Heating rates of 20–30 °C gave satisfactory results for several additives, but no effort was made to establish an optimum heating rate.

Extraction of polypropylene pellets with acetonitrile at room temperature overnight gave clear evidence for the additives, but the extraction was approximately 2% efficient. Extraction with boiling decalin (4, 5) gave 0.053 wt % UV-531 in this sample.

The samples used in this work, 1–2 mg, do not constitute either upper or lower limits on the amounts of polymer that can be used. Smaller samples allow one to study the distribution of additives within a bulk sample. This use of small samples (≤1 mg) allows determination of heterogeneities of additive concentrations in bulk samples but would not produce a good average value of additive concentration in a large batch of polymer. Care must be maintained in these studies that the bulk of the decomposition products of polypropylene do not contaminate the metal surfaces in the acceleration region of the mass spectrometer.

ACKNOWLEDGMENT

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Ion Mobility Spectrometry in Carbon Dioxide

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This work investigates the potential of using carbon dioxide as a drift and carrier gas in ion mobility spectrometry. Although separations in carbon dioxide were previously thought to be difficult due to large ion cluster formation, this study showed that under normal operating temperatures for analytical ion mobility spectrometry separation of both reactant ions and product ions is possible. Comparison of reactant ions and product ions in CO$_2$ and N$_2$ demonstrated that while ion drift times are considerably longer in CO$_2$ than in N$_2$, the patterns of the ion mobility spectra are similar for the two drift gases. Test compounds studied in this work were a series of straight-chain methyl esters ranging in molecular weight from 88 to 446.

The use of carbon dioxide as a drift gas for ion mobility spectrometry (IMS) has been limited. In fact, there has been only one brief investigation of the ion transport properties of CO$_2$ at atmospheric pressure (1). This study concluded that the "mobility of ions in CO$_2$ is largely independent of the ion species so long as the pressure is greater than about 100 torr". On the basis of this conclusion, it would seem that CO$_2$ would not be useful as a drift gas in IMS. Nevertheless, recent developments in supercritical fluid chromatography (SFC) and ion mobility spectrometry have made the continued investigation of CO$_2$ as a drift gas desirable.

The use of supercritical carbon dioxide as a mobile phase in capillary chromatography has enabled the efficient interfacing of ambient pressure ionization detection methods such as flame ionization (FID) for the sensitive detection of compounds separated by supercritical fluid chromatography (2). The highly successful nature of the SFC/FID interface suggests that other detection methods traditionally assigned to the domain of gas chromatography may also be possible with SFC. Ion mobility spectrometry has been successfully interfaced to high-resolution gas chromatography (3). Perhaps it can also serve as a sensitive and selective detection method for SFC.

Since one of the most common mobile phases employed in SFC is carbon dioxide, interfacing IMS with SFC would be facilitated if CO$_2$ could be used as a drift gas in the ion mobility spectrometer. When the chromatographic mobile phase is matched with the ion mobility drift gas, complications may be avoided when the two gases mix in the ionization region of the ion mobility spectrometer. The primary objective of the investigation reported in this paper was to provide preliminary information on the mobility behavior of ions in CO$_2$ under conditions similar to those that would be employed if the spectrometer were interfaced to a supercritical fluid chromatograph.

Despite the absence of data on atmospheric pressure IMS in CO$_2$, there has been some interest in ions formed in CO$_2$ and their mobilities at low pressures. Mobilities of O$^-$ and

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CO_3^- in CO_2 gas have been reported to be 1.34 ± 0.10 and 1.92 ± 0.14 $cm^2/(V\cdot s)$, respectively, at pressures less than 1 torr (1, 4). Positive ions observed at low pressures include $C_2O_2^+$, $C_2O_3^+$, CO_4^+, $C_2O_4^+$, CO^+, O_2^+, and CO_2^+. However, mobilities of these ions were difficult to determine due to the complex nature of reactions occurring in the drift region of the spectrometer. For O_2^+ in CO_2, mobilities of 1.35 ± 0.03 (1) and 1.32 $cm^2/(V\cdot s)$ (4) have been reported. Unfortunately, at atmospheric pressures the character of the ions formed in CO_2 changes so drastically that comparison to low-pressure mobility experiments is meaningless.

The production of positive ions in carbon dioxide at atmospheric pressure was investigated with a time-resolved atmospheric pressure ionization mass spectrometer (TRAPI) in which rapidly repeating X-ray pulses were used as the ion source (5). In these studies positive ions produced at atmospheric pressure were found to be complex clusters of ions. Also, trace amounts of impurities such as water or carbon monoxide influenced the course of the formation and decay of these cluster ions. Cluster ions that were identified included $(CO_2)_n^+$, $(CO(CO_2)_n)^+$, $((CO)_2(CO_2)_n)^+$, $(H_2O(CO_2)_n)^+$, $(H(H_2O)(CO_2)_n)^+$, and $(H(H_2O)_2(CO_2)_n)^+$. Although this study utilized a source different from the ^{63}Ni foil normally used in IMS, the study indicates that positive reactant ions generated in CO_2 may be more complex than those generated in N_2: $(H_2O)_nNH_4^+$, $(H_2O)_nNO^+$, and $(H_2O)_nH^+$.

Identities of negative ions produced in atmospheric pressure CO_2 have also been reported (1). By the use of a ^{63}Ni ionization source, two families of cluster ions have been identified to be $H_2O(CO_2)_nCO_4^-$ and $(CO_2)_nCO_4^-$. Up to 10 CO_2 molecules could be found clustered to the core ion with the most abundant ion species being $(CO_2)_6CO_4^-$. In the hydrated family of cluster ions the $H_2O(CO_2)_5CO_4^-$ species was found to be the most abundant.

The only mobility data available for ions in CO_2 at atmospheric pressure was collected at 25 °C (1). At that temperature all reactant ions in CO_2 produced essentially the same reduced mobility constant. For negative ions a mobility of 0.99 ± 0.02 $cm^2/(V\cdot s)$ was reported for the nonhydrated ions and 1.01 ± 0.02 $cm^2/(V\cdot s)$ for the hydrated ions. For positive ions, only one peak was observed at a mobility of 1.06 ± 0.02 $cm^2/(V\cdot s)$. From these and other observations the authors concluded, as was quoted earlier, that the reduced mobility of ions in CO_2 is largely independent of the ion species. According to the authors, the large induced dipole moment of CO_2 allows the drift gas to form large clusters around the "core" ion such that both the size and shape of the ion cluster are only weakly dependent on the identity of the core ion. They go on to point out, however, that the generalization of their observation may be invalid if a large macromolecular ion served as the core ion or if the temperature of the drift tube was raised above 25 °C.

EXPERIMENTAL SECTION

Instrumentation. The ion mobility spectrometer used in these studies was a Phemto-Chem 100 purchased from PCP, Inc., West Palm Beach, FL. In this system, ions are produced in the carrier gas from β particles emitted from a 12-mC ^{63}Ni radiation source. The complete instrument included an ion drift tube, a high-voltage power supply, a shutter grid controller, a digital signal averager, an oscilloscope, and an X-Y recorder.

The ion drift tube was constructed by PCP and contained a total electrical length (from the repeller to collector) of 14 cm. The reaction length (from the repeller to the shutter grid) was 6 cm, and the drift length (from the shutter grid to the ion collector) was 8 cm. The diameter of the drift region was 4.25 cm.

The high-voltage power supply was a Fluke Model 415B capable of both positive and negative variable settings from 1000 to 3000 V. Normal setting for this work was ±3000 V. With the 14-cm drift length, this voltage produced an electric field of ±214 V/cm.

Table I. Ion Mobility Spectrometry Typical Operating Conditions

parameter	value	parameter	value
electric field	214 V/cm	dwell time	24 μs
drift tube length	8 cm	gate width	0.2 ms
reaction chamber	6 cm	autostop	1024
length		vertical display	32 768
carrier gas flow rate	250 mL/min	horizontal display	1024
drift gas flow rate	350 mL/min	volts full scale	±2 V
ambient pressure	752 ± 6 torr	input filter	20 μs
temperature	220 °C	ADC resolution	9 bits
repetition period	24 ms		

The shutter grid controller was constructed by PCP and was capable of opening and closing the shutter grid every 12, 24, 60, 120, or 240 ms. The time that the grid was open (the gate width) could also be selected from among 0.05, 0.1, 0.2, 0.5, or 1.0 ms. In this work the repetition period was either 24 or 60 ms and the gate width was either 0.1 or 0.2 ms.

The digital signal averager was a Nicolet Model 1072 signal averaging system (Nicolet Instrument Corp., Madison, WI). For this work, 1024 channels were used with a dwell time/channel of either 24 or 60 μs. The number of sweeps that were averaged (Autoscan) varied from 512 to 2048, with a normal setting of 1024. The vertical scale response was controlled by both the volts full scale switch and the vertical display switch. In this work the volts full scale was maintained at ±2 V, and sensitivity was adjusted with the vertical display. This switch indicated the number of counts in memory per one centimeter of vertical deflection on the oscilloscope. A typical value for this study was 32 768 counts/cm. Full-scale response on the oscilloscope was 8 cm of vertical deflection.

Real time spectra were monitored with a Tektronix Model 5110 oscilloscope, and hard copy data were collected with a Hewlett-Packard 7010B X-Y recorder.

Generally the conditions of operation were as follows: The carrier gas (that gas that serves to sweep the sample into the ionization chamber) was either N_2 or CO_2, but the flow was always held constant at 250 mL/min. The drift gas (that gas in which the ion mobilities are measured) was also either N_2 or CO_2 with a flow rate of 350 mL/min. The two gases were never mixed; either both the carrier and drift gas were nitrogen or they both were carbon dioxide. The temperature of the drift tube was varied from 25 to 220 °C, but for most of the analytical work the temperature was maintained at the higher value. The pressure within the drift tube was considered to be ambient and was monitored twice a day with a mercury barometer located in the laboratory. Table I provides a summary of all the operating conditions that were normally used. Where conditions varied in individual experiments, specific conditions are given in the figure caption.

Experiments. The drift and carrier gases were standard grade (99.9% pure) carbon dioxide and nitrogen obtained from Watani Co., Osaka, Japan. Before use the gases were passed through a 10× molecular sieve purification tower. The test organics used in this study were a series of straight-chain methyl esters obtained from Wako Pure Chemical Industries, Ltd., Osaka, Japan. The esters used are listed in Table III.

The work was divided into three parts: First, investigations were made on the effect that temperature had on the mobility spectra of CO_2 reactant ions. Second, a comparison was concluded of the ion mobility spectra of reactant ions in both N_2 and CO_2 carrier and drift gas at elevated temperatures, and finally product ions were measured after direct introduction of 1–30 μL of head space vapors (obtained at room temperature) of the various methyl esters. In each case, care was taken not to saturate the spectrometer with the test compound. Saturation was defined as total depletion of the reactant ions.

RESULTS AND DISCUSSION

Effect of Temperature. Figure 1 shows the ion mobility spectra of both negative and positive reactant ions in CO_2 at 25 °C. The negative spectrum had a single, almost symmetrical peak at a drift time of 35.3 ms. The positive spectrum produced an asymmetrical peak with a small shoulder peak
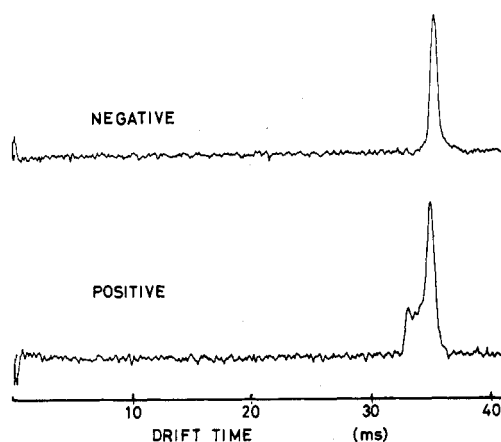
Figure 1. CO_2 reactant ion spectra at 25 °C. The upper spectrum is of the negative reactant ions. The lower spectrum is of the positive reactant ions. The operating conditions different from those listed in Table I were as follows: pressure, 748 torr; repetition period, 60 ms; dwell time, 60 μs.
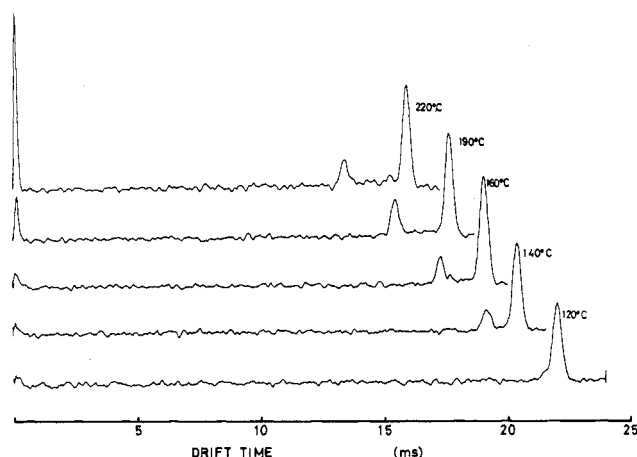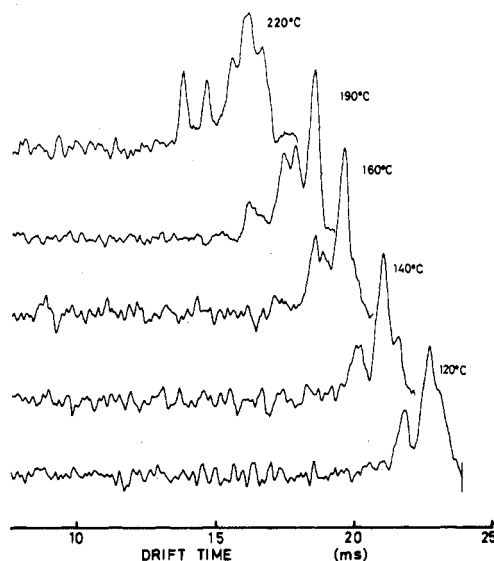

Figure 2. CO_2 negative reactant ions at various temperatures. Operating conditions different from those listed in Table I were as follows: pressure, 753 torr; gate width, 0.1 ms; autostop, 2048.

Table II. Reduced Mobility Constants of CO_2 Reactant Ions

| temp, °C	negative ion		positive ion
	minor	major	major
25		0.95	0.96
100		1.14	1.11
110		1.17	1.14
120		1.18	1.14
140	1.29	1.21	1.16
150	1.33	1.23	1.19
160	1.36	1.24	1.19
170	1.41	1.25	1.20
180	1.42	1.25	1.20
190	1.42	1.25	1.19
220	1.52	1.28	1.26

Figure 3. CO_2 positive reactant ions at various temperatures. Operating conditions different from those listed in Table I were as follows: pressure, 753; vertical display, 8.192; autostop, 2048; gate width, 0.1 ms.

on the leading edge. The shoulder occurred at 33.3 ms and the primary positive peak at 35.2 ms. Reduced mobility constants for these peaks were determined to be 0.95 ± 0.02 cm²/(V·s) for the negative peak, 0.96 ± 0.02 cm²/(V·s) for the primary positive ion, and 1.01 ± 0.02 cm²/(V·s) for the shoulder ion. These mobilities do not exactly coincide with those reported by Ellis et al. (1). One possible explanation for this difference might be the concentration of water (or other contaminants) in the CO_2 gas. Ellis et al. noted that they had accidentally contaminated their system with laboratory air prior to some of the atmospheric pressure experiments. Nevertheless, as in the work by Ellis et al., both the positive and negative reactant ion spectra produced single peaks with similar mobilities, indicating that ion identities had little effect on the mobility of the ion cluster.

As discussed in the introduction, negative reactant ions in CO_2 have been identified to be $H_2O(CO_2)_nCO_4^-$ and $(CO_2)_nCO_4^-$. At 25 °C, these two ion cluster families are presumably so large that the core ion has little effect on mobility. But, as the temperature is raised the clusters are broken sufficiently so that the core ion can influence mobility and separation occurs. Figure 2 shows a series of mobility spectra of negative reactant ions taken at different temperatures. As the temperature increases from 120 to 220 °C the drift time of the reactant ions, as would be predicted, becomes shortened. Moreover, the single peak that occurred at all temperatures below 120 °C splits into two peaks, a larger, slower one and a faster, smaller one. The small peak first

appears as a shoulder on the leading edge of the main peak at a temperature of about 120 °C. By the time the temperature is 140 °C the two peaks are completely separated. Both the drift time and the reduced mobility constant of these two peaks continued to diverge as the spectrometer was raised to its operating temperature of 220 °C.

Table II provides a comparison of the reduced mobility constants of these two peaks at various temperatures. Generally, when ions do not cluster with the drift gas (or with a contaminant contained in the drift gas) reduced mobility constants do not change when the operating temperature is varied over a limited range. The fact that the reduced mobilities of these two peaks increase with temperature indicates that they are both members of an ion cluster family. As the temperature increases, the average size of the ion cluster decreases and the average velocity of the ion increases.

One other temperature-dependent phenomenon can be observed in Figure 2. Note that as the temperature increases, a peak at the beginning of the spectrum grows in. It becomes noticeable at 160 °C and is the major peak in the spectrum at 220 °C. This peak corresponds to that expected for free electrons. The temperature dependence of free electrons in CO_2 is important to note from an analytical point of view since it may lead to temperature-selective effects for the detection of certain electrophilic compounds. Spectra shown in Figure 2 are positioned vertically to illustrate the temperature phenomenon discussed and do not represent an increase in
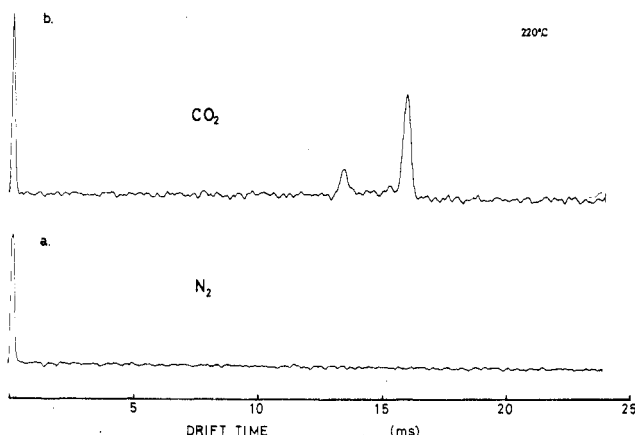
Figure 4. Comparison of N_2 negative reactant ions with CO_2 negative reactant ions. Operating conditions different from those listed in Table I were as follows: pressure, 752 torr; vertical display, 16 384; autostop, 512.

background current as a function of temperature.

Table II along with Figure 3 shows a similar process of cluster busting and ion–family separation for positive ions as the temperature is increased from 25 to 220 °C. By comparison of the positive ion mobility spectrum taken at 120 °C and shown in Figure 3 with that taken at 25 °C shown in Figure 1, it is apparent that resolution is improving. The shoulder peak seen in Figure 1 has now formed a distinct peak in Figure 3. Because of the complexity of the positive ion spectrum it was difficult to follow individual peaks as they shifted position. While all peaks shifted to lower drift times, some shifted faster than others, and the relative positions of the peaks may have changed with temperature. Thus, a reduced mobility constant was calculated only for the major peak as an indicator for the general behavior of the positive reactant ions as a function temperature. As with the negative reactant ions, and as might be expected by analogy with the behavior of positive reactant ions in nitrogen drift gas (6), reduced mobility constants were not constant. This indicated that ion cluster formation was present for the reactant ions in the positive mode as well as for those in the negative mode.

As discussed earlier, initial investigations with CO_2 drift gas were discouraging because it appeared that the extensive cluster formation prevented the separation of individual ions. These studies, however, have demonstrated that ion separation is possible at temperatures above 120 °C. Since analytical applications of ion mobility spectrometry nearly always require drift gas temperatures above 120 °C, the use of CO_2 as a drift gas may be more feasible than previously envisioned.

Reactant Ions. In general, reactant ions produced from CO_2 gas are more complex and drift with much slower velocities than do the well-characterized reactant ions produced in nitrogen drift gas. Figure 4 compares negative reactant ion mobility spectra for nitrogen and carbon dioxide drift gases. Spectrum a is the negative ion mobility spectrum for pure nitrogen. Only the peak for free electrons can be detected. After the drift and carrier gases were converted to CO_2 and sufficient time (about 10 min) was allowed to flush all of the N_2 from the system, spectrum b was obtained. Along with the free electron peak, two reactant ions were observed. The ion that migrated at the highest velocity had a drift time of 13.5 ms and a mobility constant of 1.52 cm²/(V·s). The slower negative reactant ion had a drift time of 15.9 ms and a mobility constant of 1.28 cm²/(V·s).

Switching from N_2 to CO_2 did not, however, produce new ions that grew in at drift times of 13.5 and 15.9 ms. Rather, the ions were first observed at relatively short drift times and then, over a period of about 10 min, they shifted to their stabilized positions. Immediately (within the first 5 s) a small
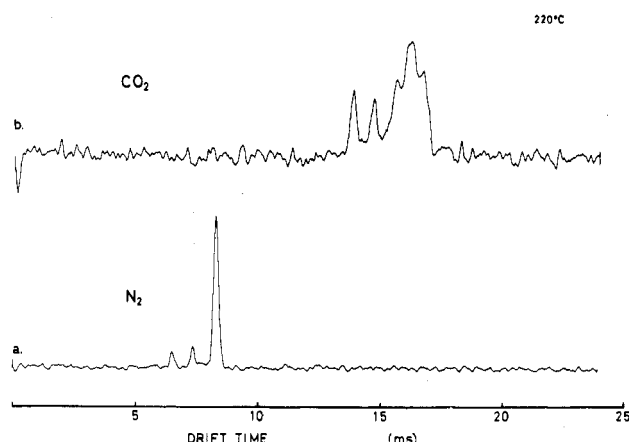
Figure 5. Comparison of N_2 positive reactant ions with CO_2 positive reactant ions. Operating conditions were the same as those shown for Figure 4.
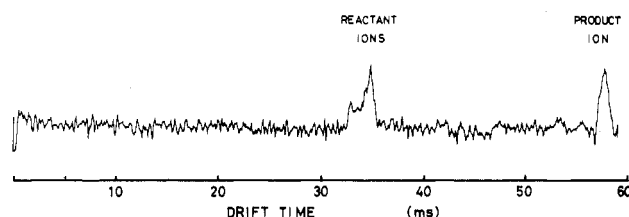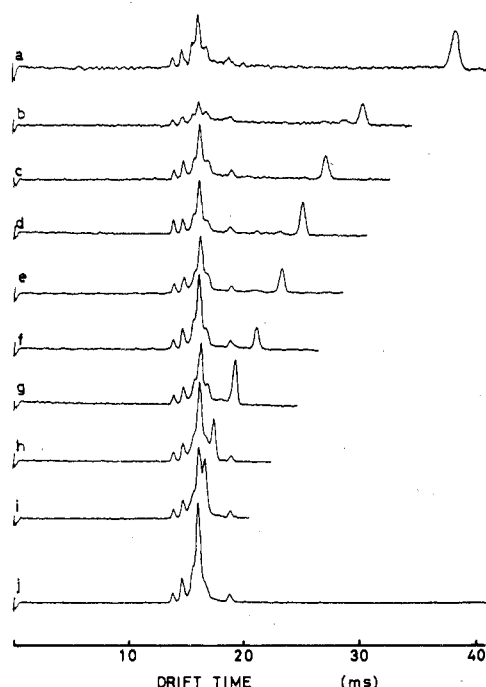

Figure 6. Positive product ion of methyl laurate measured at 25 °C in CO_2. Operating conditions different from those listed in Table I were as follows: pressure, 748 torr; vertical display, 4096; repetition period, 60 ms; dwell time, 60 μs.

peak appeared at a drift time of 8.5 ms. After about 3 min a second ion peak appeared at a drift time of 11.3 ms. Over a 10-min period both peaks grew larger in size and increased in drift time until they stabilized at drift times of 15.9 and 13.5 ms, respectively. Shifts to longer transit times of CO_2 related ion peaks have been noted before as a function of increasing concentrations of CO_2 (7).

Similarly, positive reactant ions were found to shift to longer drift times in CO_2 from their typical drift times in nitrogen. Figure 5 shows positive reactant ion spectra for both N_2 and CO_2 at 220 °C. The shift in drift times that was observed after the introduction of CO_2 is another indication that clustering in CO_2 is more pronounced than in N_2. Also, the shift in drift times may be partially credited to density differences between the two drift gases.

Note that the switch from N_2 to CO_2 was not effected gradually but rather the 350 and 250 mL/min flows of nitrogen drift and carrier gases were completely cut off and instantly replaced with 350 and 250 mL/min flows of carbon dioxide. Why then did it take 10 min for the reactant ion peaks in CO_2 to stabilize? Ion/molecule reactions under atmospheric pressure conditions usually equilibrate rapidly. Thus it does not seem reasonable that the shifts are due to nonequilibrium conditions. More probably, stabilization of the ion drift times is acquired shortly after the drift gas in the spectrometer reaches 100% CO_2. Thus, the shift in drift times occurs because, for 10 min after the instrument is switched to pure CO_2, N_2 remains as a residual gas in the drift tube.

Product Ions. Although no one has ever reported the separation of product ions from reactant ions in CO_2 gas, Ellis et al. (1) speculated that if macromolecular ions constitute the core ion of an ion cluster in CO_2, then separation might occur. We found that indeed ion separation at this low temperature was possible. Figure 6 shows an example of a product ion with the longest drift time that we could measure under our conditions. This product ion, produced from methyl laurate, was well-separated from the CO_2 reactant ions and

Figure 7. Product ions of methyl esters in CO_2: (a) methyl mellissate, (b) methyl stearate, (c) methyl myristate, (d) methyl laurate, (e) methyl caprate, (f) methyl caprylate, (g) methyl caproate, (h) methyl butyrate, (i) methyl propionate, and (j) reactant ions only. Operating conditions different from those listed in Table I were as follows: pressure, 754 torr; repetition period, 60 ms; dwell time, 60 μs.

is perhaps the slowest ion ever measured by IMS. Traveling the 8-cm drift tube in 57 ms, its velocity was only 140 cm/s, or 5.05 km/h, about the speed of a normal walk.

Product ion separation can also be achieved at more analytically useful operating temperatures. Figure 7 shows ion mobility spectra for a series of methyl esters ranging in molecular weight from 88 to 466. Spectrum a is that of methyl melissate, $CH_3(CH_2)_{28}COOCH_3$, with a product ion having a drift time more than twice that of the reactant ions. In all of the spectra from a through g the product ions of the methyl esters were well-separated from the major reactant ion peaks and from each other. Although the product ions from methyl butyrate (spectrum h) and methyl propionate (spectrum i) could be detected, they overlapped with the tail of the reactant ion peak.

In general, spectra shown in Figure 7 are similar to those obtained in N_2 except that drift times are shifted to longer times (8). Table III reports the drift times and mobility constants of these test esters and compares them to literature data of these same compounds in nitrogen. Although the temperature for the nitrogen data was about 70 °C lower than that for the carbon dioxide data, the patterns that can be

Table III. Comparison of Methyl Ester Product Ions in CO_2 and N_2 Drift Gases

compd.	drift time, ms N_2	drift time, ms CO_2	mobility, cm²/(V·s) N_2	mobility, cm²/(V·s) CO_2
A. methyl melissate		38.4		0.53
B. methyl stearate	23.4	30.2	1.02	0.68
C. methyl myristate	20.8	26.9	1.15	0.76
D. methyl laurate	19.3	25.1	1.24	0.82
E. methyl caprate	17.6	23.2	1.36	0.89
F. methyl caprylate	15.8	21.2	1.52	0.97
G. methyl caproate	14.0	19.2	1.71	1.07
H. methyl butyrate	12.4	17.4	1.93	1.18
I. methyl propionate	11.7	16.6	2.05	1.24
J. reactant ion	10.5	16.1	2.28	1.28

observed for the two sets of data are remarkably similar. From these initial observations it appears that the ionization processes that occur in CO_2 gas are similar to those that occur in N_2 gas, and that many analogous analytical detection modes may be developed with CO_2 as drift and carrier gas.

More detailed investigations are of course needed to determine the exact nature of these product ions and the reaction mechanisms that lead to their formation. Also, a more complete characterization of the analytical aspects of CO_2–IMS is needed. Do other classes of compounds produce useful ion mobility spectra? Is CO_2 a more selective chemical ionizing agent than nitrogen? Does nitrogen produce a more sensitive response? Nevertheless, this work has demonstrated that ion separation in carbon dioxide gas at atmospheric pressure is possible. Thus, the concept of employing CO_2–IMS as a detection method for CO_2–SFC appears more promising now than it did prior to this investigation.

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