

CHROM. 8322

PLASMA CHROMATOGRAPHY OF *n*-ALKYL ACETATES

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(Received March 18th, 1975)

SUMMARY

Plasma chromatography is a technique which permits characterization and analysis of trace constituents in a gaseous mixture at atmospheric pressure. It is especially well suited as a gas chromatographic detector. Operating at atmospheric pressure, the instrument uses either air or nitrogen carrier gas into which the sample is injected directly or through a gas chromatograph. The compounds are identified by their characteristic positive and negative mobility spectra, which consist of simple molecular and dissociative ions. Quantities as low as 10^{-6} to 10^{-12} g are detectable. For use as a gas chromatographic detector, reference mobility spectra of compounds are needed. Those of *n*-alkanes, alcohols, ketones, halogenated aromatics, substituted nitrobenzenes, polychlorinated biphenyls, alkyl halides, aliphatic N-nitrosamines and isomeric phthalic acids have been previously reported. This study reports the reference mobility spectra produced by *n*-alkyl acetates. These compounds display strong positive mobility spectra but no negative mobility spectra. The spectra all show characteristic MH^+ , $M(H_2O)_nH^+$ and $(M_2)H^+$ along with the alkyl fragment ions.

INTRODUCTION

Plasma chromatography is an analytical method showing much promise for ultratrace analysis of organic compounds¹⁻⁵. The technique is based on creating ion-molecule reactions and observing mobility spectra which reveal both the kind and relative abundances of the charged particles formed, with all steps being carried out at atmospheric pressure. Ions for the reactions are generated in a purified nitrogen or air carrier gas containing a trace of water vapour, by the action of 60-keV electrons emitted from a ⁶³Ni foil. Approximately 10% of the high-energy electrons are actually effective in ionizing the nitrogen carrier gas and by further ion-molecule collisions relatively stable and reactant ions are formed of the form $(H_2O)_nH^+$ and $(H_2O)_nNO^+$, whose relative abundance and value of *n* depend upon water concentration and temperature. When air is used as a carrier gas, $(H_2O)_nO_2^-$ ions are added to these groups.

The positive reactant ions induce ion-molecule reactions with trace amounts of organic compounds injected directly into the carrier gas stream, forming charac-

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teristic charged species, the product ions, which are then directed into the drift spectrometer. In the drift spectrometer the product ions drift under an electric field of several hundred volts toward the detector in an inert nitrogen atmosphere. Separation of the different product ions occurs because of differing mobilities in nitrogen. This phenomenon can be compared with that of a time-of-flight mass spectrometer, with the difference that at the atmospheric plasma chromatographic conditions the ionic velocity is determined by the collision interaction between an ion and neutral nitrogen molecules, rather than by the kinetic energy velocity of the ion in the mass spectroscopic conditions. The ion mobility is dependent upon the mass, the heavier ion moving slower, the lighter ions faster. Both positive and negative mobility spectra can be recorded by choice of the electrical field polarity.

The negative mobility spectra which consist of molecular and dissociative ions are produced only by those compounds that undergo electron attachment. All compounds studied to date⁵⁻¹⁰ exhibit positive mobility spectra. In general, the positive response is many times greater than the negative.

Plasma chromatography is an extremely sensitive method, capable of detecting 10^{-12} g or less of a compound and providing identification through the characteristic positive and negative mobility spectra. The combination of selectivity, sensitivity and operation at atmospheric pressure suggests the use of the plasma chromatograph as a detector for gas and liquid chromatography. In order that the plasma chromatograph be useful as a detector it is necessary to have at hand a large number of reference spectra as well as the knowledge of the general type of spectra produced by different classes of compounds. This study was undertaken to provide the reference spectra for *n*-alkyl acetates and to show the general relationship existing in the mobility spectra of these compounds.

EXPERIMENTAL

Instrumentation

The Beta VI plasma chromatograph (Franklin GNO Corp., West Palm Beach, Fla., U.S.A.) used in this study has been described previously^{4,5}. The experimental conditions for this study were: plasma chromatographic tube temperature, 136°; carrier gas (nitrogen) flow-rate, 115 ml/min; drift gas (nitrogen) flow-rate, 470 ml/min; electric field gradient, 250 V/cm; time base, 20 msec; recorded scan, 2.0 min; electrometer sensitivity, 3×10^{-12} a.f.s.; pressure, 724-736 torr. The carrier and drift gases were nitrogen (Linde High Purity 99.9%) passed through individual stainless-steel traps of 2.25-l capacity packed with Linde Molecular Sieve 13X to remove impurities.

n-Propyl acetate was BDH Reagent Grade, *n*-pentyl acetate Baker Reagent Grade and all the other compounds were Matheson, Coleman and Bell Division Reagent Grade of greater than 99.9% purity.

Procedure

A procedure admitting concentrations of approximately 10^{-7} - 10^{-10} g of sample compound was necessary so as not to saturate the instrument. A liquid sampling syringe of 2.5- μ l capacity was flushed three times with reagent-grade acetone and placed in a syringe cleaner (Hamilton, Reno, Nev., U.S.A.). The syringe cleaner

applies a combination of heat and vacuum to remove any residual contaminants. The syringe was then flushed with sample three times before being filled. All of the sample was ejected and the syringe inserted into the inlet tube of the plasma chromatograph. Approximately 1.0 μ l of carrier gas was drawn into the syringe and then expelled into the carrier gas stream. This technique admitted sufficient sample to produce good mobility spectra, while not overloading the instrument.

The mobility spectra of the reactant ions are very stable from day to day, as indicated by relative peak heights and reduced mobility values (K_0). The values of reduced mobilities are calculated using the expression

$$K_0 = \frac{d}{\tau E} \times \frac{273}{T} \times \frac{P}{760}$$

where d = length of cell (6 cm), τ = drift time (sec), E = field gradient (250 V/cm), T = temperature ($^{\circ}$ K), and p = pressure (mm Hg). The K_0 reported here all have a deviation of ± 0.02 .

RESULTS AND DISCUSSION

Mobility spectra were obtained for the following *n*-alkyl esters: ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, *n*-pentyl acetate, *n*-hexyl acetate, *n*-heptyl acetate, and *n*-octyl acetate.

In the plasma chromatograph *n*-alkyl esters exhibit no negative mobility spectra as has been observed in the plasma chromatographic mobility spectra of other polar oxygenated compounds such as the *n*-alkyl alcohols and 2-alkyl ketones¹¹. This behaviour is expected since these compounds give no response in the electron capture detector. However, all of them produce strong and characteristic positive mobility spectra. Their reactivity with the reactant ions is extremely high. Injecting 1.0 μ l of vapour, the sample completely consumed the reactant ions. But at this concentration the mobility spectra are extremely stable, changing predictably with the decrease in concentration of the sample in time, until the sample has disappeared completely and only the reactant ions are present. A composite mobility spectrum is illustrated in Fig. 1, where this effect can be observed. The different spectra were recorded at a certain time interval after injection of the sample, as is noted on the left-hand side of the spectrum. The first spectrum, run at high concentration, shows a large dominant signal at high drift time. This peak is assigned to a M_2H^+ ion. When the sample concentration decreases, which is recognized by the presence and intensity of the re-

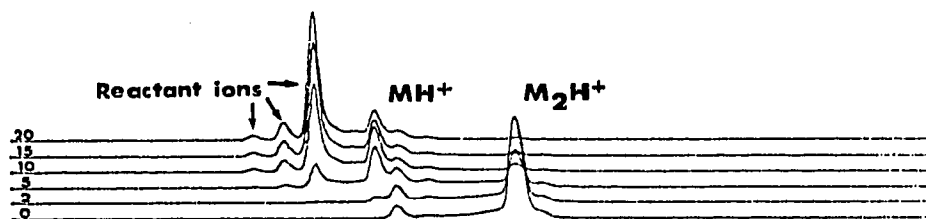


Fig. 1. Composite positive mobility spectra of *n*-propyl acetate taken at indicated times in minutes after injection of sample.

actant ion peaks, this large peak decreases in intensity to disappear completely and another peak is formed at lower drift time, which is assigned to a MH^+ ion.

Positive mobility spectra of *n*-alkyl acetates generally display four to six signals. These signals move predictably to lower mobility, with increasing molecular mass of the *n*-alkyl esters. This effect is illustrated in Fig. 2 with the normalized mobility spectra of all the compounds studied. The spectra are normalized to the major reactant ion in the reactant ion spectrum. Each compound displays a unique spectral pattern which permits identification and analysis.

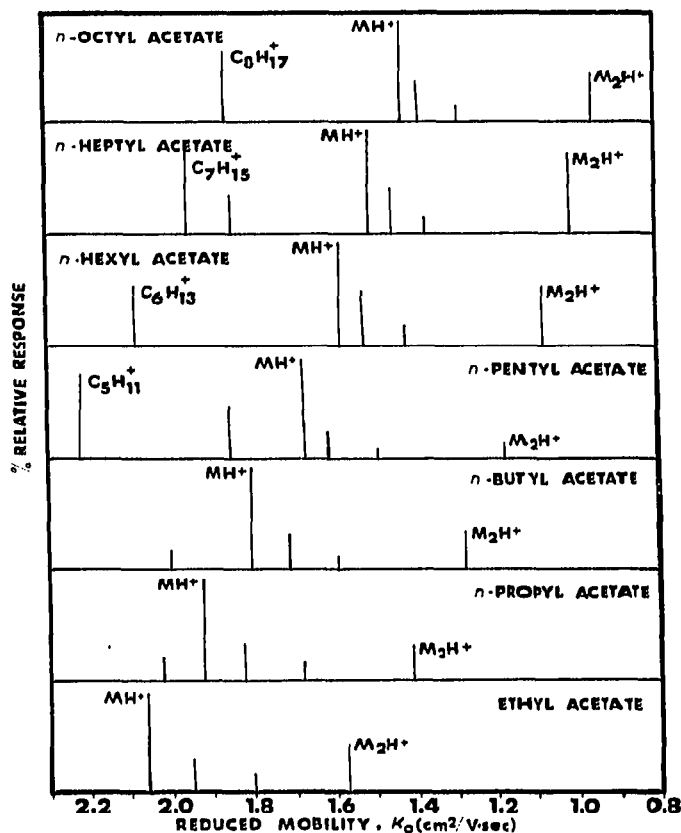


Fig. 2. Normalized plots of product ion intensities vs. reduced mobility (K_0) for the *n*-alkyl acetates.

Early work with the plasma chromatograph involved positive mass identification of the charged species in the mobility spectrum peaks by direct introduction through an interface into a quadrupole mass spectrometer. A small number of mass-mobility correlation curves were obtained in this way, most of the other data being obtained by arbitrary assignment of ion structures. However, Griffin *et al.*¹³ found that these assignments based upon mobility are in general only accurate to $\pm 20\%$, while in the correlation for structurally related compounds the accuracy can be to within $\pm 2\%$.

Kane¹⁴ has established a number of correlation curves for compounds of similar type and structure. Measuring the ionic mobilities for different series of organic compounds he has plotted mobility vs. mass, obtaining curves for each of the different classes. These curves are quite close and form a family of curves. This type of curve cannot be used for predicting accurate ionic masses, but it can be useful for spectral interpretation, to determine whether a compound forms a molecular ion, an ion cluster, or fragment ion with an accuracy of about 5% (ref. 15).

In the mobility spectra of other polar compounds such as *n*-alkyl alcohols and ketones¹² it has been observed that these compounds have a pronounced tendency to form protonated monomer ions MH^+ , protonated dimer ions $(M_2)H^+$ and hydrated monomer ions $M(H_2O)_nH^+$.

The reduced mobility data obtained for *n*-alkyl acetates fit reasonably well in the family of correlation curves established by Kane. This indicates that *n*-alkyl esters, being polar oxygenated compounds, chemically similar to those for which these curves were established, will give similar product ions and the measured reduced mobility values correspond to masses of protonated monomer ions MH^+ , hydrated monomer ions $M(H_2O)_nH^+$ and dimer ions $(M_2)H^+$.

While there are insufficient data available to determine the exact mechanism of formation of these ions, the presence of abundant amounts of protonated dimer ion $(M_2)H^+$ at higher concentration can be explained either by it being formed directly from a vapour phase M_2 molecule, or by the reaction of M with MH^+ .

The type of product ions assigned to different ion peaks, their masses and their accurately measured reduced mobilities are given in Table I.

TABLE I

REDUCED MOBILITIES OF THE PRODUCT IONS AND MASS ASSIGNMENT OF THE *n*-ALKYL ACETATES

Compound	Mass of ionic species assigned		Reduced mobility, K_0 (cm ² /V·sec)	
	MH^+	M_2H^+	MH^+	M_2H^+
Ethyl acetate	89	177	2.06	1.57
<i>n</i> -Propyl acetate	103	205	2.02	1.41
<i>n</i> -Butyl acetate	117	233	2.00	1.28
<i>n</i> -Pentyl acetate	131	261	1.85	1.18
<i>n</i> -Hexyl acetate	145	289	1.58	1.08
<i>n</i> -Heptyl acetate	159	317	1.50	1.01
<i>n</i> -Octyl acetate	173	345	1.42	0.95

A close similarity to chemical ionization mass spectrometry has been established for plasma chromatography. According to Munson and Field¹⁶, there are four products of high intensity formed in the chemical ionization mass spectra of this class of compounds. However, this fragmentation pattern was not observed in the ion mobility spectra. As an explanation can be probably cited the fact that the chemical ionization mass spectrometer functions at reduced pressure near 1 torr and more fragmentation of the molecule can take place, while plasma chromatography

functions at atmospheric pressure and the probability of stabilizing ion molecule collisions is very high.

Since the protonated monomer ion (MH^+) peak predominates at lower concentration and the protonated dimer ion (M_2H^+) peak at higher concentrations, the change in relative abundance could be used for qualitative as well as quantitative detection of those compounds.

CONCLUSIONS

n-Alkyl esters give simple, characteristic positive mobility spectra in a plasma chromatograph but no negative mobility spectra. The sensitivity of the method is very high, with identification by the mobility spectra possible. These very polar compounds form primarily ions of the type MH^+ , $M(H_2O)_nH^+$ and M_2H^+ . By establishing the general type of ions and reference spectra observed for these compounds, the data can be used to identify these specific compounds when they appear as unknown compounds in a mixture separated by gas chromatography. 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 different types of compounds to obtain more of this type of data.

ACKNOWLEDGEMENTS

The research of this paper was supported by the Defense Research Board of Canada, Grant No. 9530-116, and the National Research Council of Canada, Grant No. A5433.

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