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OXYGEN SENSITIZED RESPONSES OF THE ELECTRON CAPTURE DETECTOR AND ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETER TO DERIVATIZED ISOMERS OF AMINOANTHRACENE AND AMINOPHENANTHRENE

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SUMMARY

A comparison of the effect of oxygen on the responses of an electron capture detector and an atmospheric pressure ionization mass spectrometer to the trifluoroacetic anhydride derivatives of the eight isomers of aminoanthracene and aminophenanthrene is made. The results indicate that, while all isomers undergo the same reactions in the presence of electrons and O_2^- negative ions, the ratio of the rates of electron attachment and O_2^- charge exchange is very dependent on substituent location and provides a basis for distinguishing between individual members of this isomeric group.

INTRODUCTION

We recently reported[1] the use of oxygen-sensitized electron capture detection (ECD) for the analysis of a wide range of polycyclic aromatic amines (PAAs) and hydroxides, and the magnitude of the ECD response increase caused by oxygen was shown to depend quite strongly on subtle structural variations of the analyte. In atmospheric pressure ionization mass spectrometry (APIMS) the apparatus can be constructed in a manner such that the conditions within the ion source are nearly identical to that of ECD[2,3]. Therefore, the responses of ECD and APIMS to sample molecules are closely related and APIMS can provide insight into the electron–ion–molecule interactions which cause the ECD responses. We report here the ECD and APIMS responses of a set of eight isomeric PAAs under identical conditions of their ionization volumes. The PAAs consist of all possible substitution isomers of aminoanthracene and aminophenanthrene, and each is first converted into its trifluoroacetic anhydride derivative in order to enhance its propensity for forming negative ions.

EXPERIMENTAL

The 1-, 2- and 9-aminoanthracenes and 9-aminophenanthrene were purchased

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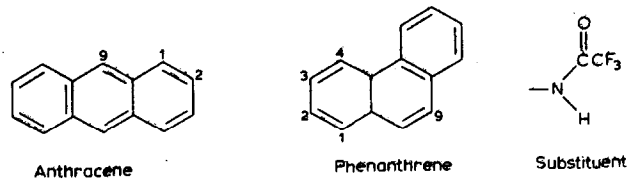
from Aldrich Chemical Company. The 1-, 2-, 3- and 4-aminophenanthrenes were kindly supplied by Doug Later and Milton Lee of Brigham Young University.

The PAAs were derivatized using a procedure similar to that used by Later *et al.*[4]. Approximately 10–20 mg of each compound were dissolved in 10 ml of benzene. A 2-ml aliquot was placed in a 5-ml flask with 0.1 ml of 0.05 *M* triethylamine in benzene. Next, 30 μl of trifluoroacetic anhydride (Aldrich) were added to the mixture. The flask was stoppered and heated in a water-bath at 60°C for 15 min. The reaction mixture was then cooled for several minutes, 1 ml of 10% aqueous ammonia solution was added to terminate the reaction and the mixture was shaken for 5 min. Finally, the organic and aqueous phases were allowed to separate and the benzene layer containing the derivatized amines was recovered and diluted in a known volume of benzene for subsequent gas chromatographic (GC)–ECD and –APIMS analyses. All organic solvents were of pesticide grade, the water was deionized and doubly distilled and the derivatization reagents were used without additional purification. The stock ammonia solution (Baker) was extracted three times with equal portions of methylene chloride to remove any organic contaminants.

The gas chromatograph was a Varian 3700 with constant-current pulse-modulated operation of its ^{63}Ni electron capture detector. A 15-m SE-52 capillary column of 0.25 mm I.D. was used with He as the carrier gas. The flow-rate of nitrogen make-up gas was 40 ml/min. When desired, oxygen was added by combining the nitrogen make-up gas with about 4 ml/min of nitrogen containing 2.0% oxygen. An oxygen concentration of 0.20% is thereby maintained in the doped detector. From one determination to another, the precise level of oxygen was adjusted by fine-tuning the oxygen flow until a preselected magnitude of baseline frequency was observed. The detector was maintained at 250°C. The GC injector temperature was 220°C and the oven temperature was held constant at 200°C.

A splitless injection of 0.4 μl was used where each injection contains a sample concentration sufficient to produce small but measurable peaks. It was estimated that approximately 10–100 pg of analyte were present in each injection. Each prepared derivative was analyzed at least three times, both with and without oxygen. For a given analysis, the peak heights were reproducible to within 5–10%. The averages of these repeated analyses were used for the response enhancements reported here. Retention times on our capillary column were also determined for all the derivatives using a flame ionization detector. Mass spectral verification of each derivative was also performed by using conventional (electron impact) GC–MS techniques.

The atmospheric pressure ionization mass spectrometer used here has been described previously[3]. An isothermal gas chromatograph with a 1.5-ft. packed column containing 4% OV-101 on Chromosorb W was used for sample introduction. The temperature of the ion source was 250°C and the column temperature was 190°C. The carrier gas was nitrogen at a flow-rate of 30 ml/min. These chromatographic parameters were chosen for the APIMS measurements so that the analyte eluted slowly for almost 1 min thus allowing its ion chemistry to be carefully examined. Again, by combining the carrier gas with about 3 ml/min of nitrogen containing 2.0% oxygen after the column, an oxygen concentration of 0.20% in nitrogen was maintained in the ion source when desired. Negative ions produced with and without oxygen present in the carrier gas were identified both by single-ion monitoring of the chromatographic effluent and by performing mass scans during the elution of samples.



Scheme 1. Structure, numbering system and substituent for compounds studied.

RESULTS AND DISCUSSION

The structures of the eight compounds studied are indicated in Scheme 1. The ECD responses to each of these were obtained as shown in Fig. 1. Chromatograms such as these were recorded without and then with 0.20% oxygen in the detector at a temperature of 250°C. The ratio of the ECD responses to each PAA derivative with and without oxygen was thereby determined for at least three separate sets of measurements. The average values of these oxygen-induced response enhancements (REs) are shown in Table I. It is seen that a very wide range of RE values are obtained, from a low value of 1.0 (no enhancement at all) for 2-aminoanthracene to an enhancement of 107 for 3-aminophenanthrene. Furthermore, the RE values measured for the other members of this isomeric group are spread almost evenly throughout the range so that each isomer is uniquely indicated by its RE fingerprint.

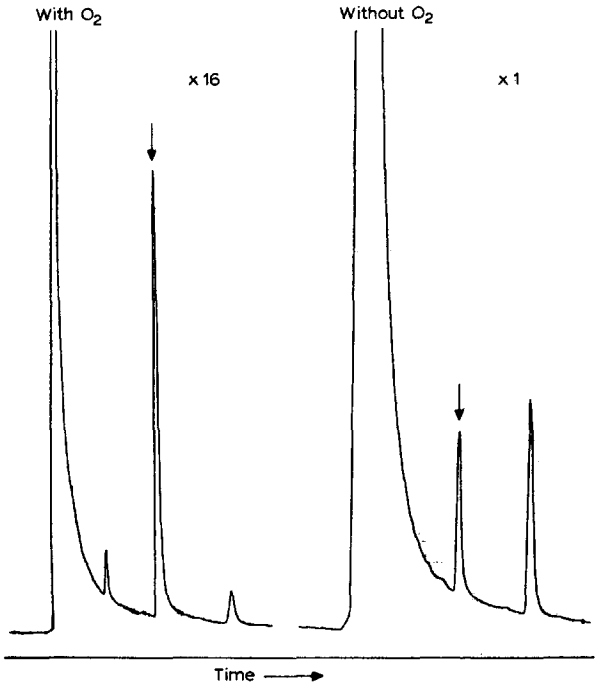


Fig. 1. ECD chromatograms from which oxygen-induced response enhancements are determined. The arrows mark the point of elution of the 9-aminophenanthrene derivative. Detector temperature is 250°C; doping O_2 concentration is 0.20%.

TABLE I

OXYGEN-INDUCED ECD AND APIMS RESPONSE ENHANCEMENTS FOR THE TRIFLUOROACETIC ANHYDRIDE DERIVATIVES OF AMINOANTHRACENES AND AMINOPHENANTHRENES

ECD and APIMS source temperature is 250°C. Oxygen concentration in doped detector is 0.20%. Reproducibility of ECD and APIMS enhancement measurements is approximately ±7% and ±15%, respectively.

Amine	*Response enhancements*	
	ECD	*APIMS*
2-Aminoanthracene	1.0	1
1-Aminoanthracene	3.1	2
9-Aminoanthracene	8.1	4
1-Aminophenanthrene	19	9
4-Aminophenanthrene	34	13
9-Aminophenanthrene	43	16
2-Aminophenanthrene	72	20
3-Aminophenanthrene	107	29

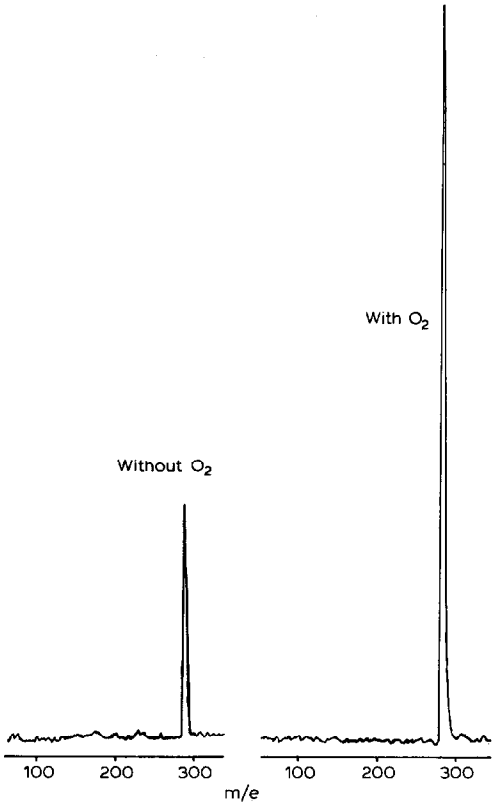


Fig. 2. Negative ion API mass spectral scans taken during elution of the derivative of 9-aminophenanthrene without and with 0.20% added oxygen.

Each PAA was then analyzed by GC–APIMS and conditions within the ion source were set nearly identical to those of the electron-capture detector. In Fig. 2, for example, API mass spectral scans during the elution of the 9-aminophenanthrene derivative with and without added O_2 are shown. As in this case, the striking feature of all mass spectra observed is that under these conditions, with or without added oxygen, the only negative ions observed for this entire set of molecules were due to the parent, M^-, ion at $m/e = 289$ and its ^{13}C isotope peak at $m/e = 290$. (The isotope peak at $m/e = 290$ is not resolved from the base peak at 289 in Fig. 2 because the response time of the pulse counting detector is too slow to follow the relatively fast mass scan rate used here. With slower scanning over the parent ion mass region, alone, these two peaks are resolved and exhibit the expected 5.7 to 1.0 ratio.) No fragment or oxygen adduct ions were seen for these compounds in spite of their frequent appearance elsewhere in the atmospheric pressure ionization of other aromatic hydrocarbons[5,6]. These results suggest that the ionization of these molecules under oxygen-free conditions occurs by simple electron capture

$$e^- + A \rightarrow A^- \quad (1)$$

and with added oxygen occurs by charge transfer

$$O_2^- + A \rightarrow A^- + O_2 \quad (2)$$

to form the parent negative ion in both cases. Clearly, the mass spectra, themselves, provide no information from which isomer identity can be determined.

By performing paired single ion monitoring experiments such as that shown in Fig. 3, the enhancement of the APIMS parent negative ion signal caused by oxygen was measured for each isomer. The magnitude of this oxygen-induced enhancement (average of at least three determinations) is also shown in Table I alongside the ECD data discussed above. As with the ECD results, the magnitude of the APIMS enhancements of parent negative ion intensities were also very dependent on the structural differences within this isomeric group. It is also evident in Table I that the relative order of the observed ECD and APIMS enhancements is the same. For both methods the 2-aminoanthracene derivative shows the lowest enhancement, the 3-aminophenanthrene derivative shows the greatest enhancement, while the enhancements of the other six compounds are relatively evenly spread throughout the observed ranges. That the oxygen-induced enhancements measured by ECD are uniformly greater than those measured by APIMS is expected. This is thought to be largely due to the nature of the frequency-based response of constant-current ECD which causes the observed ECD response enhancement to exceed the actual ratio of rates in reactions 1 and 2. This effect has been previously described in a detailed model of O_2-doped ECD[7]. The fact that the order of reactivity of the compounds listed in Table II is the same for both methods provides additional support for that model.

In summary, the experiments reported here suggest that reactions 1 and 2 provide the basis of the responses observed in the atmospheric pressure ionization cells and that the only measurable characteristic of these reactions that provides an indication of compound identity is the ratio of the rate constants for reactions 1 and 2. This measurement of rate ratio appears to be more easily and reproducibly ob-

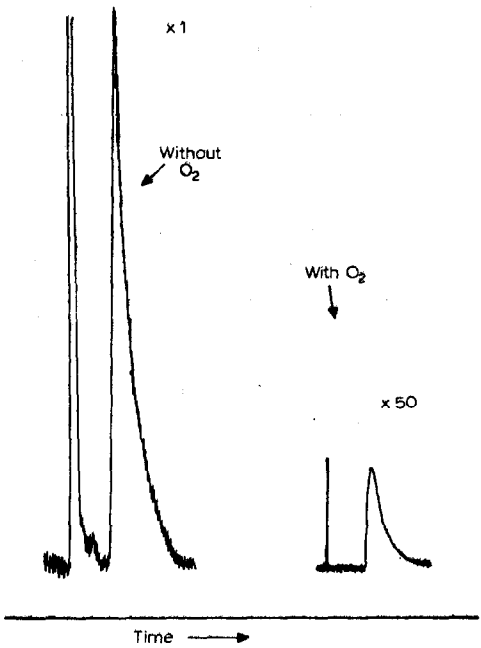


Fig. 3. Single-ion APIMS monitor of the negative ion intensity at m/e = 289 for the 1-aminophenanthrene derivative without and with 0.20% added oxygen at source temperature 250°C.

tained by ECD than by APIMS. This study further supports our earlier suggestion[7] that an analysis scheme which provides normal and oxygen-enhanced ECD responses to a chromatographic effluent (using either separate, paired GC analyses or a single analysis with an effluent splitter and two detectors) provides an instrumentally simple, but powerful aid for the identification of the components of complex organic mixtures by gas chromatography.

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