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Photodissociation of 1,2-Dibromoethylene at 248 nm: Br₂ Molecular Elimination Probed by Cavity Ring-Down Absorption Spectroscopy

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The Br₂ elimination channel is probed for $1,2-C_2H_2Br_2$ in the $B^3\Pi_{ou}^+-X^1\Sigma_g^+$ transition upon irradiation at 248 nm by using cavity ring-down absorption spectroscopy (CRDS). The nascent vibrational population ratio of $Br_2(v=1)/Br_2(v=0)$ is obtained to be 0.7 ± 0.2 , thus indicating that the Br₂ fragment is produced in hot vibrational states. The obtained Br_2 products are anticipated to result primarily from photodissociation of the ground-state cis isomer via four-center elimination or from cis/trans isomers via three-center elimination, each mechanism involving a transition state Br₂. According to ab initio potential energy calculations, the

1. Introduction

The photochemistry of ethylene^[1–8] and its halogen-substituted derivatives^[9–13] has attracted wide interest of both experimentalists and theorists for decades. Upon UV irradiation, ethylene is excited to the (π , π^*) state, which may result in dissociation to yield H+C₂H₃, 2H+HCCH, and H₂+HCCH fragments through three- and four-center elimination and H-migration reactions. The H₂ molecule can be eliminated via 1,1-, 1,2-*cis*, and 1,2-*trans* mechanisms.^[14,15] Following the 1,1-site elimination, vinylidine CCH₂ rapidly undergoes isomerization (through a barrier of 5.8 kJmol⁻¹) to form HCCH.^[15]

When chlorine atoms are substituted, the photodissociation of vinyl chloride and dichloroethylene may further cause elimination of CI and HCI, apart from the H and H₂ fragments; for instance, Blank et al. investigated the photodissociation of vinyl chloride at 193 nm, thereby observing five primary dissociation channels for H, Cl, H₂, and HCl elimination. The majority of the Cl-atom release with large translational energy follows a dissociation channel that occurs from the initially excited (π, π^*) state crossing to a repulsive $[\pi(CI), \sigma^*(C-CI)]$ state.^[10] In contrast, the remaining dissociation channels result from the ground state via internal conversion from the excited state. Morokuma and co-workers examined the probable mechanism of Cl₂ elimination from 1,1-dichloroethylene and showed that it is a difficult process involving a nonplanar transition state with an energy of 559 kJ mol⁻¹ relative to the ground state.^[16] Resende and DeAlmeida reduced the activation energy to 407 kJ mol⁻¹ by involving an intermediate of CI and a C_2H_2CI radical in the calculation.^[17] From an experimental point of view, when the dichloroethylene species were irradiated at 193 nm,^[9] no Cl₂ fragments were detected, probably because pathways that lead to Br_2 elimination may proceed either through the electronic ground state by internal conversion or through the triplet state by intersystem crossing. Temperature-dependence measurements are examined, thereby supporting the pathway that involves internal conversion—which was excluded previously by using product translational spectroscopy (PTS). The quantum yield for the Br_2 elimination reaction is determined to be 0.12 ± 0.1 , being substantially contributed by the ground-state Br_2 product. The discrepancy of this value from that (of 0.2) obtained by PTS may rise from the lack of measurements in probing the triplet-state Br_2 product.

the high energy barrier makes the dissociation process difficult. Even at a shorter wavelength (namely, 157 nm), the photodissociation of F_2CCH_2 and F_2CCFH gave rise to HF, H_2 , H, and F elimination, as well as to double-bond breaking, but not to the release of F_2 .^[18,19]

Chlorine substituents have been the main focus of interest in studies of the photodissociation of haloethylene compounds, which can be partially attributed to the fact that Cl is a well-recognized candidate to cause ozone-layer destruction. Despite the low concentration of bromine atoms in the atmosphere, their catalytic rate for depleting stratospheric ozone was proposed to be up to 100 times faster than that of chlorine atoms.^[20] Nevertheless, research on the photodissociation of bromine-substituted ethylene compounds is very limited. Vinyl bromide is the compound that has been most frequently

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investigated, especially regarding its photolysis at 193 nm; for instance, Wodtke et al. observed H and HBr elimination and determined the C-Br bond energy from the product translational energy release.^[21] Suzuki and co-workers focused on the branching ratios of Br*/Br, along with the related anisotropy parameters, thereby proposing probable dissociation mechanisms for the bromine channels associated with different translational energy releases.^[22] The Br channel carrying a smaller translational energy was anticipated to originate from the dissociation of the ground state and its yield was reported to be one order of magnitude smaller than that of the HBr elimination.^[23,24] In contrast to this case, the HBr product was not found in recent studies of the photodissociation of 1,2-dibromoethylene which were carried out at 248 nm by using product translational spectroscopy (PTS).^[11] Lin and co-workers proposed the two exclusive dissociation channels $Br_2 + C_2H_2$ and $Br(fast) + Br(slow) + C_2H_2$ with a branching ratio of about 0.2:0.8. The Br₂ elimination was proposed to be the result of a fast intersystem crossing from the (π, π^*) state, whereas the triple products were thought to occur via a simultaneous asymmetric C–Br bond rupture along the (n, σ^*) state.^[11]

Halogen molecular elimination is expected to initiate from highly vibrational levels of the electronic ground state via internal conversion,^[16,17] but this primary dissociation channel has seldom been reported, not only in haloethylene compounds but also in halomethane species. Recently, we applied cavity ring-down absorption spectroscopy (CRDS) studies to determine the quantum yields of Br₂ fragments in a variety of halomethanes.^[25-28] CRDS turns out to be superior to most spectroscopic techniques in detecting the halogen molecules. Fourier-transform infrared spectroscopy, which has been popularly employed to resolve the spectra of the hydrogen halides, does not work because the infrared fundamental transitions for Br₂ are forbidden. Probing the Br₂ fragment in the $B^{3}\Pi_{ou}^{+} \leftarrow X^{1}\Sigma_{a}^{+}$ transition around 520 nm is difficult to achieve even when a laser-induced fluorescence (LIF) technique is used-because of the low fluorescence quantum yield caused by predissociation with a repulsive $C^1 \Pi_{1u}$ state.^[29,30] To our surprise, this molecular elimination channel was rarely mentioned with the method of supersonic beam.^[26] Two possible reasons are speculated: one is that the relatively small amounts of halogen products may make the detection difficult and the other one is that when samples are prepared in a supersonic beam under jet-cooled conditions, the narrow population spread in the excited state might restrict the total rates of level-to-level couplings between the excited and ground states.

By taking advantage of the CRDS merits, this work aims to probe the optical spectra of the Br₂ fragment and to elucidate the related dissociation pathways in the photolysis of 1,2-dibromoethylene at 248 nm. As an emerging absorption technique, CRDS is based on measuring the decay rate of light trapped in an optical cavity confined between two highly reflective mirrors (R > 99.9%).^[31,32] The decay rate of the light leaking out of the cavity is related to the absorption coefficient of the sample in the cavity. With this technique, the rovibrational spectra of the Br₂ fragment are acquired. Then, the quantum yields for the production of the molecular bromine along with $Br_2(v=1)/Br_2(v=0)$ branching are determined. Temperature-dependence measurements of the Br_2 product are also examined. Finally, the molecular dissociation pathways are discussed in detail with the aid of ab initio potential energy calculations.

Experimental and Theoretical Methods

The CRDS apparatus used for the photodissociation studies has been described previously.^[25-28] In brief, a 20 ns-pulsed excimer laser (at 248 nm) was used for the photolysis of 1,2-C₂H₂Br₂ while a 5-8 ns-pulsed Nd:YAG laser-pumped dye laser working on Coumarin 503 dye (515-524 nm) was triggered after a 20 ns delay to probe the released Br₂ fragment in the $B^3\Pi^+_{ou} \leftarrow X^1\Sigma^+_{q}$ transition. The energies of the photolyzing and probe lasers were controlled in the 1–5 mJ range and at 2 mJ, respectively, prior to propagating perpendicularly into a four-armed stainless-steel ring-down cell. The photolyzing laser was focused with a 25 cm focal-length cylindrical lens onto an area of $(18 \times 1) \pm 3 \text{ mm}^2$ in the interactive region.^[25] The cell had the long arms sealed by two mirrors with high reflectances of 99.98% at 488 nm and 99.95% at 515 nm, a diameter of 25.4 mm, and a radius of curvature of 1 m. The probe beam was injected through the front mirror into the ring-down cell, while a photomultiplier tube was positioned behind the rear mirror to detect the intensity of the light pulse leaking out of the mirror.

The ring-down time for each laser pulse may be determined by a best fit to the acquired exponential decay and its value varies with the absorption coefficient of the sample introduced. The reagent 1,2-C₂H₂Br₂ was purchased with a mixture of *cis* and *trans* isomers amounting to 64 and 36%, respectively (determined by NMR). The reagent was simply degassed and then introduced into the ring-down cell with the pressure adjusted at 0.1–0.5 Torr. The Br₂ absorption spectra (with a spectral resolution of 0.1 cm⁻¹) were obtained with the aid of a lab-developed program based on a Matlab environment. For the temperature-dependence measurements, the whole chamber was wrapped with a heating tape and the temperature was monitored by using a thermocouple positioned close to the central region.

Theoretical Methods

Ab initio Electronic-Structure Calculations: The molecular (Br₂, H₂, and HBr) and atomic (Br and H) dissociation channels on the adiabatic singlet-ground-state and first-triplet-state potential energy surfaces of 1,2-C₂H₂Br₂ were characterized. The geometries and harmonic frequencies of the reactants, transition states (TS), and products were obtained at the level of the hybrid density functional theory, B3LYP/6-311G(d,p); the energies were further refined by the coupled cluster CCSD(T)/cc-pVTZ with B3LYP/6-311G(d,p) zeropoint-energy corrections. The GAUSSIAN98^[33] programs were utilized in the electronic-structure calculations. For simplicity, the spin–orbit splitting of the Br atom was not taken into account for the ab initio calculations, but this would not have any effect on the mechanism proposed for the Br₂ elimination.

RRKM Rate-Constant Calculations: The Rice-Ramsperger-Kassel-Marcus (RRKM) and variational RRKM rate constants^[15,34] for the molecular and atomic dissociations at 248 nm, on both the singlet-ground-state and first-triplet-state potential energy surfaces of 1,2-C₂H₂Br₂, were predicted. The molecule was assumed to be a collection of harmonic oscillators whose harmonic frequencies and

energies were obtained as described above. In particular, for the barrierless decomposition of the Br and H atoms on the singlet surface, intrinsic reaction coordinate (IRC) calculations of optimized geometries and corresponding harmonic frequencies as a function of the breaking C–Br and C–H bond lengths, respectively, were performed at the B3LYP/6-311G(d,p) level to locate the variational transition states.

2. Results and Discussion

2.1. Br₂ Elimination as Primary Product

CRDS spectra of the Br₂ v=0 and v=1 levels in the B³ $\Pi_{ou}^+ \leftarrow X^1 \Sigma_g^+$ transition are obtained upon photodissociation of 1,2-C₂H₂Br₂ at 248 nm. Figure 1 shows an example of the Br₂ (v=0) spectrum, which contains bands from (36,0) to (39,0) in



Figure 1. CRDS spectra of Br_2 ($\nu = 0$) obtained during the photolysis of $1,2-C_2H_2Br_2$ at a pressure of 0.44 Torr.

the 516.1–518 nm range. For the Br₂(v=1) spectrum, the bands from (39,1) to (44,1) appear in the 522–524 nm range. The Br₂ spectral assignments are referred to those reported by Barrow et al.^[35] CRDS spectra for v=2 (and other higher levels) were not observed because of the poor reflectivity of the cavity mirrors at longer wavelengths.

The bands (41,1) and (37,0) are used to estimate the population ratios of v = 1-0, assigned up to J = 33 and 35, respectively. The vibrational population amounts to the summation of each rotational line for the corresponding level. Given the Franck-Condon factors 0.00425 and 0.00499 for the bands (37,0) and (41,1), respectively, and the Hönl-London factor for each rotational line involved,^[35] the branching ratio of $Br_2(v=1)/Br_2(v=0)$ is estimated to be 0.7 ± 0.2 by summing up the area of each line intensity. Herein, only the ⁸¹Br₂ spectra are selective for the branching ratio determination. The assignments for the other two molecular isotopes are not shown in Figure 1 to avoid spectral congestion. When the photolysisprobe delay time was varied from 20 to 100 ns, the rotational feature of Br₂ remained the same. The rotational population may lose its nascent nature and become thermally equilibrated during the ring-down time which can be as long as 1000 ns.

Although information on the rate of vibrational relaxation is not available, the nascent vibrational population may be largely preserved because of inefficient vibrational energy transfer. The large uncertainty in the analysis is mainly caused by the partial spectral overlap between different isotopic variants. Ignoring the rotational lines above 33 in the summed area may not contribute much to the uncertainty, since the rotational population is expected to reach thermal equilibrium. In spite of the large uncertainty, the branching ratio shows significant evidence that the resultant Br₂ fragment is vibrationally hot compared to a Boltzmann distribution.

To verify that the obtained Br_2 species was a primary product in the 248 nm photodissociation, we conducted two further experiments involving laser energy and pressure dependence. The rotational line P(37) of the Br_2 band (35,0) at

> 519.68 nm, which may be well resolved, was selected for these experiments. As shown in Figure 2, a plot of the rotational intensity as a function of the incident laser energy yields a straight line, which is indicative of a single-photon involvement in the molecular elimination. Two photons are otherwise required for the secondary photodissociation and recombination processes. The plot takes into account the origin point in the linear regression fit, thus implying that the effects of optical or partial saturation should be negligible. Since the energy of the photolying laser was controlled in a small range (of 1-5 mJ) relative to that of 11-25 mJ usually applied in the case of CHBr₂Cl,^[28] the probability of multiphoton absorption is greatly eliminated in this case and the origin point may be reasonably treated to have the same weighing factor as the remaining points. Even if the origin point is omitted, the logarithmic plot gives a slope of 1.2, which is also indicative of an insignificant contribution of the multiphoton absorption. By using fem-

tosecond pump-probe spectroscopy, Dantus and co-workers observed the channel of dihalogen molecular elimination following the UV multiphoton photolysis of a series of dihalomethane compounds,^[36,37] but they observed the Br₂ product in the excited state. The photodissociation mechanisms occurring in the nano- and femtosecond domains actually make a signifi-



Figure 2. Plot of the line intensity of the Br_2 rotation at 519.68 nm versus the incident laser energy. The origin point was taken into account for the linear regression. The sample pressure was fixed at 100 mTorr.

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cant difference. Because of the low adjusted energy range, the data in the plots bear a relatively larger uncertainty which is not caused by a small absorption cross-section. Figure 3 shows the pressure dependence of the Br_2 rotational intensity of $1,2-C_2H_2Br_2$. A straight line is obtained, which indicates that Br_2 may be produced by a single molecular photodissociation process. These experimental results exclude the probability of atomic-Br recombination or secondary photodissociation of energized C_2Br_2 or C_2HBr_2 fragments.



Figure 3. Plot of the line intensity of the Br_2 rotation at 519.68 nm versus the 1,2- $C_2H_2Br_2$ pressure (from 0.1 to 0.3 Torr) with the photolyzing laser energy fixed at 3.0 mJ pulse⁻¹.

2.2. Quantum Yield for the Br₂ Elimination Channel

The quantum yield of Br_2 during the photolysis of $1,2-C_2H_2Br_2$ at 248 nm can be determined by Equation (1):

$$\phi = \frac{[\mathsf{Br}_2]}{N_\mathsf{p}} \tag{1}$$

where $[Br_2]$ is the Br_2 concentration produced in the beam crossed-region of the photolysis/ probe lasers and N_p is the photon number density absorbed in the same region. Following our previous work,^[28] by comparing with a reference sample that has a known quantum yield ϕ_r for the Br_2 elimination channel, the present ϕ_s may be determined by using Equation (2):

$$\frac{\phi_{\rm s}}{\phi_{\rm r}} = \frac{[{\rm Br}_2]_{\rm s}}{E_{\rm 0s} n_{\rm s} \sigma_{\rm s}} \bigg/ \frac{[{\rm Br}_2]_{\rm r}}{E_{\rm 0r} n_{\rm r} \sigma_{\rm r}}$$
(2)

where E_0 is the photolyzing laser energy before the ring-down cell; *n* is the number density of the sample in the cell, and σ is the absorption cross-section at 248 nm. The subscripts s and r denote the current and reference samples, respectively. Given the experimental conditions of E_0 and *n*—along with the measurement of a relative line intensity of Br₂ at 519.68 nm—the quantum yield of Br₂ during the photolysis of 1,2-C₂H₂Br₂ is obtained to be 0.12±0.1 by using CH₂Br₂ as a reference with a known quantum yield of 0.2±0.1.^[27] Here, $\sigma_{C_{2}H_{2}Br_{2}}$ and $\sigma_{CH_{2}Br_{2}}$ are 9.7×10^{-19[38]} and 3.7×10⁻¹⁹ cm²,^[39] respectively, for the absorption at 248 nm. The obtained quantum yield is slightly smaller than the value of 0.2 determined by using product translational spectroscopy.^[11]

2.3. Photodissociation Pathways

As shown in Figure 4, the ab initio potential energy calculations give rise to the fragmentation of $1,2-C_2H_2Br_2$ via the electronic ground state, thus yielding a variety of Br, 2Br, HBr, H₂, and Br₂ elimination channels. Here, we focus particularly on the pathway that leads to the production of Br₂. The optimized structures involved in this dissociation channel are also calculated (see Figure 5), and the corresponding energies are listed in Table 1. During photodissociation of the *trans* isomer, Br₂ formation can be accomplished through: a) Br migration to the other C atom in the intermediate step to form 1,1-dimromo-

Table 1. Calculated energies of the unrestricted B3LYP/6-311G(d,p) optimized geometries for the Br_2 dissociation channels on the adiabatic singlet-ground-state potential energy surface of $1,2-C_2H_2Br_2$.

	UB3LYP/ 6-311G(d,p) ^[a]	ZPE ^[b]	CCSD(T)/ cc-pVTZ	$\Delta E^{[c]}$ [kJ mol ⁻¹]	$\Delta E^{[d]}$ [kJ mol ⁻¹]
trans-1,2-C ₂ H ₂ Br ₂ ($^{1}A_{g}$)	-5225.667758	0.03246	-5222.62039	0	0
$cis-1,2-C_2H_2Br_2(^1A_1)$	-5225.666379	0.032767	-5222.652654	3.7	1.3
i1	-5225.57943	0.030002	-5222.558063	231.9	242.4
i2	-5225.579451	0.029986	-5222.557696	231.9	243.3
i3	-5225.552014	0.02978	-5222.535831	303.9	300.2
i4	-5225.66325	0.032295	-5222.649919	11.9	7.3
ts _{trans-i2}	-5225.557768	0.026545	-5222.535814	288.8	291.7
ts _{trans-i3}	-5225.546746	0.028648	-5222.522975	317.8	331.0
ts _{cis-i1}	-5225.5669	0.027262	-5222.543804	264.8	272.6
ts _{cis-i3}	-5225.729396	0.029489	-5222.534212	303.5	303.7
ts _{cis-Br2}	-5225.528141	0.027628	-5222.493846	366.6	404.8
ts _{i1-i2}	-5225.569668	0.030513	-5222.553519	257.6	255.7
ts _{i2-i4}	-5225.563778	0.030061	-5222.544913	273.0	277.1
ts _{i3-Br2} ^[e]	-5221.563847	0.028559	-5222.538508	256.8	289.9
ts _{i4-Br2}	5225.527286	0.028412	-5222.500316	368.8	389.8
ts _{v-a(2)}	77.257652	0.021035	-77.1121925		
$ts_{v-a(2)} + Br_2$	-5225.540887	0.021742	-5222.510737	333.1	345.0
Br ₂	-5148.283235	0.000707	-5145.398545		
C_2H_2	-77.327714	0.026984	-77.187393		
H_2C_2	-77.261775	0.02352	-77.1168718		
$C_2H_2 + Br_2$	-5225.610949	0.027691	-5222.585938	149.2	163.1
$H_2C_2 + Br_2$	-5s225.54501	0.024227	-5222.515416	322.3	339.2

[a] UB3LYP/6-311G(d,p) energy with zero-point-energy correction (in Hartree). [b] Zero-point energy obtained by UB3LYP/6-311G(d,p) (in Hartree). [c] Relative energy obtained by UB3LYP/6-311G(d,p) with zero-point-energy correction. [d] Relative energy obtained by CCSD(T)/cc-pVTZ with UB3LYP/6-311G(d,p) zero-point-energy correction. [e] The first entry is the CASSCF(6,6)/6-311G(d,p) energy with zero-point-energy correction (in Hartree), the second entry is the zero-point energy obtained by CASSCF(6,6)/6-311G(d,p) (in Hartree), the third entry is the CCSD(T)/cc-pVTZ energy at the CASSCF(6,6)/6-311G(d,p) optimized geometry, the fourth entry is the relative energy determined by CASSCF(6,6)/6-311G(d,p) with zero-point-energy correction, the fifth entry is the relative energy obtained by CCSD(T)/cc-pVTZ with CASSCF(6,6)/6-311G(d,p) zero-point-energy correction.

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Figure 4. Atomic and molecular dissociation channels of $1,2-C_2H_2Br_2$ on the adiabatic singlet-ground-state potential energy surface. The Br_2 channels are highlighted and the energies (in kJ mol⁻¹ relative to *trans*-1,2-C_2H_2Br_2) are computed using the CCSD(T)/cc-pVTZ level of theory and B3LYP/6-311G(d,p) zero-pointenergy corrections (unless otherwise stated in Table 1 and Table 3 of the Supporting Information). Note that the attempts to locate the transition states for the paths represented by dotted lines were not successful.

ethane-2-ylidene (i3), followed by elimination of Br₂ from the same C atom after surpassing a transition state (ts_{i3-Br2}) with an energy of 289.9 kJ mol⁻¹, or b) H migration to yield 1,2-dibromoethane-2-ylidene (i2), followed by Br migration to produce $1,1-C_2H_2Br_2$ (i4) and a three-center elimination to give Br_2 via the transition state ts_{i4-Br2} (at 389.8 kJ mol⁻¹). In the ts_{i3-Br2} structure along route (a), the Br-Br bond distance is stretched to 3.277 Å—much larger than the equilibrium bond distance (namely, 2.334 Å) of the ground-state Br₂ product (Br₂ may thereby be produced via an asynchronous concerted mechanism in a hot vibrational state). On the other hand, for route (b), the Br–Br distance in the ts_{i4-Br2} is shortened to 2.435 Å, in proximity to the ground-state Br₂ product, and the C-Br bond lengths are elongated asymmetrically to 2.086 and 3.325 Å. Thus, the associated Br-Br moiety may be released in a cold vibrational but hot rotational state. In contrast, the cis isomer may be photodissociated in three ways. In addition to the paths similar to those observed for the trans isomer, following a) $cis \rightarrow i3 \rightarrow C_2H_2 + Br_2$ and b) $cis \rightarrow i1 \rightarrow i4 \rightarrow H_2C_2 + Br_2$, the photodissociation of cis-1,2-C₂H₂Br₂ may undergo a four-center elimination of Br₂ in which the Br-Br bond distance is stretched to 2.866 Å and two C-Br bonds are elongated to 2.501 and 2.666 Å in the transition state (ts_{cis-Br2}) with an energy of 404.8 kJ mol⁻¹. The obtained Br₂ product is anticipated to be vibrationally hot but rotationally cold.

As 1,2-dibromoethylene is excited to the (π, π^*) state, the mutually twisted CHBr groups may enhance the level-to-level coupling between the excited and ground states to facilitate the internal conversion.^[1] Therefore, in the photolysis at 248 nm, equivalent to an energy state of 482.3 kJ mol⁻¹, it is probable for 1,2-C₂H₂Br₂ to eliminate Br₂ from the higher vibrational levels of the ground state. The obtained $Br_2(v=1)/$ $Br_2(v=0)$ branching ratio suggests that the Br_2 fragment should be vibrationally hot, as compared with the value 0.2 evaluated by the Boltzmann distribution at room temperature. Thus, the dissociation channel is anticipated to stem mainly from a fourcenter elimination in the ground-state cis isomer or from a cis/ trans isomer via a three-center elimination along route (a), as described above. This contradicts the conclusion by Lin and co-workers who excluded the possibility of Br₂ production via a ground-state dissociation.^[11]

Apart from the above mechanisms, as displayed in Figure 6, atomic and molecular elimination processes including Br, 2Br, H, HBr, H₂, and Br₂ may occur via the lowest triplet state of 1,2-dibromoethylene. The optimized structures involved in the Br₂ dissociation channels are also calculated (see Figure 7), and the corresponding energies are listed in Table 2. The structures and related energies for the remaining dissociation channels resulting from both the triplet and the ground states are collected in the Supporting Information. For the case of the Br₂

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Figure 5. B3LYP/6-311G(d,p) optimized geometries of the species along the Br_2 dissociation channels of $1,2-C_2H_2Br_2$ on the adiabatic singlet-ground-state potential energy surface. The electronic states and point groups are in parenthesis; the lengths are given in Angstroms and the angles in degrees. Note that ts_{13-Br_2} were obtained at the CASSCF/6-311G(d,p) level of theory.

elimination, the triplet state may proceed via 1,1-dibromoethane-2-ylidene (${}^{3}i3$)—an intermediate in which Br migrates to the other C atom—followed by surpassing a transition state (${}^{3}ts_{i3-Br2}$) with two Br species on the same C atom. However, the other paths along ${}^{3}i2 \rightarrow {}^{3}i4 \rightarrow H_2CC + {}^{3}Br_2$ are predicted to be inaccessible because of the much higher product energy of 510.0 kJ mol⁻¹. Note that the associated Br–Br distance in the ${}^{3}ts_{i3-Br2}$ structure is 2.722 Å, practically the same as the equilibrium distance (2.722 Å) of the triplet Br₂ product. The Br₂ product thus obtained is anticipated to be vibrationally and rotationally cold. Since the photolyzing laser energy is much larger than the ${}^{3}ts_{i3-Br2}$ energy of 330.6 kJ mol⁻¹, it is probable for 1,2-C₂H₂Br₂ to undergo Br₂ elimination through this mechanism.

If the Br₂ elimination is initiated from the *trans*-1,2-C₂H₂Br₂ ground state, the rate constants of paths a) *trans* \rightarrow i3 \rightarrow C₂H₂+Br₂ are predicted to be 1.12×10⁹ and 1.77×10¹⁵ s⁻¹, respectively, by RRKM theory, whereas those for paths b) *trans* \rightarrow i2 \rightarrow i4 \rightarrow H₂C₂+Br₂ are estimated to be 2.16×10¹⁰, 1.65×10¹² and 4.38×10⁸ s⁻¹, respectively. The net dissociation rate, as restricted by the rate-determining step, is equivalent to 1.12×10⁹ and 4.38×10⁸ s⁻¹ for routes (a) and (b), respectively. Apart from the above paths, the rate constant for the *cis*

isomer along the third route to surpass the $ts_{{\mbox{cis-Br2}}}$ barrier is calculated to be $2.78 \times 10^8 \text{ s}^{-1}$. It seems that the processes generate vibrationally hot Br₂ species [the trans(a), cis(a), and cisfour-center pathways would prevail over the vibrationally cold Br₂ paths of trans(b) and cis(b)]. The prediction by RRKM theory is consistent with our experimental results. On the other hand, the dissociation rate constants initiated from the triplet ground state give rise to 1.12×10^{13} and 1.71×10^{15} s⁻¹, required for passing through one intermediate step and one TS barrier. The statistical dissociation rate via the triplet state is surprisingly much more rapid than those via the ground state, if the rates associated with intersystem crossing and internal conversion are neglected. The complete rate constants associated with each step displayed in Figures 4 and 6 are all collected in the Supporting Information. To the best of our knowledge, the photodissociation mechanism via a triplet ground state has never been considered in previous theoretical works. Lin and co-workers were the first to adopt such a mechanism to qualitatively interpret their experimental findings.^[11] In fact, in the UV photolysis of aryl halides, a well recognized pathway that leads to halogen-atom elimination is via a spin-orbit coupling between the (π, π^*) state and the repulsive triplet (n, σ^*) state.[40-43]

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Figure 6. Atomic and molecular dissociation channels of $1,2-C_2H_2Br_2$ on the adiabatic first-triplet potential energy surface. The Br_2 channels are highlighted and the energies (in kJ mol⁻¹ relative to ground-state *trans*-1,2-C_2H_2Br_2) are computed using the CCSD(T)/cc-pVTZ level of theory and B3LYP/6-311G(d,p) zero-point-energy corrections. Note that no attempts were made to locate the transition states for the paths represented by dotted lines.

Herein, CRDS is used to probe the ground-state Br₂ species, which are contributed by the dissociation initiated from the ground state via an internal conversion and a very small fraction of products quenched from the lowest triplet state during a long ring-down time. The fact that we were not able to directly detect the triplet-state Br₂ product may explain why the obtained quantum yield of the Br₂ channel is smaller than that reported using PTS.^[11] This is yet to be determined for the Br₂ branching, as contributed between the two photodissociation channels. The internal conversion efficiency is sensitive to the temperature. As the temperature increases, higher levels of the excited state are populated so that the increased density of states may facilitate the total rates of level-to-level couplings, thereby leading to a more efficient internal conversion. In the following experiments, the rotational line P(37) of Br₂ was selected for the temperature-dependent measurements. As shown in Figure 8, the line intensity was enhanced up to 10-20% upon increasing the temperature from 300 to 335 K. Measurement of the temperature effects provides further support for the photodissociation pathway based on the ground state. In contrast, the efficiency of intersystem crossing depends on the location of the energy state prepared with respect to conical intersection between the excited- and tripletstate surfaces. The closer the energy state to the surface crossing area, the more efficient the intersystem crossing.

3. Conclusions

Optical spectra of the Br₂ product eliminated during the photodissociation of 1,2-dibromoethylene at 248 nm were obtained for the first time by using CRDS. Subsequent dissociation pathways were proposed to occur via both ground and triplet states (with the aid of ab initio potential energy calculations). According to the RRKM calculations, the photodissociation rate associated with the latter pathway prevails. Nevertheless, branching of the Br₂ products should depend on competition between internal conversion and intersystem-crossing processes. The quantum yield of this primary dissociation channel was determined; the discrepancy of this value from that obtained by using PTS may rise from the lack of measurements for probing the triplet-state Br₂ product in the present work. Temperature-dependence measurements seem to support the pathway involving ground-state photodissociation (which was nevertheless excluded previously).^[11] The obtained vibrationally hot Br₂ products favor the mechanism based on a four-center elimination from the cis isomer or a three-center elimination from the cis/trans isomers, each involving a transition state with a much larger Br-Br distance than that of ground-state Br_2 .

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2.722



b) intermediates



d) molecular dissociation products ${}^{3}Br_{2} ({}^{3}\Sigma_{a}^{*}, D_{\infty b})$ dibromine



Figure 7. B3LYP/6-311G(d,p) optimized geometries of the species along the Br_2 dissociation channels of $1,2-C_2H_2Br_2$ on the adiabatic first-triplet potential energy surface. The electronic states and point groups are in parenthesis; the lengths are given in Angstroms and the angles in degrees.

Table 2. Calculated energies of the unrestricted B3LYP/6-311G(d,p) optimized geometries for the Br_2 dissociation channels on the adiabatic triplet-state potential energy surface of $1,2-C_2H_2Br_2$.

	UB3LYP/ 6-311G(d,p) ^[a]	ZPE ^[b]	CCSD(T)/ cc-pVTZ	E ^[c] [kJ mol ⁻¹]	E ^[d] [kJ mol ⁻¹]
trans-1,2- C ₂ H ₂ Br ₂ (¹ A _q)	-5225.667758	0.03246	-5222.65284	0	0
$C_2H_2Br_2(^3B)$	-5225.585479	0.028853	-5222.557521	216.1	240.8
³ i3	-5225.555125	0.028038	-5222.530251	295.8	310.3
³ ts _{i3-Br₂}	-5225.562462	0.027588	-5222.522043	276.5	330.6
³ Br ₂	-5148.234707	0.00042	-5145.333215		
$C_2H_2 + {}^3Br_2$	-5225.562421	0.027404	-5222.520608	276.6	333.9

[a] UB3LYP/6-311G(d,p) energy with zero-point-energy correction (in Hartree). [b] Zero-point energy obtained by UB3LYP/6-311G(d,p) (in Hartree). [c] Relative energy obtained by UB3LYP/6-311G(d,p) with zero-point-energy correction. [d] Relative energy obtained by CCSD(T)/cc-pVTZ with UB3LYP/6-311G(d,p) zeropoint-energy correction.

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Keywords: ab initio calculations · bromine · cavity ring-down absorption spectroscopy · elimination · photochemistry



Figure 8. Temperature dependence of the line intensity of the Br₂ rotation at 519.68 nm during the photodissociation of 1,2-C₂H₂Br₂ at 248 nm. The photolyzing laser energy was fixed at 1.2±0.3 mJ while the sample pressure was adjusted at 110 mTorr.

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