Thus it appears that in spite of the positive micelle charge Cu^{2+} ions which would normally be repelled become complexed on the micelle surface. Atlernatively the possibility exists that the high Cl^- or Br^- ion concentration at the surface of the micelle leads first to the formation of $CuCl_2$ or $CuBr_2$, followed by a complexation of these compounds by the micelle. In either case the observable effect would be an apparent reduction of the interaction between Ps and the copper species.

References and Notes

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(13) Previous studies have shown that the interaction between Ps and Cu^{2+} in aqueous solution can best be described in terms of an oxidation of the Ps by Cu^{2+} with only a minor contribution made by the ortho to para spin conversion process caused by the paramagnetism of Cu^{2+}.[14,15]

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Potential Surfaces for the Unimolecular Reactions of Organic Ions: $C_2H_6N^+$ and $C_2H_5O^+$

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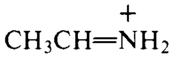
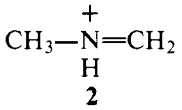
Abstract: The isomeric ions $CH_3CH{=}N^+H_2$ (**1**) and $CH_3N^+H{=}CH_2$ (**2**) are shown to decompose over the same potential surface through loss of H_2 and C_2H_2 in slow unimolecular (metastable) transitions. Deuterium labeling data, appearance potential measurements, and metastable peak widths are presented to show that **2** isomerizes to **1** in a process which has energy requirements similar to those for unimolecular dissociations of **1**. The potential energy surface for reactions of $C_2H_6N^+$ ions is compared and contrasted with the corresponding surface for $C_2H_5O^+$ ions; the approach naturally accommodates the independent behavior of $CH_3CH{=}O^+H$ and $CH_3{}^+O{=}CH_2$.

In discussing the unimolecular chemistry of species of a given chemical formula, an ultimate aim must be to describe the complete potential surface, or surfaces, over which the species can react. As a result of several years work in numerous laboratories, it is now evident that many details of the potential surfaces for unimolecular ionic reactions can be obtained by examining the slow (metastable) reactions taking place in a conventional magnetic sector mass spectrometer. The main criteria are as follows: (1) in many cases the energy levels of reactants and products can be obtained from known heats of formation, or appearance potential measurements; (2) the transition state energies for isomerization or dissociation of a reactant can be obtained from appearance potential measurements; (3) information on direct dissociation of a reactant, or isomerization prior to dissociation, can be obtained from isotope, usually ^2H or ^{13}C, labeling; and (4) reaction of species, initially generated as isomeric structures, over the same surface (or surfaces) at the same internal energies will be indicated by the same, or very similar, channeling among two or more slow (metastable) decomposition pathways.[2a] In addition, we now possess an unambiguous criterion to establish which of a set of isomeric ions are in potential wells, as opposed to those which may isomerize without activation energy to other structures, through the consideration of collision-induced dissociations.[2b] Finally, the heats of formation of species which may lie on the potential surface, but not correspond to potential energy minima, may be estimated by an isodesmic substitution procedure.[3] We now apply these criteria to a study of the potential surface for $C_2H_6N^+$ ions, which can be conveniently generated as the isomeric species **1** and **2**, both of which exist in potential wells.[2b]



$CH_3CH{=}\overset{+}{N}H_2$

1



$CH_3{-}\underset{H}{\overset{+}{N}}{=}CH_2$

2

Results and Discussion

In the present work, the two major decay pathways of $C_2H_6N^+$ ions observed in metastable transitions are loss of acetylene and molecular hydrogen. The former process, which is evidenced by the appearance of a metastable peak at *m/e* 7.36, dominates. Other reactions (e.g., loss of hydrogen radical or methane) are of negligible intensity, being responsible for only ca. 1% of the total metastable ion current.

The ratios of the metastable peak areas for C_2H_2 and H_2 loss from $C_2H_6N^+$ ions, produced from a variety of amines, are shown in Table I. Two conclusions are evident from the data; first, that the $C_2H_6N^+$ ions, irrespective of the precursor, undergo C_2H_2 and H_2 losses in similar ratios, thus suggesting at least partial equilibration of the two isomeric structures prior

Table I. Reactions for Formation, and Ratios of Competing Metastable Transitions of $C_2H_6N^+$ Ions

Precursor	Origin of *m/e* 44	Postulated ion structure at threshold	1st field-free region[a]		2nd field-free region[a]	
			C_2H_2 loss	H_2 loss	C_2H_2 loss	H_2 loss
$CH_3CH_2N^+\dot{H}_2$	$\xrightarrow{-\dot{H}}$	$CH_3CH{=}N^+H_2$ (**1**)	96	4	88	12
$(CH_3)_2CHNH_2^{+\cdot}$	$\xrightarrow{-\dot{C}H_3}$		91	9	82	18
$CH_3CH_2(CH_3)CHN^+\dot{H}_2$	$\xrightarrow{-\dot{C}_2H_5}$		98	2	86	14
$(CH_3)_2CH(CH_3)CHN^+\dot{H}_2$	$\xrightarrow{-(CH_3)_2\dot{C}H}$		96	4	89	11
$CH_3N^+\dot{H}CH_3$	$\xrightarrow{-\dot{H}}$	$CH_3N^+H{=}CH_2$ (**2**)	96	4	87	13
$CH_3N^+\dot{H}CH_2CH_3$	$\xrightarrow{-CH_3^{\cdot}}$		95	5	80	20
$CH_3N^+\dot{H}CH_2Ph$	$\xrightarrow{-\dot{P}h}$		91	9	94	6
$CH_3N^+\dot{H}CH_2CH_2CH_3$	$\xrightarrow{-\dot{C}_2H_5}$		94	6	78	22
$CH_3N^+\dot{H}CH_2CH_2OH$	$\xrightarrow{-\dot{C}H_2OH}$		95	5	81	19
$CH_3N^+\dot{H}CH_2CH(CH_3)_2$	$\xrightarrow{-(CH_3)_2\dot{C}H}$		95	5	82	18

[a] Figures normalized to a total ion current of 100 units.

to decomposition in metastable transitions;[2a] second, the minor decay channel, H_2 loss, is more favorable in the second field-free region than the first field-free region (AEI MS-902 double focusing mass spectrometer). This result indicates that, on the assumption that the two reactions are competing, the H_2 loss probably has the lower transition state energy, since it competes more successfully in ions of lower internal energies (longer lifetimes). If this is so, then it appears that H_2 loss has an unusually slow rise of k with E, since normally the lower activation energy reaction produces the more abundant metastable peak.[4] Such an effect is known to operate in the fragmentation of $C_3H_6^{+\cdot}$ radical cations, which undergo mainly loss of a hydrogen radical in metastable transitions, despite the fact that H_2 loss is the decomposition channel having the lowest activation energy.[5]

Where metastable transitions undergone by ions **1** and **2** have been previously examined[2b] from some of the precursors listed in Table I, there is reasonably good qualitative agreement between the ratios of C_2H_2 and H_2 losses. However, competing H radical loss was observed to a larger extent (6-11% where direct comparisons are possible) in the earlier work (vs. ca. 1% in the present work). Additionally, where **1** or **2** are generated from a precursor by a single simple bond homolysis, C_2H_2 loss is found to be more abundant than H_2 loss both in the present (Table I) and previous[2b] work. However, there is a tendency for H radical and/or H_2 losses to compete more successfully if **1** or **2** are generated via rearrangement or multistep routes.[2b] Although these variations are not fully understood at the present time, it has been noted[2b] that they may be due (at least in part) to differences in the P(E) functions of the precursors. Any such variations appear to be small for the precursors listed in Table I.

The shapes of the metastable peaks for the C_2H_2 and H_2 losses provide strong evidence that the reactions, irrespective of the initial structure, **1** or **2** of the ion, occur through the same transition states. Thus, the metastable peak for C_2H_2 loss is always Gaussian, even when the width of the β slit between the two sectors is greatly reduced to improve the energy resolution. In contrast, that for H_2 loss is always flat-topped under conditions of good energy resolution and corresponds to a kinetic energy release of 12 kcal mol^{-1}.

The conclusion to be drawn from the data already presented is that the barrier to interconversion of **1** and **2** must be approximately the same as, or less than, the (similar) activation energies for the C_2H_2 and H_2 losses. If this were not so, then **1** and **2** would react differently[6] either in terms of reaction type or different competition between the two channels.[4,6] In order to establish whether **1** or **2** equilibrate totally or only partially prior to unimolecular decomposition, the metastable transitions for C_2H_2, C_2HD, and C_2D_2, and H_2, HD, and D_2 losses from 13 specifically deuterated ions were examined. The data are given in Tables II and III.

From the data presented in Table II, it is evident that in the slow (metastable) decompositions leading to C_2H_2 loss, the hydrogen atom(s) initially bound to nitrogen in **1** or **2** are predominantly retained in the ammonium ion which results from the decomposition. Thus, complete equilibration of **1** and **2**, even after a very large number of vibrations at internal energies appropriate to metastable decompositions, does not occur. This conclusion follows since reversible reactions between **1** and **2** must involve transfer of hydrogen between nitrogen and carbon, and would lead eventually to complete loss of identity of the hydrogen atom(s) originally bound to nitrogen.

It should be added that a rationalization of the data based on complete equilibration of all hydrogens and deuteriums, together with a large isotope effect favoring C_2H_2 loss (over C_2HD and C_2D_2 losses), can be shown to be invalid. For example, for ions of the formula $C_2H_3D_3N^+$, $CH_3N^+D{=}CD_2$ loses more C_2D_2 than C_2H_2 in decompositions occurring in the first field-free region, and loses C_2H_2 and C_2D_2 in equal abundance in the second field-free region. Also $CD_3N^+H{=}CH_2$ and $CD_3CH{=}N^+H_2$ show a preference for C_2D_2 loss over C_2H_2 loss.

The most satisfactory model to accommodate the data presented so far is one in which **2** isomerizes to **1** prior to acetylene loss, but the reverse reaction **1** → **2** occurs only partially since the rate-determining step in passing from **1** to NH_4^+ plus C_2H_2 has a barrier very similar to that for the reaction **1** → **2**. The occurrence of **2** → **1** in all ions generated as **2** which eventually lose C_2H_2, but only partial occurrence of **1** → **2** (in ions initially generated as **2** or **1**, which eventually lose C_2H_2) not only satisfies the requirement of partial interconversion of **1** and **2**, but also satisfies the requirement of C-C bond formation in passing from **2** en route to C_2H_2 loss. Clearly, it is likely that there are one or more intermediates in

Table II. Metastable Peaks for Losses of C_2H_2, C_2HD, and C_2D_2 from ^2H-Labeled "$C_2H_6N^+$" Ions[a]

	Ion structure	1st field-free region			2nd field-free region		
Precursor	at threshold	C_2H_2 loss	C_2HD loss	C_2D_2 loss	C_2H_2 loss	C_2HD loss	C_2D_2 loss
$(CH_3)_2CH(CH_3)CDN^+H_2$	$CH_3CD{=}N^+H_2$	47	53	0	54	46	0
$(CH_3)_2CHNHD^{+\cdot}$	$CH_3CH{=}N^+HD$	*c*	*c*	*c*	90	10	0
$(CH_3)_2CHND_2^{+\cdot}$	$CH_3CH{=}N^+D_2$	83	17	*b*	82	17	1
$(CH_3)_2CH(CH_3)CDN^+HD$	$CH_3CD{=}N^+HD$	*c*	*c*	*c*	39	52	9
$(CH_3)_2CH(CH_3)CDN^+D_2$	$CH_3CD{=}N^+D_2$	27	59	14	37	56	7
$(CD_3)_2CHNH_2^{+\cdot}$	$CD_3CH{=}N^+H_2$	8	45	47	12	51	37
$(CD_3)_2CHN^+HD$	$CD_3CH{=}N^+HD$	*c*	*c*	*c*	7	48	45
$(CD_3)_2CHN^+D_2$	$CD_3CH{=}N^+D_2$	0	34	66	0	43	57
$CH_3N^+DCH_2CH_3$	$CH_3N^+D{=}CH_2$	80	20	0	85	15	0
$CH_3N^+HCD_2CH_2CH_3$	$CH_3N^+H{=}CD_2$	27	61	12	28	59	13
$CH_3N^+DCD_2CH_2CH_3$	$CH_3N^+D{=}CD_2$	12	61	27	20	60	20
$CD_3N^+HCH_2CH_2CH_3$	$CD_3N^+H{=}CH_2$	10	55	35	14	55	31
$CD_3N^+DCH_2CH_2CH_3$	$CD_3N^+D{=}CH_2$	4	51	45	6	51	43

[a] Abundances measured by peak area and normalized to a total metastable ion current for "C_2H_2" losses of 100 units. [b] Peak observed but too faint to measure accurately in 1st field-free region. [c] N-Deuterated ions which could not be produced in sufficient abundance to permit measurements.

Table III. Losses of H_2, HD, and D_2 from ^2H-Labeled "$C_2H_6N^+$" Ions in the First Field-Free Region

Ion structure	Neutral lost[a]		
at threshold	H_2	HD	D_2
$CH_3CD{=}N^+H_2$	80	20	0
$CH_3CH{=}N^+HD$	94	6	0
$CH_3CH{=}N^+D_2$	84	16	*b*
$CH_3CD{=}N^+HD$	64	36	*b*
$CH_3CD{=}N^+D_2$	47	41	12
$CD_3CH{=}N^+H_2$	37	42	21
$CD_3CH{=}N^+D_2$	0	39	61
$CH_3N^+D{=}CH_2$	82	18	0
$CH_3N^+H{=}CD_2$	44	50	6
$CH_3N^+D{=}CD_2$	33	56	11
$CD_3N^+H{=}CH_2$	27	54	19
$CD_3N^+D{=}CH_2$	13	56	33

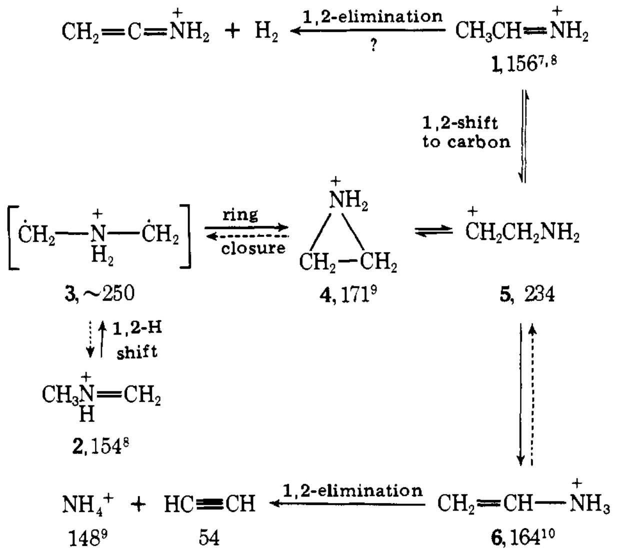
[a] Abundances measured by peak area and normalized to a total metastable ion current for "H_2" loss of 100 units. [b] Peak observed but too faint to measure accurately.

passing from **2** to $^+NH_4$ plus C_2H_2; so far as we are aware, the complete formation of a triple C≡C bond in one step would be without precedent.

The data (Table III) for competition in H_2, HD, and D_2 losses (from the same precursors as listed in Table II) are given for the first field-free region only, since the appropriate metastable transitions in the second field-free region overlap with daughter ions formed in the source. Again, it is evident that the equilibration **1** $\rightleftharpoons$ **2** is not fast relative to these reactions, since if it were, the bracketed ion pairs (Table III) would give the same ratios for H_2, HD, and D_2 losses (see later for further justification of this statement). In fact, in making comparison between such pairs, it is evident that H_2 loss increases in probability when one or two deuteriums are bound to nitrogen. Thus, there is further evidence in favor of partial retention of the original N-D (or N-H) bonds, and also evidence that the activated complex for H_2 loss does not involve the breaking of a bond to nitrogen.

Before attempting a more quantitative interpretation of the isotopic labeling data, it is worthwhile to consider possible intermediates and products in terms of their known or estimated heats of formation, and the possible barriers to reaction of each species using the organic chemist's concept of mechanism. A mechanistic scheme is given in Scheme I; where known or estimated, the heat of formation of each species is indicated (in kcal mol^{-1}) with the structure. A discussion of these values is given in the Appendix.

Scheme I



Previous experiments[2b] have established that **1** and **2** exist in potential wells. The only plausible direct dissociations from **2** would appear to be loss of CH_4 (the slow unimolecular reaction in fact observed for the oxygen analogue $CH_3{}^+O{=}CH_2$[5]), or H_2 to produce $CH_3{}^+N{\equiv}CH$. Since H_2 loss appears not to involve the N-H bond (see above), we conclude that no direct dissociation of **2** occurs. A 1,2-H shift in **2** can produce the diradical **3**; this process will have a high activation energy which can be estimated (~96 kcal mol^{-1}) from the known heat of formation (ΔH_f = 171 kcal mol^{-1} [9]) of protonated aziridine **4** on the assumption that the energy required for C-C bond homolysis will be similar to that required (76 kcal mol^{-1} [11]) in the isoelectronic molecule cyclopropane. The deuterium labeling results indicate that **3** probably represents a transition state between **2** and **4** rather than a configuration which is repeatedly accessible en route from **2** to **4**. The highly exothermic ring closure to **4** can form the first C-C bond of the potential acetylene unit, with sufficient internal energy to make the β-aminoethyl cation **5** ($\Delta H_f \simeq$ 234 kcal mol^{-1} [3]) accessible, though presumably this species in its linear form is not in a potential well; this should collapse without activation energy to **1** containing some 94 kcal mol^{-1} of internal energy. The experimental results are consistent with H_2 loss from this species with a vibrational energy in this region. Alternatively, **5** may rearrange to protonated vinylamine **6** (ΔH_f = 164 kcal mol^{-1} [10]). This process probably requires

Table IV. Comparison of Observed Decompositions of Labeled "$C_2H_6N^+$" Ions with Those Expected from Three Models

	Model A			Model B			Model C			Obsd		
Ion structure	$-C_2H_2$	$-C_2HD$	$-C_2D_2$	$-C_2H_2$	$-C_2HD$	$-C_2D_2$	$-C_2H_2$	$-C_2HD$	$-C_2D_2$	$-C_2H_2$	$-C_2HD$	$-C_2D_2$
$CH_3CD{=}N^+H_2$	50	50	0	67	33	0	58	42	0	54	46	0
$CH_3CH{=}N^+HD$	100	0	0	67	33	0	89	11	0	90	10	0
$CH_3CH{=}N^+D_2$	100	0	0	40	53	7	80	18	2	82	17	1
$CH_3CD{=}N^+HD$	50	50	0	40	53	7	47	51	2	39	52	9
$CH_3CD{=}N^+D_2$	50	50	0	20	60	20	40	53	7	37	56	7
$CD_3CH{=}N^+H_2$	0	50	50	20	60	20	7	53	40	12	51	37
$CD_3CH{=}N^+HD$	0	50	50	7	53	40	2	51	47	7	48	45
$CD_3CH{=}N^+D_2$	0	50	50	0	33	67	0	44	56	0	43	57
$CH_3N^+D{=}CH_2$	100	0	0	67	33	0	89	11	0	85	15	0
$CH_3N^+H{=}CD_2$	30	60	10	40	53	7	33	58	9	28	59	13
$CH_3N^+D{=}CD_2$	30	60	10	20	60	20	27	60	13	20	60	20
$CD_3N^+H{=}CH_2$	10	60	30	20	60	20	13	60	27	14	55	31
$CD_3N^+D{=}CH_2$	10	60	30	7	53	40	9	58	33	6	51	43

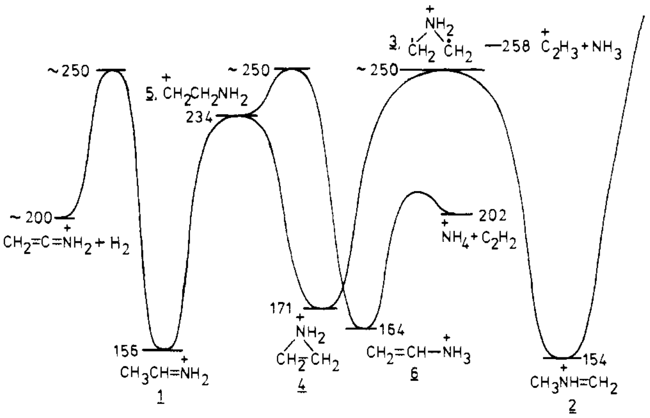
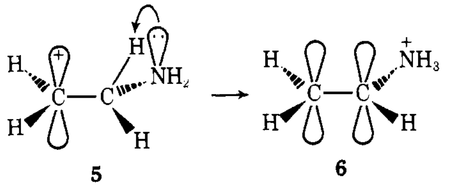


Figure 1. Proposed potential energy surface for the unimolecular reactions of $CH_3CH{=}N^+H_2$ (**1**) and $CH_3N^+H{=}CH_2$ (**2**).

a major portion of the estimated 16 kcal mol^{-1} of internal energy of **5** (since **5** $\rightleftharpoons$ **6** cannot be rapidly reversible; see deuterium labeling results).

It should be noted that the dissociation of **6** via σ-bond cleavage leading to $C_2H_3^+$ and NH_3 requires a minimum energy of 258 kcal mol^{-1} (calculated from $\Sigma\Delta H_f$ $C_2H_3^+$ and NH_3 on the basis of zero reverse activation energy). The nonoccurrence of this reaction provides strong evidence that reactions requiring an internal energy significantly greater than ca. 250 kcal mol^{-1} are unable to compete in metastable dissociations. This, in turn, suggests that the transition state energy for elimination of C_2H_2 from **6** is, at most, ca. 250 kcal mol^{-1}.

These features are incorporated in the schematic potential surface shown in Figure 1; the rate-determining steps for loss of H_2 and C_2H_2 starting from **1** have activation energies which are the same (~94 kcal mol^{-1}) within experimental error (as determined by appearance potential measurements). The same approximate total energy (~250 kcal mol^{-1}, i.e., ~96 kcal mol^{-1} internal energy of **2**) is required for H_2 and C_2H_2 losses starting from **2** (Figure 1). The significance of these barriers is considered in more detail subsequently. The existence of an activation energy for the process **5** → **6** seems plausible since it must proceed via a rather unfavorable geometrical pathway, viz.



5 **6**

A consequence of this scheme is that the sequence **1** $\rightleftharpoons$ [**5**] $\rightleftharpoons$ **4** should be rapid at the internal energies appropriate to these slow unimolecular dissociations, and it is therefore necessary that experimentally hydrogen and deuterium atoms bound to carbon in **1** or **2** should pass through equivalent states prior to the dissociations. Let us first consider a model (A) in which **2** → **4** and **5** → **6** are not significantly reversible. For ions of type **2**, regardless of whether 1,3-hydride shifts result in the statistical distribution of all hydrogens attached to carbon in **2** (prior to the rearrangement shown in Scheme I), and irrespective of the exact mechanism whereby **2** → **1**, providing only the transfer of hydrogen from carbon to nitrogen is assumed statistical, then the origin of the hydrogens finally incorporated in the NH_4^+ ion is established. One of these must be the hydrogen originally attached to nitrogen in **2**, but all the rest are selected at random from the five attached to carbon. Since in model A (1) all hydrogens originally attached to nitrogen are retained in the NH_4^+ fragment and (2) hydrogens once transferred from carbon to nitrogen are not subsequently transferred back to carbon, the relative losses of C_2H_2, C_2HD, and C_2D_2 from **1** can also be calculated. The data are presented in Table IV, with the experimental results, and calculations for two other models. Model B assumes complete equivalence of all hydrogens, and model C gives data for 67% model A plus 33% model B (i.e., one-third of the ions react after all hydrogens have become equivalent via **4** $\rightleftharpoons$ **2** and/or **6** $\rightleftharpoons$ **5**, the remaining two-thirds reacting with complete retention of the hydrogens originally bound to nitrogen). Model A, although very simple, does explain the chemistry in broad outline; model B is inadequate for cases such as $CH_3CH{=}N^+D_2$, where the postulate of complete loss of identity of all hydrogens is most obviously in error; model C provides a good explanation of the facts, especially the difference in, for example, $CH_3CD{=}N^+H_2$ and $CH_3CH{=}N^+HD$. Indeed, the greatest error between model C and experiment is 10%, while the mean error is only 4%. Thus, the experimental data are in accord with a minor fraction of the ions undergoing metastable transitions, having participated in the reactions **4** $\rightleftharpoons$ **2** and/or **6** $\rightleftharpoons$ **5** (see dotted lines in Scheme I).

Subsequent to the formulation of the models, the mass spectrum of $(CD_3)_2CDNH_2$ was obtained. The predicted and experimentally observed decompositions of the ion $CD_3CD{=}N^+H_2$ are given in Table V. The agreement with model C is again good.

A further consequence of model C is that the metastable peaks for reactions starting from **2** should be somewhat broader than those starting from **1**. This is because the isomerization of **2** to **1** is the rate-determining step for dissociation of some ions generated as **2** and a small proportion of the excess energy present in ions formed as **1** by rearrangement of **2** should appear as a broadening of the metastable peak for this process.

Table V. Predicted and Observed Decompositions of $CD_3CD{=}N^+H_2$

Model A			Model B			Model C			1st field-free region			2nd field-free region		
$-C_2H_2$	$-C_2HD$	$-C_2D_2$	$-C_2H_2$	$-C_2HD$	$-C_2D_2$	$-C_2H_2$	$-C_2HD$	$-C_2D_2$	$-C_2H_2$	$-C_2HD$	$-C_2D_2$	$-C_2H_2$	$-C_2HD$	$-C_2D_2$
0	0	100	7	53	40	2	18	80	*a*	18	82	2	27	71

[a] Peak observed but too weak (ca. 0.5%) to measure accurately.

Table VI. Kinetic Energy Release at Half-Height Associated with C_2H_2 Loss

Ion structure	$W_{1/2}$, V	$T_{1/2}$, kcal mol^{-1}
$CH_3CH{=}N^+H_2$	3.2 (±0.1)	4.1 (±0.2)
$CH_3N^+H{=}CH_2$	3.4 (±0.1)	4.6 (±0.2)

Measurement of the peak width at half-height ($W_{1/2}$) for C_2H_2 loss from **1** and **2** results in the values for the kinetic energy release at half-height ($T_{1/2}$) shown in Table VI.

The data of Table VI do reveal a somewhat broader peak for C_2H_2 loss starting from **2.** Although this difference is only slightly greater than the experimental error in determining $W_{1/2}$, it is reproducible, and it is probably significant.

The situation with regard to H_2 loss is less clear. A comparison between Tables III and IV shows that model C again gives the best fit, though in this case the mean error is larger (8%). Since this reaction is subject to more uncertainty (relative to the acetylene loss) in terms of (1) possible isotope effects and (2) doubts as to the reacting configuration, there are too many variables to allow any useful conclusions to be drawn.

A further consequence of the potential surface reproduced in Figure 1 is that protonated aziridine (**4**) should undergo C_2H_2 and H_2 losses in metastable transitions in a similar ratio to those observed for **1** and **2.** We have therefore protonated aziridine in a chemical ionization source (using CH_4 as reagent gas). Ion **4** generated in this manner undergoes (in metastable transitions) C_2H_2 and H_2 losses in the ratio 80:20 in the first field-free region of the MS50 mass spectrometer.

Finally, we should point out that since the reacting configuration for H_2 loss is in doubt (see above) the possible H_2 loss from **1** in Figure 1 could equally occur from **4** (but with a similar transition state energy).

Comparison between the Unimolecular Chemistry of $C_2H_6N^+$ and $C_2H_5O^+$. Some years ago, it was established that the oxygen analogues **7** and **8** of the ions which we have examined do not interconvert prior to unimolecular dissociations.[6] Ion **7** competitively loses C_2H_2 and CH_4 (the latter with kinetic energy release), whereas **8** loses CH_4 over a different potential surface (releasing a range of kinetic energies).[6] The reasons for the difference in behavior between the nitrogen and oxygen analogues can be understood by constructing a potential surface for isomerization and dissociation of $C_2H_5O^+$ ions (Figure 2), analogous to Figure 1.

$$\underset{\textbf{7}}{CH_3CH{=}\overset{+}{O}H} \qquad \underset{\textbf{8}}{CH_3\overset{+}{O}{=}CH_2}$$

We have previously made appearance potential measurements[12] on the dissociation of ions initially generated as **7** and **8**, by loss of C_2H_2 and CH_4, and CH_4, respectively; these values provide the transition state energies for dissociation in Figure 2.

In comparing Figures 1 and 2, it is instructive to regard $^+CH_2CH_2NH_2$ and $^+CH_2CH_2OH$ as having common energy levels, since here the NH_2 and OH functions are isolated and have yet to reflect their differing abilities to stabilize a positive charge. Points of interest which emerge from the comparison are:

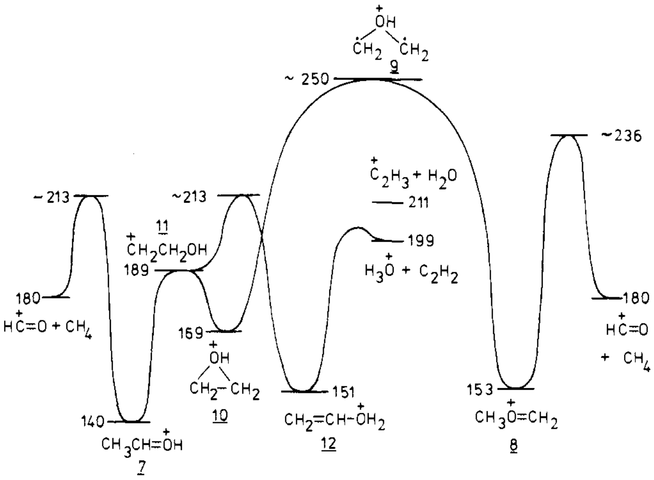


Figure 2. Proposed potential energy surface for the unimolecular reactions of $CH_3CH{=}O^+H$ (**7**) and $CH_3{}^+O{=}CH_2$ (**8**).

(1) The gas-phase rearrangements of the β-aminoethyl cation **5** to the protonated imine of acetaldehyde (**1**) by a 1,2-H shift, or to protonated aziridine **4** via cyclization, are both highly exothermic (~78 and 63 kcal mol^{-1}), whereas in the β-hydroxyethyl cation **11,** the cyclization is much less exothermic (~20 kcal mol^{-1}), and the 1,2-H shift moderately less exothermic (~49 kcal mol^{-1}).

(2) On the assumption that the energy requirements for C-C bond homolysis in **4** and **10** are similar, then the diradical **9** is at a much higher level on the $C_2H_5O^+$ surface than is the diradical **3** on the $C_2H_6N^+$ surface. Such a conclusion would in any event be reasonable on the basis of the higher proton affinity of dimethylamine (225 kcal mol^{-1})[13] relative to dimethyl ether (190 kcal mol^{-1}).[13] As a consequence, both **7** and **8** undergo unimolecular decomposition at internal energies which are insufficient to generate **9** and the potential surfaces for dissociation of **7** and **8** remain separate.

(3) The slow unimolecular dissociations (metastable peaks) of $CH_3CH{=}O^+H$ (**7**) have previously been examined by $^2H^{14,15}$ and $^{13}C^{15,16}$ labeling, with the observations that (a) the hydroxyl hydrogen remains attached to oxygen up to dissociation; (b) the carbon-bound hydrogens become equivalent; and (c) the carbon atoms become equivalent prior to unimolecular dissociations. The observations (b) and (c) are naturally accommodated by the sequence **7** $\rightleftharpoons$ [**11**] $\rightleftharpoons$ **10,** which should be rapid and reversible at energies appropriate to dissociation in metastable transitions. Observation (a) reveals that, as in the nitrogen analogues, there is a significant barrier to the reaction **11** → **12.** In the oxygen system this barrier must be rate determining starting from **7** because of the specificity[15] of retention of the hydroxyl hydrogen in the resultant H_3O^+ ion. Although appearance potential measurements[12] yield a transition state energy of 213 kcal mol^{-1} for acetylene loss, this value, which represents the height of the barrier for **11** → **12,** may be too high (by say 3-5 kcal mol^{-1}). The reason for this is that protonated vinyl alcohol **12** could undergo σ-bond cleavage yielding $C_2H_3^+ + H_2O$ ($\Sigma\Delta H_f$ = 211 kcal mol^{-1}), presumably without reverse activation energy. This process occurs only to a very small extent in metastable tran-

sitions thus indicating that the transition state for acetylene loss starting from **7** is slightly lower in energy than 211 kcal mol^{-1}. In Figure 2, the dissociative step for acetylene loss is depicted as involving only a small reverse activation energy, as indeed it appears it must. This conclusion could not have been anticipated, and is somewhat surprising. Nevertheless it is consistent with the Gaussian metastable peak which is observed for this reaction.[6]

Conclusion

Simplifying assumptions and approximations, in conjunction with appearance potential measurements and isotopic labeling, allow the construction of plausible potential surfaces for the unimolecular chemistry of $C_2H_6N^+$ and $C_2H_5O^+$. While the approach can only be an approximate one at the present time, it emphasizes that in considering the "structures" of reacting ions in a molecular beam, it is fruitful to consider the possible nature of the whole of the accessible potential surface. The internal energies required for the decomposition of stable even-electron ions will often be sufficiently high to make several isomeric structures of the reactant available prior to unimolecular decomposition, this accounting for, in a rational manner, isotopic "scrambling" processes.

Experimental Section

All unlabeled compounds were either available commercially or else synthesized by unexceptional methods. C-Deuterated amines were prepared by three main routes, summarized below.

$$RCONHR^1 \xrightarrow[\text{diglyme}]{\text{LiAlD}_4} RCD_2NHR^1$$

$$C_2H_5OCONHR \xrightarrow[\text{diglyme}]{\text{LiAlD}_4} CD_3NHR$$

$$R^1R^2C{=}NOH \xrightarrow[\text{diglyme}]{\text{LiAlD}_4} R^1R^2CDNH_2$$

N-Deuterated amines were prepared, in situ, by admission of D_2O into the all glass heated inlet system (AGHIS) containing the corresponding N-H amine.

All mass spectra were recorded using an AEI MS902 mass spectrometer, operating at 70 eV. Metastable transitions occurring in the first field-free region were examined using the refocusing technique.[17,18]

The peak widths at half-height for loss of C_2H_2 from **1** and **2** were determined for dissociations occurring in the second field-free region of a reversed geometry instrument (V. G. Micromass ZAB 2F) in the laboratory of Professor J. H. Beynon. The assistance of Dr. J. R. Kalman in making these measurements is gratefully acknowledged.

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Appendix

Heats of Formation of Relevant Species. A major problem in constructing potential surfaces for gas phase, ionic reactions is the lack of available heats of formation (ΔH_f) for reactants and postulated intermediates. In order to overcome this difficulty we have resorted to estimation techniques when no experimental values were available. These estimation techniques fall into two broad categories: (1) estimation of the proton affinities of molecules in order to obtain ΔH_f of the corresponding protonated species; (2) use of a modified isodesmic insertion[19] to obtain values for open-chain, linear configurations of ions.

The former procedure may be illustrated for protonated vinylamine. The proton affinities of various amines of general formula RNH_2 are in the region 215–225 kcal mol^{-1}. That for ethylamine is 221 kcal mol^{-1}.[13] Hence the PA of $CH_2{=}CHNH_2$ is estimated to be 220 kcal mol^{-1} (± say 5 kcal mol^{-1}). Using Franklin's group equivalents[20,21] $\Delta H_f(CH_2{=}CHNH_2) = 18$ kcal mol^{-1} and hence $\Delta H_f(CH_2{=}CHN^+H_3) = 366 - 220 + 18 = 164$ kcal mol^{-1}.

The latter method may be used to obtain $\Delta H_f(^+CH_2CH_2OH)$ as follows: ΔH_f values (kcal mol^{-1}) for C_2H_5OH,[20] C_3H_8,[20] and $C_3H_7^+$ [22] are shown in Scheme II.

Scheme II

CH_3CH_2OH	$CH_3CH_2CH_3$
-56	-25
$^+CH_2CH_2OH$	$^+CH_2CH_2CH_3$
	210

Assuming that the energy needed to remove H^- from the methyl group of CH_3CH_2OH is the same as that needed to remove H^- from the corresponding position in $CH_3CH_2CH_3$, $\Delta H_f(^+CH_2CH_2OH) = \Delta H_f(^+CH_2CH_2CH_3) - \Delta H_f(C_3H_8) + \Delta H_f(C_2H_5OH) = 210 + 25 - 56 = 179$.

This value assumes that when the methyl radical in $C_3H_7^+$ is replaced by a hydroxyl radical, the only change produced in the ΔH_f value is that reflecting the inherent difference in stability of CH_3 and OH. This isodesmic insertion[19] does not allow for the inductive destabilization of $^+CH_2CH_2OH$ caused by the β-OH. A reasonable value for this destabilization is 10 kcal mol^{-1} as revealed by calculations.[19] Use of this correction results in $\Delta H_f(^+CH_2CH_2OH) = 179 + 10 = 189$ kcal mol^{-1}.

In considering the accuracy of the estimation techniques outlined above two factors should be kept in mind: (1) The discussion presented does not critically depend on the accuracy of the ΔH_f values. Even were the values in error by 10 kcal mol^{-1}, the analysis would not be materially affected. (2) In some cases (e.g., $^+CH_2CH_2OH$) no experimental method exists for ΔH_f determination because attempts to produce open-chain configurations of ions by AP measurements (from, e.g., $BrCH_2CH_2OH$ in the case in question) will be circumvented by the formation of cyclic isomers ($\overline{CH_2CH_2O}H^+$ in this case).[3] The cyclic isomers will always be formed at threshold on account of their considerably lower heats of formation. Thus the use of an estimation method is inevitable in these cases.

Finally, it should be noted that reliable heats of formation are available for many of the ions of interest, e.g., $CH_3CH{=}O^+H$,[23] $H^+C{=}O$,[24] $CH_3CH{=}N^+H_2$,[7] together with $\overline{CH_2CH_2N}H_2^+$ and $\overline{CH_2CH_2O}H^+$ via the proton affinities of aziridine and oxirane, respectively.[9,13]

Appearance Potentials. These were determined for both ion series using either an AEI MS 9 or an AEI MS 902 double-focusing mass spectrometer. In each case the APs were measured on metastable ions in the first field-free region and analyzed by the "semilog plot" method. This method is subject to systematic errors,[25,26] and the results have therefore been used to deduce approximate transition state energies only (see Figures 1 and 2).

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An Ion Cyclotron Resonance Study of the Structures of $C_7H_7^+$ Ions

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Abstract: The $C_7H_7^+$ fragment ions formed in toluene, and the chlorinated, brominated, and iodinated toluenes, as well as the $C_7H_6F^+$ fragment ions in fluorinated toluenes have been studied in an ion cyclotron resonance spectrometer. In all these systems, it is seen that there are two populations of $C_7H_7^+$ ions, one of which reacts with the parent compound and other compounds, and one of which is totally unreactive. Because the reactive $C_7H_7^+$ ions from the different precursors all undergo the same reactions and at the same rate as the $C_7H_7^+$ ions in toluene and benzyl chloride, which have previously been shown to have the benzyl structure, this structure is assigned to the reactive $C_7H_7^+$ populations; the unreactive $C_7H_7^+$ ions are assigned the tropylium structure. The relative abundance of the unreactive tropylium ion is low (<15%) in the chloro-, bromo-, and iodotoluenes, and decreases with decreasing energy of the ionizing electrons. This is interpreted to mean that the rearrangement to the seven-membered ring structure occurs after the fragment ion is formed. In toluene and fluorotoluenes, the unreactive component comprises 30–60% of the $C_7H_6X^+$ ($X = H, F$) ions, and decreases with increasing energy of the ionizing electrons, indicating that rearrangement occurs prior to the fragmentation of the parent ion. Rate constants for the hydride transfer to the benzyl ion from cyclopentane, cyclohexane, 3-methylpentane, and 3-methylhexane are reported. An estimate that ΔH_f $(C_6H_5CH_2^+) = 219 \pm 4$ kcal/mol is based on the assumption that the maximum endothermicity of reaction is given by $-RT \ln k_{Rn}/k_{collision}$, as well as on determinations of equilibrium constants for the reactions $C_6H_5CH_2^+ + (CH_3)_3CX \rightleftarrows (CH_3)_3C^+ + C_6H_5CH_2X$ where X = Br or Cl. The relative abundances of benzyl and tropylium ions determined by this technique in various compounds are compared with analogous results from collisional activation spectra. Tolyl ions, if formed, rearrange to the more stable benzyl ion structure within 10^{-3} s.

A number of studies have examined the structures of $C_7H_7^+$ ions formed in various aromatic compounds,[1] and have presented evidence that these ions exist in the gas phase with two or more discrete structures one of which is the tropylium as suggested by Meyerson and coworkers[1a,b] in 1957. This conclusion has been based on several types of experimental observations, some of which will be discussed here.

For example, in high-pressure mass spectrometric studies,[2,3] it has been seen that $C_7H_7^+$ ions of unspecified structure react with toluene to form $C_8H_9^+$ and $C_{14}H_{15}^+$ ions:

$$C_7H_7^+ + C_6H_5CH_3 \rightarrow C_{14}H_{15}^+ \qquad (1a)$$

$$\rightarrow C_8H_9^+ + C_6H_6 \qquad (1b)$$

In both of these studies, a small fraction of the $C_7H_7^+$ ions were unreactive.

More recently, using an ICR spectrometer, Dunbar also observed that the $C_7H_7^+$ ions generated in toluene consist of two populations,[4] distinguishable by their reactivity toward toluene, and pointed out that the two populations probably represent ions of two different structures.[4,5] By studying the reaction analogous to (1b) in partially deuterium-labeled toluenes, $C_6H_5CD_3$ and $C_6D_5CH_3$, Shen et al.[5] were able to demonstrate that the product $C_8(H,D)_9^+$ ion contains three hydrogens from the methyl group of the neutral toluene reactant, four from the ring of the neutral toluene, and two from the $C_7(H,D)_7^+$ reactant with some preference to the hydrogens on the methyl group. From this result they surmised that the reactive $C_7H_7^+$ species has the benzyl structure.

In studies from that laboratory,[4,5] the hypothesis was adopted that the nonreactive $C_7H_7^+$ component has the tropylium structure; the other possible structures, the tolyl ion structures, were considered unlikely because they are known to be higher energy ions.[4,6]

More quantitative results have shown that the reactive $C_7H_7^+$ ion formed in benzyl chloride has the benzyl structure. Abboud et al.[6] determined the equilibrium constant for the