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PLASMA CHROMATOGRAPHY OF THE *n*-ALKYL HALIDES

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SUMMARY

A plasma chromatograph directly interfaced to a gas chromatograph functions as a very sensitive qualitative detector for gas chromatographic peaks. Using a nitrogen carrier gas, the plasma chromatograph creates the positive reactant ions $(\text{H}_2\text{O})_n\text{H}^+$ and $(\text{H}_2\text{O})_n\text{NO}^+$ and the negative reactant species of low-energy electrons to react with the gas chromatographic peak component and form characteristic product ions. Ion mobility spectra observed in the plasma chromatograph for a series of 1-halogenated alkanes from 1- $\text{C}_4\text{H}_9\text{X}$ to 1- $\text{C}_8\text{H}_{17}\text{X}$ display negative spectra consisting of only the halogen ion from dissociative electron capture. The positive mobility spectra appear to contain the $(\text{M}-\text{I}-\text{X})^+$ as the most abundant ion, along with smaller characteristic ion peaks. These results are consistent with plasma chromatographic spectra obtained in similar studies of halogenated aromatics, alkanes and oxygenated organic compounds.

INTRODUCTION

Functioning at atmospheric pressure, the plasma chromatograph first creates both positive and negative ions in a carrier gas using a nickel-63 source. The reactant ions undergo ion-molecule reactions with trace molecules injected into the carrier gas stream. The resultant molecular ions are separated in a coupled ion-drift spectrometer to give positive and negative spectra characteristic of the organic molecules involved and the reactant ions generated. Both the instrumentation and the technique have been described previously¹⁻⁴.

While plasma chromatography provides a method and instrumentation for trace analysis and also for fundamental studies of ion-molecule reactions, the technique has a particular relationship to gas chromatography (GC). As the plasma chromatograph operates at atmospheric pressure, only a simple interface is required for it to function as a very sensitive GC detector. In the negative mode, it can function as an electron-capture detector that produces a qualitative spectrum of the compound in a GC peak. Using nitrogen as carrier gas, which gives low-energy electrons as the only negative species, a number of studies related to the electron-capture detector have been carried out. These studies have demonstrated the existence of dissociative electron capture for monohalogenated benzenes⁵, both dissociative and associative electron capture for substituted benzenes and polychlorobiphenyl (PCB) compounds⁶⁻⁸, and the effect of the ionic species formed by oxygen in the carrier gas at

different temperatures⁴. These data show that the negative ion spectra obtained are very simple and characteristic and that even isomers such as the three chloronitrobenzenes can be distinguished⁷.

While only compounds that give a response in the electron-capture detector give a response in the negative mode with a nitrogen carrier, all compounds studied so far have exhibited a response in the positive mode. These positive spectra exhibit a sensitivity many times (at least 10^3) greater than that of the corresponding negative spectra. The positive reactant ion species formed in the nitrogen carrier gas are primarily of the type $(\text{H}_2\text{O})_n\text{H}^+$ and $(\text{H}_2\text{O})_n\text{NO}^+$. These very reactive particles react with trace molecules to give either protonated molecular ions^{5,9} or simple fragmentation patterns similar to those found in chemical ionization mass spectrometry¹⁰. Studies of the positive ion spectra produced in plasma chromatography have included those of the PCB compounds⁸, monohalogenated benzenes⁵, *n*-alkanols¹¹, oxygenated organic compounds² and the *n*-alkanes¹². The present study of a series of 1-halogenated alkanes was undertaken as part of a continuing effort to provide qualitative plasma chromatographic data for different classes of compounds.

EXPERIMENTAL

Instrumentation

The basic design and operating characteristics of the Beta-VI plasma chromatograph (Franklin GNO, West Palm Beach, Fla., U.S.A.) used in these experiments have been described previously⁴⁻⁶. Ions formed in a flowing carrier gas by a nickel-63 source are moved by an electric field through an ion-molecule reactor section toward the drift spectrometer, where separation of the ions occurs because of their different mobilities as they move through a countercurrent flow of inert drift gas (nitrogen).

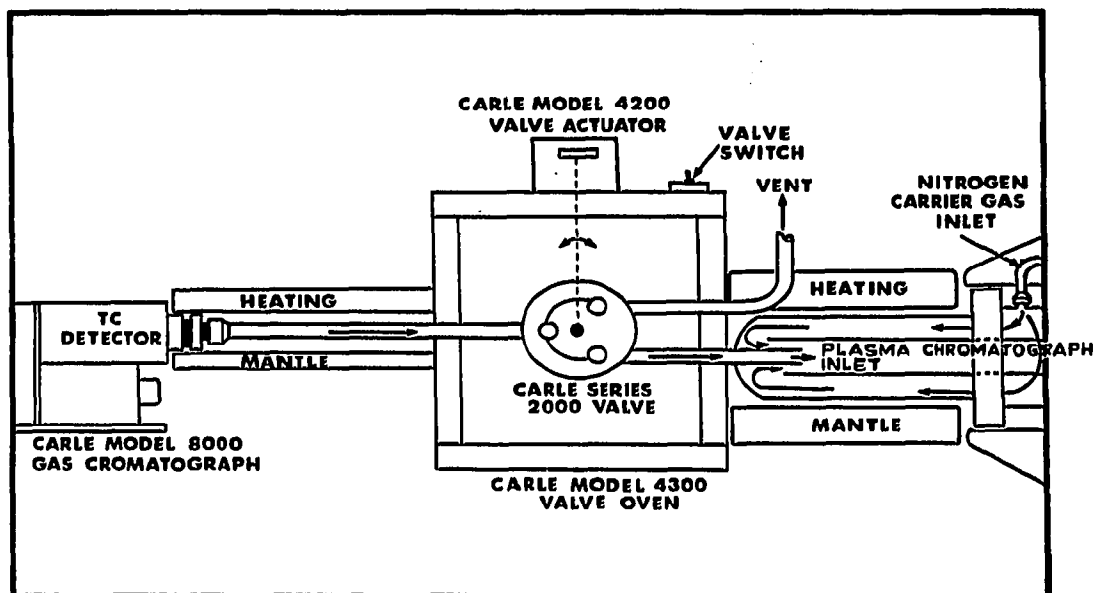


Fig. 1. Schematic diagram of the gas chromatograph-plasma chromatograph interface system.

Ions reach the detector in a series of ion peaks recorded as a plasmagram. A variable-delay gating technique on a scan grid, synchronized to the injection grid, gives a recording of the millisecond plasmagram scan in 1- to 10-min time spans.

Because of the high sensitivity of the plasma chromatograph, samples must be in the 10^{-6} – 10^{-12} -g range. To facilitate sample entry and also to ensure high purity of the sample, a direct interface of the plasma chromatograph to the effluent of a gas chromatograph was constructed. The system shown in Fig. 1 uses a Carle Series 2000 valve mounted in a Model 4300 valve oven (Carle Instruments, Fullerton, Calif., U.S.A.) to direct the GC effluent to vent, except when it is desired to inject a selected peak, or portion of a peak, into the plasma chromatograph inlet. The entire interface can be heated to 220° and is maintained 25° above the GC detector temperature.

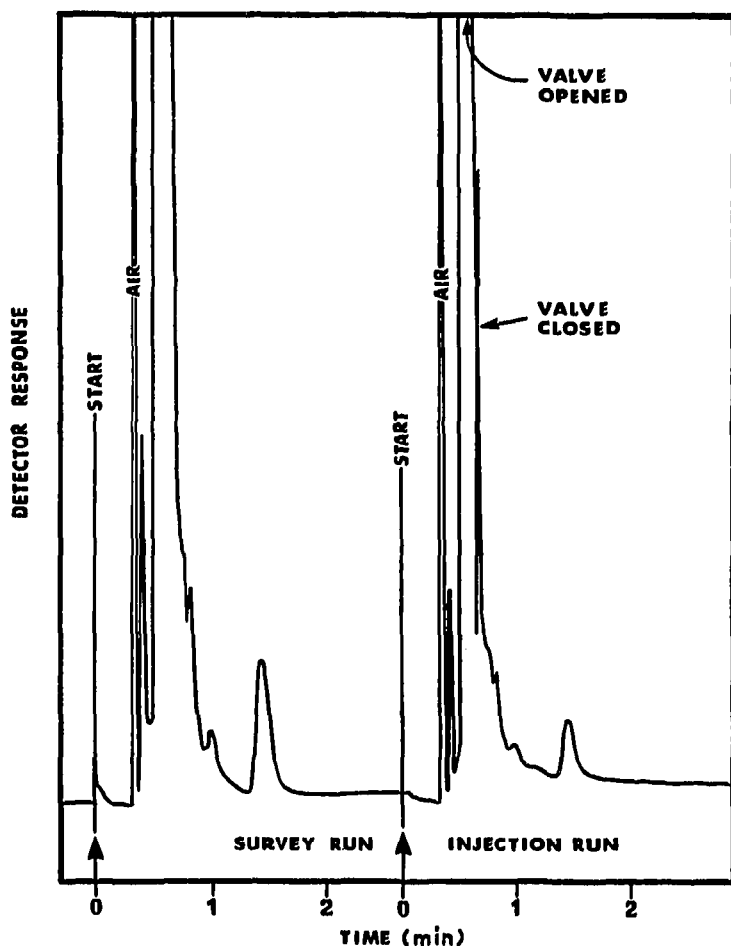


Fig. 2. Gas chromatogram showing injection of a portion of the 1-bromohexane peak into the plasma chromatograph inlet. Valve oven and line at 150° . GC conditions: 3% Dexsil 300 on Chromosorb W, 80–100 mesh; temperature, isothermal at 130° ; helium flow-rate, 30 ml/min. Plasma chromatograph conditions: temperature, 135° ; carrier gas flow-rate, 100 ml/min; drift gas flow-rate, 450 ml/min; ion-molecule reactor length, 6.0 cm; ion-drift space length, 6.0 cm; electric field, 250 V/cm; injection pulse, 0.2 msec; scan pulse, 0.2 msec; recorded scan, 2 min; pressure, atmospheric (728–735 torr); gas, nitrogen, Linde high-purity grade (99.996%).

The electrically operated switching valve functions in less than 0.2 sec per cycle. This technique avoids a continual entry of column bleed into the plasma chromatograph, which could very quickly saturate the plasma chromatograph. With this GC-plasma chromatographic interface, it is possible to inject 10^{-8} g or less of a highly purified compound. The technique is illustrated in the chromatogram in Fig. 2, showing the injection of 1-bromohexane.

Reagents

The alkyl halides were of reagent grade and were obtained from Analabs (North Haven, Conn. 06473, U.S.A.). The carrier and drift gases used were nitrogen (Linde high-purity grade, 99.996%). Prior to entry into the plasma chromatograph, both carrier and drift gases were passed through a metal trap of 2.25-litre capacity packed with Linde molecular sieve 13X. This procedure removes impurities and gives a water concentration estimated to be about 10 ppm.

Procedure

A sampling procedure that admits concentrations in the parts per 10^6 to 10^9 range is necessary so as not to saturate the plasma chromatograph. The preferred method is to use the GC-plasma chromatographic system and actuate the switching valve during a GC peak to direct a portion of the peak compound into the plasma chromatograph. An alternate method used is to inject less than $0.1 \mu\text{l}$ of sample vapor directly into the carrier-gas stream using a GC liquid sampling syringe. Both methods give samples sufficient to produce plasmagrams for 15–30 min, depending on the reactivity of the compounds. Plasmagrams of comparative concentrations can be obtained by recording each at definite time intervals after sample injection and when amounts of the reactant ions are similar. Many duplicate runs were made on each sample using both injection methods. All data reported were obtained using the GC-plasma chromatographic sampling system.

The stability of the instrument and its freedom from previous sample contamination is easily monitored by examination of the positive reactant ion spectra. These spectra are very stable from day to day, as indicated by relative peak heights, drift times under the same operating parameters and reduced mobility values (K_0) calculated from the equation given in Table I. The three ion peaks shown in Fig. 3 are found in the positive reactant spectra at all temperatures from 25° to 180° . Their relative peak intensities are a function of temperature and water concentration. Their K_0 values are slightly dependent on temperature, whereas the product-ion peaks generally are not. In general, K_0 values calculated at a given temperature have a standard deviation of 0.02. The ionic species indicated in Fig. 3 appear to be consistent with relevant published data and more recent unpublished work¹³.

RESULTS AND DISCUSSION

Both the positive and negative plasma chromatographic spectra of all halogenated compounds of the chloro-, bromo- and iodo- series from $1\text{-C}_4\text{H}_9\text{X}$ to $1\text{-C}_8\text{H}_9\text{X}$ were obtained. Taken together, the positive and negative spectra yield unique fingerprint patterns. However, in all instances, the positive spectra alone are sufficient to distinguish between any two compounds.

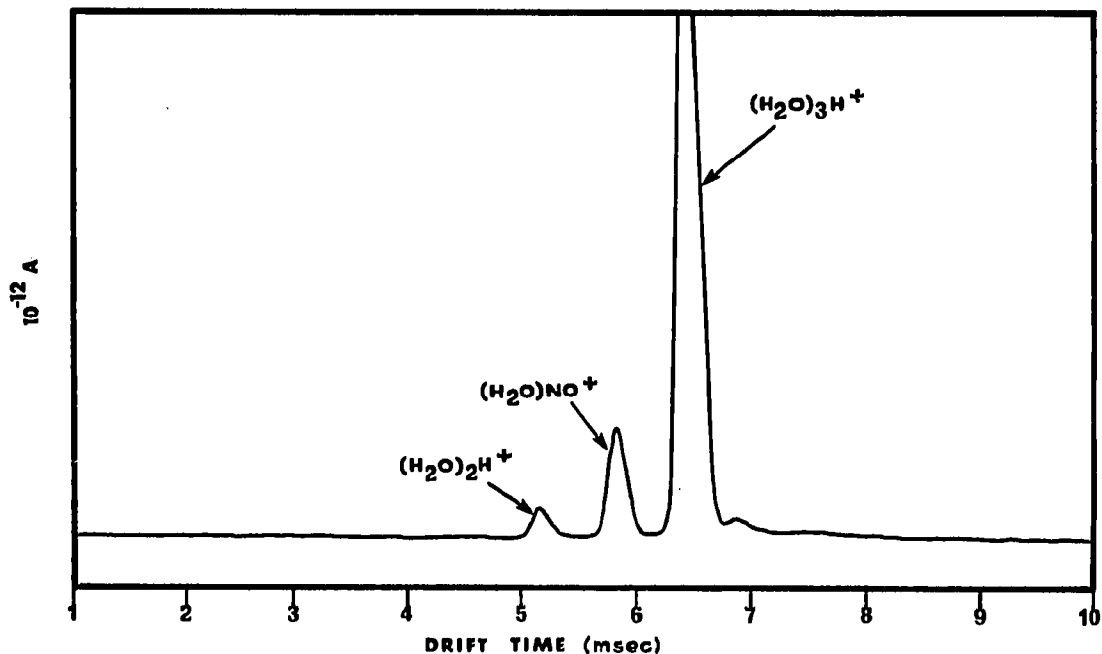


Fig. 3. Positive reactant ion spectra. Paper chromatograph conditions as in Fig. 2, except for: temperature, 137°; injection and scanning gate pulses, 0.1 msec.

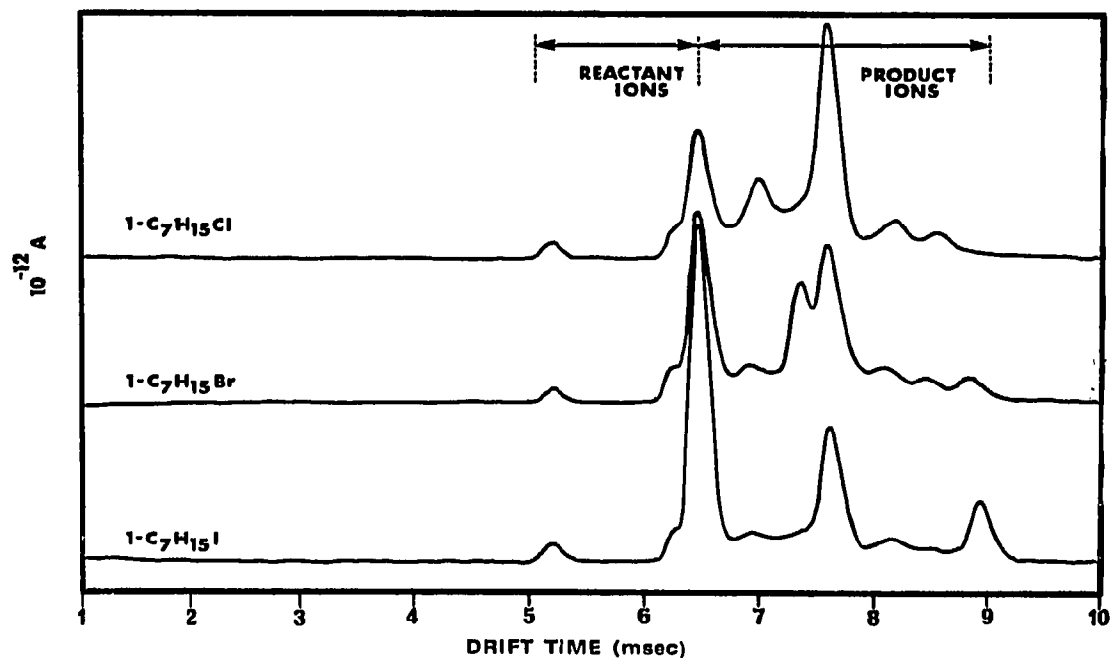


Fig. 4. Composite of the positive plasma chromatographic spectra of 1-heptyl halides. The reactant ion peak attributed in Fig. 3 to $(\text{H}_2\text{O})\text{NO}^+$ is absent, indicating its greater reactivity. Conditions as in Fig. 2.

Negative spectra

All of these compounds undergo dissociative electron capture with the formation of their respective halogen ion as the only stable product. Information appearing in the negative mode indicates the nature of the halogen atom contained in the compound. Chlorinated compounds produce a weak peak at the reduced mobility established for Cl^- . Brominated alkanes produce a Br^- peak, which, although strong for 1-bromobutane and 1-bromopentane, becomes less intense as the carbon number of the alkyl group increases. All of the iodide compounds studied gave strong ion peaks for I^- , reflecting the greater reactivity of these compounds toward dissociative electron capture. Associative electron attachment does not form stable molecular

TABLE I
MOBILITY DATA OBTAINED FOR 1-HALOGENATED ALKANES

<i>Compound</i>	<i>Reduced mobility, K_0^* ($\text{cm}^2/\text{V}\cdot\text{sec}$)</i>	<i>Compound</i>	<i>Reduced mobility, K_0^* ($\text{cm}^2/\text{V}\cdot\text{sec}$)</i>	<i>Compound</i>	<i>Reduced mobility, K_0^* ($\text{cm}^2/\text{V}\cdot\text{sec}$)</i>
<i>Positive product ions</i>					
1-Chlorobutane	2.38 2.13 1.98 1.83 1.74	1-Bromobutane	2.36 2.15 2.00 1.89 1.84	1-Iodobutane	2.33 2.20 1.98 1.67 1.57 1.37 1.18
1-Chloropentane	2.31 2.20 1.99 1.88 1.40	1-Bromopentane	2.20 2.07 1.99 1.94	1-Iodopentane	2.20 2.01 1.86 1.66
1-Chlorohexane	2.06 1.90 1.81 1.72 1.49	1-Bromohexane	2.07 1.91 1.85 1.74	1-Iodohexane	2.06 1.89 1.81 1.73
1-Chloroheptane	2.11 1.95 1.81 1.73	1-Bromoheptane	2.13 2.01 1.95 1.83 1.75 1.68	1-Iodoheptane	2.15 1.95 1.83 1.66
1-Chlorooctane	2.09 1.97 1.82 1.71 1.63	1-Bromooctane	2.20 2.00 1.82 1.72		
<i>Negative product ions</i>					
All chlorinated compounds	2.90	All brominated compounds	2.59	All iodinated compounds	2.50

* $K_0 = \left(\frac{6.55}{TX}\right) \left(\frac{P}{760}\right)$ where T = temperature ($^{\circ}\text{K}$), X = drift time (sec) and P = pressure (torr).

ions, since none were observed for these compounds. Mobility data for these halogen ions appear in Table I.

Positive spectra

All compounds gave positive spectra that were more complex than the corresponding negative spectra; in general, three to six product-ion peaks were observed. Fig. 4, showing the composite positive spectra for 1-halogenated heptanes, illustrates the type of data obtained. It can be seen that the most intense product-ion peaks formed for each halogenated heptane in this group have a coincident mobility. A coincidence of an intense product-ion peak occurs in the spectra for all three halogen derivatives (chloro-, bromo- and iodo-) of a given alkane throughout the series. This effect is best seen by examination of the normalized plot for the halogenated hexane compounds shown in Fig. 5. As the alkyl group increases in carbon number, the

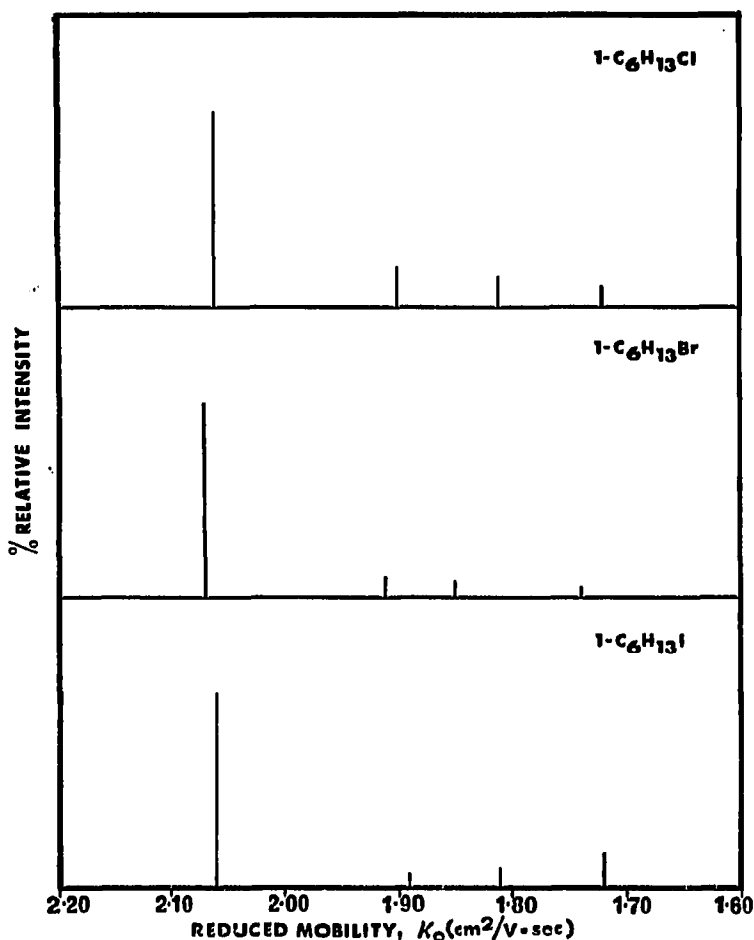


Fig. 5. Normalized plasma chromatographic spectra for the positive product ions of the 1-hexyl halides. Conditions as in Fig. 2.

coincident product-ion peak for its halogenated compounds decreases in mobility. The trend toward lower mobility of the coincident product ion as the carbon number of the alkyl radical increases is illustrated in Fig. 6, where a normalized plot of all the 1-bromoalkyl compounds appears. As the alkyl radical is the only molecular entity that is common to all three halogenated compounds in a group, and because the carbon-halogen bond ruptures easily, one can postulate that the intense product ions formed at these mobilities represent the alkyl radicals $C_4H_9^+$, $C_5H_{11}^+$, $C_6H_{13}^+$, $C_7H_{15}^+$ and $C_8H_{17}^+$. These assignments agree with the results obtained in chemical ionization mass spectrometry, where the most abundant ion for alkyl halides is usually $(M-1-X)^+$. This is also in keeping with the known sensitivity of alkyl halides to fragmentation in electron-impact ionization, where these alkyl fragments appear as the most abundant ions. Additional data that tend to confirm this postulate and the structural assignment of these product ions are given by the appearance of ions of

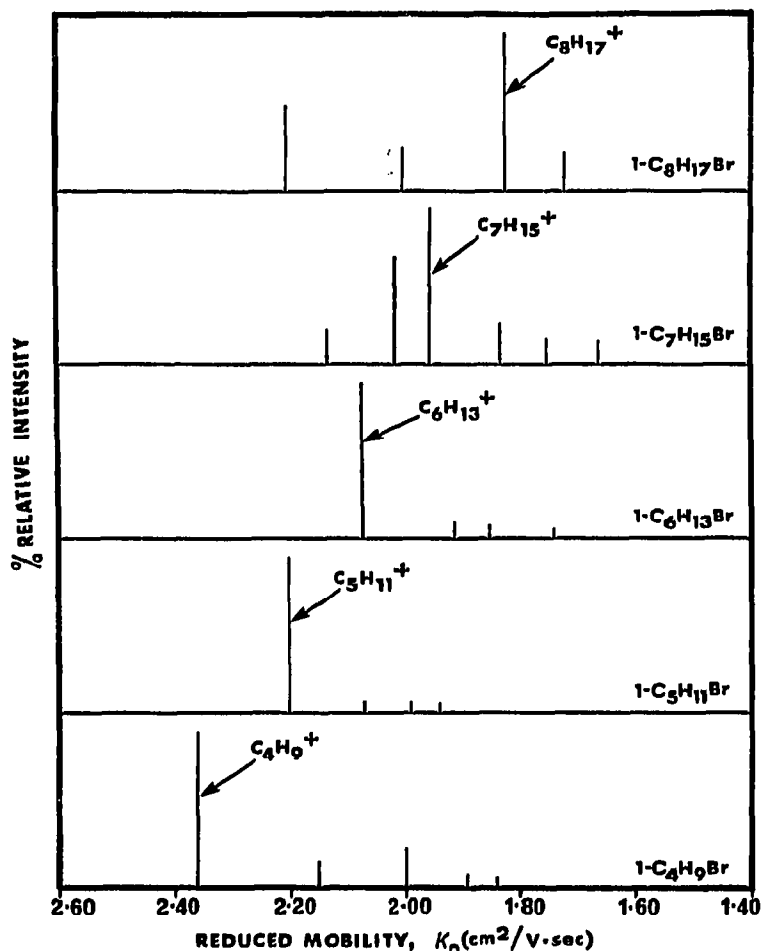


Fig. 6. Normalized plasma chromatographic spectra for the positive product ions of the 1-bromoalkanes from 1- C_4H_9Br to 1- $C_8H_{17}Br$. Positive reactant ions (mobilities of 2.78, 2.47, 2.24) are not shown in these plots. Conditions as in Fig. 2.

identical mobility as the most intense product ions given in the plasma chromatographic spectra of the *n*-alkanes¹². No attempt can be made at present to postulate the identity of the other product ions given for these compounds. The mobilities of all of the ions observed are tabulated in Table I.

CONCLUSIONS

Interfaced directly to a gas chromatograph, the plasma chromatograph provides sensitive detection of GC peaks. Taken together, the positive and negative plasma chromatographic spectra give a qualitative identification of the eluting compound. This study presents the positive and negative plasma chromatographic spectra of a series of related 1-halogenated alkanes, which together provide considerable qualitative information. Further work with many different classes of compounds and other reactant gases is expected to develop the utility of the method in GC analysis.

ACKNOWLEDGEMENTS

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