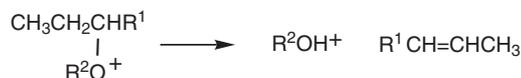


A0005 **Theoretical Models for Ion–Neutral Complexes in Unimolecular Ion Decompositions**

S0005 **1. Competing Unimolecular Pathways**

P0005 Molecular eliminations play a major role in mass spectrometry. New bonds are formed in the course of a molecular elimination (see, for example, Chapter 4 (this volume): *Unimolecular Dissociation of Organic Ions: Molecular Hydrogen Elimination*), as opposed to simple bond fissions, in which bonds are broken but not made (see Chapter 4 (this volume): *Unimolecular Dissociation of Organic Ions: Simple Bond Cleavage*). One pathway by which molecular elimination can take place involves a concerted process, in which the new bonds form at the same time as the old ones are broken. Alternatively, in nonconcerted pathways, bond making and bond breaking do not occur simultaneously but occur in a stepwise fashion. A new bond can form before an old one breaks, or an old bond can break before a new bond forms. When bond breaking precedes bond making, acyclic ions pass through ion–neutral complexes (sometimes called ion–molecule or, less correctly, ion–dipole complexes).

P0010 Alkene expulsion from positive ions of simple oxygenated compounds (Scheme 1) offers a set of examples. When  $R^1$  is an alkyl group and  $R^2$  is an aryl group (either the radical ions when  $R^2 = \text{phenyl}$  or the even-electron ions when  $R^2 = \textit{meta}\text{-Me}_2\text{NH-phenyl}$ , where the charge is on nitrogen rather than oxygen), concerted *syn*-eliminations of neutral alkene occur via four-center transition states (see Chapter 4 (this volume): *Unimolecular Dissociations of Organic Ions: Mass Spectrometric Discrimination of Acyclic Stereoisomers Via Competing Unimolecular Decompositions*). By contrast, McLafferty rearrangements of radical cations (for instance, the loss of propene from ionized *n*-propyl isovalerate,  $R^1 = \text{H}$ ,  $R^2 = (\text{CH}_3)_2\text{CHCH}_2\text{CO}$ ) are believed to be nonconcerted (see Chapter 4 (this volume): *Unimolecular Dissociations of Organic Ions: The McLafferty and Related Rearrangements*), taking place via distonic intermediates (see *Structures and Properties of Gas-Phase Organic Ions: Ion–Molecule Reactions of Distonic Radical Cations* (this chapter, this volume); and Volume 1, Chapter 9: *Organic Ion Chemistry (Positive): Distonic Radical Cations*). Finally, when  $R^1 = \text{H}$ , and  $R^2 = \text{aryl}$ , both the radical cations



F0020 **Scheme 1**

(<Bib1 Bib2>1,2) and the corresponding even-electron  $\text{MH}^+$  ions (<Bib3>3) break the  $\text{sp}^3 \text{C–O}$  bond in the first step of the decomposition, forming ion–neutral complexes en route to propene expulsion.

These three types of mechanisms for alkene loss from a radical cation ( $\text{RX}^+$ ) are illustrated schematically in Fig. 1 by the three-dimensional reaction coordinate diagram (sometimes called a More O’Ferrall-Jencks plot) (<Bib4>4). The  $z$ -axis represents energy and the  $x$ - and  $y$ -axes stand for bond-breaking and bond-making coordinates, respectively. The curves represent limiting cases for three sequences of steps. The left hand corner corresponds to one intermediate and the right hand corner to the other. The stepwise mechanisms turn the corners at their respective intermediates. The solid curve to the left shows bond making before bond breaking. The solid curve to the right shows bond breaking before bond making. The path that is preferred can be quite sensitive to subtle variations in structure, and two different mechanisms may operate in competition with one another to yield the same products. On the one hand, ionized *sec*-alkyl phenyl ethers ( $\text{X} = \text{OPh}$ , corresponding to  $\text{R}^1 = \text{alkyl}$  and  $\text{R}^2 = \text{phenyl}$  in Scheme 1) lose alkene predominantly via concerted, four-center elimination (represented by the dashed curve) (<Bib5>5). On the other hand, ionized primary alkyl phenyl ethers ( $\text{R}^1 = \text{H}$ ) expel alkene via ion–neutral complexes, the intermediates corresponding to the right hand corner of Fig. 1.

As drawn to the extreme right in Fig. 1, an ion–neutral complex is ordinarily represented within a pair of brackets by showing the charged and the neutral partners separated by blank spaces. Since electric charge does not necessarily localize on a single partner, the order in which they are written does not usually matter. In fact, it is not always obvious which partner bears the bulk of the charge.

Within a complex, one partner can flip over relative to the other. This reorientation—rotation about an axis perpendicular to the interfragment axis—constitutes a defining feature of an ion–neutral complex (<Bib6>6). Reorientation reflects the loss of directed valence. Computational methods can explore whether a putative complex satisfies the reorientation criterion: that is to say, whether one partner encounters a low barrier to flipping over.

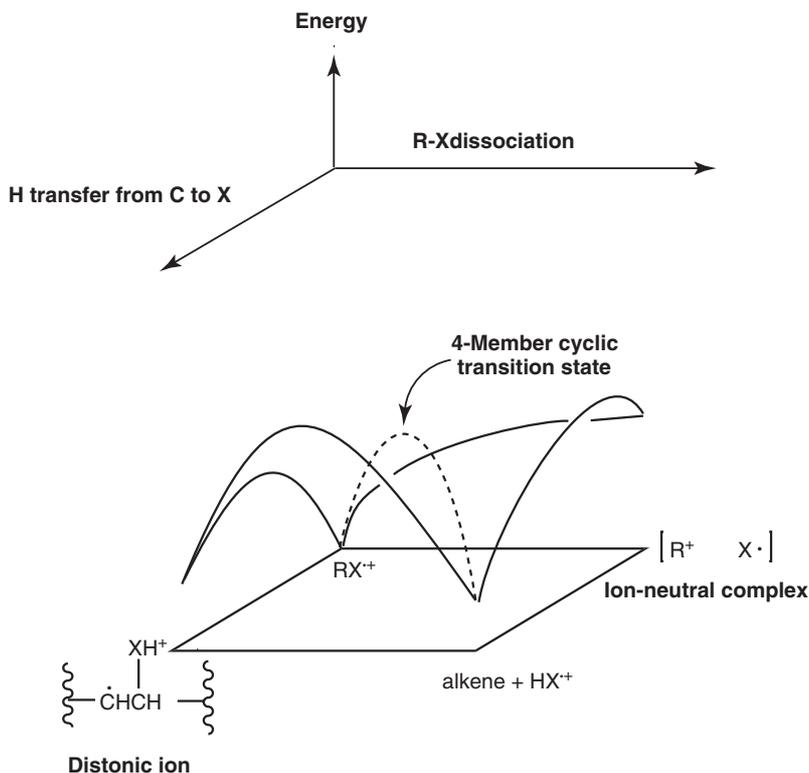
Figure 2 illustrates a thought experiment. The solid curve stands for the bond-breaking segment from Fig. 1, carried to its limit. An ion–neutral complex corresponds to where the dashed curve departs from the solid curve (i.e., where the reaction coordinate in Fig. 1 turns the corner). Reorientation can be viewed as the process by which a molecular fragment epimerizes, if the breaking bond is attached to a stereogenic center. Consider alkane loss, which comprises a class of ion decompositions in which ion–neutral complexes are thought to intervene (<Bib7>7). In general, alkane loss has a lower

P0015

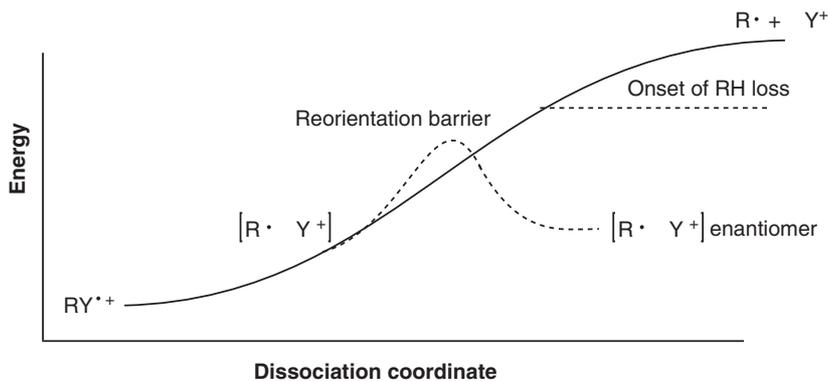
P0020

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P0030



F0005 **Figure 1**  
A schematic three-dimensional potential energy diagram showing three alternative pathways for alkene expulsion from a radical cation  $RX^{\bullet+}$  to give  $HX^{\bullet+}$  as a fragment ion. These provide a framework over which a potential energy surface can be stretched, like a sheet of rubber.



F0010 **Figure 2**  
A thought experiment illustrating the reorientation criterion.

threshold energy than does the bond fission that expels alkyl radical  $R^{\bullet}$ , and the dashed straight line to the right stands for the energy of its onset. The

reaction coordinate connecting the complex to this outcome (i.e., after turning the corner in Fig. 1) is not shown.

P0035 Suppose a radical cation,  $\text{RY}^+$ , contains a single asymmetric carbon, to which the R–Y bond is connected. If the R–Y bond breaks and the two fragments remain together (bound by electrostatic attraction), one side of the  $\text{R}^\bullet$  radical faces  $\text{Y}^+$  and one side of  $\text{Y}^+$  faces R. Satisfying the reorientation criterion means that the barrier to interconverting the two mirror images of  $[\text{R}^\bullet\text{Y}^+]$  (epimerization) is lower than the threshold for expelling the neutral alkane RH. If this criterion is not met, then the intermediate cannot be correctly called an ion–neutral complex. The foregoing description is intentionally vague, in the sense that the asymmetric carbon might be in R or in Y. It could happen that a chiral R might not epimerize, but that a chiral Y will (or vice versa). All that the criterion requires is for one partner to reorient.

P0040 Needless to say, such an experiment has not been performed in a mass spectrometer (although the competition between epimerization and dissociation has been examined by other means for ion–molecule reactions near atmospheric pressure ( $\langle \text{Bib8} \rangle 8$ )), but it can be explored computationally. Ion–neutral complexes pose problems for the experimentalist because, for the most part, they represent transient intermediates. Complexes challenge current methods of computational chemistry, too, because they do not necessarily correspond to stationary points on a potential energy surface. For the purposes of the discussion below, ion–neutral complexes will be classified into four categories, of which three will be considered in detail. Type 1 complexes represent local minima on the potential energy surface that are isomeric with covalently bonded structures having similar topology. The example that will be discussed is  $[(\text{CH}_3)_2\text{C}=\text{NH}_2^+\text{CH}_3^\ddagger]$  from the unimolecular dissociation of ionized *tert*-butylamine.

P0045 Type 2 complexes represent ions held together by weak bonding, whose vibrationally excited states can exhibit reorientation. This category embraces complexes that have been explored theoretically, such as  $[\text{NH}_4^+\text{FH}]$  ( $\langle \text{Bib9} \rangle 9$ ),  $[\text{P}_4\text{Li}^+]$  ( $\langle \text{Bib10} \rangle 10$ ), and  $[\text{NH}_4^+\text{FCH}_3]$  ( $\langle \text{Bib11} \rangle 11$ ). The low-barrier reorientations correspond to  $360^\circ$  rotations of the tetrahedral partner and have been called ‘planetary motions’ ( $\langle \text{Bib10} \rangle 10$ ). The Type 2 complex discussed below will be the radical cation of  $(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{OH}$ , which has never been observed directly by experiment, but which expels alkane at the threshold of ionization. Here the major question arises regarding the order of a highly elongated bond within a stable geometry and the reorientation barrier relative to the appearance energy seen in the laboratory.

P0050 Type 3 complexes present the most serious obstacles to computational study, because they do not correspond to stationary states on their potential energy surfaces (see Chapter 1 (this volume): *General Concepts: Potential Energy Surfaces*). Entropic bottlenecks separate Type 3 complexes from their

covalent isomers, even though the potential energy surface exhibits no potential energy barrier between them. The complexes depicted schematically in Fig. 1, where X = phenoxy (PhO), fall into this category. Experiments implicate Type 3 complexes in the unimolecular decompositions of the even-electron, protonated parent ions from alkyl phenyl ethers, as well. For the purposes of computation, a highly approximate model has been put forth to describe Type 3 complexes, for example, the  $[\text{O}=\text{C}=\text{NH}_2^+\text{CH}_3^\ddagger]$  intermediate that intervenes in methane loss from ionized acetamide. However, it is clear that deeper theoretical insight is needed.

Type 4 complexes correspond to local minima on the effective potential energy curve for separating an ion and a neutral, which result from a centrifugal barrier that does not exist in the absence of rotational angular momentum. For most unimolecular ion decompositions, the angular momentum distribution of decomposing ions is virtually the same as that of the parent neutrals, which contributes a negligible centrifugal barrier. For this reason, this article will treat only complexes of Types 1–3 and will omit complexes formed by bimolecular reactions ( $\langle \text{Bib8} \rangle 8$ ).

A careful distinction must be made between energy barriers calculated for predicting vibrational energy levels and those used for kinetic arguments. A normal mode must leave a molecule’s center of mass and its angular momentum unchanged. A potential energy surface used to describe large-amplitude motions must not violate these constraints. This has been discussed in some detail for small systems ( $\langle \text{Bib9} \rangle 9$ ). For isomerizations of large polyatomic molecules, it can be assumed that there are so many internal degrees of freedom that this constraint need not be imposed along a reaction coordinate that considers only a few of them. Thus, the top of a calculated kinetic barrier usually corresponds to the highest electronic energy along the minimum energy pathway, and a saddle point optimization is usually deemed appropriate.

This article will not attempt to survey the literature describing potential energy surfaces on which ion–neutral complexes have been posited. Instead, a small set of selected cases will outline issues that contemporary computational methods can address, as well as some questions that remain to be answered. The examples chosen are all derived from radical cations, but there is ample evidence (both experimental and theoretical) that ion–neutral complexes intervene in the unimolecular decompositions of anions and of even-electron ions, as well.

S0010 **2. Topological Analysis**

S0015 **2.1 Atoms in Molecules**

P0070 The topology of a molecule reflects the number of rings and cages that it possesses. A monocyclic molecule (such as styrene) has a different topology from an acyclic isomer (such as dipropargylethylene ( $\text{HC}\equiv\text{CCH}_2$ )<sub>2</sub> $\text{C}=\text{CH}_2$ ) or a caged isomer (such as cubane). Two monocyclic isomers (styrene and cyclooctatetraene, for instance) have the same topology, although they have different connectivities. The electron density distribution of a molecule defines its topology, which should not be sensitive to the method by which its electronic wavefunction is approximated.

P0075 At present, the vast majority of theoretical investigations of gaseous ions explore structure and energetics by means of computation. Algorithms and methods improve constantly, and it is evident that the widely used techniques, which are currently popular at present, will soon become outmoded. Topological analysis of electron densities provides a picture that does not depend so critically upon the calculational method. This approach can be applied to experimental electron densities (as measured by X-ray crystallography) (<Bib12>12), as well as to those computed by *ab initio* or density functional theory (DFT). Among the general topological methods, atoms in molecules (AIM) and electron localization function (ELF) techniques have become available. Despite debate between the practitioners of AIM and ELF regarding relative merits and defects (<Bib13 Bib14 Bib15>13–15), both seek the same objective: to partition physical quantities among subsystems within a molecule.

P0080 This article makes use of the AIM approach (<Bib16>16). Various AIM programs are available, including the AIMPAC code, which can be downloaded from R.F.W. Bader's website, <http://www.chemistry.mcmaster.ca/aimpac/>; the AIM module within various versions of GAUSSIAN; and the AIM2000 code (SBK Software, <http://www.aim2000.de/>), which has a convenient graphical interface. The cases described below will outline uses of AIM to analyze wavefunctions based upon single Slater determinants. It may be reasonably argued that energies and geometries are more appropriately treated using wavefunctions containing multiple Slater determinants. For the purposes of topological analyses, however, the level of calculation used here provides a suitable basis for a qualitative discussion.

P0085 In brief, AIM divides the electron density of a molecule into separate, nonoverlapping regions belonging to each atom (sometimes called atomic basins). A subset of these regions is connected by bond paths. The point where a bond path crosses the boundary between two atomic basins has special importance and is called a bond critical point. The

electron density at the bond critical point will be symbolized below as  $\rho$ . The set of bond paths does not always stand in a one-to-one relationship with the bonds a chemist might draw based on valence theory: sometimes more bond paths emerge than there are conventional bonds. Two atoms that happen to be close to one another may exhibit a bond path between them. This implies that they are interacting, but the interaction might be that they repel one another sterically. It is not always easy to distinguish a weakly bonding interaction (such as a hydrogen bond) from a nonbonded repulsion. But strong single bonds show an unmistakable characteristic; namely, the Laplacian of the electron density at the bond critical point,  $\nabla^2\rho$ , has a negative value.

AIM assigns electric charges to each atom by integrating the electron density within an atomic basin and subtracting that value from the nuclear charge. AIM charges tend to differ substantially from charges assigned by other methods, and they are often at variance with the formal charges assigned using Lewis dot structures. Although the interpretation of AIM charges themselves is controversial, chemical insight can be gained from seeing how they change as a function of structure. P0090

2.2 Bond Order S0020

The notion of a chemical bond lies at the heart of chemists' understanding of molecular structure. This concept holds such sway that it pervades ideas regarding how reactions take place. Hence, it is habitual to talk about bonding within transient intermediates and transition states, as well as for stable entities whose structure can be examined at leisure. P0095

Using AIM, bond order can be assigned based on the value of  $\rho$  at a bond critical point. Bond lengths in calculated transition states change with  $\rho$  in a systematic fashion as substituents are varied (<Bib17>17). An exponential relationship between  $\rho$  and bond order  $n$  has been put forth,  $n = e^{C(\rho-\rho_1)}$ , where  $\rho_1$  symbolizes the electron density at the bond critical point of a single bond between the two atoms in question (<Bib12 Bib16>12,16), and parameter  $C$  is determined from the value of  $\rho$  calculated for a multiple bond between these same two atoms. This expression does not give a bond order of zero when  $\rho=0$ , so a modified expression, eqn (1), has been proposed, which uses the same two data points ( $\rho$  for a multiple bond and  $\rho_1$ ) to extract parameters  $A$  and  $B$ . Equation (1) does give  $n=0$  for  $\rho=0$  and can be used to assign fractional bond orders  $n<1$  for weak bonds (<Bib18>18): P0100

$$n = e^{A(\rho-B)} - e^{-AB} \quad (1)$$

P0105 As noted above, two isomers very often have the same topology but different connectivities. For acyclic systems, two structures may differ by the connectivity of one bond (e.g.,  $\text{CH}_3\text{CN}$  versus  $\text{CH}_3\text{NC}$ ) and are sometimes called linkage isomers. Removing an electron from a stable molecule frequently gives a radical cation with the same topology and connectivity as the neutral precursor. AIM portrays some Type 1 ion–neutral complexes as being linkage isomers of such radical cations.

### S0025 3. Categories of Ion–Neutral Complexes

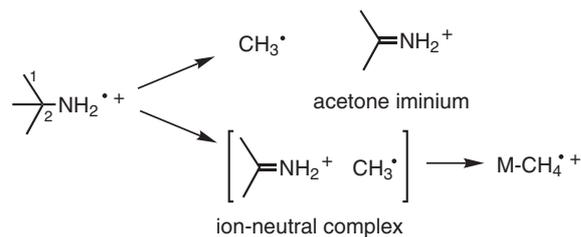
#### S0030 3.1 Type 1 Complexes

P0110 The first category embraces ion–neutral complexes that have well-defined positions on their potential energy surfaces. They correspond to local minima, where there is an energy barrier for reforming covalent bonds, as Fig. 3 portrays. In order for the well to correspond to an ion–neutral complex, the reorientation barrier must be less than the magnitude of the well depth.

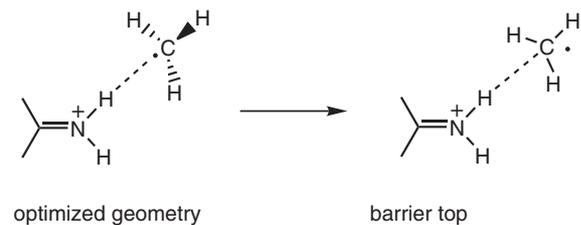
P0115 Such a case pertains to methyl cleavage from ionized *tert*-butylamine (the example shown schematically in Fig. 3), for which experiments demonstrate a substantial reverse activation barrier ( $\ll \text{Bib19} \gg 19$ ). The mass spectrum of *tert*-butylamine shows a small amount of methane expulsion in addition to a prominent fragmentation via  $\alpha$ -cleavage of methyl radical. Scheme 2 summarizes these two ion decompositions, although experiments indicate that methane loss is not as straightforward as represented: a  $^{13}\text{C}$  label in position 2 is completely retained in the  $\alpha$ -cleavage ion (consistent with the acetone iminium structure), but the  $^{13}\text{C}$  label is reportedly lost in about one-third of the  $\text{M}-\text{CH}_4$  ions ( $\ll \text{Bib20} \gg 20$ ). Nevertheless, the ion–neutral complex containing acetone iminium and methyl radical, as drawn in Scheme 2, can be explored computationally. The theoretical

picture gives an idea as to the origin of the reorientation barrier.

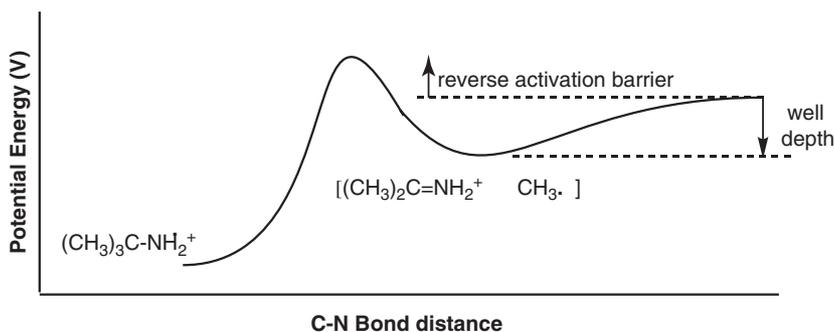
Geometry optimizations of the P0120  $[(\text{CH}_3)_2\text{C}=\text{NH}_2^+ \text{CH}_3^\cdot]$  complex at various levels give the structure drawn to the left in Scheme 3. Topological analysis shows a bond path between the carbon of the methyl radical and one of the NH hydrogens, represented by the dashed line. The methyl radical is slightly pyramidalized, and the plane of its three hydrogens is perpendicular to the plane of the  $\text{NH}_2$ . The connectivity of the complex differs from that of ionized *tert*-butylamine, in that one methyl-C bond path has been replaced by the methyl-H bond path. The ion–neutral complex has the same topology as the molecular ion (i.e., no



F0025



F0030



F0015 **Figure 3** Schematic potential energy curve illustrating the position of a Type 1 ion-neutral complex on the dissociation curve for ionized *tert*-butylamine.

rings), but, from the standpoint of the change in connectivity, the complex represents a linkage isomer of ionized *tert*-butylamine.

P0125 The interaction between the methyl radical and the NH draws electron density away from the hydrogen with which the carbon is associated. In other words, that NH bears a slightly greater positive charge than does the NH that is further away from the methyl radical. At the same time the methyl radical carries a small net positive charge. When the methyl radical is rotated so that it lies in the plane of the NH<sub>2</sub> (the top of the barrier for reorientation of the methyl), the topology does not change: the bond path remains between the methyl carbon and the NH, and the associated hydrogen still carries a greater positive charge. However, the methyl radical becomes more electron withdrawing. At MP2/6-31G\*\*//MP2/6-31G\*\* the net charge on the methyl radical shifts from positive to slightly negative. In other words, rotating the *p*-orbital of the radical out of the plane, so that it is parallel to the  $\pi$ -orbitals of the C=N bond, prevents the radical from donating electron density to the cationic partner. This displacement of charge accounts for the reorientation barrier.

P0130 It must be noted that it is not necessary for a Type 1 complex to have a reverse activation barrier  $>0$ . That is, the magnitude of the well depth can be greater than the potential energy barrier for returning to a covalent isomer. A satisfactory geometry optimization can be performed on any local minimum, regardless of whether the well depth (the thermodynamic barrier to dissociation to the right) or the barrier on the left (the potential energy maximum for isomerization to a covalent structure) has a greater magnitude. Furthermore, the latter barrier can represent a reaction more complicated than a bond fission (e.g., a molecular elimination). However, the existence of such potential energy maxima does not guarantee that a decomposing ion will actually spend any time in the corresponding potential energy well. For instance, a substantial barrier separates the (CH<sub>3</sub>)<sub>2</sub>CF<sup>+</sup> ion from its noncovalent [CH<sub>3</sub>C=CH<sub>2</sub><sup>+</sup>FH] isomer (<Bib21>21), yet the large translational kinetic energy release in the metastable ion decomposition (see Volume 1, Chapter 3: Instrumentation: Metastable Ions) that expels HF to produce

CH<sub>3</sub>C=CH<sub>2</sub><sup>+</sup> (of the order of 1 eV (<Bib17>17)) indicates that the outgoing products fly apart as though the potential energy minimum did not exist.

### 3.2 Type 2 Complexes

S0035

P0135 Ionization of some molecules leads to pronounced weakening of a bond. As a result, calculations predict dramatic elongation, such as in the case of the C<sub>2</sub>–C<sub>3</sub> bond of thexyl alcohol, shown in Scheme 4. The optimized structure of the radical cation looks like protonated acetone associated with an isopropyl radical, as drawn in the center of Scheme 4. The calculated bond distance has a value  $r > 2\text{Å}$ , and the thermodynamic threshold for complete dissociation is predicted to be of the order of 0.5 eV. The calculated bond order is approximately  $n = 0.1$ .

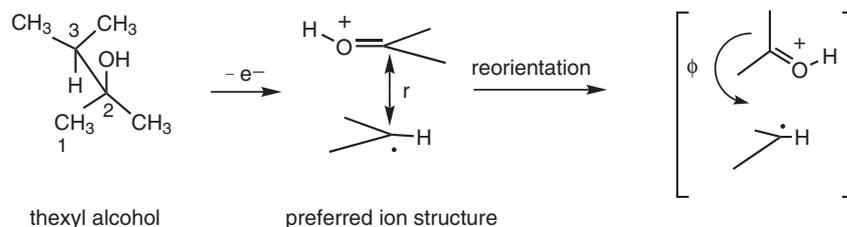
P0140 Not surprisingly, the radical cation of thexyl alcohol has never been observed. At the photoionization onset (see Chapter 1 (this volume): *General Concepts: Appearance Energies*) only the fragment from propane loss can be detected. Flipping over the protonated acetone has a calculated barrier that is lower than the experimentally observed photoionization threshold (<Bib18>18).

P0145 This example typifies a Type 2 complex. The topology and connectivity of the molecular ion are the same as that of the parent neutral. The potential energy surface shows no evidence of a stable linkage isomer. Rotating one partner to the top of the reorientation barrier changes the connectivity (unlike the example in Scheme 3) but nevertheless does not cost a great deal of energy. In the case of ionized thexyl alcohol, turning the protonated acetone approximately 90°, so that the C<sub>1</sub>–C<sub>2</sub>–C<sub>3</sub> bond angle has a value of  $\Phi = 180^\circ$ , replaces the central carbon–carbon bond path with a bond path between C<sub>2</sub> and one of the hydrogens on C<sub>1</sub>.

### 3.3 Type 3 Complexes

S0040

P0150 Type 1 and Type 2 complexes are ions in which a stationary state can be found by geometry optimization, in which directed valence is greatly reduced. A Type 1 complex has a covalent isomer, separated


 F0035 **Scheme 4**

from it by an energy barrier. A Type 2 complex does not. Type 3 complexes occur in ions for which geometry optimizations exhibit only covalent structures. Experiment provides evidence for intermediates in which reorientation takes place, but no such stationary states are to be found on the respective potential energy surfaces.

P0155 Failure to find potential energy minima does not mean that they do not exist. Nevertheless, some potential energy surfaces have been closely examined without revealing one. The  $[(\text{CH}_3)_2\text{CH}^+\text{PhO}^*]$  complex, whose existence is strongly supported by experiment ( $\langle \text{Bib1} \rangle 1$ ), is calculated to collapse to a covalent structure without any detectable energy barrier ( $\langle \text{Bib22} \rangle 22$ ). Similarly, the potential energy surface of ionized acetamide has been studied in detail ( $\langle \text{Bib23} \rangle 23$ ). A number of Type 1 complexes have been reported for ionized acetamide, but none that would account for the expulsion of methane (a decomposition that is observed experimentally ( $\langle \text{Bib24} \rangle 24$ )). These results support the conclusion that a potential energy barrier is not necessary in order for a unimolecular ion decomposition to pass through an intermediate that behaves as though it were a Type 1 complex. Such intermediates are classed as Type 3 ion–neutral complexes.

P0160 What sort of barrier might separate a Type 3 ion–neutral complex from its covalent isomer in the absence of an energy maximum? It has been argued that entropic bottlenecks can exert the same effect as a potential energy barrier ( $\langle \text{Bib25} \rangle 25$ ). The underlying notion is that, as a charged and a neutral fragment separate, large amplitude bending motions become progressively easier, until they reach a point where they transform into internal rotations that correspond to reorientation ( $\langle \text{Bib26} \rangle 26$ ). The resulting increase in the density of vibrational states has the same consequences as a potential energy well. In order to return to covalency, these internal rotations within the complex must be frozen in the correct orientation, providing an effective barrier.

P0165 The following analogy can be drawn. If a cork is removed from the bottle, reinserting it requires that the cork point toward the bottle and that the mouth of the bottle point toward the cork. If either the cork or the bottle (or both) is spinning about some arbitrary axis, not only must that rotation be stopped in order to put in the cork, but the correct orientation must also be restored. The probability is low that random motions will lock the cork and the bottle into the proper geometry.

P0170 Finding a region of a multidimensional potential energy surface that corresponds to this entropic barrier presents a formidable task that has yet to be attempted. One computational approach has been to guess a domain in which the Type 3 complex exists and estimate the density of states as a function of internal energy ( $\langle \text{Bib24} \text{ Bib27} \rangle 24, 27$ ). This density

of states can be compared with the transition state flux for the corresponding simple bond fission.

P0175 Such a comparison bears a resemblance to calculating a translational kinetic energy distribution (see Volume 1, Chapter 1: *Theory (Reactions): Kinetic Energy Release Distributions in Mass Spectrometry*), but here the translational kinetic energy is negative. That is to say, the kinetic energy of the fragments is insufficient to overcome their mutual attraction. Since a density of states and a transition state flux have different dimensions, the former must be integrated or multiplied by a factor with units of energy in order to gauge the probability of forming an ion–neutral complex relative to simple bond fission. Simple models have been put forth for how to predict the relative rate constants using a combination of experiment and theory ( $\langle \text{Bib24} \text{ Bib27} \rangle 24, 27$ ).

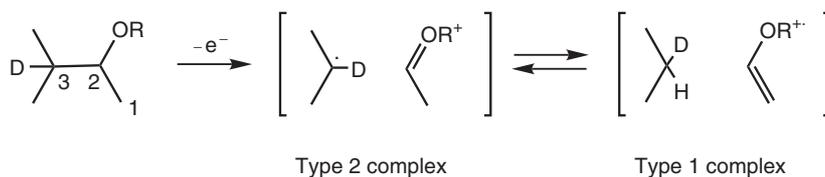
P0180 Sophisticated techniques are now available for constructing multidimensional potential energy surfaces and integrating over regions, so as to calculate densities of states. Application of these approaches to Type 3 ion–neutral complexes remains a challenge for the future.

### 3.4 Is it an Ion–Neutral Complex?

S0045

P0185 The reorientation criterion was originally presented as a way for experimentalists to assess whether a dissociation proceeds via an ion–neutral complex ( $\langle \text{Bib28} \rangle 28$ ). This criterion is supposed to clarify how to partition Fig. 1 among alternative mechanisms. The three curves in Fig. 1 illustrate three limiting-cases, and a surface connects them. In general, a reaction will find the favored pathway on this surface somewhere between the dashed curve and one of the solid curves. The question arises: how far from concerted do bond breaking and bond making have to be, in order to warrant the inference of a bona fide intermediate? It is clear that, in the case of ion–neutral complexes, if one partner flips over many times relative to the other, such a conclusion is justified.

P0190 Propane expulsion from ionized 3-methyl-2-butanol has been reported as a clear-cut case where experimental evidence documents that the reorientation criterion has been met. The metastable ion decomposition shows isotopic exchange between positions 1 and 3, and the sequence of two interconverting ion–neutral complexes shown in Scheme 5 ( $\text{R} = \text{H}$ ) provides an efficient explanation ( $\langle \text{Bib29} \rangle 29$ ). Before looking more closely at this dissociation, first consider what theory predicts regarding the case where  $\text{R} = \text{CH}_3$ . Calculations show that the molecular ion of this methyl ether has an elongated  $\text{C}_2\text{--C}_3$  bond. This bond length does not have as great a value as does  $r$  for the preferred ion structure in Scheme 4, but the  $\text{C}_2\text{--C}_3$  bond still


 F0040 *Scheme 5*

has a bond order of only about  $n=0.3$  (with a negative value of  $\nabla^2\rho$ , unlike the ion in Scheme 4). The calculated reorientation barrier for the radical cation is correspondingly higher than in Scheme 4. The question as to whether the methyl ether molecular ion corresponds to a Type 2 complex (as represented by the first species in brackets in Scheme 5) hinges on whether the experimental appearance energy for dissociation (which has yet to be measured) is greater than the reorientation barrier.

P0195 A different kind of barrier separates the radical cation of the methyl ether from a second complex, which looks like a molecule of propane electrostatically bound to ionized methyl vinyl ether. This represents a Type 1 complex. Within the complex, propane has a structure virtually unchanged from that of the isolated hydrocarbon, but three of its hydrogens (one on each carbon) make contact with the ion. Each of the three has a bond path connecting it to the ion, but the propane does not acquire a net positive charge (unlike the methyl radical in the optimized geometry in Scheme 3). These bond paths represent the steric interactions that prevent the neutral from approaching the ion more closely.

P0200 The case where  $R=H$  gives a different computational result. Both DFT (B3LYP/6-31G\*\*) and MP2 geometry optimizations show a stable structure that lies in between the two complexes, drawn to the left in Scheme 6. This structure is a linkage isomer of the parent radical cation. The transferring hydrogen is bonded to two carbons, with a pair of bond critical points each having  $\nabla^2\rho < 0$ . The dashed lines in Scheme 6 represent partial bonds.

P0205 The bond order of the two partial CH bonds is difficult to assign, because there are no standard multiple bonds to hydrogen from which to determine the parameters A and B in eqn (1). However, the bond order of the  $C_1-C_2$  bond is  $n=1.6$ , only slightly lower than the calculated bond order for ionized vinyl alcohol by itself. If the calculated geometry is to be believed, the observed isotopic interchange could be interpreted as a result of switching between two configurations at carbon 3, as shown in Scheme 6, in combination with interconversion between the parent radical cation and its linkage isomer. It is not clear at present whether that interconversion takes place in a stepwise or a concerted fashion. Nor is it clear how many times carbon 3 has to rock back and forth in order to give rise to the observed levels of isotopic



Scheme 6

F0045

exchange. Given the unusual nature of the bonding depicted in Scheme 6, considerable ingenuity will be required of both experimentalists and theoreticians alike to resolve questions like this.

### Abbreviations

S0050

AIM	Atoms in molecules	P0210
DFT	Density functional theory	P0215
ELF	Electron localization function	P0220

### Bibliography

- <Bib1>(1) Traeger, J. C.; Morton, T. H. Mechanisms for the Expulsion of Propene from Ionized Propyl Phenyl Ethers in the Gas Phase. *J. Am. Chem. Soc.* **1996**, *118*, 9661–9668.
- <Bib2>(2) Molenaar-Langeveld, T. S.; Gremmen, C.; Ingemann, S.; Nibbering, N. M. M. Isomeric Dependences of the Formation of Ion/Neutral Complexes in Dissociation Reactions of Ionized Propoxypropyridines. *Int. J. Mass Spectrom.* **2000**, *199*, 1–16.
- <Bib3>(3) Jacquet, J.-P.; Morton, T. H. Chemical Ionization of *n*-Propyl Phenyl Ether with  $D_2O$  Reagent Gas. A Test of Statistical Models. *J. Mass Spectrom.* **1997**, *32*, 251–252.
- <Bib4>(4) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd edn. Harper & Row: New York, 1987, pp. 211–229.
- <Bib5>(5) Traeger, J. C.; Luna, A.; Tortajada, J. C.; Morton, T. H. Regio- and Stereochemistry of Alkene Expulsions from Ionized *sec*-Alkyl Phenyl Ethers. *J. Phys. Chem. A* **1999**, *103*, 2348–2358.
- <Bib6>(6) Morton, T. H. The Reorientation Criterion and Positive Ion–Neutral Complexes. *Org. Mass Spectrom.* **1992**, *27*, 353–368.

- <Bib7>(7) McAdoo, D. J.; Bowen, R. D. Alkane Eliminations from Ions in the Gas Phase. *Eur. Mass Spectrom.* **1999**, *5*, 389–409.
- <Bib8>(8) Filippi, A.; Speranza, M. Gaseous Ion Activation Dynamics: the Role of the Bulk Gas in the Racemization of Chiral Oxonium Ions. *Chem. Eur. J.*, submitted for publication.
- <Bib9>(9) Midland, M. M.; Morton, T. H. Is Protonated Ammonium Fluoride an Ion-Neutral Complex in the Gas Phase? *J. Am. Chem. Soc.* **1993**, *115*, 9596–9601.
- <Bib10>(10) Abboud, J. L. M.; Alkorta, I.; Davalos, J. Z.; Gal, J. F.; Herreros, M.; Maria, P.-C.; M6, O.; Molina, M. T.; Notario, R.; Y6ñez, M. The P<sub>4</sub>⋯Li<sup>+</sup> Ion in the Gas Phase: A Planetary System. *J. Am. Chem. Soc.* **2000**, *122*, 4451–4454.
- <Bib11>(11) Illies, A. J.; Morton, T. H. Strong Hydrogen Bonding in the Gas Phase: Fluoromethane⋯hydronium versus fluoromethane⋯ammonium. *Int. J. Mass Spectrom. Ion Proc.* **1997**, *167/168*, 431–445.
- <Bib12>(12) Coppens, P. X-ray Charge Densities and Chemical Bonding. .
- <Bib13>(13) Cassam-Chenaï, P.; Jayatilaka, D. Some Fundamental Problems with Zero Flux Partitioning of Electron Densities. *Theor. Chim. Acta* **2001**, *105*, 213–218.
- <Bib14>(14) Bader, R. F. W. The Zero Flux Surface and the Topological and Quantum Mechanical Definitions of an Atom in a Molecule. *Theor. Chim. Acta* **2001**, *105*, 276–283.
- <Bib15>(15) Cassam-Chenaï, P. Frequently Asked Questions on ‘Some Fundamental Problems With Zero Flux Partitioning of Electron Densities’. *J. Math. Chem.* **2002**, *31*, 145–153.
- <Bib16>(16) Bader, R. F. W. *Atoms in Molecules, A Quantum Theory*. Clarendon Press: Oxford, 1994.
- <Bib17>(17) Nguyen, V.; Mayer, P. S.; Morton, T. H. Intramolecular Fluorine Transfer via 4-Member Cyclic Transition States. *J. Org. Chem.* **2000**, *65*, 8032–8040.
- <Bib18>(18) Traeger, J. C.; Morton, T. H. Photoionization of 2,3-Dimethyl-2-Butanol (Thexyl Alcohol). Interaction Between the Charged and Expelled Fragments. *J. Am. Soc. Mass Spectrom.*, in press.
- <Bib19>(19) Hammerum, S.; Derrick, P. J. Alpha-Cleavage in Amine Molecular Ions. A not-so-simple Cleavage. *Chem. Commun.* **1985**, 996–997.
- <Bib20>(20) Siegel, A. S. Rearrangement Ions—II: Mass Spectra of the C-13 Labeled 2-Methyl-Hydroxypropanes and 2-Methyl-2-Aminopropanes. *Org. Mass Spectrom.* **1970**, *3*, 1417–1421.
- <Bib21>(21) Stams, D. A.; Johri, K. K.; Morton, T. H. Vicinal Elimination from 2-Fluoroisopropyl Cation. *J. Am. Chem. Soc.* **1988**, *110*, 699–706.
- <Bib22>(22) Weddle, G. H.; Dunbar, R. C.; Song, K.; Morton, T. H. Time-Resolved Photodissociation of the Molecular Ions of Propyl Phenyl Ethers. *J. Am. Chem. Soc.* **1995**, *117*, 2573–2580.
- <Bib23>(23) Heinrich, N.; Schwarz, H. Ion/Molecule Complexes as Central Intermediates in Unimolecular Decompositions of Metastable Radical Cations of some Keto/Enol Tautomers: Theory and Experiment in Concert. In *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989, pp 329–372.
- <Bib24>(24) Morton, T. H. Competition in the Formation of Ion-Neutral Complexes. Expulsion of Methane from the Molecular Ion of Acetamide. *Org. Mass Spectrom.* **1991**, *26*, 18–23.
- <Bib25>(25) Morton, T. H. Gas Phase Analogues of Solvolysis Reactions. *Tetrahedron* **1982**, *38*, 3195–3243.
- <Bib26>(26) McAdoo, D. J.; Morton, T. H. Gas Phase Analogues of Cage Effects. *Acc. Chem. Res.* **1993**, *26*, 295–302.
- <Bib27>(27) Chronister, E. L.; Morton, T. H. Internal Energy Effects on Ion-Neutral Complexes from Unimolecular Dissociation of *n*-Propyl Phenyl Ether Radical Cations. *J. Am. Chem. Soc.* **1990**, *112*, 133–139.
- <Bib28>(28) Morton, T. H. The Reorientation Criterion and Positive Ion-Neutral Complexes. *Org. Mass Spectrom.* **1992**, *27*, 353–368.
- <Bib29>(29) Hammerum, S.; Audier, H. E. Experimental Verification of the Intermediacy and Interconversion of Ion-Neutral Complexes as Radical Cations Dissociate. *J. Chem. Soc. Chem. Commun.* **1988**, 860–861.

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