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C−H Bond Strength of Naphthalene Ion. A Reevaluation Using New Time-Resolved Photodissociation Results

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Abstract: The dissociation rates and branching ratios for naphthalene ion (naphthalene-d_8 ion) have been measured by time-resolved photodissociation at an internal energy of 7.10 (7.13) eV. Dissociation rate constants of 6450 (2360) s^{-1} were observed, with acetylene loss being somewhat favored over hydrogen atom and hydrogen molecule losses. Using simple RRKM theory, these results were modeled along with prior information from time-resolved dissociative photoionization and from photoelectron photoion coincidence to give rate−energy curves. Extrapolated to threshold, bond energies of 4.48 eV for H atom loss and 4.41 eV for acetylene loss were derived, in agreement with predictions from independent thermochemical data. The C−H bond energy (4.48 eV) is discussed relative to those for neutral aromatic hydrocarbons (4.8 eV) and benzene ion (3.7 eV).

Introduction

The C−H bond dissociation thresholds of benzene and naphthalene ions have fundamental interest as giving the most direct measures of the corresponding C−H bond strengths in the cations. These bond strengths are of interest in comparison with each other, and also in comparison with the neutral aromatic C−H bonds (whose bond strengths are about 4.8 eV[1]). However, the hydrogen-loss reactions observed from these cation dissociations are particularly poorly behaved from the point of view of obtaining accurate thermochemical thresholds. The rate−energy curves are quite flat, which gives large kinetic shifts and makes it hard to estimate true threshold energies. It is worth reemphasizing that for ions as large as naphthalene the appearance energy of a dissociation fragment ion is largely worthless as an estimate of the thermochemical threshold, since kinetic shifts of the order of 1 eV or more are normal and expected.[2−5]

It has been possible to surmount these problems in the benzene ion case by combining accurate dissociation rate measurements at low and well-known internal energies with careful extrapolation to zero rate by RRKM modeling. This was done with success by Neusser et al.[6] using REMPI (resonance multiphoton ionization) data and simple RRKM extrapolation, giving an E_0 assignment of 3.65 eV (later reassigned as 3.72 eV by Klots[7] using the thermodynamic modeling approach). Recently[8] the rate−energy measurements were extended to lower energy by TRPD measurements, and a more refined variational RRKM analysis was applied, giving a revised E_0 value of 3.88 eV. It was suggested in the latter analysis that direct benzene ion dissociation leaves the phenyl cation with about 0.2 eV of electronic excitation, indicating a ground-state dissociation energy of about 3.7 eV. These direct-dissociation experiments are in reasonable agreement with the thermochemical bond strength (3.81 eV) obtained from heats of formation.[9,10] The tabulated heat of formation of phenyl cation[9] is primarily based on dissociation of halobenzene cations, so that this agreement gives an independent confirmation that the E_0 value for benzene ion hydrogen loss is a true estimate of the thermochemical dissociation limit.

Understanding of naphthalene ion dissociation kinetics has approached a point where a similar resolution of the thermochemical uncertainties should be possible, but a final, definitive conclusion has been elusive. Two recent, careful studies of naphthalene ion fragmentation kinetics using PEPICO (photoelectron−photoion coincidence)[11] and TPIMS (time-resolved photoionization mass spectrometry)[12] gave extrapolated assignments of the activation energy E_0 for the loss of acetylene neutral from parent ion. These values diverge by 1.1 eV, showing that major uncertainty still surrounds the dissociation thermochemistry of naphthalene ion. This divergence persists because the data are somewhat scattered in both of these experiments, and because of limitations in each of the experiments. The PEPICO rate−energy measurements of Rühl et al.[11] span only a limited energy range located at quite high internal energy, so that there is major uncertainty in the slope of the rate−energy curve and in the appropriate extrapolation to the threshold. The time-resolved (but not fully energy resolved) photoionization measurements of Gotkis et al.[12] sample dissociating ions over a usefully wide energy range, but uncertainty arises in the data deconvolution because of the need for rather strong assumptions about the energy deposition function and the photoionization threshold law.

The time-resolved photodissociation (TRPD) method is particularly well suited to energy-resolved measurements of slow dissociation processes.[2−5,8,13,14] Using it, we have been able to

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acquire time- and energy-resolved data for naphthalene ion much lower on the rate–energy curve than the Leach group's PEPICO measurements.[11] The resulting refinement of the slope of the rate–energy curves clarifies the origin of the discrepancies among previous measurements and enables us to suggest refined values of E_0 and to assign bond strengths for the naphthalene ion with greater confidence than before. A variational RRKM analysis at the same high level of sophistication as for benzene ion[8] is not yet available, but the present lower-level RRKM extrapolations use an approach which experience suggests to be reliable within one- or two-tenths of an electronvolt for assignment of the critical energy for direct dissociation of an atom from a polyatomic ion.

Experimental Section

The TRPD experiment has been described in previous publications. The present work used TRPD techniques and apparatus similar to those used, for example in the study of tri-*tert*-butylbenzene ion.[14] In the TRPD approach, ions are prepared (by multiphoton ionization in this case) and trapped in the ion cyclotron resonance (ICR) ion trap. After thorough thermalization by collisional and radiative relaxation of excess internal energy, the ions are photoexcited by a laser pulse, which deposits a precisely known increment of internal energy. The subsequent dissociation of the ions is followed using the detection capabilities of the Fourier-transform ICR spectrometer.

Since dissociation of naphthalene ion at a usefully large rate requires about 7 eV or more of internal energy, this must be a two- or more-photon process for ordinary laser light sources. Two photons at 355 nm turned out to give a convenient dissociation rate, and also to fall at a wavelength of substantial absorption intensity for the parent ion.[15] The light was provided by the tripled output of the Lumonics HY 1200 Nd:YAG laser (15 mJ/pulse).

Neutral naphthalene was ionized by multiphoton ionization at 193 nm using a Lumonics excimer laser operating with ArF. Neutral pressure was $1 \times 10^{-8} - 6 \times 10^{-8}$ Torr. The ions were thoroughly thermalized at 300 K by collisional and radiative cooling during a 4–6 s thermalization delay before the YAG laser pulse. In ion cooling experiments to be described later,[16] it was shown that these thermalization conditions were ample for complete thermalization, and this was reconfirmed by showing that longer thermalization times gave no change in the observed TRPD rate constant. Daughter ions formed by MPI were ejected before the YAG laser pulse was applied.

Care was taken to minimize peak-ratio artifacts in the branching ratio determination. Mass discrimination (attributed to space charge effects[17]) can be severe for peaks lying close together in mass. It is expected that this problem will be least severe using impulse excitation at the highest possible amplitude not giving ion ejection, as was done here. The ^{13}C isotope peak at *m/z* 137 in $C_{10}D_8^+$ was equal to the expected 11%, giving us confidence that the peak ratios of close-lying peaks were accurate.

Results and Discussion

TRPD Results. There are three low-energy dissociation channels for naphthalene ion:

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

$$C_{10}H_8^+ \rightarrow C_{10}H_6^+ + H_2 \qquad (2)$$

$$C_{10}H_8^+ \rightarrow C_8H_6^+ + C_2H_2 \qquad (3)$$

Figures 1 and 2 show representative TRPD results for acetylene loss (eq 3) from the h_8 and d_8 ions. The fitted lines are derived in the standard way,[8] by convoluting the ICR signal equation, the 300 K thermal distribution of ion internal energies, and the rate–energy curve. The fits are seen to be entirely satisfactory, and from them we assign the parent ion dissociation rate constants shown in Table 1 at an internal energy of 7.10 eV (7.13 eV for the d_8 ion), calculated as the energy of two photons plus the average 300 K thermal internal energy.

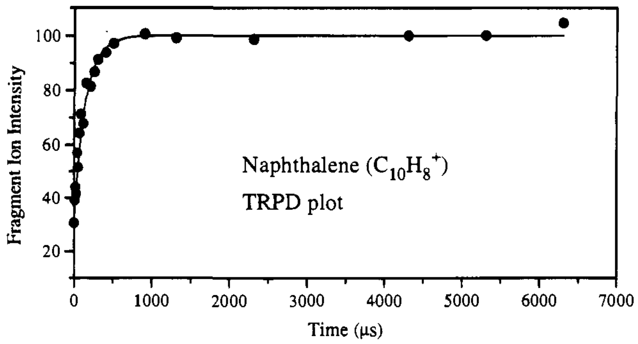

Figure 1. TRPD points for dissociation of $C_{10}H_8^+$ by two photons at 355 nm. The points are the relative signal intensities of the $C_8H_6^+$ fragment peak. The solid curve is the simulated TRPD curve based on the present RRKM rate–energy curve convoluted with the 300 K thermal distribution and the TRPD ICR signal equation.

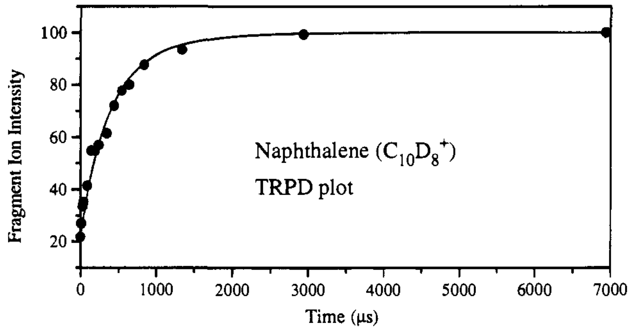

Figure 2. TRPD curve similar to Figure 1, for dissociation of $C_{10}D_8^+$.

Table 1. Experimental and Derived Kinetic Results for TRPD of Naphthalene Ions at 355 nm

	$C_{10}H_8^+$	$C_{10}D_8^+$
total dissociation rate (s^{-1})[a]	6450	2360
$H:H_2:C_2H_2$	1.0:0.6:1.3	1.0:0.8:2.0
k(H) (s^{-1})	2230	620
$k(H_2)$ (s^{-1})	1340	500
$k(C_2H_2)$ (s^{-1})	2890	1240

[a] Measured inverse time constant.

Figure 3 displays an illustrative d_8 photodissociation mass spectrum, showing that the fragment ions $C_{10}D_7^+$, $C_{10}D_6^+$, and $C_8D_6^+$ are all formed in observable abundance. The branching ratios (averaged over a number of spectra) are shown in Table 1. From the parent ion dissociation rate and the branching ratios, the individual rates for the three channels are derived[18] as shown in the table. In using the branching ratios to derive rate constants for the H-loss and H_2-loss channels, whose time dependence could not be observed directly, we have made the assumption that all three of these fragmentation channels are competitive, deriving from the same pool of parent ions. The limitations of the TRPD experiment (the daughter-ion dephasing time must be short compared with the dissociation rate) unfortunately did not allow us to monitor the H-loss and H_2-loss channels to verify this assumption.

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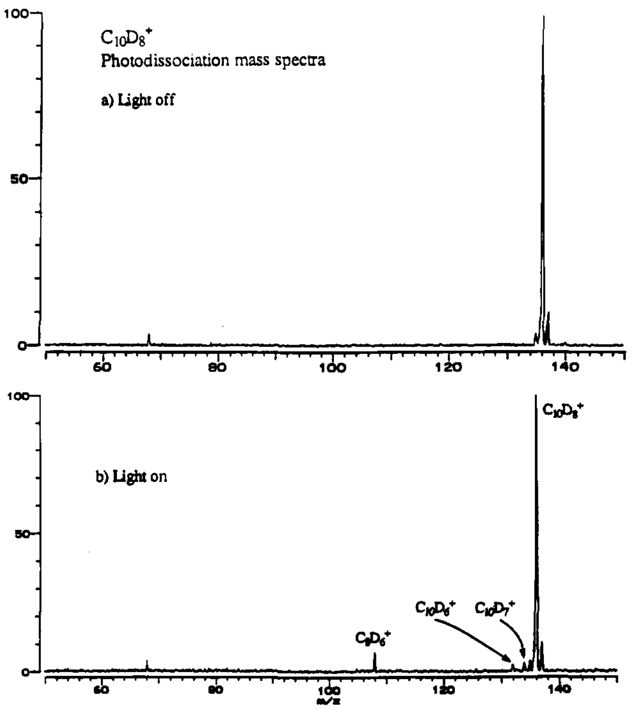

Figure 3. Photodissociation mass spectra for dissociation of $C_{10}D_8^+$ by two-photon dissociation at 355 nm: (a) light off; (b) light on. The small light-independent peak at *m/z* 68 is believed to be $C_{10}D_8^{2+}$.

Table 2. Literature Thermochemical Values

species	$\Delta H_f°(0\ K)$ (kJ mol^{-1})
$C_{10}H_8^+$	959[a]
$C_{10}H_7^+$	1176 ± 12[b]
$C_8H_6^+$	1175 ± 4[a,c]
H	216[a]
C_2H_2	229[a]

[a] Reference 9. [b] Reference 12. [c] Reference 19.

Table 3. Dissociation Energies Predicted from Literature Thermochemistry

reaction	$\Delta H_{reaction}(0\ K)$
$C_{10}H_8^+ \rightarrow C_{10}H_7^+ + H$	433 kJ (4.48 eV)
$C_{10}H_8^+ \rightarrow C_8H_6^+ + C_2H_2$	445 kJ (4.61 eV)

Evaluation of Dissociation Energies. The goal of the present work is to correlate all the available information and assign the C−H bond strength of naphthalene ion as well as possible. A number of different sources of information seem credible enough to provide useful constraints on the final assignment:

1. The heat of formation of naphthyl cation $C_{10}H_7^+$ has been independently derived from various sources, of which the most recent (and we think most reliable) is the dissociation of bromonaphthalene ion.[5] The 0 K value $\Delta H_f°(C_{10}H_7^+)$ of 281 kcal mol^{-1} gives a $\Delta H_{diss}{}^{0\ K}$ for eq 1 of 4.48 eV (see Tables 2 and 3).

2. A second independent thermochemical value comes from the heat of formation of phenylacetylene cation. This is the likely product of eq 3, and no lower-energy $C_8H_6^+$ structure is known.[19] The thermochemical estimate of this dissociation energy is thus a lower limit, since it would be higher if the product ion were a less stable isomer. Using the literature[9] $\Delta H_f°$(298 K) and correcting to zero K, the thermochemical lower limit for the dissociation energy for eq 3 is calculated as 4.61 eV (see Tables 2 and 3).

Table 4. RRKM Parameters Fitted to TRPD and TPIMS Data

	E_0 (eV)	$\Delta S^{\ddagger}_{1000\ K}$ (cal K^{-1} mol^{-1})
$C_{10}H_8^+ \rightarrow C_{10}H_7^+ + H$	4.48 ± 0.10	5.6 ± 2
$C_{10}D_8^+ \rightarrow C_{10}D_7^+ + D$	4.48 ± 0.10	6.1 ± 2
$C_{10}H_8^+ \rightarrow C_8H_6^+ + C_2H_2$	4.41 ± 0.20	3.5 ± 3
$C_{10}D_8^+ \rightarrow C_8D_6^+ + C_2D_2$	4.41 ± 0.20	4.7 ± 3

3. The present TRPD results give dissociation rates for hydrogen loss from both naphthalene ion and naphthalene-d_8 ion, along with branching ratios for the different loss channels, at a single value of internal energy (7.10 or 7.13 eV).

4. The TPIMS data[12] for naphthalene ion and naphthalene-d_8 ion severely constrain the acceptable range of rate−energy curves. The experiments sample the energy range 7.5−9 eV (with some weaker information about the 7.0−7.5 eV range) and give strong information about the rate−energy curves in the energy region above 7.5 eV.

5. The PEPICO results[11] give dissociation rates for C_2D_2 loss from naphthalene-d_8 ion in the energy range 8.3−9.7 eV, as well as some indication of branching ratios.[20]

6. All of the experiments indicate branching ratios not greatly different from unity for C_2H_2 loss relative to H loss, so it is clear that the energies for cleaving H and C_2H_2 from naphthalene ion are quite similar.

In making the extrapolations of observed dissociation rates to threshold, we will assume that the rate energy curves for the different reactions are given by simple RRKM theory,[21] with the following constraints on the RRKM parameters:

7. The E_0 values (for H loss and for C_2H_2 loss) are the same for the h_8 and the d_8 cases. Isotopic zero-point energy differences are estimated to be negligible (0.02 eV).

8. The $\Delta S^{\ddagger}_{1000\ K}$ values for H loss (and D loss) should be strongly positive, which is appropriate for a simple bond cleavage and is parallel to the benzene ion case. The $\Delta S^{\ddagger}_{1000\ K}$ values for acetylene loss are unconstrained. The $\Delta S^{\ddagger}_{1000\ K}$ values need not be the same for the h_8 and the d_8 cases, although it would be cause for concern if a proposed model involved large $\Delta S^{\ddagger}$ isotope effects. In generating rate−energy curves via RRKM theory, the frequency sets for molecule and activated complex used the values given by Rühl et al.[11] as a starting point, and the $\Delta S^{\ddagger}_{1000\ K}$ values were varied by making small changes in the activated complex frequencies. A reaction path degeneracy of 8 was used, on the assumption that all eight hydrogens are accessible to dissociation. Changing to a degeneracy of 4, corresponding to dissociation of only one of the two inequivalent sets of hydrogens, would have a nearly insignificant effect on the E_0 assignment.[22] In ref 12 allowance was made in the modeling for rather high assumed rates of relaxation of the parent ions due to radiative and collisional relaxation effects. There is no collisional relaxation under the present TRPD conditions. Experimental observation of naph-

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(19) Jochims, H. W.; Rasekh, H.; Rühl, E.; Baumgärtel, H.; Leach, S. *J. Phys. Chem.* **1993**, *97*, 1312.

(20) It appears that the experimental values derived by Rühl et al.[11] are the rate constants for overall disappearance of parent ion. As has been noted in connection with other ion dissociation work,[18] the rate constant for each individual reaction channel is derived from the parent ion disappearance rate constant by correcting for the branching ratio. In this case, making this correction reduces the dissociation rate values of Rühl et al. by about a factor of 2. This worsens the fit of their data to our model but appears to be a necessary correction to their interpretation.

(21) Lifshitz, C. *Adv. Mass Spectrom.* **1989**, *11*, 113.

(22) We may note that Rühl et al. (ref 11) apparently used a reaction path degeneracy of 1 in their calculations, which seems definitely unreasonable. We estimate that a recomputation of their fit using a degeneracy of 8 leads to an increase in the fitted E_0 from their value of 3.5 eV to a revised value of 3.85 eV, which is still in strong disagreement both with the independent thermochemical values and with our best fit described in the text.

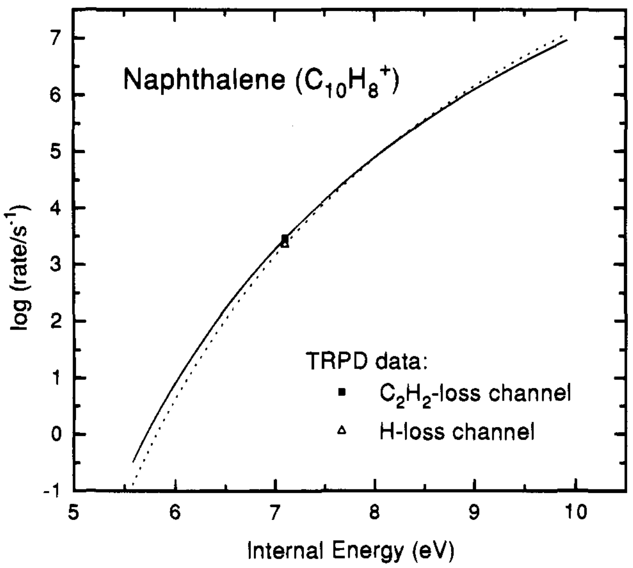

Figure 4. TRPD experimental values for the rate constants of eq 1 (△ and dashed line) and eq 3 (■ and solid line). The curves are the RRKM rate−energy curves corresponding to the present model. Note that these curves, in addition to passing through the TRPD points, are strongly constrained to agree with the TPIMS results, as well as being constrained by the other considerations detailed in the text.

Table 5. Modeled Rate−Energy Points for the Dissociation of $C_{10}D_8^+$ (Sum of All Dissociation Channels), Compared with Experimental Results

	total dissociation rate constant (s^{-1})		
internal energy (eV)	theoretical model	present work	Rühl *et al.*[a]
7.13	2.4×10^3	2.4×10^3	
8.27	1.7×10^5		2.9×10^5
8.52	3.7×10^5		3.2×10^5
8.65	5.3×10^5		3.0×10^5
8.77	7.5×10^6		3.8×10^5
9.02	1.5×10^6		6.0×10^5
9.72	8.1×10^6		2.1×10^6

[a] See ref 20 for discussion of the interpretation of these numbers.

thalene ion radiative cooling[23] suggests such low radiative rates that radiative relaxation is unlikely to compete to a significant extent with dissociation at the internal energy of the present TRPD experiment. Accordingly, this effect was not included in the present modeling.

To some extent these different criteria are contradictory, and no model can satisfy all of them exactly. However, making reasonable allowances for the uncertainties of the various experimental results, an overall model can be defined which is in satisfactory accord with the eight criteria given. The RRKM parameters for the resulting rate−energy curves are given in Table 4. Figure 4 shows rate−energy curves corresponding to these RRKM parameters, and Table 5 gives calculated rate−energy points for the d_8 case at energies relevant for comparison with experimental results. If we equate the RRKM E_0 parameter with the thermochemical bond strength, which is a reasonable assumption for a simple bond cleavage process, we arrive at a final value of the C−H bond energy in naphthalene ion of 4.48 eV, with a realistic uncertainty of 0.2 eV.

The final assigned C−H dissociation energy from RRKM fitting to the dissociation experimental results is equal to the independent thermochemical value of Table 3, although this was not imposed as a necessary condition on the modeling. The E_0 value of 4.48 eV for H loss seems quite robust, in that it gives both the best overall fit and also a good fit to the TPIMS data. The PEPICO results for $C_{10}D_8^+$ diverge somewhat from the present model at the higher internal energies (as seen in Table 5), which may reflect experimental uncertainties.[24]

Table 6. C−H Bond Strengths (eV)

	benzene	naphthalene
neutral	4.78[a]	4.8[b]
radical cation	3.7	4.48

[a] Reference 10. [b] Reference 25.

The new assignment of the acetylene loss energetics of this ion is substantially higher than that derived by Rühl et al.[11] (3.5 eV[22]) from the PEPICO measurements; it is not unreasonably far from the thermochemical value (4.61 eV) and from the value derived by Gotkis et al.[12] (4.60 eV) solely from deconvolution of TPIMS results. For hydrogen atom loss, the present assignment is slightly higher than that derived by Gotkis et al.[12] (4.23−4.33 eV). If we compare our Table 5 with Figure 6 of Rühl et al., the deviation of the PEPICO analysis from the present assignment is attributable both to data scatter and to the PEPICO data not spanning a large enough energy range to give a realistic estimate of the slope of the rate−energy curve. With regard to the TPIMS analysis, the deconvolution of TPIMS data gives useful constraints on the rate−energy curve but is sufficiently flexible so that the extracted E_0 is uncertain by several tenths of an electronvolt unless it is anchored by at least one absolute energy-resolved rate−energy point like that provided by TRPD in the present analysis.

The difficulty encountered in the extrapolation of PEPICO data by Rühl et al.[11] is clearly evident: Using their extrapolated rate−energy curve (as given in ref 19), the rate constant for $C_{10}H_8^+$ disappearance is predicted to be 2.5×10^4 s^{-1} at the TRPD energy of 7.10 eV, compared with the observed value of 6.6×10^3 s^{-1}. Similarly, the rate constant for $C_{10}D_8^+$ disappearance is predicted to be 7.7×10^3 s^{-1}, compared with the observed value of 2.4×10^3 s^{-1}.

For benzene ion, Neusser and collaborators[6] assign the acetylene loss channel 0.50 eV higher than the hydrogen loss channel, and they observe that the acetylene loss channel is almost an order of magnitude slower than the hydrogen loss channel in the metastable ion dissociation energy region. This is in contrast to the naphthalene ion case, where the two channels have comparable dissociation rates in the metastable ion dissociation region. This difference between the benzene and naphthalene ions is primarily a reflection of the much higher C−H bond strength in the naphthalene ion case.

Table 6 compares bond strengths for the molecules of interest here. The C−H bond strength of naphthalene ion is greater by 0.8 eV than that of benzene ion. It is, however, less than the value for neutral naphthalene by about 0.3 eV. There is evidently an effect of the positive charge which weakens the aromatic C−H bond, but as the aromatic framework is enlarged from benzene to naphthalene, this effect is attenuated. In ref 5 a generalization was suggested to the effect that the peripheral bond strengths are weaker by about 15% for the benzene-derived cations as compared with the corresponding naphthalene-derived cations. The present assignment of a slightly higher C−H bond

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(23) Dunbar, R. C.; Chen, J. H.; So, H. Y.; Asamoto, B. *J. Chem. Phys.* **1987**, *86*, 2081.

(24) There are features of the results of ref 11 which suggest substantial uncertainty in these values. For one thing, the slope suggested by the points is definitely inconsistent with the present results. For another, there is a substantial, unexplained residue of undissociated parent ions at high nominal internal energy, suggesting that a significant fraction of the ions contained less than the intended internal energy. Finally, the tailing of the time-of-flight peaks used to extract the dissociation rates was apparently comparable with the intrinsic peak widths at the higher internal energies.

(25) Chechneff, I.; Barker, J. R. *Astrophys. J.* **1992**, *394*, 703.

strength for naphthalene cation than in ref 5 gives a benzene/naphthalene cation difference somewhat larger than this 15%, but still qualitatively of this magnitude.

Conclusions

The new points on the dissociation rate−energy curves coming from the TRPD results, along with reconsideration of previous results, give new assignments for the critical dissociation energies for the two low-energy dissociation channels of naphthalene ion. The values (Table 4) are in accord with the bond-strength values inferred from independent thermochemistry (Table 3). It is gratifying to find the direct dissociation determinations agreeing with the thermochemical estimates, which strengthens our confidence in the bond strength assignments.

It is noteworthy that for the naphthalene case, the experimental determination of the C−H bond strength may be more precise and reliable for the ion than experimental values available for the neutral molecule. This situation is likely to become increasingly common as the powerful new tools available for measuring energy-resolved ion dissociation kinetics are applied to more polyatomic ions.

The comparisons between benzene and naphthalene, and between neutral and ionized molecules, displayed in Table 6, should provide fuel for theoretical analysis beyond the simple ideas presented here. The contrast between the large bond weakening upon ionization for benzene, and the much smaller bond-weakening upon ionizing naphthalene, is unexpected and worthy of further consideration.

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