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Comparison of the fragmentations of phenanthrene and anthracene by low-energy electron impact

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Abstract. We have measured sets of mass spectra for positive ions produced by low-energy electron impact on phenanthrene. Ions have been mass resolved using a reflectron time-of-flight mass spectrometer, and the electron impact energy has been varied from 0 to 100 eV in steps of 0.5 eV. Ion yield curves of most of the fragment ions have been determined by fitting groups of adjacent peaks in the mass spectra with sequences of normalized Gaussians. The aim of this paper is to provide a detailed comparison of phenanthrene with its isomer anthracene, for which we have published results in a previous paper [1]. Appearance energies for a selection of fragment ions of phenanthrene have been determined, and are compared with anthracene. The most significant differences are observed in the ion yield curves of the ions containing 12 carbon atoms. The ion yield curves of phenanthrene have higher maximum yields and lower appearance energies compared to anthracene. For the fragments containing 9 and 10 carbon atoms the phenanthrene yields are slightly lower, but the appearance energies are the same as for anthracene. Small differences in yields are also observed for the fragments with 6 and 7 carbon atoms. The double and triple ionization energies of phenanthrene have been determined and are in agreement with anthracene.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are relevant in astrophysical processes and in environmental chemistry, and these molecules have been the focus of much scientific research. Emission bands in the infrared spectra of many interstellar objects are commonly attributed to PAH molecules [2]. PAHs are susceptible to hydrogen attachment and are considered to play a key role as catalysts in the formation of molecular hydrogen in the interstellar medium [3, 4]. PAHs are also considered as essential components in the pathway to the origin of life [5]. In the Earth's environment, PAHs are widespread pollutants generated by the combustion of organic materials, and are of concern because many have toxic, mutagenic and/or carcinogenic properties [6, 7]. Electron induced processes are important in the interstellar medium where irradiation of molecules in interstellar dust grains by ultraviolet light and cosmic rays releases many secondary electrons which may themselves induce chemical reactions [8]. Electron induced processes are also important in gaseous environments such as discharges, gas lasers and the Earth's atmosphere [9].

Several research groups have investigated collision induced fragmentation of PAHs in collisions with photons, electrons and ions. We have given an overview of studies with anthracene ($C_{14}H_{10}$) and other PAHs in our previous paper [1]. The focus of this paper is on the electron induced fragmentation of phenanthrene and the comparison with its isomer anthracene.



For both phenanthrene and anthracene we have measured mass spectra for electron impact energies from 0 to 100 eV in steps of 0.5 eV. For anthracene we have obtained ion yield curves of most of the fragment ions, and we have determined the appearance energies for these ions, see ref. [1]. We identify groups of peaks in the mass spectra by the number of carbon atoms contained in the fragments. The most abundant groups in the mass spectra are group 14 (containing the parent ion at 178 u), and groups 7 and 6. In the mass spectra at 70 eV, 45% of the ion yield is contained in the parent ion group, 17% of the ion yield is in groups 8-13, and 38% of the ion yield is in groups 1-7. These percentages are the same for phenanthrene and anthracene.

We concluded [1] that the groups of anthracene fragments containing 8-13 carbon atoms provide evidence for hydrogen rearrangements during the fragmentation, involving retention or loss of one or two additional hydrogen atoms. Groups of fragments with 6 and 7 carbon atoms clearly show the presence of doubly-charged fragments. The smaller fragments with 1-4 carbon atoms all show broadened peaks, and above the double ionization threshold these fragments may for a large part be due to energetic charge separation fragmentations of doubly-charged anthracene. Group 5 is possibly partly attributable to doubly-charged fragments and partly to singly-charged fragments from charge separation reactions of doubly-charged anthracene.

On phenanthrene we noted [1]: “Comparison of the mass spectra of phenanthrene and anthracene by stepping through all electron energies does not reveal any clear systematic difference, and we suspect that there are no substantial differences in the electron-induced fragmentation pathways between anthracene and phenanthrene.” The purpose of the present paper is to examine the differences between phenanthrene and anthracene in more detail, and on close examination we do indeed find small differences in the fragmentation patterns of these isomers.

2. Experiment and data analysis

The experiment is contained in a vacuum chamber and consists of an oven containing anthracene or phenanthrene powder, a pulsed electron beam, and a reflectron time-of-flight mass spectrometer (see [1] for further details). A beam of anthracene or phenanthrene emerges from a capillary in the resistively heated oven (100 °C), and is crossed by a pulsed electron beam (0.3 μ s, 8 kHz). Positively charged fragments are extracted into a reflectron time-of-flight mass spectrometer. Data acquisition using LabVIEW code enables us to measure mass spectra as a function of electron impact energy. Ion yield curves are obtained by fitting adjacent peaks in the mass spectra with sequences of normalized Gaussians. Appearance energies of the fragment ions are determined by fitting onset functions to the ion yield curves.

3. Results and discussion

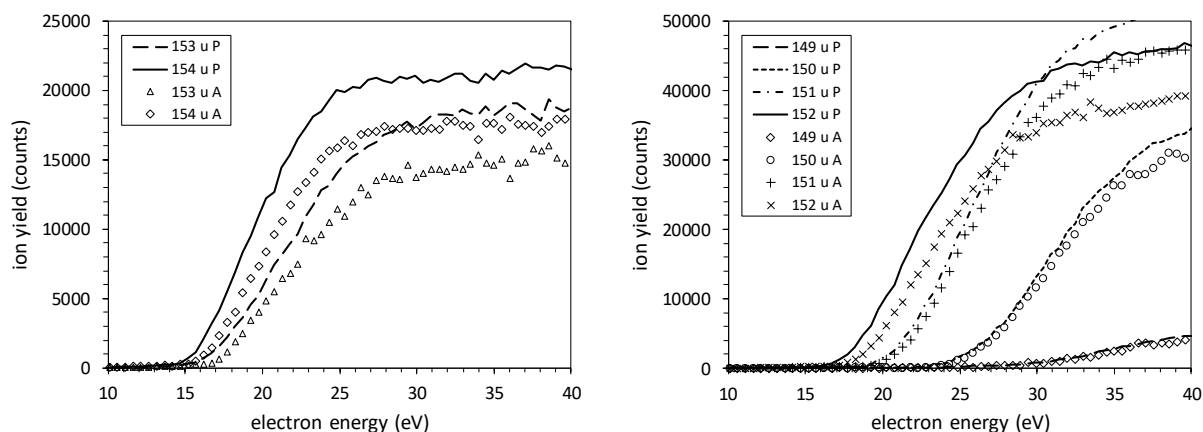
In order to be able to compare ion yield curves of phenanthrene and anthracene, we have multiplied all ion yields of anthracene with a normalization factor, such that the total ion yield (174-180 u) in the parent ion group of anthracene becomes the same as for phenanthrene. The estimated error in this normalisation factor is $\pm 2\%$. If, for a given ion, the ion yield curves for phenanthrene and for anthracene have the same shape and are within $\pm 2\%$ in agreement after normalisation, then we consider the ion yield curves for this ion to be the same.

Based on this normalisation, the ion yield curves for all fragments in groups 1 to 5, group 8, group 11 and group 13 are the same for anthracene and phenanthrene. Small differences are observed for some of the ion yield curves in the other groups. Table 1 shows phenanthrene to anthracene yield ratios averaged over 90-100 eV for those ions for which the ratio differs significantly from 1.

The most significant differences are observed in the ion yield curves of group 12. Figure 1 shows the ion yield curves for the six main ions in this group. Figure 1 shows that, apart from 149 u, the ion yield curves of phenanthrene have higher maximum yields and lower appearance energies. Table 2 compares the appearance energies.

Table 1. Phenanthrene to anthracene yield ratios averaged over 90-100 eV for several ions in groups 6, 7, 9, 10, and 12.

m/q	assignment	yield ratio
76 u	$C_6H_4^+ / C_{12}H_8^{2+}$	1.12 ± 0.01
76.5 u	$C_{12}H_9^{2+}$	1.09 ± 0.03
77 u	$C_{12}H_{10}^{2+} / C_6H_5^+$	0.88 ± 0.02
77.5 u	$C_{11}^{13}CH_{10}^{2+}$	0.99 ± 0.05
88 u	$C_7H_7^+ / C_{14}H_8^{2+}$	1.13 ± 0.02
88.5 u	$C_{14}H_9^{2+}$	1.07 ± 0.05
89 u	$C_{14}H_{10}^{2+} (/ C_7H_5^+)$	0.91 ± 0.01
89.5 u	$C_{13}^{13}CH_{10}^{2+}$	0.92 ± 0.04
114 u	$C_7H_7^+$	0.98 ± 0.09
115 u	$C_7H_7^+$	0.87 ± 0.04
125 u	$C_{10}H_5^+$	1.03 ± 0.05
126 u	$C_{10}H_6^+$	0.95 ± 0.02
127 u	$C_{10}H_7^+$	0.83 ± 0.03
128 u	$C_{10}H_8^+$	0.81 ± 0.03
149 u	$C_{12}H_5^+$	1.06 ± 0.05
150 u	$C_{12}H_6^+$	1.05 ± 0.01
151 u	$C_{12}H_7^+$	1.09 ± 0.02
152 u	$C_{12}H_8^+$	1.15 ± 0.02
153 u	$C_{12}H_9^+$	1.22 ± 0.04
154 u	$C_{12}H_{10}^+$	1.22 ± 0.02

**Figure 1.** The ion yield curves for group 12 fragments of phenanthrene (P) compared with those of anthracene (A). Apart from 149 u, the ion yield curves of phenanthrene have higher maximum yields and lower appearance energies.

The ion yield curves in figure 1 provide evidence for hydrogen rearrangements during the fragmentation. As noted already in ref. [1], if one would assume that the most abundant fragment in group 12 would be formed by the breakage of two C-C bonds in one of the terminal rings, one would expect that 152 u ($C_{12}H_8^+$ formed by C_2H_2 loss) would have the highest yield and the lowest appearance energy. Both in phenanthrene and in anthracene, 152 u and 151 u are the fragments with the highest abundance above 25 eV, but 154 u has the lowest appearance energy. This indicates that the transfer of two hydrogen atoms during the fragmentation resulting in C_2 loss is energetically favourable at low

electron energies. The 22% higher 154 u yield in phenanthrene indicates that the non-linear structure of the molecule enhances the probability of C_2 loss.

Table 2. Appearance energies (AEs) in eV for group 12 fragments of phenanthrene compared with those of anthracene from ref. [1].

m/q	assignment	AE	
		phenanthrene	anthracene
149 u	$C_{12}H_7^+$	28.1 ± 0.8	27.2 ± 0.6
150 u	$C_{12}H_8^+$	22.0 ± 0.3	23.0 ± 0.2
151 u	$C_{12}H_9^+$	17.8 ± 0.3	18.6 ± 0.2
152 u	$C_{12}H_{10}^+$	15.3 ± 0.3	17.0 ± 0.2
153 u	$C_{12}H_{11}^+$	14.6 ± 0.4	16.9 ± 0.2
154 u	$C_{12}H_{10}^+$	14.2 ± 0.3	15.5 ± 0.2
155 u	$C_{11}^{13}CH_{10}^+$	14.1 ± 0.4	16.4 ± 0.2

Comparing groups 9 and 10 in phenanthrene with anthracene, there are differences in the maximum yield for some of the ions in these groups, see table 1, but comparison of the ion yield curves shows that the appearance energies are the same. Figure 2 shows the ion yield curves for group 10. Contrary to group 12, here the phenanthrene yields for 128 u, 127 u and 126 u are lower for phenanthrene than for anthracene. The same is observed for 115 u in group 9.

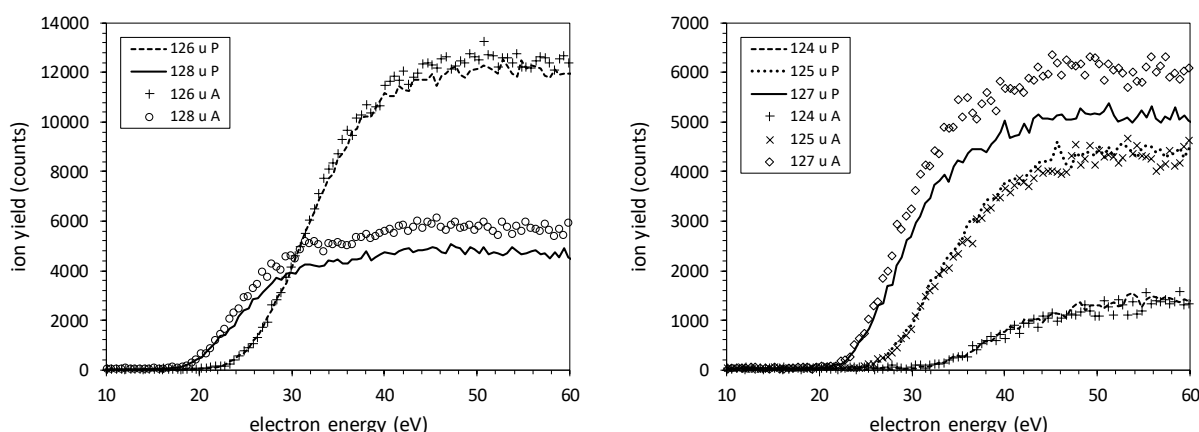


Figure 2. The ion yield curves for group 10 fragments of phenanthrene (P) compared with those of anthracene (A). Some of the ion yield curves of phenanthrene have lower maximum yields but the appearance energies are the same.

As noted already in ref. [1], one would expect that 126 u ($C_{10}H_6^+$ formed by C_2H_4 loss from one of the terminal rings) would have the highest yield and the lowest appearance energy. This is indeed the fragment with the highest abundance at higher electron energies, but in both phenanthrene and anthracene 128 u has a significantly lower appearance energy, indicating that the transfer of two hydrogen atoms during the fragmentation is energetically favorable at low electron energies. The 19% lower 128 u yield in phenanthrene indicates that this rearrangement is slightly less likely in the fragmentation of phenanthrene.

Both in phenanthrene and in anthracene, groups 6 and 7 clearly show the presence of doubly-charged fragments. In the phenanthrene mass spectra the 89.5 u / 89 u ratio is equal to the isotope ratio 179 u / 178 u, and because the only possible configuration for 89.5 u is $C_{13}^{13}CH_{10}^{2+}$, we conclude that the 89 u anthracene fragment is almost entirely $C_{14}H_{10}^{2+}$. Similarly, from the 77.5 u / 77 u ratio we conclude that 77 u is mostly $C_{12}H_{10}^{2+}$. We have observed the same for anthracene [1].

Table 1 also shows the phenanthrene to anthracene yield ratios for several ions in groups 6 and 7. Noticeable here is that the yield ratios are somewhat lower than 1 for 89 u and 77 u, and somewhat higher than 1 for 88 u and 76 u. The same is observed for the half-integer fragments. This indicates that doubly-ionised anthracene has a slight tendency to retain one more hydrogen atom compared to phenanthrene.

We have also determined the double and triple ionization energies of phenanthrene. Directly to the left of the 60 u peak in group 5 is a small but distinct peak at 59.333 u, attributed to triply-charged phenanthrene. Table 3 compares the ionisation energies with those of anthracene. The triple-ionisation energies are in agreement. The weighted average of the double ionisation energies of phenanthrene is 20.4 ± 0.4 eV, slightly lower than 20.8 ± 0.4 eV for anthracene.

Table 3. Double and triple ionisation energies of phenanthrene in eV compared with those of anthracene from ref. [1].

m/q	assignment	AE	
		phenanthrene	anthracene
59.333 u	$C_{14}H_{10}^{+++}$	45.6 ± 0.4	45.5 ± 0.5
89 u	$C_{14}H_{10}^{++}$ ($/ C_7H_5^+$)	20.1 ± 0.9	20.2 ± 0.7
89.5 u	$C_{13}^{13}CH_{10}^{++}$	20.5 ± 0.5	21.1 ± 0.5

4. Conclusions

We have closely examined the mass spectra and the ion yield curves of phenanthrene and its isomer anthracene. The mass spectra are very similar, showing that the overall fragmentation pathways for both molecules are very similar. On close examination we have found several small differences. The most significant differences are in group 12, for which the ion yield curves of phenanthrene have higher maximum yields and lower appearance energies. For some of the ions in groups 9 and 10 the anthracene yields are somewhat higher than the phenanthrene yields. Ion yields in groups 6 and 7 show that doubly-ionised anthracene has a slightly higher tendency to retain one more hydrogen atom than phenanthrene. The double and triple ionization energies of phenanthrene and anthracene are the same within experimental error.

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