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# IONIC SPECIES OF ORGANIC COMPOUNDS OBSERVED IN MOBILITY SPECTRA BY PLASMA CHROMATOGRAPHY

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## SUMMARY

A plasma chromatograph functions as a very sensitive qualitative detector for a gas chromatograph. Compounds in a gas chromatographic peak are detected in nanogram or less quantities and identified by their characteristic positive and negative mobility spectra. General relationships observed indicate that all compounds show simple positive mobility spectra similar to those obtained in chemical ionization mass spectrometry, giving prominent molecular-type ions, occasionally associated with fragment ions. The simple negative mobility spectra which consist of molecular and dissociative ions are produced only by those compounds that undergo electron attachment. Reference mobility spectra for the different compound classes of *n*-alkanes, alcohols, ketones, halogenated aromatics, substituted nitrobenzenes, polychlorinated biphenyls, alkyl halides and 1-nitropropane are given.

## INTRODUCTION

Functioning at atmospheric pressure, the plasma chromatograph first creates both positive and negative ions in a carrier gas using a $^{63}$Ni source. These reactant ions undergo ion–molecule reactions with trace molecules injected into the carrier gas stream. The resultant ion–molecules are separated in a coupled ion drift spectrometer to give positive and negative mobility spectra characteristic of the organic molecules involved and the reactant ions generated. Both the instrumentation and technique have been described previously[1–4].

While plasma chromatography provides a method and instrumentation for trace analysis and fundamental studies of ion–molecule reactions, the instrumentation has a very real application as a sensitive qualitative detector for gas chromatography (GC). Since the plasma chromatograph operates at atmospheric pressure, only a simple interface is required for it to function as a GC detector.

In the negative mode it can function as an electron-capture detector (ECD) that produces a qualitative mobility spectrum of the compound in a GC peak. Using a nitrogen carrier gas, which gives thermal electrons as the only negative species, a

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number of studies related to the ECD have been completed. These studies have demonstrated the existence of dissociative electron capture for monohalogenated benzenes[5], both dissociative and associative capture for substituted benzenes and polychlorinated biphenyl (PCB) compounds[6-8], the effect of the ionic species formed by oxygen in the carrier gas at different temperatures[4], and halide ion formation by dissociative capture for the alkyl halides[9]. The plasma chromatography data show that the negative ion mobility spectra obtained are simple and characteristic and that even isomers such as the three monochloronitrobenzenes can be distinguished[7].

While only compounds that give a response in the ECD give a response in the negative mode with a nitrogen carrier gas, all compounds studied to date exhibit a response in the positive mode. Many of these positive spectra exhibit an intensity many times greater than that of the corresponding negative spectra. The positive reactant ion species formed in the nitrogen carrier gas are primarily of the type $(H_2O)_nH^+$ and $(H_2O)_nNO^+$. These very reactant species react with trace molecules to give protonated molecular ions[10,11], simple fragmentation patterns similar to those found in chemical ionization mass spectrometry[12,13], or more complex ion–molecules of the form $(M)_x(H_2O)_yH^+$ or $(M)_x(H_2O)_yNO^+$ for polar compounds like alcohols and ethers[14]. Studies of the positive ion mobility spectra produced in plasma chromatography have included those of the PCB compounds[8], monohalogenated benzenes[5], *n*-alkyl alcohols[14], oxygenated organic compounds[2], *n*-alkanes[13] and 1-haloalkanes[9].

To be useful as a qualitative GC detector it is necessary to develop a general knowledge of the type of positive and negative mobility spectra produced by different classes of compounds and to have reference spectra available for a wide range of specific compounds. This study presents the general relationships observable in the mobility spectra of compound classes and presents new reference spectra for a series of compounds.

## EXPERIMENTAL

The basic design and operating characteristics of the Beta-VI Model plasma chromatograph (Franklin GNO Corp., West Palm Beach, Fla., U.S.A.) used to obtain these results have been described previously[4]. Unless otherwise indicated in figure captions, the experimental parameters used to obtain these data are: carrier gas flow-rate, 100 ml/min; drift gas flow-rate, 410 ml/min; electric field gradient, 250 V/cm; ion injection pulse, 0.2 msec; scan pulse, 0.2 msec; recorded scan time, 2 min; pressure, atmospheric (727–748 torr). Nitrogen (Linde, high purity grade) was used as both carrier and drift gas and was passed through separate metal traps of 2.25-l capacity packed with Linde molecular sieve 13X. This procedure removes impurities and gives a very low water concentration on the order of 10 ppm.

Because of the high sensitivity of the plasma chromatograph, samples must be introduced in the $10^{-6}$–$10^{-12}$-g range. Several techniques are used to introduce samples to the instrument. For compounds of fairly low ion–molecule reactivity, introduction is achieved by injecting sample vapour (of the order of $10^{-6}$–$10^{-7}$ g) with a microlitre syringe. For solids and high-boiling liquids, a solution in benzene, toluene or other suitable solvent, including water, is prepared and a platinum wire introduced into the solution. The solvent is allowed to evaporate and the sample remaining on the wire is introduced to the instrument. Samples introduced in this way are in the $10^{-7}$–$10^{-8}$-g range. For accurate work at low concentrations the solution is dispensed onto the wire from a microlitre syringe. During the exploration of using the plasma chromatograph as a qualitative detector for a gas chromatograph, a direct valved interface to inject a portion of a GC peak into the plasma chromatograph was constructed[9]. With this interface it is possible to inject a highly pure compound from the gas chromatograph to the plasma chromatograph at concentrations down to and even below the limit of detection of the GC flame ionization detector.

### *Procedure*

Sample introduction was achieved by using all three of the methods described above. All methods give sample concentrations sufficient to produce mobility spectra for 5 to 30 min depending upon the amount of sample introduced, reactivity of the compound with the reactant ions, and the temperature of the inlet. Mobility spectra of comparable sample concentrations can be obtained by recording each at definite time intervals after sample injection and making observations when reactant ion concentrations are similar. All sample quantities reported are quantities injected into the instrument, but peaks observed in the mobility spectra may represent sample concentrations several orders of magnitude lower. This is because of exponential dilution of the sample by the instrument carrier gas in time.

The stability of the instrument and its freedom from previous sample contamination are easily monitored by examination of the positive reactant ion mobility spectra. These are very stable from day to day as indicated by relative peak heights, drift times under the same operating conditions and reduced mobility values ($K_0$). $K_0$ values are calculated from the equation,

$$K_0 = \frac{6.55}{\tau \cdot T} \cdot \frac{p}{760}$$

where

$\tau$ = drift time (sec)
$T$ = absolute temperature (°K)
$p$ = atmospheric pressure (mmHg)

and the factor 6.55 incorporates cell length (6 cm), electric field gradient (250 V/cm) and correction to 273 °K.

All $K_0$ values reported have a standard deviation of $\pm 0.02$.

## RESULTS AND DISCUSSION

### *Negative mobility spectra*

When using nitrogen carrier gas to create reactant ions, the negative species are thermal electrons with average energies of about 0.5 eV. This allows one to observe both dissociative and associative electron attachment and study these processes over a wide range of conditions for many compounds. Only compounds that undergo associative or dissociative electron attachment give negative mobility spectra. No negative mobility spectra have been observed for aliphatic and aromatic hydrocarbons, aliphatic alcohols, aldehydes, ketones, amines, esters, ethers or fluorinated hydrocarbons.

When electrons react with monohalogenated benzenes, toluenes or xylenes, dissociative capture occurs to give only a negative halide ion[5]. This phenomenon also occurs for halogenated aliphatic compounds. With compounds containing mixed halogen substitution, only the most reactive halogen ion is dissociated. This reactivity is in the order $I^- > Br^- > Cl^-$. This order of reactivity is supported by data reported by Steelhammer and Wentworth[15], who measured activation energies for dissociative capture of electrons exhibited by a series of haloaromatic compounds using swarm-beam and electron attachment methods. They report activation energies for halide dissociation from chloro-, bromo- and iodobenzene to be in the order 0.42, 0.25 and 0.05 eV/molecule respectively. Christophorou *et al.*[16] carried out similar studies using a swarm-beam technique reporting the same order of reactivity and similar activation energies.

PCB compounds exhibit either dissociative capture to produce $Cl^-$, or dissociative and associative capture to produce $Cl^-$ and a molecular ion. This process depends on the degree of chlorination of the sample compound, associative capture occurring only for the higher molecular weight PCB compounds. Decachlorobiphenyl exhibits further dissociative capture producing $C_{12}Cl_8^-$ as well as $Cl^-$ and $C_{12}Cl_{10}^-$. These results are illustrated in Fig. 1.

The negative spectrum of 1-nitropropane is extremely weak. A $10^{-4}$-g sample

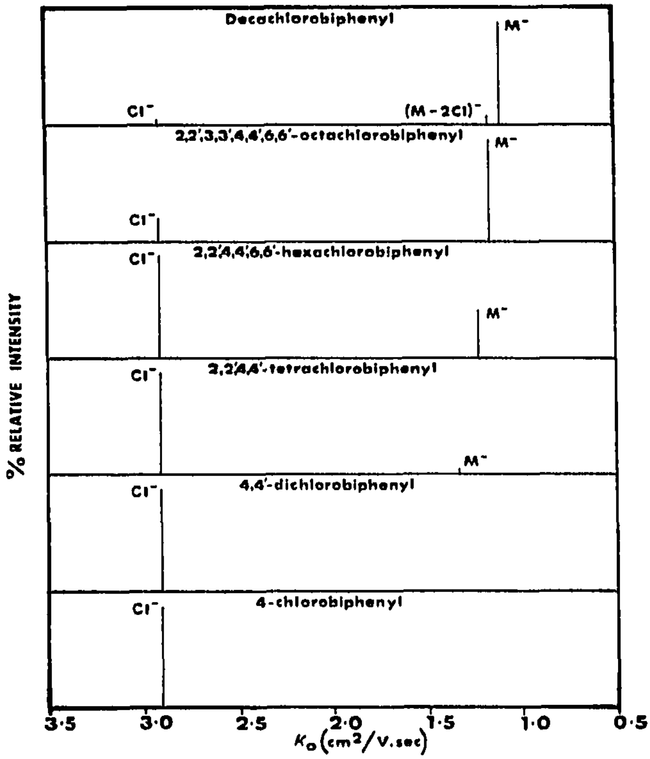

Fig. 1. Normalized plots of negative ion intensities *vs.* reduced mobility ($K_0$) for a series of polychlorinated biphenyls. All data are obtained at a temperature of 127°C. Higher molecular weights are associated with lower mobilities.

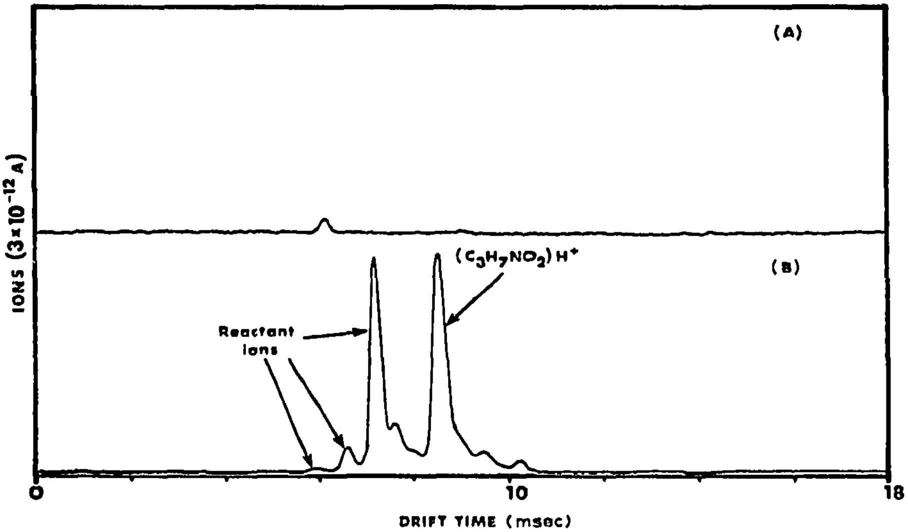

Fig. 2. Positive and negative mobility spectra of 1-nitropropane obtained at 108°C. (A) Negative mobility spectrum, $10^{-6}$-g sample injection; (B) positive mobility spectrum, $10^{-9}$-g sample injection.

injected into the plasma chromatograph produces several peaks, including a large peak that shifts position as the nitropropane concentration in the instrument depletes. The shift is from $K_0 = 2.35$ to $K_0 = 2.68$ cm$^2\cdot$V$^{-1}\cdot$sec$^{-1}$. Quantities of sample injected into the plasma chromatograph in the $10^{-4}$–$10^{-6}$-g range overload the instrument and no interpretation of ion peaks observed in the mobility spectrum is advisable. This is because the number density of sample molecules is so great at the high pressure involved that a complicated series of ion–molecule reactions involving more than one sample molecule is possible. For injected sample quantities between $10^{-6}$ and $10^{-7}$ g one small peak is seen at $K_0 = 2.68$ cm$^2\cdot$V$^{-1}\cdot$sec$^{-1}$. This ion we postulate as $NO_2^-$, but insufficient evidence exists at this time to prove its identity. For sample injections below $10^{-7}$ g, no peak is observed in the negative mode. By contrast, the positive mobility spectrum is obtainable at much lower 1-nitropropane concentrations (Fig. 2).

Christophorou *et al.*[16] reported that nitrobenzene captures electrons non-dissociatively at electron energies between 0 and 0.3 eV, only undergoing dissociative capture to form $NO_2^-$ at electron energies above 1.0 eV. In the plasma chromatograph with its low energy electrons only associative electron capture occurs for nitrobenzene with formation of $C_6H_5NO_2^-$, no $NO_2^-$ being noted[6]. The identity of the $C_6H_5NO_2^-$ observed is confirmed by coincidence of its mobility peak with that obtained for this compound in the positive mobility spectrum. Using a coupled mass spectrometer it has been established that for aromatic compounds a positive molecular type ion, $MH^+$, is obtained in the plasma chromatograph[5,11], thus such an ion for nitrobenzene could be expected to have a mobility similar to that of its equivalent negative ion.

Halonitroaromatic compounds exhibit both dissociative and associative electron capture. *Ortho*- and *para*-monohalonitrobenzenes exhibit complete dissociative capture to give the corresponding halide ion and the nitrophenyl fragment ion. The

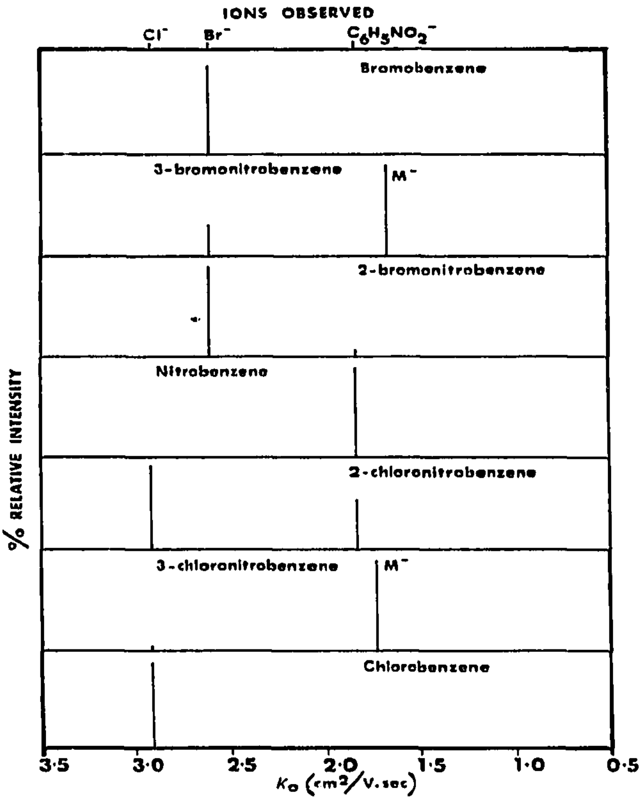

Fig. 3. Normalized plots of negative ion intensities *vs.* $K_0$, for a series of halo- and nitro-substituted benzenes. All data are obtained at 127°C.

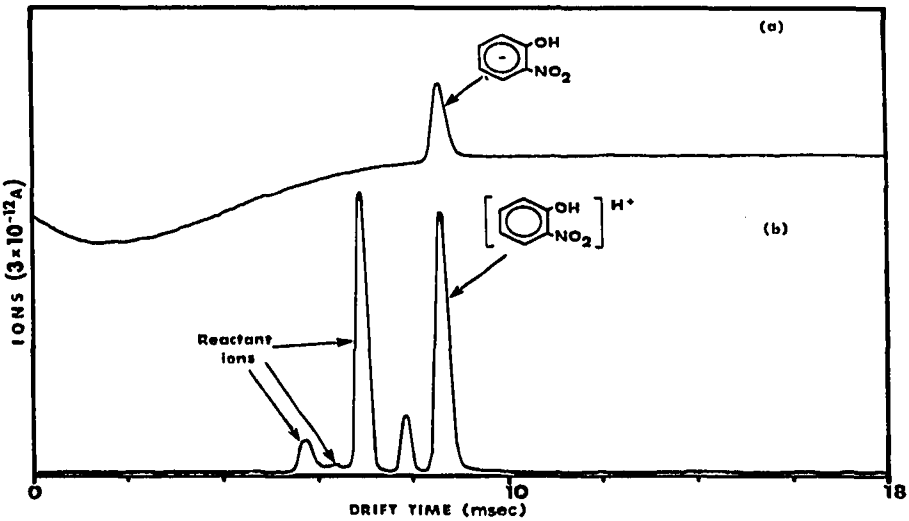

Fig. 4. Positive and negative mobility spectra of *o*-nitrophenol obtained at 136°C from a $10^{-7}$-g sample injection. (A) Negative mobility spectrum, (B) positive mobility spectrum.

corresponding *meta*-isomers exhibit primarily associative capture to give the molecular halonitrobenzene ion with a small amount of $Cl^-$ being formed by dissociative capture. Dihalosubstituted nitrobenzene compounds exhibit dissociative capture to give the halide ion and a monohalonitrophenyl ion[7]. Fig. 3 shows a comparison between several halo- and nitro-substituted benzenes. Other substituted nitrobenzene compounds show only a molecular ion, except for *m*-nitrophenol which shows a peak which may be due to a dimer ion.

Fig. 4 illustrates the positive and negative mobility spectra obtained for *o*-nitrophenol. A $10^{-7}$-g sample was injected in the plasma chromatograph and the negative mobility spectrum obtained. The instrument was then switched over to the positive mode and the positive mobility spectrum obtained. This may be compared to the spectra illustrated for 1-nitropropane in Fig. 2, whose negative and positive mobility spectra were obtained separately using a $10^{-6}$-g injection to obtain the negative mobility spectrum and a $10^{-9}$-g injection to obtain the positive mobility spectrum. This difference in reactivity and type of negative mobility spectra between *o*-nitrophenol and 1-nitropropane, which in this case can be used to distinguish between nitro-substituted aromatic and aliphatic compounds, is typical of results obtained with other types of compound.

Figs. 2 and 4 illustrate the way data are recorded directly from the plasma chromatograph. Figs. 1, 3 and 5–8 illustrate data plotted as normalized ion intensity

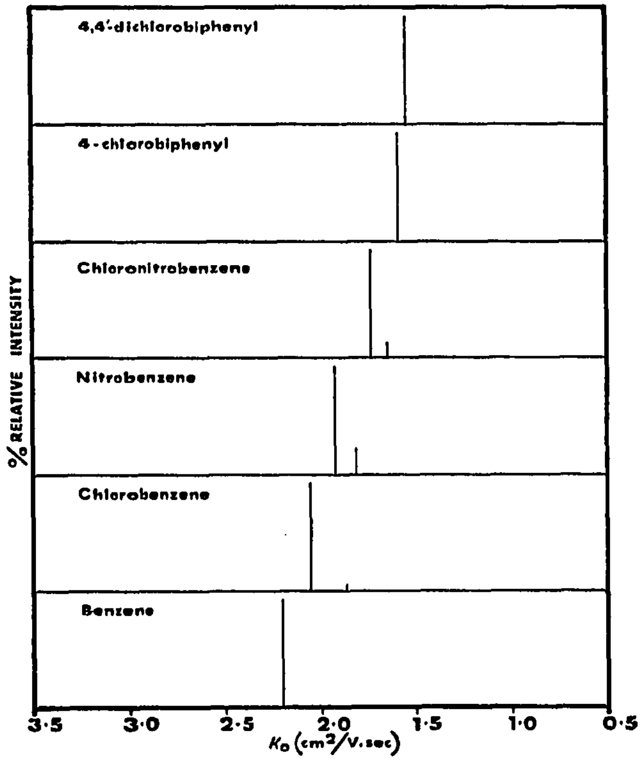

Fig. 5. Normalized plots of positive product ion intensities *vs*. $K_0$ for a series of substituted benzenes. All data are obtained at 127°C. The major ion shown is $MH^+$; the minor ion is $(M+NO)^+$.

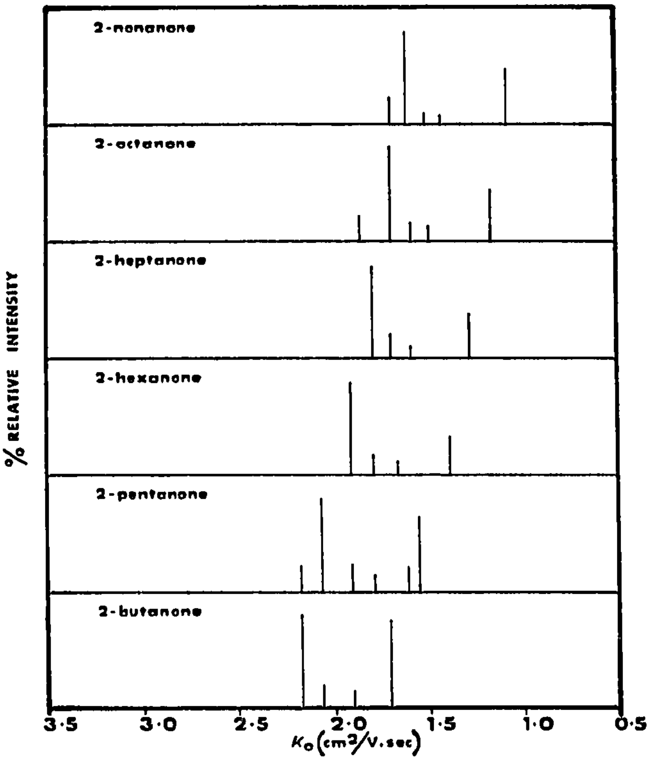

Fig. 6. Normalized plots of positive product ion intensities *vs.* $K_0$ for the 2-alkyl ketones. All data are obtained at a temperature of 127°C. No negative mobility spectra are observed.

*versus* reduced mobility. These normalized plots of data are the preferred way to present reference spectra, since the effect of different operating parameters of the instrument as well as temperature, pressure and sample concentration are eliminated.

*Positive mobility spectra*

The positive reactant species formed in a nitrogen carrier gas are of the type $(H_2O)_nH^+$ and $(H_2O)_nNO^+$. Nitrobenzene and the halonitrobenzenes described above all react primarily with the $(H_2O)_nH^+$ species to give positive ion–molecules of the form $MH^+$. Correspondence of this $MH^+$ with $M^-$ in the negative mode is used as a method of identifying these ion-mobility peaks. A small amount of $(M+NO)^+$ is also seen for these compounds.

Fig. 5 illustrates the positive mobility spectra for a series of substituted aromatic compounds of increasing molecular weight. The major peak observed for each compound is due to the $MH^+$ species. It should be noted that if the $K_0$ values of the protonated molecular ions observed for 4-chlorobiphenyl and 4,4′-dichlorobiphenyl are plotted, along with the negative molecular ions observed for higher PCB compounds (Fig. 1), *versus* their molecular weight a smooth curve is obtained. This mass correlation is expected from previous experimental observations[11].

The positive mobility spectrum of 1-nitropropane (Fig. 2) exhibits a strong

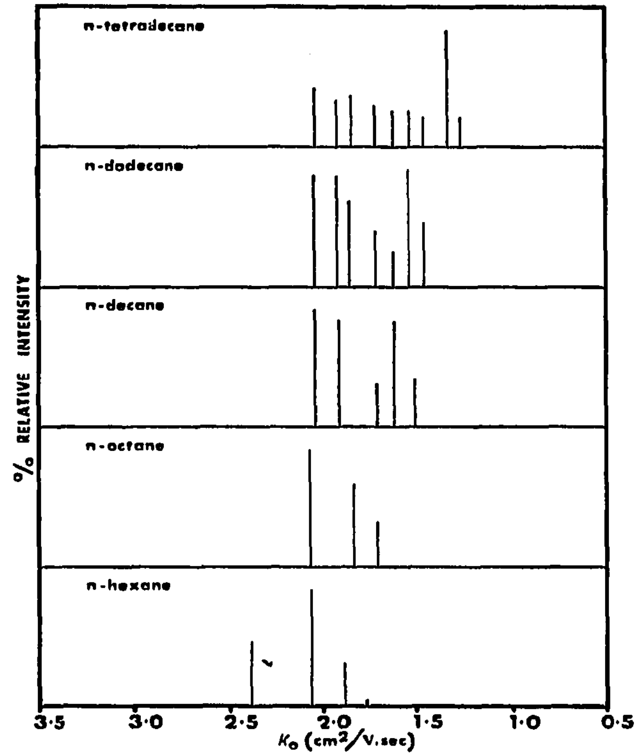

Fig. 7. Normalized plots of positive product ion intensities *vs.* $K_0$ for a series of *n*-alkanes. All data are obtained at 136°C. No negative mobility spectra are observed.

peak at $K_0 = 1.89\ \mathrm{cm^2 \cdot V^{-1} \cdot sec^{-1}}$, which is most probably due to the $(C_3H_7NO_2)H^+$ species. This peak is still observed after injecting nitropropane sample quantities in the $10^{-13}$–$10^{-14}$-g range.

Aliphatic alcohols give peaks which appear to correspond to monomer, dimer, and trimer hydrated species. As the plasma chromatograph temperature is raised, the lower mass ions become more prominent. The 2-alkyl ketones show two major peaks. The one at higher $K_0$ values is due to a hydrated molecular type ion $M(H_2O)H^+$, and the one at lower $K_0$ value to a dimer ion of the form $M_2H^+$. A series of 2-alkyl ketones is illustrated in Fig. 6. Both the hydrated monomer and dimer protonated ions show a progression to lower $K_0$ value as the molecular weights of the ketones increase along their homologous series. A plot of these $K_0$ values *versus* mass produces a smooth curve. The relative intensities seen in Fig. 6 are plotted from the mobility spectra using as a comparative reference point when the heights of the major reactant ion peak in the spectra are approximatley equal. Under these conditions, spectral patterns of pure compounds appear to be quite stable down to minimum detectable concentrations. When sample quantities of polar compounds that overload the instrument are introduced ($10^{-4}$–$10^{-6}$ g), dimer product ions predominate in the spectra.

The *n*-alkane hydrocarbons produce positive mobility spectra strikingly similar to those formed in chemical ionization mass spectrometry with a prominent molecular type ion, $(M+NO)^+$, and a series of simple fragment ions[14]. This is illustrated for

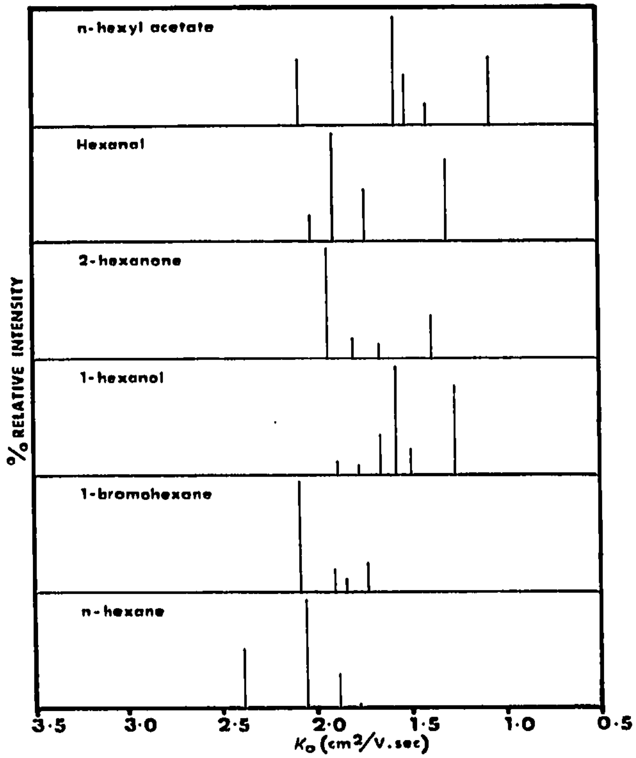

Fig. 8. Normalized plots of positive product ion intensities *vs.* $K_0$ for a series of substituted hexane compounds. Data for *n*-hexane, 1-bromohexane and *n*-hexyl acetate are obtained at 136°C, for 2-hexanone and hexanal at 127°C, and 1-hexanol at 100°C. Only 1-bromohexane produces a negative mobility spectrum of the compounds shown.

these compounds in Fig. 7. By analogy to chemical ionization mass spectrometry the major ion is assigned as $(M-1)^+$. Additional evidence for this assignment appears in the coincident mobility of this ion and the major ion in the corresponding alkyl halides where $(M-1)^+$ is formed[9].

Fig. 8 illustrates the normalized mobility spectra of a series of substituted hexanes. Both *n*-hexane and 1-bromohexane show a peak at $K_0 = 2.06(\pm 0.02)$ $cm^2 \cdot V^{-1} \cdot sec^{-1}$ as their major ion, postulated[10] as $C_6H_{13}^+$. As the polarity of the functional group on the hexane substrate increases, the compounds show greater tendency to form ions of the type $M(H_2O)_nH^+$ and $M(H_2O)_nNO^+$, dimers and trimers. Hexanol and 2-hexanone show major peaks at $K_0 = 1.90$ and $1.93\ cm^2 \cdot V^{-1} \cdot sec^{-1}$ respectively, which are postulated as $(M)_2H^+$. The *n*-hexyl acetate, which has a polarity intermediate between *n*-hexane and 2-hexanone, shows a peak corresponding to $C_6H_{13}^+$ as well as peaks postulated as due to hydrated molecular type species and dimer species.

## CONCLUSIONS

Taken together the positive and negative spectra provide considerable qualitative information about the particular compound being studied. Since the mobility spectra are quite dependent upon having small concentration and extreme purity of sample, delivery of the sample as a GC peak is ideal for this technique. Thus the plasma chromatograph can function as a sensitive qualitative detector in the GC of many different compounds. The results obtained for electron-capturing compounds give qualitative information about the species formed in the electron-capture process and can be used to elucidate electron-capture mechanisms. Correlations between positive and negative mobility spectra and comparison to existing reference spectra can be used to identify an unknown compound in a mixture separated by GC. To become effective in this application, the plasma chromatographic mobility spectra of many classes of compounds need to be determined. Further work is now underway with many different types of compounds to obtain more of this type of data.

## ACKNOWLEDGEMENTS

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