J. Am. Chem. Soc. **1993,** *115,* 7402–7406

Time-Resolved Dissociation of Bromonaphthalene Ion Studied by TPIMS and TRPD. Heat of Formation of Naphthyl Ion

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Received January 8, 1993

Abstract: Dissociation of 1-bromonaphthalene and 2-bromonaphthalene molecular ions was studied by time-resolved photodissociation (TRPD) in the ion cyclotron resonance spectrometer at ultraviolet wavelengths and by time-resolved photoionization mass spectrometry (TPIMS) in the vacuum ultraviolet. TRPD of the 1-bromonaphthalene ion gave rate constants of 3.4×10^3 s^{-1} at 266 nm (4.93 eV ion internal energy) and 1.6×10^4 s^{-1} at 252 nm (5.19 eV internal energy). The TRPD results, and the time-resolved PIE curves for the parent, $C_{10}H_7Br^+$, and the daughter, $C_{10}H_7^+$, were modeled by RRKM calculations. The critical energies and 1000 K activation entropies obtained were $E_0 = 3.23 \pm 0.07$ eV and $\Delta S^{\ddagger}_{1000K} = 7.7 \pm 2.5$ eu for 1-bromonaphthalene and $E_0 = 3.08 \pm 0.07$ eV and $\Delta S^{\ddagger}_{1000K} = 5.2 \pm 1.2$ eu for 2-bromonaphthalene. The reactions demonstrate loose transition states characteristic of simple bond cleavages. Kinetic shifts are much higher than for the analogous $Br^{\bullet}$ loss reaction in the bromobenzene ion. The conventional kinetic shift is 1.6 eV and the intrinsic shift, due to infrared radiative decay, is 1.1 eV. The heat of formation of the α-naphthyl cation is deduced to be $\Delta H^{\circ}_{f,0}(C_{10}H_7^+) = 281 \pm 3$ kcal/mol. The correlation between bond energies for benzene and naphthalene derivatives is discussed.

Introduction

Ionized polycyclic aromatic hydrocarbons (PAHs) are thought to be important species in interstellar space, giving infrared emission bands and participating in large-molecule-building sequences. They may also be key participants in combustion and soot formation. Benzene ion, the lowest member of the family, has received much attention, but knowledge of the higher members, and especially the energetics and dynamics of their reactions is limited. The present work addresses the naphthalene ion system, with the application of powerful new techniques for examining fragmentation reactions of naphthalene ion derivatives.

Dissociative photoionization processes in naphthalene were studied recently.[1] Carbon–carbon and carbon–hydrogen bond cleavage reactions were observed. Through an RRKM fit to the experimental dissociation rates good understanding of the acetylene loss channel was gained. However, satisfactory knowledge is not yet available for the carbon–hydrogen bond cleavage reaction,

$$C_{10}H_8^{\bullet+} \rightarrow C_{10}H_7^+ + H^{\bullet} \qquad (1)$$

There is little reliable information about the thermochemistry, kinetics, or dynamics of reaction 1, and the present study was aimed at clarifying some of these aspects through study of the related bromonaphthalene ion dissociations.

Hydrogen losses from PAHs constitute the major fragmentation reactions for various activation techniques of the isolated ions.[3] It is thus important to have accurate C–H bond dissociation energies; in particular the heat of formation of the naphthyl ion $C_{10}H_7^+$ is of considerable interest. Appearance energies have been determined[1,2] for $C_{10}H_7^+$ from naphthalene and naphthalene-d_8. However, these are probably affected by large kinetic shifts, and are uncertain at best. A similar problem arose some years ago in connection with the C–H bond cleavage reaction in benzene, which also is affected by large kinetic shifts and parallel dissociation channels, and did not yield thermochemically useful direct appearance thresholds. This was circumvented by Baer,[4] Rosenstock,[5] Dunbar,[6] and their co-workers through studying the bromobenzene ion dissociation reaction. While benzene, naphthalene, and other PAH radical cations undergo several parallel primary reactions,[1–3] bromobenzene ion undergoes one simple bond cleavage reaction forming the phenyl cation and a bromine atom, reaction (2):

$$C_6H_5Br^{\bullet+} \rightarrow C_6H_5^+ + Br^{\bullet} \qquad (2)$$

This reaction, as well as the analogous ones in chlorobenzene and iodobenzene, lends itself to reliable RRKM modeling, and it led to a fairly well established value for the heat of formation of the phenyl cation, and thus to the $C_6H_5^+$–$H^{\bullet}$ bond energy in the benzene radical cation.[7–12] The bromonaphthalene radical cation similarly undergoes a simple bond cleavage reaction

$$C_{10}H_7Br^{\bullet+} \rightarrow C_{10}H_7^+ + Br^{\bullet} \qquad (3)$$

The primary goal of this work was thus the study of reaction 3 in order to obtain information concerning the energetics of reaction 1.

In addition to obtaining information about the energetics, the original studies of the analogous bromobenzene ion reaction were

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fruitful in considering three additional questions, which are also interesting in the bromonaphthalene case: (i) whether reaction 3 is in fact a simple bond cleavage as it appears formally to be; (ii) what evidence there might be for transition state switching (TSS),[12] which may be important for this type of fragmentation reaction; and (iii) the magnitude of the kinetic shift of the reaction threshold[13] and its relation to the time scale of the measurements and other experimental conditions.

For the bromobenzene ion reaction 2, extensive study has clarified these questions. The reaction proceeds along a single-well potential energy surface without any significant reverse activation barrier. The activation entropy, $\Delta S^{*}_{1000\mathrm{K}} = 8.07$ eu, determined by Rosenstock et al.[7] and Malinovich et al.,[10] indicates a totally loose, orbiting transition state (OTS). This means that the activation energy $E_0 = 2.76$ eV[7,10] or 2.83 eV as determined by Pratt and Chupka[9,12] must be close to the C–Br bond energy in the bromobenzene radical cation, $D_0(C_6H_5^+\text{–Br.})$. This allows the assignment of the formation enthalpy of the phenyl cation as $\Delta H^\circ_{f,0}(C_6H_5^+) = 270$ kcal/mol[5] or perhaps slightly higher, $\Delta H^\circ_{f,0}(C_6H_5^+) = 274$ kcal/mol.[9,12] It was demonstrated[10,12] that at least up to 1 eV above threshold the OTS adequately describes the reaction dynamics and there is no need to involve TSS to a tight transition state (TTS).

Two methods have been developed in recent years to study slow ion decompositions at near-threshold energies: (1) time resolved ion photodissociation (TRPD)[6,14,15] and (2) time-resolved photoionization mass spectrometry (TPIMS).[10,11] Both methods rely on ion trapping to observe dissociation kinetics on previously inaccessible time scales. They are complementary in a useful way: TRPD gives absolute dissociation rates for ions with well-defined internal energies, but it is often restricted to a limited range of internal energies by limitations of available photon wavelengths and photoabsorption cross sections. TPIMS, on the other hand, is generally convenient over a wide range of ion internal energies, but it yields spectra convoluted over a broad range of ion internal energies which must be deconvoluted by modeling. It has proven useful to use TRPD results to give reliable absolute dissociation rate values, combined with TPIMS results to define the shape of the dissociation rate–energy curve over an extended energy range. A successful combination of these techniques was described in the study of thiophenol ion.[16a]

These methods gave results on the fragmentation energetics and kinetics of bromobenzene and iodobenzene ions which were in excellent agreement.[6,10,11,14] The bromobenzene cation fragmentation reaction demonstrates a substantial kinetic shift which naturally decreases with increasing reaction time. Up to 2 ms reaction time the decay by infrared emission has no effect on the photoionization efficiency (PIE) curve for $C_6H_5^+$ production even though the radiative decay rate at the dissociation threshold is more than two orders of magnitude faster than the dissociation rate.[10] In the present study we have applied TRPD as well as TPIMS to the dissociation reaction 3 in 1- and 2-bromonaphthalene ions, respectively, expecting that this reaction would behave similarly to the bromobenzene cation reaction 2 in having a totally loose transition state. Straightforward kinetic modeling will then allow us to obtain information on the formation enthalpy of the naphthyl cation, $\Delta H^\circ_{f,0}(C_{10}H_7^+)$.

Experimental Section

The techniques of ion cyclotron resonance TRPD and TPIMS have been described in previous combined work.[16] The ICR-TRPD experiments were carried out as has been described in detail in previous publications[15,17] using the phase-sensitive-detection ICR spectrometer. In the present experiments parent ions, formed by electron impact, were allowed to undergo 20 to 30 thermalizing collisions with parent neutral during a 3 or 4 s cooling time. Measurement of the fragmentation rate as a function of cooling time indicated that these conditions were more than sufficient to thermalize the parent ions to 375 K. The thermalized parent ion population was then photoexcited by a 10 ns monochromatic laser pulse. The ensuing photodissociation reaction was followed by monitoring the appearance of daughter ion as a function of time using the detection capabilities of the ICR spectrometer. The abundance of daughter ions was plotted as a function of delay after the laser pulse. Since absorption of a photon gives a parent ion of precisely known internal energy (within the spread of initial thermal energies), each TRPD curve gives a single, well-defined point on the rate–energy curve.

Table I. Ionization and Appearance Energies (eV) for 1-Bromo- and 2-Bromonaphthalene

	ionization energy		$C_{10}H_7^+$ appearance energy	
species	present data	lit[a]	24 μs	2 ms
1-bromonaphthalene	8.08 ± 0.03	8.09	13.1 ± 0.1	12.1 ± 0.1
2-bromonaphthalene	8.18 ± 0.03		13.1 ± 0.1	12.1 ± 0.1

[a] Reference 20.

With the electron beam turned off, a small $C_{10}H_7^+$ signal was present at 252 nm, presumably from dissociative multiphoton ionization of the parent neutral. Since this ion showed no time dependence and constituted only 10% of the total daughter ion signal, its contribution was easily subtracted in the data analysis.

The fundamental of a Lumonics Nd/YAG Model HY 1200 pulsed laser was quadrupled to provide light at 266 nm (about 50 mJ in a 1 cm^2 spot). The 252-nm light (about 3 mJ in a 5 mm^2 spot) was obtained by doubling the output from a Lumonics Model 300 dye laser (Coumarin 500 dye) pumped by the third harmonic of the Nd/YAG laser.

The TPIMS technique has been described in detail recently.[18] Briefly, photoionization is induced by a pulsed VUV light source. In the present case we employed the Hopfield continuum in helium for short-time measurements and the Hinteregger discharge, producing the many line spectrum in hydrogen, for long-time measurements. Photoions formed in the central region of the cylindrical ion trap (CIT) are trapped by an RF electrical field and are ejected after a given delay time into a quadrupole mass filter by a short drawout pulse. In this study, ions were trapped from ~20 μs to 2 ms. The radio frequency of the potential applied to the cylindrical barrel electrode in the CIT is 0.5 MHz ($\omega/2\pi$). The radio frequency field is superimposed throughout the full cycle. A detection pulse gates the ion counter. TPIMS provides time-resolved PIE curves. Appearance energies at different storage times are derived by the vanishing current approach used in previous studies.

The effective wavelength resolution employed in the TPIMS experiment is 5.0 Å. This corresponds to an energy resolution of about 0.025 eV near the ionization thresholds of the bromonaphthalenes and ~0.05 eV near their fragmentation onsets.

Since the early combined study of TRPD and TPIMS[16] both techniques have been improved. The mass resolution and sensitivity of our TPIMS ion source were improved and storage times of up to ~0.5 s are now possible. One recent detailed experiment on methylnaphthalenes[19] performed with this new source demonstrated the possibilities of the TPIMS technique in determining critical energies of activation, E_0, to within ±0.5 kcal/mol, activation entropies, $\Delta S^{*}_{1000\mathrm{K}}$, to within ±1.5 eu, and microcanonical rate constants, $k(E)$, to within 40–50%.

1-Bromonaphthalene and 2-bromonaphthalene were obtained from Aldrich with a stated minimum purity of 98%.

Results and Discussion

Time-Resolved Photoionization Mass Spectrometry. The ionization energies obtained in the present study for 1- and 2-bromonaphthalene are given in Table I. The value for 1-bromonaphthalene is in excellent agreement with the only previous result available from photoelectron spectroscopy.[20]

The PIE curves obtained for the parent $C_{10}H_7Br^{\bullet+}$ and daughter $C_{10}H_7^+$ ions from 1-bromonaphthalene at $t = 24$ μs and 2 ms are represented in Figures 1 and 2, respectively. Several clear changes

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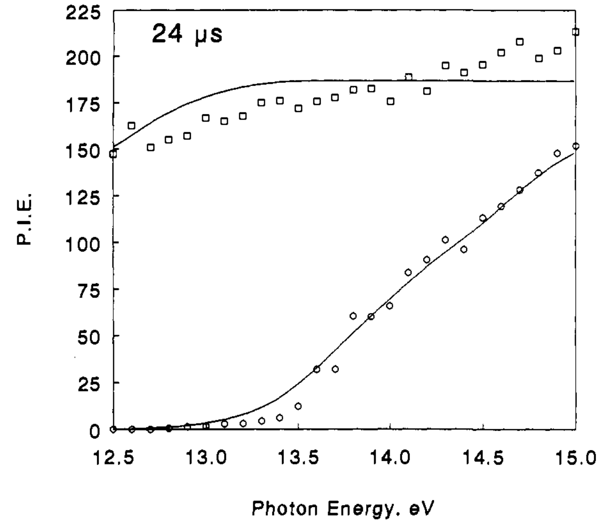

Figure 1. Parent ion, $C_{10}H_7Br^+$ (□), and daughter ion, $C_{10}H_7^+$ (○), PIE curves for 1-bromonaphthalene, the PIE (arbitrary units) is plotted versus the photon energy (in eV) at 24 μs: o, □ experimental results; lines, calculated (see text).

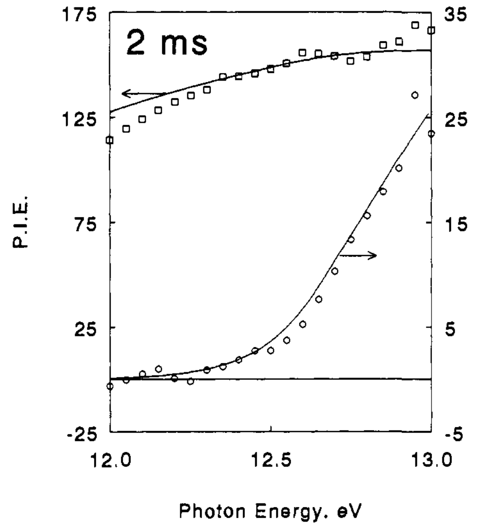

Figure 2. Experimental and calculated PIE curves at $t = 2$ ms; see caption to Figure 1; note the different PIE scales for the parent (□) and daughter ions (○).

are observed as a result of the extension of ion storage time: (i) the sharply rising onset for the daughter ion shifts to lower photon energies and time resolved appearance energies are included in Table I; (ii) the abundance of the daughter ion relative to the parent increases; and (iii) the leveling off of the parent ion, which occurs at the daughter ion appearance energy, shifts to lower energies.

Time-Resolved Photodissociation. Time-resolved appearance curves for the production of $C_{10}H_7^+$ from thermalized 1-bromonaphthalene cation were measured at 266 and 252 nm. With an average vibrational energy of 0.27 eV, for a parent ion population at 375 K, the two wavelengths correspond to average energies of 4.93 and 5.19 eV, respectively. Experimental appearance curves for both wavelengths are reproduced in Figure 3 with the same time axis. The expected increase in rate with photon energy is clearly shown.

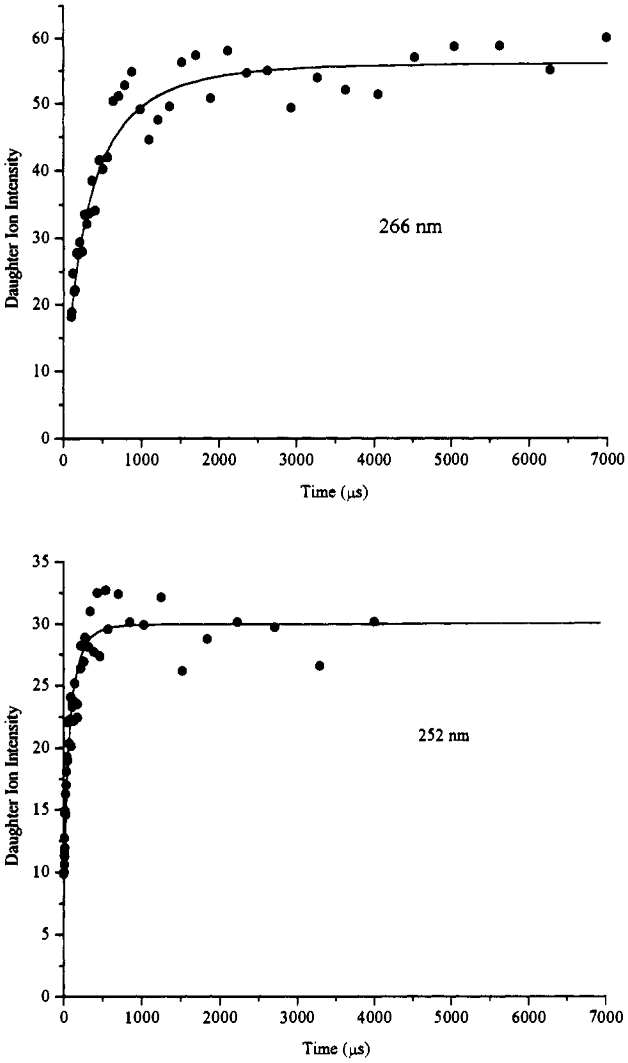

Figure 3. TRPD curve for $C_{10}H_7^+$ photoproduction at 266 and 252 nm.

As has been discussed,[16b,17] the TRPD curve for a thermal ion population deviates in general from exponential decay. Because of the thermal spread of internal energies of the dissociating parent ion population, the appearance curves of Figure 3 cannot conveniently be reduced to a plot of dissociation rate as a function of ion energy. The most straightforward approach to displaying the results is to find a rate–energy curve which, when convoluted with the Boltzmann distribution, gives predicted daughter ion appearance curves agreeing with each of the experimental curves. Following this approach the rate–energy curve shown in Figure 4 (open circles) was assigned, and the solid lines in Figure 3 were obtained by convoluting it with the thermal distribution. The rates given in Table II were taken from this rate–energy curve at energies corresponding to the photon energy plus the average thermal energy.

RRKM/QET Calculations. RRKM calculations of the dissociation rate–energy curves were carried out using neutral 1-bromonaphthalene frequencies[21] for the activated molecules of both 1- and 2-bromonaphthalene cations. For the transition state, one mode of 584 cm^{-1} was deleted from this frequency set to represent the C–Br stretch reaction coordinate and the frequencies of several other modes were varied to increase the looseness of the transition state. It is widely accepted that the details of the frequency changes used in the transition state are not very important;[22] what is important, is the resulting tightness or looseness of the transition state, which is usefully characterized by the single parameter $\Delta S^{\ddagger}_{1000\mathrm{K}}$. The critical energy, E_o, and 1000 K activation entropy, $\Delta S^{\ddagger}_{1000\mathrm{K}}$, were treated as parameters to obtain a best fit to the TRPD and TPIMS results. The resultant $k(E)$ dependences are represented in Figure 4.

Time-resolved PIE curves were modeled by RRKM/QET calculations as described previously.[10,18,19,23] Time-resolved parent

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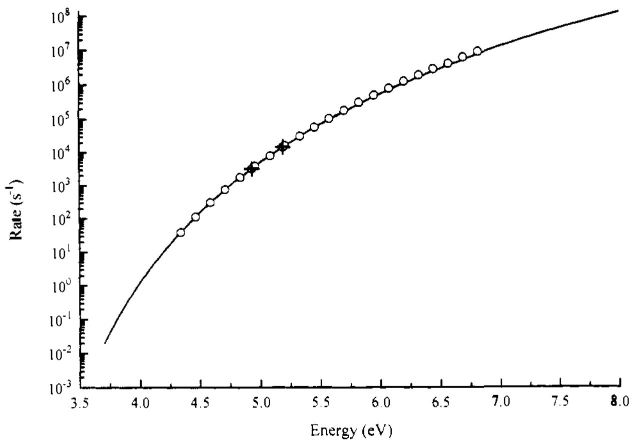

Figure 4. Rate–energy curves calculated by RRKM modeling for the 1-bromonaphthalene ion dissociation: (○) $E_0 = 3.2$ eV, $\Delta S^{\ddagger}_{1000K} = 8.6$ eu; (—) $E_0 = 3.23$ eV, $\Delta S^{\ddagger}_{1000K} = 7.7$ eu; (+) experimental points from the TRPD experiments.

Table II. Experimental Rate–Energy Data Points for 1-Bromonaphthalene

wavelength (nm)	total internal energy[a] (eV)	fragmentation rate (s^{-1})
266	4.93	3390
252	5.19	1.62×10^4

[a] Includes the energy of the photon and 0.27 eV of thermal energy.

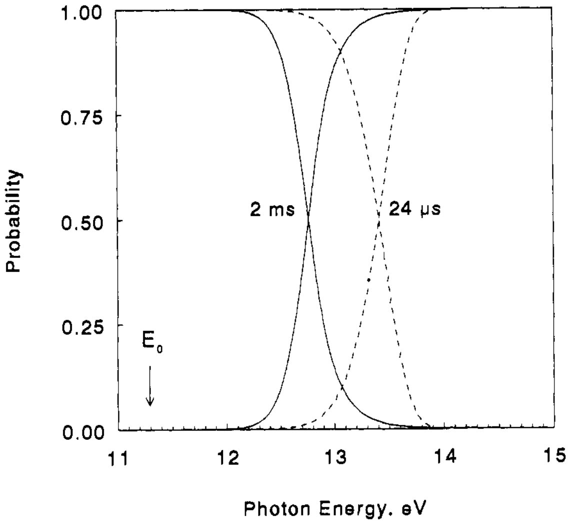

Figure 5. Calculated time-resolved 0 K breakdown curves for parent and daughter ions ($C_{10}H_7Br^+$ and $C_{10}H_7^+$, respectively) of 1-bromonaphthalene at the two indicated reaction times. The crossover shift, which is the shift in crossover energies (equal parent and daughter ion probabilities) between 24 μs and 2 ms, is calculated to be 0.71 eV.

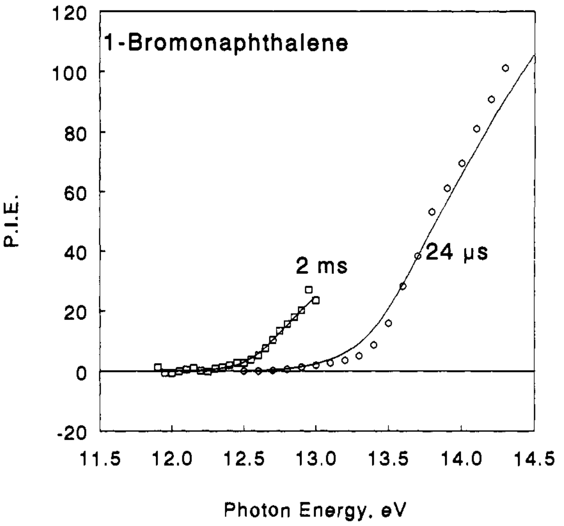

Figure 6. Time-resolved experimental [(○) 24 μs; (□) 2 ms] and calculated (—) daughter ion ($C_{10}H_7^+$) PIE curves. The relative intensities of the experimental PIE curves of the parent served to scale the experimental daughter ion PIEs.

Table III. RRKM Activation and Rate Parameters for 1- and 2-Bromonaphthalene Cation Br-Loss Reactions

	1-bromonaphthalene			2-bromonaphthalene		
experiment	E_0 (eV)	$\Delta S^{\ddagger}$ (eu)	k_{rad} (s^{-1})	E_0 (eV)	$\Delta S^{\ddagger}$ (eu)	k_{rad} (s^{-1})
TRPD	3.2	8.6				
TPIMS[a]	3.25	8.95	500	3.11	5.77	100
TPIMS[b]	3.17	6.23	500	3.0	3.95	100
TPIMS[c]	3.17–3.32	6.2–10.0	500	3.11	5.77	100
TPIMS (av ± 2σ)	3.23 ± 0.07	7.7 ± 2.5		3.08 ± 0.07	5.2 ± 1.2	

[a] Short time experiment (Figure 1 for 1-bromonaphthalene). [b] Long time experiment (Figure 2 for 1-bromonaphthalene). [c] Time-resolved daughter ion PIE's (Figure 6 for 1-bromonaphthalene).

and daughter ion breakdown curves were calculated from the $k(E)$ dependence at 0 K. These give the internal energy dependence of the fractional abundance of the ions. They can be converted into time-resolved breakdown graphs as a function of photon energy by adding the ionization energy of the neutral molecule to the internal energy. The results at 24 μs and 2 ms for 1-bromonaphthalene are summarized in Figure 5. In these calculated curves we have employed the dissociative rate constants of Figure 4 as well as an energy-independent rate constant for radiative decay in the infrared region. A similar approach was employed previously.[10,19,24] The radiative relaxation rates of naphthalene and methylnaphthalene ions are of the order of 10^2 s^{-1}.[25] We found best agreement with the TPIMS data with a value of ~500 s^{-1} for the relaxation rate constant of 1-bromonaphthalene and 100 s^{-1} for 2-bromonaphthalene. In addition to radiative relaxation, these values may reflect contributions from collisional relaxation under the higher pressures which prevail in the TPIMS ion source compared with the ICR.[19,25]

The 0 K breakdown graphs were convoluted with the instrumental slit function, with the calculated thermal energy distribution, and with the energy deposition function. The resultant curves represent the calculated first derivatives of the PIE curves of the ions, provided that the threshold law for photoionization is a step function.[26] These curves were integrated to compare them with the experimental time-resolved PIE curves and they are included in Figures 1 and 2, for both reactant parent and product daughter ions. A comparison between experimental and calculated daughter ion PIE curves at two storage times is given in Figure 6.

The photoelectron spectrum (PES) of 1-bromonaphthalene taken from ref 20 was adopted as the energy deposition function for both bromonaphthalenes, since the PES for 2-bromonaphthalene is not available. The photoelectron spectra of 1- and 2-chloronaphthalene, and 1- and 2-fluoronaphthalene, respectively, are rather similar,[20] justifying the assumption of similarity also in the case of the bromine isomers.

The activation parameters which best fit the TRPD and TPIMS results are given in Table III. The critical energies of activation

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Table IV. Comparison of Bond Energies for Benzene and Naphthalene Ion Derivatives

compd	bond	bond energy (eV)	ref	ratio[a]	ionization energy (eV)
benzene	$C_6H_5^+ - H^{\bullet}$	3.65	28	0.83	9.25
naphthalene	$C_{10}H_7^+ - H^{\bullet}$	4.4	29 and present results		8.14
bromobenzene	$C_6H_5^+ - Br^{\bullet}$	2.76	7, 10	0.85	8.98
bromonaphthalene	$C_{10}H_7^+ - Br^{\bullet}$	3.23	present data		8.08, 8.18
toluene	$C_7H_7^+ - H^{\bullet}$	2.11	30	0.87	8.81
methylnaphthalene	$C_{11}H_9^+ - H^{\bullet}$	2.41	19, 25b		7.85

[a] Bond energy ratio for benzene derivative divided by naphthalene derivative. Average ratio = 0.85 ± 0.02.

(E_0) from the TRPD and TPIMS experiments are in excellent agreement. The activation entropies are very similar, although as before,[19] the error limits on $\Delta S^{\ddagger}_{1000\text{K}}$ are quite large. Even so, it is quite clear that the transition state is a loose ("orbiting") transition state with a highly positive ΔS, as in the case of bromobenzene ion.[11,12] The resultant $k(E)$ rate/energy dependences based on the TRPD experiments and on the average TPIMS results are included in Figure 4. The two curves diverge only very slightly at higher energies.

Thermochemical Information. The loose transition states for the bromonaphthalene dissociation reactions 3 are indicative of a negligible reverse activation energy. As a result, the critical energies of activation (E_0) may be equated with the corresponding ion C–Br bond dissociation energies. This information, combined with additional thermochemical data,[27] allows one to estimate the heat of formation of the naphthyl cation. The heat of formation of 1-bromonaphthalene has been estimated[27] from group contributions to be $\Delta H^{\circ}_{f,298}(C_{10}H_7Br) = 42$ kcal/mol. The heat of formation at 0 K was calculated from the room temperature value and from the frequencies,[21] using standard statistical mechanics methods: $\Delta H^{\circ}_{f,0}(C_{10}H_7Br) = 48.4$ kcal/mol. Employing the ionization energy of 1-bromonaphthalene (Table I) gives $\Delta H^{\circ}_{f,0}(C_{10}H_7Br^+) = 235$ kcal/mol. Since $\Delta H^{\circ}_{f,0}(Br^{\bullet}) = 28.2$ kcal/mol,[27] we can calculate the heat of formation of the α-naphthyl cation, $\Delta H^{\circ}_{f,0}(C_{10}H_7^+) = 281$ kcal/mol. Assuming validity of the basic kinetic modeling approach used here to obtain E_0 from the TRPD and TPIMS data, the greatest uncertainty in the $\Delta H^{\circ}_{f,0}(C_{10}H_7^+)$ value comes from the uncertainty in the heat of formation of the neutral precursor. We estimate the error limits to be ±3 kcal/mol.

We can look at the effect of expansion from the benzene to the naphthalene ring system on C–H and C–Br bond energies, as shown in Table IV. Within the uncertainties in the values, an approximately constant bond energy ratio is observed for the respective pairs—the naphthalene derivatives form more stable bonds. As shown in the last column of Table IV, a similar framework expansion effect is seen for the ionization energies. Expansion of the ring system lowers the ionization energy by about 1 eV in all three cases. In all of these compounds the highest occupied orbital (HOMO) is a π-orbital, and this orbital is higher in energy in the naphthalene system by about 1 eV.

While halosubstitution in benzene leads to a decrease in the π-ionization energy, i.e. to a destabilizing perturbation of the HOMO, an opposite effect is observed in the case of naphthalene Br substitution.[21] In other words, substitution leads to slightly stabilizing interactions of the edge atom and the π-orbitals of the naphthalene condensed-double-ring system in contrast to the destabilizing repulsive interactions in the case of the benzene ring system. The stabilization may arise from the higher polarizability of the system, reflecting the larger size of naphthalene. This stabilization causes increased bond energies in the naphthalene derivatives.

Appearance Energies and Kinetic Shifts. The calculated minimum energy required for the reaction

$$C_{10}H_7Br \rightarrow C_{10}H_7^+ + Br^{\bullet} + e^- \qquad (4)$$

is equal to the ionization energy, which for 1-bromonaphthalene is 8.08 ± 0.03 eV (Table I), plus the critical energy for dissociation of the ion, 3.23 ± 0.07 eV (Table III), i.e. 11.3 ± 0.1 eV. The appearance energies (Table I) are considerably higher than this calculated value, reflecting large kinetic shifts in this system. The "conventional" kinetic shift (CKS) has been defined[25b,c,26a] as the excess energy required to observe detectable (1%) dissociation within 10 μs, appropriate to conventional mass spectrometer appearance energy measurements. Recently the "intrinsic" shift (IKS) has been defined[25b,c] as the energy needed for 10% fragmentation in competition with radiative relaxation of the excited ion. From the rate energy dependence (Figure 4), CKS = 1.6 eV and IKS $\simeq$ 1.1 eV for 1-bromonaphthalene. In other words, the predicted appearance energy (at 0 K) for ~10 μs is 12.9 eV, while the value predicted for an ion-trap appearance-energy experiment, unlimited by ion containment time, is 12.4 eV (again at 0 K). The lowest value we have observed experimentally is 12.1 ± 0.1 eV (Table I). It is not surprising that this value is lower than the predicted limit, since it was obtained at 298 K and contains a compensating effect due to the thermal internal energy of the dissociating parent ion. By comparison, the values for bromobenzene are CKS = 0.3 eV and IKS ≤ 0.07 eV[10,12,16] and those for methylnaphthalene are CKS = 2.15 eV and IKS = 1.05 eV.[25b]

Comparing the bromobenzene and bromonaphthalene systems illustrates the strong effect of ion size on kinetic shift effects. Going from a hydrocarbon molecule of about 12 atoms to a molecule of about 20 atoms, the magnitude of the kinetic shift increases from being rather minor to being very important. Because of the large kinetic shifts, and also the effects of thermal internal energy, the observed appearance energies of fragment ions from large ions have little direct quantitative value. Kinetic modeling like that carried out in the present study is essential for deriving useful thermochemical values from fragmentation data.

We began this project because of the interest in the unsubstituted naphthalene system. The minimum energy required for the reaction

$$C_{10}H_8 \rightarrow C_{10}H_7^+ + H^{\bullet} + e^- \qquad (5)$$

in naphthalene is calculated from the thermochemistry reported here to be approximately 12.5 eV. The experimental appearance energies of about 15.4 eV[1,2] demonstrate large conventional kinetic shifts. We are in the process of determining direct time-resolved appearance energies and intrinsic shifts in the naphthalene system.

Acknowledgment. This research was supported by the Basic Research Foundation administered by the Israel Academy of Science and Humanities, by the US National Science Foundation, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Y.G. thanks the Israeli Ministry of Absorption and Ministry of Science and Development for their support.

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