Experimental Evidence for the Existence of Cyanovinylidene :C=C(H)CN. Gas-Phase Characterization of a Possible Interstellar Molecule

Norman Goldberg and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni, D-10623 Berlin, Germany

Received: November 9, 1993; In Final Form: January 12, 1994*

Experiments on the first successful gas-phase generation of the theoretically predicted cyanovinylidene :C—C-(H)CN are reported by applying the technique of neutralization-reionization mass spectrometry.

Introduction

Over the previous years unsaturated carbene molecules of the type :C—CR₂ have been intensively investigated by experimentalists as well as theoretical chemists. Not only their chemical behavior but also their physical properties have been studied in great detail. The evaluation of the chemistry of these species will be helpful in understanding a number of mechanistic aspects of organic chemistry as several of these molecules are thought to be involved as highly reactive intermediates in condensed-phase processes.¹ This viewpoint, however, is not the only reason why these carbenes have been examined so extensively. Several of them have been discovered to exist in interstellar matter² and due to their reactivity are believed to play an important role in the chemical processes taking place in interstellar clouds.

The archetype of these molecules, the vinylidene :C=CH₂ has formed the subject of numerous investigations,³ and theoretical and experimental studies have demonstrated that vinylidene possesses an \tilde{X}^1A_1 ground state calculated to be 46.6 kcal/mol separated from its low-lying triplet state $\tilde{a}^3B_2^{3c}$ (calculated at the TZ2P CCSD(T) level).^{3b} The experimentally derived energy difference was determined to be 47.6 kcal/mol.

In a very recent theoretical paper, Hu and Schaefer reported⁴ that according to their calculations the analogous cyanovinylidene :C=C(H)CN (1)should also be an experimentally observable



species. In this ab initio study the isomerization barrier on the singlet surface for the process :C=C(H)CN (1) \rightarrow HC=CCN (2) was determined to be only 2.2 kcal/mol; the singlet-triplet splitting between the \tilde{X}^1A' and \tilde{a}^3A' states was calculated to be 42.0 kcal/mol at the TZ2P CCSD(T) level of theory. It was suggested that a carbene radical anion of 1 is a reasonable precursor to generate the triplet cyanovinylidene in an electron detachment process. The isomeric cyanoacetylene HC=CCN (2) which corresponds to the global minimum on the [C₃NH] surface has been well characterized by spectroscopic methods⁵ and is among the most abundant molecules in interstellar matter.^{5a} According to Hu and Schaefer,⁴ 2 is calculated to lie 47.2 kcal/mol below 1.

To date a number of cyanoacetylenes $H(C=C)_nCN$ have been detected in the interstellar nebulaes and planetary atmospheres of several solar systems, and in recent studies several cumulated carbenes have been observed,² thus strongly suggesting that if

the cyanovinylidene is a stable species it should exist in these regions. However, experimental evidence for the existence of cyanovinylidene (1) has *not* been reported in the literature. In this paper we wish to demonstrate that, in line with the theoretical prediction,⁴ the cyanovinylidene 1 is indeed a viable molecule in the gas phase. It can be readily generated when starting from its corresponding radical anion and is distinguishable from HCCN (2) by means of neutralization-reionization mass spectrometry (NRMS).⁶

Carbene radical anions can be conveniently generated in the gas phase by the ion-molecule reaction of the corresponding alkenes with the atomic oxygen radical anion according to eq $1.3^{3c,7,8}$

$$H_2C = CR_1R_2 + O^{*-} \rightarrow :C = CR_1R_2^{*-} + H_2O \qquad (1)$$

By starting from the so-obtained anions and examining these species by means of charge reversal $(CR)^9$ and neutralization-reionization mass spectrometry,⁶ the neutral counterparts can be generated and characterized. We were thus able to characterize recently the long-sought-after vinylidene :C=CH₂^{3c} as well as butatrienylidene :C=CH₂.⁷

Experimental Part

The collision experiments were performed using a modified ZAB four-sector tandem mass spectrometer with a BEBE configuration (B stands for magnetic and E for electrostatic analyzer). The details of the instrument have been described in previous publications.¹⁰ Acrylnitrile and the reactant gas were introduced into the source via the direct inlet system. The HCCCN⁺⁺ radical cations were generated upon dissociative electron-impact ionization of acrylnitrile. The :CC(H)CN-radical anions were obtained by reacting acrylnitrile with O*- (eq 2) which itself was produced in the electron-impact ionization of on N₂O (N₂O + $e^- \rightarrow N_2$ + O⁻⁻). Typical source conditions were: electron energy 50-100 eV, repeller voltage ca. 0 V, ion source temperature 200 °C, accelerating voltage 8 kV. The ions of interest were mass selected by means of the first magnetic (B1) and electrostatic (E1) analyzers (mass resolution $m/\Delta m \approx$ 2000). To ensure single-collision conditions, the experiments were performed at a transmission of 80% of the ion beam.¹¹ For the neutralization-reionization experiments of the cationic species, xenon was used as a neutralization agent in the first part of a tandem collision cell. The remaining ions were deflected from the beam by charging the deflector electrode (1000 V), which is situated between the two differentially pumped collision cells. The neutral molecules were reionized by colliding them with oxygen. For a particle having been accelerated to 8-keV kinetic energy, it takes approximately 4 μ s to travel from the first to the second collision cell. This value defines a minimal lifetime of the neutral molecule. In the charge-reversal experiments (CR),

^{*} Abstract published in Advance ACS Abstracts, March 1, 1994.



Figure 1. CA mass spectrum of :CCHCN⁻⁻ (collision gas helium; 80% transmission (T)).

oxygen was employed as a charge-stripping gas. For the neutralization-reionization study of the anionic species, oxygen was used as collision gas in the neutralization as well as in the reionization step. The collisional activation (CA) experiments were performed by using helium as a collision gas. In the CRNR-CA experiments the anions were neutralized and ionized with oxygen to the corresponding cations in the third field-free region of the mass spectrometer. Ions were then mass-selected with the second magnetic analyzer (B2) and collided with helium in a collision cell situated in the fourth field-free region of the machine. The resulting fragment ions were recorded by scanning the second electrostatic analyzer (E2). To improve the signal-to-noise ratio of the spectra, 10-30 scans were accumulated and on-line processed with the AMD-Intectra data system.

Results and Discussion

Reactions of O^{\leftarrow} with organic molecules have found wide application for the generation of highly reactive intermediates.⁸ Many of the former "H₂^{•+}" transfer reactions to O^{\leftarrow} have been shown to produce carbenic radical anions, proceeding via a 1,1 elimination.^{3c,7,8} The high efficiency of the abstraction process in these oxidation reactions can be rationalized by the strong driving force for the formation of the thermochemically stable water molecule. The cyanovinylidene radical anion can therefore be readily generated in the ion-molecule reaction of acrylnitrile H₂C=CHCN and O^{•-} (eq 2).

$$H_2C = C(H)CN + O^{-} \rightarrow :C = C(H)CN^{-} + H_2O$$
 (2)

The collisional-activation mass spectrum of 1^{-} is given in Figure 1. The most abundant fragment ion observed upon colliding the anions with helium corresponds to the H[•] loss (m/z 50). The intense HCCN⁻⁻ signal (m/z 39) results from the structure-indicative loss of a carbon atom. The other fragments cannot be related to a specific ion structure. Nevertheless, the strong signal for the cyanocarbene anion HCCN⁻⁻ clearly suggests that the radical anion generated from H₂C=C(H)CN corresponds to :C=C(H)CN⁻⁻ (1⁻⁻).

For a further assessment of the ion connectivity the beam of $:C \longrightarrow C(H)CN^{-1}$ radical anions was subjected to a charge reversal experiment. The spectrum (Figure 2) exhibits a strong survivor signal for the charge-reversed anions. Furthermore, as in the CA spectrum of 1⁻⁻, a strong signal for the structure-indicative C_1 loss is observed. This HCCN⁺⁺ ion is certainly not very likely to result from a molecule possessing a terminal C-H group, as the expulsion of a carbon atom from such a structure would necessarily involve multiple rearrangement processes prior to fragmentation. All other fragments can be assigned to the carbonic as well as the acetylenic linear structure and do not permit a further interpretation.



Figure 2. CR mass spectrum of :CC(H)CN⁻⁻ (collision gas oxygen; 80% T).



Figure 3. CR-NR mass spectrum of :CC(H)CN⁻⁻ (collision gases oxygen; 80% T//oxygen; 80% T).

To provide evidence for the existence of the theoretically predicted,⁴ neutral cyanovinylidene 1, the anion 1^{•-} was subjected to a CR-NRMS experiment. In this two-step collision experiment the ion beam was oxidized by using molecular oxygen as a target gas in both collision events. The CRNS spectrum (Figure 3) reveals a strong survivor signal at m/z 51. This observation not only demonstrates that cyanovinylidene 1 is a viable species in the gas phase surviving the transit time between the two collision processes but points to quite favorable Franck-Condon factors in the vertical electron transfers of the two ionization steps.¹² In keeping with the structural assignment of :C=C(H)CN, a relatively strong HCCN⁺⁺ signal (m/z 39) is observed, which results from the elimination of a carbon atom. The fact that this fragmentation process, which is disfavored by ca. 28 kcal/mol over the HCC⁺ + CN⁻ dissociation path,¹³ does take place at such a high rate underscores the assessment of the correct ion and neutral structure. In addition, the spectrum exhibits a notable fragment ion at m/z 12, corresponding to C^{*+} loss from the cumulated carbene. The other observed ions do not reveal structure-specific fragmentation processes characteristic of either 1 and 2.

To firmly establish that no rearrangement processes have taken place after the neutralization step of 1^{•-} and to ensure that the survivor signal in the CR-NR spectrum does indeed consist of the ionized carbene 1, ^{•+} a collisional activation spectrum of the survivor ions:CC(H)CN⁺⁺ was recorded. This CR-NR-CA mass spectrum, corresponding to an MS/MS/MS experiment, is displayed in Figure 4. The strongest peak observed corresponds to H[•] loss. Again, as in the fragmentations of the charge-reversed and neutralized-reionized cyanovinylidene anions, the structureindicative C₁ loss giving rise to HCCN⁺⁺ (m/z 39) occurs with a high abundance, thus demonstrating that the molecule has preserved its structural integrity in the CRNR process. This



Figure 4. CR-NR-CA mass spectrum of :CC(H)CN^{*-} (collision gases oxygen; 80% T//oxygen; 80% T//helium 80% T).



Figure 5. CA mass spectrum of HCCCN⁺⁺ (collision gas helium; 80% T).

observation clearly demonstrates that neutral cyanovinylidene 1 is indeed a stable species within the time frame of the mass spectroscopic experiment. In addition, it shows that also the cationic form 1^{++} is stable and does not undergo facile isomerization in the gas phase.

For a further experimental support of our assignment, the cyanoacetylene radical cation 2.+ was generated and subjected to CA as well as an NRMS experiment. This ion can be generated from acrylnitrile under dissociative electron-impact ionization. The acrylnitrile radical cation readily loses H₂ presumably in a 1,2-elimination process. The CA spectrum of the cyanoacetylene radical cation 2^{•+} is given in Figure 5. In contrast to the CA spectrum of the cyanovinylidene cations produced in the CR-NR process, only a negligible signal at m/z 39, corresponding to HCCN⁺⁺, was observed. This result is in keeping with the structure of a linear acetylene. The radical cation possesses terminal HC and CN groups and cannot fragment into HCCN*+ and C in a one-step unimolecular process. Another striking difference is the considerably stronger H[•] loss from 2^{•+} as compared with 1*+. This indicates that the vinylidene species 2*+ seems to possess enough initial energy to fragment into other more endothermic products in contrast to the cyanoacetylene radical cation 1*+ which preferably decomposes to CCCN+ and H[•]. This reaction channel is probably the lowest pathway for both systems.

For comparison the corresponding NR spectrum of 2^{*+} is given in Figure 6. In this experiment the radical cation 2^{*+} was neutralized and reionized under the same experimental conditions that were employed for recording the CRNR spectrum of 1. The NR spectrum of 2^{*+} displays distinct differences to 1^{*+} giving essentially no signal for the HCCN*+ fragment (loss of C₁).



Figure 6. NR mass spectrum of HCCCN^{*+} (collision gases xenon, 80% T//oxygen 80% T).

These experiments clearly demonstrate that the neutral cyanovinylidene 1 is indeed a viable molecule that can be generated and structurally characterized by means of mass spectroscopic techniques. As indicated by the theoretical investigations,⁴ the neutral molecule :C=C(H)CN is most likely generated in the triplet state \tilde{a}^3A^1 . Furthermore, experimental evidence for the existence of the corresponding cyanovinylidene anion 1^{•-} as well as the cation^{*+} has been presented.

Acknowledgment. The financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is appreciated.

References and Notes

(1) Stang, P. J. Chem. Rev. 1978, 78, 383.

(2) (a) Smith, D. Chem. Rev. 1992, 92, 1473.
 (b) Böhme, D. K. Chem. Rev. 1992, 92, 1487.

(3) (a) Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W.
C. Chem. Phys. Lett. 1983, 100, 124. (b) Ervin, K. M.; Ho, J.; Lineberger,
W. C. Chem. Phys. 1989, 91, 5974. (c) Sülzie, D.; Schwarz, H. Chem. Phys. Lett. 1989, 156, 397. (d) Collins, C. L.; Meredith, C.; Yamaguchi, Y.; Schaefer, III, H. F. J. Am. Chem. Soc. 1992, 114, 8694. (e) Vacek, G.; Russell, T. J.; DeLeeuw, B. J.; Yamaguchi, Y.; Schaefer, III; H. F. J. Chem. Phys. 1993, 98, 4766.

(4) Hu, C.-H.; Schaefer, III, H. F. J. Phys. Chem. 1993, 97, 10681.

(4) Int. C-I., Schalter, II., I. I. J. Int. I. J. Inf. Comm. 1205, 17, 16001.
 (5) (a) Morris, M.; Turner, B. E.; Palmer, P.; Zuckerman, B. Astrophys.
 J. 1976, 205, 82. (b) Cresswell, W. A.; Winnewisser, G.; Gerry, M. C. L. J.
 Mol. Spectrosc. 1977, 65, 421. (c) DeFrees, D. J.; McLean, A. D. Chem.
 Phys. Lett. 1989, 158, 540.

(6) (a) Terlouw, J. K.; Burgers, P. C.; van Baar, B. L. M.; Weiske, T.;
Schwarz, H. Chimia 1986, 40, 357. (b) Wesdemiotis, C.; McLafferty, F. W.
Chem. Rev. 1987, 87, 485. (c) Terlouw, J. K.; Schwarz, H. Angew. Chem.,
Int. Ed. Engl. 1987, 26, 805. (d) Schwarz, H. Pure Appl. Chem. 1989, 61,
685. (e) Holmes, J. L. Mass Spectrom. Rev. 1989, 8, 513. (f) Terlouw, J.
K. Adv. Mass Spectrom. 1989, 11, 984. (g) McLafferty, F. W. Science 1990,
247, 925. (h) McLafferty, F. W. Int. J. Mass Spectrom. Ion Processes 1992,
118/119, 221.

(7) Goldberg, N.; Sülzle, D.; Schwarz, H. Chem. Phys. Lett. 1993, 213, 593.

(8) For a review of the reactions of O[⊷] with organic molecules, see: Lee, J.; Grabowski, J. J. Chem. Rev. 1992, 92, 1611.

(9) Reviews: (a) Bowie, J. H. Mass Spectrom. Rev. 1984, 3, 161. (b)
Levsen, K.; Schwarz, H. Mass. Spectrom. Rev. 1985, 4, 77. (c) Bursey, M.
M. Mass Spectrom. Rev. 1990, 9, 55.

(10) (a) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H.
 J. Am. Chem. Soc. 1991, 113, 5970. (b) Srinivas, R.; Böhme, D. K.; Sülzle,
 D.; Schwarz, H. J. Phys. Chem. 1991, 95, 9836. (c) Srinivas, R.; Sülzle, D.;
 Weiske, T.; Schwarz, H. Int. J. Mass Spectrom. Ion Processes 1991, 107, 369.
 (11) Holmes, L. Org. Mass. Spectrom. 1985, 20, 5874.

Weiske, 1.; Schwarz, H. Int. J. Mass Spectrom. 10n Processes 1991, 107, 369.
(11) Holmes, J. L. Org. Mass Spectrom. 1985, 20, 5874.
(12) (a) Fournier, P.; Appell, J.; Fehsenfeld, F. C.; Durup, J. J. Phys. B
1972, 5, L58. (b) Fehsenfeld, F. C.; Appell, J.; Fournier, P.; Durup, J. Phys. B
1973, 6, L268. (c) Lorquet, J. C.; Leyh-Nihaut, B.; McLafferty, F. W. Int. J. Mass Spectrom. Ion Processes 1990, 100, 465.

(13) This value was derived from an estimation of the enthalpies of formation for both processes. The data were taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. Phys. Chem. Ref. Data 1988, 17, Suppl. 1.