Journal of Chromatography, 234 (1982) 13–23
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,228

NEGATIVE IONS OF DICARBOXYLIC ACIDS OBSERVED BY PLASMA CHROMATOGRAPHY AND ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETRY

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(Received July 22nd, 1981)

SUMMARY

The negative ions observed by plasma chromatography (PIC) and atmospheric pressure ionization mass spectrometry (APIMS) were compared for maleic acid, fumaric acid, and the isomeric phthalic acids. Although the product ionic species observed by PIC and APIMS are expected to be the same, based on similar ionization mechanisms and conditions, there are some exceptions. All three isomers of phthalic acid show the identical ionic species of $(M - 18)^-$ and $(M + O)^-$ in APIMS, while phthalic acid and isophthalic acid show a single ionic species with different ion mobilities in PIC. Maleic acid and fumaric acid display the same patterns of negative product ions in either PIC or APIMS. It may be concluded that if the ion survival time τ of product ion from a compound is longer than the time of PIC detection, *i.e.* $\tau \geqslant 10^{-2}$ sec, then the ion can be observed by both techniques; if $\tau \leqslant 10^{-5}$ sec then the ion can be observed only by APIMS.

INTRODUCTION

Plasma chromatography (PIC)[1] and atmospheric pressure ionization mass spectrometry (APIMS)[2] utilize a Ni-63 β-ray emitter as an ionization source at atmospheric pressure. These two techniques are virtually identical with respect to the ionization mechanism for organic compounds in the vapour phase, producting both positive and negative ions. The negative ion modes of PIC and APIMS are essentially those of an electron-capture detector (ECD) in which negative ions as well as electron standing current can be simultaneously measured.

The ECD is one of the most sensitive and selective devices available for detection in gas chromatography[3]. This detector has been widely used for the analysis of trace compounds in biomedical samples and for environmental pollutants, in spite of its anomalous responses and linearity limits[4]. Wentworth *et al.* have reported electron-capture mechanisms, electron-capture coefficients, and relative electron affinities for a

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0021-9673/82/0000–0000/$02.75

wide range of organic compounds[5,6]. Karasek and Kane reported the oxygen effect on ECD response using the negative ion mode of PIC[7]. The mobility data of negative ions formed in PIC can be used to distinguish isomeric phthalic acids[8]. A summary of ECD response mechanisms for polynuclear aromatic compounds was reported using the negative ion mode of APIMS[9]. Most organic compounds, except some halogenated compounds, usually show less sensitive responses in the negative ion mode compared to the positive ion mode in PIC and APIMS. This lower sensitivity has been an obstacle to its use as an analytical method. However, it has been found that minor impurities, such as oxygen, in the nitrogen carrier gas appear to be involved in electron–molecule reactions displaying strong negative ion response. *p*-Chloronitrobenzene is one such example, exhibiting strong negative phenoxide ion $(M + O - Cl)^-$ with the same level as that of positive product ion in intensity[10]. This result suggests that intentional doping of electrophilic gas molecules, such as NO, O_2, SO_2 or N_2O into nitrogen carrier gas could enhance the response for organic compounds. Recently an enhancement of ECD sensitivity to non-electron-attaching compounds by addition of N_2O to the carrier gas has been reported[11].

Grimsrud and Miller reported an oxygen effect in ECD response enhancement of two or three orders of magnitude for halogenated hydrocarbons[12]. Research on the response enhancement by intentionally doping oxygen or other gases into nitrogen carrier gas has been expanded to a wide range of organic and environmentally interesting compounds. Some results for polynuclear aromatic compounds and observation on the dependence of ion signals on electrostatic fields applied to the ionization cell, as a new insight into the role of ions in influencing the measured ECD current, have been reported[13]. Meanwhile, very sensitive responses were reported with a d.c. mode of ECD using various mixtures of gases[14,15].

For these reasons it is meaningful to compare the negative product ions formed by both techniques of PIC and APIMS when adopting similar experimental conditions. It is currently thought that the resultant ions observed by both techniques are the same. We report here some comparisons for isomeric phthalic acids, and maleic and fumaric acids in forming their negative ions by these two techniques.

EXPERIMENTAL

All of the PIC data used in this study were obtained using the Beta VI plasma chromatograph. Fig. 1 shows the schematic diagram of the PIC tube. The details of the instrument and its operation have been described previously[1]. Experimental conditions for this study were: PIC tube, 150°C; inlet temperature, 150°C; carrier gas flow-rate 100 ml/min; drift gas flow-rate 400 ml/min; electric field gradient, 250 V/cm; injection and scan gate width, 0.2 msec; time base, 20 msec; recorded scan time, 2 min; ambient pressure, 724–746 torr. The carrier and drift gases were nitrogen (Linde high purity 99.996%) passed through individual stainless steel traps of 2.25-l capacity with Linde Molecular Sieve 13X to remove impurities.

The API mass spectrometer used in this study has been described in detail previously[13]. The schematic diagram of this instrument is also shown in Fig. 1. A sample can be introduced to the API source either via the injection port of a Autoprep Aerograph Model A-700 gas chromatograph using a stainless steel column (1.5 ft. × $\frac{1}{8}$ in. O.D.) packed with 3% OV-17 directly via a direct injection port connected the

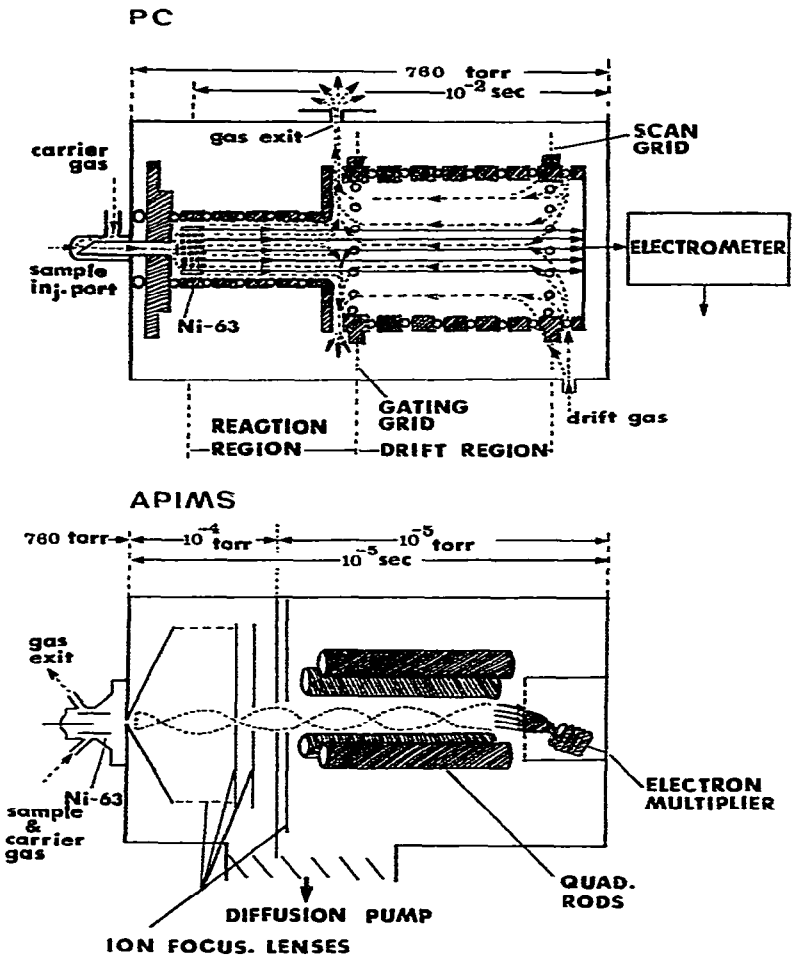

Fig. 1. A schematic diagram for PIC tube (top) and for APIMS (bottom).

API source. Alternate sample injection can also be made into a 3.7-l dilutor located between the carrier gas cylinder and the API source. Experimental conditions of the APIMS were: nitrogen carrier gas (Matheson, ultra high purity) flow-rate, 50 ml/min; injection port temperature, 140°C; API source temperature, 150°C. The electron standing current was measured with a pulse mode (pulse period 300 μsec, pulse width 2 μsec), and the individual m/z ion measurement was made by monitoring one single ion by tuning at specific m/z ion during the course of an experiment with pulse mode off.

Samples were prepared as 10^{-4}–10^{-5} g/ml solutions in ethanol and introduced directly to the PIC or APIMS system using a 1-μl syringe Alternatively, for direct injection for PIC, sample solution (1.0 μl solution) was dispensed onto a clean platinum wire, and the solvent was allowed to evaporate before introducing it into the PIC inlet system.

The phthalic and isophthalic acids were from J. T. Baker (Phillipsburg, NJ, U.S.A.). The terephthalic acid was reagent grade from BDH (Poole, Great Britain).

The maleic acid was reagent grade from Eastern Organic (Hauppauge, NY, U.S.A.). The fumaric acid was reagent grade from Aldrich (Milwaukee, WI, U.S.A.). The ethanol used as solvent was absolute (100%) ethanol for spectroscopic use from J. T. Baker.

RESULTS AND DISCUSSION

APIMS and PIC

Either a Ni-63 or a corona discharge ionization source is used as a β-ray source in both APIMS and PIC at atmospheric pressure. Schematic diagrams of both techniques are shown in Fig. 1. Sample vapour introduced to the ionization source via a GC column or a direct inlet system undergoes ion–molecule reactions with the reactant ions of $(H_2O)_nH^-$, $(H_2O)_nNO^-$, and $(H_2O)_nNH_4^+$ when nitrogen is used as a carrier gas. In the negative ion mode, sample molecules undergo electron–molecule reactions producing negative ions via associative electron capture, dissociative electron capture, or additive rearrangement reaction with negatively charged ions from trace molecules in the carrier gas. In APIMS the product ions are drawn through the same aperture via adiabatic expansion into the mass analyzer, while in PIC the product ions move through a nitrogen drift gas stream in the counter-current direction under the influence of an electric field. Positive and negative polarizing voltages are applied to observe positive and negative ions. The API sources in both techniques are always under an electric field influence; an API source is under a 107–250 V/cm field gradient in PIC. In APIMS, the field gradient is 15–25 V/cm in the d.c. model and in a 1–2 μsec pulse period of the pulse mode. The details of d.c. and pulse mode effects to the negative ions formed with polynuclear aromatic compounds in an ECD adopted APIMS have been previously reported[13]. The negative ionic species from polynuclear aromatic compounds such as anthracene, 1,2-benzanthracene, pyrene, and tetracene appear to be M^-, $(M + O - 1)^-$, and $(M + O_2 - 2)^-$ when a pulse mode is adopted in APIMS[16]. The formation mechanisms of these ions have previously been reported[9,16]. If a d.c. mode is adopted in APIMS, then neither product ion nor an ECD standing current decrease appears unless the sample size reaches the level of saturation for these polynuclear aromatics[12]. However, neither an ECD standing current decrease nor a product ion is observed in the negative ion mode of PIC, even with fairly large sample size. Presumably, the d.c. mode of the negative APIMS roughly corresponds to the API source environment of PIC except for the field gradient difference. These results indicate that electrons barely undergo electron–molecule reaction with sample species under constant electric field. Further, we could predict the following two reasons which might explain the absence of response.

(i) Electrons are drawn so rapidly to the electrode extended into the center of the ionization source due to the attraction force of the applied voltage in APIMS, and toward the ion collector due to the repulsive force in PIC, that electron-capturing sample species seldom have a chance to capture electrons or to react with them. The small portion of the ions formed by electron capture, assuming some electron-capture reaction still occurs under these conditions, might undergo recombination reactions between negative ions and positive product ions or charge neutralization reactions between negative ions and positive reactant ions, which presumably exist as space charge not only inside the wall of the ionization source cell but also along the inner wall of at least the first guard ring of the reaction region. If these assumptions are correct, the recombination or charge neutralization effect must be more profound in

PIC than in APIMS, since no such effect can be expected in the mass analyzer used in APIMS. In a PIC–MS system, the collected total ion current appears to be only 10% of the total ion current obtainable from the source[17]. Another possible path for the removal of the electron from the small portion of the negative ions formed under the conditions mentioned above is an electron decapturing process in the equilibrium state achieved between an electron and a molecular ion produced by an associative electron capture: Suppose a sample molecule "M" captures an electron via reaction 1

$$M + e \rightleftharpoons M^- \quad (1)$$

to form a negative molecular ion, M^-. This system can be considered an equilibrium mixture that depends upon the concentration of the sample, if the electron concentration is almost constant before the system reaches a saturation condition. Electron affinities (EA) of most organic compounds are reported to be below 1.0 eV and the EA of halide ions and of some nitrocompounds lies in the range 2.0–4.0 eV[6]. The negative ions formed via electron capture may be stabilized by a collision with neutral molecules or the captured electrons will be ejected if the energy level of the charged particles is quenched abruptly via a collision with neutral molecules. The reversible reaction

$$M^- \rightleftharpoons M + e \quad (2)$$

will occur. This reversible reaction can cause the decapturing of electrons from negative ions through several millions of collisions per second. The free electrons ejected thus might be detected by the PIC detedtor. This effect would be advantageous for the compounds of bulky structure such as polynuclear aromatic hydrocarbons (PAHs) having larger collisional cross-sections than those of relatively small ions such as the halide ions, Cl^-, I^-, and Br^-.

(ii) Another alternate view which might be responsible for the absence of response is the strength of electron energy in the source. The energy of electrons under PIC conditions appears to be $\sim$ 0.33 V cm^{-1} $torr^{-1}$, which corresponds to 0.58 eV at 165°C. The energy under APIMS conditions is 0.115 V cm^{-1} $torr^{-1}$ or 0.015 eV. The difference in the electron energy level between these two techniques might be responsible for the difference in ECD response for the aromatic compounds and for the lack of response from PAHs, since the EA of these compounds varies. The electron–molecule reaction is a function of the electron energy, and the electron energy is at or near the thermal energy level when no electric field is applied. However, the electron energy is considerably higher if an electric field is present[18,19]. Associative electron-capture responses were reported to be observed at 0.03 eV for both *o*-nitrotoluene and *m*-nitrotoluene[20]. The EA of naphthalene, anthracene, pyrene, benz[*a*]anthracene, and azulene were reported by Wentworth[5] to be 0.152, 0.552, 0.579, 0.696 and 0.587 eV, respectively.

The ECD conditions in APIMS used in this investigation are similar to those of the ECD used widely in ECD–gas chromatography. By applying 35 V to the ionization source of APIMS, the electron energy with a pulse mode operation is 0.115 V cm^{-1} $torr^{-1}$ or 0.015 eV, which corresponds roughly to one tenth of the reported values of electron affinities. The EA reported by Wentworth seem to be too high to be

supported by the data of ECD response obtained by ECD adopted negative APIMS[13]. These affinities appear to be close to the energy level of electrons in the PIC ionization source. However, no electron-capture response is obtained in PIC from PAHs. This discrepancy means that the reported EA values for these particular compounds might not be correct.

The ECD standing current, which is higher with the d.c. mode than with the pulse mode, and the absence of response with such structurally bulky compounds as polynuclear aromatics support view (i), because the ions formed from these compounds are expected to have slower ion mobilities. If view (ii) is responsible for the absence of response, the electron energy in PIC must be too strong to be captured by polynuclear aromatics.

Once view (i) is assumed correct, the charge neutralization reactions between positive reactant ions and the sluggish negative ions are expected to occur very rapidly based on Lovelock's model[3].

Under these circumstances, the neutralization reaction between positive and negative ions will occur and can be expressed as follows:

$$(H_2O)_nH^+ \text{ (or } MH^+) + M^- + N_2 \rightleftharpoons MH \text{ (or } M_2H) + nH_2O + N_2 \qquad (3)$$

The three-body recombination represented by eqn. 3 is the most important mechanism occurring in the range of a few torr to atmospheric pressure[21]. If the number of neutralization or recombination events is R, then eqn. 4 can be used to express the neutralization or recombination events as a unit of the number of events per second:

$$R = \alpha n^+ n^- \qquad (4)$$

where α is the neutralization or recombination coefficient, and n^+ and n^- are the number of positive and negative ions, respectively. Thomson[21] set up a model criterion for condition of recombination events between two oppositely charged particles and defined the coefficient α as follows: recombination will occur if the kinetic energy of the charged particles is at the same level as the average of the thermal energy. According to the premises suggested by Thomson, an ion pair will combine if its total relative energy ever becomes negative. De-excitation by collision with a third body is necessary to restore the kinetic energy to the average thermal value within a critical distance "r" of the other ion for recombination. The critical distance is determined by the relation of $3/2\,kT = e^2/r$ (or $r = 2e^2/3kT$), where k is the Boltzman constant, e is the electronic charge (e.s.u.), and T is the Kelvin temperature. Further, Thomson took into account collision probabilities between positive and negative ions, which are a function of the mean free paths of both positive and negative ions, and finalized the neutralization or recombination coefficient α for the pressure range from a few torr to 1 atm:

$$\alpha = \left(\frac{32\,(2\pi e^6)^{\frac{1}{2}}}{27\,(M_r)^{\frac{1}{2}}}\right)\left(\frac{1}{(kT)^{5/2}}\right)\left(\frac{1}{\lambda^+} + \frac{1}{\lambda^-}\right) \qquad (5)$$

where M_r is the reduced mass between ion and neutral gas, and λ^+ and λ^- are the mean free paths for positive and negative ions, respectively. At constant temperature,

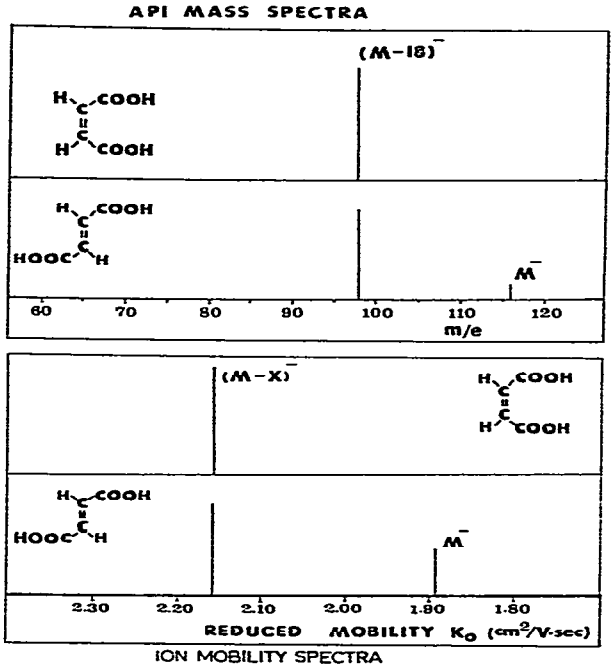

Fig. 2. Negative APIMS data for maleic and fumaric acid (top), and negative PIC ion mobility data (bottom). See the text for discussion.

α increases linearly with pressure up to 1 atm and becomes pressure independent at high pressure (see Fig. 12-4-1 in ref. 21). If the temperature is fixed, α is a function of the mean free path λ^{-}, which depends upon pressure. This means that a thousand-fold more recombination events will occur at atmospheric pressure than will occur at a pressure of 1 torr, and 10^7 times more than at 10^{-4} torr, which corresponds to the pressure of the ion focusing section in APIMS. It is apparent that recombination reactions between positive and negative ions cause shorter ion survival time and lower density of ions for the product ions formed in the API source. It takes $\sim 10^{-5}$ sec for the ions to reach the detector via a quadrupole mass filter in APIMS and $\sim 10^{-2}$ sec in PIC, depending on the ionic size and mass. Therefore the thousand-fold longer detection time in PIC could be responsible for the further recombination and neutralization of charges. This may mean that the charge neutralization probability is 10^7 times higher in PIC than in APIMS. Accordingly it is probable that the ions which have survival times shorter than 10^{-2} sec would not be detected in PIC, while such ions could still be detected in APIMS. If the absence of ECD response from PAHs were caused by the reason based on view (ii), a sensitive response from PAHs has to be obtained by applying a low ion polarizing voltage to the ionization source. Under these circumstances, the negative product ions of isomeric phthalic acids, maleic acid and fumaric acid which are geometric isomers were observed by both APIMS and PIC.

Ion mobility spectra of dicarboxylic acids

It is well known that phthalic acid loses one molecule of H_2O from the two

neighboring carboxylic groups to form phthalic anhydride, when the compound is heated above 150°C[22]. This type of dehydration is not believed to occur for isophthalic acid, terephthalic acid or fumaric acid, when we consider the position of the two carboxylic groups of these dicarboxylic acids and the impossible rotation mode between the two C=C carbons of fumaric acid. This means that thermal dehydration is responsible partly for the dehydrated ion $(M - 18)^-$ observed from phthalic acid and maleic acid. Fig. 2 shows the APIMS negative product ion spectra (top) and PIC ion mobility spectra (bottom) for maleic acid and its geometric isomer, fumaric acid. As one can see, the patterns of the APIMS and PIC ion mobility spectra for maleic acid and fumaric acid are identical: *i.e.* one single prominent ion $(M - 18)^-$ for maleic acid and two ion peaks, $(M - 18)^-$ and M^-, for fumaric acid. Obviously, $(M - 18)^-$ of the APIMS from maleic acid is the negative maleic anhydride ion with *m/e* 98. The $(M - 18)^-$ ion from fumaric acid is also considered to be $(M - H_2O)^-$, although the course of elimination of H_2O between the OH of the carboxyl groups and the hydrogen attached to the C=C group has not been reported. Presently, it is not clear whether one single ion of the PIC ion mobility spectra labelled as $(M - X)^-$ from maleic acid corresponds to the $(M - H_2O)^-$ of the APIMS spectra. The data of the positive ion mobility spectra of maleic and fumaric acids are available in ref. 22 as shown in Table I. No investigation has been made of the course of H_2O elimination and the accurate ionic mass formed from fumaric acid. The point we would like to make clear though is that these two geometric isomers display exactly the same pattern of spectra in both APIMS and PIC.

TABLE I

APIMS AND PIC DATA FOR MALEIC AND FUMARIC ACIDS

Compounds	*m/e*	*Ion*	*Abundance (%)*		*Reduced mobilities**
			APIMS	*PIC*	K_0 *(cm²/V sec)*
Maleic acid	98	$(M - 18)^-$	100.0	100.0	2.15
	99	$(M - Y)H^-$	–	100.0	1.99
	117	MH^-	–	20.0	1.89
Fumaric acid	98	$(M - X)^-$	100.0	100.0	2.15
	116	M^-	20.8	50.0	1.89
	99	$(M - Y)H^-$	–	100.0	1.99
	117	MH^-	–	60.0	1.89

* Calculated from $K_0 = \frac{L}{td \cdot E} \frac{273}{T} \cdot \frac{P}{760}$, where L = drift length (cm), td = drift time (sec), E = electric field gradient of drift (V), T = temp. (°K), and P = tube pressure (torr) (see ref. 22).

Fig. 3 shows a comparison of the APIMS and ion mobility spectra for isomeric phthalic acids. Unlike the spectra of maleic and fumaric acids, responses from these isomers are identical for the three isomers, while one single ion mobility peak is observed from phthalic acid and isophthalic acid with a mobility difference: from terephthalic acid, no negative ion is observed in PIC[8]; however, a prominent $(M - 18)^-$ with a weak $(M + 16)^-$ ion was observed in APIMS. No argument is

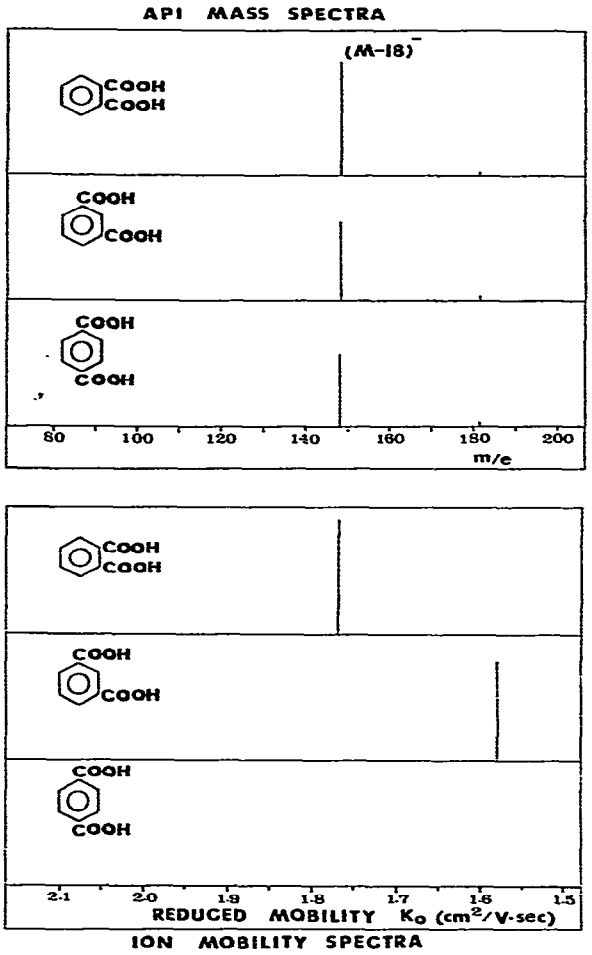

Fig. 3. Negative APIMS data (top) and PIC ion mobility data (bottom) for isomeric phthalic acids. See the text for discussion.

necessary for the $(M - H_2O)^-$ ion formation from phthalic acid; however, the observation of the identical pattern of ions from iso- and terephthalic acids forces us to conclude that H_2O elimination reactions may also occur in the two isomers by some elimination path under the conditions employed in this work. It is well known that a conversion of these three isomers into another is impossible under the conditions employed in this work, considering the synthesis routes of the three isomers.

Similar comments on the mechanism of dehydration of these compounds could be made for maleic acid and fumaric acid. What we are interested in is that the negative ion mobility data of isomeric phthalic acids obtained by PIC can be used for the identification of these three isomers[8], while APIMS data of the negative ions do not distinguish these isomers. The resultant ionic structures of the three dehydrated isomeric phthalic acids may be attributed to ion mobility differences in spite of identical ionic masses. Although Hagen[24] reported that terephthalic acid (*para* form) has a smaller collisional cross-section than that of isophthalic acid (*meta* form), it seems to

be reasonable to predict that the $(M - H_2O)^-$ ions formed from terephthalic acid apparently have a large ionic size because of the *para* position of the two carboxylic groups. As a result of random motions of the ion, the negative ion of the dehydrated terephthalic acid could be expected to have the largest collisional cross-section, which causes the highest chance of recombination with positive ions. This may mean that the $(M - H_2O)^-$ ion from terephthalic acid could be neutralized completely during the drift time of 10^{-2} sec. Indeed, the weakest intensity of this ion is observed in APIMS data as shown in Table II. The additional ionic mass and ionic radii of the $(M + 16)^-$ ion, which can be interpreted as the $(M + O)^-$ ion for phthalic acid and isophthalic acid, will also certainly be a factor for these ion mobilities, if these two different ions drift together in PIC. However, this effect should not be great when we consider the observed relative intensities between these two ions, which is less than 10%. Details of negative ions from isomeric phthalic acids are presented in Table II.

TABLE II

APIMS AND PIC DATA FOR ISOMERIC PHTHALIC ACIDS

Compound	*m/z*	*Ion*	*Abundance**		*Reduced mobility* K_0 ($cm^2/V \cdot sec$)
			APIMS	*PIC*	
Phthalic acid	148	$(M - 18)^-$	100.0 (2.5K)	100.0	1.77 (ref. 8)
	166	M^-	1.7		
	182	$(M + 16)^-$	1.7		
Isophthalic acid	148	$(M - 18)^-$	100.0 (1.7K)	100.0	1.58 (ref. 8)
	166	M^-	5.3		
	182	$(M + 16)^-$	8.8		
Terephthalic acid	148	$(M - 18)^-$	100.0 (1.6K)	None	
	166	M^-	6.4		
	182	$(M + 16)^-$	6.4		

* The values in parentheses for $(M - 18)^-$ ions denote the ion intensities observed by APIMS with 10^{-9} g sample size for the three isomers.

To confirm the absence of response from terephthalic acids in PIC, careful measurements have been repeated several times with time bases of 20 msec and 50 msec, respectively, to search further for any possible heavily clustered ion (ion with slower ion mobility due to its bulky structure). However, no such ion was observed. These results again force us to predict that the ion survival time of the $(M - H_2O)^-$ ion from terephthalic acid must be shorter than 10^{-2} sec. In other words, the ion survival time, τ, of the $(M - H_2O)^-$ ion from terephthalic acid could be between 10^{-5} and 10^{-2} sec; these are the detection time limits for APIMS and PIC, respectively. This may mean that the ionic species observed by PIC reveal the truly stabilized ionic species at atmospheric pressure.

Thus we may conclude that the most probable reasons for the absence of response of polynuclear aromatics could be the low electron density at the source because of the existence of an electric field, as well as view of (ii) related to the energy of the electrons in the ionization source.

ACKNOWLEDGEMENTS

The research for this paper was supported by the Natural Sciences and Engineering Research Council of Canada. The authors thank E. Grimsrud, Chemistry Department, Montana State University, for valuable assistance in obtaining the negative APIMS data for the compounds used in this study.

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