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THE EFFECT OF TRIALKYLAMINES ON THE RESPONSE OF THE ELECTRON-CAPTURE DETECTOR TO ACRIDINE

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SUMMARY

The normal electron-capture detector response to acridine is shown to be complicated by a positive ion-molecule reaction sequence. Because of its very high proton affinity, acridine is readily protonated in the electron-capture detector when clean carrier gas is used. This positive ion-molecule sequence has an effect on electron density which is dominant over the electron capture reaction with small concentrations of acridine so that an inverted response is then observed. At higher concentrations of acridine, complex peak shapes are observed which reflect the competition between the electron capture reaction and the positive ion sequence. The positive ion sequence is partially stabilized and the electron-capture detector response to acridine is simplified by the addition of trimethylamine to the carrier gas. The positive ion sequence is completely stabilized by triethylamine. The positive ions formed by the presence of the alkylamines are not simply the $(M + 1)^+$ ions as were expected. Rather, for trimethylamine the $(M - 1)^+$ ion and for triethylamine the $(M - 15)^+$ ion are dominant. It is shown that these ions are produced in abundance only in a relatively pure nitrogen medium. These ions are shown to be more stable than the corresponding $(M + 1)^+$ ions which are also observed in lower abundance.

INTRODUCTION

In a recent report[1] we demonstrated that the response of the electron-capture detector to anthracene is complicated by a sequence of positive ion-molecule reactions which overwhelm anthracene's weak tendency to capture electrons. It was shown that in clean carrier gas the $(M + 1)^+$ ion of anthracene is readily formed within the electron-capture detector and that this event is accompanied by an increase in the population of both total positive ions and electrons. It was suggested that the increase in electron population occurred because the rate constant for the recombination of electrons with the protonated anthracene positive ions is smaller than those with the positive ions normally present. It was also shown that this complicating effect could be removed by the intentional addition of methylamine to the carrier gas. Since the gas phase proton affinity of methylamine exceeds that of anthracene (214 *versus* 207 kcal/mole, respectively[2]), protonation of anthracene did not then

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occur and no changes in the positive ions of the methylamine-doped electron-capture detector occurred throughout the elution of anthracene.

In that earlier report, we speculated that a dopant other than methylamine, one with a still greater proton affinity, would be more generally successful as a stabilizer of positive ions in the general analysis of electron-capture-active analytes which possess unusually high proton affinities. For example, polynuclear aromatic hydrocarbons (PAH's) which contain heteroatoms either as substituents to the fused ring system (as in the case of the amino PAHs) or as atoms integrated within the fused ring system will have proton affinities considerably greater than that of anthracene. Acridine is a specific example of such a compound, and its electron-capture detector response is examined here. In order to eliminate detrimental effects of the positive ion chemistry which are predicted to accompany this molecule, the carrier gas dopants trimethylamine and triethylamine will be tested. These are known to have very high proton affinities, 225 and 232 kcal/mole (ref. 2), respectively. Also, with the aid of the mass spectrometric function of a specialized electron-capture detector ion source, the specific positive ions formed in the presence of the alkylamines and the analyte acridine have been identified and their reactivities characterized.

EXPERIMENTAL

The apparatus and procedures used here were identical to those described in a previous study[1]. Briefly, the electron-capture detector also serves as the ion source for atmospheric pressure ionization mass spectrometry (APIMS). With this instrument the electron-capture detector current is measured by applying +50-V pulses every 200 μsec to the cell's anode. Simultaneously, the positive ions of the electron-capture detector are measured by the APIMS function of the instrument. A simple isothermal gas chromatograph was used to introduce samples to the electron-capture detector–atmospheric pressure ionization mass spectrometer. Nitrogen and argon–methane (90:10) (Matheson) carrier gases are first passed through oxygen-removing (Alltech OxyTrap) and water-removing (calcium sulphate and 5 Å molecular sieve) traps. A simple 15 ft. × 1/8 in. stainless-steel column was packed with 4% OV-101 on Chromosorb W. This column is directly attached to the electron-capture detector–atmospheric pressure ionization mass spectrometer source by a 6 × 1/8 in. glass-lined stainless-steel tube. The flow-rate through the detector was about 45 ml/min. The column temperature was 140°C. The detector temperature was 250°C. In order to allow the addition of chemical dopants to the carrier gas, a 3-l stainless-steel exponential dilution sphere was added to the flow system just before the gas chromatograph.

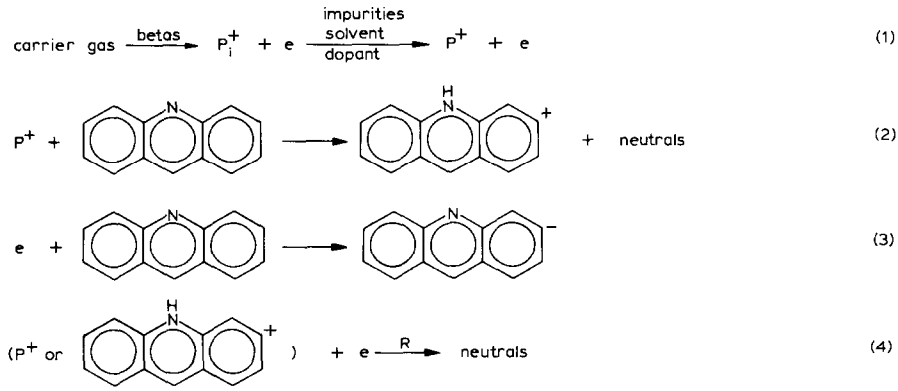
Ammonia (Matheson) and trimethylamine (Aldrich) were injected into the dilution sphere in pure gaseous form, while triethylamine (Aldrich) was added as the pure liquid. To establish a concentration of 100 ppm in the dilutor, 1.0 ml of the gases and 6.0 μl of triethylamine were required. Acridine samples were prepared by successive dilution of the pure, weighed material (Aldrich) into benzene.

RESULTS AND DISCUSSION

The response of the electron-capture detector–atmospheric pressure ionization

mass spectrometer to three acridine samples is shown in Fig. 1A. Both the electron-capture detector current and the positive ion signal at *m/e* 180 have been monitored. The electron-capture detector response is quite complicated. With the smallest sample (2.5 ng) an inverted peak is observed which indicates an increase in electron population as acridine passes through the detector. With larger sample sizes a more complex peak shape is observed where, for the 50-ng sample, the peak is inverted on the low-concentration edges of the peak, but is normal and quite sensitive at its center. The intensity of the positive ion signal at *m/e* 180 indicates the effective formation of the $(M + 1)^+$ ion of acridine, as was expected. The production of this ion is saturated with the 12-ng sample. That is, with this sample size and larger, all positive ions within the electron-capture detector using clean carrier gas become the $(M + 1)^+$ ion of acridine at the point in time corresponding to the center of the peak.

Based on our previous study of anthracene[1], the results shown in Fig. 1A were expected. The model previously suggested for anthracene can be applied to the case of acridine as shown in reactions 1–4. In clean carrier gas the terminal positive ions,



P^+, which are formed by reactions with short-lived intermediate positive ions, P_i^+, will depend on the impurities which are present in the carrier gas. We have previously shown that these positive ions will be composed of trace water, column bleed molecules, and traces of the injection solvent which persist throughout the chromatogram. All of these P^+ ions react rapidly with acridine, as symbolized by reaction 2, to form the ion at *m/e* 180. Electron capture reaction 3 is also occurring and is undoubtedly the cause of the strong decrease in electron-capture detector current observed for the 50-ng sample in Fig. 1A. Reaction 4 indicates the recombination of electrons with the positive ions which happen to be present at any moment. In clean carrier gas, the terminal positive ions will either be the P^+ ions described above or the $(M + 1)^+$ ions of acridine during its elution. It is suggested that the rate constant for recombination, *R*, is smaller when the $(M + 1)^+$ ion of acridine is predominant (due to its large π-resonance system over which charge can be effectively spread). It then follows that the slowing of reaction 4 as acridine passes through the detector causes an increase in electron population and an inverted response for the smallest sample size. Since this positive ion sequence is saturated with the 12-ng sample, the electron capture reaction competes effectively at the center of the 50-ng peak. At

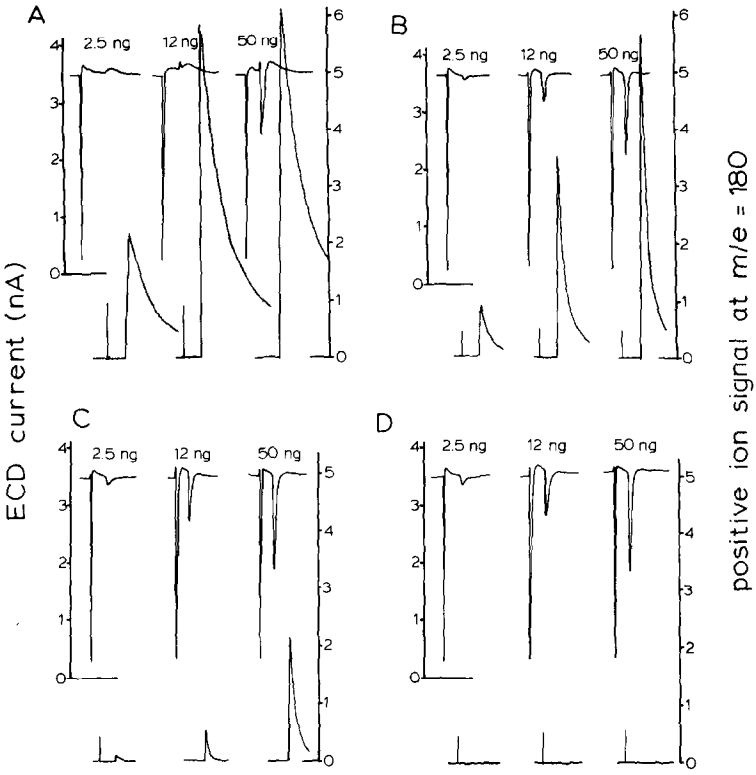


Fig. 1. Repeated analysis of three acridine samples in clean nitrogen carrier gas (A), and with 100 ppm of NH_3 (B), $(CH_3)_3N$ (C) and $(CH_3CH_2)_3N$ (D) added to nitrogen carrier gas. Both the electron-capture detection current (fixed frequency, pulsed mode) and the APIMS positive ion signal at *m/e* 180 have been monitored. Source temperature is 250°C.

concentrations lower than 12 ng, the positive ion sequence is dominant over the electron-capture reaction.

In Fig. 1B–D three amine dopants with successively stronger proton affinities have been added to the carrier gas. The proton affinities of ammonia, trimethylamine, and triethylamine are 204, 225, and 232 kcal/mole (ref. 2), respectively. The proton affinity of acridine is also 232 kcal/mole[2,3]. As might be expected from the relative proton affinities of these dopants, the extent of acridine protonation (as indicated by the intensities of the positive signals at *m/e* 180) continuously decreases in Fig. 1B–D. That is, reaction 2 becomes progressively less favorable as the proton affinity of the dopant is increased. With triethylamine, which has the highest proton affinity of the dopants (232 kcal/mole), no positive ionization of acridine is observed.

Along with the retardation of acridine protonation, the electron-capture detector responses in Fig. 1B–D indicate dramatic improvements relative to those in Fig. 1A. With ammonia in Fig. 1B, the electron-capture detector responses appear to be normal and uncomplicated by competitive processes. However, the positive ion signals indicate that reaction 2 may still be sufficiently favorable as to affect the electron-capture detector response. Upon considering the electron-capture detector

responses in Fig. 1C and D, it is seen that the electron-capture detector responses in Fig. 1B are, indeed, somewhat retarded. With trimethylamine and triethylamine, the electron-capture detector responses to the acridine samples are about 50% greater for the 2.5- and 12.0-ng samples than was observed with ammonia. For the most effective elimination of positive ion effects on the response of the electron-capture detector to acridine, it appears that the use of triethylamine is to be recommended. Trimethylamine provided an identical electron-capture detector response even though it did not completely retard the positive ionization of acridine.

In terms of the proposed mechanism consisting of reactions 1–4, the results in Fig. 1 suggest that with the dopants of higher proton affinity, reaction 2 is retarded due to the formation of a more stable set of positive ions. With triethylamine, reaction 2 is stopped entirely. In this case, the identity of the positive ions, P^+, is never measurably altered as acridine passes through the detector. The rate of electron recombination, reaction 4, is therefore stabilized at an unchanging magnitude. When acridine then passes through the detector, only the electron capture reaction 3 causes the population of electrons to change, and a normal, well-behaved response is observed.

The detrimental effects of the positive ion sequence on the electron-capture detector response are not unique to the use of nitrogen carrier gas. In Fig. 2, the same three acridine samples have been analyzed by electron-capture detection–APIMS using argon–methane (90:10) as the carrier gas. In Fig. 2A, clean argon–methane is used, and in Fig. 2B this carrier has been doped with 100 ppm triethylamine. Essentially the same results reported above for nitrogen are observed. That is, the changes caused by triethylamine are that the positive ionization of acridine is eliminated, and normal, well-behaved electron-capture detector responses are created. The primary difference observed with argon–methane is an increase in total electron-capture detector standing current and responses of about 25% relative to those observed with nitrogen. This change was entirely expected because of the argon's greater atomic density of electrons (18 *versus* 14 for molecular nitrogen), which increases its ability to be ionized by the beta radiation emitted from the ^{63}Ni nuclides attached to the source walls.

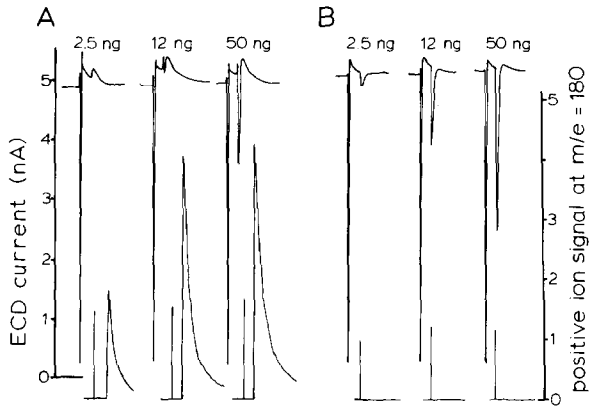


Fig. 2. Analysis of three acridine samples (A) in clean argon–methane (90:10) carrier gas (A) and in argon–methane (90:10) doped with 100 ppm $(CH_3CH_2)_3N$ (B). Both the electron-capture detection current and the APIMS positive ion signal at *m/e* 180 have been monitored.

At this point, we will turn our attention to the nature of the terminal positive ions (represented as P^+ in reaction 1) formed in the trialkylamine-doped electron-capture detector. Due to the high proton affinity of the trialkylamines, we initially expected to see only ions of the type $(M + H)^+$, where M is the trialkylamine molecule. Particularly in nitrogen carrier gas, however, this expectation was not observed. The positive APIMS spectrum of nitrogen carrier gas doped with 20 ppm trimethylamine is shown in Fig. 3a. It is seen that the most intense ion is at *m/e* 58 which corresponds to $(M - 1)^+$, while the expected ion at *m/e* 60 corresponding to $(M + 1)^+$ is only one-third as intense. In each of the other spectra shown in Fig. 3b–e, aliquots of cyclohexane were added in amounts corresponding to 20 ppm increase for each spectrum. In Fig. 3f, the nitrogen carrier gas contains 140 ppm cyclohexane along with 20 ppm trimethylamine. It is noted that the presence of cyclohexane has a dramatic effect on the ratio of the $(M - 1)^+$ and $(M + 1)^+$ ions of trimethylamine. No ions characteristic of cyclohexane, itself, are observed.

In Fig. 4, the corresponding experiment with triethylamine is shown. Again, Fig. 4a is with 20 ppm triethylamine in nitrogen, while Fig. 4b–f are with cyclohexane again added successively in amounts as previously described for Fig. 3b–f. For triethylamine in Fig. 4a, the predominant ion at *m/e* 86 corresponds to $(M - 15)^+$, and is presumed to result from the loss of methyl. The relative intensity of the $(M + 1)^+$ ion is only 0.16. An $(M - 1)^+$ ion is again observed, but with a relative intensity of only 0.11. Again, as cyclohexane is added to the triethylamine-doped nitrogen carrier gas, the relative intensities of the ions continuously change so that in Fig. 4f with 140 ppm cyclohexane present, the once intense ion at *m/e* 86 is now small and the $(M + 1)^+$ ion is dominant. It is interesting to note that in this case the intensity ratio of the $(M - 1)^+$ and $(M + 1)^+$ ions remain relatively constant with addition of cyclohexane. Fig. 4g is that obtained with 20 ppm triethylamine in argon–methane (90:10) carrier gas. Noteworthy features here are that the $(M - 15)^+$

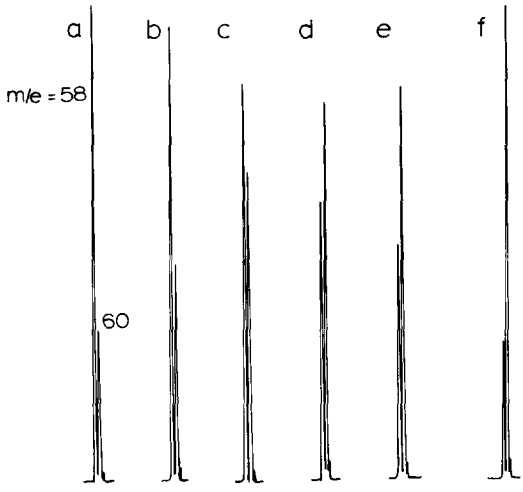
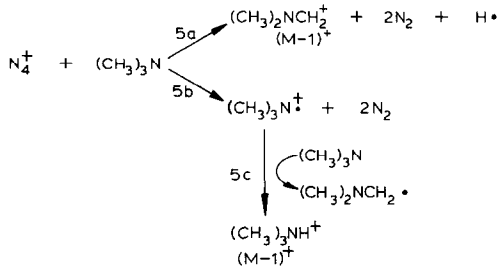


Fig. 3. Positive ion APIMS spectra of 20 ppm $(CH_3)_3N$ in nitrogen with the following amounts of cyclohexane added: (a) none, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 140 ppm.

and $(M - 1)^+$ ions are still easily measurable, while the $(M + 1)^+$ ion is clearly dominant.

The spectra in Figs. 3 and 4 can be explained by closer examination of the initial positive ionization process in nitrogen which was expressed previously as reaction 1. According to Siegel and Fite[4], the intermediate ions in reaction 1, symbolized as P_i^+, will primarily be N_4^+ and N_3^+ in a 3:1 abundance ratio. In an APIMS source with ionization by ^{63}Ni, the lifetime of all positive ions against recombination will be on the order of several milliseconds[5]. In that time in an atmospheric pressure medium, it can be shown that an ion will undergo approximately 10^7 collisions. Therefore, the terminal ions which are observed by APIMS may reflect impurities which are present at concentrations of 1 ppm or greater. (This point has been explained thoroughly by Siegel and Fite[4].) If dopants are added to the carrier gas in concentrations of tens or hundreds of ppm, the first reactive collisions of the species, N_4^+ and N_3^+, will be with the dopant molecules. We suggest here that the spectrum of trimethylamine in nitrogen shown in Fig. 3a results from the following reaction sequence:



(5)

Reaction 5a is hydride abstraction and 5b is charge exchange followed by hydrogen atom abstraction in step 5c. Within this mechanism the relative rates of reactions 5a and b determine the intensity ratio of the $(M - 1)^+$ and $(M + 1)^+$ ions, which in Fig. 3a was shown to be about 3:1. Reaction pathway 5a is a higher energy pathway than 5b because a carbon–hydrogen bond is broken in it. Nevertheless it can be dominant over pathway 5b because the reagent ion, N_4^+, is a relatively high energy ion (the ionization potential of N_2 is 356 kcal/mole)[6]. In Fig. 3 it was noted that the intensity of the $(M - 1)^+$ ion decreased as cyclohexane was added to the trimethylamine-doped carrier. This occurs because with cyclohexane in excess of trimethylamine, the first collisions of N_4^+ and N_3^+ will then tend to be with cyclohexane. The product of this reaction will be a lower energy cyclohexane-derived positive ion. This ion will soon collide and react with a trimethylamine molecule, but the energy available from this reaction will be much less than that where N_4^+ was involved (the ionization potential of cyclohexane is 225 kcal/mole)[7]. Therefore, with excess cyclohexane producing the greater share of reactive positive ions which first collide with trimethylamine, a lower energy pathway similar to reaction 5b will be favored over the higher energy route, analogous to pathway 5a.

A similar explanation can be applied to the spectra of triethylamine shown in Fig. 4. The production of the $(M - 15)^+$ ion is favored in clean nitrogen. However, like the $(M - 1)^+$ ion of trimethylamine, its production appears to require the par-

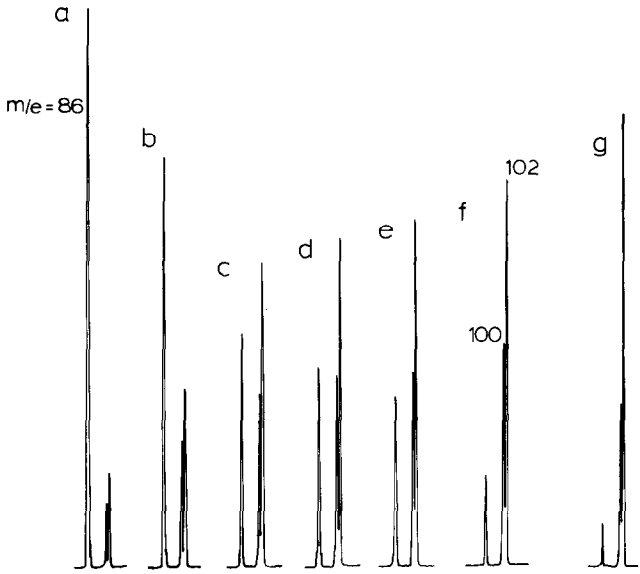
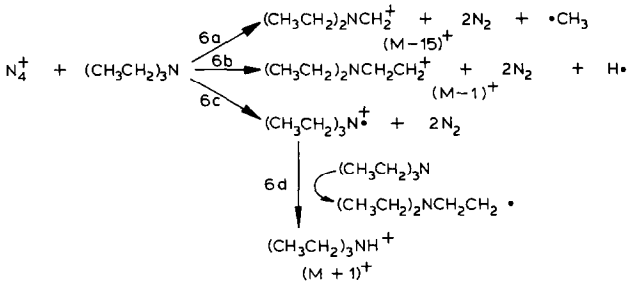


Fig. 4. Positive ion APIMS spectra of 20 ppm $(CH_3CH_2)_3N$ in nitrogen (a–f) with the following amounts of cyclohexane added: (a) none, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 140 ppm. Spectrum g was obtained with 20 ppm $(CH_3CH_3)_3N$ in clean argon–methane (90:10).

ticipation of the high energy reagent ions, N_4^+ and N_3^+, since its intensity is drastically diminished by the addition of cyclohexane. Thus, the following reaction scheme might be proposed for the formation of positive ions in triethylamine-doped nitrogen carrier gas.



(6)

Within this mechanism the high energy reaction 6a is favored in the presence of the high energy reagent, N_4^+. With excess cyclohexane added, the lower energy cyclohexane positive ions which then first collide with triethylamine cause reactions which proceed by pathways 6b and 6c to form the $(M - 1)^+$ and $(M + 1)^+$ ions. It is interesting to note that for triethylamine the production of an $(M - 1)^+$ ion is a lower energy process than it is with trimethylamine.

The final point to be examined concerning the positive ions formed in alkylamine-doped carrier gas is whether the fragment ions which have been observed here

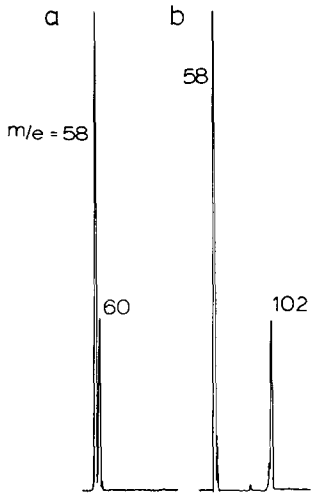


Fig. 5. Positive ion APIMS spectra of 100 ppm $(CH_3)_3N$ in nitrogen before (a) and after (b) adding 1 ppm $(CH_3CH_2)_3N$.

have greater or less stability against reaction with strongly basic molecules than do the $(M + 1)^+$ ions. An answer to this question is suggested in Fig. 5. Fig. 5a shows the positive ion APIMS spectrum of nitrogen carrier gas doped with 100 ppm trimethylamine. In Fig. 5b about 1 ppm triethylamine has also been added to the same carrier gas. It is seen in Fig. 5b that the signal at *m/e* 60 [the $(M + 1)^+$ ion of trimethylamine] has been replaced by an ion at *m/e* 102 [the $(M + 1)^+$ ion of triethylamine]. This result indicates that the reaction,

$$(CH_3)_3NH^+ + (CH_3CH_2)_3N \rightarrow (CH_3)_3N + (CH_3CH_2)_3NH^+ \quad (7)$$

occurs readily as it should, because of the greater proton affinity of triethylamine. More significantly, however, Fig. 5 indicates that the ion of *m/e* 58, which is $(CH_3)_2NCH_2^+$, does not react with triethylamine either by proton transfer or hydride abstraction. Therefore, it appears that the $(M - 1)^+$ ion of trimethylamine is more stable than its $(M + 1)^+$ ion against reaction with a stronger base. Since the $(M - 15)^+$ ion of triethylamine (shown in Fig. 4a) has a structure analogous to that of the $(M - 1)^+$ ion of trimethylamine, it might also be expected to be more stable than its $(M + 1)^+$ form.

CONCLUSIONS

It has been shown here that alkylamines can be used as carrier gas dopants for the stabilization of positive ions in the analysis of strongly basic, electron-capture-active compounds. In nitrogen carrier gas, the predominant positive ions which are formed from trimethylamine and triethylamine are not the $(M + 1)^+$ ions as might have been expected due to their high proton affinity. Rather, the most intense ions are the $(M - H)^+$ and the $(M - CH_3)^+$ ions for trimethylamine and triethylamine, respectively. Both of these ions would have a common structure of the type,

$R_2NCH_2^+$. The stability of these ions against reaction with strong gas phase bases appears to be even greater than that of their corresponding $(M + 1)^+$ ions. In argon–methane (90:10) carrier gas, the $(M + 1)^+$ ions of both trialkylamines are predominant.

The addition of the alkylamines to the carrier gas of a gas-chromatograph–electron-capture detector appears to cause no detrimental effects. In fact, a small increase in the electron-capture detector standing current has consistently been observed here upon addition of either trimethylamine or triethylamine to the carrier gas. For routine analytical use, it is anticipated that the easiest way to introduce the alkylamines to the carrier gas will be by the use of a gaseous permeation device which is placed in line with the makeup gas to electron-capture detector. Precise control of the concentration of the amine dopant is not necessary, since little effect on response has been generally noted with changes in dopant concentration between approximately 50 and 150 ppm. With the positive ions stabilized by this procedure another potential complication of the response of the electron-capture detector can be eliminated.

ACKNOWLEDGEMENT

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