ALTERATION OF THE ELECTRON-CAPTURE DETECTOR RESPONSE TO POLYCYCLIC AROMATIC HYDROCARBONS BY OXYGEN DOPING OF THE CARRIER GAS

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SUMMARY

A constant-current electron-capture detector (ECD) has been used to study the effects of oxygen added intentionally to the carrier gas on the response of the instrument to five polycyclic aromatic hydrocarbons (PAHs). At a detector temperature of 250°C the responses of anthracene, pyrene and 1,2-benzanthracene are increased very substantially, while those of phenanthrene and tetracene are increased only slightly. The basis of these observations is discussed, and mass spectrometric measurements of the negative ions formed in an ECD as a result of oxygen doping are reported. It is suggested that the structure-dependent oxygen-caused response enhancements observed for PAH molecules might assist in the identification of these in their analysis by gas chromatography.

INTRODUCTION

Because of the carcinogenic properties of certain polycyclic aromatic hydrocarbons (PAHs), the analysis of this class of compounds in the environment has received a great deal of attention in recent years. Very early in the development of the electron-capture detector (ECD) for gas chromatographic (GC) detection, it was noted that PAHs produce responses with this detector that are strong relative to non-aromatic hydrocarbons[1,2]. In the analysis of atmospheric particulates, the ECD has been shown to provide useful complementary information regarding the presence of PAHs when paired with simultaneous flame-ionization detection (FID)[3,4].

In our first investigation of the effects of oxygen intentionally added to the carrier gas of a GC–ECD system[5], it was noted that the ECD response to certain compounds, one being anthracene, was significantly increased with added oxygen. Since then we have characterized the effects of oxygen doping on the responses to halogenated compounds and have described instrumental effects to be expected (baseline current, noise, basis of response, etc.)[6,7]. It was deduced in these studies that increased responses occur due to the assistance provided by O_2^- in the formation of stable negative ions of the sample molecule. Since then, a similar method of

altering ECD responses, by the addition of nitrous oxide to the carrier gas, thereby creating a reagent flux of O^- rather than O_2^- ions, has also been described[8].

In this paper we report the effect of addition of oxygen to the carrier gas on the response of a pulsed ECD to several PAHs. It will be shown that response enhancement caused by the presence of oxygen is dependent on the structures of the PAHs. The oxygen-caused response enhancements are discussed relative to the differing reactivities of each PAH toward the thermal electron and the negative ion, O_2^-. Using atmospheric pressure ionization mass spectrometry (API-MS), identifications of the oxygen-incorporated negative ions for several PAHs are reported.

EXPERIMENTAL

The gas chromatograph used was a Varian 3700 Aerograph with constant-current, pulse-modulated operation of a ^{63}Ni detector. The carrier gas was ultra-high-purity nitrogen (Matheson Gas Products, East Rutherford, NJ, U.S.A.), maintained at a flow-rate of 40 ml min^{-1}. The column was a 1.5 ft. × 1/8 in. I.D. stainless-steel tube packed with 3% OV-101 on Chromosorb W.

Oxygen was mixed with the carrier gas by one of two different methods. In the first, oxygen was mixed into a 5-l stainless-steel reservoir which was part of the carrier gas flow system. With this approach, described in detail previously[6], the oxygen is present in the carrier gas prior to the injector or column. Because of the ease with which the oxygen concentration can be reliably controlled and varied with this approach, it was used for most analyses. Oxygen was also added as a make-up gas after the column just prior to the detector by combining the carrier gas flow at this point with about 4 ml min^{-1} of nitrogen containing 2% of oxygen. The results obtained for each PAH were found to be independent of the choice of method for introducing oxygen.

Most of the measurements reported here were obtained at a detector temperature of 250°C. The high temperatures available to the ^{63}Ni ionization source were tested (300 and 350°C), but the results were unsatisfactory for purposes of analysis. Reproducibility and sensitivity, both with and without added oxygen, were much less favorable than at 250°C. The responses to some of the PAHs, in fact, were observed to be inverted. The choice of 250°C was made arbitrarily so as to maintain a detector temperature 50°C above the maximum column temperature.

The compounds studied were purchased from commercial suppliers. Standards of each were prepared by dilution into benzene. Aliquots of 2 μl were syringe-injected into the normal injection ports. Sample sizes sufficient to produce small, but easily measured peaks were used. These were about 200, 20, 100, 20 and 1 ng per sample injection for phenanthrene, anthracene, pyrene, 1,2-benzanthracene and tetracene, respectively. The retention time of each substance was determined using an FID prior to its ECD analysis. In comparing the detection limits obtainable by the ECD (undoped) with those of the FID, it was found that anthracene, pyrene and 1,2-benzanthracene produced similar signal-to-noise responses for a given sample with the two detectors. The relative ECD response of phenanthrene is about 0.02 and that of tetracene about 100 times that obtained with the FID.

RESULTS AND DISCUSSION

Fig. 1 shows the results of the repeated GC–ECD analysis of a prepared standard containing 20 ng per injection of 1,2-benzanthracene where the oxygen content of the carrier gas was increased with each analysis. The first peak, corresponding to 1,2-benzanthracene, increases in magnitude continuously with oxygen addition. Two other peaks are very prominent in the first chromatogram, but do not increase significantly with oxygen addition, and in the later chromatograms are nearly lost in the attenuation increase and increased baseline noise. These two peaks are thought to reflect the presence of contaminants in the sample, possibly oxygenated aromatic molecules, which have ECD response coefficients much higher than those of the PAHs. These responses are not increased as significantly by oxygen addition (see the case of anthraquinone, for example, ref. 5).
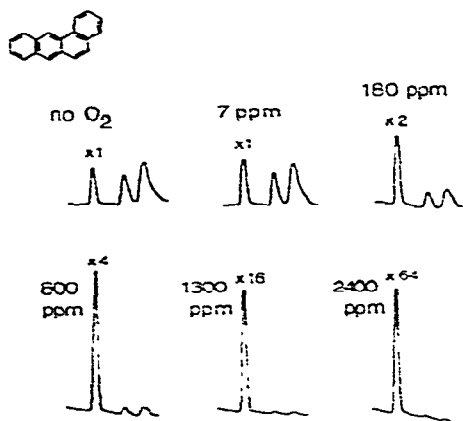

Fig. 1. Response of ECD to a 20-ng 1,2-benzanthracene sample with various amounts of oxygen added to the carrier gas. The second and third peaks observed in each analysis are due to impurities.

Experiments similar to that shown in Fig. 1 were performed for five PAHs at a detector temperature of 250°C. The results are shown in Fig. 2, where the oxygen-caused response enhancement minus 1.0 (so that all curves pass through the origin) is plotted against oxygen concentration. The response enhancement values were determined from the ratio of peak heights with and without oxygen. It can be seen in Fig. 2 that anthracene, pyrene and 1,2-benzanthracene exhibit large response increases with added oxygen. The responses of tetracene and phenanthrene increase only slightly.

The use of higher detector temperatures does not seem to offer any advantages for PAH analysis. The ECD response is weakened by increased temperature, as expected for a resonance capture-electron attachment process[2]. We find, in fact, that at detector temperatures in excess of 300°C, reverse responses are observed for some PAHs (this is discussed further for anthracene, below.) The magnitude of the oxygen-caused response also is observed to be lower at higher detector temperatures. This was expected, as the instantaneous O_2^- concentration is lowered by increasing the gas temperature[7].
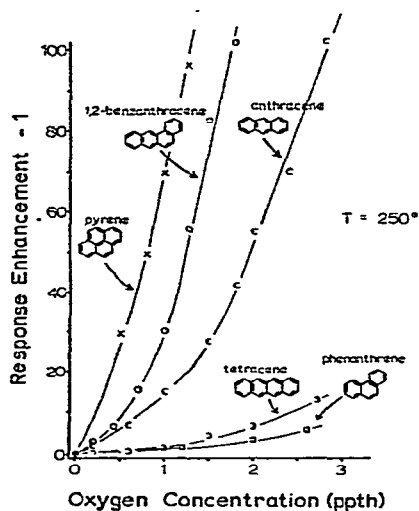
Fig. 2. Response enhancements for each PAH as a function of oxygen concentration in the carrier gas.

To establish the reason why response enhancements do or do not occur in each instance in Fig. 2, it is necessary to consider individually the relative ECD responses (R_{ECD}) and the relative oxygen-caused responses (R_{O_2}) in each instance. The latter value can be obtained from the measured response enhancements (RE) and R_{ECD} using the relationship $R_{O_2} = R_{ECD} (RE - 1)$ (ref. 7). Values for R_{ECD}, RE (at 2 parts per 10^3 of oxygen), and R_{O_2} shown in Table I are normalized with respect to the corresponding phenanthrene values. By inspection of the five compounds listed in Table I, the basis of measured RE values in Fig. 2 can be better appreciated. For example, while phenanthrene has a low R_{ECD}, its R_{O_2} is also the lowest and its RE is only 4.6. The reason for the relatively low RE value of 7.4 for tetracene, on the other hand, is due entirely to its normally high R_{ECD}, as its R_{O_2} value is the highest of those observed. Large response enhancements are observed for anthracene, pyrene

TABLE I

ELECTRON-CAPTURE RESPONSES, RESPONSE ENHANCEMENTS, RELATIVE RATES OF REACTION WITH O_2^- AND CALCULATED HÜCKEL PARAMETERS FOR EACH PAH

R_{ECD} = normal ECD molar responses relative to phenanthrene at 250°C; RE = response increase caused by presence of 2.0 parts per thousand of oxygen in the carrier gas; R_{O_2} = rate of oxygen-caused reaction relative to case of phenanthrene; E_{LUMO} = calculated energy of lowest unoccupied molecular orbital; L^- = calculated resonance energy lost by removal of a specific carbon atom from the π-electron system.

PAH	R_{ECD}	RE	R_{O_2}	E_{LUMO}	L^-
Phenanthrene	1	4.6	1	0.60β	2.30β
Anthracene	57	56	870	0.41β	2.01β
Pyrene	14	185	720	0.44β	2.19β
1,2-Benzanthracene	130	134	4800	0.45β	2.05β
Tetracene	4500	7.4	8000	0.29β	1.93β

and 1,2-benzanthracene because their normal ECD responses are low relative to that of tetracene, while their reactivity towards O_2^- is high.

We also measured with a specialized mass spectrometer the negative ions thought to accompany the electron-capture reactions of the PAHs. The ion source of this instrument is, in fact, a pulsed ECD at 1 atm pressure and has been described in detail elsewhere[9,10]. Fig. 3 shows an analysis of anthracene with this instrumentation using a source temperature of 280°C. Both the pulsed ECD function of the ion source and the single-ion monitor function of the mass spectrometer are shown as a function of the amount of oxygen added to the nitrogen carrier gas. The paired ECD and mass spectral traces were obtained in separate rather than simultaneous determinations. This is necessary because with pulses applied to the cell for the ECD function, the negative ions formed within the cell cannot be observed by the mass spectrometer under certain conditions. This effect, which relates to the fundamental physics of the ECD, is described in detail elsewhere[10]. To observe the negative ion chemistry independent of this complication, the source must be pulse-free.
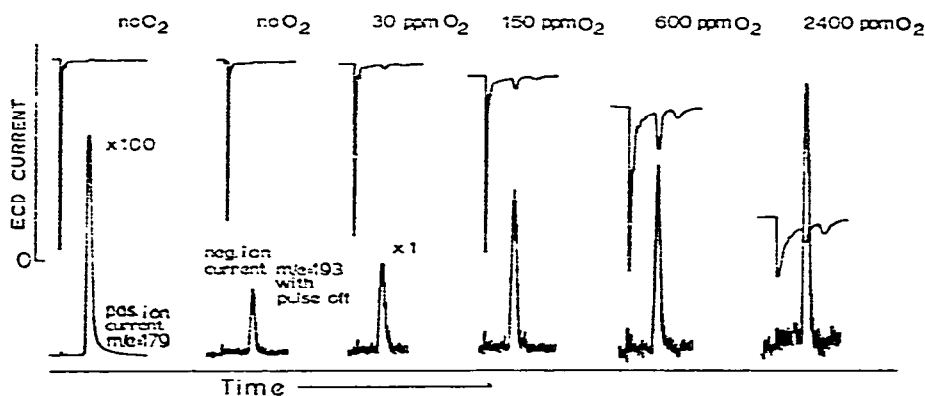

Fig. 3. Repeated analyses of a 20-ng sample of anthracene using a specialized ECD–API-MS detector for various concentrations of oxygen added to the carrier gas. Along with the ECD response, the intensity of either the M + H positive ion or the M + O − H negative ion was monitored. Source temperature: 280°C.

With no oxygen added, the ECD trace in Fig. 3 indicates a reverse peak at 280°C as anthracene elutes from the column. Reverse peaks such as these have frequently been observed for the PAHs at elevated temperatures in purified nitrogen carrier gas. At a temperature of 250°C, normal ECD responses are observed. In Fig. 3 a temperature of 280°C was chosen to illustrate this reversal and to suggest its cause. With no oxygen added, the positive ion signal at m/e 179 (the M + 1 peak for anthracene) has also been monitored. As this anthracene sample (10 ng) passes through the source, the positive ion mass spectral signal at m/e 179 reaches a saturation level, indicating that all positive ions within the ECD are converted to ions of this type. It is reasonable to expect that such a pronounced alteration of positive ion character will affect to some extent the electron density by a slight alteration of the rate of positive ion–electron recombiantion[10,11]. Thus, a slight increase in electron

density is possibly caused by this effect, which masks any electron attachment reaction that may also be occurring. The second chromatogram showing the "no O_2" condition, again while monitoring the negative ion at m/e 193 (M + O − H), indicates that some electron attachment to anthracene has, indeed, occurred, even though the ECD response does not reflect it. As oxygen is added to the carrier gas, a normal and increased ECD response to anthracene is observed. Meanwhile, the most intense negative ion observed at m/e 193 also increases with added oxygen. The magnitude of the negative ion signal at m/e 193 remains relatively small in all instances. A larger negative ion signal might have been expected, based on our comparisons with other electron-attaching molecules we have studied[9] and the ECD response they cause. We suspect that a significant portion of the PAH negative charge carriers do not survive transport through the API aperture and transmission to the ion detector. It seems likely that these ions are of the M⁻ type which detach their relatively weakly held electron during the orifice sampling or transmission period. Horning *et al.*[12] have also described difficulties in detecting negative ions of a PAH by API-MS.

We have measured the negative ion mass spectrum of each of the five PAHs shown in Table I. For each, the most intense negative ions observed are due to either the M + O − H or the M + 2O − 2H species. Small and variable signals for the M⁻ species are also seen. With the exception of tetracene, the M + O − H ion was in greater abundance than the M + 2O − 2H ion. Because of our above suspicions concerning the lack of detection of species of the M⁻ type, we do not know if the oxygenated negative ions are the most important ion products accompanying oxygen doping. It therefore remains conceivable that ECD enhancement to PAHs occurs partially by charge exchange from O_2^- to form M⁻.

Theoretically calculated values for the energy of the lowest unoccupied molecular orbital, E_{LUMO}, are also listed in Table I. These values (derived from simple Hückel theory) have been calculated by Coulson and Streitwieser[13] for numerous polycyclic aromatic hydrocarbons. The magnitude of E_{LUMO} might be expected to be related inversely to the relative ease with which electron attachment occurs, as it is into this molecular orbital that the captured electron goes. It is seen that a rough inverse correlation between E_{LUMO} and the respective R_{ECD} value does indeed exist. Tetracene has the lowest E_{LUMO} value and the largest R_{ECD} value, while the opposite is true of phenanthrene. The other three instances are intermediate with respect to R_{ECD} and E_{LUMO}. Within this group of three the correlation appears to fail. However, this may be due to the presence of trace amounts of oxygen in the carrier gas, which assists the "normal" ECD response to 1,2-benzanthracene more than it does that of anthracene and pyrene. Also, as described above, the observed ECD response at 250°C is undoubtedly complicated to some extent by positive ion effects.

Another theoretically calculated value, L^-, is listed in Table I for the first five compounds shown. This value (which has also been calculated from simple Hückel theory and is available for numerous PAHs[13]) is the amount of resonance energy lost

$$O_2^- \; + \; \text{(anthracene)} \longrightarrow \left[\text{(hydroxyanthracene radical)} \right]^- \tag{1}$$
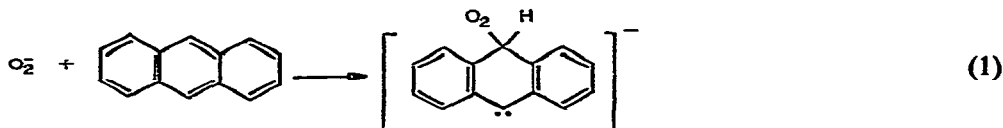
by each molecule when one of its carbon atoms is removed from the total resonance system. This value might be expected to provide an estimate of the relative ease with which nucleophilic attachment by O_2^- on some site in the molecule might occur, as shown in reaction 1.

Following the formation of the intermediate $[M + O_2]^-$, negative ion species such as M^-, $M + O - H$ or $M + 2O - 2H$ observed in the mass spectral studies could be formed. The rate of the overall reactions might be limited by the rate of reaction 1, for which the value of L^- contributes to the activation energy.

Inspection of Table I indicates that within each group of 3-ring and 4-ring PAHs an inverse correlation of L^- with the measured value of R_{O_2} for each case exists. And again, tetracene is predicted to be the most reactive and phenanthrene the least reactive. It appears from the above comparisons of measurements and simple theory that the ECD signals observed with and without oxygen are consistent with the relative reactivities of the electron and O_2^- that might have been expected for each molecule. Conversely, the values of E_{LUMO} and L^-, which are readily available[13] or easily calculated for PAHs, may provide a useful guide to the behavior of all PAHs in the ECD, with and without oxygen doping.

These initial observations prompt us to explore further the behavior of additional PAHs in the ECD. In the development of these methods for the trace analysis of PAHs, it has become apparent that the proper choice of the GC column and the minimization of column bleeding will be even more critical than in normal ECD analysis. Unfortunately, the oxygen enhancement process can enhance the instrument's sensitivity to column bleed molecules as well as to the analyte of interest. Therefore, in order to maintain the ECD baseline as low as possible (determined ideally by the electron–O_2 equilibrium[7]), it will be desirable to determine which stationary phases and column technologies produce the least amount of O_2^--reactive impurities at the required oven temperatures. The effect of oxygen doping for a relatively clean system on baseline current and noise has been described in detail[6].

Also under further study is the fundamental basis of the oxygen-caused enhancements. It cannot at this point be ruled out, for example, that the enhancements observed are due simply to surface-catalyzed oxidations of a portion of the PAHs as they pass through the stainless-steel transfer line to the detector. Determination of the precise cause of the enhancements will also assist in the determination of the optimum experimental conditions for taking full advantage of the effects described here.

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