Fast Atom Bombardment Combined with Mass Spectrometry for Characterization of Polycyclic Aromatic Hydrocarbons

Chhabil Dass

Charles B. Stout Neuroscience Mass Spectrometry Laboratory and the Department of Neurology, University of Tennessee-Memphis, Memphis, Tennessee, USA

A new approach using fast atom bombardment combined with mass spectrometry to characterize polycyclic aromatic hydrocarbons (PAHs) in the range of 128–252 u molecular weight is described. Sulfolane was employed as a liquid matrix for these π -conjugated hydrocarbons. Bombardment of sulfolane solution of certain PAHs with an atom beam produces both radical cation ($M^{+\cdot}$) and protonated molecule $[(M + H)^+]$, with no evidence of fragmentation. Collisional activation of the fast atom bombardment-desorbed $M^{+\cdot}$ ions, however, results in several structure-specific fragment ions. Structural differences in a few isomeric hydrocarbons can be detected using the $[(M + H)^+]/[M^{+\cdot}]$ abundance ratio and in the pyrene-fluoranthene pair by the B/E linked-field-collision-activated dissociation data. The $[(M + H)^+]/[M^{+\cdot}]$ was found to be compound-specific and correlated well with certain properties (resonance energy, proton affinity, and ionizing energy) of PAHs. (*J Am Soc Mass Spectrom* 1990, 1, 405–412)

Polycyclic aromatic hydrocarbons (PAHs) are highly carcinogenic and ubiquitous in combustion products [1], and thus require highly innovative analytical methods capable of providing greater sensitivity and structure specificity [1, 2]. Of critical importance is differentiation of isomeric PAHs because carcinogenicity is attributable to specific structural features of a PAH. For example, benzo[a]pyrene is carcinogenic, but benzo[e]pyrene is not [1]. Electron ionization (EI) mass spectrometry has been used traditionally to identify PAHs [3–6]. The low vapor pressure of PAHs with a molecular weight (M_r) > 300 u, however, limits the use of this technique to low mass hydrocarbons only. Furthermore, EI mass spectra are not isomer-specific because deposition of a large amount of internal energy during ionization increases the extent of isomerization.

Several mass spectrometry approaches have been investigated to characterize PAHs. Charge-exchange chemical ionization (CI) with an argon/methane mixture was used successfully to distinguish isomeric PAHs [7]. Because the $[(M + H)^+]/[M^{+\cdot}]$ ratio was found to be a function of the ionizing energy (IE) of the PAH in question [8], it was used as an isomer-specific diagnostic probe [7]. In an electron capture (EC) negative ion (NI) CI study, it was demonstrated that a correlation between the electron affinity and ionization response exists for certain PAHs [9]. The

PAHs with an electron affinity below 0.5 eV were found to be unresponsive to EC/NICI. Hunt et al. [10] employed pulsed positive ion (PI) and negative ion CI mass spectrometry to analyze PAHs. Certain isomeric PAHs could be differentiated in terms of their relative abundances of $M^{+\cdot}$ and $(M + 15)^+$ ions formed by NICI with oxygen as the reagent gas. Ochme [11] developed high-resolution gas chromatography/NICI by using a methane/nitrous oxide mixture for isomer characterization. The use of NICI with carbon dioxide alone [12, 13] or in combination with a nitrogen/oxygen mixture [14, 15] was also reported recently. Pyrene and fluoranthene were shown to display different CI mass spectra [12]. Similarly, a group of isomeric PAHs of $M_r = 228$ were found to exhibit isomer-specific NICI mass spectra [13]. Keough [16] differentiated anthracene from phenanthrene on the basis of its reactivity towards the $CH_2 = \dot{O} - CH_3$ ion to form Diels-Alder products.

Zakett and co-workers [17, 18] developed tandem mass spectrometry (MS/MS) methods as possible means of identifying PAHs in coal samples. MS/MS provides compound-specific data and can be employed for mixture analysis [19]. The isomer-specific MS/MS data were obtained by Shushan and co-workers [20, 21] by using a B/E (E and B are electric and magnetic fields, respectively) linked-field scan [22]. An elegant study by Pachuta et al. [23] investigated in detail the energetic requirements for fragmentation of several PAHs by using a variety of experimental techniques including collision-activated dissociation (CAD) of low (eV) and high (keV) translational energy ions [19], multiphoton ionization (MPI)

Address reprint requests to Chhabil Dass, Charles B. Stout Neuroscience Mass Spectrometry Laboratory, Department of Neurology, University of Tennessee-Memphis, Memphis, TN 38163.

[24], and surface-induced dissociation [25]. These researchers concluded that the extent of fragmentation of an ionized PAH depends upon the particular activation method used, and also, the rate of isomerization is fast enough to compete with direct dissociation. These two factors may make isomer differentiation more difficult [23]. It was further suggested that singly charged ions that have lost no carbon units may retain partial or complete structural identity and, thus, may be helpful in distinguishing isomers.

Fast atom bombardment combined with mass spectrometry (FAB/MS) has emerged as a powerful analytical technique for analysis of several classes of polar, thermally labile, and nonvolatile compounds [26]. The success of FAB is attributed to the use of a liquid matrix, the choice of which depends upon the chemical and physical properties of the individual analyte. The most important criteria for selecting a matrix are its potent solvent properties, volatility, and acidity or basicity [27, 28]. The analyte must be basic compared to the matrix so that transfer of a proton from the matrix to the analyte occurs readily to yield a strong signal due to the protonated molecule. Glycerol, thioglycerol, and a mixture of dithiothreitol and dithioerythritol are the most widely used FAB solvents [29, 30]. Using these polar matrices, $(M + H)^+$ and $(M - H)^-$ even-electron ions are produced as characteristic molecular species in the positive and negative ionization modes, respectively. The important physical properties of several common matrices were compiled recently [27].

Because of their weak polar character PAHs are unresponsive to FAB/MS when polar matrices are used. Recently, we reported FAB/MS analysis of anthracene antibiotics using sulfolane (tetramethylene sulfone; 1) as a matrix [31]. One of the interesting features of FAB/MS of these compounds is that the radical cation ($M^{\cdot+}$) dominates the molecular ion region. The $(M + H)^+$ ion was found to be less significant in these spectra. In other words, removal of an electron from these compounds is more facile than their protonation when sulfolane is used as a matrix. Two factors are envisioned as the plausible reasons for the ease of formation of $M^{\cdot+}$. First, the aglycone portion of these antibiotics contains a conjugated π -electron system that can easily assimilate a positive charge. Second, the absence of a labile H atom in sulfolane makes transfer of a proton more difficult in this liquid medium. Formation of the $(M + H)^+$ ions of those anthracenes is perhaps a consequence of the proton transfer reaction from the protonated molecule of sulfolane to those analytes. Use of sulfolane as a matrix in FAB/MS analysis of the group IV organometallic halides was also discussed by Miller and Fulcher [32].

Because PAHs also contain a network of conjugated π -electrons, it is reasonable to assume that these compounds may be accessible to FAB/MS if sulfolane is employed as a liquid matrix. Significantly,

Figure 1. The structures of the PAHs under study.

sulfolane has been used as a solvent for extraction of PAHs from natural sources [33].

This article describes FAB/MS analysis of certain PAHs (shown in Figure 1) that include naphthalene (2), 1-methylnaphthalene (3), fluorene (4), anthracene (5), phenanthrene (6), pyrene (7), fluoranthene (8), benz[a]anthracene (9), tetracene (10), chrysene (11), triphenylene (12), pentacene (13), and perylene (14). Fast atom bombardment of a sulfolane solution of these compounds produces both $M^{\cdot+}$ and $(M + H)^+$ ions. In some cases, isomer characterization is possible by monitoring the $[(M + H)^+]/[M^{\cdot+}]$ ratio and also by using the MS/MS spectra, which were acquired by using B/E linked-field scan and CAD techniques.

Previous efforts in using a particle beam to ionize PAHs met with limited success. Dynamic secondary ion mass spectrometry (SIMS) of certain PAHs deposited on liquid gallium [34] and carbon black [35] was shown to produce $M^{\cdot+}$ ions. Those hydrocarbons, however, were found to be unresponsive to SIMS when mounted on silver or indium foil, or dissolved in glycerol [34]. Anthracene deposited on metal surfaces undergoes cationization in static SIMS [36]. Groenewold et al. [37] employed liquid $SbCl_3$ as a solvent in SIMS experiments. Pyrene was shown to exhibit a strong signal due to the $M^{\cdot+}$ ion. Sulfuric acid has also found utility as a solvent in SIMS analysis of several substituted PAHs [38]. The research discussed in this article is the first report of the use of FAB to analyze PAHs.

Experimental

The experiments described here were performed on a VG 7070E-HF (VG Analytical Ltd, Wythenshawe, Manchester, UK) double-focusing forward-geometry (E,B) instrument outfitted with an Ion Tech B11NF (Ion Tech Ltd, Teddington, UK) saddle-field fast atom gun. The data were acquired under computer-con-

Table 1. Variation of the $[M^+ \cdot]/[m/z\ 241]$ and the $[(M + H)^+]/[M^+ \cdot]$ ratios with the amount of pyrene*

Amount (nmol)	$[M^+ \cdot]/[m/z\ 241]$	$[(M + H)^+]/[M^+ \cdot]$
10	0.049	0.431
25	0.155	0.433
40	0.306	0.431
50	0.653	0.457
75	1.204	0.458

* Pyrene was dissolved in 1 μ L sulfolane.

trolled scans by using a Digital PDP 11/24 (Digital Equipment Corp., Maynard, MA) minicomputer-based VG 11-250 M+ data system. A beam of Xe atoms of approximately 7-keV impact energy and equivalent to 1-mA emission current was employed to ionize PAHs dissolved in sulfolane. The vapor pressure of sulfolane is higher compared to other commonly used FAB matrices (as noted by increased pressure in the ion source). Two microliters of sulfolane, however, lasted well over 2 min in our FAB ion source (see Table 2). The FAB-produced ions exited the ion source at a potential of 6 kV. The MS/MS spectra of the mass-selected $M^+ \cdot$ ions of PAHs were generated by using the B/E linked-field scan in the 5-350 u mass range with an exponential-down scan of 5 s per decade, and 7-10 scans were accumulated by operating the data system in the multichannel acquisition (MCA) mode. The β -slit was closed until the intensity of the precursor ion beam began to reduce. The MCA data were smoothed and processed to provide peak heights and were subsequently mass-measured using a calibration file acquired under the magnet scan. Helium was used as the collision gas to

Table 2. Variation of the $[M^+ \cdot]/[m/z\ 241]$ and the $[(M + H)^+]/[M^+ \cdot]$ ratios with the time of irradiation of pyrene*

Time (sec)	$[M^+ \cdot]/[m/z\ 241]$	$[(M + H)^+]/[M^+ \cdot]$
17	0.231	0.431
33	0.250	0.431
50	0.385	0.431
66	0.519	0.430
83	0.739	0.421
100	1.238	0.442
116	2.261	0.442
133	14.385	0.442

* Pyrene, 75 nmol, was dissolved in 2 μ L sulfolane.

effect CAD in the first field-free region (FFR). The pressure of helium (1×10^{-6} torr as read on the ionization gauge located in the analyzer region) was adjusted to reduce the precursor-ion intensity by one third.

For the data reported in Table 1, 1 μ L of sulfolane containing 10-75 nmol of a PAH was applied separately to the FAB probe, the magnet was scanned across the 170-250 u mass range, and ten scans were summed using the MCA. The time-dependence of the two ratios $[M^+ \cdot]/[m/z\ 241]$ (where the $m/z\ 241$ is the protonated dimer of sulfolane) and $[(M + H)^+]/[M^+ \cdot]$ (the data of Table 2) was studied by dissolving 75 nmol of pyrene in 2 μ L sulfolane and acquiring the data over the 170-250 u mass range. For the sake of brevity, the data corresponding to every ninth scan are reported in Table 2. To obtain the $[(M + H)^+]/[M^+ \cdot]$ ratio (Table 3), a few crystals of PAHs were dissolved separately in sulfolane, and the solution (probably saturated) was applied to the FAB

Table 3. A list of M_r , IE, LUMO energies, RE, PA, and the $[(M + H)^+]/[M^+ \cdot]$ ratio of PAHs

PAH	M_r (u)	IE ^a (eV)	LUMO energy ^b (eV)	RE ^{c,d}	Proton affinity ^e (kcal/mol)	$[(M + H)^+]/[M^+ \cdot]$	
						Ratio	σ
Naphthalene	128	8.15	-0.331	0.59	196.3	0.2473	0.0165
1-Methylnaphthalene	142	—	-0.388	—	—	0.3320	0.0166
Fluorene	166	7.91	-0.369	—	202.4	0.2860	0.0188
Phenanthrene	178	7.90	-0.480	0.85	201.1	0.3442	0.0149
Anthracene	178	7.42	-0.841	0.71	209.4	0.4792	0.0135
Pyrene	202	7.43	-0.878	0.95	208.5	0.4398	0.0071
Fluoranthene	202	7.95	-0.939	—	201.7	0.5051	0.0347
Benz[<i>a</i>]anthracene	228	7.46	-0.829	1.00	210.5	0.5459	0.0185
Tetracene	228	7.01	-1.182	0.83	218.7	0.7989	0.0178
Chrysene	228	7.60	-0.716	1.07	203.3	0.5829	0.0156
Triphenylene	228	7.87	-0.558	1.13	199.7	0.4670	0.0156
Perylene	252	6.98	-1.088	1.15	213.0	0.5685	0.0246

^a These experimental values are from refs 8, 40.^b LUMO = lowest unoccupied molecular orbital; from ref 41.^c In β units, where β is the resonance integral.^d From ref 42.^e From ref 40 except for benz[*a*]anthracene, the value for which was estimated by extrapolation of the proton affinities of the remaining three C₁₈H₁₂ isomers.

Figure 2. The FAB mass spectra of pyrene in (a) sulfolane and in (b) glycerol. The matrix ions are labeled as S and G, respectively.

probe tip. The magnet was scanned over a narrow mass range (10 u wide) centered around the M^+ ion of each one of the PAHs, and ten scans were accumulated and signal-averaged by using the MCA mode. The data reported in Table 3 are an average of at least five such measurements with a precision of $< \pm 7\%$ (RSD). The precision of the data acquired on different days was within $\pm 10\%$ (RSD).

Sulfolane and all of the PAHs studied here were purchased from Aldrich Chemical Co. (Milwaukee, WI), and were used without further purification.

Results and Discussion

Fast Atom Bombardment Mass Spectra

The conventional magnet scan FAB mass spectrum of pyrene dissolved in sulfolane is shown in Figure 2a. As was demonstrated for anthracenes [31], FAB of pyrene also produces a radical cation at m/z 202. The $(M+H)^+$ ion of ca. 45% abundance relative to the M^+ ion is also formed. This observation suggests that one-electron oxidation of pyrene is a facile process under these experimental conditions. All other ions present in Figure 2a are attributable to sulfolane. The absence of fragments related to pyrene in the FAB mass spectrum is not surprising. The conjugated π -electrons network imparts high thermodynamic stability to pyrene. Consequently, pyrene and other PAHs can accommodate a large amount of excess energy before undergoing any bond fragmentation [23].

The FAB mass spectrum of pyrene obtained using glycerol as the matrix is depicted in Figure 2b. This spectrum demonstrates that by using polar matrices no meaningful FAB data are obtained for nonpolar compounds. When the molecular ion region was multiplied by a factor of 400, a very small ion-signal due to the $(M+H)^+$ ion was found at m/z 203 (see inset). A similar situation exists when nitrobenzyl alcohol and thioglycerol are used as matrices for the FAB/MS analysis of pyrene.

The FAB mass spectra acquired in sulfolane of all other PAHs of Figure 1 (except for pentacene) are similar to pyrene in that all compounds form M^+ and $(M+H)^+$ ions of varying abundance, and no evidence of fragmentation. The proclivity of different PAHs to FAB ionization was determined in terms of the abundance ratio $[M^+]/[m/z\ 241]$, where the m/z 241 is the protonated sulfolane dimer. For these experiments, 1 μ L sulfolane containing 75 nmol of a PAH was deposited onto the FAB probe tip. The following values of the $[M^+]/[m/z\ 241]$ (reported in parentheses) were obtained for some of the PAHs; anthracene (0.215), phenanthrene (0.221), pyrene (1.204), fluoranthene (0.213), benz[a]anthracene (0.231), chrysene (0.152), triphenylene (0.515), and perylene (0.081). Fluorene and tetracene did not produce meaningful data at this low concentration. A change in the $[M^+]/[m/z\ 241]$ with concentration was also studied using pyrene as an example (see Table 1). The variation of the $[M^+]/[m/z\ 241]$ with the time of irradiation is reported in Table 2, which also includes the corresponding data for the $[(M+H)^+]/[M^+]$. To obtain these data, 2 μ L sulfolane containing 75 nmol pyrene was applied to the FAB probe. The steep increase in the $[M^+]/[m/z\ 241]$ is a consequence of the high evaporation rate of sulfolane.

One of the limitations of the present method is the solubility of a PAH in sulfolane. In general, it was observed visually on the probe tip that linear PAHs are less soluble in sulfolane than the corresponding nonlinear isomers. Also, the solubility was found to decrease with increasing M_n . For example, anthracene displays a good ion signal. In contrast, tetracene exhibits a poor FAB response, and pentacene, which appears to be insoluble in sulfolane, is not amenable to FAB ionization.

To study the behavior of these PAHs under negative-ion FAB, the spectrum of pyrene was acquired. Pyrene, however, was found to be unresponsive to this mode of ionization. Lloyd and Cotter [39], while working with quinones, reported that only those quinones that have electron affinities > 1.1 eV produce a negative ion FAB signal in sulfolane. In that study, it was rationalized that negative ions are formed as a result of charge transfer from SO_2^- , the electron affinity of which is 1.1 eV. The electron affinities of PAHs are below 0.8 eV [9]. Therefore, the response of PAHs to negative ion FAB noted here is consistent with the observation of Lloyd and Cotter [39].

Isomer Differentiation

In searching for a method to distinguish isomeric PAHs, the $[(M+H)^+]/[M^+]$ ratio was determined. The rationale for choosing this property is that proton affinity and IE are functions of the structure of a molecule. Protonation of aromatic compounds is less favorable compared to one-electron oxidation because the π -electrons involved in σ -bond formation with an electrophile (here H^+) are removed out of conjugation with the remaining π -electrons. Increasing the size of π -conjugated system permits an increase in delocalization of the charge in both radical and protonated ions. Consequently, IE decreases and proton affinity (PA) increases with the size of a PAH (see Table 3). Ionizing energy, however, decreases faster because of additional delocalization of spin density in the radical cation [40]. Thus, it is expected that the $[(M+H)^+]/[M^+]$ is a structure-specific property.

The data concerning the $[(M+H)^+]/[M^+]$ were obtained in a more precise fashion by scanning the magnet over a narrow mass range (10 u wide) encompassing the M^+ ion region of the PAHs listed in Figure 1. The observed $[(M+H)^+]/[M^+]$, along with the standard deviation of five replicate measurements, are reported in Table 3, which also lists other properties of PAHs, including M_r , IE [7, 40], lowest unoccupied molecular orbital energies [41], resonance energies (RE) [42], and PA [40]. The $[(M+H)^+]/[M^+]$ were obtained with saturated solutions of PAHs. It was important to use high concentrations because for some PAHs (e.g., fluorene, anthracene, chrysene, and tetracene) the matrix background contributed to the M^+ and $(M+H)^+$ ions abundances at lower concentrations. However, it was observed for pyrene that the $[(M+H)^+]/[M^+]$ remains constant within the experimental error with concentration (see Table 1). The $[(M+H)^+]/[M^+]$ for pyrene was also found to be constant within the time of irradiation (Table 2).

The data presented in Table 3 demonstrate that the $[(M+H)^+]/[M^+]$ is diagnostic of the structures of certain PAHs. For example, phenanthrene and anthracene are distinguishable readily on the basis of different values of the $[(M+H)^+]/[M^+]$. These ratios for the pyrene-fluoranthene isomeric pair are very close to each other, yet are characteristic of the isomer in question. The four isomers of $C_{18}H_{12}$ composition ($M_r = 228$ u), benz[a]anthracene, tetracene, chrysene, and triphenylene, all exhibit different values of the $[(M+H)^+]/[M^+]$. The difference in the values of this ratio, however, is small for benz[a]anthracene and chrysene, and must be used with caution to differentiate these two isomers.

It is of interest to search for a structural feature that can be correlated with the observed $[(M+H)^+]/[M^+]$. Several researchers in the past looked for similar correlations. Shushan and co-workers [20, 21] found correlation between the metastable ion intensi-

Figure 3. The relation between the $[(M+H)^+]/[M^+]$ ratio and the resonance energy (in β units). The linear coefficients for the straight lines connecting the linear isomers, the pericondensed isomers, and the isomers of $M_r = 228$ are 0.992, 0.563, and 0.895, respectively.

ties ratios $M^+/(M-H)^+$ and $(M-H)^+/(M-2H)^+$ with number of hydrogens per molecule capable of benzointeractions and with RE. Proton affinities were shown to correlate with the structure of PAHs [40]. Pericondensed and linear PAHs fall on different correlation lines. Gallegos [5] found that the IE of PAHs decreases with an increasing number of π -electrons in the molecule, if comparison is made for molecules belonging to the same symmetry group. A similar correlation was obtained by Natalis and Franklin [6] between appearance energy of certain fragments and the RE of the parent PAH. A CI mass spectrometry study also found a good correlation between the $[(M+H)^+]/[M^+]$ and IE of several PAHs [7].

As mentioned above, protonation localizes the π -electrons involved in σ -bond formation with H^+ . This process affects the aromaticity of the resulting ion. Furthermore, a large network of conjugated π -electrons will facilitate delocalization of the charge in both the radical cation and the protonated molecule. Thus, localization energy, RE, proton affinity, and IE are some of the properties that might correlate with the observed $[(M+H)^+]/[M^+]$ of a PAH. Indeed, the plots of the $[(M+H)^+]/[M^+]$ versus RE (Figure 3) and PA (Figure 4) demonstrate clearly that the linear acenes and pericondensed PAHs follow distinct correlation curves. The $[(M+H)^+]/[M^+]$ increases with increasing RE (Figure 3). Likewise, the $[(M+H)^+]/[M^+]$ also increases with increasing PA of these PAHs (Figure 4). These trends are consistent with the expected relations of RE and proton affinity with the size of PAHs. The correlation of the $[(M+H)^+]/[M^+]$ with proton affinity, however, produces more scatter than the corresponding correlation with RE. In fact, no clear correlation is seen between the $[(M+H)^+]/[M^+]$ and the proton affinities for pericondensed PAHs. It is also observed that the $[(M+H)^+]/[M^+]$ is smaller for a nonlinear PAH compared to its linear isomer. Anthracene-phenanthrene and benz[a]anthracene-tetracene are examples of this observation.

Figure 4. The relation between the $[(M+H)^+]/[M^{\bullet}]$ ratio and the proton affinity (kcal mol^{-1}). The curve joining the pericondensed PAHs (6, 7, 8, 9, 11, 12, and 14) is not plotted because of a large scatter of the data. The linear coefficients for the straight lines connecting the linear isomers and the isomers of $M_r = 228$ are 0.965 and 0.789, respectively.

Correlation of the $[(M+H)^+]/[M^{\bullet}]$ with RE and PA was also tested for $\text{C}_{18}\text{H}_{12}$ ($M_r = 228$) isomers. The corresponding plots are also included in Figures 3 and 4, respectively. The PA and RE both decrease with an increasing number of benzointeractions. The $[(M+H)^+]/[M^{\bullet}]$ follows to a large extent the expected correlation with these two properties.

The $[(M+H)^+]/[M^{\bullet}]$ was also found to correlate with IE for linear acenes and isomeric PAHs of $\text{C}_{18}\text{H}_{12}$ composition (not shown). Similar to the corresponding correlation with proton affinities, the data for pericondensed PAHs leads to a scatter plot.

B/E Linked-field Collision-activated Dissociation Spectra

As mentioned above, the thermodynamic stability of PAHs, coupled with the small amount of excess energy deposited by FAB ionization, did not produce fragment ions in the conventional FAB mass spectrum. However, collisional activation of a mass-selected ion in the FFRs of multisector instruments is known to increase fragmentation [19]. The average energy deposition in collisional activation of high-energy ions is of the order of ca. 1–3 eV with tail of the energy function extending beyond 15 eV [43]. In general, the CAD technique samples nondecomposing ions. Coupled with the fact that FAB-desorbed ions are formed with low internal energies, it is realized that FAB, in combination with collisional-activation mode of ion activation, may produce a structurally diagnostic mass spectrum for PAHs.

With this objective in mind, the B/E linked-field CAD MS/MS spectra of the $M^{\bullet}$ ions of the pyrene-fluoranthene isomeric pair was acquired. A typical example of these spectra for each of the two isomers is shown in Figure 5. In this mode of a linked-field scan, B and E are both scanned in such a way that the ratio B/E is maintained constant. The preselected precursor ion is allowed to fragment in the first FFR of a

forward-geometry (EB) instrument either unimolecularly (metastable ion spectrum) or by collisions with a neutral target (CAD spectrum). In this way, a spectrum of the product ions formed exclusively from that mass-selected precursor is obtained [22]. Mass selection of a precursor ion, however, is poor in the B/E linked-field technique using an EB instrument. For example, the ions of m/z 203 and m/z 204 in Figure 5 are a consequence of a poor precursor-ion resolution. Thus, a B/E spectrum is susceptible to contributions from neighboring ions due to the analyte (e.g., m/z 203 and m/z 204 in the present case) and the FAB matrix. One advantage of the B/E linked-field technique over the mass-analyzed ion kinetic energy (MIKE) mode of MS/MS [44] is increased mass resolution of the daughter ions.

The B/E-CAD spectra of the pyrene-fluoranthene isomeric pair are characterized by the presence of several diagnostic ions. The prominent fragments, apart from the losses of H radicals, are formed by the expulsion of CH_3 , C_2H_2 , C_2H_3 , and C_2H_4 neutral moieties. The ions of m/z 126, m/z 138, m/z 150, m/z 162, and m/z 174 are part of a series of fragment ions that are formed by the loss of C_nH_4 neutral species. This series is also associated with another series consisting of ions 1 u higher. At the lower mass end of the spectrum a number of ions belong to the $\text{C}_n\text{H}_2^{\bullet}$ (e.g., m/z 38, m/z 50, m/z 62, m/z 74, m/z 86, etc.) and $\text{C}_n\text{H}_3^{\bullet}$ -type (e.g., m/z 51, m/z 63, m/z 75, m/z 87, etc.) H-deficient ions, which are formed by the expulsion of C_nH_8 and C_nH_7 species, respectively. A similar trend of fragment ions is observed in the B/E-CAD spectrum of phenanthrene (see Figure 6).

These general patterns of the B/E-CAD spectra are consistent with those observed by the MIKE-CAD

Figure 5. The B/E linked-field CAD mass spectra of (a) pyrene and (b) fluoranthene. These two spectra are normalized with respect to m/z 187 and m/z 174, respectively.

Figure 6. The B/E linked-field CAD mass spectrum of phenanthrene.

experiments reported earlier [23]. In that study, it was proposed that the low-mass fragments must arise from a common intermediate having a linear structure with cumulated double bonds, and the precursor ions responsible for high-mass fragments may retain structural identity to a certain extent. Thus, it is expected that significant differences may exist in the relative abundances of the ions in the high-mass region of the spectra. The data obtained here for pyrene and fluoranthene support this expectation. For example, m/z 187 (i.e., the loss of CH_3) forms the base peak in the B/E-CAD spectrum of pyrene, whereas the loss of C_2H_4 to yield m/z 174 is the most prominent fragmentation of the M^+ ion of fluoranthene. The relative abundances of m/z 176, m/z 163, m/z 150, m/z 99, and m/z 74 also differ slightly in the two B/E-CAD spectra. The artifact peaks, possibly from the m/z 225 of the matrix, contribute significantly to the spectra of M^+ ions (m/z 228) of $\text{C}_{18}\text{H}_{12}$ isomers and, therefore, generality of the present technique to characterize isomeric hydrocarbons could not be tested. The distinction of the pyrene-fluoranthene pair by FAB-B/E-CAD may be regarded at best an exception until additional data are obtained by combined FAB and MIKE-CAD technique for several isomeric PAHs. The MIKE mode of MS/MS would eliminate these interfering peaks. Sulfolane also contributes artifact peaks to the B/E-CAD spectra of pyrene/fluoranthene and phenanthrene. The ions of m/z 55, m/z 69, m/z 121, m/z 137, and m/z 149 and m/z 55, m/z 69, m/z 111, m/z 121, m/z 123, and m/z 159 in Figures 5 and 6, respectively, are recognized as contributions from the matrix.

Conclusions

This study has demonstrated that FAB/MS, which is a proven analytical technique largely for polar molecules, can also be employed successfully to characterize less polar aromatic hydrocarbons. In order to obtain a good quality FAB mass spectrum, the analyte must be soluble in an appropriate matrix. Sulfolane was found to be a suitable FAB matrix for PAHs. The PAHs yield both M^+ and $(\text{M} + \text{H})^+$ ions. The slope of the curve between the $[(\text{M} + \text{H})^+]/[\text{M}^+]$ and the resonance energies of PAHs was found to be struc-

ture-specific. The FAB-desorbed ions are conveniently utilized in obtaining MS/MS spectra of PAHs.

Low vapor pressure of analytes is not a limitation in FAB/MS analysis. Therefore, the method reported here could be applied to high-mass PAHs, provided they are soluble in sulfolane. Analytical applications of FAB using sulfolane as a liquid matrix for other nonpolar compounds are also foreseen. The formation of odd-electron ions in sulfolane by FAB is quite significant. These FAB-formed ions may not have enough energy to isomerize. Fast atom bombardment, combined with CAD, thus holds potential for distinguishing isomeric compounds. Simultaneous generation of M^+ and $(\text{M} + \text{H})^+$ ions will be an added advantage in obtaining their MS/MS spectra.

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