Slow Metastable Dissociation of Chemically Activated Adduct Ions. The Fourier Transform Ion Cyclotron Resonance Analogue of the MIKES Experiment

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Abstract: A new experimental technique is presented in which Fourier transform ion cyclotron resonance spectra may be used to examine the metastable dissociations of chemically activated adduct ions undergoing unimolecular dissociation on time scales greater than 50 μs. The technique involves taking the difference between two spectra, one in which continuous rf irradiation at the cyclotron frequency of the transient adduct ion is carried out during a reaction delay and another in which no such irradiation occurs during the same reaction delay. The difference spectrum then yields a mass spectrum of all those adduct ions with metastable lifetimes greater than the time required to effect the ejection. The technique is applied to examples in mechanistic ion chemistry where the product distribution arising from unimolecular dissociation of the metastable ion is examined as a function of the lifetime probed, and this information is then used to deduce a probable reaction mechanism. The potential of the technique for direct determination of metastable ion lifetimes is noted.

Introduction

Ion cyclotron resonance spectrometry and, more recently, Fourier transform ion cyclotron resonance spectrometry (FTICR) have been abundantly demonstrated to be powerful techniques for the elucidation of mechanisms and energetics of gas phase ion–molecule reactions.[1] With the ability to isolate mass-selected reactant ions and to follow the subsequent temporal evolution of reactant and product ions, rate constants may be readily determined and, from these, insight into the nature of the potential energy surface developed. For example, on this basis, Brauman and co-workers[2] were able to deduce that simple gas phase S_N2 reactions proceed on a double-minimum potential energy surface. In addition, by virtue of the very long trapping time capability, reversible bimolecular processes can be followed for sufficiently long periods of time that thermal equilibrium between reaction partners is established and, from the experimentally measured equilibrium constants, accurate free energy changes for ion–molecule reactions can be obtained.[3] Thus, both qualitative and quantitative insights into the potential energy profiles for ion–molecule reactions are readily deduced from FTICR experiments.

A further area of investigation, in which ICR techniques have proven to be of somewhat lesser general utility, involves the dynamics and mechanisms of dissociation of the intermediates involved in a given ion–molecule reaction. In FTICR experiments, the pressures are usually sufficiently low that, in reactions such as eq 1, adduct ions, $(AB^+)^*$, will all undergo unimolecular

$$A^+ + B \rightleftharpoons (AB^+)^* \begin{cases} \rightarrow C^+ + N_1 \\ \rightarrow D^+ + N_2 \\ \rightarrow E^+ + N_3 \end{cases} \quad (1)$$

dissociation within the time scale of the experiment, either back to reactants, $A^+ + B$, or to products. However, even though ions $(AB^+)^*$ are too short lived to be observed in the mass spectrum, they can in fact live for significant periods of time. Studies of collisional stabilization and radiative relaxation of chemically activated adduct ions[4] have shown that for symmetric proton bound dimers of CH_3CN, $(CH_3)_2O$, $(CH_3)_2CO$, and $(C_2H_5)_2O$, where the internal energy of the initially formed adduct ions, $(B_2H^+)^*$, is 31 ± 1 kcal mol^{-1} in each case, the mean lifetimes vary between 5 μs and 2 ms. In general, as the adduct size increases, for a fixed internal energy, the lifetime for unimolecular dissociation to $BH^+ + B$ will increase, as predicted by simple RRKM considerations.[5] In these latter, simple cases, no net reaction occurs and the only products of dissociation of the chemically activated intermediate are the initial reactants. In the more complicated, and more usual, case represented by eq 1, several products of the intermediate dissociation, including initial reactants, are possible, but in ICR experiments, only the overall product distribution of the products different from reactants can be obtained. The fraction of intermediate complexes returning to reactants may be estimated, however, if accurate rate constant measurements are made from a comparison of the observed disappearance rate constant for reactant ion and the calculated collision rate. A further point of considerable importance for understanding the mechanism of reaction is the product distribution as a function of the internal energy of the intermediate complex. The adduct ions formed in eq 1 will have a thermal energy distribution superimposed on the internal energy arising from the chemical activation of bond formation between A^+ and B.[5] However, in conventional FTICR experiments, since the $(AB^+)^*$ lifetimes are all shorter than the observational time scale, only the average behavior is observed.

In contrast to this situation for FTICR experiments, the study of unimolecular dissociation of ions outside the ion source in the electric field free regions of sector mass spectrometers (MIKES) has proved to be a powerful means for probing the structure and reaction mechanisms of ions decomposing on the 1–10 μs time scale.[6,7] These so-called metastable ions normally represent a slice through the distribution of ion internal energies. In the

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(1) Freiser, B. S. In *Techniques for the Study of Ion-Molecule Reactions*; Farrar, J. M., Saunders, W. H., Eds.;Wiley-Interscience: New York, 1988.

(2) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(3) See, for example: Larson, J. W.; Szulejko, J. E.; McMahon,T. B. *J. Am. Chem. Soc.* **1988**, *110*, 7604.

(4) (a) Fisher, J. J.; McMahon,T. B. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 701. (b) Thölmann, D.; McCormick, A.; McMahon, T. B. *J. Phys. Chem.*, submitted for publication. (c) Fisher, J. J. Ph.D. Thesis, University of Waterloo, ON, Canada, 1990.

(5) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular Reactions*; Blackwell: Oxford, U.K., 1990.

(6) Williams, D. H. *Acc. Chem. Res.* **1977**, *10*, 280.

(7) Cooks, R. G. *Metastable Ions*; Elsevier: Amsterdam, 1973.

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most common experimental arrangement, a spectrometer with a reverse (BE) geometry, ions with energies greater than this slice will decompose either in the ion source or before undergoing mass selection in the magnetic sector. Ions of lower internal energy will survive transit through the field free region between the magnetic and electric sectors. Ions formed by different ionization methods such as electron impact or chemical ionization will usually exhibit dramatically different internal energy distributions. In the case of ions $(AB^+)^*$ formed by a simple association reaction in a chemical ionization source, the ions leaving the ion source will have a complex distribution of internal energies determined by the exothermicity of the association reaction, the source temperature, the pressure dependent extent of collisional thermalization, and the fraction of ions having already undergone decomposition. However, since the MIKES experiment probes only those ions with a narrowly defined range of lifetimes, the metastable dissociation spectra of a given ion can be remarkably similar regardless of the means of formation. The magnetic sector instrument also provides a very simple means of examination of the effect of internal energy on the metastable dissociation by variation of the accelerating potential. At lower values of accelerating voltage, the ion transit time through the spectrometer is greater and metastable ions of longer lifetime, and presumably lower internal energy content, will be sampled. Thus the behavior of the product distribution with change in internal energy and intermediate ion lifetime can be determined and usefully applied to mechanistic interpretation.

As noted above, chemically activated adduct ions formed under FTICR conditions can have a range of lifetimes from a few microseconds to several milliseconds. This range of lifetimes, while too short to permit acquisition of a FTICR signal transient, includes the range of times required to eject ions from the ICR cell. This fact has been previously exploited in a type of "double-resonance" experiment where the mass of an adduct ion AB^+ is ejected from the ICR cell while the intensity of the product ion is monitored in order to confirm that A^+ and B are the reactants giving rise to product ions C^+ in a complex mixture of ions and neutrals.[4c] It would therefore seem possible, under carefully controlled experimental conditions, to probe the unimolecular dissociation of these chemically activated adduct ions as a function of ion lifetime and, in so doing, to obtain a metastable dissociation spectrum in the FTICR spectrometer. If successful, such an endeavor would dramatically enhance the power and utility of the FTICR technique for the elucidation of the reaction mechanisms for decomposing ions. The development of such a FTICR analogue of the MIKES experiment and the demonstration of its applicability to a number of mechanistic problems are described herein.

Experimental Section

All experiments were performed with a Bruker-Spectrospin CMS-47X FTICR spectrometer. Briefly, ions generated in an external ion source by electron impact on appropriate neutral precursors are transferred to the ICR cell and the desired reactant ion is isolated in the ICR cell by a series of radio frequency ejection pulses to eliminate undesired ions. In order to ensure complete relaxation of any excess kinetic energy in the isolated ions, either as a result of the ion transfer or ejection pulses, a 20–100-fold excess of an inert gas (usually Ar or CH_4) relative to the neutral reactant of interest was used. Typical pressures were 2×10^{-8} mbar of reactant and 5×10^{-7} to 2×10^{-6} mbar of inert gas. The CMS-47X and FTICR principles, in general, have been described in detail elsewhere.[8,9]

All chemicals used were commercial samples and were used without further purification, with the exception of degassing *via* successive freeze–pump–thaw cycles.

(8) Allemann, M.; Kellerhals, Hp.; Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1983**, *46*, 139.
(9) Marshall, A. G.; Verdun, F. *Fourier Transforms in Optical, NMR, and Mass Spectrometry: A User's Handbook*; Elsevier: Amsterdam, 1990.

Table 1. RF Voltages and Associated Ejection Times[a]

V_{pp} (V)	t_{rf}^{ej} (μs)
34	610
124	170
141	147
160	130
181	115
206	101
233	89
265	78
300	70
340	60
386	54

[a] Calculated according to eq 1 with $B = 4.7$ T and $S_{E'} = 0.814$.

The method to be developed for observation of metastable dissociations involves the ejection of the metastable ion from the FTICR cell in a time shorter than the unimolecular dissociation lifetime of the metastable ion. In order to determine the times required for ion ejection, the rf voltages used for ejection were accurately measured with an oscilloscope as a function of the attenuator setting. According to the theory for charged particles in a finite cylindrical electric field, the time for ion ejection is given by eq 2),[10] where r is the cell radius, B the magnetic field strength,

$$t_{ej} = \frac{4r^2}{S_{E'}V_{pp}}B \qquad (2)$$

V_{pp} the peak-to-peak rf voltage applied across opposite cell plates, and $S_{E'}$ a constant determined by the cell geometry (length and radius).[10] For a series of typical values of V_{pp}, the calculated ejection times are shown in Table 1. The conditions used span a range of approximately 10 in V_{pp} and t_{ej} with the latter corresponding to a range of 50–600 μs. In order to test the validity of the calculated ejection times, a series of experiments was carried out in which the signal strength was examined as a function of the excitation pulse width. As previously demonstrated by Grosshans and Marshall,[11] the signal strength monotonically increases until the excitation pulse width corresponds to the minimum time necessary for ion ejection, after which the signal decreases rapidly. In each case, it was found that the decrease in signal strength began at a time within 5% of the calculated ejection time. Because of the coupling of axial and radial ion motions, this calculated time is the minimum ion ejection time. However, as discussed below, since the experiment is intended to sample the dissociations of all metastable ions with lifetimes greater than this calculated time, this does not represent an experimental limitation. The *average* time required for ion ejection is ~25% greater than the calculated time; however, as noted above, ion ejection begins at very close to the calculated time. In this respect, the behavior is essentially identical to that reported by Grosshans and Marshall.

Results and Discussion

Methodology. As previously noted, adducts formed by association of a gaseous ion with a stable neutral molecule may have lifetimes ranging up to several milliseconds while, as shown in Table 1, the time required to eject an ion from the FTICR cell may be as little as 50 μs. It is then logical to expect that, if a rf ejection pulse is continuously applied at a frequency corresponding to the mass of the metastable adduct ion during a reaction time in which a significant extent of conversion of reactant to product is expected, then the intensity of the product ion may be reduced compared to that in a spectrum where no rf ejection of the adduct was attempted. This reduction should occur only in the case that the time taken to eject the adduct ion is less than the lifetime of at least some fraction of the adduct ions formed. This procedure then yields qualitative information about which product ions are reactively coupled to which reactant ions in a complex mixture. However, with the aid of the signal processing software routinely available in FTICR spectrometers, a substantially more powerful experiment can be carried out to extract

(10) Kofel, P.; Allemann, M.; Kellerhals, Hp.; Wanczek K. P. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 1.
(11) Grosshans, P. B.; Marshall, A. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 347.

more quantitative details of the metastable dissociation. For example, consider the following procedure as a means to obtain the metastable dissociation spectrum of $(AB^+)^*$ ions of a given minimum lifetime:

(i) A FTICR spectrum is taken in which the reaction delay is sufficiently long to permit a readily observable extent of conversion to product ions (~10–20%).

(ii) A second spectrum is taken in which, during the same reaction delay, an rf electric field at the exact mass of AB^+ is continuously applied. If the complex $(AB^+)^*$ has a sufficiently long lifetime to be ejected, diminished intensities of both reactant and product ions may be observed.

(iii) The *difference* between these two spectra is then taken. This spectrum is then the spectrum due to the dissociation of all $(AB^+)^*$ ions with lifetimes greater than the time required to eject AB^+. Since the difference between two spectra is taken, it is imperative that the spectra be acquired in such a fashion that the signal strength of the second is compared in terms of absolute intensity to the first. If the difference between signal transients is taken, this is automatically accomplished. However, if the difference between transformed spectra is taken, the second must be scaled with respect to the first to obtain the real difference in absolute intensities. In principle, if product ions do not react further after dissociation of $(AB^+)^*$ with the neutral B present in the ICR cell, the spectrum obtained should be independent of the reaction time used. If very few AB^+ ions survive sufficiently long to be ejected, the two spectra should be nearly identical with the result that the difference spectrum will have a poor signal to noise ratio. If this is the case, a large number of scans may be necessary.

In the experiments described below, typically 256 transients were coadded for each spectrum before subtraction to generate the metastable dissociation spectrum. This large number of scans was necessary to generate acceptable S/N within a reasonable experimental time scale and was the result of the fact that the systems chosen for study had average unimolecular dissociation lifetimes significantly shorter than the 60–120 μs readily attainable with the rf amplifier available. Thus, only the dissociations of that small fraction of ions with lifetimes greater than this range are detected. Studies of metastable dissociation of adducts with longer lifetimes give significantly improved S/N with many fewer scans; however, none have been found which exhibit the competition between reaction channels of the type illustrated below.

Caveats. The metastable FTICR technique outlined above, while conceptually simple, has a number of pitfalls which must be avoided, in so far as possible, in order to obtain meaningful dissociation spectra of the chemically activated adduct ion. The first of these concerns the fact that during the unimolecular dissociation process the products of the dissociation may be formed at radii ranging from near the center of the cell to virtually at the cell walls themselves. However, in order that all ions be detected with equal sensitivity, ideally they must have the same radial (and axial) position in the cell. Further, since two spectra are to be subtracted to obtain the MICR spectrum and since the spectrum without continuous ejection has ions confined at the cell center, it is essential that the spectrum with continuous ejection attempts to duplicate this situation. For this reason, the presence of the 20–100-fold excess of inert gas (Ar or CH_4 in the present experiments) in the cell was found to be essential to the experiment. This excess of inert gas serves as a means of collisional relaxation for some fraction of the ions back toward the center of the cell after they are formed from dissociation of the translationally excited adduct ions. However, the larger the radius of such ions the smaller is the fraction of ions which are collisionally relaxed toward the cell center since a greater fraction will be scattered toward the cell walls where they will be lost. For this reason the experiment will discriminate against those fragment ions formed at larger radii and thus the upper limit to the lifetime probed will be less than that calculated from eq 2. In the absence of this inert gas, the resulting MICR spectra were found frequently to contain "negative" parent peaks corresponding to the fact that the intensity of the initial reactant ion was greater in the spectrum with continuous ejection than that without. This could be due either to the fact that the reaction of a translationally excited ion is slower than that of the thermal ion or to the fact that the intensity of the reactant ion is greater if it is further away from the cell center at the start of the detection event. Dunbar[12] has previously demonstrated the effect of cell position on induced image current. In either case, the presence of such negative peaks was completely suppressed if excess inert gas was employed. Typically, pressures 5–10 times greater than that required to eliminate the negative peaks were employed; however, no significant changes in the MICR spectra were observed with increasing the inert gas pressure beyond the minimum required for the elimination of the negative peak. In all cases, MICR spectra were found to have relative intensities which were reproducible within 5% when the same operating conditions were employed.

It is also important to note that when an adduct ion, AB^+, undergoes unimolecular dissociation at a large radius it will generate an ion A^+ of the same velocity but greater cyclotron frequency due to its lower mass. This fragment ion must then decay to an orbit of smaller radius in order to satisfy conservation of energy. The radius of the new orbit will depend upon the A^+:AB^+ mass ratio; however, the centers of the orbits will no longer be at the cell center. In the examples discussed below, this ratio is typically on the order of 0.5. Thus fragment ions formed initially at large radii will execute trajectories that take them both near the cell walls and toward the center of the cell. It is important to note, however, that when two competing fragmentation channels are monitored there may be mass discrimination against higher mass fragments formed at large radii for this reason. As discussed below, alternative techniques for relaxing ions to the cell center should greatly enhance the quantitative potential of the MICR experiment.

Nevertheless, although identical detection efficiencies for the population of unimolecular dissociation products formed cannot be expected, it should be sufficient to permit formulation of qualitative arguments on the relative unimolecular rate constant *vs* energy behavior which are invaluable in the deduction of mechanism in traditional MIKES experiments. It is also noteworthy that "null" metastable dissociation spectra are very readily obtainable when the adduct lifetime is too short to be ejected to any discernible extent. In these cases, evidently those ions formed in the unimolecular event of dissociation away from the cell center are detected with high efficiency after collisional relaxation.

Applications. In principle, this metastable FTICR technique (henceforth abbreviated MICR) should be generally applicable to any adduct ion unimolecular dissociation where the lifetime is greater than the minimum ejection time determined by the maximum output of the rf amplifier. If the nature of the potential energy surface for the reaction is such that products are of significantly lower energy than reactants and no significant intermediate barriers separate products from reactants, the reaction should be nearly unit collision efficient and the metastable dissociation spectrum will exhibit a single peak due to the product ion. Alternatively, if no exothermic reaction channel exists, all $(AB^+)^*$ adducts will dissociate back to reactants and the MICR spectrum will exhibit a single peak due to reactant ion, A^+. While these two situations may provide information regarding the lifetime of $(AB^+)^*$, they are of little interest for deduction of mechanisms of decomposing ions. In order to illustrate the feasibility and applicability of the MICR technique, examples have been chosen involving multiminima potential energy surfaces where at least two competitive dissociation pathways for $(AB^+)^*$ exist and which forcefully demonstrate the power of the technique.

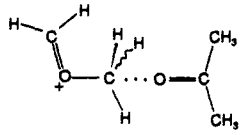
(12) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1984**, *56*, 1.

(1) Methyl Cation Transfer Reactions of $CH_3OCH_2^+$. Methyl cation transfer reactions have previously been shown frequently to proceed *via* double-minimum potential energy surfaces[13,14] and, as such, potentially provide a good test situation to demonstrate the versatility of the MICR technique. The methoxymethyl cation has been found to be a methyl cation donor to a number of species with base strengths greater than that of formaldehyde.[15,16] In particular, Nibbering and co-workers[15] have shown that methyl cation transfer occurs to both acetaldehyde and acetone (eqs 3 and 4). In the latter case, with the aid of both deuterium and

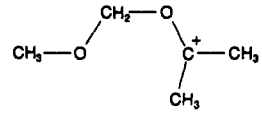
$$CH_3OCH_2^+ + CH_3CHO \rightarrow CH_3CHOCH_3^+ + CH_2O \quad (3)$$

$$CH_3OCH_2^+ + (CH_3)_2CO \rightarrow (CH_3)_2COCH_3^+ + CH_2O \quad (4)$$

^{18}O-labeled acetone, it was deduced that the mechanism involved in the methyl cation transfer is direct, that is, one in which a methyl cation is transferred from formaldehyde to acetone *via* a methyl cation bound intermediate (I) upon a collision of the appropriate orientation. A mechanism involving the presumably energetically more favorable covalent adduct (II), in which the



I



II

carbocation center of the methoxymethyl cation is bound to the basic carbonyl oxygen of the acetone, was ruled out on the basis of failure to observe loss of the ^{18}O label in the methyl cation transfer product. In the case of acetone, for the covalent structure II, a value of $\Delta H°_f$ may be estimated from the proton affinity of the appropriate (methoxymethyl)propenyl ether[17] and from this the methoxymethyl cation can be determined to be bound to acetone by ~38 kcal mol^{-1}. High-pressure mass spectrometric studies of methyl cation bound dimers[18] can also be used to estimate a binding energy of ~15 kcal mol^{-1} for I. On the basis of a simple RRKM analysis, it is then clear that if complexes of both type I and type II are formed on encounters of $CH_3OCH_2^+$ with acetone then type II complexes should have a significantly greater lifetime derived from their much greater binding energies. Therefore an analysis of the evolution of the dissociation product ratio for metastable adducts between acetone and methoxymethyl cation should be mechanistically informative.

The results of the MICR experiment are shown in Figure 1 for the reaction of CD_3OCD_2+ with acetone eq 5. When ions of

$$\underset{m/z\,50}{CD_3OCD_2^+} + (CH_3)_2CO \rightleftharpoons [(CH_3)_2CO, CD_3OCD_2^+]^* \quad (5)$$

$$\downarrow$$

$$\underset{m/z\,76}{(CH_3)_2COCD_3^+} + CH_2O$$

lifetime greater than 60 μs are sampled, roughly equivalent amounts of simple dissociation and methyl cation transfer products are observed (Figure 1a). However, when the ions sampled have

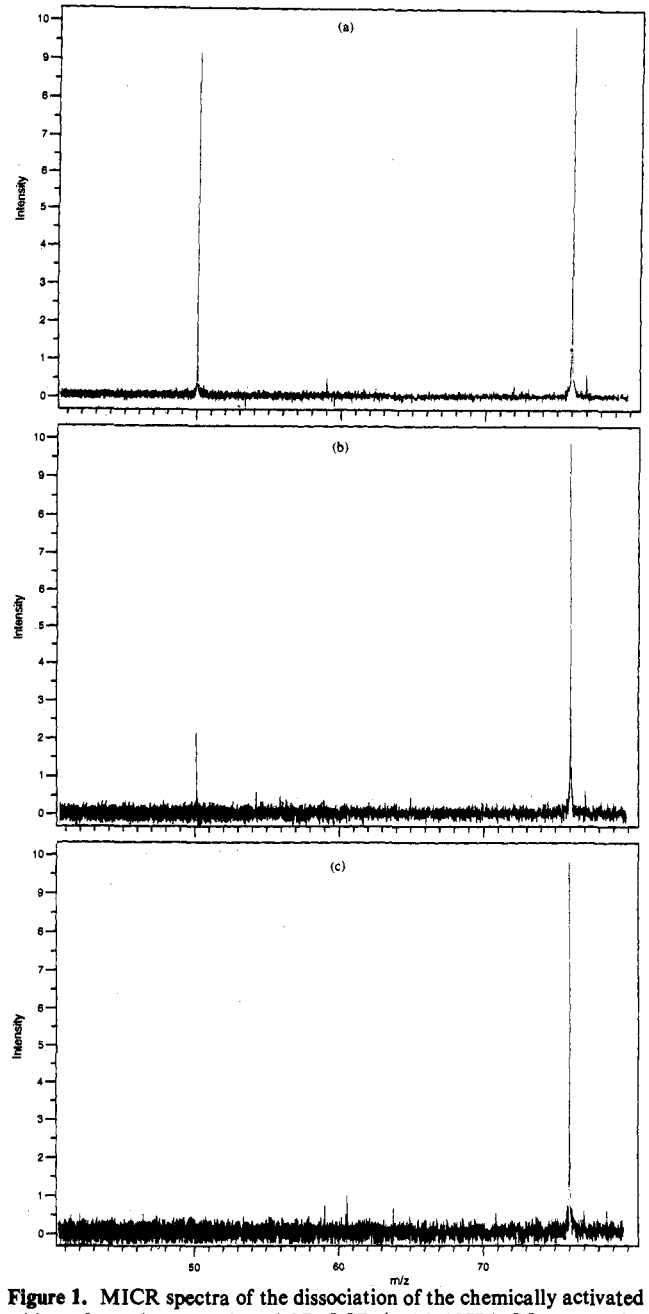


Figure 1. MICR spectra of the dissociation of the chemically activated adducts formed *via* reaction of $CD_3OCD_2^+$ with $(CH_3)_2CO$ at a partial pressure of acetone of 5×10^{-8} mbar during a reaction delay of 2 s for various minimum adduct lifetimes: (a) 60 μs, (b) 90 μs, (c) 115 μs. The pressure of Ar was 1.0×10^{-6} mbar in all cases. The peak at m/z 50 corresponds to $CD_3OCD_2^+$ and that at m/z 76 to $(CH_3)_2COCD_3^+$.

lifetimes greater than 115 μs, only the methyl cation transfer product is observed (Figure 1c). An intermediate lifetime situation is shown in Figure 1b (90 μs). If competitive formation of intermediates of types I and II were occurring, the much less stable I ions would dissociate more rapidly. In such a case then, as the lifetime of metastable adduct ions increases, the proportion of methyl cation transfer product to simple dissociation product would be expected to decrease. Since exactly the opposite behavior is observed in the data shown in Figure 1, it is highly unlikely that this mechanism is valid. Consider, then, the possibility that initially only the covalent adduct II is formed. The distribution of ion internal energies for the chemically activated adducts is a simple Maxwell–Boltzmann distribution superimposed on the binding energy of the adduct at the mean of the distribution. Those ions with the lowest internal energies will have the longest lifetimes with respect to dissociation to $CD_3OCD_2^+ + (CH_3)_2CO$

(13) Olmsted, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.
(14) McMahon, T. B.; Heinis, T.; Nicol, G.; Hovey, J. K.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 7591.
(15) van Doorn, R.; Nibbering, N. M. M. *Org Mass Spectrom.* **1978**, *13*, 527.
(16) Okada, S.; Abe, Y.; Taniguchi, S.; Yamabe, S. *J. Am. Chem. Soc.* **1987**, *109*, 295.
(17) Szulejko, J. E.; Fisher, J. J.; McMahon, T. B.; Wronka, J. W. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 147.
(18) Szulejko, J. E.; McMahon, T. B. *Org. Mass Spectrom.* **1993**, *28*, 1009.

and therefore will be the ions most likely to traverse an intermediate barrier to a structure such as I which can subsequently eliminate CH_2O. The observed behavior, shown in Figure 1, is then consistent with a distribution of adduct ion internal energies in which the higher energy end of the distribution more rapidly dissociates predominantly to $CD_3OCD_2^+$ while ions in the lower energy portion of the distribution survive sufficiently long to overcome an intermediate barrier to a second complex which yields the methyl cation transfer product. A determination of the rate constant for the methyl cation transfer reaction[19] revealed that roughly one collision in 10 is reactive. Therefore, the majority of adduct ions formed have lifetimes shorter than the minimum observable with the MICR technique. The product distribution resulting from the MICR experiments depends upon the internal energy content of the covalent adduct formed, the height of the intermediate barrier relative to the energy of initial reactants, the covalent well depth, and the number of atoms in the system. As the lifetime of the covalent intermediate complexes sampled increases, the probability of crossing the central barrier increases and the behavior illustrated by Figure 1 results. Extensive studies of the methyl cation transfer reactions of the methoxymethyl cation involving FTICR kinetics studies and conventional MIKES spectra for a large number of aldehydes and ketones support this conclusion.[19]

(2) Deuterium Exchange in Intermediate Complexes. A further example serves to illustrate the range of uses of the MICR technique. The extent of isotope scrambling in metastable dissociations is frequently an invaluable tool in the deduction of mechanisms for unimolecular rearrangements and dissociations.[20] For example, the bimolecular reaction of *tert*-butyl cation with isopropyl alcohol has previously been shown[21] to yield protonated acetone formally by a hydride abstraction reaction (eq 6).

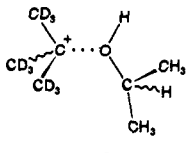
$$t\text{-}C_4H_9^+ + (CH_3)_2CHOH \rightarrow (CH_3)_2COH^+ + i\text{-}C_4H_{10} \quad (6)$$

Significantly, however, when the MIKES spectrum of the adduct formed via chemical ionization reaction of t-$C_4D_9^+$ with isopropyl alcohol is examined, deuterium incorporation in the protonated acetone and hydrogen incorporation in the *tert*-butyl cation are observed (eq 7). Moreover, the exchange involving the *tert*-butyl

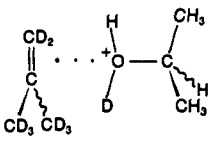
$$t\text{-}C_4D_9^+ + (CH_3)_2CHOH \rightleftharpoons [t\text{-}C_4D_9\text{-}O\text{-}CH(CH_3)_2]^* \quad (7)$$

$$t\text{-}C_4D_8H^+ + (CH_3)_2CHOD \qquad (CH_3)_2COD^+ + t\text{-}C_4D_8H_2$$

cation is observed to be statistical with a ratio of t-$C_4D_8H^+$:t-$C_4D_9^+ \approx 9$. In order to accomplish this, an exchange *via* the intermediates III and IV can be proposed.[22] In attempts to



III



IV

examine this type of exchange by a conventional FTICR experiment in the reaction between t-$C_4D_9^+$ and i-$(CH_3)_2CHOH$, the deduction of the extent of exchange is complicated by the presence of unreacted t-C_4D_9+ and continued exchange of t-$C_4D_8H^+$ when a subsequent collision with $(CH_3)_2CHOH$ occurs. These problems can be largely overcome in the MICR experiment however. Figure 2a shows the metastable dissociation spectrum of [t-$C_4D_9^+$, $(CH_3)_2CHOH$] adducts with lifetimes greater than 60 μs formed in a short reaction delay during which roughly 15% of the initial t-$C_4D_9^+$ has reacted. This 60 μs spectrum shows a t-$C_4D_8H^+$:t-$C_4D_9^+$ ratio of less than 1, indicating that complete statistical scrambling has not yet occurred. However, as the adduct lifetime probed is increased, as in Figure 2b, to 90 μs, a pronounced increase in the proportion of exchanged products is observed. Finally, at adduct lifetimes greater than 115 μs (Figure 2c), despite the fact that the signal to noise is reduced, a near statistical ratio of 9:1 for t-$C_4D_8H^+$:t-$C_4D_9^+$ is observed. The other peaks present, $C_4D_7H_2^+$ and $C_4D_6H_3^+$, are the result of subsequent exchanges of $C_4D_8H^+$ and are of necessity also present in the MICR spectrum since they are the secondary products of the ions formed in dissociation of the initially formed adduct.

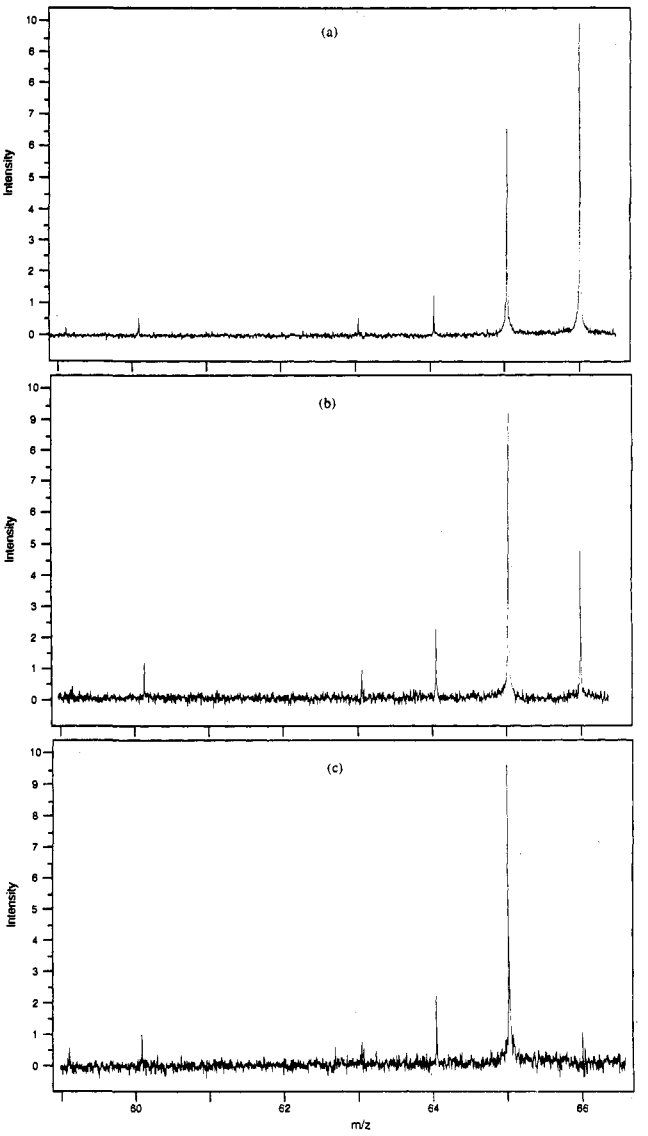


Figure 2. MICR spectra of the dissociation of the chemically activated adducts formed *via* reaction of t-$C_4D_9^+$ with $(CH_3)_2CHOH$ at a partial pressure of isopropyl alcohol of 3×10^{-8} mbar during a 2 s reaction delay for various minimum adduct lifetimes: (a) 60 μs, (b) 90 μs, (c) 115 μs. The pressure of Ar was 1.0×10^{-6} mbar in all cases. The peak at m/z 66 corresponds to $(CD_3)_3C^+$ and that at m/z 65 to $(CD_3)_2(CD_2H)C^+$. Peaks at lower masses are due to subsequent exchange *via* bimolecular reaction of m/z 65.

(19) Audier, H. E.; McMahon, T. B. Unpublished results.
(20) See, for example: Audier, H. E.; Monteiro, C.; Berthomieu, D.; Tortajada, J. *Int. J. Mass Spectrom. Ion Processes* **1991**, *104*, 145.
(21) Monteiro, C.; Mourgues, P.; Audier, H. E.; Berthomieu, D.; Tortajada, J. *New J. Chem.* **1990**, *14*, 625.
(22) See, for example: (a) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665. (b) Reference 18. (c) Audier, H. E.; Berthomieu, D.; LeBlanc, D.; McMahon, T. B.; Morton, T. H. *Int J. Mass Spectrom. Ion Processes* **1992**, *117*, 327.

Importantly, however, the ratio of *tert*-butyl cation products, $t\text{-}C_4D_6H_3^+$:$t\text{-}C_4D_7H_2^+$:$t\text{-}C_4D_8H^+$, does not change with the metastable lifetime probed despite the fact that the $t\text{-}C_4D_8H^+$:$t\text{-}C_4D_9^+$ ratio has changed by a factor of 10. This is to be expected for product ions which are the result of subsequent reaction of the ions derived from the unimolecular dissociation of the adduct probed. The overall reduction in signal intensity with increased adduct lifetime shows that most adducts formed dissociate to yield unexchanged $t\text{-}C_4D_9^+$ and it is the lowest energy, longest lived adducts which sample structures such as III and IV to effect the isotope exchange. Evidently, in the conventional MIKES spectrum of adducts of $t\text{-}C_4D_9^+$ and $(CH_3)_2CHOH$, the population sampled has been collisionally deactivated to a sufficient extent to greatly enhance the probability of isotope exchange.

Potential for the Determination of Unimolecular Dissociation Rate Constants of Chemically Activated Adduct Ions. Ideally, the technique outlined above could be refined to permit the examination of the disappearance of the reactant ion intensity as a function of the ejection time and, in this way, to obtain the unimolecular dissociation rate constant of the chemically activated intermediate. For the systems described above, the majority (>90%) of adducts have unimolecular dissociation lifetimes less than the minimum ~50 μs attainable here and therefore only the "tail" of the exponential decay is observable. Systems with longer intermediate lifetimes do exhibit such exponential decay. Because of the potential uncertainties in the ejection time described under Caveats above, we are in the process of accurately determining the unimolecular dissociation lifetimes of a number of trimethylsilyl cation adducts (eq 8) by techniques previously employed

$$(CH_3)_3Si^+ + B \rightleftharpoons [(CH_3)_3SiB^+]^* \rightarrow [(CH_3)_3SiB^+] \quad (8)$$

to determine both unimolecular dissociation and radiative lifetimes of chemically activated intermediates.[4] Following this, these lifetimes will be compared with those derived from the MICR technique to "calibrate" the latter method.

Also for the reasons outlined in Caveats above, the MICR technique will suffer from the disadvantage that neither quantitative unimolecular product distributions nor quantitative lifetimes will be obtainable with absolute confidence unless the efficient detection of ions formed at large radii can be achieved. As described recently by Marshall and co-workers,[23] the quadrupolar excitation technique can potentially provide the solution to this shortcoming. In this technique, an azimuthal quadrupolar excitation at the combination frequency of the cyclotron and magnetron ion motions in conjunction with a pressure of inert gas can cause collisions to drive the ions back to the cell center. Such excitation converts magnetron motion to cyclotron motion which is then collisionally damped. Since the usual increase in magnetron radius which normally accompanies collisions is thus avoided, the ions are in effect axialized to the cell center. If this procedure is used to axialize the unimolecular dissociation products in a MICR experiment, the desired result of equal detection efficiencies of unreacted ions and unimolecular dissociation product ions could be achieved and the MICR experiment would become a viable quantiative procedure. Means to implement quadrupolar excitation in this way are currently being explored.

Conclusion

The new MICR experiment described above and the examples given show that the MICR technique adds a significant new dimension to the study of ion–molecule reactions using FTICR. The possibility of carrying out quantitative determination of unimolecular dissociation lifetimes of chemically activated adduct ions is currently under investigation, as is the possibility of obtaining a difference between two MICR spectra for different adduct lifetimes to yield the metastable dissociation spectrum of ions of a very narrow range of lifetimes. However, the initial, more qualitative studies described here demonstrate that it is possible to examine the evolution of unimolecular dissociation products with the lifetime of the adduct under study and to learn a great deal about the nature of the potential energy surface on which the dissociation takes place.

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(23) Schweikard, L.; Guan, S.; Marshall, A. G. *Int. J. Mass Spectrom. Ion Processes* **1992**, *120*, 71.