Ion Decomposition versus Molecular Size Probed by Vacuum Ultraviolet Photoionization

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The molecular size dependence of primary fragmentation is studied for a series of β -naphthyl esters having alkyl chain lengths from C_2 to C_{18} . The esters are vaporized at a known temperature and ionized by coherent vacuum ultraviolet radiation at 10.5 eV. The photoionization wavelength is energetic enough to cause both metastable and nonmetastable primary fragmentation to m/z 144, but not energetic enough to cause secondary fragmentation to m/z 115 or 116. Under these conditions, the ratio of the nonmetastable-to-metastable daughter ion current, D/m_D , is expected to give a rough indication of the average parent ion dissociation rate. The D/m_D ratio decreases with increasing molecular size, but not as quickly as expected by simple RRK theory. This behavior along with temperature dependence studies suggests that the internal energy required for dissociation is provided in substantial part by both the initial thermal internal energy and the energy imparted by the photoionization step. The role of thermal energy in the dissociation of large ions is discussed. (*J Am Soc Mass Spectrom* 1991, 2, 103-107)

Ion decomposition in a mass spectrometer is determined by the internal energy dependence of the parent ion dissociation rate, $k(E)$, and the distribution of parent ion internal energies produced in the experiment, $P(E)$ [1]. As the size of the parent ion increases, changes in the form of $k(E)$ will affect the $P(E)$ required to observe sufficient fragmentation [2-4]. By measuring changes in the parent ion dissociation rate as a function of molecular size, it should be possible to predict the ionization and/or activation step $P(E)$'s necessary to dissociate large ions. Most ionization/activation techniques create parent ions over a broad range of internal energies. Therefore, a single dissociation rate cannot be assigned to the ion ensemble. In these cases, measurement of the ratio of the nonmetastable-to-metastable daughter ion current can give an indication of the "average" dissociation rate. Changes in this ratio as a function of molecular size should, therefore, reflect the molecular size dependence of the dissociation rate.

For such an experiment to succeed, other factors that can affect the ratio must be controlled. Metastable and/or nonmetastable ion currents for a given primary daughter ion are determined by: (1) $P(E)$ of the parent ion, (2) $k(E)$ for the fragmentation process, (3) competing primary fragmentations, and (4) secondary fragmentation of the primary daughter ion. These factors are determined by the molecular system studied and the ion preparation method used. The choice of molecular system affects the identities and $k(E)$ relationships of primary and secondary fragmentation

channels, and the way these values change as a function of molecular size. The ion preparation method directly influences the $P(E)$ distributions and whether or not secondary or competing primary fragmentations are observed. Given the large number of potential variables, it is not surprising that consistent, assignable trends in primary fragmentation with increasing molecular size have not been reported. Consistent trends in secondary fragmentation with increasing molecular size, however, are routinely observed and give rise to the so-called degrees-of-freedom effect [5-8]. Secondary fragmentation is apparently easier to study because the effects of most of the variables are either eliminated or "averaged out" by the primary fragmentation step [9].

We propose a new method of ion preparation that simplifies studying the molecular size dependence of primary fragmentation. Gas-phase molecules are ionized by vacuum ultraviolet photoionization with coherent, monochromatic radiation. The wavelength chosen is energetic enough to produce both metastable and nonmetastable primary fragmentation but not energetic enough to cause secondary fragmentation. If the ionization energies and Franck-Condon factors for vertical transitions in the photoionization process do not change significantly across the molecular series, then the $P(E)$ arising from photoionization will be constant. By eliminating secondary fragmentation and variations in $P(E)$, changes in the nonmetastable-to-metastable primary daughter ion ratio with molecular size should give a rough indication of the dissociation rate dependence. This approach is tested for a homologous series of β -naphthyl esters using 10.5 eV photoionization. The esters represent a good choice

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for study because the ionization energies and Franck-Condon factors should be largely determined by the naphthyl group rather than the alkyl chain and because all parent ions in the series fragment by a similar process to the same mass-to-charge ratio primary daughter ion.

Aside from demonstrating the viability of the photoionization approach to molecular size dependences, our results show that the nonmetastable-to-metastable primary daughter ion ratio is only a weak function of molecular size for this set of compounds. This ratio appears to be governed by the net effect of two competing molecular size dependences: changes in the form of $k(E)$ and changes in the amount of thermal internal energy. These dependences are qualitatively discussed along with their implications for the dissociation of large ions.

Experimental

In this experiment, 10.5-eV (118-nm) radiation was used for photoionization. This wavelength was generated by frequency tripling the third harmonic of a Nd:YAG laser (355 nm) in a phase-matched mixture of xenon and argon [10]. Ionization occurred in the source region of a linear time-of-flight mass spectrometer. Spectra were obtained by averaging 2000 laser pulses. The frequency tripling cell and mass spectrometer have been described in a separate publication [11].

As evident from the Results and Discussion sections, it was important to heat all compounds to the same temperature. This was accomplished by using an oven with an effusive orifice located directly over the source region. The orifice was a laser-drilled pinhole in a stainless steel disk mounted on the oven. The disk was interchangeable so that several different orifice diameters could be used. Since the volatilities of the naphthyl esters changed so much across the series, it was not possible to study all compounds at the same temperature even with a wide selection of pinholes. Therefore, the C_2 - C_{10} compounds were studied at 100 °C whereas the C_{12} - C_{18} compounds were studied at 150 °C. For each compound, the signal-to-noise ratio of the corresponding mass spectrum was determined by the vapor pressure at the oven temperature and by the orifice diameter.

All of the β -naphthyl esters were purchased from Sigma (St. Louis, MO). Each was vacuum distilled in successive stages to remove trace impurities of the remaining compounds in the series.

Results

Scheme I shows the main fragmentation sequence of the β -naphthyl esters. Alkyl chain lengths from C_2 to C_{18} are included in this study. For each parent ion in the series, the primary (m/z 144) and secondary (m/z 116 and 115) daughter ions are the same.

Scheme I

The 10.5-eV photoionization mass spectrum of β -naphthyl myristate is shown in Figure 1 as a representative example. The large peak widths in this and other spectra arise from metastable decomposition rather than the intrinsic resolution of the mass analyzer. The small amount of ion current at m/z 116 and 115 is probably due to absorption of a 355-nm photon after 10.5-eV photoionization, because the relative abundances of these ions are strongly dependent upon the incident 355-nm pulse energy. This observation is consistent with the rather high appearance energies of these ions from the β -naphthyl alcohol parent ion at m/z 144: 11.27 eV for m/z 116 and 13.91 eV for m/z 115 [12]. It is unlikely that m/z 144 arises from absorption of an additional 355-nm photon, because its relative abundance and peak shape are independent of laser pulse energy.

Figures 2 and 3 show expanded portions of the mass spectra in the m/z 144 region. These spectra are normalized to the same height of the (nominally) nonmetastable m/z 144 peak. The spectra in Figure 2, C_2 - C_{10} , were all taken with an oven temperature of 100 °C. The spectra in Figure 3, C_{12} - C_{18} , were all taken with a temperature of 150 °C.

The C_2 and C_4 spectra are superimposable. For C_6 and beyond, there is a monotonic increase in the size of the metastable tail (high-mass side of the m/z 144 peak) with increasing alkyl chain length. The metastable tail is caused by ion decomposition on the 10^5 - 10^6 s $^{-1}$ time scale in the source and acceleration regions. Since these spectra are normalized to the (nominally) nonmetastable m/z 144 peak height, the metastable tails show that the D/m_D ratio (D = nonmetastable daughter ion current, m_D = metastable

Figure 1. 10.5-eV photoionization mass spectrum of β -naphthyl myristate.

Figure 2. 10.5-eV photoionization mass spectra of β -naphthyl esters, C_2 - C_{10} , in the m/z 144 region. (Oven temperature 100 °C.)

daughter ion current) decreases monotonically with increasing alkyl chain length. Unfortunately, a quantitative measure of the D/m_D ratio cannot be made with our mass analyzer configuration. However, by integrating the metastable ion current beyond m/z 145 (the ^{13}C isotopic peak for m/z 144), we can determine that the magnitude of the D/m_D decrease is no more than ca. 2 across the series in either Figure 2 or Figure 3.

Metastable decay is also observed in the molecular ion region of the spectrum because there is a short postacceleration field adjacent to the microchannel plate detector. In this case, metastable decay in the flight tube (10^4 s $^{-1}$ time scale) causes broadening of the molecular ion peak and/or appearance of a broad hump underneath the molecular ion peak. Unfortunately, our mass analyzer design does not allow adequate separation of the metastable vs. nonmetastable contributions in this region, so ion abundance trends with molecular size cannot be determined. Another logical correlation to consider is the ratio of the parent-to-daughter ion current (P/D). Studying this

Figure 3. 10.5-eV photoionization mass spectra of β -naphthyl esters, C_{12} - C_{18} , in the m/z 144 region. (Oven temperature 150 °C.)

Figure 4. 10.5-eV photoionization mass spectra of β -naphthyl laurate with different oven temperatures.

molecular size dependence, however, requires a precise calibration of detector response vs. mass-to-charge ratio, which is not currently available for our instrument.

The role of oven temperature is shown in Figure 4 with β -naphthyl laurate as a representative example. As before, these spectra are normalized to the same (nominally) nonmetastable m/z 144 peak height. The size of the metastable tail decreases monotonically with increasing temperature. Therefore, D/m_D increases with increasing temperature. The difference in D/m_D between the 100 °C and 150 °C laurate spectra is similar to that between the myristate and laurate spectra at 150 °C. The temperature dependence of the parent ion to m/z 144 daughter ion ratio (P/D) for β -naphthyl laurate can be studied without a precise calibration of the detector response vs. mass-to-charge ratio. This ratio decreases monotonically with increasing temperature, going from 0.36 at 100 °C to 0.21 at 150 °C.

Discussion

Figures 2, 3, and 4 show that D/m_D depends upon both molecular size and temperature. The magnitudes of the size and temperature dependences are comparable. These results suggest that the observed trend in D/m_D with molecular size is a net effect of two competing molecular size dependences: "intrinsic" changes in the form of $k(E)$ (internal energy constant) and changes in the thermal internal energy. The interplay between these two factors can be illustrated simply through the RRR relationship between the dissociation rate constant (k) and the ion internal energy (E) [13],

$$k = \nu \left(\frac{E - E_0}{E} \right)^{N-1} \quad (1)$$

where ν is the frequency factor, E_0 is the critical energy for decomposition, and N is the number of

Table 1. RRK calculations of $k(E)$ vs. N

Case I: $E = \text{constant}^a$		Case II: $E = \rho N^b$	
k (s^{-1})	N	k (s^{-1})	N
1.4×10^{10}	50	1.78×10^8	50
1.8×10^7	100	2.95×10^8	100
2.9×10^1	200	3.69×10^8	200
1.2×10^{-16}	500	4.19×10^8	500
1.2×10^{-45}	1000	4.36×10^8	1000
—	5000	4.50×10^8	5000

^a $\nu = 10^{13} \text{ s}^{-1}$, $E_0 = 0.5 \text{ eV}$, $E = 4.0 \text{ eV}$.^b $\nu = 10^{13} \text{ s}^{-1}$, $E_0 = 0.5 \text{ eV}$, $\rho/E_0 = 0.1$.

vibrational modes in the molecule and hence determined by the molecular size. Two limiting cases must be considered. If E is constant as N increases, then k decreases rapidly with increasing N . This intrinsic dependence ($E = \text{constant}$) corresponds to the situation where essentially all of the molecular ion internal energy comes from the photoionization step. E will be constant with increasing N if the ionization energies and Franck-Condon factors for vertical electronic transitions in the photoionization process are the same for all compounds in the series.

If E is proportional to N , then eq 1 can be rewritten in terms of the energy density $\rho = E/N$,

$$k = \nu \left(1 - \frac{E_0}{\rho N} \right)^{N-1} \quad (2)$$

If ρ is a constant, then E increases with increasing N , and k actually increases slightly with increasing N . This dependence corresponds to a situation where essentially none of the molecular ion internal energy comes from the photoionization step. If E is determined by the initial thermal energy of the molecule, then E will increase linearly with N when all compounds in the series are heated to the same temperature. The two limiting cases are illustrated in Table 1, where values of k vs. N are calculated by using "reasonable" values for the remaining parameters. For comparison, the β -naphthyl esters in this study have total vibrational degrees of freedom (N) ranging from 66 for C_2 to 210 for C_{18} .

Within this simple picture, the spectra in Figures 2 and 3 can be explained by an intermediate situation between the two limiting cases. Assuming that D/m_D gives a rough approximation of the average k over the range of ion internal energies accessed in the experiment, k decreases with increasing N but not by the orders of magnitude suggested by the case where E is independent of N . For example, a factor of 2 increase in N should yield a 10^2 – 10^5 decrease in k , depending upon the values of E and E_0 chosen. Therefore, the energy required for molecular ion dissociation is probably provided in substantial part by both the photoionization step and the initial thermal internal energy. When both sources contribute substantially to

the molecular ion internal energy, they counteract the k vs. N dependence of each other. As a result, k only decreases slowly with N .

Significant participation of the thermal internal energy in the primary fragmentation process is demonstrated by the temperature dependence results. Figure 4 shows that D/m_D can be affected by temperature as strongly as it is by the length of the alkyl chain. For β -naphthyl laurate, both D/m_D and P/D change as expected by simple RRK theory: the former increases and the latter decreases as temperature, and hence thermal internal energy, increases.

Of course, the above discussion is meant only to give an initial, qualitative illustration of the interplay between changes in the form of $k(E)$ and the thermal internal energy as a function of increasing molecular size. A more quantitative description will require detailed RRKM calculations in concert with quantitative measurements of either $k(E)$ or D/m_D . Detailed calculations will benefit from precise determinations of molecular ionization energies, appearance energies, and photoionization $P(E)$'s, which are not currently available. Quantitative measurements of $k(E)$ and/or D/m_D can be made with time-of-flight analyzers possessing a reflecting geometry to separate stable and metastable ion currents via kinetic energy differences [14, 15]. Finally, one must consider the possibility that the internal energy imparted by photoionization is not statistically randomized throughout the parent ion before decomposition. Although this phenomenon may play a role with larger molecules [4], it is an unlikely contributor to the β -naphthyl ester spectra. Smalley [16] has reviewed vibrational randomization measurements on alkyl benzene molecules having chain lengths similar to those considered here. As long as the density of states is sufficient ($> 10^3$ states per cm^{-1}), randomization occurs on a subnanosecond time scale. Energy randomization as a function of molecular size can potentially be studied by comparing wavelength and temperature-dependent photoionization mass spectra [17].

Conclusions

Metastable tails in the 10.5-eV photoionization mass spectra of β -naphthyl esters allow trends in the non-metastable-to-metastable m/z 144 daughter ion ratio (D/m_D) to be studied as a function of molecular size. This ratio decreases slowly with increasing alkyl chain length and is temperature dependent. These results suggest that the observed molecular size dependence is really a net effect of two competing factors: changes in $k(E)$ and changes in the thermal internal energy with increasing molecular size. This conclusion has significant implications for the dissociation of high-mass molecules. Several methods have been developed to vaporize large molecules, including laser desorption [18], electrospray ionization [19], plasma desorption [20], and fast atom [21] or ion [22] bombard-

ment. If the internal energy imparted to the neutral/ion during the vaporization step scales with increasing molecular size, then the additional energy required from the activation step to maintain a reasonable dissociation rate with increasing molecular size is substantially reduced. Therefore, it is important to understand the internal energy vs. molecular size dependences of the different vaporization methods as well as the intrinsic $k(E)$ dependence. Vacuum ultraviolet photoionization is a unique way to study the net effect of these two dependences because the internal energy imparted to the molecular ion during the ionization/activation step can be independent of molecular size.

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