Formation and Structure of $C_2H_4N^+$. Effect of Pressure and Reaction Exothermicity on Collision-Induced Dissociation Spectra

A. J. Illies, Shuying Liu, and M. T. Bowers*

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received February 12, 1981*

Abstract: $C_2H_4N^+$ ions generated by proton-transfer reactions on acetonitrile and methyl isocyanide as well as from the association reaction between CH_3^+ and HCN are studied by means of MIKES-CID. It is shown that two distinct species occur. The ion produced in the association reaction has the same structure as that produced from the proton transfer on acetonitrile. The protonated isocyanide definitely has a different structure. The CID spectra are dependent on the internal energy of the ion as demonstrated by the variation with ion source pressure and with reaction exothermicity.

I. Introduction

In this study MIKES-CID (Mass Analyzed Ion Kinetic Energy Spectroscopy-Collision Induced Dissociation)[1] is used to probe the structure of $C_2H_4N^+$. Evidence exists that this ion might be produced by the radiative association reaction[2]

$$CH_3^+ + HCN \underset{k_b}{\overset{k_c}{\rightleftharpoons}} (C_2H_4N^+)^* \qquad (1a)$$

$$(C_2H_4N^+)^* \xrightarrow{k_r} C_2H_4N^+ + h\nu \qquad (1b)$$

Reactions of this sort have been invoked[3,4] to explain the observed number densities of some molecules in dense interstellar clouds where the pressure is too low for three-body association reactions. Knowledge of the structure of this ion would be useful for theoretical modeling of the unimolecular rate constant, k_b, as well as for kinetic modeling of other products produced in any reaction involving this ion.

Reaction 1a forms a $C_2H_4N^+$ ion with 4.2 eV internal energy. As pressures are increased in the ion source it is expected that collisional stabilization will dominate

$$(C_2H_4N^+)^* + M \rightarrow C_2H_4N^+ + M \qquad (1c)$$

where M is a neutral molecule in the source. The resultant $C_2H_4N^+$ ions will have internal energies between thermal and 4.2 eV. Hence, the MIKES-CID spectrum could vary with source pressure since the internal energy in $C_2H_4N^+$ varies with ion source pressure. Two kinds of experiments were performed to investigate this effect. First the MIKES-CID spectra of the $C_2H_4N^+$ ion formed in reaction 1 were measured as a function of ion source pressure. Second, the reactions

$$BH^+ + C_2H_3N \rightarrow C_2H_4N^+ + B \qquad (2)$$

were studied for B = CH_3OH and H_2 for two C_2H_3N isomers (methyl isocyanide and acetonitrile) as a function of ion source pressure. For B = CH_3OH near thermal energy $C_2H_4N^+$ ions are formed while for B = H_2, the $C_2H_4N^+$ ions will have a very large amount of internal energy. The comparison of the two sets of data provide a rational basis for structure identification of the $C_2H_4N^+$ ion formed by reaction 1 and for investigating the effect of source pressure (and hence internal energy) on MIKES-CID spectra.

Table I. MIKES-CID of $C_2H_4N^+$ Ions[a,b]

m/z	$(CH_3NC)H^+$	$(CH_3CN)H^+$	CH_3^+ + HCN
12			
13	0.015		0.002
14	0.060		0.003
15	0.274	0.008	0.008
26	0.20	0.25	0.20
27	0.62	0.45	0.38
28	0.80	0.44	0.41
38	1.00	1.00	1.00
39	1.21	1.23	1.21
40	2.42	2.86	2.79
41	2.75	3.93	3.75
20[c]	0.04	0.003	0.004
20.5[c]	0.18	0.039	0.037
21[c]	0.012	0.017	0.011

[a] Ion intensities are normalized by the m/z 38 (CCN^+) intensity. [b] The ion gauge pressure was 8×10^{-5} torr. [c] Charge stripping reaction.

The paper is organized as follows. Section II describes the experimental method. The results are summarized and discussed in Section III, and conclusions are stated in Section IV.

II. Experimental Section

Measurements were performed on a high-resolution commercial reversed-geometry double-focusing mass spectrometer, the V.G. Micromass ZAB-2F.[5] In these experiments, $C_2H_4N^+$ ions were formed by chemical ionization, accelerated to 8 kV, and mass analyzed. The ions were then collided with helium in a collision cell placed at the focal point between the magnet and the electrostatic analyzer (ESA). All experiments were carried out at a collision gas pressure which resulted in a 50% reduction of the main beam (parent ion beam). The MIKES-CID spectra are then obtained by scanning the ESA.

The commercial EI/CI ion source on this instrument was modified to obtain higher source pressures by reducing the electron entrance hole to 0.020 in. and by covering all re-entrants with stainless steel plates (except for the one being used as a gas inlet). The pressure in this source cannot be directly measured. Instead an ion gauge at the entrance to the diffusion pump is used to estimate the pressure. The ion repeller was set at 0 V for all experiments and the source temperature at 225 °C. The total emission current and electron energy were 1 mA and 200 eV, respectively. At the highest ion source pressures used, the results did not depend upon the electron energy in the range of 50-200 eV.

High-mass-resolution spectra were taken at all pressures studied in order to ensure that impurities at m/e 42 ($C_2H_4N^+$ nominal mass) were less than 1% of the $C_2H_4N^+$ ion intensity.

Research grade acetonitrile, methanol, and hydrogen were used. The methyl isocyanide was prepared by reacting *N*-methylformamide, toluene-*p*-sulfonyl chloride, and quinoline and was used without further purification.[6]

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(1) R. G. Cooks in "Collision Spectroscopy", R. G. Cooks, Ed., Plenum Press, New York, 1978. R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973. See also: N. M. M. Nibbering, T. Nishishita, C. C. van de Sande, and F. W. McLafferty, *J. Am. Chem. Soc.*, **96**, 5668 (1974); F. W. McLafferty, *ACS Symp. Ser.*, No. **70**, 45-47 (1978).

(2) (a) M. J. McEwan, V. G. Anicich, W. T. Huntress, P. R. Kemper, and M. T. Bowers, *Chem. Phys. Lett.*, **75**, 278 (1980). (b) L. M. Bass, P. R. Kemper, and M. T. Bowers, *J. Am. Chem. Soc.*, in press.

(3) W. T. Huntress and G. F. Mitchell, *Ap. J.*, **231**, 456 (1979).

(4) C. G. Freeman, P. W. Harland, and M. J. McEwan, *Astrophys. Lett.*, **19**, 133 (1978).

(5) R. P. Morgan, J. H. Beynon, R. H. Bateman, and B. N. Green, *Int. J. Mass Spectrum. Ion Phys.*, **28**, 171 (1978).

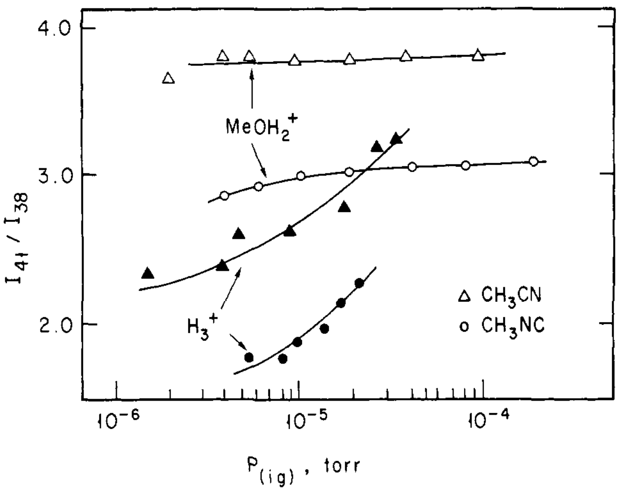


Figure 1. The ratio I_{41}/I_{38} in the CID spectra of $C_2H_4N^+$ as a function of ion source pressure. The $C_2H_4N^+$ ion is produced by: protonation of CH_3CN with $CH_3OH_2^+$ (△); CH_3CN with H_3^+ (▲); CH_3NC with $CH_3OH_2^+$ (○); CH_3NC with H_3^+ (●).

III. Results and Discussion

A. Proton Transfer to CH_3CN and CH_3NC. The MIKES-CID of $C_2H_4N^+$ ions produced by proton transfer to methyl isocyanide and acetonitrile were found to depend upon the ion source pressure and the protonating agent. The following four reactions were therefore extensively studied as a function of the ion source pressure. Although we can draw at least six reasonable structures

$$CH_3CN + CH_3OH_2^+ \rightarrow C_2H_4N^+ + CH_3OH \quad (3)$$

$$\Delta H = -6 \text{ kcal/mol}^7$$

$$CH_3CN + H_3^+ \rightarrow C_2H_4N^+ + H_2 \quad (4)$$

$$\Delta H = -90 \text{ kcal/mol}^7$$

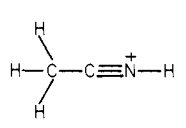
$$CH_3NC + CH_3OH_2^+ \rightarrow C_2H_4N^+ + CH_3OH \quad (5)$$

$$\Delta H = -16 \text{ kcal/mol}^7$$

$$CH_3NC + H_3^+ \rightarrow C_2H_4N^+ + H_2 \quad (6)$$

$$\Delta H = -101 \text{ kcal/mol}^7$$

a–f for the $C_2H_4N^+$ ion, intuition suggests that the ion formed from protonation of acetonitrile has the structure a while that produced from methyl isocyanide has the structure b. That at least two distinct structures are formed is supported by the experimental data in Table I and Figures 1 and 2.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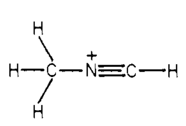
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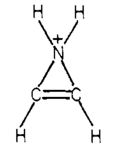
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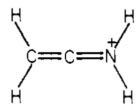
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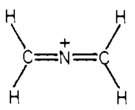
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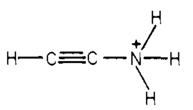
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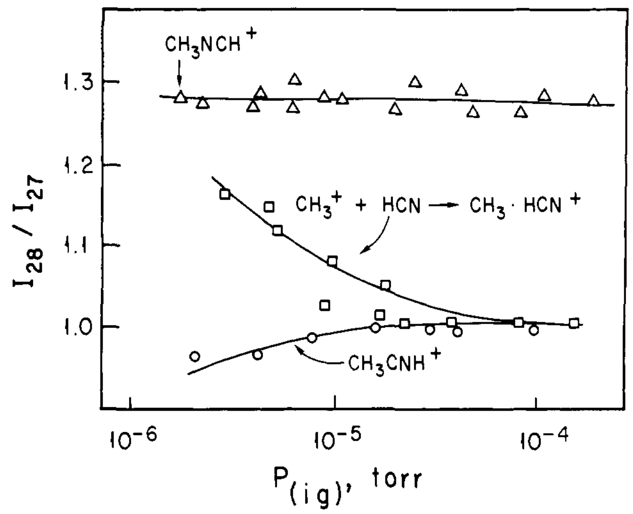

Figure 2. The ratio I_{28}/I_{27} in the CID spectra of $C_2H_4N^+$ as a function of ion source pressure: (△) $CH_3CN + CH_3OH_2^+ \rightarrow 42^+$, (○) $CH_3NC + CH_3OH_2^+ \rightarrow 42^+$, (□) $CH_3^+ + HCN \rightarrow 42^+$.

A substantial number of products are formed in the MIKES-CID experiment (Table I). Only those that are intense and diagnostic of differences in structure or internal energy content will be discussed in detail here. Figure 1 demonstrates that the ratio I_{41}/I_{38} in the CID spectrum of $C_2H_4N^+$ varies only slightly as a function of the ion source pressure for reactions 3 and 5 where $CH_3OH_2^+$ is used as the protonating agent. In reactions 4 and 6 H_3^+ is used for the protonating agent. These reactions are very exothermic and the results shown in Figure 1 demonstrate a strong dependence on the ion source pressure. As the pressure in the ion source is increased, the ratios for the highly exothermic reactions approach those of the weakly exothermic reactions.

These results may be understood by considering the internal energy content of the $C_2H_4N^+$ ions. The highly exothermic reactions 4 and 6 will produce $C_2H_4N^+$ ions with a substantial amount of internal energy which will be primarily distributed among the vibrational degrees of freedom. The pressure dependence is due to the increase in the number of stabilizing collisions as the ion source pressure is increased, reaction 1c. In reactions 3 and 5, however, the ions are produced with little or no internal energy and therefore few or no stabilizing collisions are required to yield the low internal energy CID spectra.

Figure 2 shows the ratio I_{28}/I_{27} for reactions 3 and 5, and again the dependence on pressure is weak when the exothermicity is low. The data presented in Figures 1 and 2 clearly show that protonation of CH_3CN and CH_3NC produces two distinctly different species which retain their integrity throughout the pressure regime studied.

An examination of the data in Table I indicates that the differences between $(CH_3CN)H^+$ and $(CH_3NC)H^+$ shown in Figures 1 and 2 show up in other fragment ions as well. For example, the charge stripping products, *m/e* 20, 20.5, and 21, have substantially different patterns for the two isomers. An even more dramatic difference occurs in the propensity for formation of CH_3^+ ion, *m/e* 15. The $(CH_3NC)H^+$ ion forms substantial amounts of CH_3^+ on collision with He while $(CH_3CH)H^+$ forms almost no CH_3^+. This result can be rationalized with use of structures a and b. The collision between 8 keV ions and He imparts substantial amounts of energy into the $C_2H_4N^+$ projectile ion. Hence, direct processes will be favored over those requiring substantial rearrangement. In the case of reaction 7 the thermodynamically most stable products, CH_3^+ + NCH, are formed by simple C–N bond cleavage. In the case of reaction 8 the less stable CH_3^+/CNH products would be formed by direct bond cleavage which may account for the virtual absence of CH_3^+ product ions in this system (Table I). It may also be indicative of the fact that

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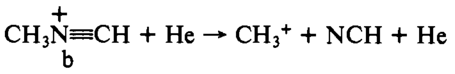
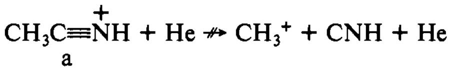
(6) J. Casanova, Jr., R. E. Schuster, and N. D. Werner, *J. Chem. Soc.*, 4280 (1963).

(7) (a) Ground state reagents are assumed in the calculation of the heat of reaction. (b) Proton affinities of acetonitrile and methylisocyanide were determined by D. Aue, M. Pedley, and M. T. Bowers, private communication. The remaining heats of formation are from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, 6 (1977).

(8) Measurements by Bass et al. have shown that some of the $C_2H_4N^+$ ion intensity is due to the reaction $CH_4^+ + HCN \rightarrow C_2H_4N^+ + H$, see ref 2b. This complication was not considered in our analysis.



$$\underset{b}{CH_3\overset{+}{N}{\equiv}CH} + He \rightarrow CH_3^+ + NCH + He \tag{7}$$

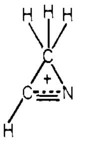


$$\underset{a}{CH_3C{\equiv}\overset{+}{N}H} + He \not\rightarrow CH_3^+ + CNH + He \tag{8}$$

structure a does not result from protonation of CH_3CN but isomerization occurs to one of the structures c–f. Further study is necessary to sort this out.

B. Reaction of CH_3^+ with HCN.[8] The exothermicity of reaction 1 is 95 kcal/mol. The ratios I_{28}/I_{27} and I_{41}/I_{38} for this reaction are plotted as a function of ion source pressure in Figures 2 and 3, respectively, and demonstrate that the CID product intensities depend upon the ion source pressure and therefore the ion internal energy as did the highly exothermic proton transfer reactions 4 and 6. These figures also show that as the ion source pressure is increased, the ratios approach those of protonated acetonitrile produced by protonation with $CH_3OH_2^+$ under low-energy conditions. Examination of the data for this reaction at high ion source pressure in Table I clearly shows that the ion produced has the same structure as protonated acetonitrile. In particular those product ions already discussed as being diagnostic *m/z* 15, (27/28), and 41 and the charge stripping ions 20, 20.5, and 21 strongly support this assignment.

Intuitively one might have expected this reaction to produce an ion with the structure b. Apparently, however, in reaction 1a the methyl cation attacks the carbon center rather than the nitrogen lone pair, possibly via the cyclic intermediate g. The



g

association complex formed can then rearrange to the same isomer as formed from protonation of CH_3CN. This latter isomer presumably has structure a but, as discussed following reaction 8, might have one of the structures c–f. An alternative explanation is that CH_3^+ + HCN react to initially form protonated methyl isocyanide which then isomerizes to protonated acetonitrile. Since this process does not occur for protonation with H_3^+ (reaction 6), a large amount of kinetic energy must be released in reaction 6 if this explanation is correct. This possibility could be checked experimentally.

Conclusions

(1) It has been generally accepted that MIKES–CID spectra for all but the lowest energy pathways depend only on the ion's structure and not on its internal energy.[9] However, the relative abundance of ions resulting from the low-energy pathways can depend upon the precursor ions' internal energy.[9,10] In the usual analysis of CID spectra[9] these low-energy processes are omitted to facilitate the comparison and analysis of spectra. In this paper we have demonstrated that careful analysis of these low-energy pathways may also be useful in structural analysis. However, since the relative importance of these processes depends upon ion source conditions extreme care must be exercised in obtaining the necessary data.

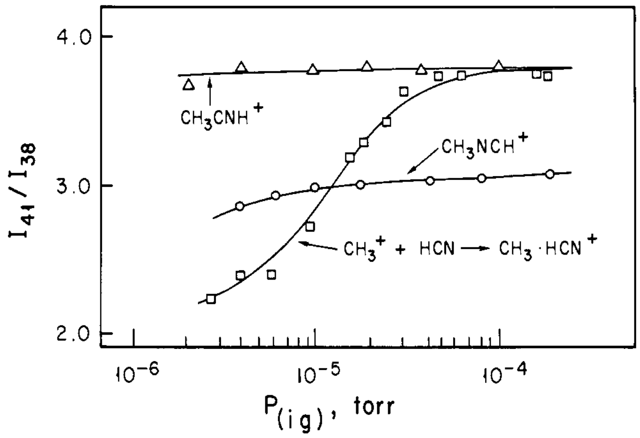


Figure 3. The ratio I_{41}/I_{38} as shown in Figure 1 with $CH_3OH_2^+$ as the protonating agent along with the data for the reaction between CH_3^+ and HCN (□).

(2) Protonated CH_3CH and CH_3NC definitely have different structures. Protonated CH_3NC is almost certainly structure b based on the propensity of the *m/e* 15 ion in its CID spectrum. Protonated CH_3CN is probably structure a but this result cannot be stated with certainly given the data in hand.

(3) The structure of the ion formed by reaction 1 under conditions when collisional stabilization dominates radiative stabilization is the same as that obtained by protonating CH_3CN with use of low-energy protonating agents.

Acknowledgment. The support of the National Science Foundation under Grant CHE77-15449 is gratefully acknowledged. We also acknowledge D. H. Aue for useful discussions and for help in synthesizing CH_3NC.

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[9] (a) See, for example: F. W. McLafferty, R. Kornfeld, W. F. Haddon, Karsten Levsen, Ikuo Sakai, P. F. Bente III, Shih-Chuan Tsai, and H. D. R. Schuddemage, *J. Am. Chem. Soc.*, **95**, 3886 (1973). (b) T. Wachs, C. C. van de Sande, P. F. Bente, P. P. Dymesaki, and F. W. McLafferty, *Int. J. Mass. Spectrum. Ion Phys.*, **23**, 21 (1977).

[10] A. J. Illies, P. A. M. Kemper, and M. T. Bowers, *Org. Mass Spectrom.*, to be submitted.