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THE PLASMA CHROMATOGRAPH AS A QUALITATIVE DETECTOR FOR GAS CHROMATOGRAPHY

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SUMMARY

A plasma chromatograph can function as a very sensitive, qualitative detector for a gas chromatograph. Sample components in a gas chromatographic peak can be detected in quantities of 10^{-6} to 10^{-12} g and be identified by their characteristic positive and negative mobility spectra. The types of reference mobility spectra produced by alkanes, aromatics, esters, halogenated and nitrated compounds have been previously reported. This study presents the reference mobility spectra produced for benzoic and isomeric phthalic acids and some of their esters. All these compounds display strong positive mobility spectra containing abundant ions of the MH^+, $(M - H_2O)H^+$, $(M)NO^+$ and $(M - R)H^+$ type. Benzoic acid, benzaldehyde and terephthalic acid give no negative mobility spectra, while the other compounds and esters show negative mobility spectra whose prominent ions are of the M^- or $(M - H_2O)^-$ type.

INTRODUCTION

Plasma chromatography shows promise as a method for ultra-trace qualitative and quantitative analysis of organic compounds and is particularly useful when employed to detect gas chromatographic (GC) effluents. The technique is based on creating an ion–molecule reaction involving the organic compound 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 reaction are generated by the action of 60-keV electrons emitted from a ^{63}Ni foil into a purified nitrogen or air carrier gas containing a trace of water vapor. In nitrogen, the primary ions formed undergo a series of reaction steps to evolve the stable species of $(H_2O)_nH^+$ and $(H_2O)_nNO^+$ ions, whose relative abundances and the value of n depends upon water concentration and temperature. The negative particles are low-energy ($\sim$0.5 eV) electrons.

The reactant ions and electrons undergo ion–molecule reactions with trace molecules injected into the nitrogen carrier gas stream. The resultant product 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 technique have been described previously[1–5]. Since 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 (ECD) that produces a qualitative spectrum of the compound in a GC peak. A number of studies related to the ECD and its mechanism have been carried out. These studies have demonstrated the existence of dissociative electron capture for monohalogenated benzenes[6], both dissociative and associative electron capture for substituted benzenes and polychlorinated biphenyl (PCB) compounds[7-9], 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[10]. These 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[8].

While only compounds that give a response in the ECD give a response in the negative mode using nitrogen carrier gas, all compounds studied so far exhibit a response in the positive mode. Many of these positive spectra exhibit intensities many times greater than those of the corresponding negative spectra. The very reactive positive ion species of type $(H_2O)_nH^+$ and $(H_2O)_nNO^+$ react with trace molecules to give protonated molecular ions[11,12], simple fragmentation patterns similar to those found in chemical ionization mass spectrometry[13,14] or more complex ion molecules of the form $(M)_x(H_2O)_yH^+$ and $(M)_x(H_2O)_yNO^+$ for polar compounds like alcohols and ethers[13]. Studies of the positive ion mobility spectra produced in plasma chromatography have included those of the PCB compounds[9], monohalogenated benzene[6], *n*-alkyl alcohols[15], oxygenated compounds[2], *n*-alkanes[14] and 1-haloalkanes[10].

The plasma chromatograph can be employed as a qualitative GC detector only if the user has developed a general knowledge of the type of positive and negative mobility spectra produced by different classes of compounds, and has reference spectra available for a wide range of specific compounds. This study was undertaken as part of a continuing effort to provide qualitative plasma chromatographic data for different classes of compounds. New reference spectra are presented for a series of aromatic mono- and dicarboxylic acids and their esters. The general relationships observable in their mobility spectra are explored to establish the type of spectra produced by compounds of this class.

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 previously[4-7]. Ions formed in a flowing carrier gas by a ^{63}Ni source are moved by an electric field through an ion–molecule reactor section toward a drift spectrometer, where separation of the ions occurs because of their different mobilities as they move through a countercurrent flow of inert nitrogen drift gas. Ions reach the detector in a series of ion peaks recorded as an ion mobility spectrum. A variable delay gating technique on a scan grid, synchronized to the injection grid, gives a recording of the millisecond mobility spectrum scan in 1- to 10-min time scan. Because of the high sensitivity of the plasma chromatograph, samples must be in the 10^{-6}- to 10^{-12}-g range in order not to saturate the instrument. To facilitate sample entry and also to provide an interface directly to the effluent of a gas chromatograph,

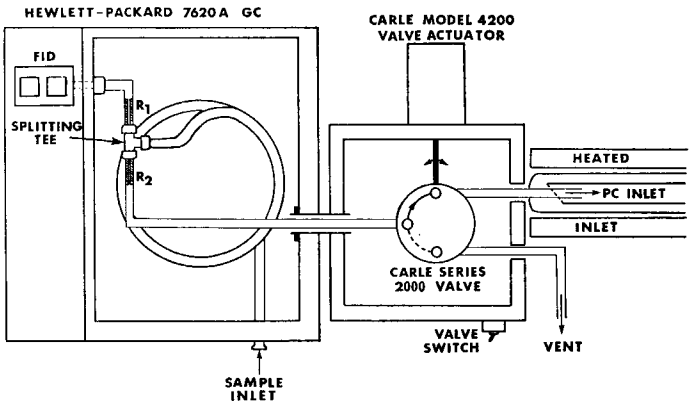

Fig. 1. Schematic diagram of the gas chromatograph–plasma chromatograph interface system. Restrictions R_1 and R_2 are 2 × 0.010-in. capillary tubes to give the split ratio 1:1 (FID:plasma chromatograph).

the system shown in Fig. 1 was constructed[16] using a Hewlett-Packard Model 7620A gas chromatograph equipped with flame ionization detectors (FID). The GC effluent is split approximately equally between the FID of the GC and the plasma chromatograph inlet by use of a splitting tee followed by flow restrictors. The restrictors are made from 2-in. length of 0.010-in.-I.D. capillary tubing. They provide a resistance to flow which maintains the split ratio in spite of slight changes in FID and plasma chromatograph inlet pressure change. The entire interface can be heated to 220° and is maintained 25° above the GC detector temperature. 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 instrument. With this technique a sufficient quantity of sample from a GC peak can be injected to obtain both a negative and a positive mobility spectrum to identify a compound. All plasma chromatographic data were taken at the following conditions, unless otherwise shown in the figure captions: plasma chromatograph tube temperature, 150 °C; carrier gas flow-rate, 120 ml/min; drift gas flow-rate, 380 ml/min; ion–molecule reactor length, 6.0 cm; ion drift space length, 6.0 cm; electric field gradient, 250 V/cm; injection pulse, 0.2 msec; scan pulse, 0.2 msec; recorded scan, 2 min; pressure, 724–736 torr; gas, Linde high-purity nitrogen, 99.996%.

Reagents

The phthalic acid, isophthalic acid, phthalic anhydride, dimethyl terephthalate, methyl benzoate, benzaldehyde and benzoic acid samples are Becker Reagent Grade. The terephthalic acid is BDH reagent grade. The carrier and drift gases are Linde high-purity nitrogen 99.996%. Prior to entry into the plasma chromatograph, both carrier and drift gases were passed through a metal trap of 2.25-l capacity packed with Linde molecular sieve 13X. This procedure removes impurities and gives a water concentration estimated to be about 10 ppm.

Procedure

To avoid saturation of the plasma chromatograph the sample concentrations

are controlled in the range of 10^{-6} to 10^{-9} g. The preferred method is to use the gas chromatograph–plasma chromatograph interface system and actuate the switching valve during a GC peak to direct a portion of the compound peak into the plasma chromatograph. An alternative, very rapid and simple method to introduce pure samples is to use a Pt wire onto which sample solutions are dispensed using a microliter syringe followed by evaporation of the solvent prior to sample introduction. Both methods give sample concentrations sufficient to produce mobility spectra for 5–10 min depending on the amount of sample introduced, reactivity of the compound with the reactant ions, and the temperature of the inlet. Both methods were used to obtain these data. Plasma chromatographic mobility spectra of comparable sample concentrations can be obtained by recording each at definite time intervals after injection and making observations when reactant ion concentrations are approximately similar. Observation of the abundance of reactant ions is useful for following the reaction between the reactant ions and trace molecules of the sample. All sample quantities reported, except for phthalic acid, are quantities injected into the instrument, but peaks observed in the mobility spectra may represent sample concentrations several orders of magnitude lower, because the sample is diluted exponentially by instrument carrier gas with time. The stability of the instrument and its freedom from previous sample contamination is easily monitored by examination of the initial 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

$$K_0 = \frac{6.55}{\tau T} \times \frac{P}{760}$$

where τ = drift time (sec), T = absolute temperature (°K), and P = pressure (torr). 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 ± 0.02. Table I lists accurately measured K_0 values for the ionic species observed, while the data plotted in Fig. 6 serve to show relative ion abundances in the observed spectra.

RESULTS AND DISCUSSION

The positive and negative mobility spectra of the aromatic mono- and dicarboxylic acids and some of their esters were obtained. All compounds produced positive spectra, while only the phthalic acid, isophthalic acid, dimethyl phthalate, phthalic anhydride, and methyl benzoate gave negative spectra. When observed, the negative spectra are generally much weaker than the corresponding positive spectra. Most of these compounds show MH^+, $(M - H_2O)H^+$ or $(M - R)H^+$ ion peaks with spectral patterns that permit one to distinguish between isomeric compounds. Interpretation of these mobility spectra is greatly facilitated by comparison to the stable ions observed for these compounds in both electron impact and chemical ionization mass spectra.

Negative mobility spectra

The negative reactant ionic species observed using nitrogen carrier gas are thermal electrons with average energies of 0.5 eV. Reaction of sample molecules with

TABLE I

CALCULATED MOBILITY VALUES (K_0) FOR IONIC SPECIES OBSERVED IN PLASMA CHROMATOGRAPHIC SPECTRA

Compound	K_0 *(cm²/V·sec)*		*Compound*	K_0 *(cm²/V·sec)*	
	Positive	*Negative*		*Positive*	*Negative*
Phthalic acid	2.15	2.15	Benzoic acid	2.05	
	1.77	1.77		1.82	
	1.64			1.74	
	1.52			1.63	
Isophthalic acid	2.14		Phthalic anhydride	2.15	
	1.91			1.77	1.77
	1.76			1.64	
	1.57	1.58		1.52	
	1.52		Benzaldehyde	2.03	
		1.15		1.91	
Terephthalic acid	2.14			1.84	
	1.91			1.40	
	1.76		Methylbenzoate	2.05	
	1.57			1.82	1.82
	1.52			1.52	
Dimethyl terephthalate	1.69				
	1.51	1.53			
	1.32				

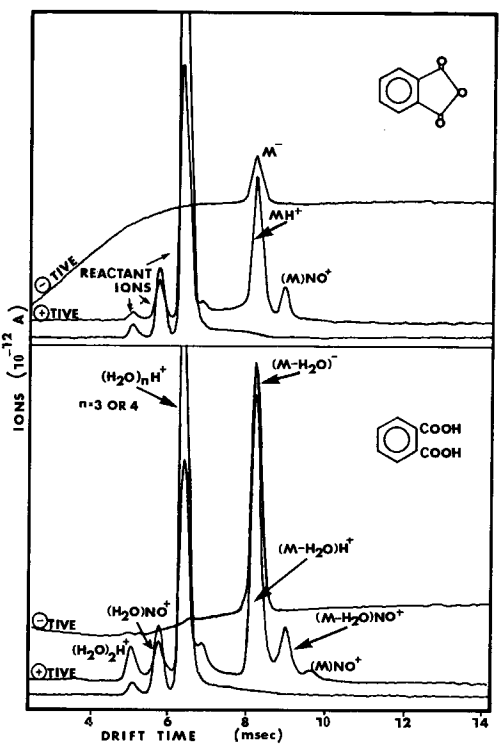

Fig. 2. Positive and negative mobility spectra of phthalic anhydride and phthalic acid at 150 °C for a 10^{-7}-g sample injection.

these low-energy electrons permits observation of both associative and dissociative electron attachment in the negative mobility spectra. These compounds undergo both electron attachment processes. Both phthalic and isophthalic acids show that associative electron capture occurs, but the associative capture for phthalic acid occurs after dehydration to phthalic anhydride to give the $(M - H_2O)^-$ ion. As shown in Fig. 2, the spectrum of phthalic anhydride corresponds completely to that of phthalic acid, and contains both the negative and positive molecular M^- and MH^+ ions that are coincident in mobility. Hence, the negative ion of phthalic acid appears to be the $(M - H_2O)^-$ ion. This same situation and spectral coincidence exists for these compounds in conventional mass spectrometry, as reported by Beynon *et al.*[17] and Benoit *et al.*[18], who recognized that above 150 °C phthalic acid undergoes dehydration and the anhydride is stable up to 250 °C. Also, Ito *et al.*[19] reported the negative ion of $(M - H_2O)^-$ as the prominent ion in electron impact negative mass spectra. This abundant ion in the plasma chromatographic mobility spectra permits a very sensitive identification for these compounds. Isophthalic acid also gives an abundant negative ion and another weak negative ion at higher mass position, which is assigned as the $(M_2 - 2H_2O)^-$ ion (Fig. 3). The prominent negative ion of isophthalic acid appears to be the M^- ion, indicating that dehydration does not occur in this compound. Since the positive mobility spectra of iso- and terephthalic acids exhibit very much the same patterns, the absence of a negative ion peak for terephthalic acid provides a definite

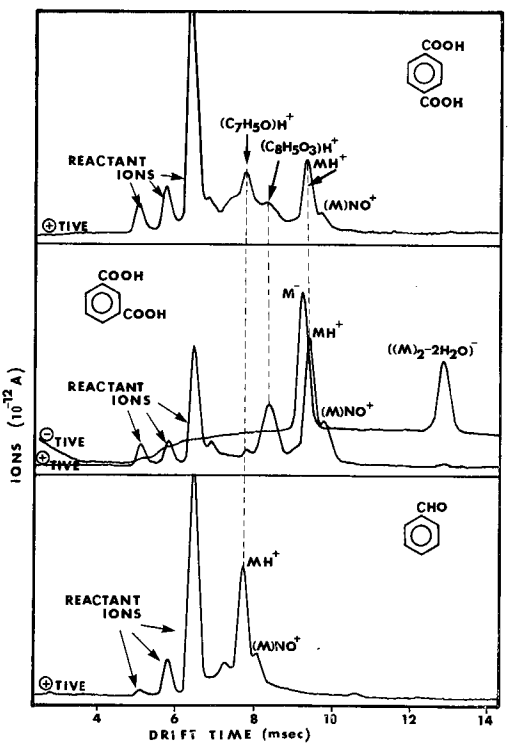

Fig. 3. Positive and negative mobility spectra for terephthalic acid, isophthalic acid and benzaldehyde at 150 °C for a 10^{-7}-g sample injection.

method of distinguishing the terephthalic acid from isophthalic acid. Methyl benzoate also shows a weak negative peak with the same K_0 value as the positive peak. No negative mobility spectra for benzoic acid or benzaldehyde are observed (see Figs. 3 and 4). Dimethyl terephthalate shows a strong negative ionic peak, which appears to be the $(M - CH_3)^-$ ion from dissociative electron capture.

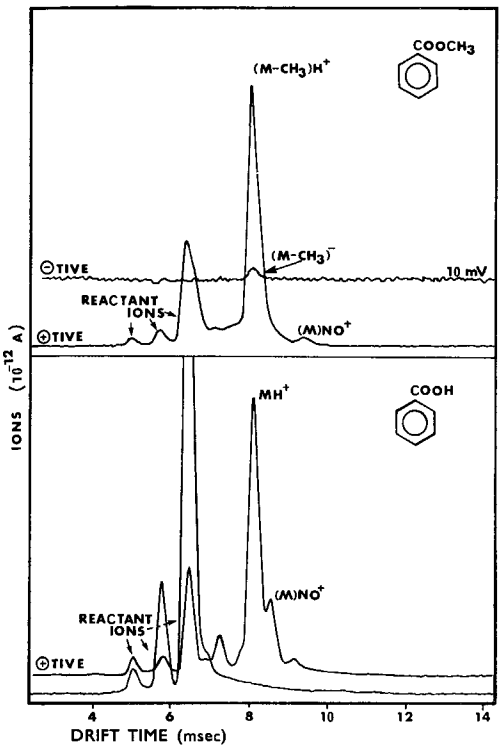

Fig. 4. Positive and negative spectra of methyl benzoate and benzoic acid at 150 °C for a 10^{-7}-g sample injection.

As a further aid to identification of ions observed in plasma chromatography, correlation curves of K_0 *vs.* ionic mass can be used. These curves will correlate to $\pm 20\%$ for all ions, and even closer for ions of similar composition and structure. A family of correlation curves for compounds of similar type and structure has been established[20]. The curve in Fig. 5 of mass *vs.* K_0, established specifically for oxygen-containing aliphatic and aromatic compounds, shows a reasonable agreement when the values of our compounds studied here are plotted.

Positive mobility spectra

In the plasma chromatograph the positive reactant ions are of the type $(H_2O)_nH^+$ and $(H_2O)_nNO^+$. These ions undergo systematic ion–molecule reactions with organic molecules by charge or proton transfer as previously described[9,11]. The trace compounds react with these ionic species to give ion molecules in the form of MH^+, $(M)NO^+$ and $M(H_2O)_nH^+$ or $M(H_2O)_nNO^+$. All the compounds studied here

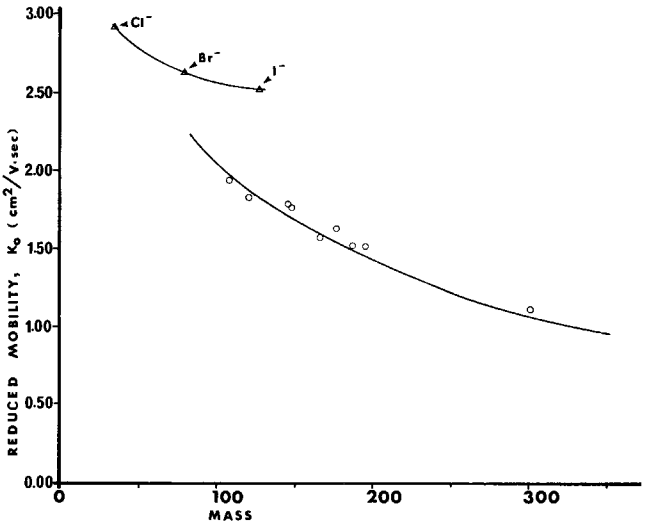

Fig. 5. Correlation curve of the relation of mass *vs.* reduced mobilities (K_0) for oxygen-containing aliphatic and aromatic compounds. ○ (Circle) data points show those ionic species for mono- and dicarboxylic acids and esters. Mobility behavior of halogen ions is shown.

produce characteristic positive spectra that in general are more complex than the negative ones, showing two to six ion peaks, as revealed in Figs. 2–4 and 6. The composite K_0 plots of the compounds seen in Fig. 6 show the several types of common ionic species that are observed formed from similarly structured compounds.

The mobility spectrum of phthalic anhydride was investigated to explain the spectrum of phthalic acid. As already mentioned, the anhydride is formed above 150 °C and quite stable to 250 °C once it is dehydrated. The most abundant peak of the anhydride at $K_0 = 1.77$ appears to be the MH^+ ion along with the $(M)NO^+$ ion at K_0 of 1.64, and these two ions exactly coincide with those of phthalic acid. Also, these most abundant peaks coincide with those of negative peaks in these two compounds, as seen in Fig. 2. The weak peak observed at $K_0 = 1.52$ for phthalic acid could be $(M)NO^+$ for phthalic acid representing some partially undehydrated molecules still present. Beynon *et al.*[17], McLafferty and Gohlke[21] and Fales *et al.*[22] report that the iso- and terephthalic acids and esters give the same fragmentations in the electron impact mass spectra. The same situation is observed in the positive plasma chromatographic mobility spectra. The tere- and isophthalic acids give exactly the same mobility spectra. Benzoic acid and phthalic acid give very similar fragmentation patterns in electron impact mass spectra; but their positive mobility spectra differ considerably. Furthermore, phthalic acid gives a strong negative mobility spectrum, while benzoic acid gives none. The plasma chromatographic spectra, therefore, provide a good method of distinguishing between these two compounds.

The composited positive and negative spectra of benzaldehyde, isophthalic acid, and terephthalic acid show the coincident mobilities of the $(C_7H_5O)H^+$ and $(C_8H_5O_3)H^+$ ions formed by the respective compounds. Isophthalic acid also shows prominent dimer ions, $(M_2 - 2H_2O)H^+$ and $(M_2 - 2H_2O)^-$ in both the positive and negative spectra.

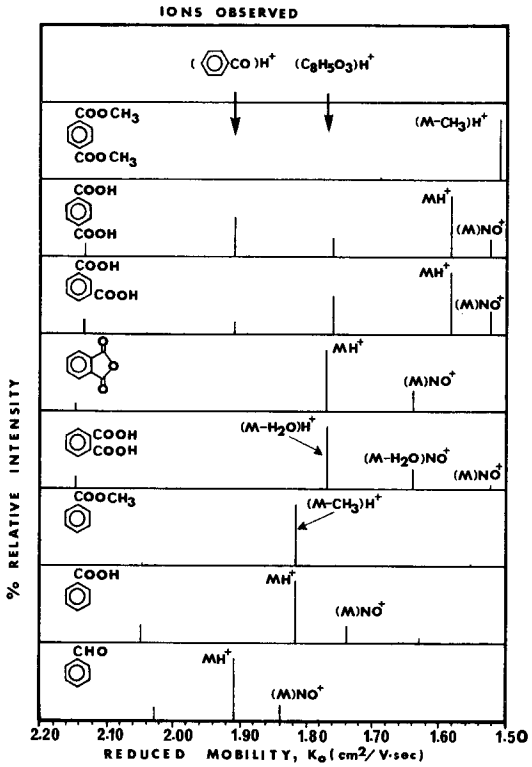

Fig. 6. Reference spectra of normalized plots of positive ionic species intensities *vs.* reduced mobility (K_0) for the series of aromatic mono- and dicarboxylic acids and esters studied. All data were obtained at 150 °C and no negative mobility spectra are shown in this figure.

Aromatic acids generally display intense molecular ions in conventional electron impact mass spectra, reflecting the high resonance stability of the benzoyl system[21]. The positive mobility spectrum of benzoic acid shows both the MH^+ and $(M)NO^+$ ions (Fig. 4), and also a weak ion which might be $M(H_2O)_3H^+$ or an impurity. The mobility spectrum of methyl benzoate was also investigated and compared to that of benzoic acid. The most prominent peak at $K_0 = 1.82$ coincides with the MH^+ of benzoic acid, indicating this ion to be the $(M - CH_3)H^+$ in methyl benzoate. Dimethyl terephthalate also was studied to compare its spectral patterns with the terephthalic acid and other compounds. The results are shown at the top of Fig. 6. This spectrum is much simpler compared to the spectrum of the corresponding acid, displaying only a single prominent positive peak which corresponds to $(M - CH_3)H^+$ ionic species. The negative spectrum also contains a single $(M - CH_3)^-$ ion.

The normalized mobility spectra shown in Fig. 6 compare the spectral patterns of all the compounds studied. Several coincided ionic species are seen, but each compound gives characteristic and useful spectral patterns for identification. Assignments of masses for ionic species observed correlate with the results obtained in chemical ionization mass spectrometry and those of major fragment ions in electron impact mass spectrometry. In addition, a plot of K_0 *vs.* ionic mass for these results agrees

favorably with the similar plot made by Karasek and co-workers for aliphatic and aromatic oxygen-containing compounds[20,23].

CONCLUSION

Since the plasma chromatographic mobility spectra are quite dependent upon the low sample concentration with high purity, introduction of the sample by a GC interface system is the most favorable technique to obtain spectra for identification. Taken together, the positive and negative plasma chromatographic spectra of these aromatic mono- and dicarboxylic acids give characteristic ions of the type MH^+, M^-, $(M - H_2O)H^+$, $(M - H_2O)^-$, $(M - R)H^+$, $(M)NO^+$ and $(M - R)^-$. By establishing the general types 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 GC. To become effective in this application, the plasma chromatographic mobility spectra of many classes of compounds need to be accurately established. It should be emphasized, however, that while the plasma chromatographic instrumentation used to obtain these qualitative data is adequate for that purpose, further development of the instrumentation specifically as a GC detector is necessary to provide a system with the proper speed and design for the application.

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REFERENCES

1 F. W. Karasek, *Res. Develop.*, 21 (1970) 3, 34.
2 F. W. Karasek, W. D. Kilpatrick and M. J. Cohen, *Anal. Chem.*, 43 (1971) 1441.
3 M. J. Cohen and F. W. Karasek, *J. Chromatogr. Sci.*, 8 (1970) 330.
4 F. W. Karasek and D. M. Kane, *Anal. Chem.*, 45 (1973) 576.
5 F. W. Karasek, *Can. Res. Develop.*, 6, No. 4 (1973) 19.
6 F. W. Karasek and O. S. Tatone, *Anal. Chem.*, 44 (1972) 1758.
7 F. W. Karasek, O. S. Tatone and D. M. Kane, *Anal. Chem.*, 45 (1973) 1210.
8 F. W. Karasek and D. M. Kane, *Anal. Chem.*, 46 (1974) 780.
9 F. W. Karasek, *Anal. Chem.*, 43 (1971) 1982.
10 F. W. Karasek, O. S. Tatone and D. W. Denney, *J. Chromatogr.*, 87 (1973) 137.
11 F. W. Karasek and D. W. Denney, *Anal. Chem.*, 46 (1974) 633.
12 G. W. Griffin, I. D. Zidic, D. I. Carroll, R. N. Stillwell and E. C. Horning, *Anal. Chem.*, 45 (1973) 1204.
13 F. W. Karasek, D. M. Kane and O. S. Tatone, *Proc. Annu. Conf. Amer. Soc. Mass Spectrom., 21st, San Francisco, Calif., May, 1973*, ASTM Press, Philadelphia, Pa., p. 45.
14 F. W. Karasek, D. W. Denney and E. H. Dedeker, *Anal. Chem.*, 46 (1974) 970.
15 F. W. Karasek and D. M. Kane, *J. Chromatogr. Sci.*, 10 (1973) 673.
16 D. W. Denney, *M.Sc. Thesis*, University of Waterloo, Waterloo, Ontario, 1974, pp. 52–56.
17 J. H. Beynon, B. E. Job and A. E. Williams, *Z. Naturforsch.*, 209 (1965) 883.
18 F. Benoit, J. L. Holmes and N. S. Isaacs, *Org. Mass Spectrom.*, 2 (1969) 6, 591.
19 A. Ito, K. Matsumoto and T. Takeuchi, *Org. Mass Spectrom.*, 7 (1973) 1279.
20 F. W. Karasek, *Anal. Chem.*, 46 (1974) 710A.
21 F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, 31 (1959) 2076.
22 H. M. Fales, G. W. A. Milne and R. S. Nicholson, *Anal. Chem.*, 43 (1971) 13, 1785.
23 F. W. Karasek and D. M. Kane, *J. Chromatogr.*, 93 (1974) 129.