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NEW SCHEMES FOR THE ELECTRON-CAPTURE SENSITIZATION OF AROMATIC HYDROCARBONS

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SUMMARY

In recent years it has been shown that the response characteristics of an electron-capture detector can be altered dramatically by the intentional addition of either oxygen or nitrous oxide to the carrier gas. These dopants produce negative ions whose reactions with molecules can cause enhanced responses. In these instances the dopant gas serves as a "catalyst" for electron capture (EC) by the sample molecule. A new EC detection scheme is described in which the roles of the dopant and the sample molecule are reversed in that the sample molecule serves as the catalyst for EC by a normally inactive dopant molecule. Specifically, it is shown that by doping the carrier gas with ethyl chloride, a very sensitive EC response to anthracene is then observed. Another problem encountered in the analysis of anthracene and polynuclear aromatic hydrocarbons (PAHs) with EC detection, in general, is the detrimental effect on the response caused by positive ion–molecule reactions. The means for its control and elimination is also described. These improvements are significant, because the normal EC response to anthracene and other PAHs is weak and non-linear at the detector temperatures required for general chromatographic analysis.

INTRODUCTION

The electron-capture detector for gas chromatography (GC) offers an extremely high detection sensitivity for numerous compounds of environmental interest. Generally, high sensitivity is observed for compounds that contain heteroatoms with a high electronegativity[1]. Perhaps the greatest analytical use of electron-capture detection (ECD) has been for the analysis of halogenated hydrocarbons. High sensitivity is also achieved when nitro or carbonyl functional groups are incorporated into an aromatic hydrocarbon system. These molecules rapidly attach and hold thermalized gaseous electrons by forming stable negative ions by either the resonance electron capture (EC) or the dissociative EC mechanism[2].

Although unsubstituted polynuclear aromatic hydrocarbons (PAHs) are known to attach electrons under favorable conditions[3,4], ECD has not been used extensively in their analysis by GC, because relatively low sensitivities to PAHs are observed at the relatively high temperatures generally required for the detector when used with a chromatographic column and oven. The basis of this problem is explained

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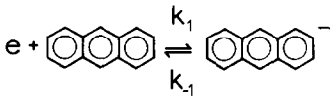


$$\frac{k_1}{k_{-1}} = \frac{5 \times 10^{-9} \text{ ml sec}^{-1}}{1.0 \times 10^{7} T^{3/2} e^{-(12 \text{ kcal/RT})} \text{ sec}^{-1}}$$

	100°	150°	200°	250°	300°	350°C
τ_{-1} (μsec)	103	13	2.3	0.6	0.2	0.07

Fig. 1. Resonance EC mechanism of anthracene. Rate constants and lifetimes of negative anthracene ion (τ_{-1}) were obtained from ref. 4.

in more detail in Fig. 1, where the measurements of Wojnárovits and Földiák[4] have been used to describe the EC dynamics of anthracene. The PAH molecules and anthracene, in this instance, attach electrons by the resonance capture process. The parent molecule simply attaches an electron to form a molecular negative ion which, on stabilization by collisions with the buffer gas, will survive for a period of time characterized by the magnitude of the auto-detachment constant, k_{-1}. For anthracene, the rate constant for electron attachment, k_1, is actually fairly high at all temperatures. The corresponding EC coefficients for the most strongly electron-attaching molecules such as CCl_4 and SF_6 are about $2 \cdot 10^{-7}$ ml sec^{-1} (ref. 5). Thus, the k_1 value of $5 \cdot 10^{-9}$ ml sec^{-1} listed in Fig. 1 for anthracene is within two orders of magnitude of the very fastest electron attachment constants and could, by itself, provide the basis for a sensitive ECD response to anthracene. The problem is caused by the strong temperature dependence of the auto-detachment constant, k_{-1}. The lifetime ($1/k_{-1}$) of the molecular negative ion is also shown in Fig. 1 for various temperatures from 100 to 350°C, and is shown to decrease strongly with increasing temperature. Between 200 and 350°C, where a detector might normally be maintained for a typical PAH analysis, the lifetime of the negative anthracene ion is on the order of microseconds or tenths of microseconds. The electron population of a pulsed electron-capture detector is typically sampled at intervals of hundreds of microseconds. Therefore, at the instant the electron density measurement is made by application of a pulse, the degree of electron attachment to anthracene is very small relative to the total number of attachments that have occurred during the entire period between pulses. Further, as the width of an applied pulse is typically about 1 μsec, a significant degree of auto-detachment and signal loss can actually occur during the time of the pulse itself.

In view of the kinetic parameters indicated in Fig. 1, it is not surprising that the ECD sensitivity to anthracene at temperatures greater than 200°C is low. Even worse than this expectation, however, the chromatographic ECD peaks of many PAHs have also been found to display complex and anomalous shapes[6,7]. These observations suggest that additional complicating processes are also operative and dominate over the weak EC response.

In this paper, a study of the response of anthracene in a specialized electron-capture detector is reported. This instrument is also an atmospheric pressure ion-

ization mass spectrometric (APIMS) instrument which allows the observation of positive and negative ions within the electron-capture detector. The most significant conclusion of this study is that a dramatic improvement in the ECD response to anthracene can be caused by appropriate tailoring of the ionic reactions occurring within this detector. This is accomplished by two means. The first is by chemical stabilization of the terminal positive ions which are otherwise reactive towards anthracene, and the second occurs by inducing further reaction of the negative anthracene ion with an additional dopant molecule so that a more stable negative ion is formed. The conclusions to be drawn here are supported by the observed effects of numerous carrier gas chemical dopants on the response of the ECD/APIMS instrument.

EXPERIMENTAL

The ion source for the APIMS instrument is shown in Fig. 2. The entire APIMS system, which includes mass analysis with quadrupoles and positive or negative ion detection by the ion-counting technique, has been described previously[8,9]. A 20-μm aperture allows about 4 ml min^{-1} of carrier gas to flow from the ion source at atmospheric pressure into the adjacent vacuum region where the ions are mass-analyzed and detected. These ion measurements provide a measure of the ionic reactions occurring throughout the cell[9].

The stainless-steel pin that protrudes through the center of the source in Fig. 2 is the electrode by which the ECD function is obtained. Pulses of +50 V and 1 μsec duration are applied to this pin with a constant frequency of 5 kHz. The negative current thereby produced is measured with an electrometer and recorder.

Positive ion signals are measured simultaneously with the ECD current, as the application of voltage pulses has little effect on the observed positive ions[9]. When negative ion signals are measured, however, the ECD pulses must be turned off[9].

A simple isothermal gas chromatograph with a conventional injection port was

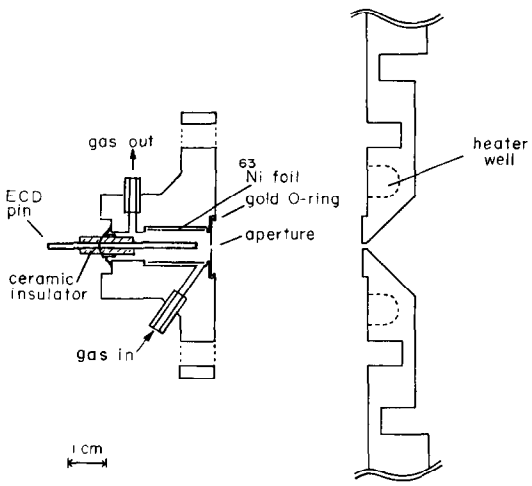


Fig. 2. Specialized ECD/APIMS ion source by which the ECD signal and ion measurements are made.

used to introduce samples to the APIMS system. Nitrogen carrier gas was first passed through oxygen-removing (Alltech Oxy-Trap) and water-removing ($CaSO_4$ and molecular sieve 5A) traps. A simple 1/8 in. × 1.5 ft. stainless-steel column was packed with 4% OV-101 on Chromosorb W. The column and APIMS system were connected by a 1/8 in. × 6 in. glass-lined, heated transfer tube. The flow-rate of carrier gas was 45 ml min^{-1}, the column temperature was 140°C and the source temperature was 250°C.

In order to add chemical dopants to the carrier gas, a 3-l stainless-steel exponential dilution sphere was added to the flow system immediately before the gas chromatograph. This device has an injection port at its inlet through which gaseous or liquid dopants were added. The dilution half-life of this device was about 2 h at the flow-rate indicated above.

Gaseous dopants were added to the carrier gas dilutor by injection with a 3-ml ground-glass syringe. About 1 ml was required to create a concentration of 100 ppm in the dilutor. The gases CH_3CH_2Cl, NH_3 and $(CH_3)_3N$ were obtained in gaseous form from Matheson and Aldrich, and gaseous CH_3NH_2 was obtained by warming a 40% aqueous solution of CH_3NH_2 (Eastman Organic Chemicals) in a small volumetric flask. The liquid dopants, including toluene, cyclohexane, diethyl ether, methanol, acetone and isopropyl chloride (all reagent grade, J. B. Baker), were added to the dilution sphere by injection of the pure liquid with a 10-μl syringe. About 1–2 μl of the liquid dopant was required to create a concentration of 100 ppm in the carrier gas.

Measurements are also reported that were obtained with a Varian 3700 GC–ECD system. The column, dilution sphere and carrier gases used in these experiments are of the same types as described above. The detector, however, differs considerably in that it uses the displaced coaxial geometry and the constant-current mode of signal processing. This detector has been described in detail by Patterson[10].

RESULTS AND DISCUSSION

Fig. 3 shows the ECD responses of the cell presented in Fig. 2 to three amounts of anthracene. The responses to all three samples at 250°C are inverted, in that an increase rather than the usual decrease in current is observed as anthracene passes through the source. As little difference is observed between the responses to the 20- and 50-ng samples, this inverse response appears to have reached a point of saturation with the 20-ng sample. These chromatograms indicate not only that the ECD reaction is weak at 250°C, as expected, but also that some other reactions of anthracene are occurring within the detector that actually increase the population of electrons as anthracene passes through the detector.

We have recently considered the cause of the inverse peaks with anthracene in some detail[11] and concluded that they are related to positive ion–molecule reactions between the set of terminal positive ions present in the detector and anthracene. The dynamic nature of the positive ion chemistry in the ECD with clean carrier gas is shown in Fig. 4, where the most intense positive ion signals have been individually monitored during the repeated analysis of the 2-ng anthracene sample. Together with the $(M+1)^+$ ion of anthracene at m/e = 179, the ions at m/e 37, 78 and 224 have been monitored. These ions are the most intense ones prior to sample injection and

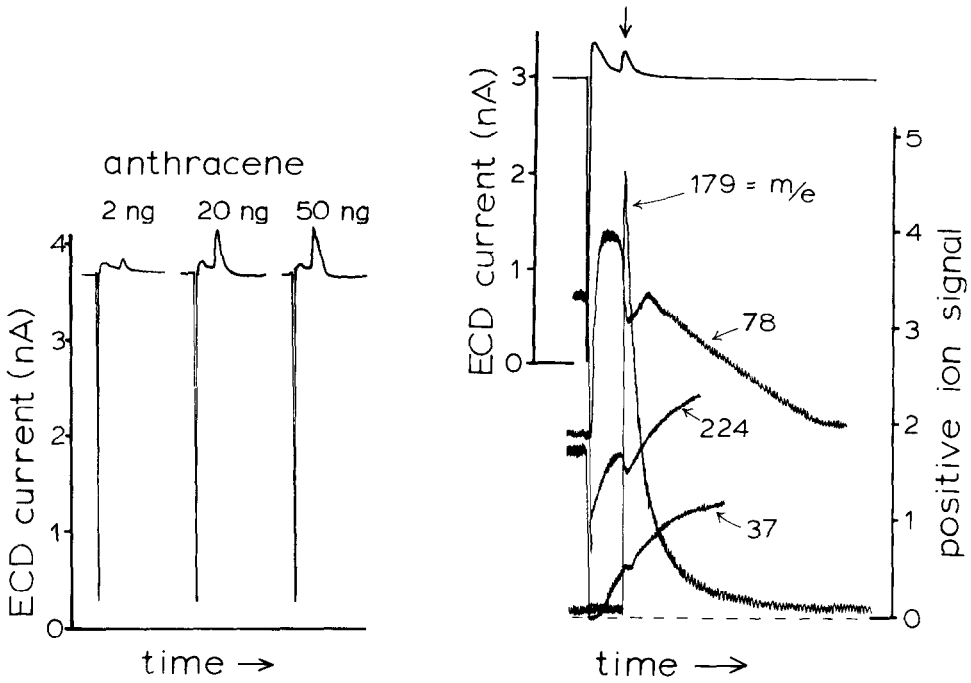


Fig. 3. ECD response to three anthracene samples with clean nitrogen as the carrier gas. Detector temperature, 250°C; pulse frequency, 5 kHz.

Fig. 4. Four repeated analyses of 2-ng anthracene samples with nitrogen as the carrier gas with simultaneous measurement of the ECD current and the intensity of various positive ions.

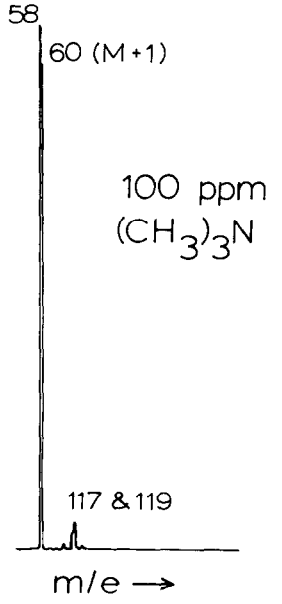


Fig. 5. Positive ion atmospheric pressure ionization mass spectrum of nitrogen carrier gas doped with 100 ppm of trimethylamine.

are due to the trace presence of water [$H^+(H_2O)_2$], benzene (analyte solvent) and column bleed in the detector. With very clean nitrogen carrier gas, these positive ions are the most stable ones possible until anthracene enters the detectors. The proton affinity (PA) of anthracene is high, 206.4 kcal/mole (ref. 12) [all PA values quoted here have been adjusted to a scale where PA_{NH_3} = 204 kcal/mole (ref. 13)], relative to the proton affinities of the continuously present carrier gas impurities such as water [PA = 171 kcal/mole (ref. 13)] and benzene [PA = 188 kcal/mole (ref. 12)]. At the point of elution of the 2-ng sample shown in Fig. 4, a large portion of the total population of positive ions become the $(M+1)^+$ ion of anthracene. In an experiment (not shown in Fig. 4), in which the 20-ng sample was used, almost all of the positive ions became the anthracene $(M+1)^+$ ion at the point of elution. Thus, the production of the $(M+1)^+$ anthracene ion, like the observed ECD response shown in Fig. 2, becomes saturated with about 20 ng of anthracene.

The positive ion chemistry can be stabilized by the addition to the carrier gas of a compound that has a very high proton affinity. Previously, CH_3NH_2 has been used for this purpose[11]. In this study $(CH_3)_3N$ was used. Fig. 5 shows the APIMS positive ion spectrum of the carrier gas with 100 ppm of trimethylamine added. The most intense ions observed occur at *m/e* 58 and 60. Because $(CH_3)_3N$ has a very high proton affinity of 224 kcal/mole (ref. 14) the intense ion at *m/e* 60 [$(M+1)^+$] was expected. The ion at *m/e* 58 could be due to $(M-1)^+$ or might reflect the presence of an impurity having an even greater proton affinity than $(CH_3)_3N$. As Bombick *et*

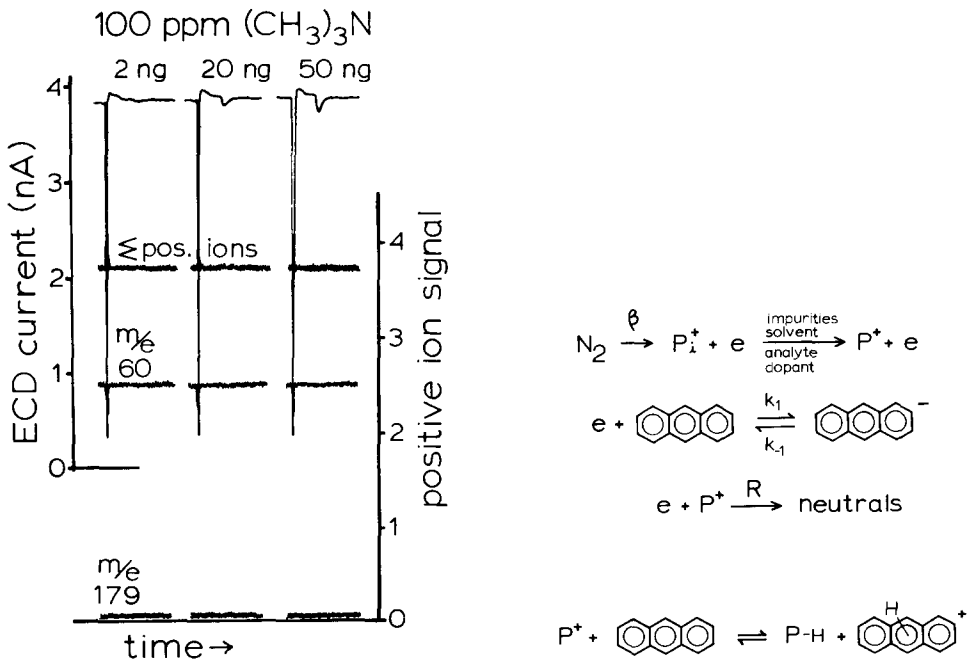


Fig. 6. Analyses of anthracene samples with nitrogen doped with 100 ppm of $(CH_3)_3N$ as the carrier gas with simultaneous measurements of ECD current and various APIMS positive ion signals.

Fig. 7. Proposed mechanism for the effect positive reactions on the ECD response to anthracene.

al.[15] reported intense $(M+1)^+$ and $(M-1)^+$ ions for the chemical ionization of triethylamine, the ion at *m/e* 58 in Fig. 5 is tentatively assumed to be the $(M-1)^+$ ion of trimethylamine. The low-intensity ions at *m/e* 117 and 119 are undoubtedly due to an additional $(CH_3)_3N$ molecule attached to the ions of *m/e* 58 and 60.

Analyses of the three anthracene samples with 100 ppm of $(CH_3)_3N$ in the carrier gas are shown in Fig. 6. Total positive ions, as well as the positive ion signals at *m/e* 60 and 179, were monitored throughout the analysis. As opposed to the previous analysis with clean nitrogen carrier gas, the positive ion chemistry is now stable and unchanging even as anthracene passes through the detector. The ECD response has also been altered in that weak, but normal, EC responses are now observed as anthracene passes through the detector.

In comparing the results shown in Figs. 4 and 6, a strong correlation between the stabilization of the positive ion chemistry and the creation of normal EC responses is suggested. As an explanation of this correlation we currently favor the mechanism shown in Fig. 7. The reactions shown symbolize the production of positive ions and electrons, the EC reaction of anthracene, the destruction of electrons and positive ions by their recombination and a positive ion–molecule reaction between the set of terminal positive ions, P^+, and anthracene. The identity of the set of terminal positive ions is determined by the molecules that are unintentionally or intentionally present as impurities or dopants in the nitrogen carrier gas. The P^+ ions are formed by the reaction of impurities with the ions, P_i^+, which are those initially formed by the beta radiation. The P_i^+ ions are very reactive ions such as N_3^+ and N_4^+ (ref. 16), and survive only until they collide with an impurity or dopant molecule. As shown in Fig. 4, with clean carrier gas the terminal positive ions are those formed by the trace presence of water, benzene and column bleed. These ions are reactive towards anthracene and the $(M+1)^+$ ion of anthracene is formed with great facility. This reaction alone does not affect the electron density and the measured current. However, if the rate constant, *R*, for the recombination reaction shown in Fig. 7 is altered by this drastic change in the identity of the positive ions, then the steady-state electron density will also be changed. As the protonated anthracene ion has a large π-resonance system over which the positive charge can be effectively spread, it seems reasonable to expect that the rate constant for the recombination of this ion with electrons might be lower than those of smaller and less resonant positive ions.

When the carrier gas is doped with $(CH_3)_3N$, as shown in Fig. 6, the set of terminal P^+ ions formed are those derived from $(CH_3)_3N$ at all times during the analysis. Because the proton affinity of $(CH_3)_3N$ is about 18 kcal/mole greater than that of anthracene, a positive ion–molecule reaction of this set of P^+ ions with anthracene does not occur. Therefore, the recombination of electrons with positive ions always involves the same set of $(CH_3)_3N$-derived ions, and the rate constant for this reaction, *R*, is unchanged throughout the analysis. With the positive ion sequence stabilized, no alteration in the electron density is caused by it, and the weak resonance EC reaction of anthracene can then be observed.

In further studies of the response of anthracene, the effects of several different chemical dopants in addition to $(CH_3)_3N$ have been assessed. From these measurement it has become apparant that further improvement in the response of anthracene over that provided by positive ion control is possible. This point becomes clear after consideration of the twelve experiments shown in Fig. 8, where the ECD responses

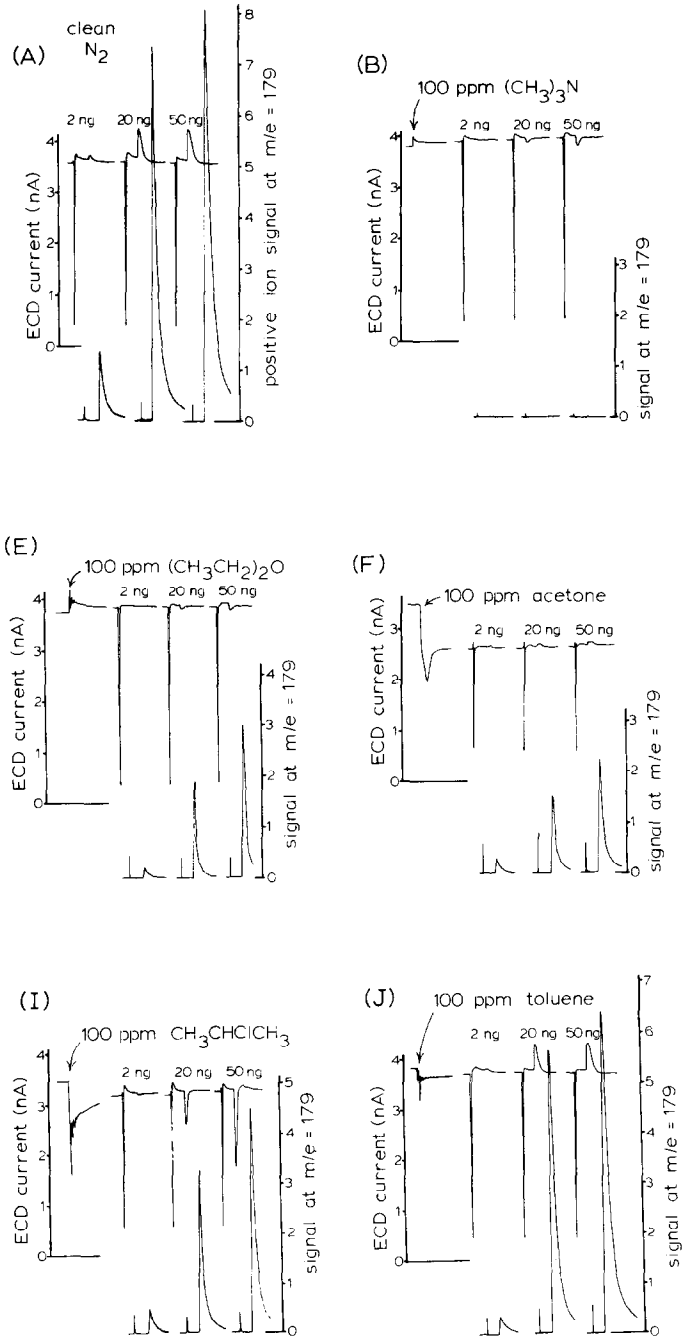

(A)
clean
N_2
2 ng
20 ng
50 ng
ECD current (nA)
positive ion signal at m/e = 179
(B)
100 ppm $(CH_3)_3N$
2 ng
20 ng
50 ng
ECD current (nA)
signal at m/e = 179
(E)
100 ppm $(CH_3CH_2)_2O$
2 ng
20 ng
50 ng
ECD current (nA)
signal at m/e = 179
(F)
100 ppm acetone
2 ng
20 ng
50 ng
ECD current (nA)
signal at m/e = 179
(I)
100 ppm $CH_3CHClCH_3$
2 ng
20 ng
50 ng
ECD current (nA)
signal at m/e = 179
(J)
100 ppm toluene
2 ng
20 ng
50 ng
ECD current (nA)
signal at m/e = 179

Fig. 8.

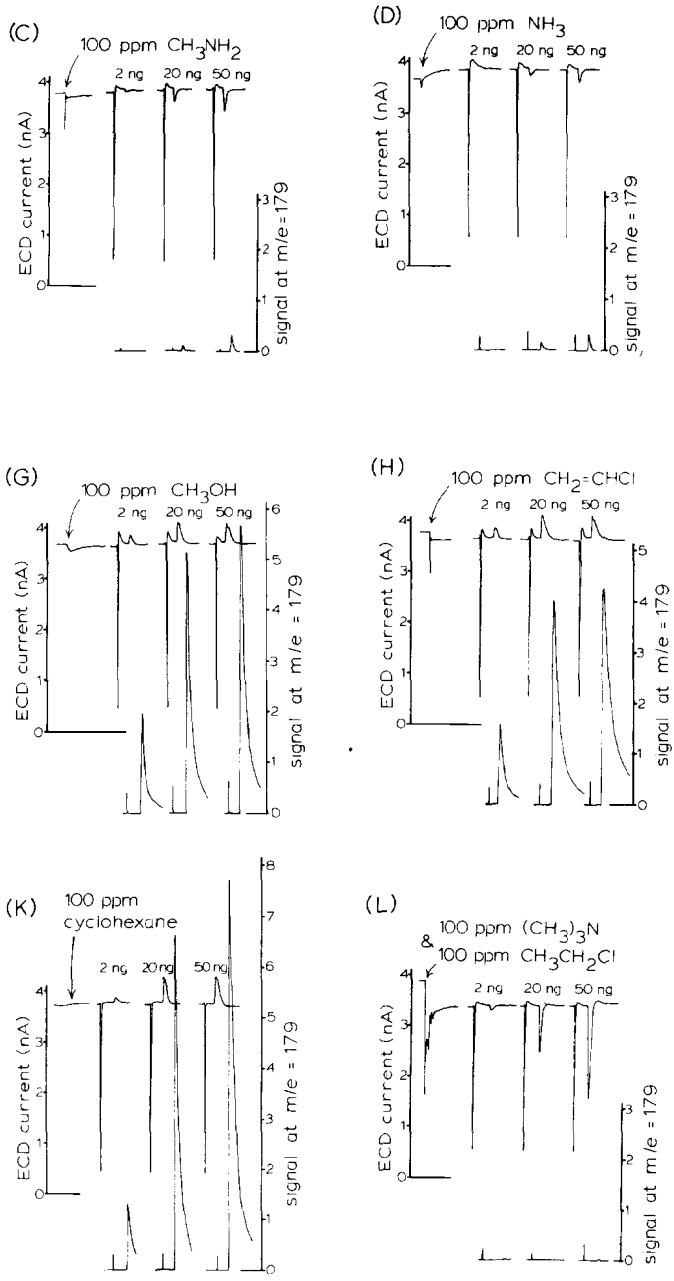


Fig. 8. Repeated analyses of anthracene samples with various chemical dopants added to the carrier gas. In addition to the ECD current, the positive ion intensity at *m/e* 179 [$(M + 1)^+$ ion] was monitored. In each instance, the effect of addition of the dopant to the carrier gas on the ECD standing current is also shown.

and the APIMS signal for the $(M+1)^+$ ion of anthracene are monitored with various chemical dopants added to the carrier gas. In each of the figures the effect of the addition of each dopant to the carrier gas on the ECD standing current is also indicated. Fig. 8A is the reference experiment in which clean carrier gas was used. In Fig. 8B the $(CH_3)_3N$ experiment previously discussed is shown, where the positive ionization of anthracene has been completely stopped and the weak EC reaction of anthracene is observed. In Fig. 8C and D CH_3NH_2 and NH_3, respectively, were used; their proton affinities are 213 and 204 kcal/mole, respectively. With both of these only a small degree of positive anthracene ionization is indicated and normal EC peaks are observed. Actually, the ECD response with CH_3NH_2 appears to be greater than that with $(CH_3)_3N$, in spite of the fact that $(CH_3)_3N$ more effectively blocks the positive ion–molecule reaction of anthracene. A possible reasons for this apparent inconsistency may be that an impurity that enhances the EC response has also been added to the carrier gas with the CH_3NH_2. This possibility is supported by the small reduction in the ECD current that accompanies the addition of CH_3NH_2.

In Fig. 8E the presence of diethyl ether has also significantly reduced the production of the anthracene $(M+1)^+$ ion (relative to the clean N_2 case), and normal ECD responses are again observed. Diethyl ether has a proton affinity of 199 kcal/mole, and its $(M+1)^+$ ion is additionally stabilized by a strong clustering reaction so that the $H^+(Et_2O)_2$ ion was observed to be the predominant ion.

Acetone has a proton affinity of 194 kcal/mole (ref. 14). With it as the dopant (Fig. 8F), positive ionization of anthracene was significantly retarded, but the ECD peaks indicate that the positive ion sequence is again beginning to cause an increased electron density when anthracene passes through the detector. With CH_3OH in the carrier gas, shown in Fig. 8G, all beneficial effects of positive ion stabilization appear to be lost. Neither the ECD responses nor the positive ion signals differ significantly from the undoped case in Fig. 8A. Methanol's lower proton affinity of 184 is apparently insufficient to prevent extensive proton transfer to anthracene.

The next four cases, Fig. 8H–K, show the effects of relatively non-basic hydrocarbons. For all of these cases the positive ionization of anthracene occurs readily, and for vinyl chloride, toluene and cyclohexane no improvement in the ECD response is observed. It is extremely interesting, therefore, that for the relatively non-basic isopropyl chloride dopant (Fig. 8I) a spectacular improvement in the EC response is obtained. It appears that the cause of this improvement is not related to positive ion stabilization, but rather to some other, yet to be defined, reaction involving isopropyl chloride. The last experiment, shown in Fig. 8L, indicates that this beneficial enhancement of response to anthracene is also caused by ethyl chloride. In this experiment $(CH_3)_3N$ is also present so that the positive ion interference has also been eliminated. By using the combined beneficial effects of $(CH_3)_3N$ and CH_3CH_2Cl in Fig. 8L, the most favorable ECD responses to anthracene have been created.

Additional experiments were performed to determine the mechanism by which ethyl and isopropyl chloride enhance the ECD response to anthracene. One of these experiments is shown in Fig. 9, where the response of the Varian 3700 GC–ECD system to an anthracene sample is shown as a function of ethyl chloride concentration in the carrier gas. It can be seen that with an increase in ethyl chloride concentration above a few tenths of a ppm, the anthracene response increases rapidly until the

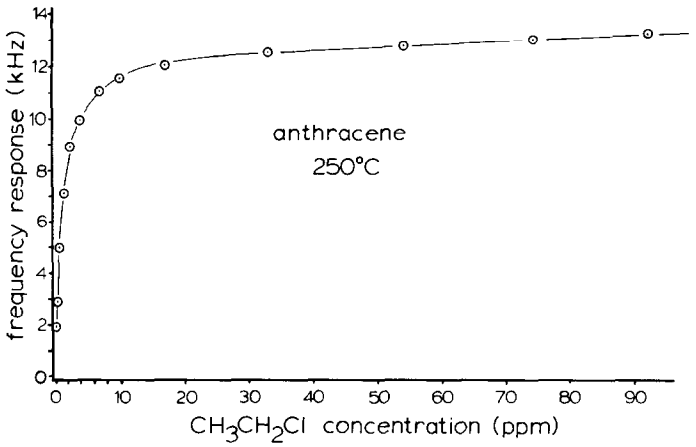
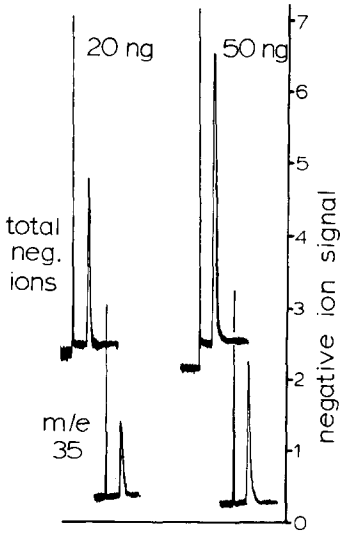


Fig. 9. Effect of ethyl chloride concentration in the carrier gas on the response to anthracene of a commercial GC–ECD instrument (constant-current mode).

effect reaches a saturation point at about 10 ppm of ethyl chloride. With further increases in ethyl chloride concentration (up to 400 ppm), relatively little additional effect on the anthracene response was observed.

Another experiment with ethyl chloride is shown in Fig. 10, where negative ion APIMS signals were monitored during the repeated analysis of two anthracene samples. It can be seen that the intensity of the Cl^- ion signal at *m/e* 35 is nearly half as great as the observed intensities of the total negative ion signals. This result suggests that most of the negative ions formed when anthracene passes through the detector in the presence of ethyl chloride are Cl^- ions.



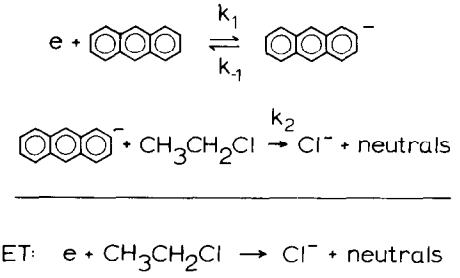


Fig. 10. APIMS total negative ion signal and Cl^- response at *m/e* 35 to two anthracene samples.

Fig. 11. Proposed mechanism for the enhancement of the ECD response to anthracene caused by ethyl chloride.

The above observations lead to the mechanism for the enhancement of the ECD response to anthracene by ethyl and isopropyl chloride proposed in Fig. 11. It is suggested that the alkyl chlorides "trap" the otherwise short-lived anthracene negative ion by reaction with it to form Cl^- and unknown neutral species. The data in Fig. 9 suggest that the trapping of the anthracene anion is nearly 100% effective with about 10 ppm or more of CH_3CH_2Cl in the carrier gas. Therefore, with 100 ppm of ethyl chloride, the rate-limiting step in the negative ion sequence shown in Fig. 11 is the forward EC step by anthracene, k_1. The overall reaction sequence is similar to direct EC by ethyl chloride, but the rate is determined by the magnitude of k_1 for anthracene, as the anthracene anion serves as a limiting reagent for the formation of a stable Cl^- negative ion.

The mechanism proposed in Fig. 11 is analogous to that proposed previously[17] for the EC-enhancing effects of oxygen where oxygen played the role that anthracene does here. Also, it appears here that the compounds that were previously shown to react rapidly with O_2^- also react rapidly with anthracene anion. That is, in this study ethyl chloride and isopropyl chloride have been shown to react rapidly with the anthracene anion, whereas vinyl chloride did not (Fig. 8H). Among these three organic chlorides, the same trend of reactivity toward O_2^- was noted previously[17]. The significant difference in the use of this negative ion sequence here is that the analyte plays the role of the catalyst, whereas the dopant serves as the substrate for the EC reaction.

The negative ion sequence shown in Fig. 11 also possesses another advantage

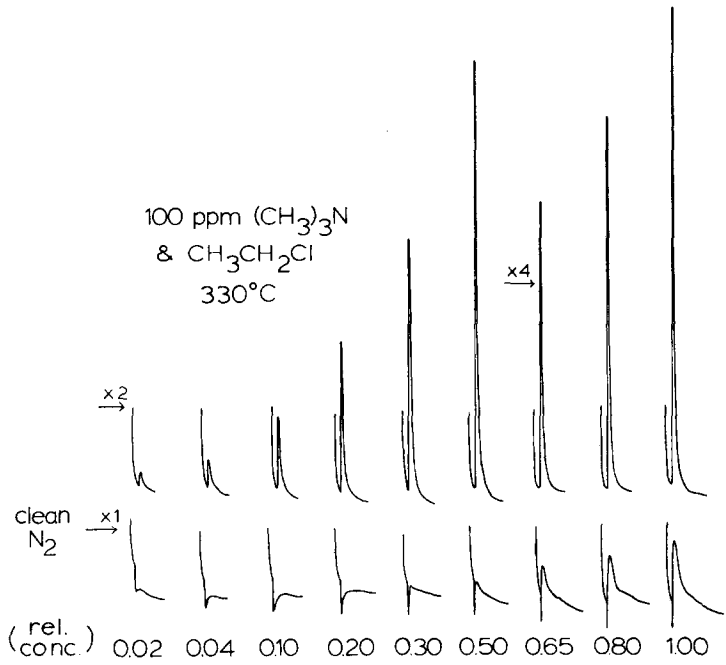


Fig. 12. Responses of a commercial GC–ECD instrument to anthracene samples by use of clean carrier gas and carrier gas doped with $(CH_3)_3N$ and CH_3CH_2Cl. Detector temperature, 330°C. Anthracene concentrations listed are relative to 1.00 = 170 ng/μl.

over the previously described[15] use of the catalyst, oxygen, for EC enhancement of the substrate molecule, that is, that the baseline current (or frequency, if the instrument utilizes the constant-current mode of signal processing) is only slightly impared by the presence of ethyl chloride or propyl chloride in the carrier gas. As shown in Fig. 8I and L, the ECD current was reduced less than 15% by the addition of either of the alkyl chlorides to the carrier gas. Further, in a previous study we have shown that for ethyl chloride this reduction in the standing current is not due to simple EC by ethyl chloride[18]. That is, at 250°C ethyl chloride does not undergo EC without the assistance of a catalyst, such as oxygen, anthracene or an unknown carrier gas impurity.

We also tested the effects of $(CH_3)_3N$ and ethyl chloride on the responses to anthracene with a commercial GC–ECD system. The recorded responses obtained with and without the combined use of these dopants are shown in Fig. 12. A detector temperature of 330°C was chosen to demonstrate that useful responses to anthracene can be created even at this relatively high temperature. With clean N_2 carrier, the responses to anthracene are very weak and assume unusual shapes. The leading edge of the anthracene peak occurs on the trailing shoulder of the solvent (benzene) peak. With low sample concentrations only an inverted response occurs. With higher concentrations, a more complex response with both inverted and normal deflections of the recorder are observed. With the two dopants added, one for positive ion control and the other for EC response enhancement, entirely useful and well behaved responses to anthracene are created, even at this relatively high temperature. In Fig. 13 the responses shown in Fig. 12 are plotted against relative sample concentration,

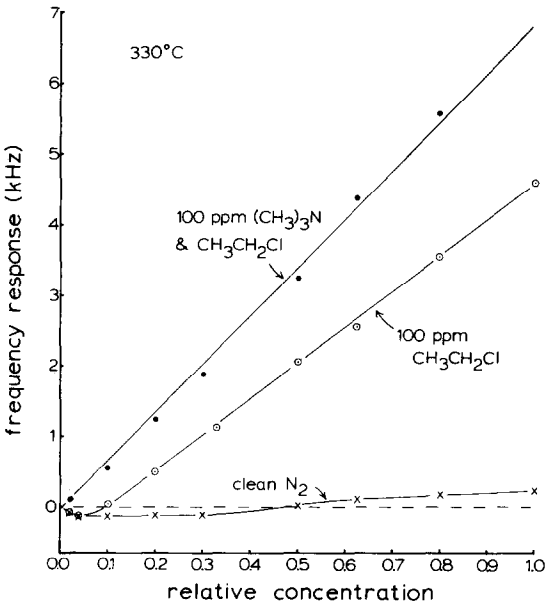


Fig. 13. Calibration graphs for the peak heights responses of a commercial GC–ECD instrument to anthracene samples with clean nitrogen as the carrier gas, nitrogen carrier doped with ethyl chloride and nitrogen carrier doped with trimethylamine and ethyl chloride. Detector temperature, 330°C.

together with the additional case where only ethyl chloride was used as the dopant. The superior nature of the calibration graph obtained with both $(CH_3)_3N$ and CH_3CH_2Cl added to the carrier gas is evident. It should be noted that the use of ethyl chloride alone does not produce optimal results in that inverse peaks are observed for the low-concentration anthracene samples. Hence this calibration graph does not pass through the origin and is non-linear in the low-concentration region. In view of the experiments described above, these inverted peaks are also thought to reflect a complicating positive ion sequence, which again requires elimination by the presence of $(CH_3)_3N$.

CONCLUSIONS

The results and concepts described here should lead to a significant extension of the use of the electron-capture detector for the chemical analysis of aromatic compounds. It seems likely that numerous compounds that normally depend on an inefficient resonance capture equilibrium for their EC response will be rendered more sensitively detected by the enhancement provided by a dopant such as ethyl chloride. As the aromatic hydrocarbons generally possess relatively high proton affinities, the use of positive ion stabilizers such as trimethylamine may also be required to make their responses well behaved over the entire response range of the instrument.

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