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NEGATIVE ION CHEMICAL IONIZATION MASS SPECTRA OF POLYCYCLIC AROMATIC HYDROCARBONS

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Negative ion chemical ionization mass spectra were evaluated for 21 polycyclic aromatic hydrocarbons. The spectra exhibited some peculiar peaks corresponding to $(M-H)^-$, $M^{\overline{\cdot}}$ and MH^-. These ions were found to be useful to identify and detect such polycyclic aromatic hydrocarbons and also to distinguish the isomers.

The negative ion chemical ionization (NCI) mass spectra of some polycyclic aromatic hydrocarbons (PAHs) have been reported by Hunt using an oxygen/hydrogen(9:1) reagent gas to generate $O_2^{\overline{\cdot}}$ as a reactant ion .[1] However , the reagent gas cannot be used in an ion source due to oxidation of a filament. Furthermore the method proved to be unappropriate to give useful positive ion chemical ionization (PCI) spectra. In contrast , methane as a reagent gas is not only favorable for practical use but also attractive for both the PCI and NCI mass spectrometry. In the present work , the NCI spectra with methane were first evaluated for PAHs with the intention of disclosing the characteristics and also the possibility of identifying the PAHs.

PAH samples were dissolved in benzene to prepare 1 $\mu g \cdot \mu \ell^{-1}$ solutions. One to five $\mu \ell$ of the solutions were introduced into a Finnigan 4023 GC/MS/DS equipped with an OV-17 column (2 mm i.d. x 0.5 m). The spectra were measured using 99.95% methane over the range from m/z 70 to the molecular weights plus 50 , at 1 sec/scan and a 1 sec interval. Ion source temperature and ionization chamber pressure were maintained at 250°C and 0.20 Torr. Electron accelerating voltage was fixed at 70 V.

Negative reactant ions were observed at m/z 12 to 17 corresponding to C^- , CH^- , $CH_2^{\overline{\cdot}}$, CH_3^- , $O^{\overline{\cdot}}$ and OH^- when methane was used as the reagent gas. Their relative intensities (%Σ) were about 1 , 2 , 7 , 38 , 48 and 2 % , respectively. It seemed that the C^- ions were produced by electron impact , the $O^{\overline{\cdot}}$ ions by the reaction of background O_2 with C^- ions [2] and the OH^- ions by the reaction of background H_2O with H^- ions gene-

Table 1 Relative ion intensities (%Σ)[a] of PAHs in negative ion chemical ionization mass spectra (CH_4 reagent gas)

No.	Compound	Formula	MW.	$(M-H)^-$	$M^{\cdot-}$	MH^-	Others(m/z)
1	Indene	C_9H_8	116	91.1*	8.8	-	
2	Naphthalene	$C_{10}H_8$	128	68.5*	13.9	13.2	
3	Azulene	$C_{10}H_8$	128	-	85.9*	13.1	
4	Acenaphthylene	$C_{12}H_8$	152	11.2	59.3*	26.4	
5	Fluorene	$C_{13}H_{10}$	166	77.7*	10.9	2.3	6.0(180)
6	Anthracene	$C_{14}H_{10}$	178	22.6	8.5	57.5*	
7	Phenanthrene	$C_{14}H_{10}$	178	48.1*	8.5	31.9	2.6(208)
8	Fluoranthene	$C_{16}H_{10}$	202	3.2	70.5*	22.6	
9	Pyrene	$C_{16}H_{10}$	202	28.3	8.5	53.0*	
10	Naphthacene	$C_{18}H_{12}$	228	21.7	52.0*	22.1	
11	Chrysene	$C_{18}H_{12}$	228	52.5*	12.1	27.3	
12	Triphenylene	$C_{18}H_{12}$	228	54.7*	12.1	26.7	
13	Benz(a)anthracene	$C_{18}H_{12}$	228	19.2	18.3	52.0*	1.2(226)
14	Benzo(c)phenanthrene	$C_{18}H_{12}$	228	42.3*	9.9	31.2	8.9(226)
15	Perylene	$C_{20}H_{12}$	252	9.8	62.3*	23.6	
16	Benzo(a)pyrene	$C_{20}H_{12}$	252	9.8	66.5*	20.7	
17	Benzo(e)pyrene	$C_{20}H_{12}$	252	23.6	13.9	49.6*	2.1(250)
18	Benzo(b)fluoranthene	$C_{20}H_{12}$	252	3.1	76.4*	17.6	
19	Benzo(j)fluoranthene	$C_{20}H_{12}$	252	-	80.2*	16.6	
20	Picene	$C_{22}H_{14}$	278	44.2*	11.8	34.1	
21	Dibenz(a,h)anthracene	$C_{22}H_{14}$	278	27.8	16.7	33.7*	

a) These values were not corrected for ^{13}C contributions.

* ; base peak , - ; less than 1 percent

rated from CH_4.[1] The total amount of these ions were about 2 % of the positive reactant ions such as CH_5^+, $C_2H_5^+$ and $C_3H_5^+$. Besides , a large number of thermal electrons and hydride ions which were not identified may also participate in the formation of the negative ions in the ion source under the conditions used.

The spectra of PAHs are shown in Table 1 as relative ion intensities. Major ions were $(M-H)^-$, $M^{\cdot-}$ and MH^- in all cases , and $(M-2H)^{\cdot-}$ and $(M+m)^-$ were formed in certain compounds. $(M-H)^-$ ions were produced by proton abstraction from a molecule in question , since the proton affinities of the reactant ions such as $O^{\cdot-}$ and H^- are fairly large , i.e. 1590 $KJ\cdot mol^{-1}$ for $O^{\cdot-}$ and 1673 $KJ\cdot mol^{-1}$ for H^-.[3] The $(M-H)^-$ ions were responsible for base peaks in some PAHs spectra and smaller peaks in others. Therefore , the $(M-H)^-$ ions may be useful to distinguish PAHs. As molecular ions , $M^{\cdot-}$, are produced primary by resonance electron capture reactions ,[4] $M^{\cdot-}$ ions are observed more abundantly for PAHs of larger electron affinity.

MH^- ions were observed with high intensity in some PAHs spectra, although the formation of MH^- ions have not been reported in literature, except for the case of 7,7,8,8-tetracyanoquinodimethane by McEwen.[5] He pointed out that MH^- ions are formed by the fast radical reactions such as

$$M^{\cdot-} + H \longrightarrow MH^-$$

$$M^{\cdot-} + CH_3\cdot \longrightarrow (M+CH_3)^-$$

The predominance of such MH^- ions suggests that the radical (H) concentration greatly exceeds the reactant ion and thermal electron concentrations in a methane plasma and the rate of the radical addition reaction approaches a diffusion controlled rate. Although the formation process of MH^- ions from PAHs seems to be similar to that of McEwen's estimation, other reactions such as

$$M + H^- \longrightarrow MH^- \quad , \quad M + CH_3^- \longrightarrow MH^- + CH_2$$

seem also possible to occur in addition to the above process, since some unsaturated compounds show positive hydride affinities.[6]

Table 2 Base peaks and ion intensity ratios[a)] of PAHs

No. of Compound	Base peak	N/P(base peak)	N/P(total)
1	$(M-H)^-$	0.14	0.10
2	$(M-H)^-$	0.04	0.04
3	$M^{\cdot-}$	0.76	0.59
4	$M^{\cdot-}$	0.55	0.55
5	$(M-H)^-$	0.21	0.16
6	MH^-	0.13	0.10
7	$(M-H)^-$	0.10	0.13
8	$M^{\cdot-}$	0.59	0.44
9	MH^-	0.13	0.13
10	$M^{\cdot-}$	0.18	0.11
11	$(M-H)^-$	0.10	0.09
12	$(M-H)^-$	0.14	0.15
13	MH^-	0.05	0.05
14	MH^-	0.07	0.08
15	$M^{\cdot-}$	0.43	0.36
16	$M^{\cdot-}$	1.2	0.89
17	MH^-	0.07	0.07
18	$M^{\cdot-}$	4.8	3.4
19	$M^{\cdot-}$	12	7.7
20	$(M-H)^-$	0.14	0.22
21	MH^-	0.12	0.18

a) Intensity ratios were determined with the GC/MS ajusted to give the $M^{\cdot-}/MH^+$ ratio to be 20 ± 2 with 1 ng injection of 9,10-anthraquinone.

Ion intensity ratios of negative ions to positive ions (N/P) are given in Table 2. In general, N/P were less than 1, but those of azulene, benzo(a)pyrene [B(a)P], benzo(b)fluoranthene and benzo(j)fluoranthene were in the range 1 to 10, on account of the relatively high electron affinities of these compounds, e.g. 0.77 eV (calcd. value) for azulene, 0.88 eV for B(a)P.[7],[8] Furthermore, considerable difference in N/P values was observed among isomers, and this made possible to distinguish the isomers of PAHs.

While the base peaks were MH^+ in all cases and the total ion intensities scarcely varied in the PCI spectra,[9] the base peaks in the NCI spectra were $(M-H)^-$, $M^{\bar{\cdot}}$ or MH^- and the total ion and/or the specific ion intensities varied as much as two orders of magnitude. For example, the absolute intensity of $M^{\bar{\cdot}}$ in B(a)P was about 50 times higher than that of benzo(e)pyrene [B(e)P]. Thus B(a)P was confirmed to be detected and determined separately from B(e)P by the use of GC/NCIMS with a short capillary column.

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