Infrared Multiphoton Dissociation of Some Oxygen-Containing Hydrocarbon Ions. Differentiation of Isomeric Ion Structures in the Gas Phase

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Abstract: Infrared multiphoton dissociation of gaseous ions formed from several ethers and esters, trapped in a Fourier transform mass spectrometer, and irradiated with a grating-tuned continuous wave CO_2 laser has been observed. Ions of the same empirical formula arising from different precursors exhibited different photodissociation behavior. The $C_4H_9O_2^+$ (m/z 89) ion formed in 1,4-dioxane and 2-(2-ethoxyethoxy)ethanol fragmented after multiphoton infrared absorption to produce a $C_2H_5O^+$ (m/z 45) ion, while the $C_4H_9O_2^+$ ion formed in bis(2-methoxyethyl) ether (diglyme), 1,2-dimethoxyethane, and 2-methoxyethanol fragmented under similar conditions to produce a $C_3H_7O^+$ (m/z 59) ion. The $C_4H_9O_2^+$ ion formed in ethyl acetate fragmented to produce $C_2H_5O_2^+$ (m/z 61), and the $C_4H_9O_2^+$ ion formed in methyl propionate did not undergo photodissociation. The $C_5H_{11}O_2^+$ (m/z 103) ion formed in diglyme and 2-methoxyethanol photodissociated to form $C_3H_7O^+$, while the $C_5H_{11}O_2^+$ ion formed in propyl acetate under similar conditions yielded $C_2H_5O_2^+$. Explanation of these phenomena in terms of the lowest activation energy dissociation channels of different structural isomers is presented, and this method of isomeric differentiation is compared with the more widespread techniques of collisional activation (CA) spectroscopy.

Introduction

Mass spectrometric methods can provide a wide range of information about chemical compounds and have been applied in an increasing number of chemical subdisciplines in recent years. However, the often important problem of determining, or at least differentiating between, the structures of several isomeric forms of an ion with a given mass-to-charge (m/z) ratio has not yet been solved. Several approaches to the problem, which are successful with certain classes of ions, have been developed. The most widespread of these is the technique of collision-induced dissociation (CID), one of the processes occuring in collisional activation (CA) spectroscopy[1,2] which has been applied not only in various magnetic sector instruments[1,2] but also in the triple quadrupole mass spectrometer[3] and in Fourier transform mass spectrometers.[4]

An alternate approach to isomeric differentiation involves the use of bimolecular ion/molecule reactions to distinguish between various ionic structural isomers based on their differing reactivity. This approach has most often employed an ion cyclotron resonance (ICR) mass spectrometer.[5] Many of the species investigated have been small hydrocarbon ions.[6-8] A similar technique involving the use of low-energy reactive collisions has also recently been reported[9] for isomeric differentiation of $C_3H_3^+$ isomers in a triple quadrupole mass spectrometer.

The use of conventional light sources or UV/visible lasers to photodissociate gaseous ions of interest is another quite promising approach to isomeric differentiation.[10] For favorable cases, the photodissociation spectrum of various structural isomers can be

obtained[11,12] and used, for example, to probe the structure of ion/molecule reaction products.[13] In order to observe photodissociation, the ions of interest must possess an allowed transition in the range of output wavelengths available from the light source and must also have available energetically allowed dissociation pathways from the excited states which are reached upon photon absorption. While these conditions are met for a wide range of ions, there are other classes for which they do not hold and hence for which this approach to isomeric differentiation is not possible.

Several groups have reported work involving photodissociation of gaseous ions with relatively low powered infrared (CO_2) lasers (continuous wave (CW) and pulsed).[14-17] Again, most of these studies have been carried out in ICR mass spectrometers, where ions can be trapped for long periods of time during which they may sequentially absorb many infrared (IR) photons. Since ion photodissociation can be followed as a function of (the relatively limited range of CO_2) laser wavelength, this type of experiment raises the possibility of isomeric differentiation based on the observed infrared photodissociation spectrum. Indeed, at least two reports have been published on the subject, one dealing with $C_3F_6^+$ photodissociation,[18] and one with $C_7H_7^-$ photodetachment[19] (which also can be induced by infrared radiation).

There are a number of significant differences between dissociation of neutrals (or ions) brought about by high-power, pulsed CO_2 lasers and the dissociation of ions trapped in an ICR mass spectrometer subjected to irradiation from a chopped or gated CW CO_2 laser of relatively low power. In the latter process, if the rate of absorption of photons by the trapped ions exceeds the rates of radiative and collisional relaxation, increasing amounts of vibrational energy are accumulated in the ion, eventually re-

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sulting in its dissociation. The best discussion of the many aspects of this type of experiment has been given by Thorne and Beauchamp,[20] who noted two general cases involving small and large ions. For small ions, resonant absorption of one or more infrared photons could be expected (and was suggested experimentally) before eventual absorption of numerous photons into the quasicontinuum completed the energy input necessary to produce dissociation. Large ions already possessed a density of states sufficiently high that even absorption of the first infrared photon was expected to be into the quasicontinuum. For almost all ions studied, since photons were absorbed sequentially by the trapped ions over a time period of many milliseconds, complete randomization of energy throughout all of the normal modes of the ion was postulated, resulting in dissociation via the lowest activation energy pathway, as soon as sufficient energy had been accumulated in the ion. This point has also been discussed for photodissociation of neutrals.[21] Such dissociation via the channel of lowest activation energy leads to the possibility of a second means of isomeric differentiation with IR multiphoton photodissociation (MPD). Instead of noting the wavelength dependence of ionic dissociation for different isomers, which may not be significant as the ions approach the large molecule limit, one might observe differences in the *dissociation products* of different isomers, since different structures might be expected to possess different lowest energy dissociation pathways. One example of this approach, where different dissociation products were observed for isomeric proton-bound alcohol dimers, has been reported.[22]

An area of active research in this laboratory in recent years has been investigation of the visible laser photodissociation of gaseous ions.[23-25] More recently, studies of small hydrocarbon ions[26,27] have prompted a search for improved methods of isomeric differentiation,[8,9] since the structures of these ions, particularly any cyclic structures, are quite important in assessing the viability of an ionic mechanism of soot nucleation. Thus the possibility of using tunable infrared irradiation to differentiate structural isomers of gaseous ions was particularly attractive.

For the initial work reported here, a number of oxygen-containing hydrocarbon ions were chosen, in part because earlier reports[14,20] had predicted a high probability that these compounds would absorb CO_2 laser radiation in the 10.6 μm wavelength range, presumably due to excitation of a C–O–C asymmetric stretching mode in the ions. Demonstration of the potential for isomeric differentiation in classes of ions different from the proton-bound alcohol dimers previously[22] studied was also sought. The infrared multiphoton dissociation of two ions, $C_4H_9O_2^+$ (m/z 89) and $C_5H_{11}O_2^+$ (m/z 103), has been studied, and quite different dissociation pathways depending on the ionic precursor have been observed. The photodissociation behavior of four distinct $C_4H_9O_2^+$ isomers is presented in some detail, with limited results for $C_5H_{11}O_2^+$ used to corroborate dissociation pathways suggested for the smaller ion. Implications of this controlled means of dissociating ions of moderate to large molecular weight are also discussed.

Experimental Section

All experiments were carried out with a Nicolet FT/MS-1000 Fourier transform mass spectrometer[28] equipped with a 3 T superconducting magnet. The cubic ion cyclotron resonance cell (2.54 cm) was modified to allow irradiation of trapped ions by replacing the stainless steel trapping plate through which the electron beam exits the cell with one containing a 1.34 cm diameter hole covered by a copper mesh of approxi-
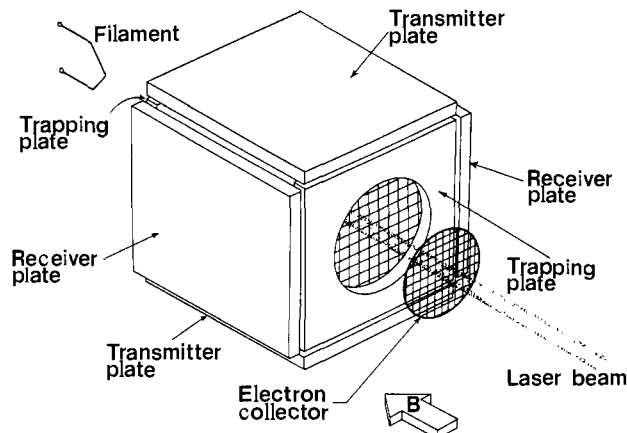
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(28) Nicolet Analytical Instruments, 5225 Verona Road, P.O. Box 4508, Madison, WI 53711.

Figure 1. Cubic ICR cell modified for irradiation of trapped ions. Direction of the magnetic field (B) is as indicated.
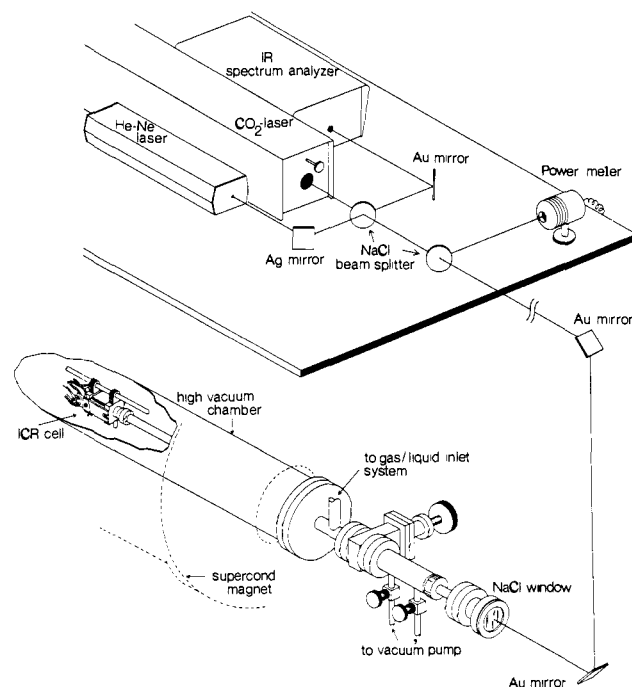

Figure 2. Laser table and cutaway view of relevant portions of the FTMS instrumentation. The He/Ne laser was used only for alignment of the CO_2 laser, and the two NaCl beam splitters were removed during ion irradiation.

mately 80% transparency, as shown in Figure 1. Positive ions were produced by electron impact (EI) (ionizing energies ranged from 9.2 to 50 eV) and trapped in the cell by the magnetic field and an electric trapping field produced by a +1 V potential applied to the trapping plates. Ion irradiation was carried out with an Apollo Model 570 CW tunable CO_2 laser[29] gated by a trigger pulse from the FTMS instrument which could be chosen to coincide with any pulse in the experimental sequence under software control.

As shown in Figure 2, the laser beam was reflected by a NaCl beam splitter and an Au mirror into a spectrum analyzer (Optical Engineering, Model 16-A)[30] for wavelength determination. The main beam was split again by another NaCl beam splitter for power measurement with a Coherent Radiation Model 410 power meter.[31] These two beam splitters were removed during actual ion irradiation. Finally, the main laser beam was reflected by using two gold mirrors into the vacuum chamber of the mass spectrometer, passing through a NaCl window sealed to a vacuum flange with viton O-rings. The flange was at the end of a 1.27 cm diameter stainless steel tube which was inserted into the vacuum chamber

(29) Apollo Laser Inc., 9201 Independence Avenue, Chatsworth, CA 91311.
(30) Optical Engineering Inc., 2495 Bluebell Drive, Santa Rosa, CA.
(31) Coherent Components Group (formerly Coherent Radiation), 2301 Lindbergh Street, Auburn, CA 95603.
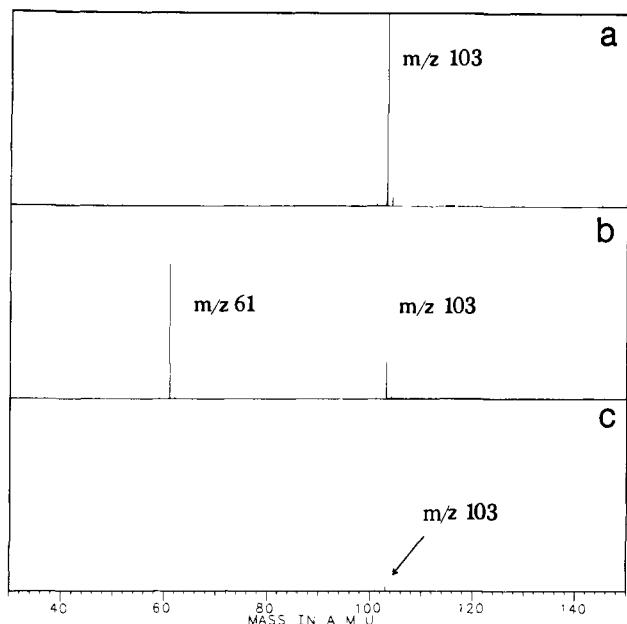
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Figure 3. Photodissociation of protonated propyl acetate ($C_5H_{11}O_2^+$) with (a) laser off, (b) laser on for 500 ms, and (c) laser on and m/z 61 photoproduct ejected during irradiation.

with use of the solid sample inlet system. Before passing through the mesh on the trapping plate (Figure 1) the laser beam passed through another mesh of ca. 50% transparency which was used as the electron collector of the cyclotron resonance cell. The IR laser beam was aligned with use of a He–Ne laser whose beam was reflected by an Ag mirror and the first beam splitter into the path of the CO_2 laser (Figure 2).

Although a wavelength dependence for multiphoton dissociation of lower molecular weight ions as well as some of those studied here has been observed,[32] for these studies a fixed wavelength of 10.6 μm was used with CW power levels of 25–50 W. Following formation by electron impact or ion/molecule reaction the ion of interest was typically subjected to laser irradiation for 500 ms. The effect of the mirrors, window, and meshes described above was to reduce the actual laser power entering the cell by approximately a factor of 10 (to ca. 2.5–5 W in a beam of ca. 1 cm^2 cross section). Since the cell interior consists of highly polished stainless steel, the laser beam was reflected from the trapping plate opposite the one through which it entered the cell. This reflection effectively doubled the laser irradiance to a value of 5–10 W/cm^2. Under these conditions photodissociation rate constants[33] of ca. 10 s^{-1} were observed.

Pressures of neutrals from which the ions were formed were maintained in the $2–5 \times 10^{-8}$ torr range as measured on an ionization gauge (Granville-Phillips Series 280).[34] These pressures were sufficiently high to produce adequate ion intensities but low enough that reactions of photoproduced ions to reform their parents were relatively slow (vide infra). For CID experiments Ar was added as a collision gas to a total pressure of $1–2 \times 10^{-6}$ torr.

In order to avoid interference which might arise from either competing ion–molecule formation reactions or competing multiphoton dissociation pathways, photodissociation of an ion was carried out after ejection from the cell of all ions except the one under study. Many of the ions of interest were formed as products in ion/molecule reactions, and for these ions an additional reaction time, usually 500 ms, was added to the experimental sequence before ion selection and irradiation. Since reactive ions can undergo ion/molecule reactions during the laser irradiation period, all spectra were taken both with and without laser irradiation with the same pulse sequence.

In some cases the photoproduct ions reacted with neutral molecules present in the system to reform the photodissociating ion. These back reactions complicated study of the photodissociation effect and made it difficult to observe the actual extent of photodissociation. In order to eliminate this problem, the photoproduct ion was continually ejected

during the laser irradiation period and the extent of photodissociation was determined from the decrease of the parent peak. An example of this effect for the $C_5H_{11}O_2^+$ ion formed in propyl acetate is shown in Figure 3. Figure 3a shows the mass spectrum after ejection of all ions but m/z 103 ($C_5H_{11}O_2^+$), and the mass spectrum following 500 ms of laser irradiation is shown in Figure 3b. If the m/z 61 photoproduct ion was continually ejected from the cell during laser irradiation, the mass spectrum shown in Figure 3c was obtained. In this case, the m/z 61 ions were unable to react with propyl acetate to reform the $C_5H_{11}O_2^+$ ion and virtually 100% photodissociation of the latter ion was observed; hence photodissociation was markedly more effective than might be surmised from Figure 3b.

All of the compounds used were commercially available analytical grade chemicals. 1,4-Dioxane and bis(2-methoxyethyl) ether were obtained from Mallinckrodt (Paris, KY), 2-(2-ethoxyethoxy)ethanol, propyl acetate, and methyl propionate from Aldrich (Milwaukee, WI), ethyl acetate from Fisher Scientific Co. (Ft. Lauderdale, FL), 2-methoxyethanol from Eastman-Kodak Co. (Rochester, NY), and 1,2-dimethoxyethane from Chem Service Inc. (West Chester, PA). All compounds were additionally purified by several freeze–pump–thaw cycles before introduction into the mass spectrometer. No significant level of any impurity was detected by standard FTMS wide mass range analysis prior to laser irradiation experiments.

Results and Discussion

Differing photodissociation pathways for ions of the same mass-to-charge ratio formed from different precursors have been observed in this work. Such an observation strongly suggests that structural isomers are being formed and differentiated by infrared multiphoton dissociation. The long time scales of our experiments (ca. 1 s for ion formation, irradiation, and detection) help to ensure that only stable, long-lived isomers are being studied. All observed dissociations were checked at both high (50 eV) and low (vide infra) electron energies to assess the effect on the photodissociation process of excess internal energy in the ions prior to photodissociation. The absence of any observed effect indicates that different dissociation pathways were not caused merely by differing internal energy in ions of the same structure.

The photodissociation pathways observed for each ionic system can be used as guides to the probable structure of the ions prior to photodissociation. Thermochemical data are not available for several of the postulated isomeric structures so the energetics of most of the pathways observed cannot be calculated. Nonetheless, with use of those data which are available, it appears that dissociation pathways of lowest activation energy (which are observed in MPD) correspond to those of lowest calculated endoergicity (i.e., there is no case II behavior[35]). As indicated in the following discussion, quite reasonable choices for ion structures and lowest energy dissociation are in excellent agreement with experimental results.

$C_4H_9O_2^+$. Photodissociation of this ion (m/z 89) as produced from seven different precursors was studied. In each case reactions which produce the m/z 89 ion are reported and discussed, followed by the photodissociation behavior.

1,4-Dioxane. In this system $C_4H_9O_2^+$ is formed by proton-transfer reactions to the dioxane molecule. For example, the molecular ion of dioxane undergoes a reaction with neutral dioxane:

$$C_4H_8O_2^+ + C_4H_8O_2 \rightarrow C_4H_9O_2^+ + C_4H_7O_2 \qquad (1)$$
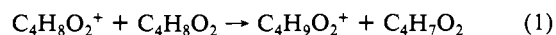
The electron impact induced fragment $C_2H_5O^+$ also reacts with the parent molecule and produces protonated dioxane:

$$C_2H_5O^+ + C_4H_8O_2^+ \rightarrow C_4H_9O_2^+ + C_2H_4O \qquad (2)$$

The neutral molecule produced in reaction 2 may be acetaldehyde (although the identity of neutrals cannot be established in the ICR technique). $C_2H_5O^+$, in addition to being produced by electron impact ionization, is formed by an ion/molecule reaction involving the molecular ion:

$$C_4H_8O_2^+ + C_4H_8O_2 \rightarrow C_2H_5O^+ + (C_6H_{11}O_3) \qquad (3)$$
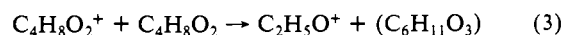
Thus production of $C_4H_9O_2^+$ also occurs via the consecutive re-

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(32) Watson, C. H.; Baykut, G.; Eyler, J. R., manuscript in preparation.

(33) The photodissociation process followed first-order kinetics, $I/I_0 = \exp(-k_D t)$, where I is the signal intensity at the end of the irradiation period of length t, I_0 the intensity at the end of the same period without irradiation, and k_d is the dissociation rate constant.

(34) Granville-Phillips Co., 5675 East Arapahoe Avenue, Boulder, CO 80303.

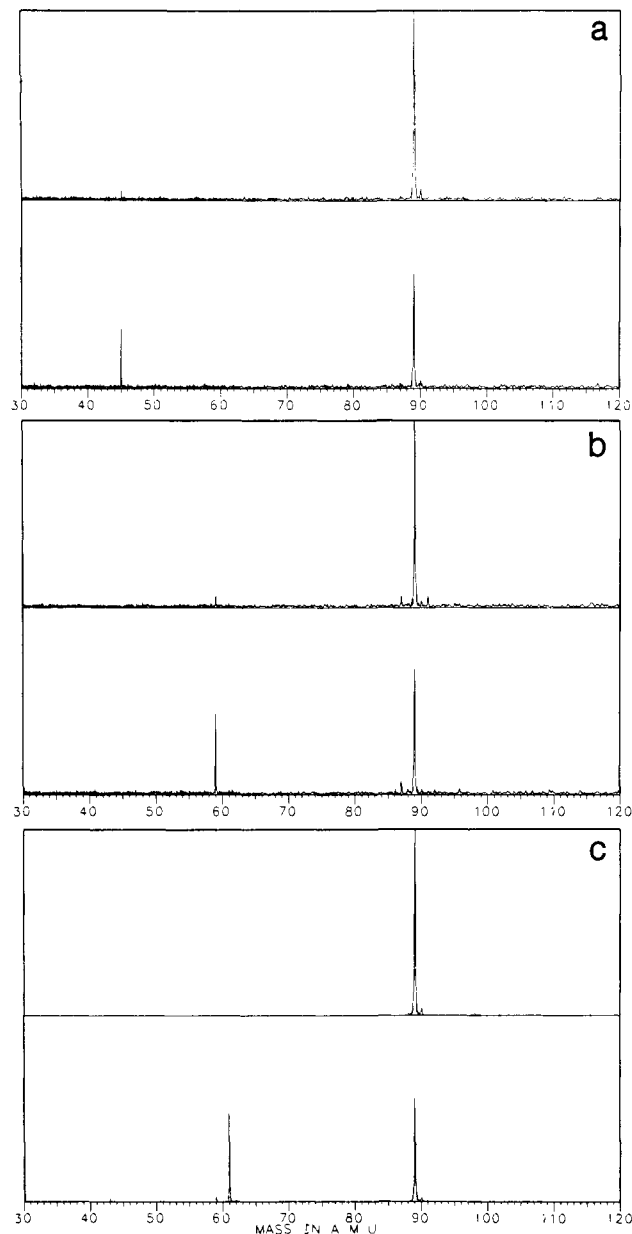(35) Thorne, L. R.; Beauchamp, J. L., ref 20, p 75.

Figure 4. Photodissociation of $C_4H_9O_2^+$ from different precursors: (a) photoproduction of $C_2H_5O^+$ (m/z 45) from protonated 1,4-dioxane; (b) photoproduction of $C_3H_7O^+$ (m/z 59) from the $C_4H_9O_2^+$ fragment ion in bis(2-methoxyethyl) ether; and (c) photoproduction of $C_2H_5O_2^+$ (m/z 61) from protonated ethyl acetate. (Upper spectrum in each case is laser off; lower spectrum is laser on.)

action system $C_4H_8O_2^+ \rightarrow C_2H_5O^+ \rightarrow C_4H_9O_2^+$.

Irradiation of protonated dioxane by the CO_2 laser tuned to a wavelength of 10.6 μm leads to photodissociation of the ion, producing $C_2H_5O^+$:

$$C_4H_9O_2^+ + nh\nu \rightarrow C_2H_5O^+ + C_2H_4O \qquad (I)$$
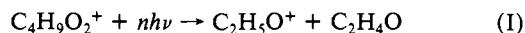
(see Figure 4a).

Most studies were carried out on ions formed with 50 eV ionizing electron energy. To lessen the chances of significant internal excitation in primary and product ions, the electron energy was reduced to 11 eV and photodissociation of the protonated dioxane was again studied. Under these conditions, all ions except the parent ion, $C_4H_8O_2^+$, were ejected from the cell and $C_4H_9O_2^+$ was produced exclusively by reaction 1. Only process I was observed. Since the photodissociation product $C_2H_5O^+$ is also a precursor of $C_4H_9O_2^+$ (reaction 2), it reacts with dioxane as soon as it is produced by photodissociation to reform protonated dioxane. To avoid complication due to this process, $C_2H_5O^+$ was continuously ejected from the analyzer cell during the laser ir-

radiation period in experiments where the extent of dissociation was determined.

The m/z 89 ion formed via reactions 1 and 2 might retain the cyclic neutral structure upon protonation, with a proton on one of the oxygens or alternatively located between the two oxygens in a "boat" conformation of the dioxane. Such a cyclic $C_4H_9O_2^+$ structure requires cleavage of two bonds during photodissociation, since $C_2H_5O^+$ is observed as the dissociation product. The first cleavage would produce a ring-opened ion of the same mass as
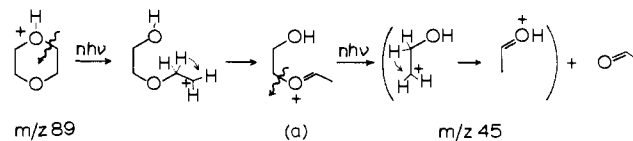
the cyclic one and the second step would involve cleavage of a carbon–oxygen bond with loss of acetaldehyde most probable. On the other hand, protonation of dioxane might impart sufficient internal energy to open the ring, with photodissociation then proceeding via the second half of the pathway shown above: (In Scheme A
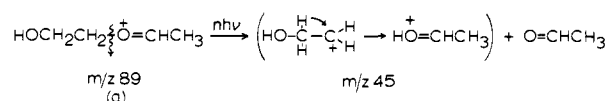

this discussion, each proposed isomeric structure will be labeled by a lower case letter, and the photodissociation scheme postulated for that isomer will be labeled with the same upper case letter.) A three-membered ring intermediate ion formed by neighboring group participation[36] is also possible during the photodissociation process, in which case the mechanism would be:
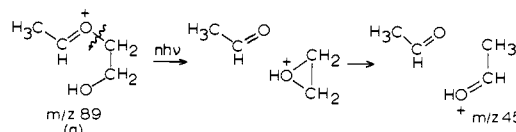

Further evidence supporting structure a and its dissociation via Scheme A is obtained by studying the subsequent behavior of the m/z 45 ion produced in this photodissociation. After its formation during laser irradiation, this ion reacts completely with dioxane via proton transfer. Such behavior is characteristic[37] of the most stable[38] m/z 45 isomer, protonated acetaldehyde, shown in Scheme A.

2-(2-Ethoxyethoxy)ethanol. A $C_4H_9O_2^+$ ion is also produced in 2-(2-ethoxyethoxy)ethanol, mainly as a reaction product of the major fragment ion, $C_2H_5O^+$;

$$C_2H_5O^+ + C_6H_{14}O_3 \rightarrow C_4H_9O_2^+ + C_4H_{10}O_2 \qquad (4)$$
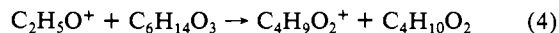
The same photodissociation process was observed for this ion as for the m/z 89 ion produced in 1,4-dioxane, namely process I above. Considering the formation of the ion via reaction 4, the structure a which dissociates via Scheme A would again be expected. Again in this system photoproduced m/z 45 ions react
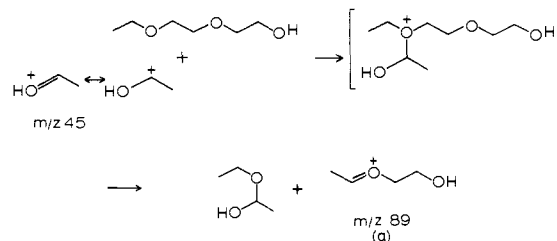
completely to protonate the parent neutral, indicating a protonated

(36) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms and Structure"; McGraw Hill: New York, 1977; p 279.

(37) Beauchamp, J. L.; Dunbar, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 1477.

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acetaldehyde structure for these photofragment ions and supporting structure a as the best assignment for the $C_4H_9O_2^+$ isomer undergoing photodissociation.

Bis(2-methoxyethyl) Ether (Diglyme). A $C_4H_9O_2^+$ fragment ion is produced by electron impact ionization of diglyme. After ejection of all other ions, irradiation of this ion results in photofragmentation, producing $C_3H_7O^+$, m/z 59:

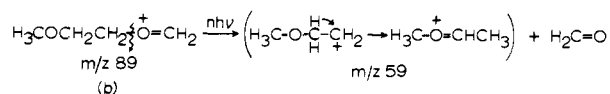$$C_4H_9O_2^+ + nh\nu \rightarrow C_3H_7O^+ + CH_2O \qquad (II)$$
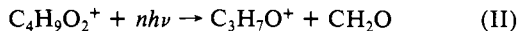
(see Figure 4b). Experiments at an electron energy of 10 eV, slightly above the m/z 89 ion's appearance potential, gave the same results as those seen with 50 eV ionizing energy.

The EI induced fragmentation of diglyme cleaves a carbon–carbon bond and causes loss of CH_2OCH_3 as the neutral species.

$$(H_3COCH_2CH_2OCH_2CH_2OCH_3)^{+\cdot} \rightarrow H_3COCH_2CH_2O^+=CH_2 + H_2COCH_3$$
$$m/z\ 89$$
$$(b)$$
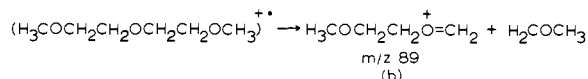
Thus, the resultant $C_4H_9O_2^+$ most likely has a methylene and not a hydroxyl group at the end of a linear ion. The photodissociation process then involves cleavage of a carbon–oxygen bond and a neutral formaldehyde molecule is apparently lost. Again invoking
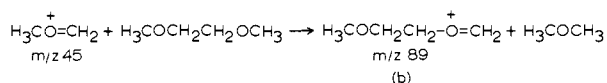
Scheme B

$$H_3COCH_2CH_2\overset{+}{O}=CH_2 \xrightarrow{nh\nu} \left(H_3C-O-\overset{H\curvearrowleft}{\underset{H}{C}}-\overset{+}{C}H_2 \rightarrow H_3C-\overset{+}{O}=CHCH_3 \right) + H_2C=O$$
$$m/z\ 89 \qquad\qquad m/z\ 59$$
$$(b)$$

neighboring group participation the mechanism can be alternately formulated with a three-membered ring intermediate ion:

[structure] m/z 89 (b) $\xrightarrow{nh\nu}$ [structures] m/z 59
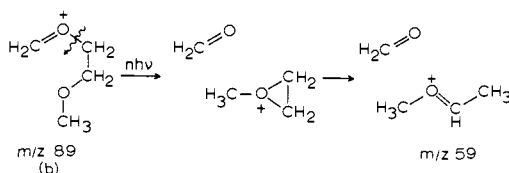
1,2-Dimethoxyethane. The electron impact mass spectrum of 1,2-dimethoxyethane contains very little $C_4H_9O_2^+$. However, the ion is formed by ion/molecule reactions, primarily from $C_2H_5O^+$, which is a major fragment ion in the mass spectrum:
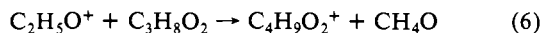
$$C_2H_5O^+ + C_4H_{10}O_2 \rightarrow C_4H_9O_2^+ + C_2H_6O \qquad (5)$$

Thus it appears that $C_2H_5O^+$ forms dimethyl ether by a hydride transfer reaction involving the 1,2-dimethoxyethane neutral.

$$H_3C\overset{+}{O}=CH_2 + H_3COCH_2CH_2OCH_3 \rightarrow H_3COCH_2CH_2-\overset{+}{O}=CH_2 + H_3COCH_3$$
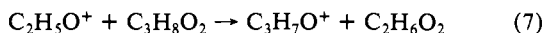$$m/z\ 45 \qquad\qquad\qquad m/z\ 89$$
$$(b)$$

Hydride transfer is a characteristic reaction[37] of the methoxymethyl cation isomeric form of m/z 45 shown above.

Photodissociation of this $C_4H_9O_2^+$ isomer was observed at both high and low electron energies, down to the appearance potential of its $C_2H_5O^+$ precursor. MPD gave rise to the photofragment $C_3H_7O^+$, as shown in process II above. Formation of isomer b, which dissociates via Scheme B, is quite reasonable given its formation via hydride transfer from the parent molecule.

2-Methoxyethanol. A $C_4H_9O_2^+$ ion is formed in 2-methoxyethanol. The fragment ion $C_2H_5O^+$ produces $C_4H_9O_2^+$ by a reaction with the neutral,
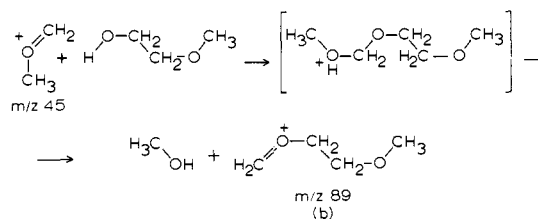
$$C_2H_5O^+ + C_3H_8O_2 \rightarrow C_4H_9O_2^+ + CH_4O \qquad (6)$$

or by two consecutive reactions via $C_3H_7O^+$;

$$C_2H_5O^+ + C_3H_8O_2 \rightarrow C_3H_7O^+ + C_2H_6O_2 \qquad (7)$$

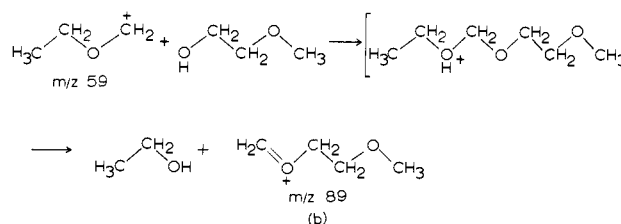$$C_3H_7O^+ + C_3H_8O_2 \rightarrow C_4H_9O_2^+ + C_2H_6O \qquad (8)$$

Multiphoton dissociation of this $C_4H_9O_2^+$ ion yields $C_3H_7O^+$ as shown in process II above. This photodissociation was studied at low electron energies (11 eV) after ejection of all ions but $C_2H_5O^+$, which then formed $C_4H_9O_2^+$, and it still proceeded as shown in (II).

Reaction 6 most likely involves elimination of methanol, as shown below.

[reaction scheme]
m/z 45 $\rightarrow$ [bracketed intermediate] $\rightarrow$
$$H_3C\overset{}{\underset{OH}{\diagdown}} + H_2C\overset{+}{=}O-CH_2-CH_2-O-CH_3$$
$$m/z\ 89$$
$$(b)$$

The photodissociation then proceeds as shown in Scheme B. Observation of this photodissociation pathway gives strong evidence for a $C_4H_9O_2^+$ ion with no terminal OH but rather two etheric oxygens in the central portion of the chain. Such a structure would result from reaction of the less stable methoxymethyl cation, known[37] to form in etheric systems. Reaction of the more stable protonated acetaldehyde m/z 45 isomer with 2-methoxyethanol would lead to $C_4H_9O_2^+$ with a terminal OH, as in the case of dioxane and 2-(2-ethoxyethoxy)ethanol. Those ions, however, photodissociate to form $C_2H_5O^+$ rather than $C_3H_7O^+$.

Formation of the m/z 89 ion via reaction 8, with probable loss of ethanol, can proceed as shown below. The $C_4H_9O_2^+$ ion would again be predicted to photodissociate as shown in Scheme B.

[reaction scheme]
m/z 59 $\rightarrow$ [bracketed intermediate]

$$\rightarrow H_3C\overset{}{\underset{OH}{\diagdown}} + H_2C\overset{}{=}O-CH_2-O-CH_3$$
$$m/z\ 89$$
$$(b)$$

Ethyl Acetate. Protonated ethyl acetate also possesses the formula $C_4H_9O_2^+$. Protonation occurs via reaction of the fragment ions $C_2H_3O^+$, $C_2H_5O^+$, $C_2H_5O_2^+$, and $C_4H_6O^+$:

$$C_2H_3O^+ + C_4H_8O_2 \rightarrow C_4H_9O_2^+ + C_2H_2O \qquad (9)$$

$$C_2H_5O^+ + C_4H_8O_2^+ \rightarrow C_4H_9O_2^+ + C_2H_4O \qquad (10)$$

$$C_2H_5O_2^+ + C_4H_8O_2 \rightarrow C_4H_9O_2^+ + C_2H_4O_2 \qquad (11)$$

$$C_4H_6O^+ + C_4H_8O_2 \rightarrow C_4H_9O_2^+ + C_4H_5O \qquad (12)$$

The fragments $C_4H_6O^+$, $C_2H_5O^+$, and $C_2H_5O_2^+$ also contribute to formation of $C_4H_9O_2^+$ by producing $C_2H_3O^+$ in ion–molecule reactions, which are then followed by reaction 9.

Photodissociation of $C_4H_9O_2^+$ ions formed by reactions 9–12 was studied at electron impact energies of 50 and 11 eV. Photodissociation with a similar cross section was observed for both electron energies, leading to $C_2H_5O_2^+$:

$$C_4H_9O_2^+ + nh\nu \rightarrow C_2H_5O_2^+ + C_2H_4 \qquad (III)$$
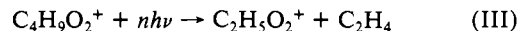
(see Figure 4c). Again the extent of photodissociation was more easily studied by ejecting the photoproduct $C_2H_5O_2^+$ during the laser irradiation time, since it reacted to reform $C_4H_9O_2^+$ as shown in reaction 11. Photofragmentation consistent with a McLafferty-type rearrangement[39] best explains the loss of ethylene and formation of an m/z 61 ion in this system.

Scheme C

[reaction scheme]
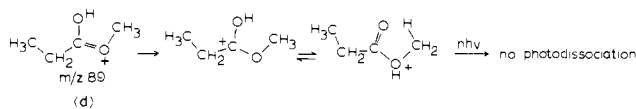m/z 89 $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ m/z 61
(c)
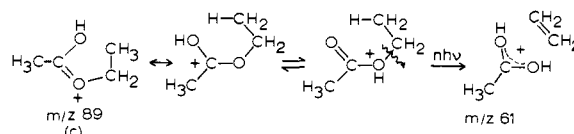
Methyl Propionate. Protonated methyl propionate is obtained primarily by reaction of a fragment ion, $C_3H_5O^+$, with the neutral molecule:

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(39) McLafferty, F. W. *Anal. Chem.* **1959**, *31*, 82.

$$C_3H_5O^+ + C_4H_8O_2 \rightarrow C_4H_9O_2^+ + C_3H_4O \qquad (13)$$

This $C_4H_9O_2^+$ isomer exhibited no photodissociation over the range of wavelengths available. The absence of photodissociation in
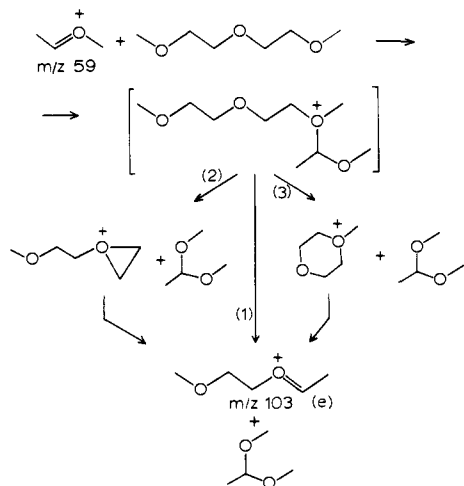
Scheme D

this case is reasonable, since thermochemical calculations[40,41] show that abstraction of a CH_2 radical from protonated methyl propionate requires much more energy (103 kcal/mol) than ethylene abstraction from protonated ethyl acetate (30 kcal/mol) shown in Scheme C. An alternate dissociation to give CH_3^+ and propionic acid is probably the lowest energy pathway available to protonated methyl propionate, but it still requires ca. 97 kcal/mol, apparently more than can be supplied in this type of photodissociation process.

$C_5H_{11}O_2^+$. Photodissociation pathways observed for ions of empirical formula $C_5H_{11}O_2^+$ (m/z 103) strengthen conclusions drawn about m/z 89 structural isomers. Two distinct photodissociation pathways were seen for $C_5H_{11}O_2^+$ ions formed from three different precursors.

**Bis(2-methoxyethyl) Ether (diglyme).** In diglyme $C_5H_{11}O_2^+$ is produced as the product of an ion/molecule reaction involving $C_3H_7O^+$:

$$C_3H_7O^+ + C_6H_{14}O_3 \rightarrow C_5H_{11}O_2^+ + C_4H_{10}O_2 \qquad (14)$$
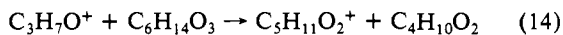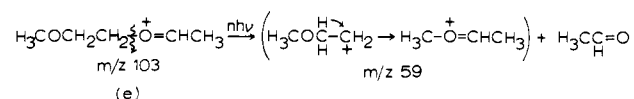
Three different pathways for ion formation can be envisioned: (1) simple C–O bond cleavage in the m/z 193 ion/molecule collision complex; (2) neighboring group participation involving a three-membered ring intermediate; or (3) formation of a 6-membered ring intermediate.

Multiphoton dissociation of this ion yielded $C_3H_7O^+$:

$$C_5H_{11}O_2^+ + nh\nu \rightarrow C_3H_7O^+ + C_2H_4O \qquad (IV)$$
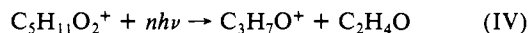
The photodissociation process once again involves C–O bond cleavage, perhaps preceded by ring opening if the ion retains one of the cyclic structures shown above. Scheme E is identical with Scheme B, with an additional methyl group added to the photodissociating ion and subsequent formation of acetaldehyde rather than formaldehyde.

Scheme E

Scheme B, with an additional methyl group added to the photodissociating ion and subsequent formation of acetaldehyde rather than formaldehyde.

2-Methoxyethanol. The fragment ion $C_3H_7O^+$ reacts with 2-methoxyethanol to produce $C_5H_{11}O_2^+$:

$$C_3H_7O^+ + C_3H_8O_2 \rightarrow C_5H_{11}O_2^+ + CH_4O \qquad (15)$$
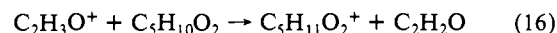
Addition of $C_3H_7O^+$ ion followed by rearrangement and loss of methanol is entirely analogous to reaction 6, which involved addition of $C_2H_5O^+$, rearrangement, and loss of methanol. As would
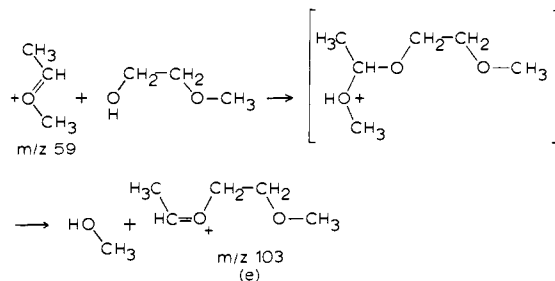
be expected, this ion dissociates via C–O bond cleavage to form an m/z 59 ion and acetaldehyde, following Scheme E above.

Propyl Acetate. The fragments $C_2H_3O^+$, $C_2H_5O_2^+$, and $C_3H_5O_2^+$ produced a $C_5H_{11}O_2^+$ ion by ion/molecule reactions:

$$C_2H_3O^+ + C_5H_{10}O_2 \rightarrow C_5H_{11}O_2^+ + C_2H_2O \qquad (16)$$

$$C_2H_5O_2^+ + C_5H_{10}O_2 \rightarrow C_5H_{11}O_2^+ + C_2H_4O \qquad (17)$$

$$C_3H_5O_2^+ + C_5H_{10}O_2 \rightarrow C_5H_{11}O_2^+ + C_3H_4O_2 \qquad (18)$$

At 11 eV electron energy the only fragment ion observed is m/z 61, $C_2H_5O_2^+$, which then reacts solely via reaction 17 to produce $C_5H_{11}O_2^+$. An ion/molecule reaction of m/z 43, $C_2H_3O^+$, also produces $C_2H_5O_2^+$, which in turn reacts to form the protonated molecule via reaction 17.

Infrared photodissociation in this case gave

$$C_5H_{11}O_2^+ + nh\nu \rightarrow C_2H_5O_2^+ + C_3H_6 \qquad (V)$$

This photodissociation behavior is best explained by a McLafferty-type rearrangement similar to that shown in Scheme C for protonated ethyl acetate: The products of this photodissociation

Scheme F
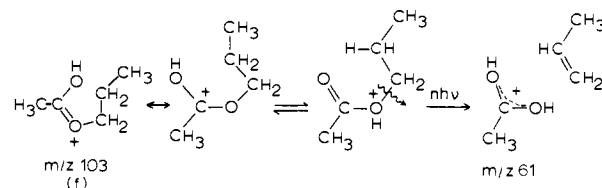
are most likely protonated acetic acid and a propylene molecule. Thermochemical calculations[40,41] show that such a photodissociation requires about the same amount of energy (31 kcal/mol) as ethylene loss from protonated ethyl acetate (30 kcal/mol).

All of the photodissociation pathways observed in this study involved C–O rather than C–C bond cleavages. While either of these bond types requires approximately the same energy for homolytic bond cleavage in neutral species (ca. 80–90 kcal/mol), this equality apparently does not hold true for the ionized, often protonated, oxygen-containing hydrocarbons studied in this work. Heats of formation of the many ions involved in the processes observed are not uniformly available, but sample calculations for smaller ions can be performed. Thus, for example, cleavage of the C–O bond in protonated methyl *n*-propyl ether to produce methanol and *n*-$C_3H_7^+$ requires ca. 14 kcal/mol less energy than cleavage of the C–C bond to form dimethyl ether and $C_2H_5^+$.[40,41]

(40) Thermochemical calculations have utilized heats of formation of gaseous ions and neutrals given in the following: (a) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Ions"; National Bureau of Standards: Washington, D.C., 1969; NSRDS-NBS 26. (b) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.

(41) The following references have been used for proton affinity data: (a) Long, J.; Munson, B. *J. Am. Chem. Soc.* **1973**, *95*, 2427. (b) Aue, D. H.; Bowers, M. T. In "Chemistry of Gaseous Ions"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 1.

Table I

ion	precursor	m/z of dissociation products	
		CID (Ar collision gas)	MPD
$C_4H_9O_2^+$	dioxane	*45*,[a] 29	45
(m/z 89)	2-(2-ethoxyethoxy)ethanol	*45*, 73, 61	45
	bis(2-methoxyethyl) ether	*59*, 31, 29	59
	1,2-dimethoxyethane	*59*, 45, 31, 29	59
	2-methoxyethanol	*59*, 31, 29	59
	ethyl acetate	*61*, 43, 29, 27	61
	methyl propionate	*57*, 45, 29, 27	
$C_5H_{11}O_2^+$	bis(2-methoxyethyl) ether	*59*, 31, 29	59
(m/z 103)	2-methoxyethanol	*59*, 45, 31, 29	59
	propyl acetate	*61*, 43, 27	61

[a] The fragment ion observed in highest abundance is in italics.

Formation of formaldehyde and n-$C_3H_7^+$ by C–O bond cleavage in CH_3–CH_2–CH_2–O^+=CH_2 requires ca. 17 kcal/mol less than formation of 1,2-epoxyethane and $C_2H_5^+$ via C–C bond cleavage.[40,41] Also protonation of the hydroxyl oxygen on n-propanol lowers the C–O bond strength from 93 to 36 kcal/mol![40,41]

Collision-induced dissociation techniques are widely used to obtain structural information about gaseous ions, In these methods, collisions impart a distribution of internal energies to the ions of interest, which then dissociate, often producing a number of different fragment ions. Multiphoton photodissociation utilizing a CW CO_2 laser is a more controlled, low-energy process. For the systems reported here only one dissociation pathway was seen, corresponding to the fragmentation process of lowest activation energy available to the ion. CID studies have been performed in our FTMS instrument for all of the ions for which multiphoton dissociation was reported in this paper, and in every case multiple dissociation pathways were seen. Results are presented in Table I, For the ions studied in this work the fragment ion observed in highest abundance after CID corresponded to the only ion produced by multiphoton dissociation. However, for other oxygen- and nitrogen-containing ions this has not always proven to be the case.[43]

Thus infrared multiphoton dissociation can complement CID studies by identifying unambiguously the lowest activation energy

fragmentation pathway (most often corresponding to the weakest bond) in the ion under study. While the technique described here is limited to those ions which absorb in the 9,2–10.8 μm wavelength region, the effect has been observed for many classes of compounds, particularly those containing heteroatoms. Larger ions with sufficient degrees of freedom to guarantee absorption directly into a quasicontinuum should be especially suited for the technique. Since collisions of these ions with typical (much lighter) target gases in CID experiments may not impart sufficient internal energy to cause fragmentation, infrared multiphoton dissociation should prove to be most advantageously applied to such high mass ions, for which the technique should also be most universally applicable. We have observed multiphoton dissociation of ions in the m/z 500–700 range and are extending this work to ions of even higher mass,

Conclusions

Use of Fourier transform ion cyclotron resonance mass spectrometry enhances study of gaseous ion MPD. Long ion trapping times are afforded by the high magnetic fields available (3 T) and (often multiple) ion ejection can be employed at any time during the experimental sequence to remove complicating reactions or unwanted ions. Differentiation of several $C_4H_9O_2^+$ (m/z 89) and $C_5H_{11}O_2^+$ (m/z 103) ions produced in some oxygen-containing hydrocarbon systems has been demonstrated. A $C_4H_9O_2^+$ ion of structure a is found in p-dioxane and 2-(2-ethoxyethoxy)ethanol, while structure b is produced in bis(2-methoxyethyl) ether, 1,2-dimethoxyethane, and 2-methoxyethanol, structure c results from protonation of ethyl acetate, and structure d results from protonation of methyl propionate. $C_5H_{11}O_2^+$ ions of structure e are formed in bis(2-methoxyethyl) ether and 2-methoxyethanol, and protonation of propyl acetate produces an ion of structure f. As compared to CID, where numerous fragment ions are produced, infrared MPD is a highly efficient, low-energy means of generating usually only one fragment ion. For the ions studied here, the one fragment ion produced by MPD corresponded to the highest intensity ion resulting from CID.

(42) Sharma, R. B.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 510.

(43) Watson, C. H.; Baykut, G.; Battiste, M. A.; Eyler, J. R. *Anal. Chim. Acta*, in press.