

such rates are certainly low enough for the mechanism we discuss.

Finally it is worth noting that simple hydrated Cu^{2+} fails to oxidize acetyl and similar negatively substituted radicals in contrast to many examples of such oxidation by Cu^{2+} -halide complexes,²⁷ supporting the idea that here another path, direct displacement on the ligand, is taking place.

Experimental Section

Stoichiometry of the Fe^{2+} - H_2O_2 -substrate reactions was determined as in our previous papers^{2,3} by slow addition of H_2O_2 to

stirred Fe^{2+} -substrate solutions under N_2 , followed by determination of Fe^{2+} consumed by dichromate titration or of Fe^{3+} formed by spectrophotometric determination of its thiocyanate complex. DMSO systems developed a pronounced yellow color during reaction and products were apparently unstable since Fe^{3+} titers changed on standing. Accordingly products were analyzed immediately after reaction *via* the thiocyanate method.

Isobutyl alcohol products were determined qualitatively by flame ionization glc of reaction solutions. Isobutylene glycol (2-methyl-1,2-propanediol) was detected in approximately 20% yield both with and without added Fe^{3+} . In the presence of 0.04 M Cu^{2+} the yield was 14% plus 8% methallyl alcohol, present only in traces in the absence of Cu^{2+} . Evidently some oxidative elimination occurs with copper in this system.

Structure and Unimolecular Reactions of Gaseous $\text{C}_2\text{H}_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ Ions¹

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Abstract: Collisional activation (CA) spectra of $\text{C}_2(\text{H},\text{D})_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ ions from a wide variety of compounds show that the immonium ion isomers, and only those isomers, are the stable structures of lifetimes $>10^{-5}$ sec. Ions formed initially as $^+\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{N}^+\text{H}$ isomerize to $\text{CH}_3\text{CH}=\text{N}^+\text{H}_2$ (b), and those formed as $\text{CH}_3\text{-N}^+\text{CH}_3$ isomerize to $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2$ (d). Deuterium labeling shows that a substantial proportion of the decompositions of b and d do not involve loss of the positional identity of the hydrogen atoms. $\text{C}_3\text{H}_8\text{N}^+$ ions of the immonium structures $\text{CH}_3\text{CH}_2\text{N}^+\text{H}=\text{CH}_2$ (f), $(\text{CH}_3)_2\text{C}=\text{N}^+\text{NH}_2$ (g), $\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+\text{H}_2$ (h), $\text{CH}_3\text{N}^+\text{H}=\text{CHCH}_3$ (i), and $(\text{CH}_3)_2\text{N}^+=\text{CH}_2$ (j) have lifetimes $>10^{-5}$ sec. Contrary to previous evidence,³ g does not isomerize completely to h before metastable decomposition, nor does f isomerize to i, unless the activation energy for the latter isomerization is nearly as high as that for decomposition. Thus in several cases the information supplied by metastable ion decompositions, including the width of flat-topped peaks, has provided misleading evidence as to the structure of the corresponding undecomposed ions in the mass spectrum. In contrast, CA spectra provide reliable evidence for the structures of $\text{C}_2\text{H}_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ ions, and thus for the structure of molecules giving such ions in their mass spectra.

Structure and reactivity of gaseous organic cations have been examined in a variety of recent investigations.^{1,3,4} Such information on ion behavior free of solvent interactions has been valuable in application to, for example, fundamental concepts of basicity,^{4a} theoretical prediction of ion structure and properties,^{4b,c} and understanding of mass spectral reactions.^{1,3,4} The study reported here of $\text{C}_2\text{H}_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ ions was undertaken because of conflicting evidence of the behavior of such ions, which are simple examples of the important class of even-electron $\text{C}_n\text{H}_{2n+2}\text{N}^+$ ions found in the mass spectra of saturated amines.

The saturated amine group is well known for its unusual ability to direct mass spectral fragmentations;⁵

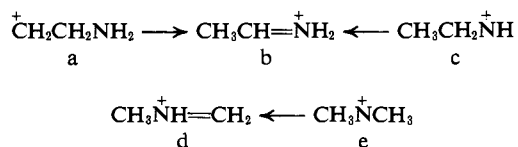
(1) Metastable Ion Characteristics. XXVII. Part XXVI: K. Levsen, F. W. McLafferty, and D. M. Jerina, *J. Amer. Chem. Soc.*, **95**, 6332 (1973).

(2) (a) Postdoctoral Fellow, 1972. (b) John Simon Guggenheim Memorial Foundation Fellow, 1972. (c) We are indebted to the National Institutes of Health (GM 16575 and 16609) and the Army Research Office (8246-C) for generous financial support.

(3) N. A. Uccella, I. Howe, and D. H. Williams, *J. Chem. Soc. B*, 1933 (1971).

(4) (a) E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972); (b) P. Ausloos, R. E. Rebert, L. W. Sieck, and T. O. Tiernan, *ibid.*, **94**, 8939 (1972); (c) D. J. McAdoo, F. W. McLafferty, and P. F. Bente III, *ibid.*, **94**, 2027 (1972); (d) N. A. Uccella and D. H. Williams, *ibid.*, **94**, 8778 (1972).

— NH_2 and — $\text{N}(\text{CH}_3)_2$ have been ranked as the most effective groups of the common functionalities.⁶ Addition of a single amine group can have a profound influence on the mass spectrum of a large molecule; for example, the mass spectrum of *n*-octadecylamine has CH_2N^+ as its largest peak, and other $\text{C}_n\text{H}_{2n+2}\text{N}^+$ ions account for a large part of the remaining ion abundance.⁵ This has been assumed to be due in substantial part to the high stability of the $\text{C}_n\text{H}_{2n+2}\text{N}^+$ ions, which stability is thought to result from the unusual electron-donating ability of nitrogen, for example, $^+\text{CH}_2\text{NH}_2 \leftrightarrow \text{CH}_2=\text{N}^+\text{H}_2$. This would predict that the quaternary immonium ions b and d would be the most stable of the possible $\text{C}_2\text{H}_6\text{N}^+$ isomers a–e (the indicated isomerizations will be discussed below). The $\text{CH}_3\text{CH}=\text{O}^+\text{H}$ and $\text{CH}_3\text{O}^+=$

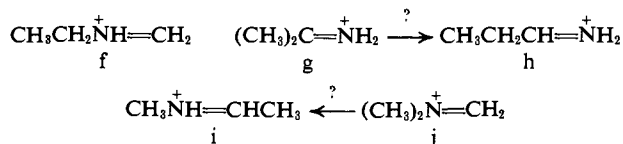


(5) R. S. Gohlke and F. W. McLafferty, *Anal. Chem.*, **34**, 1281 (1962); H. Budziklewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 8.

(6) G. Remberg and G. Spiteller, *Chem. Ber.*, **103**, 3640 (1970).

CH₂ ions, which correspond to b and d, have been shown to be the most stable of the analogous C₂H₅O⁺ isomers using evidence from their metastable ion decompositions (MI spectra) and ion cyclotron resonance (icr) spectra.⁷ Ions formed as ⁺CH₂CH₂OH and CH₃CH₂O⁺, corresponding to a and c, apparently isomerize spontaneously to CH₃CH=O⁺H, but CH₃-CH=O⁺H and CH₃O⁺=CH₂ ions of internal energies necessary for metastable decomposition retain their isomeric integrity.^{7a}

In contrast to this behavior, however, from a recent detailed investigation of the structure and isomerization of C₃H₈N⁺ metastable ions utilizing ²H and ¹³C labeling it was concluded that skeletal isomerizations take place readily for some of these immonium ions.³ The ions f-j are the possible C₃H₈N⁺ structures which should be stabilized by electron sharing. Comparison of their



MI spectra led to the conclusion that g and h decompose from the same structure, as do i and j, possibly due to the prior isomerizations g → h and j → i. This was supported by the observation of a unique flat-topped metastable corresponding to 58⁺ → 30⁺ for g and h, and of one corresponding to 58⁺ → 56⁺ for i and j. Evidence from isotopic labeling indicated that the isomerization i → f precedes loss of C₂H₄ from i.³ These indicated isomerizations of the immonium ions g, i, and j, requiring less energy than any decomposition of the ions, limit our previous assumptions concerning the general stability of immonium ions.

This study seeks further information on the structures and behavior of C₂H₆N⁺ and C₃H₈N⁺ ions utilizing collisional activation (CA) spectra, which are produced by causing ions to collide with an inert gas during passage through a field-free drift region of the mass spectrometer. The relative abundances of product ions in CA spectra resulting from higher energy processes are virtually independent of the distribution of internal energy values, P(E), of the precursor ions.⁸ In contrast, the usefulness of icr and MI spectra for characterizing ion structures is compromised by their dependence on P(E) of the precursor ions.^{7b,9} A recent study¹⁰ of the CA spectra of C₃H₇O⁺ ions found CH₃-CH₂O⁺=CH₂, (CH₃)₂C=O⁺H, CH₃CH₂CH=O⁺H, and CH₃O⁺=CHCH₃ to be stable structures which do *not* undergo isomerization; note that these structures are directly analogous to f-i, respectively (the oxygen analog of j is not possible). C₃H₇O⁺ ions formed initially in structures other than these were found to isomerize to these by hydrogen rearrangement and ring opening, but not by skeletal reorganization. (In some cases skeletal rearrangement occurs during ion formation,

(7) (a) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966); (b) J. L. Beauchamp and R. C. Dunbar, *ibid.*, **92**, 1477 (1970).

(8) (a) F. W. McLafferty, P. F. Bente III, R. Kornfeld, S.-C. Tsai, and I. Howe, *J. Amer. Chem. Soc.*, **95**, 2120 (1973); (b) F. W. McLafferty, R. Kornfeld, W. F. Haddon, I. Sakai, K. Levsen, P. F. Bente III, S.-C. Tsai, and H. D. R. Schuddege, *ibid.*, **95**, 3886 (1973).

(9) J. L. Occolowitz, *J. Amer. Chem. Soc.*, **91**, 5202 (1969); A. N. H. Yeo and D. H. Williams, *ibid.*, **93**, 395 (1971).

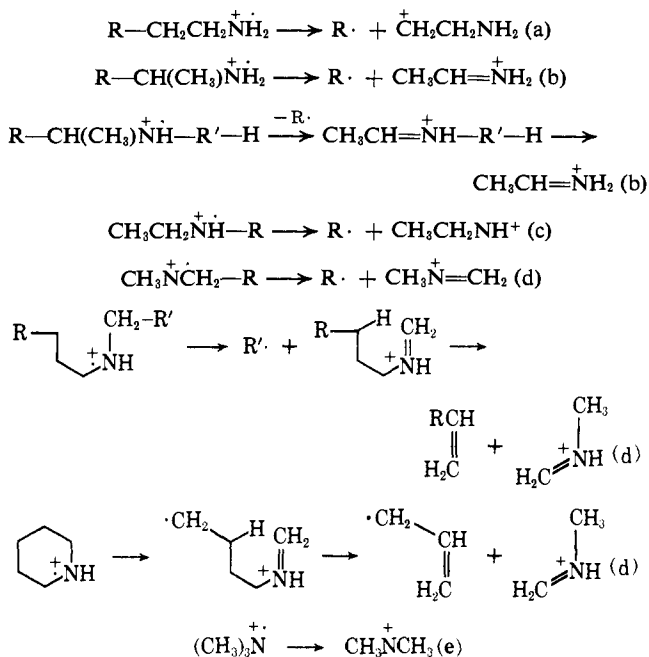
(10) F. W. McLafferty and I. Sakai, *Org. Mass Spectrom.*, **7**, 971 (1973).

such as through anchimeric assistance.¹⁰) If the stabilization of the oxonium and immonium ions is due to the electron-donating ability of the heteroatom, this would predict that the C₃H₈N⁺ ions should exhibit an even smaller tendency to undergo such skeletal rearrangements. Molecular orbital calculations reported recently¹¹ indicate that CH₂OH⁺ and CH₂NH₂⁺ are resonance stabilized by 48 and 66 kcal/mol, respectively, relative to the methyl cation.

Results and Discussion

Structures of C₂H₆N⁺ Ions. The variety of reactions outlined in Scheme I would be expected⁵ to give initially

Scheme I



ions of structures a-e. The structures expected in greatest abundance for the compounds examined are listed in Table I. Alternative reactions can be visualized,⁵ for example, C₂H₅NH₂ could form ⁺CH₂-CH₂NH₂ (a) as well as CH₃CH=N⁺H₂ (b), and the 1-methyl primary amines could first form RCH=N⁺H₂ by α-CH₃ loss followed by δ-H rearrangement with C^β-C^γ bond cleavage to give CH₂=CH-N⁺H₃.¹² The MI spectra of the C₂H₆N⁺ ions from the compounds of Table I show three peaks of widely varying abundances: *m/e* 18, 9-86%; *m/e* 42, 5-59%; and *m/e* 43, 5-66%. In contrast to the MI spectra of the analogous C₂H₅O⁺ ions,^{7a} *these abundances bear little relationship to the expected ion structures.* For example, there are large differences in the MI spectra of the C₂H₆N⁺ ions from the homologous series of 1-methyl primary amines, and the spectrum of C₂H₆N⁺ from ethylamine most closely resembles that from dimethylamine. These peaks are of very low abundance relative to the precursor C₂H₆N⁺ ions (5 × 10⁻⁷ - 3 × 10⁻⁵), which may make the MI spectra subject to wider variations with changes in either precursor ion internal energy or concentration of ions in isolated electronic states.

(11) P. A. Kollman, W. F. Trager, S. Rothenberg, and J. E. Williams, *J. Amer. Chem. Soc.*, **95**, 458 (1973).

(12) H. C. Hill, "Introduction to Mass Spectrometry," Heyden, London, 1966, p 68.

Table I. MI and CA Spectra of $C_2H_6N^+$ Ions

<i>m/e</i>	Un-decyl-amine	Ethyl-amine	1-Methylethyl-amine		1-Methyl-butyl-amine	1-Methyl-octyl-amine	1,2-Di-methyl-butyl-amine	Diiso-propyl-amine	Bis(1-methyl-heptyl-amine)	AcAla-AlaAla-OMe	Diethyl-amine	Benzyl-N-ethyl-amine	Di-methyl-amine	N-Methyl-isobutyl-amine	N-Methyl-pentyl-amine	N-Methyl-phen-ethyl-amine	Dibutyl-amine ^d	Di-heptyl-amine ^d	Piperi-dine	Tri-methyl-amine
Unimolecular Metastable Spectra ^a																				
43	35	6	7	<i>b</i>	21	60	9	13	37	<i>b</i>	5	66	7	11	19	6	47	32	27	12
42	51	8	26		24	19	27	40	46		27	5	11	29	38	13	24	59	11	25
18	14	86	67		55	21	64	47	17		68	29	82	60	43	81	29	9	62	63
Collisional Activation Spectra ^c																				
43	(68)	(41)	(45)	(74)	(50)	(54)	(53)	(47)	(60)	(69)	(34)	(62)	(55)	(55)	(66)	(62)	(79)	(69)	(73)	(62)
42	(60)	(83)	(77)	(58)	(66)	(61)	(75)	(78)	(69)	(78)	(71)	(62)	(68)	(56)	(58)	(56)	(50)	(46)	(59)	(71)
41	26	31	32	30	30	30	33	31	32	30	30	31	22	25	23	23	22	21	20	27
40	17	17	15	16	14	14	15	16	16	17	15	16	17	16	16	17	15	16	17	14
39	7	6	6	7	6	5	6	6	6	4	6	5	6	5	6	5	5	5	6	7
38	3	3	3	2	3	3	3	3	3	3	3	4	3	4	4	3	4	3	4	4
30	1.1	0.4	1.1	<2	1.0	0.4	0.5	0.7	0.7	0.7	0.6	1.2	2	2	2	2	1.5	2	2	2
29	5	3	4	7	4	4	3	3	5	3	3	4	4	4	4	4	5	4	5	5
28	18	17	17	19	17	18	19	19	18	17	17	18	31	31	32	32	30	31	32	29
27	9	11	10	7	10	10	9	10	8	9	11	9	7	5	5	5	5	5	5	5
26	4	5	4	5	5	5	4	5	5	5	5	4	0.7	0.6	<0.8	0.6	<0.8	<0.6	0.9	<1.0
25	1.3	1.1	1.0	<2	1.2	1.5	1.2	1.4	1.0	1.5	1.4	1.4	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
18	(4)	(44)	(21)	(7)	(15)	(10)	(16)	(17)	(8)	(6)	(38)	(8)	(22)	(10)	(7)	(6)	(5)	(2)	(7)	(18.3)
15	8	5	6	7	8	8	5	5	7	8	7	5	7	6	7	7	12	12	8	7
Structure:																				
Initial	a	b	b	b	b	b	b	b	b	b	b or c	c	d	d	d	d	d	d	d	e
Final	CH ₃ CH=N ⁺ H ₂ (b)											CH ₂ N ⁺ H=CH ₂ (d)								

^a Abundances relative to the sum of all metastables. ^b Not recorded due to low sensitivity. ^c Abundances relative to the sum of all peaks except *m/e* 18, 42, and 43. ^d The CA spectra of diisobutyl-amine and diisopentylamine are identical with these CA spectra within experimental error.

Figure 1. Peak shape of *m/e* 30 in the MI spectra of $C_2H_6N^+$ from *tert*-butylamine (bottom) and diisopropylamine (top).

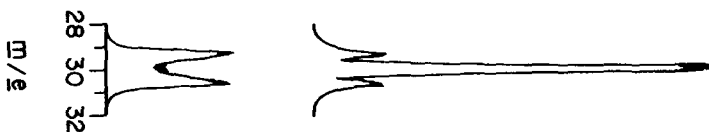


Table II. Partial CA Spectra of ^3H -Labeled $\text{C}_2\text{H}_6\text{N}^+$ Ions^a

m/e	$\text{CH}_3\text{CH}=\text{N}^+\text{H}_2^b$	$\text{CH}_3\text{CH}=\text{N}^+\text{D}_2^b$	$\text{CH}_3\text{N}^+\text{H}=\text{CH}_2^c$	$\text{CH}_3\text{N}^+\text{D}=\text{CH}_2^c$	$\text{CH}_3\text{N}^+\text{H}=\text{CH}_2^d$	$\text{CD}_3\text{N}^+\text{H}=\text{CH}_2^d$
46						16.4
45		16.8				21.0
44		13.4		22.5		10.2
43	19.4	14.0	23.5	11.1	30.9	5.1
42	23.1	6.6	19.3	9.7	17.1	3.7
41	9.4	3.4	8.1	5.5	5.5	2.5
40	5.2	1.6	5.7	3.5	4.0	1.7
39	1.6	0.8	1.9	1.3	1.5	
32		0.3				
31		2.5		1.3		
30	0.3	1.5 ^e	1.2	3.2		3.4
29	2.1 ^e	7.0	3.1	20.2	5.1	7.8
28	10.3	1.4 ^e	20.6	6.1	20.0	13.8
27	5.6 ^e	4.7	3.8	2.1	5.1	2.4
26	2.6	2.6	0.6	0.5		
25	0.6	0.6				
21						0.3
20		14.9				2.6
19		2.1		4.0		1.4
18	14.0	0.5	4.6	0.8	5.5	2.6
17	0.6	0.4				1.9
16	0.3	1.9		1.3		1.8
15	3.1	1.4	5.4	4.2	4.7	0.8
14	1.1	0.5	1.4	1.2	0.7	0.5

^a Abundances relative to the sum of all peaks in the spectrum, not corrected for contributions from the MI spectrum. Differences in comparison to other data for these ions are due mainly to the replacement of the electron gun filament.⁸ ^b Precursors: $(\text{CH}_3)_2\text{CHNH}_2$ and $(\text{CH}_3)_2\text{CHND}_2$. ^c Precursors: $n\text{-C}_3\text{H}_{11}\text{NHCH}_3$ and $n\text{-C}_3\text{H}_{11}\text{NDCH}_3$. ^d Precursors: $\text{CH}_3\text{CON}(\text{CH}_3)\text{CH}(\text{CH}_2\text{C}_6\text{H}_5)\text{CON}(\text{CH}_3)\text{CH}_2\text{CON}(\text{CH}_3)\text{CH}_2\text{COOCH}_3$ and $\text{CH}_3\text{CON}(\text{CD}_3)\text{CH}(\text{CH}_2\text{C}_6\text{H}_5)\text{CON}(\text{CD}_3)\text{CH}_2\text{CON}(\text{CD}_3)\text{CH}_2\text{COOCD}_3$. ^e Value less accurate due to interference from neighboring flat-topped peak.

The CA spectra of these $\text{C}_2\text{H}_6\text{N}^+$ ions, however, are useful for the characterization of their structures, despite their differences in internal energy. The abundances of peaks from low energy processes (values in parentheses, Table I) are, as expected,⁸ dependent on $P(E)$ of the precursor $\text{C}_2\text{H}_6\text{N}^+$ ions. Decreasing the average internal energy of the $\text{C}_2\text{H}_6\text{N}^+$ ions from 1-methylethylamine by lowering the electron energy decreases the m/e 18 and 42 peaks while increasing m/e 43; the same trend is observed in both the MI and CA spectra for the homologous series $\text{RCH}(\text{CH}_3)\text{-NH}_2$ from $\text{R} = \text{H}$ to C_7H_{15} , consistent with the expected decrease in the average internal energy of the $\text{C}_2\text{H}_6\text{N}^+$ ions with increasing number of degrees of freedom of the molecule.¹³ Note, however, that these changes in $P(E)$ of the precursor ions have a *negligible* effect on other peaks of the CA spectra.

Despite the close similarity in the abundances of many of the remaining peaks in these CA spectra, there are some peaks whose abundances differ by much more than the experimental reproducibility of the values. The most logical explanation of these data is that only two different ion structures remain after the $\sim 10^{-5}$ sec required to reach the collision region; for the m/e 25, 26, 27, 28, and 30 peaks those ions of the first structure show abundances of >0.9 , >3 , >8 , <20 , and <1.3 , respectively, while those of the other structure are <0.2 , <1.0 , <8 , >28 , and >1.4 , respectively. Ions originally formed as a, b, and c have apparently isomerized to a common structure, as have ions d and e; by analogy to the behavior of the $\text{C}_2\text{H}_5\text{O}^+$ ions, these more stable ions would be expected to have the immonium structures b and d, respectively.⁷ It must be pointed out that, without knowledge of the true CA spectra of the unrearranged ions, the presence of

some ions of structures a or c with b, or of e with d, cannot be ruled out. However, the isomerizations $a \rightarrow b$, $c \rightarrow b$, and $e \rightarrow d$ are also logical in that they involve only hydrogen migration, not skeletal rearrangement, consistent with the low energy isomerizations of $\text{C}_2\text{H}_5\text{O}^+$ and $\text{C}_3\text{H}_7\text{O}^+$ ions reported previously.^{7,8,10} To confirm these conclusions concerning the stability of b and d, the CA spectra of some deuterium-labeled analogs were examined.

Unimolecular Decomposition of $\text{C}_2\text{H}_6\text{N}^+$ Ions. For the CA spectra of both types of $\text{C}_2\text{H}_6\text{N}^+$ ions, the major peaks observed (CH_3^+ and ions due to the losses of H_2 , CH_4 , and C_2H_2) are analogous to those found in the CA spectra of both $\text{CH}_3\text{CH}=\text{O}^+\text{H}$ and $\text{CH}_3\text{O}^+=\text{CH}_2$.^{8b} Isotopic labeling was used to study the origins of these peaks. Comparison of the CA spectra of ions formed as b and as $\text{CH}_3\text{CH}=\text{N}^+\text{D}_2$ (b') (Table II) shows for several of these processes that the deuterium atoms of b' retain their positional identity to a substantial degree. Williams and coworkers observed that N-H bonds of $\text{C}_3\text{H}_8\text{N}^+$ ions remain structurally distinct in decomposition, and Collin¹⁴ reported similar behavior for the molecular ion of ethylamine. The NH_4^+ ion at m/e 18 in the CA spectrum of b moves mainly to m/e 20 (NH_2D_2) in the spectrum of b', ruling out the isomerization to c as a common structure. The m/e 28 and 29 peaks should represent mainly the $\text{HC}\equiv\text{N}^+\text{H}$ and $\text{HC}^+=\text{NH}_2$ ions, as these peaks move in substantial part to m/e 29 and 31 in the spectrum of b', consistent with b as the common ion structure. As found in the mass spectrum of ethylamine,¹⁴ the ions at m/e 25, 26, and 27 appear to be mainly C_2H^+ , C_2H_2^+ , C_2H_3^+ ; their abundances are reduced to only a small extent in the CA spectrum of b'. Again, this is inconsistent with c as the common ion structure.

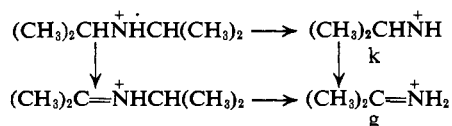
(13) F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, **89**, 5951 (1967).

(14) J. E. Collin, M. J. Franskin, and D. Hyatt, *Bull. Soc. Roy. Sci. Liege*, **35**, 744 (1966).

In the CA spectra (Table IV), the ions which arise from low energy processes in any spectra have been excluded from the normalization of ion abundances; these processes were identified both from CA spectra of $C_3H_8N^+$ ions formed using 15 eV electrons for ionization and from the MI spectra.⁸ For 18 compounds these data give five distinct and characteristic CA spectra; these spectra correspond to the five proposed immonium ions f-j and show that the $C_3H_8N^+$ ions in the mass spectra of these compounds have not undergone substantial isomerization. (The only anomalous spectrum is that for the ions from diisopropylamine, which will be discussed below.)

This evidence for the structural integrity of i and j contrasts with conclusions based on the similarity of their MI spectra;³ this apparent discrepancy could arise from several factors. MI spectra represent precursor ions of a narrow range of internal energies at the metastable decomposition threshold, while CA spectra arise from ions which have energies before collision ranging from the lowest up to this threshold energy. If the threshold energy for isomerization is below that for decomposition, only part of the ions giving rise to the CA spectra would be isomerized; this cannot have occurred to an appreciable extent for any of the ions f-j, however, as the $C_3H_8N^+$ ions produced by 15 eV ionizing electrons give the same CA spectrum (higher energy ions) as that using 70 eV electrons. Thus the similarity in the MI spectra of i and j could be a coincidence, or the isomerization and decomposition reactions could have similar energy requirements. The fact that both i and j, as well as g and h, give rise to the same flat-topped metastable peaks is strong evidence that for this particular reaction these ions decompose through a common transition state. In the case of g and h, however, this cannot be due to a prior isomerization of all ions with the internal energy necessary for metastable decomposition because of the differences in their MI spectra, as discussed above.

The m/e 30 ions in the MI spectrum of $C_3H_8N^+$ from diisopropylamine are made up of both a normal and a flat-topped metastable peak (Figure 1), indicative of the presence of isomers of both the group f, i, and j (normal³) and the group g and h (flat-topped³). The CA spectrum is consistent with g as the major component, possibly accompanied by i, although the quantitative agreement is not too satisfactory. The CA spectrum of the $C_3H_7O^+$ ion from diisopropyl ether agreed closely with that of $(CH_3)_2C=O+H$;¹⁰ at least two pathways to g can be visualized. Forma-



tion of i is more difficult to rationalize; isomerization of k through methyl rearrangement or C_2H_4 loss from $(CH_3)_2CHN^+H=CHCH_3$ are possibilities. Further investigation with isotopically labeled ions is necessary to determine which isomers other than g are present; stable structures other than f-j, such as cyclic or unsaturated ammonium ions, are conceivable.

Conclusions

The recently reported³ tendency for hydrogen and skeletal isomerization for $C_3H_8N^+$ ions f-j which undergo metastable decomposition is not found for these ions which have the lifetimes required for detection in the mass spectrometer. The immonium ion structure, at least for the seven examples studied here, is of high stability with regard to isomerization as well as to decomposition.⁵ The CA spectra of the possible immonium ion structures for $C_2H_6N^+$ and $C_3H_8N^+$ ions are sufficiently different that these spectra can serve as distinctive characteristics of ions b, d, f, g, h, i, and j; the ions f, g, and h can also be characterized from their MI spectra. Thus these spectra should prove useful for the determination of complex molecular structures and for the elucidation of mass spectral decomposition mechanisms.⁸

Experimental Section

Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer in which the positions of ion source and electron multiplier were interchanged as described previously.¹⁶ An ion accelerating potential of 3.8 kV, ionizing electrons of 100 μ A and 70 eV (or lower where noted), and sample reservoir and ion source temperature of 200° were used. Unimolecular metastable decompositions of the precursor ion selected by the magnetic field occurring in the field-free drift region between the magnetic and electrostatic (ESA) analyzers are measured by scanning the ESA potential. The pressure in the field-free drift region between the magnet and the ESA is then increased with helium until the precursor ion intensity is reduced to 10% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan.⁸ The contributions from MI products (corrected as described⁸) are subtracted from these values to obtain the CA spectrum. The values reported are the averages of at least ten scans in at least two separate determinations, and were reproducible within $\pm 5\%$ (relative) except for the least abundant peaks and the low voltage data.

Samples. N-Deuterated amines were prepared by exchange with D_2O in the inlet system of the mass spectrometer. The peptide PheGlyGly was derivatized as described previously.¹⁷ All other compounds were obtained from commercial sources, checked for purity by mass spectrometry, and purified by gas chromatography where necessary.

Acknowledgment. We are indebted to Drs. Timothy Wachs, Johann Winkler, and Paul F. Bente III for helpful advice and assistance.

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