

# Photoelectron-photoion coincidence study of the bromobenzene ion

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The technique of variable time photoelectron-photoion coincidence mass spectrometry has been applied to the fragmentation of bromobenzene ion producing a phenyl ion. A detailed analysis of the variation of the breakdown curve with parent ion residence time was performed. The results lead to  $\Delta H_{f_0}^\circ$  (phenyl ion) = 270 kcal/mole in close agreement with recalculated results from an earlier study on chlorobenzene. This, combined with other photoionization results leads to  $\Delta H_{f_0}^\circ$  (phenyl radical) =  $83 \pm 3$  kcal/mole, slightly higher than the value  $80.9 \pm 2$  kcal/mole obtained from neutral kinetics. The analysis leads to a rate-energy dependence for the fragmentation process and an equivalent 1000 K Arrhenius pre-exponential factor of  $\sim 9.4 \times 10^{14} \text{ sec}^{-1}$ , which may be compared to the value  $2 \times 10^{15} \text{ sec}^{-1}$  for the analogous neutral process. The possible contribution of spin orbit splitting is discussed.

## INTRODUCTION

The recently developed techniques of photoelectron-photoion coincidence mass spectrometry have become a powerful tool for detailed investigation of ion fragmentation processes.<sup>1-6</sup> The strength of the techniques lies in the ability to select for study a restricted class of ionization-fragmentation processes for which the excitation energy imparted at ionization is rather accurately specified. This is accomplished by selecting ionization events for which the energy of the ejected photoelectron is kept essentially zero while varying the photon energy, or selecting events producing a narrow band of photoelectron energies about some nominal value and varying this nominal value while keeping the photon energy fixed (usually at 21.21 eV, He 58.4 nm resonance radiation). The actual value of the total internal energy of the photoion is composed of the photon energy less the photoelectron energy and the adiabatic ionization potential, along with the nonnegligible internal energy distribution of the room temperature molecules which are being ionized.

Different experimental systems have been realized in which the data can be treated to yield either parent-daughter ion ratios at various excitation energies (breakdown curves) or ion time-of-flight distributions resulting from fragmentation processes occurring during ion acceleration. Despite the superficial difference in analyzing breakdown curves or TOF distributions, all these experiments yield data which originate in essence from the energy dependence of the unimolecular rate constant for fragmentation.

Recently, the present authors have extended the threshold electron-ion coincidence technique along the time domain, studying parent-daughter branching ratios not only as a function of photon energy (i. e., breakdown curves) but also as a function of parent ion residence

time prior to ion ejection and TOF mass analysis.<sup>7,8</sup> This additional experimental variable made possible a systematic analysis leading to the kinetic parameters [i. e., activation energy and activated complex parameters (activation entropy)] of an ion fragmentation process.

A detailed analysis<sup>8</sup> of the time dependence of the breakdown curve of chlorobenzene ion fragmenting to a phenyl ion and a chlorine atom led to a quite precise determination of the rate-energy dependence of the process in the  $10^5$ - $10^7 \text{ s}^{-1}$  rate constant range, along with determination of the kinetic parameters for the fragmentation.

In the present paper we report on a similar study of the bromobenzene ion fragmentation process and also present some minor refinements in the analysis of the results. These refinements bring about some changes in the values of the kinetic parameters for chlorobenzene ion; these are reported here as well. This study represents a further application of the sensitivity analysis developed earlier and affords an independent check of validity through the  $\Delta H_{f_0}^\circ$  (phenyl ion) value deduced here. Although the two processes are similar, it is expected that the kinetic parameters will differ enough from those of the chlorobenzene ion to produce a significantly different time dependence of the breakdown curve. In addition, the results can be compared with earlier work by Baer *et al.*<sup>9</sup> and Bouchoux<sup>10</sup> as was done for chlorobenzene.<sup>8</sup>

## EXPERIMENTAL

The experimental breakdown curves were obtained on the photoelectron-photoion coincidence mass spectrometer previously described.<sup>11</sup> The sample gas is ionized with monochromatic photons and zero energy photoelectrons are selected by a steradiancy analyzer followed by a 127° cylindrical energy analyzer. Following detection of an electron, a drawout pulse is applied to the ion source region after an accurately known and variable delay time. The ions then pass through a series of accel-

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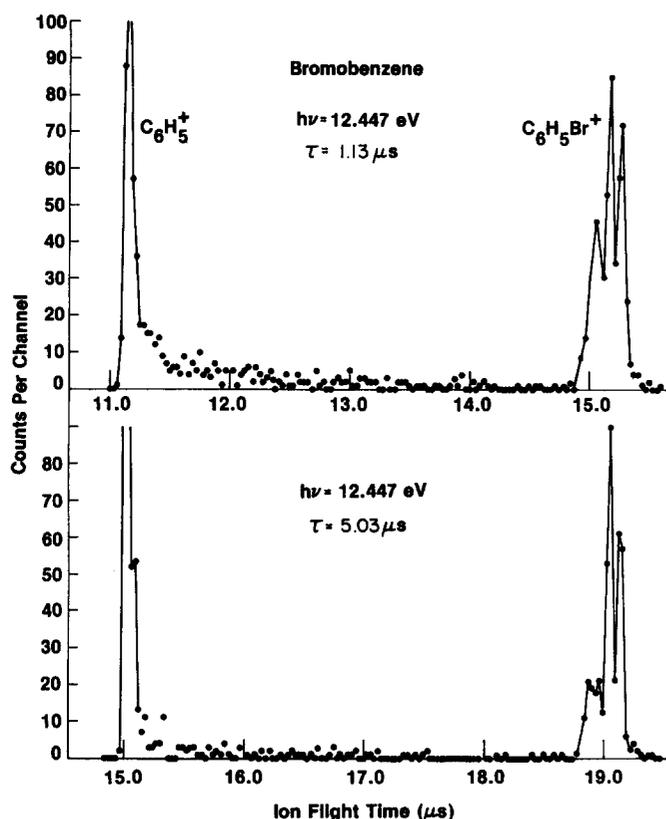


FIG. 1. Coincidence time of flight spectra for bromobenzene experimentally observed for 1.13 and 5.03  $\mu\text{s}$  effective ion residence times ( $\tau$ ), with a photon energy of 12.447 eV.

erating and focusing fields allowed to travel through a drift region and finally accelerated to high energy and detected on a multiplier. Mass analysis is carried out by standard time-to-pulse-height conversion and delayed coincidence techniques.

Two TOF coincidence spectra are shown in Fig. 1. Both were obtained at the same photon energy (12.447 eV) but with different drawout pulse delay times, i. e., residence time. As expected, the parent ion relative intensity is lower at the longer residence time. In addition to the parent and daughter peaks, there is a continuous distribution of ion counts between the two peaks. These arise from parent ions decomposing in the acceleration region. Those decomposing shortly after acceleration begins will have a total travel time close to that of the fragment ion; those decomposing near the end of the accelerating region will have a travel time close to that of the parent. On the basis of these considerations it is possible to define two distinct effective residence times in a given experiment.

The fragment peak is broadened due to three distinct factors:  $\text{C}^{13}$  isotope contributions, the overall effect of initial velocity and imperfect space focusing, and fragmentation of the ion immediately after application of the drawout pulse. The fragmentation effect produces a continuous distribution of flight times, depending on the time at which fragmentation occurs. As a result of the first two smearing factors, some of these delayed fragmentations are included in the nominal fragment peak

distribution. Calculations showed that processes occurring within about 0.43  $\mu\text{s}$  for bromobenzene ion and 0.30  $\mu\text{s}$  for chlorobenzene ion fell within the travel time distribution which was defined as the fragment. Hence, the effective decomposition times were 1.13  $\mu\text{s}$  (bromobenzene) 1.00  $\mu\text{s}$  (chlorobenzene). The previously published chlorobenzene results were recalculated using this 1.00  $\mu\text{s}$  decomposition time. Taking this definition of the decomposition time, the entire distribution of ion counts at intermediate travel times is included with the parent ion and represents ions which have not decomposed within 1.13 or 1.00  $\mu\text{s}$ , respectively.

Alternately, it is possible to include the ion counts at intermediate travel times with the fragment, thus defining parent ions as those which have not decomposed in the time interval defined by the pulse delay and the parent ion transit time through the accelerating-focusing region. This was done in the earlier work on chlorobenzene. However, a closer analysis of the actual potential distribution in the accelerating-focusing region showed that the potential well near the end of this region makes such a definition rather imprecise. Fragmentation processes occurring in the potential well produce total travel times equal to or even slightly in excess of that of the parent ion. Other fragmentation processes occurring at slightly higher potential (earlier times) produce total ion travel times a little below that of the parent. The third prominent peak in the parent ion region (see Fig. 1) is no doubt due to these processes. Hence, this definition is much less precise and is not used in the analysis.

## ANALYSIS OF THE DATA

The data were analyzed in precisely the same manner as was done previously for chlorobenzene<sup>8</sup> and allene.<sup>7</sup> Sets of activated complex frequencies and activation energies (i. e., reaction threshold energies) were chosen and for each set a breakdown curve was calculated, taking into account the apparatus function as well as the internal thermal energy and the rotational energy distribution. The sensitivity analysis consisted of calculating the location on the energy scale of the point at which 50% fragmentation takes place at long residence time (5.03  $\mu\text{s}$ ) and calculating the shift in the 50% fragmentation energy as the residence time is decreased to the lower value (1.13  $\mu\text{s}$ ). These define the so-called crossover energy and crossover shift. These calculations were carried out for several values of the activation energy and several sets of values for the activated complex frequencies (or equivalent activation entropies). With these results it was possible to define a curvilinear grid from which the value of the activation energy and entropy could be related to the two experimental parameters—i. e., crossover energy and crossover shift. The activated complex frequencies were taken the same as for the reactant ion (and neutral molecule<sup>12</sup>) except for the six halogen-dependent normal modes. One of these (670  $\text{cm}^{-1}$ ) was taken as the reaction coordinate,<sup>8,9</sup> and the other five were set equal and varied in a systematic manner in the calculations. The results are shown in Fig. 2.

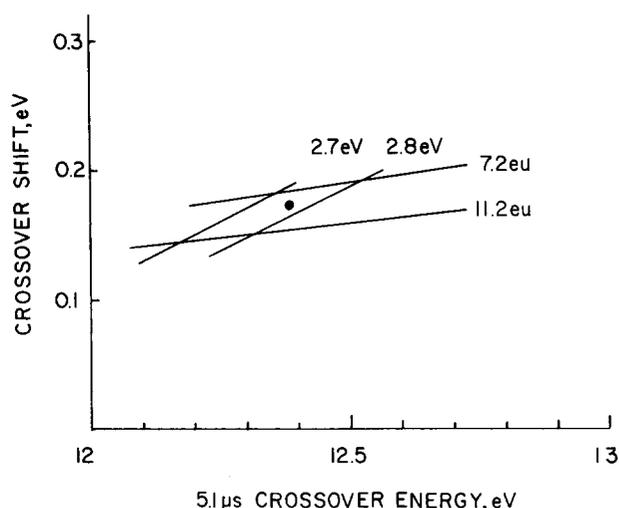


FIG. 2. Sensitivity of the calculated bromobenzene breakdown curves to activation energy  $E_{act}$  and activation entropy. The curves show the dependence of the crossover energy (i.e., energy for 50% fragmentation at long residence time) and crossover shift (i.e., difference in crossover energy between long and short ion residence times) on activated complex parameters. The steep curves show the dependence on activation entropy for two values of the activation energy and the near-horizontal curves the dependence on activation energy for two values of the activation entropy. (●) Crossover energy and shift obtained from Fig. 3.

## RESULTS AND DISCUSSION

The sensitivity analysis leads to a best fit of the crossover energy and shift with an activation energy of 2.76 eV and an equivalent 1000 K entropy of activation of 8.6 e.u., corresponding to a lowering of all five halogen dependent frequencies to  $\sim 130 \text{ cm}^{-1}$  (see Fig. 2). We estimate the error in the activation energy to be no more than  $\pm 0.02 \text{ eV}$  and in the equivalent entropy to about  $\pm 0.5 \text{ e.u.}$  at most. The activation energy (2.76 eV) when combined with the ionization potential of 8.97 eV corresponds to a 0 K fragmentation threshold of  $11.73 \pm 0.04 \text{ eV}$ .

The convoluted breakdown curves calculated with these parameters and the two effective residence times are compared with the experimental points in Fig. 3. The agreement is good near the crossover regions but the experimental points deviate markedly at both lower and higher energies. At first sight this would imply a weaker rate-energy dependence for the process, but this would be inconsistent with the crossover shift which is observed as the residence time is changed. Second, as pointed out in our earlier work,<sup>7,8</sup> the apparatus sampling function might be seriously distorted by autoionization. We have no way of testing this. Lastly, a new possibility arises here, namely, that the observed fragmentation process is actually a superposition of several processes. The ground state of the bromobenzene ion as well as that of the bromine atom is split by spin-orbit interaction; the magnitude of the splitting is 0.3–0.4 eV.<sup>13</sup> Thus, there arises the possibility of four distinct processes involving, on the one hand, the formation of  $^2P_{3/2}$  and  $^2P_{1/2}$  bromine atoms and, on the other, the  $^2E_{3/2}$  and  $^2E_{1/2}$  spin-orbit doublet states of the parent ion act-

ing as independent unimolecular reactants with distinct activation energies. Again, this must remain speculative in the absence of more detailed experimental and theoretical information.

With this caveat we proceed to the thermochemical and kinetic implications of the results. The room temperature heat of formation of bromobenzene is  $104.3 \pm 3.1 \text{ kJ/mol}$  ( $24.9 \pm 0.7 \text{ kcal/mol}$ ).<sup>14</sup> This can be corrected to absolute zero using the vibrational frequencies measured by Whiffen<sup>12</sup> and other thermochemical data.<sup>15</sup> Thus,  $\Delta H_{f_0}^\circ$  is  $119.0 \pm 3.1 \text{ kJ/mol}$  ( $28.4 \pm 0.7 \text{ kcal/mol}$ ). Combining this with  $\Delta H_{f_0}^\circ(\text{Br}) = 117.9 \text{ kJ/mol}$  ( $28.2 \text{ kcal/mol}$ ),<sup>15</sup> the activation energy for the process of  $266 \text{ kJ/mol}$  (2.76 eV) determined here, and the ionization potential of  $865.5 \text{ kJ/mol}$  (8.97 eV), we obtain  $\Delta H_{f_0}^\circ(\text{phenyl ion}) = 1133 \pm 5 \text{ kJ/mol}$  ( $271 \pm \text{kcal/mol}$ ).

Recalculation of the earlier results on chlorobenzene using the new effective fragmentation time of  $1.00 \mu\text{s}$  leads to an activation energy of  $308 \text{ kJ/mol}$  (3.19 eV) and to  $\Delta H_{f_0}^\circ(\text{phenyl ion}) = 1130 \pm 5 \text{ kJ/mol}$ , in excellent agreement with the present results.

With this confirmed value for  $\Delta H_{f_0}^\circ(\text{phenyl ion})$  it is of interest to compute the dissociation energy of the C–H bond in benzene. Sergeev, Akopyan, and Vilesov<sup>16</sup> have measured the phenyl radical ionization potential by photoionization techniques, obtaining  $\text{I.P.} = 8.1 \pm 0.1 \text{ eV}$ . This combined with our numbers gives  $\Delta H_{f_0}^\circ(\text{phenyl radical}) = 349 \pm 12 \text{ kJ/mol}$  ( $83 \pm 3 \text{ kcal/mol}$ ) and a benzene bond dissociation energy (at 0 K of  $467 \pm 12 \text{ kJ/mol}$  ( $112 \pm 3 \text{ kcal/mol}$ ). The corresponding results from thermal kinetics<sup>17</sup> are  $\Delta H_{f_0}^\circ(\text{phenyl radical}) = 338 \pm 8 \text{ kJ/mol}$  ( $80.9 \pm 2 \text{ kcal/mol}$ ) and a bond energy of  $471 \pm 8 \text{ kJ/mol}$  ( $113 \pm 2 \text{ kcal/mol}$ ), when corrected to absolute zero. Thus, the present coincidence results are slightly higher

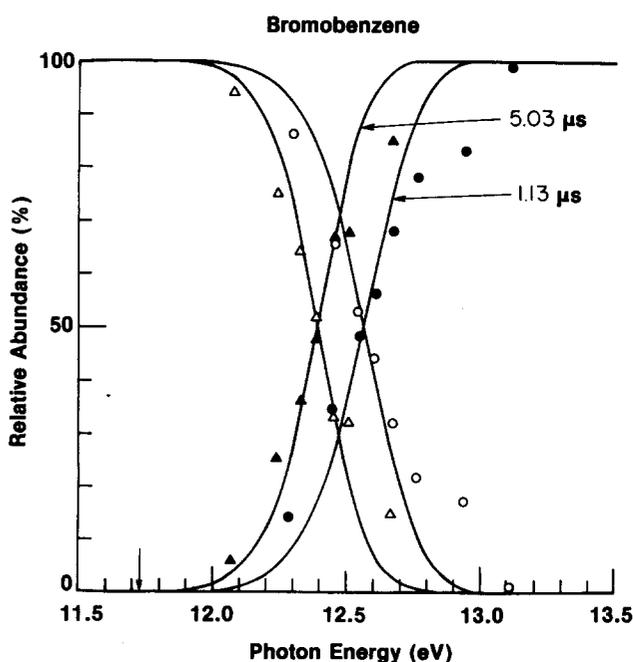


FIG. 3. Breakdown curves for bromobenzene for 1.13 and  $5.03 \mu\text{s}$  effective residence times. Experimental points: (○), (Δ)  $\text{C}_6\text{H}_5\text{Br}^+$  parent; (●), (▲)  $\text{C}_6\text{H}_5^+$  fragment; (—) best fit calculations. The arrow indicates the thermochemical threshold.

than the kinetic results. These are all summarized in Table I.

A comparison with neutral kinetics and with earlier work of Baer *et al.*<sup>9</sup> is also of interest. The activated complex parameters derived here can be converted to a hypothetical unimolecular thermal *A* factor at any temperature using transition state theory. We obtain at 1000 K the value of  $9.4 \times 10^{14} \text{ s}^{-1}$ . The corresponding thermal carbon-bromine bond scission reaction for neutral bromobenzene has an experimental Arrhenius *A* factor of about  $2 \times 10^{15} \text{ s}^{-1}$ .<sup>18</sup> This value of the *A* factor for the ion suggests that one is not dealing with an extremely loose activated complex, as is occasionally suggested for some ionic fragmentations. Also, the *A* factor for bromobenzene ion determined here is about a factor of 5 higher than the recalculated value for chlorobenzene ion.

Our results show significant disagreement with the results of Baer *et al.*, as was the case with chlorobenzene.<sup>8</sup> The rate-energy dependence defined by the kinetic parameters is shown in Fig. 4, both for our best fit parameters and for those used by Baer *et al.* It is seen that the present results lead to a more steeply rising rate-energy curve but at higher energy. This is qualitatively the same disagreement as was noted in chlorobenzene. Also, the parameters deduced by Baer *et al.* do not fit our crossover results, since they predict a crossover at a considerably lower energy. Lastly, the results of Baer lead to a "tight" complex for bromine loss, with an activation entropy of  $-1.2 \text{ e.u.}$  at 1000 K. This is most implausible. The present results along with our earlier results on chlorobenzene appear to give a much more sensible picture. It should be noted that although the two experiments are conceptually identical, the details of the apparatus and especially the method of data handling are considerably different. The experiments of Baer *et al.* focus on analysis of in-flight decomposition whereas ours focus on parent-daughter ratios prior to or after accelerations. As noted earlier, we have also observed in-flight decompositions in both ions. An analysis of these observations is in progress.

## CONCLUSIONS

The internal consistency of the present results with earlier work on chlorobenzene and with information from thermal kinetics provides support for the useful-

TABLE I. Energetic and kinetic parameters for halobenzene fragmentation.

Process	$E_{\text{act}}$ (eV)	$A_{1000}$	$\Delta H_0^\ddagger$ (kJ/mol)		Reference
			$\text{C}_6\text{H}_5^+$	$\text{C}_6\text{H}_5$	
$\text{C}_6\text{H}_5\text{Cl}^+ \rightarrow \text{C}_6\text{H}_5^+ + \text{Cl}$	$3.19 \pm 0.02$	$1.7 \times 10^{14}$	$1130 \pm 5$	$348 \pm 12$	This work
$\text{C}_6\text{H}_5\text{Br}^+ \rightarrow \text{C}_6\text{H}_5^+ + \text{Br}$	$2.76 \pm 0.02$	$9.4 \times 10^{14}$	$1133 \pm 5$	$351 \pm 12$	This work
$\text{C}_6\text{H}_5\text{Cl} \rightarrow \text{C}_6\text{H}_5 + \text{Cl}$	$4.06^a$	...	...	...	a
$\text{C}_6\text{H}_5\text{Br} \rightarrow \text{C}_6\text{H}_5 + \text{Br}$	$3.5^a$	$2.0 \times 10^{15}$	...	...	a, b
...	...	...	...	$338 \pm 8$	17

<sup>a</sup>Calculated from the tabulated  $\Delta H_0^\ddagger$  ( $\text{C}_6\text{H}_5$ ) and appropriate 0 K thermochemical quantities.

<sup>b</sup>Arrhenius factor from Ref. 18.

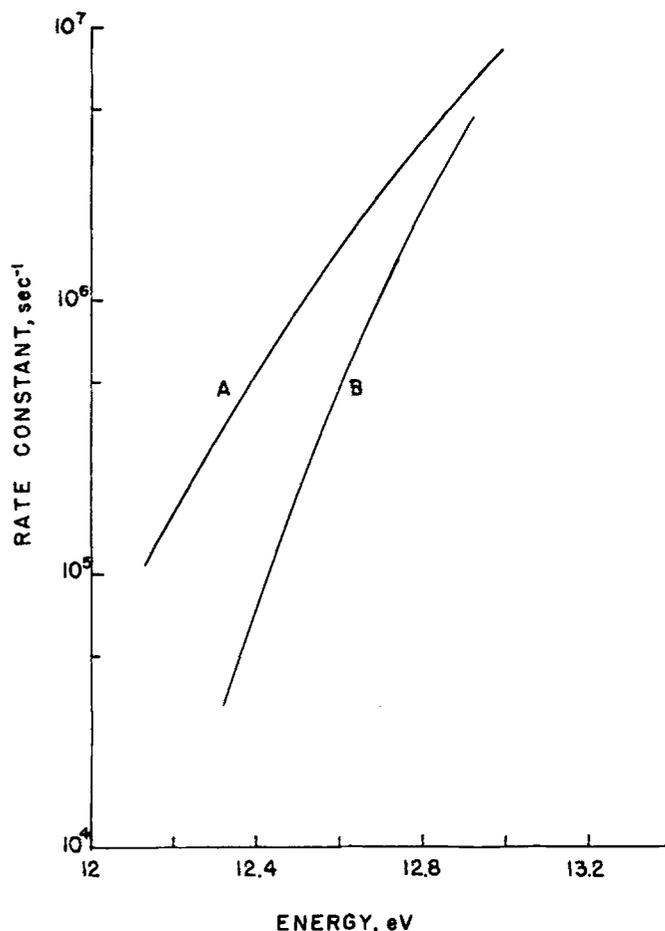


FIG. 4. Calculated rate energy curves for bromobenzene. (A) Present calculations with activated complex parameters used by Baer *et al.*<sup>9</sup> (B) Present calculations with activated complex parameters with reproduce the data in Fig. 2.

ness of the present technique and method of analysis of crossover energy and shift. However, the spread of the parent daughter transition region in the experimental results is troublesome and remains to be explained. It is possible to extract meaningful kinetic and thermochemical information even from processes in which there is a large kinetic shift. The problem of disparate results obtained from studies on in-flight dissociation requires further analysis. Lastly, the possibility of complications from spin-orbit splitting must be further examined, although it does not seem to strongly distort the present analysis.

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