

Evidence for a difference in the dissociation mechanisms of acetylene (HCCH) and vinylidene ($\text{H}_2\text{C}=\text{C}:$) from charge inversion mass spectrometry

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Received 9th January 2003, Accepted 11th April 2003

First published as an Advance Article on the web 1st May 2003

Vinylidene and acetylene are the simplest hydrocarbon isomers, and vinylidene is the simplest unsaturated carbene. The charge inversion mass spectra of C_2H_2^+ cations derived from acetylene using Na, K, Rb and Cs targets were found to be clearly different from those derived from vinylidenechloride (1,1-dichloroethylene). The process of formation of the negative ions in charge inversion mass spectrometry is *via* near-resonant neutralization followed by spontaneous dissociation, and then endothermic negative ion formation. The intensity of the C_2^- peak relative to the C_2H^- peak in these spectra increased with decreasing ionization potential of the targets for both of the isomeric C_2H_2^+ cations. The formation of the C_2^- anion is proposed to result from the dissociation of excited C_2H_2 neutrals into C_2 and H_2 . The dependence on target species of the intensities of the C_2^- peak relative to the C_2H^- peak for HCCH and $\text{H}_2\text{C}=\text{C}:$ cannot be rationalized by the internal energy of the excited C_2H_2 neutrals. The differences indicate that the isomeric C_2H_2 neutrals dissociate into C_2H and H prior to 1,2-hydrogen atom migration.

1. Introduction

Isomerization reactions that involve migration of hydrogen atoms, such as 1,2-hydrogen shifts, play a critical role in a number of complex chemical reactions. Vinylidene ($\text{CH}_2=\text{C}:$) is the simplest unsaturated carbene and is important as an intermediate in many chemical reactions.¹ Since vinylidene and acetylene (HCCH) are the simplest hydrocarbon isomers, the 1,2-hydrogen atom migration between the cations,²⁻⁴ the neutral species,⁵⁻⁸ and the anions^{2,9} of vinylidene and acetylene has been the subject of numerous recent experimental and theoretical investigations. The lifetime of vinylidene has also been reported.^{3,8,9} A few years ago, it was suggested from both experimental and theoretical results¹⁰⁻¹⁷ that the ground-state of vinylidene has a shallow minimum in the potential energy surface and exists only on the picosecond timescale. In 1998, Levin *et al.*⁸ used a coulomb explosion imaging technique¹⁸ to show that more than 50% of the initial population of the vinylidene formed by electron detachment from vinylidene anion still remained 3.5 μs after the electron detachment. Hayes *et al.*⁵ attempted to reconcile the apparent violation of conventional transition-state theory suggested by these experimental results by using *ab initio* molecular dynamics calculations.

We have demonstrated previously³ using charge inversion mass spectrometry that the C_2H_2^+ cation formed from vinylidene chloride (CH_2CCl_2) has vinylidene structure and a lifetime longer than 8.5 μs . At the same time, Jursic² reported results from high-level *ab initio* calculations indicating that there is practically no activation barrier for rearrangement of the vinylidene radical cation into the acetylene radical cation.

In our present work, the existence of a long-lived vinylidene cation is confirmed and the dissociation of vinylidene and acetylene formed *via* near-resonant neutralization from corresponding cations is investigated.

2. Experimental

In our charge inversion mass spectrometer, mass-selected positive ions are made to collide with alkali metal targets, and the resulting negative ions formed upon two-electron transfer are mass analyzed.¹⁹ The MS/MS instrument utilizes a double focusing mass spectrometer as MS-I to mass-separate precursor ions, and a cylindrical electrostatic analyzer (ESA) as MS-II to mass-analyze secondary ions. Positive precursor ions are formed by electron impact ionization and are accelerated to 3 keV kinetic energy. The mass-separated precursor ions enter a 3 cm long target chamber which is located between the two analyzers. The alkali metal target is supplied as a vapor from a reservoir through a ball valve. The target chamber, the ball valve and the reservoir are thermally controlled in order to control the alkali metal density in the target chamber. Neutralization, dissociation and anionization take place in the target chamber filled with alkali metal vapor.

3. Results

Fig. 1A and B show the charge inversion spectra measured using the Rb target for the isomeric C_2H_2^+ cations obtained by electron impact on acetylene (HCCH) and vinylidene

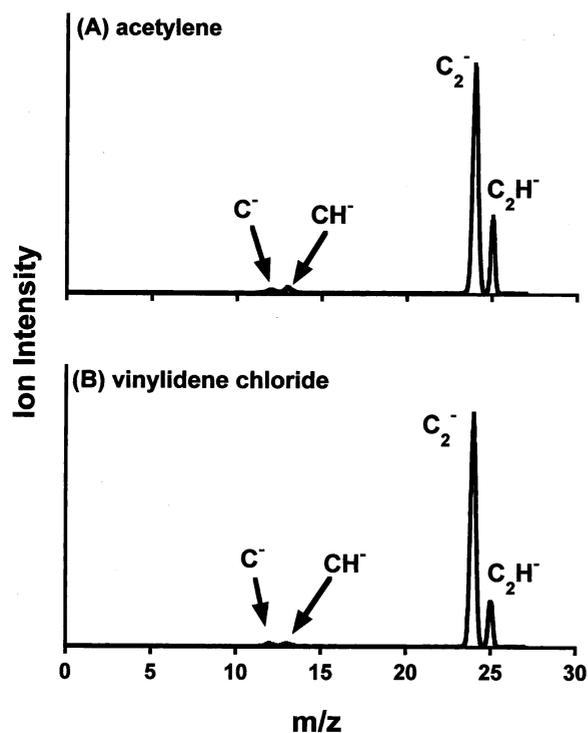


Fig. 1 Charge inversion mass spectra of $C_2H_2^+$ ions obtained by electron impact on acetylene (A) and vinylidene chloride (B). The target was Rb and the collision energy was 3 keV. A clear difference in the charge inversion mass spectra of the $C_2H_2^+$ ions for acetylene and vinylidene chloride is evident in the mass region of 24–25.

chloride (CH_2CCl_2), respectively. In both spectra, the dominant peaks are those associated with $C_2H_n^-$ ($n = 0, 1$) ($m/z = 24, 25$), resulting from loss of hydrogen atoms, whereas the peaks associated with CH_n^- ($n = 0-2$) ($m/z = 12-14$), resulting from C–C bond cleavage, have significantly lower intensity. There is a clear difference in the intensity of the C_2^- peak relative to the C_2H^- peak for the acetylene and vinylidene chloride spectra shown in Fig. 1. This difference is attributed to the $C_2H_2^+$ ions formed from CH_2CCl_2 having vinylidene structure as discussed in our previous work.³ The charge inversion mass spectra using Na, K, and Cs targets were also measured for the isomeric $C_2H_2^+$ cations. The peaks associated with $C_2H_n^-$ ($n = 0, 1$) were dominant, whereas the peaks associated with CH_n^- ($n = 0-2$) were of significantly lower intensity.

The magnified charge inversion spectra of $C_2H_2^+$ ions obtained from vinylidene chloride on collision with Cs (A), Rb (B), K (C), and Na (D) targets are shown in Fig. 2. The relative intensities of C_2^- peaks to C_2H^- peaks depend strongly on the target species, as shown clearly in Fig. 2. The non-dissociative $C_2H_2^-$ ion peak was not observed for any of the targets used. We have reported previously¹⁹ the charge inversion spectra of $C_2H_2^+$ ions obtained from acetylene using Cs, K, and Na targets. Fig. 3 shows the intensities of the C_2^- peak relative to the C_2H^- peak for both of the isomeric $C_2H_2^+$ cations. These data have been corrected for the influence of $^{13}CCH^+$ ions, as discussed previously.³ It is evident from Fig. 3 that a clear difference exists between these ratios for acetylene and vinylidene for each of the targets used. For both isomeric $C_2H_2^+$ cations, the intensity of the C_2^- peak relative to the C_2H^- peak decreases with increasing of ionization potential of the targets, and the relative intensities are larger for the vinylidene cation than the acetylene cation for each of the alkali metal targets. Though Jursic reported² that the activation barrier for the vinylidene cation rearrangement into the acetylene cation does not exist, these clear differences in

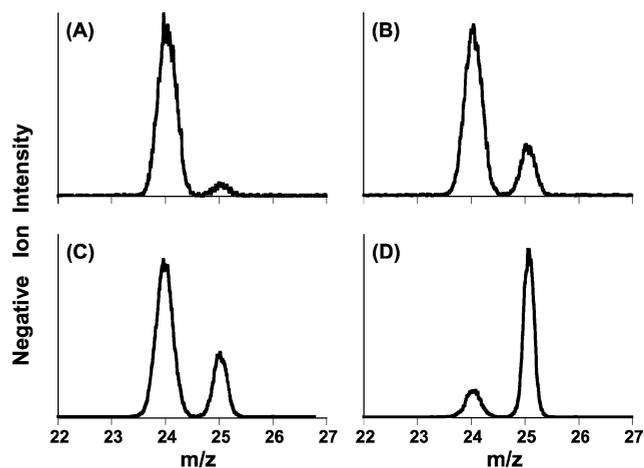


Fig. 2 The charge inversion spectra of $C_2H_2^+$ cation in the mass range of 22–27 on collision with Cs (A), Rb (B), K (C), and Na (D) targets. The projectile ion was $C_2H_2^+$ ion obtained from the vinylidene chloride and the collision energy was 3 keV.

relative intensities in the charge inversion spectra of the isomeric $C_2H_2^+$ cations demonstrate that the long-lived vinylidene cation does exist.

4. Discussion

The reaction process

In the charge inversion spectra shown in Fig. 1 and 2, dissociative negative ions formed from positive ions by transfer two electrons are overwhelmingly more abundant than non-dissociative negative ions. The formation of the negative product ions produced by transfer of two electrons in the charge inversion mass spectrometer may involve either double electron transfer in one collision or successive single electron transfer in two collisions. The reaction process for double electron transfer in a single collision is shown in reactions (1) and (2), where AB^+ , T and A^- are a projectile positive ion, a target and a product negative ion, respectively. In this process, dissociation takes place after negative ion formation.

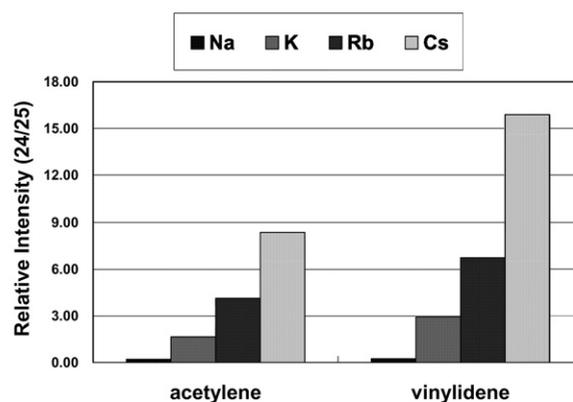
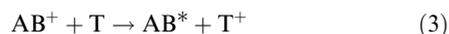


Fig. 3 Relative intensities of C_2^- peak to C_2H^- peak in the charge inversion mass spectra of $C_2H_2^+$ ions obtained by electron impact on acetylene and vinylidene chloride. The targets were Cs, Rb, K, and Na. Clear differences between acetylene and vinylidene in these relative intensities are evident for each of the targets used.

The reaction process for successive single electron transfers in two collisions is shown in reactions (3)–(5), where the dissociation takes place after neutralization.



By using the single-focusing charge inversion mass spectrometer with an alkali metal target, we have measured the target density dependence of the product negative ions by monitoring the target density using surface ionization of the alkali metal target.^{20,21} Dissociative C_2^- and C_2H^- ion formation from the acetylene cation showed a quadratic dependence on the target density, while non-dissociative C_2^- and C_2H^- ion formation from C_2^+ and C_2H^+ observed only for a Cs target showed a linear dependence. From this measurement, it was confirmed that non-dissociative C_2^- and C_2H^- ions were formed by double electron transfer in a single collision, whereas dissociative C_2^- and C_2H^- ions from $C_2H_2^+$ ions were formed by successive single electron transfer in two collisions.

The endothermicity for reaction (1) in which all of the components are in their ground states is given by:

$$\Delta E = IE(T) + IE(T^+) - IE(AB) - EA(AB) \quad (6)$$

where IE and EA are the ionization energy and electron affinity, respectively. The ionization energies of the alkali metals are shown in Table 1. While alkali metals have small ionization energies, IE(T), alkali metal cations have large ionization energies, IE(T^+), as shown in Table 1. While the electron affinity of acetylene is negative, the electron affinity of vinylidene was reported to be 0.490 ± 0.006 eV.¹⁰ The ionization energy of vinylidene was calculated to be 11.33 eV by using the energy difference between acetylene cation and vinylidene cation calculated by Jursic.² The endothermicities for reaction (1) evaluated using these values for the vinylidene cation are also shown in Table 1.

The experimental^{22–24} and theoretical^{25,26} treatment for double electron transfer in one collision indicates the existence of a reaction window for the reaction. Griffiths *et al.* reported²⁴ that the cross-section for double electron transfer for OH^+ and F^+ ions maximized when the reaction endothermicity has a value between 10 and 14 eV. The estimated endothermicities for vinylidene are much larger than the value of reaction window. The absolute cross-sections measured for C_2^- and C_2H^- ion formation by way of double electron transfer in one collision with a Cs target whose endothermicities are 13.59 and 14.04 eV, respectively, are in the order of 10^{-18} – 10^{-17} cm².²⁷ The peak intensities associated with these non-dissociative C_2^- and C_2H^- ion formations were much lower than those for dissociative C_2^- and C_2H^- ion formation from $C_2H_2^+$ ions on collision with alkali metal targets.²⁸

Although the vinylidene anion is metastable, the lifetime of the anion is reported to be 110 s,⁹ which is much longer than the estimated flight time of the vinylidene anions from the target chamber to the detector of 3.9 μ s. If the vinylidene anion is

formed by the double electron transfer in reaction (1), then it would be expected that $C_2H_2^-$ ions would be detected by the charge inversion mass spectrometer. The fact that vinylidene negative ions were not observed in the charge inversion spectra is explained by the large endothermicities of double electron transfer in one collision of reaction (1). If dissociative negative ions are formed from double electron transfer in a single collision by reactions (1) and (2), then the bond energy for the dissociation must be added to the endothermicities of the double electron transfer reactions. As a result of the large endothermicity, the cross-sections of double electron transfer accompanied with the bond dissociation are estimated to be very small.

In previous work, collisionally activated dissociation (CAD) spectra and charge inversion spectra were measured for two types of so-called thermometer molecules, namely partially deuterated methanol²⁹ and $W(CO)_6$.³⁰ The differences between the CAD spectra and the charge inversion spectra of partially deuterated methanols demonstrated that the major process in the charge inversion involves dissociation of the excited neutral species as shown in reaction (4). The internal energy deposition of the charge inversion measured for $W(CO)_n^+$ ($n = 4–6$) ions indicated that dissociation occurs in the energy-selected neutrals formed by way of near resonant neutralization. This fact confirmed that the neutralization reaction (3) is a near-resonant process. These discussions for the reaction processes in the charge inversion mass spectrometer were in accordance with the explanation in the recent review.¹⁹ On the basis of these findings, it was concluded that the process of formation of the negative ions in charge inversion mass spectrometry is *via* near-resonant neutralization followed by spontaneous dissociation, and then endothermic negative ion formation, as shown in eqn. (3)–(5). Fig. 4 shows the schematic description of near-resonant neutralization. A near-resonant process is one in which the energy level of the reactants AB^+ and T is almost as same as that of the products, AB^* and T^+ . In comparison with the energy level of AB, AB^* has an energy lower than the energy level of AB^+ by an amount equal to the ionization energy of the alkali metal target, as shown in Fig. 4. The ionization energy of the projectile is usually much higher than the ionization energies of alkali metals. Since the energy level of AB^* is higher than that of the fragments A and B when using an alkali metal as a target, AB^* dissociates spontaneously, as shown in reaction (4).

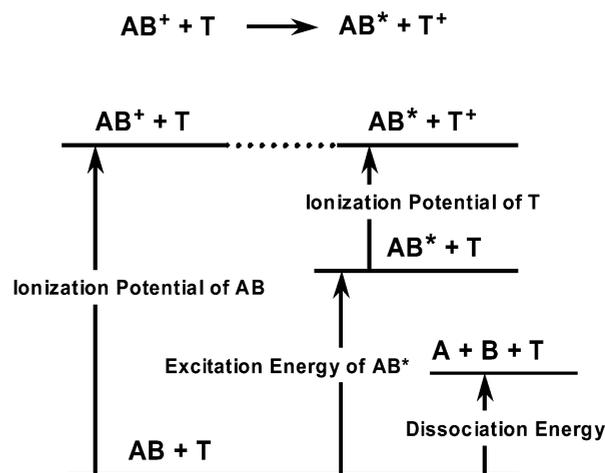


Fig. 4 The schematic description of near-resonant neutralization. The energy level of AB^* formed near-resonant neutralization are usually higher than that of the fragments A and B when using an alkali metal as a target.

Table 1 Ionization energies (IEs) and endothermicities evaluated using the ionization energies for the reaction (1). IEs are cited from ref. 31

Species	Cs	Rb	K	Na
First IE	3.893	4.176	4.339	5.138
Second IE	25.08	27.51	31.81	47.29
Endothermicity	17.15	19.87	24.33	40.61

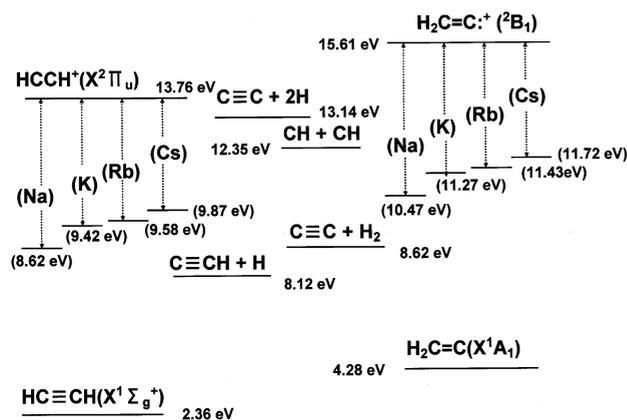


Fig. 5 Heats of formation of C_2H_2 , its fragments, and $C_2H_2^+$ ions in electron volts. The $CH_2=C^+$ shown in this figure is the 2B_1 ground state. The values shown in parentheses are the energy values predicted for near-resonant neutralization.

Interpretation of the results

The heats of formation for C_2H_2 , its fragments, and $C_2H_2^+$ ions are shown in Fig. 5, with most of the thermochemical data shown in this figure being taken from ref. 32. The near-resonant levels, which have energies lower than the energy level of the corresponding cations by an amount equal to the ionization potentials of the alkali metal targets, are also shown in Fig. 5. The thermochemical data for vinylidene and its cation have not been reported experimentally, so these levels were estimated using the energy difference between acetylene and vinylidene calculated by Jursic.²

Fig. 5 shows that two independent C–H bond cleavages to form $CC + 2H$ is endothermic by 0.79 eV compared with CC triple bond cleavage, and H_2 loss to form C_2 is exothermic by 3.73 eV compared with the CC triple bond cleavage. Two endothermic C–H bond cleavages should result in a smaller branching ratio than the CC bond cleavage because simple bond cleavages do not generally have activation energies. The energy levels of the neutral species formed by near-resonant neutralization from $HCCH^+$, as shown in Fig. 5, are much lower than those of $CC + 2H$ and $CH + CH$, and a few eV higher than that of $CC + H_2$. The excited neutrals cannot dissociate into fragments with higher energy levels, but dissociate spontaneously into those with lower energy levels. The large intensity ratios of the C_2^- peak to the CH^- peak for all of the targets indicates that C_2 does not result from two C–H bond cleavages but rather from loss of H_2 .

For both isomeric cations, the intensities of the C_2^- peak relative to the C_2H^- peak decrease with increasing ionization potential of the target, as shown in Fig. 3. The $C_2 + H_2$ level is a little higher than that of $CCH + H$. Processes which involve both bond dissociation and bond formation together with structural rearrangement usually require higher activation energy than that for a simple bond cleavage. Therefore, the transition state in the formation of $C_2 + H_2$ from the C_2H_2 isomers is expected to have a higher activation energy than that for the simple cleavage into $CCH + H$. The higher internal energy of excited neutrals formed using targets with lower ionization potential make it easier for these excited neutrals to dissociate into fragments with higher activation energy. The observed dependence of relative intensities of the C_2^- peak to the C_2H^- peak on target species is explained by this difference in activation energy for bond cleavage accompanied by structural rearrangement into $C_2 + H_2$ compared with simple bond cleavage to form $C_2H + H$.

The heat of formation of the vinylidene cation has not been determined experimentally, but is calculated to be 1.85 eV higher than that of the acetylene cation.² The energy levels

of the neutral species formed by near-resonant neutralization were assumed to have the same difference in energies for both of the isomeric cations. If these neutral species isomerize before dissociation, then the branching ratios of the dissociation will depend only on the internal energy of acetylene and vinylidene. As shown in Fig. 5, the energy level of excited acetylene formed *via* near-resonant neutralization with a Cs target, having the lowest ionization potential, is lower than that of the excited vinylidene formed with a Na target having the largest ionization potential in the alkali metals used in the present work. Fig. 3 shows that the intensities of the C_2^- peak relative to the C_2H^- peak for acetylene with a Cs target is much larger than that of the vinylidene with a Na target. This difference in relative intensity cannot be rationalized by the internal energy of the excited neutrals, so is attributed to a difference between the structures of the acetylene and vinylidene cations. The differences in these relative intensities for acetylene and vinylidene demonstrate that excited C_2H_2 neutrals formed *via* neutralization dissociate prior to isomerization.

Since the dissociation process to form $C_2H + H$ from both acetylene and vinylidene involves a simple cleavage of a C–H bond, the barrier to the dissociation is expected to be smaller than that for the process associated with the structural rearrangement to form $C_2 + H_2$. While the barrier involved in the dissociation process to form $C_2 + H_2$ from vinylidene is estimated to be very small, the barrier to formation of $C_2 + H_2$ from acetylene is expected to be larger due to the structural deformation required to form the H–H bond.³³ Therefore, the observed difference in the intensities of the C_2^- peak relative to the C_2H^- peak between acetylene and vinylidene is attributed to this difference in the barrier to dissociation into $C_2 + H_2$. It is currently unclear whether the dissociation mechanism from acetylene to form $C_2 + H_2$ proceeds *via* a transition state to dissociation, or *via* a vinylidene structure prior to dissociation. It should be possible to determine the dominant process by comparison with theoretical calculations.

The present work has demonstrated that the dissociation mechanism of highly excited neutral C_2H_2 isomers formed from isomeric $C_2H_2^+$ cations involves dissociation into $C_2H + H$ prior to isomerization. This is the same behaviour as for ground-state vinylidene formed from the vinylidene anion as reported by Hayes *et al.*⁵ and Levin *et al.*⁸

Acknowledgements

Grants in aid for scientific research for the Ministry of Education, Culture, Sports, Science and Technology under Grant No.13640515 are gratefully acknowledged.

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