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Photodissociation of 2-Bromobutane by Ion-velocity Map Imaging Technique

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The photodissociation dynamics of 2-bromobutane has been investigated at 233.62 and 233.95 nm by ion-velocity map imaging technique coupled with resonance-enhanced multiphoton ionization. The speed and angular distribution of Br and Br* fragments were determined from the map images. The two Gaussian components, shown in the speed distributions of Br and Br* atoms, are suggested to attribute to the two independent reaction paths of photodissociation of 2-bromobutane at 233.62 and 233.95 nm. The high-energy component is related to the prompt dissociation along the C−Br stretching mode, and the low-energy component to the dissociation from the repulsive mode with bending and C−Br stretching combination. The contributions of the excited $^3\text{Q}_0$, $^3\text{Q}_1$, and $^1\text{Q}_1$ states to the products (Br and Br*) were discussed. Relative quantum yield of 0.924 for Br($^2\text{P}_{3/2}$) at about 234 nm in the photodissociation of 2-bromobutane is derived.

Key words: Ion-velocity imaging, Photodissociation, 2-bromobutane

I. INTRODUCTION

The photodissociation of alkyl bromides in the A band has attracted substantial attention because of the ozone depletion potential of the halogen-containing radicals [1, 2]. The A band is formed via an $\sigma^*\leftrightarrow n$ transition localized on the C−Br bond and consists of overlapping transitions to three excited states, $^3\text{Q}_1$, $^3\text{Q}_0$, and $^1\text{Q}_1$ in Mulliken’s notation [3], which are dipole allowed from a ground state of alkyl bromide. The excitation of the A band could lead to the breaking of a C−Br bond, thereby, to the forming of an alkyl radical and the bromine atom in the ground state Br ($^2\text{P}_{3/2}$) or in the excited state Br* ($^2\text{P}_{1/2}$). It is known that the Br* is produced from the $^3\text{Q}_0$ state, whose dipole moment is aligned parallelly to the C−Br bond, while the Br is produced from the $^3\text{Q}_1$ and $^1\text{Q}_1$ states through perpendicular transition [3].

In recent years, the time-sliced ion velocity imaging technique [4–6] combined with resonance enhanced multiphoton ionization (REMPI) is widely used to study the photodissociation of alkyl halides [7–21]. For example, CH$_3$Br [14], C$_2$H$_5$Br [15], iso-C$_3$H$_7$Br [16], n-C$_4$H$_9$Br [17], iso-C$_4$H$_9$Br [18], and tert-C$_4$H$_9$Br [18] have been investigated by this sensitive technique. From the analysis of the photodissociation processes of alkyl bromides, different dissociation mechanisms are revealed in the previous studies [14–18]. For n-C$_4$H$_9$Br [17] and iso-C$_4$H$_9$Br [18], the images of the Br fragments show the characteristics of a direct dissociation along the C−Br stretching mode. While for tert-C$_4$H$_9$Br [18], in addition to the direct dissociation, a second dissociation channel is proposed from the images of Br and Br* fragments, which is related to the potential energy surfaces with the combination of bending and C−Br stretching modes. Similar dissociation processes had been observed for CH$_2$I$_2$ [9, 10] and N$_2$O$^+$ molecules [11], as revealed from ion velocity imaging experiments.

From previous studies it is obvious that the branch number on the carbon atom of the C−Br bond can play an important role in the dissociation to produce Br fragment for C$_4$H$_9$Br isomers [17, 18]. Among these isomers the 2-C$_4$H$_9$Br (2-bromobutane) has two branches on the carbon atom of the C−Br bond, while n-C$_4$H$_9$Br, iso-C$_4$H$_9$Br have one branch and tert-C$_4$H$_9$Br has three branches. Our interest is to study the photodissociation paths of 2-bromobutane, which has two branches on the carbon atom of the C−Br bond, at about 234 nm. The photolysis of 2-bromobutane at 233.62 and 233.95 nm is investigated using ion-velocity map imaging technique coupled with resonance-enhanced multiphoton ionization. With the aid of the speed and angular distribution of Br and Br* fragments measured from the map images at about 234 nm, the photodissociation paths and the contributions of the excited $^3\text{Q}_0$, $^3\text{Q}_1$, and $^1\text{Q}_1$ states to produce Br and Br* have been studied for 2-C$_4$H$_9$Br.

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II. EXPERIMENTS

The experiments were performed in a home-built ion velocity imaging apparatus, details of which can be found elsewhere [22]. Briefly, sample gas seeded in He (about 2.5%) at a stagnation pressure of about 200 kPa was expanded through a pulsed nozzle (Series 9, General Valve) with an orifice diameter of 0.5 mm in a source chamber and skimmed to form a super-sonically expanded molecular beam into a differentially pumped detection chamber. The operating pressures in the source and detection chambers were maintained at about 133 and 26.6 µPa, respectively. After passing through a 1 mm hole on the repeller plate, the molecular beam directed along the time-of-flight (TOF) axis was intersected at right angles by the laser beam in the detection zone. For all ion velocity imaging measurements, the electric vectors of both linearly polarized lasers were set perpendicularly to the TOF axis and thus paralleled to the front face of the microchannel plates (MCP’s) that form part of the ion detection system. The about 234 nm laser is the output of a neodymium-doped yttrium aluminum garnet (Nd:YAG) (GCR-170, Spectra Physics) pumped dye laser (PrecisionScan, Sirah) and focused by an f=210 mm lens.

Br and Br* were probed at 233.62 and 233.95 nm (usually denoted about 234 nm) via the 6p(4P3/2)←4p5(2P3/2) and 6p(5S1/2)←4p5(2P1/2) transitions, respectively, using a (2+1) REMPI technology. Within a set of ion optics designed for the ion velocity imaging measurements, the Br+ were accelerated by the focusing electric fields and projected onto a 40 mm-diameter Chevron-type dual MCP’s coupled to a P-47 phosphor screen (APD 3040FM, Burle Electro-Optics). A fast high-voltage switch (PVM-4210, DEI; typical duration about 50 ns) was pulsed to gate the gain of the MCP’s for mass selection as well as the time slicing of the ion packet.

The transient images from the phosphor screen were captured by a charge-coupled device (CCD) camera (Imager Compact QE 1376×1024 pixels, LaVision) and transferred to a computer on an every shot basis for event counting [23] and data analysis. Timing of the pulsed nozzle, the laser, and the gate pulse applied on the MCP’s were controlled by a multichannel digital delay pulse generator (SRS, DG 535).

III. RESULTS AND DISCUSSION

The images of Br and Br* fragments were obtained from the photolysis of 2-bromobutane at 233.62 and 233.95 nm, as shown in Fig.1. The polarization vector of the photolysis laser is parallel to the vertical direction of the image plane.

The available energies for the photodissociation of 2-bromobutane can be obtained by the energy conservation relationships,

\[ E_{avl} = h\nu - D_0 - E_{el} + E_{int}^P = E_t + E_{int} \]  

where \( E_{avl} \), \( h\nu \), and \( D_0 \) denote the available energy, the photon energy, and the bond dissociation energy of C–Br (300 kJ/mol [24]), respectively, \( E_{el} \), \( E_{int}^P \), \( E_t \), and \( E_{int} \) denote the electronic energy level of the Br atom (0 kJ/mol for Br and 44 kJ/mol for Br*), the internal energy of parent molecules, the average translational energy of fragments, and the internal energy of C2H5 radical. \( E_t \) is average translational energy of each component, which can be calculated by the following equation

\[ E_t = \frac{1}{2} \left( m_{Br} + \frac{m_{Br}^2}{m_{C_2H_5}} \right) v_{Br}^2 \]

where \( m \) and \( v \) represent mass and velocity, respectively. The value of \( v_{Br} \) is obtained from the fitting functions of speed distribution. The fraction of \( E_t \) over \( E_{avl} \) is defined as

\[ f_T = \frac{E_t}{E_{avl}} \]

The values of \( E_t \) and \( f_T \) together with the relative contribution of each component are listed in Table I.

The branching ratio \( N(\text{Br}^*)/N(\text{Br}) \) can be determined by the following equation:

\[ \frac{N(\text{Br}^*)}{N(\text{Br})} = k \frac{S(\text{Br}^*)}{S(\text{Br})} \]

where \( N(X) \) is the number of species \( X \), \( S(X) \) is the measured mass spectrum signal intensity of species \( X \), and \( k \) is the proportional constant. The \( k \) value is determined by the REMPI probability ratios, relative detection efficiencies, and other instrumentation factors. By performing a calibration experiment of Br2 photolysis under the same condition [25], the value of \( k \) at about 234 nm is found to be 0.37. The ratio of \( N(\text{Br}^*)/N(\text{Br}) \) is obtained to be 0.082 at about 234 nm.

FIG. 1 The raw images of Br and Br* fragments following the photodissociation of 2-bromobutane at about 234 nm. (a) Br at 233.62 nm and (b) Br* at 233.95 nm. The arrow shows the linear polarization direction of the photolysis laser which is parallel to the vertical direction of the image plane.
TABLE I Energy partitioning, anisotropy parameters, and relative contribution of each component in 2-C₄H₉+Br(Br⁺) channel. Energies are in kJ/mol.

<table>
<thead>
<tr>
<th>Wavelength/nm</th>
<th>Product</th>
<th>hν (kJ/mol)</th>
<th>E_{avl} (kJ/mol)</th>
<th>E_{t} (kJ/mol)</th>
<th>f_{T}</th>
<th>β</th>
<th>Relative contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>233.62</td>
<td>Br(2P_{3/2})</td>
<td>512.1</td>
<td>212.1</td>
<td>83.2</td>
<td>0.39</td>
<td>1.55</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40.3</td>
<td>0.19</td>
<td>0.84</td>
<td>0.34</td>
</tr>
<tr>
<td>233.95</td>
<td>Br⁺(2P_{1/2})</td>
<td>511.3</td>
<td>167.3</td>
<td>72.7</td>
<td>0.43</td>
<td>1.83</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>42.8</td>
<td>0.26</td>
<td>1.01</td>
<td>0.35</td>
</tr>
</tbody>
</table>

FIG. 2 The velocity distributions of Br and Br⁺ following the photodissociation of 2-bromobutane at about 234 nm. The circles represent the experimental results, the solid lines a show the Gaussian-fitting lines, and the solid lines b are the sum of the simulated distributions.

The relative quantum yields of Φ(Br) and Φ(Br⁺) can be derived from the product ratio according to the following relations:

\[ \Phi (\text{Br}⁺) = \frac{N (\text{Br}⁺)}{N (\text{Br}) + N (\text{Br}⁺)} \]  
\[ \Phi (\text{Br}) = 1 - \Phi (\text{Br}⁺) \]  

The resultant relative quantum yield of Φ(Br) is 0.924 at about 234 nm.

The speed distribution of bromine, \( P(v) \), can be extracted by integrating a three-dimensional speed distribution over all angles at each speed. The center-of-mass translational energy distribution \( P(E) \) is calculated by converting \( P(v) \) with the following relationship:

\[ P(E) = P(v) \frac{dv}{dE} \]  

The derived speed distributions for Br and Br⁺ are shown in Fig. 2, which can be decomposed into two Gaussian components.

FIG. 3 The angular distributions of the Br and Br⁺ fragments from the photolysis of 2-C₄H₉Br at about 234 nm. (a) Br at 233.62 nm, \( \beta = 1.55 \). (b) Br at 233.62 nm, \( \beta = 0.84 \). (c) Br⁺ at 233.95 nm, \( \beta = 1.83 \). (d) Br⁺ at 233.95 nm, \( \beta = 1.01 \). The circles represent the experimental data, and the solid lines show the best-fitting profiles.

By integrating a three-dimensional velocity distribution over an appropriate range of speed at each angle, the angular distributions \( P(\theta) \) of the bromine fragments were extracted, where the parameter \( \theta \) is the angle between the laser polarization and the recoil axis of the Br fragments (C–Br). Figure 3 shows \( P(\theta) \) of the bromine fragments for the photolysis of 2-C₄H₉Br at 233.62 and 233.95 nm. The anisotropy parameter \( \beta \) has been fitted using

\[ P(\theta) \propto 1 + \beta P_2(\cos \theta) \]  

where \( P_2(\cos \theta) \) is the second-order Legendre polynomial. The \( \beta \) values for Br and Br⁺ are listed in Table I.

To estimate the relative contributions of the parallel and perpendicular transitions to the experimental anisotropy parameters \( \beta \), the measured \( \beta \) can be roughly regarded as a linear combination of the two limiting cases, \( \beta_{//} = 2 \) and \( \beta_{\perp} = -1 \), corresponding to par-
TABLE II The parallel and perpendicular weighting factors of the high-$E_t$ components for the photodissociation of 2-C$_4$H$_9$Br at about 234 nm together with the contribution of each state to the product at about 234 nm.

<table>
<thead>
<tr>
<th>(\lambda/\text{nm})</th>
<th>Product</th>
<th>(\Phi)</th>
<th>(\beta)</th>
<th>(\alpha_{//})</th>
<th>(\alpha_{\perp})</th>
<th>Initial excitation</th>
<th>Curve crossing</th>
</tr>
</thead>
<tbody>
<tr>
<td>233.62</td>
<td>Br</td>
<td>0.924</td>
<td>1.55</td>
<td>0.85</td>
<td>0.15</td>
<td>(f(1^3Q_1_1)+f(1^1Q_1_1)=0.139)</td>
<td>(f(1^3Q_1_1-1^3Q_0)=0.785)</td>
</tr>
<tr>
<td>233.95</td>
<td>Br$^*$</td>
<td>0.076</td>
<td>1.83</td>
<td>0.94</td>
<td>0.06</td>
<td>(f(1^3Q_0)=0.071)</td>
<td>(f(1^3Q_0-1^3Q_1)=0.005)</td>
</tr>
</tbody>
</table>

parallel (to $^3Q_0$ state) and perpendicular (to $^1Q_1$ or $^3Q_1$ state) transitions, respectively [20]. The corresponding relations are

\[
\beta = \alpha_{//}/\beta_{//} + \alpha_{\perp}/\beta_{\perp}, \quad \alpha_{//} + \alpha_{\perp} = 1
\]  

where \(\beta_{//}=2\) and \(\beta_{\perp}=-1\) are the limit values for the pure parallel transition and the perpendicular transition, respectively. \(\alpha_{//}\) and \(\alpha_{\perp}\) are the parallel and perpendicular weighting factors. For 2-C$_4$H$_9$Br, \(\beta\) of the high-$E_t$ Gaussian components for Br and Br$^*$ are 1.55 and 1.83, respectively (see Table I). These \(\beta\) values indicate that the angle distributions of the two Gaussian components correlated mainly with a parallel anisotropy. As listed in Table II, the \(\alpha_{//}\) values for Br and Br$^*$ fragments are 0.85 and 0.94, the \(\alpha_{\perp}\) values are 0.15 and 0.06, respectively. It is obvious that all \(\alpha_{//}\) values are much higher than that of \(\alpha_{\perp}\). This indicates that the molecule is mainly excited to the $^3Q_0$ state by parallel transitions.

With the aid of \(\beta\) values of 1.55 and 1.83 for Br and Br$^*$, respectively, the above analysis shows that the initial excitation is main to the $^3Q_0$ state. On the other hand, the $^3Q_0$ state correlates with Br$^*$ product, and the dipole moment is aligned parallelly to the C–Br bond, while the $^3Q_1$ and $^1Q_1$ states lead to the Br formation through perpendicular transition [18]. Therefore, we expect that in this situation the nonadiabatic $^1Q_1-^3Q_0$ transition plays an important role for Br$^*$ photofragment in the dissociation of 2-C$_4$H$_9$Br. That is, the conical intersection between $^1Q_1$ and $^3Q_0$ states leads to the Br$^*$ production. Furthermore, \(\beta\) of the low $E_t$ components for Br and Br$^*$ fragments are 0.84 and 1.01, respectively (see Table I). These \(\beta\) values of 0.84 and 1.01 for low $E_t$ Gaussian components are obviously lower than those of 1.55 and 1.83 for high $E_t$ components. This phenomena indicate that the contribution of parallel transition excited to the $^3Q_0$ state decreases, and the contribution of perpendicular transition excited to the $^3Q_1$, and $^1Q_1$ states increases a lot for Br and Br$^*$ photofragments of 2-C$_4$H$_9$Br. The relative fractions of individual pathways to produce Br and Br$^*$ can be determined using the following relations [18, 24]:

\[
\begin{pmatrix}
\Phi_{Br} \chi_{Br//} \\
\Phi_{Br^*} \chi_{Br//} \\
\Phi_{Br} \chi_{Br//} \\
\Phi_{Br^*} \chi_{Br//}
\end{pmatrix} =
\begin{pmatrix}
 f(1^3Q_1_1-3^Q_0) & f(1^1Q_1_1) + f(3^Q_1_1) \\
 f(3^Q_0) & f(3^Q_0-1^3Q_1_1)
\end{pmatrix}
\]

(10)

where $\chi_{Br//}$, $\chi_{Br\perp}$, $\chi_{Br^*//}$, and $\chi_{Br^*\perp}$ represent the portion of Br and Br$^*$ which come from a parallel or perpendicular transitions, $\Phi_{Br}$ and $\Phi_{Br^*}$ are relative quantum yields listed in Table II. The probability of the nonadiabatic $^1Q_1-^3Q_0$ curve crossing, \(f(1^3Q_1-3^Q_0)=0.785\) was determined to be 0.785.

Using the speed distribution of Br(Br$^*$), the anisotropy parameter, and the energy partitioning, we can investigate the photodissociation paths of 2-C$_4$H$_9$Br(Br$^*$). At 233.62 nm, the speed distribution of Br can be fitted with two Gaussian curves which are centered at 647.3 and 930.5 m/s, respectively (Fig.2(a)). At 233.95 nm, the speed distribution of Br$^*$ can also be fitted with two Gaussian curves which are centered at 667.5 and 869.8 m/s, respectively (Fig.2(b)). Furthermore, the high $E_t$ Gaussian component of Br accounts for 66% of the sum of two Gaussian components. In view of the two Gaussian components of the speed distribution of Br and Br$^*$ atoms, two independent reaction paths are suggested to attribute to the photodissociation of 2-bromobutane both at 233.62 and 233.95 nm. The high $E_t$ component is related to the prompt dissociation along the C–Br stretching mode, which can be explained reasonably by the classic impulsive model [18, 26]. For this prompt dissociation, two models have been proposed to present two limiting cases [26]. One is the rigid model that ignores the flow of energy into the vibrational degrees of freedom of the fragments, the other is the soft radical limit [18]. The values of $E_t/E_{avol}$ corresponding to the soft and rigid radical limit are 0.31 and 1, respectively [18]. In the present work, for the high $E_t$ channels of Br and Br$^*$, the values of $E_t/E_{avol}$ are 0.39 and 0.43 (see Table I), respectively, which are close to those of the soft radical limit.

Therefore, the high $E_t$ channels of Br and Br$^*$ can be explained by direct dissociation along the C–Br bond. However, for the low $E_t$ channels of Br and Br$^*$, the values of $E_t/E_{avol}$ are 0.19 and 0.26 (see Table I), respectively, which are lower than that of the soft radical limit (0.31). Therefore, the low $E_t$ components of Br and Br$^*$ cannot be accommodated by the prompt impulsive dissociation, as in the case of tert-C$_4$H$_9$Br [18]. The low $E_t$ components are suggested to be correlated to the dissociation from the repulsive mode with bending and C–Br stretching combination. The bending-stretching motions have been observed widely in recent photodissociation experiments of alkyl halide, such as C$_3$H$_7$I, i-C$_3$H$_7$I, and t-C$_3$H$_7$I, using resonance Raman emission [27]. The values of $E_t/E_{avol}$ for the low $E_t$ components of Br and Br$^*$ in the present work are also very close to that observed in the photodissociation of t-C$_4$H$_9$I.
ity between the C–Br stretching and C–Br repulsive modes with bending and C–Br stretching mode and the dissociation channel from the carbon atom of the C–Br bond, respectively. All of these observations imply that we can correlate the number of dissociation channel for Br at about 234 nm.

Figure 4 shows schematically the relevant energy levels to illustrate the photodissociation of 2-C\textsubscript{4}H\textsubscript{9}Br and the ionization of Br and Br\textsuperscript{*} fragments at about 234 nm. At first, 2-C\textsubscript{4}H\textsubscript{9}Br absorbs about 234 nm photon to produce Br(\textsuperscript{2}P\textsubscript{3/2}) or Br\textsuperscript{*}(\textsuperscript{2}P\textsubscript{1/2}), then, the Br\textsuperscript{*} are produced via the [2+1] resonance enhanced multiphoton ionization of Br or Br\textsuperscript{*} at about 234 nm. The photodissociation and ionization process of 2-C\textsubscript{4}H\textsubscript{9}Br for generation of Br\textsuperscript{*} can be expressed as follows

\[
2\text{-C}_4\text{H}_9\text{Br} \xrightarrow{\hbar\nu} 2\text{-C}_4\text{H}_9 + \text{Br(}^2\text{P}_{3/2}) \text{ or Br}^*\left(^2\text{P}_{1/2}\right) \quad (11)
\]

Br or Br\textsuperscript{*} \xrightarrow{(2+1)\hbar\nu} \text{Br}^* \quad (12)

IV. CONCLUSION

Based on the photodissociation investigation of 2-bromobutane at 233.62 and 233.95 nm by ion-velocity map imaging technique, two dissociation channels in the photodissociation of 2-bromobutane are suggested. The channel of high-E\textsubscript{t} component is related to the prompt dissociation along the C–Br stretching mode, and the channel of low-E\textsubscript{t} component is related to the dissociation from the repulsive mode with bending and C–Br stretching combination. The contributions of the excited 3Q\textsubscript{0}, 3Q\textsubscript{1}, and 1Q\textsubscript{1} states to the products (Br and Br\textsuperscript{*}) were estimated at about 234 nm. Relative quantum yield of 0.924 for Br(\textsuperscript{2}P\textsubscript{3/2}) at about 234 nm in the photodissociation of 2-bromobutane was derived.

V. ACKNOWLEDGMENTS

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