative (or T). v₅ is also marked as tentative due to some interference by a peak from an unknown species. The band intensities are in reasonable agreement among our experimental results, our calculations and the results by Huang and Lee.

To conclude, the matrix-isolated IR absorption spectrum of the bromomethylperoxy radical CH₂BrOO has been detected in an Ar matrix. Six vibrational bands of the CH₂BrOO radical in a 5 K Ar matrix have been observed: v₄ = 1274.3, v₅ = 1229.9, v₆ = 1086.7, v₇ = 961.8, v₈ = 879.9, and v₁₀ = 515.4. Two of them, v₅ and v₁₀, are observed for the first time.

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References

[17] The ANO Basis Sets for the SF2XC-1e Scheme Used in the Present Calculations have been Obtained by Recontracting the Primitive Functions in Refs. [18,19] Using SF2XC-1e CCSD Atomic Density Matrices. They are available on <www.cfour.de>.