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The Protonation of Allene and Some Heteroallenes, a Computational Study

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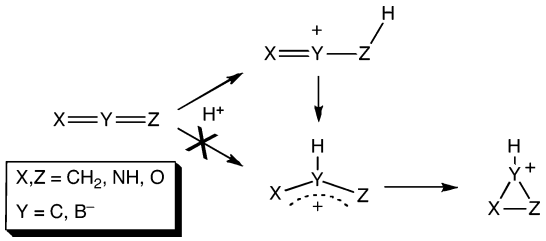

Protonation of allene and seven heteroallenes, X = Y = Z, at the terminal and central positions has been studied computationally at the MP2/6-311+G**, B3LYP/6-31+G**, and G3 levels. In all but one case protonation at a terminal position is preferred thermodynamically. The exception is allene, where protonation at C2 giving allyl cation prevails by about 10 kcal/mol over end-protonation, which gives the 2-propenyl cation. In the heteroallenes, protonation at a terminal carbon is strongly favored, activated by electron donation from the other terminal atom. Transition states for identity proton-transfer reactions were found for 10 of the "end-to-end" proton transfers. When the transfer termini are heteroatoms these processes are barrier free. We found no first-order saddle point structures for "center-to-center" proton transfers. An estimate of $\Delta H^{\ddagger}$ for an identity center-to-center proton transfer could be made only for the reaction between the allyl cation and allene; it is ~22 kcal/mol higher than $\Delta H^{\ddagger}$ for the end-to-end proton transfer between the 2-propenyl cation and allene. First-order saddle points for the proton transfer from H_3S^+ to both C1 and C2 of allene were found. The difference in activation enthalpies is 9.9 kcal/mol favoring protonation at C1 in spite of the thermodynamic disadvantage. We infer that protonation of X = Y = Z at central atoms passes through transition states much like primary carbenium (nitrenium, oxenium) cations, poorly conjugated with the attached vinylic or heterovinylic group. Several other processes following upon center protonation were studied and are discussed in the text, special attention being given to comparison of open and cyclic isomers.

Introduction

Allenes and heteroallenes may formally be considered as variants of the generalized structure X = Y = Z, for which the most simple, unsubstituted heteroallene category includes ketene, ketenimine, diazomethane, carbodiimide, carbon dioxide, isocyanic acid, and other, similar combinations of atoms X, Y, and Z. Electrophilic addition reactions of these compounds are common, including acid-catalyzed hydration, hydrohalogenation, and, in the case of diazomethane, the methylation of nucleophiles.

Acid-catalyzed addition of substances, H-Nu, to allene proceeds through the 2-propenyl cation leading to $CH_2{=}C(Nu){-}CH_3$ rather than via the allyl cation that would deliver $CH_2{=}CH{-}CH_2{-}Nu$, even though the allyl cation is the more stable ion by 10 kcal/mol (gas phase).[1] Good examples include addition

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of the hydrogen halides[2a] and acid-catalyzed hydration that produces acetone, via its enol.[2b] Clearly formation of the 2-propenyl cation is kinetically favored, a result that has been discussed previously,[2c,d] and not only for the reaction in solution, but in the gas phase as well.[2e,f] Similarly, protonation of ketene is known to occur at the outer, CH_2 group, rather than at the inner carbon,[3] and the well-known methylation of carboxylic acids and related compounds by diazomethane occurs by protonation at the carbon.[4]

We were interested to see if protonation at one of the terminal atoms, X or Z, is a general preference, kinetically and/or thermodynamically, among allenic compounds. We have carried out an ab initio study at the G3 level of the proton affinities ($PA = -\Delta H°_{ACID}$) and at the MP2/6-311+G** level of transition state structures for identity proton-transfer reactions, where proton transfer occurs both at terminal and at central atoms of allene, ketene, ketenimine, diazomethane, carbodiimide, carbon dioxide, isocyanic acid, and the 2-boraallene anion. Proton affinities and heats of isomerization were also obtained for several of the isomers of these species. Additional calculations on the X = Y = Z species, their isomers, and their conjugate acids were made at the B3LYP/6-31+G** level. General references to the chemistry of X = Y = Z compounds include the following: allenes,[2] ketenes,[3] ketenimines,[5] diazoalkanes,[4,6] and isocyanic acid.[7] A useful account of the boron−carbon double bond is given by Eisch.[8] Our previous computational work in this area contains many references to gas-phase experimental and computational studies on proton-transfer reactions.[9]

Methods

All structures were built and optimized at the HF/3-21 or HF/6-31G* level by using the MacSpartan Plus software package.[10] Conformational preferences were established at these or higher levels, before completing the geometry optimizations at the HF/6-311+G** and MP2/6-311+G** levels with use of the GAUSSIAN 03 quantum mechanical package.[11] Frequencies and zero-point vibrational energy (ZPVE) corrections were calculated at HF/6-311+G** for all structures and, to verify that electronic energy minimization had been attained, at MP2/6-311+G** for X = Y = Z compounds, their isomers, and their conjugate acids as well. ZPVEs were scaled by 0.9135 (HF) or 0.9748 (MP2).[12] B3LYP/6-31+G** and G3 calculations were completed for the X = Y = Z compounds, their isomers, and conjugate acids. Complexes and transition states were only calculated at the MP2/6-311+G** level except for structure **10**, the cyclopropyl cation, which is the ts for disrotatory ring opening to the allyl cation. Only the G3 values include thermal corrections. With two exceptions all reported structures had the correct number of imaginary frequencies: none for the reactants and complexes and one (the transfer coordinate) for the transition states. The first exception is structure **7**, the ts for rotation about a CC bond in the allyl cation, for which a first-order saddle point was found at the HF level, but not at MP2. The other is structure **9**, a model for the ts for the identity proton-transfer reaction between the central carbons of the allyl cation and allene. A fully optimized structure was not obtained; the structure reported here, a second-order saddle point, was found by constraining the partial C−H bond lengths to 1.42 Å. Attention is called to these results in the tables. In several cases an Intrinsic Reaction Coordinate (irc) calculation was made to confirm the link between a ts structure and purported reactant and product structures. These cases are pointed out in the text and/or tables.

Results and Discussion

Energetics and Geometries. The electronic energies, zero-point vibrational energies, and imaginary frequencies calculated in this study are tabulated in Table S1 of the Supporting Information.[13] Cartesian coordinates for all structures at the MP2/6-311+G** level are contained in Table S2 (Supporting

(1) (a) *NIST Standard Reference Database, No. 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, May 2007. (b) Aue, D. H. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P., Eds.; Wiley: New York, 1997 (for a clarification of the difference in the heats of formation of allyl and 2-propenyl cations). (c) Dixon, D. A.; de Jong, W. A.; Peterson, K. A.; McMahon, T. A. *J. Phys. Chem. A* **2005**, *109*, 4073 (for diazomethane data). (d) Wight, C. A.; Beauchamp, J. L. *J. Phys. Chem.* **1980**, *84*, 2503 (for isocyanic acid data).

(2) (a) Griesbaum, K.; Naegele, W.; Wanless, G. G. *J. Am. Chem. Soc.* **1965**, *87*, 3151, including references to earlier work on these reactions. These authors also reported formation of 1,3-dihalo-1,3-dimethylcyclobutanes, attributable to cycloaddition of 2-propenyl cation to allene followed by product-forming steps. Our attempted computation of the ion−molecule complex formed by 2-propenyl cation and allene produces the cyclic (homoallylic) cation intermediate proposed by Griesbaum and coworkers. (b) See the following for a kinetic and mechanistic study with leading references to early work: Cramer, P.; Tidwell, T. T. *J. Org. Chem.* **1981**, *46*, 2683. (c) Jacobs, T. L., Jr. In *The Chemistry of the Allenes*, Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. 2, Chapter 5. (d) Siehl, H.-U. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.: Wiley-Interscience: New York, 1997; Chapter 5. (e) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 6700. See also: Bowers, M. T.; Shuying, L.; Kemper, P.; Stradling, R.; Webb, H.; Aue, D. H.; Gilbert, J. R.; Jennings, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 4832. (f) Fornarini, S.; Speranza, M.; Attinà, M.; Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1984**, *106*, 2498.

(3) Tidwell, T. T. *Ketenes*, 2nd ed.; Wiley: New York, 2006.

(4) Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; Wiley-Interscience: New York, 2001; pp 447, 464, 470, 490.

(5) (a) Krow, G. R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435. (b) Gambaryan, N. P. *Russ. Chem. Rev.* **1976**, *45*, 1251. (c) Barker, M. W.; McHenry, W. E. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley-Interscience: Chicherster, UK, 1980; Part 2, p 701. (d) Perst, H. *Houben-Weyl*: *Methoden der Organischen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, Germany, 1993; Vol. E15, Part 3, p 2531. (e) Alajarín, M.; Vidal, Á.; Tovar, F. *Targets Heterocycl. Syst.* **2000**, *4*, 293.

(6) (a) Regitz, M.; Maas, G. *Diazo Compounds*; Academic Press: New York, 1986. (b) Hegarty, A. F. In *The Chemistry of Diazonium and Diazo Groups*: Patai, S., Ed.; Wiley: New York, 1978; Part 2, pp 511, 571−575. (c) Zollinger, H. *Diazo Chemistry*; VCH: New York, 1994, 1995; Vols. 1 and 2.

(7) Ulrich, H. *The Chemistry and Technology of Isocyanates*; Wiley: New York, 1996.

(8) Eisch, J. J. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1996; Vol. 39, pp 355−391. For recent high-level computations on BC_2H_5 isomers see: Galland, N.; Hannachi, Y.; Lansizera, D. V.; Andrews, L. *Chem. Phys.* **2000**, *255*, 205.

(9) (a) Keeffe, J. R.; Gronert, S.; Colvin, M. E.; Tran, N. L. *J. Am. Chem. Soc.* **2003**, *125*, 11730. (b) Gronert, S.; Keeffe, J. R. *J. Org. Chem.* **2006**, *71*, 5959.

(10) Wavefunction, Inc.: 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612.

(11) Frisch, M. J., et al. *GAUSSIAN 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(12) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. Computations made in this study and previously[9] have established with over 100 examples that enthalpies of reaction and activation obtained by using scaled ZPVEs calculated at HF/6−311+G** and MP2/6−311+G** differ by an average of -0.1 ± 0.5 kcal/mol.

(13) See the Supporting Information paragraph at the end of this paper. Electronic energies, zero-point vibrational energies, point group assignments, and transition state (ts) imaginary frequency values are reported therein.

Information), and selected (MP2) calculated geometric features, including point-group designations, of the reactants, products, several complexes, and transition state structures are in Table S3 (Supporting Information). G3 enthalpies are listed in Table S4 (Supporting Information). Enthalpies of protonation are found in Table 1, with enthalpies of isomerization and miscellaneous activation processes in Table 2. $\Delta H°$ values pertinent to the comparison of isomeric open and cyclic structures for the centrally protonated X = Y = Z cations are given along with structural drawings in Figure 2. The enthalpies of formation of the ion−molecule complexes poised for proton transfer ($\Delta H°_{cx}$) and enthalpies of activation ($\Delta H^{‡}$) for the proton-transfer reactions are in Table 3, while $\Delta H°$ values needed for discussion of the mechanism of positional exchange within the allyl cation are given in Table 4. All enthalpy changes were calculated by using scaled ZPVE corrections as identified in the tables.[12] The G3 values include thermal corrections using scaled vibrational frequencies (0.9135). Further details are found in the Methods section.

A number of covalent complexes formed between cations and their neutral precursors were calculated. The resulting structures, compounds **24**, **25**, **26**, **59**, **60**, **72**, and **73**, are not directly relevant to this study, and are omitted from the tables. Electronic energies, ZPVE values, and Cartesian coordinates for these structures can be found in the Supporting Information.[13]

Agreement with available experimental results[1] is mixed for the MP2 and B3LYP calculations. For the nine systems with reliable experimental proton affinities, the MP2 calculations give good agreement in five cases and poor agreement (error ≥3 kcal/mol) in four cases. In the B3LYP calculations, only four of the nine cases gave values within 3 kcal/mol of experiment. These results highlight the computational challenge of characterizing systems where sp-hybridized carbons are formed or rehybridized in a reaction process. This led us to apply the G3 composite method to the problem. In general, the G3 method gives excellent agreement with the experimental proton affinities and isomerization energies. Moreover, these calculations point to three cases where the NIST database values appear to be in error. First, the value in the database for cyclopropene (195.6 kcal/mol) is not consistent with the known thermochemistry of the neutral C_3H_4 isomers—cyclopropene is over 20 kcal/mol less stable than allene, but the database proton affinity is only 10 kcal/mol above that of allene (both giving the allyl cation). Of course any measured value for cyclopropene is an apparent basicity because it ring-opens to give the allyl cation when protonated. We have used the known heat of formation of cyclopropene and the allyl cation to obtain the value listed in Table 1. The value of propyne giving the 2-propenyl cation is also in error in the database. Aue[1b] has remeasured the value for propyne and it is included in Table 1. The G3 calculations match Aue's value. The value for diazomethane also appears to be an error. Surprisingly, there does not seem to be a reliable heat of formation for diazomethane itself—high-level calculations point to errors of up to 10 kcal/mol in the experimental value.[1c] This error is propagated into the NIST proton affinity value. Without a good experimental heat of formation for diazomethane, its experimental proton affinity cannot be calculated accurately. Finally, the value for isocyanic acid is not consistent with earlier gas-phase equilibrium measurements.[1d] It was derived from an appearance energy and seems to be 7 kcal/mol too high (180 kcal/mol). The equilibrium measurement value, when adjusted to the modern proton affinity scale, is in good agreement with the G3 value. In the systems without experimental values, it can be seen that the B3LYP and MP2 values give modest agreement with significant scatter relative to the more reliable G3 values.

Equilibrium Protonation: General. Enthalpies of protonation were calculated for protonation at both termini and at the central position of the X = Y = Z compounds in this study. These values are compared with available experimental (298 K) gas-phase values for allene, some of the heteroallenes, and several of their isomers in Table 1.[1] Agreement with experiment is sufficiently good to establish the equilibrium site of protonation in cases where that choice is not obvious. That is, even when experimental data are unavailable, the differences in calculated $\Delta H°$ values for protonation at different sites are large enough to allow specification of the preferred position of protonation.

In all cases but one, protonation at one end of the X = Y = Z system dominates strongly. Structures of these "end-protonated" species are shown in Figure 1. Thus, equilibrium protonation of ketene, ketenimine, and diazomethane, all of which have a CH_2 group at one end, takes place at that group, leading respectively to $CH_3C{\equiv}O^+$ (**14**), $CH_3C{\equiv}NH^+$ (**33**), and $CH_3N{\equiv}N^+$ (**46**). These ions are favored over the alternative end-protonated cations by 41 (ketene), 15 l (ketenimine), and 33 kcal/mol (diazomethane). Protonation of carbodiimide and carbon dioxide occurs at a heteroatom terminus rather than at the central carbon. For isocyanic acid protonation at the nitrogen is favored by 16 kcal/mol giving [$H_2N^+{=}C{=}O \leftrightarrow H_2N{-}C{\equiv}O^+$] (**75**). Each of the preferred protonation sites is activated by π-electron donation from the heteroatom at the other end.

The single case in which protonation at the central atom is preferred is allene, for which the allyl cation is calculated (G3) to be more stable than the 2-propenyl cation by 7.8 kcal/mol. Center protonation is of further interest because it leads to the possibility of open, allyl-like structures as well as closed, three-membered cyclic structures. This issue is addressed below within a larger context.

Protonation of 2-boraallene$^-$, **78**, at the center boron atom leads to a cyclic structure, borirane (**82**), only 11.5 kcal/mol less stable than the preferred, end-protonated **80**. Other than that, protonation at the central atom of heteroallenes gives structures that are less stable than their end-protonated isomers by large amounts ranging from 42 to 98 kcal/mol. The smaller differences, 42 to 56 kcal/mol, are for ketene, ketenimine, and diazomethane, for which center protonation also leads to cyclization or bridging giving cations which have a bonding interaction between the CH_2 group and the heteroatom at the other end. For example, ion **21**, formed by protonation at the central carbon of ketene, is better thought of as carbon-protonated oxirene; the oxygen atom bridges to the methylene group with a $CH_2{-}O$ distance of 1.62 Å.[14] Likewise, ketenimine and diazomethane, protonated at the central atom, give ions **39** and **53a**, having bridging $CH_2{-}N$ distances of 1.51 and 1.53 Å, respectively.

Centrally Protonated Allenes and Heteroallenes: Subsequent Events. Although formation of the center-protonated allenes and heteroallenes is generally disfavored, both thermodynamically and kinetically, some of them are potentially accessible by gas-phase proton transfer from a strong acid or by fragmentation of a suitable precursor ion. Center protonation

(14) van Alem, K.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2002**, *116*, 10681.

TABLE 1. Calculated Enthalpies of Protonation for the Cumulenes and Their Isomers in This Study (kcal/mol)[a]

reactant	product	$\Delta H^\circ_{protonation}$ (exptl)[b]	$\Delta H^\circ_{protonation}$ (calcd)[c] MP2	DFT	G3
		allene and isomers			
1 allene	**6** allyl$^+$	−185.3	−183.5	−185.9	−183.2
	4 2-propenyl$^+$	−175.4	−173.5	−178.8	−175.4
2 propyne	**4** 2-propenyl$^+$	−174.9	−168.7	−181.8	−174.8
3 cyclopropene	**6** allyl$^+$[d]	−205.8	−202.8	−211.6	−206.6
		ketene and isomers			
11 ketene	**14** acetyl$^+$	−197.3	−199.0	−192.1	−196.4
	17 CH_2=C=OH^+		−149.3	−154.6	−154.8
	21 CH_2CHO^+ [e]		−138.5	−138.4	−140.3
12 ethynol	**17** CH_2=C=OH^+		−184.2	−192.4	−189.1
13 2-oxirene	**21** CH_2CHO^+ [e]		−216.7	−214.3	−217.4
		ketenimine and isomers			
27 ketenimine	**33** CH_3CNH^+		−215.0	−210.1	−213.9
	35 CH_2=C=NH_2^+		−191.7	−198.3	−198.3
	39 CH_2CHNH^+ [f]		−168.2	−169.3	−171.4
	38 CH_2CHNH^+ [g]		−143.1	−150.5	−148.2
28 acetonitrile	**33** CH_3CNH^+	−186.2	−182.7	−186.7	−187.1
29 methyl isonitrile	**40** CH_3NCH^+	−200.5	−200.2	−197.5	−200.0
30 ethynamine	**35** CH_2=C=NH_2^+		−204.6	−216.4	−213.5
	41 HC≡CNH_3^+		−188.7	−187.0	−189.7
31 2-azirine	**39** CH_2CHNH^+ [f]		−225.0	−226.9	−225.8
32 1-azirine	**39** CH_2CHNH^+ [f]		−188.8	−192.5	−192.7
		diazomethane, carbodiimide and isomers			
42 diazomethane	**46** CH_3N≡N^+	−205.3[k]	−214.6	−204.3	−210.5
	49 CH_2=NNH^+		−169.9	−176.2	−177.0
	53 CH_2NHN^+		−74.0	−89.9	−90.7
	53a CH_2NHN^+ [h]		−151.8	−150.0	−153.9
44 2-diazirine	**58** $CHNHNH^+$ [h]		−172.0	−177.8	−176.3
	57 $HNCHNH^+$ [i]		−142.4		
45 carbodiimide	**54** H_2NC≡NH^+		−194.7	−193.2	−195.2
45 carbodiimide	**58** $CHNHNH^+$ [h]		−112.1	−114.5	−115.7
	57 $HNCHNH^+$ [i]		−82.6		
61 cyanamide	**54** H_2NC≡NH^+	−192.5	−189.1	−193.3	−193.0
	64 N≡CNH_3^+		−166.1	−163.4	−166.3
		carbon dioxide and isocyanic acid (HN=C=O)			
65 carbon dioxide	**67** $OCOH^+$		−128.0	−125.9	−128.9
	71 $OCHO^+$		−23.8	−24.3	−30.6
74 isocyanic acid	**75** H_2N−C≡O^+	−172.4[l]	−173.0	−170.0	−172.9
	76 HN≡COH^+		−154.5	−154.0	−157.0
	77 $HNCHO^+$		−73.5[j]	−76.3	−79.8
		CH_2−B−CH_2^-			
78 CH_2−B−CH_2^-	**80** CH_3BCH_2		−358.3	−359.1	−358.7
	82 borirane		−348.2	−347.2	−347.2

[a] Energies at the MP2/6-311+G**, B3LYP/6-31+G**, or G3 level unless otherwise noted. $\Delta H^\circ_{protonation}$ is equivalent to −(proton affinity) and $-\Delta H^\circ_{acid}$ of the protonation product. ΔH°_{cx} and $\Delta H^\ddagger$ values for identity proton-transfer processes are found in Table 3. [b] *NIST Standard Reference Database, No. 69;* Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, 2005. For the proton affinity of propyne and heats of formation of allyl and 2-propenyl cations see also: Aue, D. H. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P., Eds.; Wiley: New York, 1997. Experimental values refer to 298 K for reactions **1** → **4** and **3** → **6**, the experimental proton affinity was calculated on the basis of known heats of formation, not direct acidity measurements. [c] $\Delta H°$ values were calculated by using scaled ZPVE values as recommended by Scott and Radom; see: Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. Thermal corrections were not made for MP2 or DFT calculations. The main effect of including a thermal correction would be due to the thermal energy of the proton. This would make calculated $\Delta H^\circ_{protonation}$ values more negative by $^5/_2$ *RT*, or about 1.5 kcal/mol. The G3 values contain scaled thermal corrections. The use of HF ZPVE values in place of MP2 ZPVE values has been found to cause insignificant differences in over 100 ΔH calculations: this work, and also: Gronert, S.; Keeffe, J. R. *J. Org. Chem.* **2006**, *71*, 5959. [d] Ring opens during protonation at correlated levels. Proton affinity in NIST table appears to be for formation of 2-propenyl cation or is an error. [e] An oxygen-bridged cation identical with carbon-protonated oxirene. [f] A nitrogen-bridged cation identical with that of nitrogen-protonated azirene. [g] The unbridged isomer of **39**. [h] Structure **53a** is the N−CH_2 bridged isomer of open, planar **53**, while **58** is a three-membered ring with a long (1.638 Å) N−N bond. [i] Structure **57** is an open "sickle-shaped" cation. At the MP2 and B3LYP levels it is a transition state for isomerization of **58**. [j] Structure **77** has a short N−O distance.[k] The value from the NIST database is likely an error and the PA is probably considerably higher. The ΔH°_f of diazomethane in the database appears to be too low by over 10 kcal/mol: Dixon, D. A.; de Jong, W. A.; Peterson, K. A.; McMahon, T. A. *J. Phys. Chem. A* **2005**, *109*, 4073. [l] The value from the NIST database (180.0 kcal/mol) is based on appearance energies and appears to be an error. The value given in the table is derived from an equilibrium measurement against formaldehyde indicating that isocyanic acid is more basic by 2 kcal/mol. The value differs from that in the original paper because the proton affinity scale has been shifted and the PA of formaldehyde has changed: Wight, C. A.; Beauchamp, J. L. *J. Phys. Chem.* **1980**, *84*, 2503.

leads to the allyl cation, **6**, and a set of heteroallylic structures, the open forms of which are compounds **22**‡, **38**, **53**, **57**, **71**, **77**, and **81**‡, shown in Figure 2. These species are isoelectronic with the allyl cation, and are generalized as X−YH−Z^+. All X−YH−Z^+ species can, in principle, undergo several further changes, shown in Scheme 1.

ΔH°_{isom} values for (reversible) isomerization between end-protonated and center-protonated cations can be found in Table

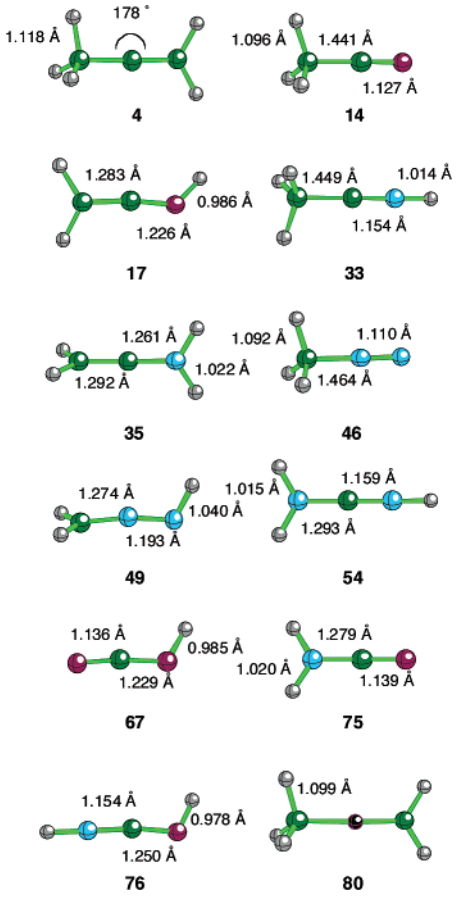


FIGURE 1. MP2/6-311+G** structures of end-protonated allene and heteroanalogues. Color coding: carbon is green, hydrogen is gray, oxygen is red, boron is black, and nitrogen is blue.

2. Additionally, covalent addition of $X-YH-Z^+$ to its neutral precursor is a common and exothermic possibility. This category of reaction was not investigated thoroughly, but several such complexes are reported in the Supporting Information.[13] A third possibility is unimolecular, ring-closing isomerization to a three-membered ring, e.g., cyclopropyl cation, **10**, in the case of the allyl cation. Structures of these closed forms and their heats of isomerization from the open forms are shown in Figure 2 alongside the structures of the open forms. The first six entries all have YH = CH as the central fragment while compounds **53** and **81** have NH and BH, respectively, at the center. All are cations except for the boron compounds, which are neutral.

For center-protonated CO_2, **71**, and HNCO, **77**, the ions are cyclic, but with a long O−O or O−N distance. Open forms were not found for these species. In all other cases, both isomers were found and except for the allyl cation to cyclopropyl cation interconversion, the cyclic isomer is strongly favored in each case. A number of factors affect the relative stabilities of the open and closed forms. Regarding the open isomers, Wiberg and co-workers have made several generalizations: (1) Allylic π-charge delocalization is best when the three atoms composing the allylic framework have similar electronegativities. (2) Changes at positions X and Z which stabilize positive charge, as in 1,1,3,3-tetramethylallyl cation, will reduce the need for charge distribution. (3) Substitution of atoms or groups at X and Z which are more electronegative than Y will also reduce charge delocalization to those positions and place more positive

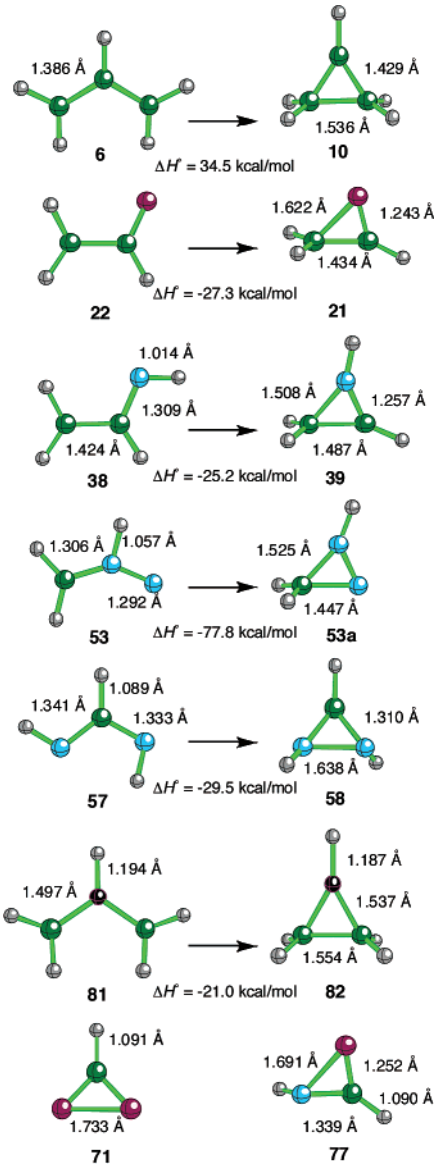
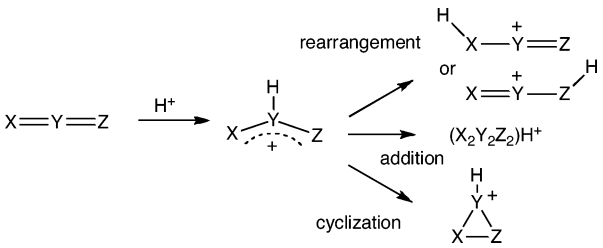


FIGURE 2. Structures of open, centrally protonated allene and heteroanalogues, their closed, cyclic isomers, and their enthalpies of isomerization. Color coding: carbon is green, hydrogen is gray, oxygen is red, boron is black, and nitrogen is blue. $\Delta H°$ values are calculated at MP2/6-311+G** with ZPVE corrections at HF/6-311+G**.

SCHEME 1. Reactions of Center-Protonated Species



charge at the Y position.[15] Regarding the closed isomer there is a potential advantage in that a formal "σ" (bent) bond has taken the place of the π bonding in the open form. An obvious

(15) Wiberg, K. B.; Cheeseman, J. R.; Ochterski, J. W.; Frisch, M. J. *J. Am. Chem Soc.* **1995**, *117*, 6535.
(16) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Organometallics* **1985**, *4*, 429.

TABLE 2. Calculated Enthalpies of Isomerization and Miscellaneous Activation Processes for the Cumulenes and Their Isomers in This Study[a]

reactant(s)	product	$\Delta H°$, kcal/mol (exptl)[b]	$\Delta H°$ or $\Delta H^{‡}$, kcal/mol (calcd)[c] MP2	DFT	G3
		Isomerization			
		allene and isomers			
1 allene	**2** propyne	−1.6	−4.8	3.0	−0.6
	3 cyclopropene	20.3	19.3	25.7	23.4
4 2-propenyl$^+$	**6** allyl$^+$	−9.9	−10.0	−7.1	−7.8
		ketene and isomers			
11 ketene	**12** ethynol	30.8	34.9	37.8	34.3
	13 2-oxirene		80.6	75.8	77.1
14 acetyl$^+$	**17** CH_2═C═OH$^+$		49.8	37.5	41.6
	21 CH_2CH═O$^+$ [d]		60.5	53.7	56.0
		ketenimine and isomers			
27 ketenimine	**28** acetonitrile		−32.3[e]	−23.4	−26.8
	30 ethynamine		12.9	18.1	15.2
	31 2-azirine		53.5	57.6	54.4
	32 1-azirine		17.3	23.2	21.4
28 acetonitrile	**29** methyl isonitrile	23.7	27.3	22.3	24.4
33 CH_3C≡NH^+	**35** CH_2═C═NH_2^+		23.3	11.8	15.7
35 CH_2═C═NH_2^+	**39** CH_2CHNH^+ [f]		23.5	29.0	26.9
39 CH_2CHNH^+[f]	**38** CH_2CHNH^+ [g]		25.2	18.8	23.2
		diazomethane, carbodiimide, and isomers			
42 diazomethane	**43** 1-diazirine	12.6	9.4	14.1	11.8
	44 2-diazirine		31.5	35.2	31.6
	45 carbodiimide		−28.4	−28.1	−29.0
	61 cyanamide		−33.9	−30.6	−31.3
46 CH_3N≡N^+	**49** CH_2NNH^+		44.7	28.1	32.0
	58 $CHNHNH^+$ [h]		74.1	61.7	65.8
	53 CH_2═NHN^+		140.6	114.3	118.3
58 $CHNHNH^+$ [h]	**57** $HNCHNH^+$ [i]		29.5		
54 H_2NC≡NH^+	**64** N≡CNH_3^+		23.0	29.9	26.7
53 CH_2NHN^+	**53a** CH_2NHN^+ [h]		−77.8	−60.1	−64.6
		carbon dioxide and isocyanic acid (HN═C═O)			
65 carbon dioxide	**66** CO_2 cyclic		148.6	139.9	140.2
67 $OCOH^+$	**71** $OCHO^+$		104.2	101.7	98.3
75 H_2N-C≡O^+	**76** HN≡COH^+		18.5	16.0	16.0
	77 $HNCHO^+$[j]		99.5	93.8	93.1
		$CH_2-B-CH_2^-$			
80 CH_3BCH_2	**82** borirane		10.1	11.9	11.5
		Miscellaneous Activation Processes			
		allene and isomers			
6 allyl$^+$	**7** (rotational ts)[k]		35.1		
6	**8** (ts)[l]		28.2		
6	**10** (ts)[m]		34.5	33.1	
4 2-propenyl$^+$	**8** (ts)[l]		18.4		
		ketene and isomers			
17 CH_2═C═OH^+	**18** (rotational ts)[n]		16.1		
21 CH_2CHO^+	**22** (ts)[o]		27.3		
17	**23** (ts)[p]		53.1		
		diazomethane, carbodiimide, and isomers			
49 CH_2NNH^+	**50** (ts)[q]		21.4		
61 cyanamide	**62** (ts)[r]		0.9		
		$CH_2-B-CH_2^-$			
78 CH_2BCH_2	**79** (ts)[s]		24.7		
82 borirane	**81** (ts)[t]		21.0		

[a] Energies at the MP2/6-311+G**, B3LYP/6-31+G**, or G3 level unless otherwise noted. Transition states are denoted by ts. $\Delta H°_{cx}$ and $\Delta H^{‡}$ values for identity proton-transfer processes are found in Table 3. [b] Bartmess, J. E. In *NIST Standard Reference Database, No. 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, 2005. For the heats of formation of 2-propenyl and allyl cations see also: Aue, D. H. In *Dicoordinated Carbocations*; Rapport, Z., Stang, P., Eds.; Wiley: New York, 1997. Experimental values refer to 298 K. The MP2 and DFT calculations do not contain thermal corrections, but scaled corrections are included in the G3 values. [c] $\Delta H°$ values were calculated by using scaled ZPVE values as recommended by Scott and Radom; see: Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. The use of HF ZPVE values in place of MP2 ZPVE values has been found to cause insignificant differences in over 100 ΔH calculations: this work, and see also: Gronert, S.; Keeffe, J. R. *J. Org. Chem.* **2006**, *71*, 5959. [d] An oxygen-bridged cation identical with that formed by loss of hydride from the methyl group of acetaldehyde. [e] An aqueous phase ΔG value for the isomerization of ketenimine to acetonitrile has been calculated at −30.7 kcal/mol by: Richard, J. P.; Williams, G.; Gao, J. *J. Am. Chem. Soc.* **1999**, *121*, 715. [f] A nitrogen-bridged cation identical with that of nitrogen-protonated azirene. [g] The unbridged isomer of **39**. [h] Structure **53a** is the N−CH_2 bridged isomer of open, planar **53**, while **58** is a three-membered ring with a long (1.638-Å) N−N bond. [i] Structure **57** is an open "sickle-shaped" cation. At the MP2 and B3LYP levels it is a transition state for isomerization of **58**. [j] Structure **77** has a short N−O distance. [k] MP2/6-311+G**//HF/6-311+G** value. This is the ts for rotation about an allyl$^+$ C−C bond. A "perpendicular" allyl cation could not be found at MP2/6-311+G**. [l] This ts is for rearrangement of allyl$^+$ to 2-propenyl$^+$, and its reverse. An irc calculation demonstrated the connection between the two cations. [m] Structure **10**, cyclopropyl$^+$, is a transition state for disrotatory ring opening leading to allyl$^+$, shown by an irc calculation. [n] Structure **18** is the ts for rotation about the CO bond in H_2C═C═OH^+. [o] Structure **22** is flat; it is the ts for rotation about the CC bond of structure **21**, carbon-protonated oxirene. [p] S [q] Structure **50** is the ts for rehybridization at the NH nitrogen. In **49** the NNH angle is bent; in ts **50** it is linear. [r] Structure **62** is the ts for flattening at the NH_2 nitrogen. [s] Structure **79** is the ts for rotation about a CB bond in **78**. [t] Structure **81**, a planar species with allyl$^+$ (C_{2v}) symmetry, is the ts for disrotatory ring closure to **82**.

disadvantage is the introduction of considerable ring strain. Schleyer and co-workers have estimated the ring strain of cyclopropyl cation to be about 56 kcal/mol and that of borirane (**82**) to be about 44 kcal/mol.[16]

Of the systems studied here the preference for the open, allyl cation over the closed, cyclopropyl cation, **10**, can be assigned to a combination of excellent π-charge delocalization in the open form along with the strain energy in the closed form, these two factors being sufficient to overcome the introduction of the "σ" bond in the three-membered ring. Indeed, our calculations suggest that disruption of π delocalization in the allyl cation caused by a 90° rotation about a C−C bond amounts to about 35 kcal/mol (see Table 2).[17] This factor must be greatly reduced in the heteroallylic cations[15] allowing the cyclic forms to prevail despite the introduction of ring strain.

The boron analogue of the cyclopropyl cation is neutral borirane, **82**. Compared with the all-carbon system, the opposite behavior is found as the cyclic isomer is 21 kcal/mol *more* stable than the open, C_{2v}, singlet transition state, **81**. This system has been analyzed by Taylor, Zerner, and Ramsey,[18] who note that whereas in **10** the weakest bond in the ring is the CH_2-CH_2 bond, a factor contributing to barrier-free, disrotatory ring opening, the weakest bonds in **82** are the CH_2-B bonds. Cleavage of a C−B bond does not lead to **81**. Cyclization in all systems places more positive charge at the central fragment, YH. In the all-carbon system the increase in the npa charge (MP2/6-311+G**) at YH is 0.79 unit. In the boron system the change is also large, +0.54 unit, despite the fact that this system is neutral. In open **81** charge density is almost equally divided between the terminal CH_2 units and the central BH unit, but in closed **82** the CH_2 groups are substantially negative.

The boron and all-carbon systems differ from all the other systems reported here in that cyclization does not produce a structure for which all ring atoms can be written with complete valence octets. This deficiency is more critical for positive carbon than for neutral boron, and is perhaps another of the factors favoring the open, allyl cation over the cyclopropyl cation.

Several other systems in Figure 2 offer special features. Cation **57**, a "sickle-shaped" structure, is formed by protonation of carbodiimide at carbon. This structure has a net charge of 0.44 at the central CH position. Closure leads to a diazacyclopropyl cation, **58**, with a charge of 0.73 at that site. The open form, **57**, however is only a minimum at the HF level and represents a transition state for the isomerization of **58** at correlated levels. Compound **58**, like other closed structures in which *both* X and Z are first-row heteroatoms, has a formal, antiaromatic, four-π-electron cyclic array. However, in **58** this outcome is mitigated by two factors: the N−N bond is unusually long at 1.64 Å (that in *trans*-diaziridine is calculated at 1.505 Å) and *both* nitrogens are pyramidal. The *trans* N−H bonds result in a pair of lone-pair/N−H eclipsing interactions rather than the more costly lone-pair/lone-pair eclipsing.[19] Stabilization by π-electron donation to the central carbon is indicated by the short C−N bond lengths, 1.31 Å.

Ions **71** and **77**, formed by protonation at the carbon atom of carbon dioxide and isocyanic acid, respectively, are placed in the cyclic category even though the O−O and N−O distances are longer (1.73 and 1.69 Å, respectively) than for the other cyclic structures, evidence of weak bonding. Full closure would give cyclic structures which, like **58**, could be antiaromatic. Moreover, bond-weakening, lone-pair/lone-pair eclipsing interactions could not be avoided. Charge at the central CH unit is large in both cases: +0.89 for **71** and +0.72 for **77** at MP2. The terminal oxygens are essentially neutral in these structures, but the NH unit in **77** bears some of the positive charge.

Ions **22** and **38** are the open forms of the more stable bridged isomers, **21** and **39**. Bridging by the heteroatom turns an open, planar primary carbocation (attached to an electron withdrawing group) into the more stable bridged form wherein positivity at the CH_2 group is greatly reduced. Structure **22** is, in fact, the transition state for rotation about the CH_2-CH bond of **21**.[14,15] Surprisingly, open **38** is a stable state albeit much less stable than cyclic **39**.

Ion **53** is the open form obtained by protonation at the inner nitrogen of diazomethane. The CH_2 group and especially the terminal "nitrene" nitrogen in **53** are considerably electron deficient with 37% of the positive charge at that nitrogen. Strongly exothermic cyclization to **53a** transfers most of this charge plus some of that on the CH_2 group to the central NH group leaving only 14% on the other nitrogen.

Kinetic Protonation. To explore the kinetics of protonation without introducing a thermodynamic bias, we have examined identity proton transfers between the protonated cumulenes and their neutral precursors. We were able to find true transition states only for the end-to-end identity proton transfers of carbon (C−H) acids. In transfers involving heteroatoms, barrierless processes, with effectively single-well potentials, were observed at the highest level of theory. The transition structure in these cases is a symmetric (or nearly so), proton-bound dimer complex. For the identity proton transfers of center-protonated species, transition state searches were not successful, and led to structures involved in other processes such as bond-forming addition reactions. We have concluded that there are no minimum energy pathways linking center-protonated species via identity proton-transfer processes. Enthalpies of ion−molecule complexation and transition state formation for the identity end-to-end proton-transfer reactions in this study are listed in Table 3. Selected geometric features of the calculated transition structures are in Table S3 (Supporting Information),[13] and pictures of these structures are shown in Figure 3.

Identity proton transfer in the parent allene system presents a particularly interesting situation because the center-protonated species, the allyl cation, is significantly more stable than the end-protonated species, the 2-propenyl cation, yet we could find no pathways for the identity proton transfer from the allyl cation to allene. To explore this issue in more detail, we have forced the system to follow such a pathway. By constraining both the partial C−H bond lengths to 1.42 Å, a typical distance for identity proton transfers to and from carbon,[9] a ts structure for center-to-center proton transfer between the allyl cation and allene was found (**9** in Figure 3). At the MP2 level, this structure

(17) Calculated at the MP2/6-311+G**//HF/6-311+G** level. Wiberg et al.[15] report a value of 33 kcal/mol. Attempted optimation at the MP2 level leads to the 2-propenyl cation, **4**; see also: Foresman, J. B.; Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2220.

(18) Taylor, C. A.; Zerner, M. C.; Ramsey, B. *J. Organomet. Chem.* **1986**, *317*, 1. These workers obtained $\Delta H = 24.5$ kcal/mol for ring opening of **82** at the MP4/6-31G** level. A ΔH value of 31 kcal/mol was calculated at a lower level by Budzelaar et al.[2]

(19) At MP2/6-311+G** *trans*-diaziridine is 5.8 kcal/mol more stable than *cis*-diaziridine. The latter has a lone-pair/lone-pair eclipse and a NH/NH eclipse. Moreover, the N−N bond length in the *cis* isomer is slightly longer (1.509 Å) than that in the *trans* form, and the HNN angles (presumably those defined by the lone pair axis and the two nitrogens as well) are relatively more splayed in the *cis* isomer.

TABLE 3. Calculated Enthalpies of Complexation and Activation for Identity Proton-Transfer Reactions of the Cumulenes in This Study[a]

reactant(s)	complex or transition structure	ΔH°_{cx} or $\Delta H^\ddagger$, kcal/mol[b]
1 allene + **4** 2-propenyl$^+$	**5** (ts)	−9.9
1 allene + H_3S^+ (non-identity reaction)	**5a** (ts)	−12.3
1 allene + **6** allyl$^+$	**9** (ts)[c]	∼12
1 allene + H_3S^+ (non-identity reaction)	**9a** (ts)	−2.4
11 ketene + **14**, acetyl$^+$	**15** (cx)[d]	−6.8
11 ketene + **14**, acetyl$^+$	**16** (ts)[d]	−5.3
11 ketene + **17**, $H_2C{=}C{=}OH^+$	**19** (cx)[e]	−22.0
11 ketene + **17**, $H_2C{=}C{=}OH^+$	**20** (ts)[e]	−24.5
27 ketenimine + **33**, $CH_3C{\equiv}NH^+$	**34** (ts)[f]	3.6
27 ketenimine + **35**, $H_2C{=}C{=}NH_2^+$	**36** (cx)[g]	−19.8
27 ketenimine + **35**, $H_2C{=}C{=}NH_2^+$	**37** (ts)[g]	−22.2
42 diazomethane + **46**, $CH_3N{\equiv}N^+$	**47** (cx)[h]	−10.1
42 diazomethane + **46**, $CH_3N{\equiv}N^+$	**48** (ts)[h]	−8.9
42 diazomethane + **49**, H_2CNNH^+	**51** (cx)[i]	−15.8
42 diazomethane + **49**, H_2CNNH^+	**52** (ts)[i]	−17.6
45 carbodimide + **54**, $H_2N{=}C{=}NH^+$	**55** (cx)[j]	−20.4
45 carbodimide + **54**, $H_2N{=}C{=}NH^+$	**56** (ts)[j]	−22.3
65 carbon dioxide + **67**, $OCOH^+$	**68** (cx)[k]	−19.4
65 carbon dioxide + **67**, $OCOH^+$	**69** (ts)[k]	−21.9
67 $OCOH^+$	**70** (ts)[l]	82.8
78 $CH_2BCH_2^-$ + **80**, CH_3BCH_2	**83** (ts)[m]	−2.6

[a] Structures are optimized at MP2/6-311+G** unless otherwise noted. Complexes and transition structures are denoted by cx and ts, respectively. [b] ΔH°_{cx} and $\Delta H^\ddagger$ values were calculated by using scaled ZPVE values as recommended by Scott and Radom; see: Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. The use of HF ZPVE values in place of MP2 ZPVE values has been found to cause insignificant differences in over 100 ΔH calculations: this work, and see also: Keeffe, J. R.; Gronert, S.; Colvin, M. E.; Tran, N. L. *J. Am. Chem. Soc.* **2003**, *125*, 11730−11745. [c] This is a hypothetical model for the center-to-center proton-transfer ts between allyl$^+$ and allene. It is a second-order saddle point, found only by constraining the partial C−H distances to 1.42 Å. The quoted value is therefore approximate. No ion−molecule complexes lying on the proton-transfer reaction coordinate were found for the allene reactions. [d] Structure **15** is the ion−molecule complex between ketene and acetyl$^+$. Structure **16** is the corresponding proton-transfer ts. [e] Structure **19** is the ion−molecule complex between ketene and $H_2C{=}C{=}OH^+$. Structure **20** is the corresponding proton-transfer ts. [f] Structure **34** is the ts for the identity carbon-to-carbon proton transfer between $CH_3C{\equiv}NH^+$ and ketenimine. [g] Structure **36** is the complex between ketenimine and $H_2C{=}C{=}NH_2^+$. Structure **37** is the identity nitrogen-to-nitrogen proton-transfer ts. [h] Structure **47** is the complex between diazomethane and $CH_3N{\equiv}N^+$. Structure **48** is the identity carbon-to-carbon proton-transfer ts. [i] Structure **51** is the complex between diazomethane and **49**, while **52** is the proton-transfer ts between the terminal nitrogens. [j] Structure **55** is the complex between diazomethane and $H_2N{=}C{=}NH^+$, and **56** is the ts for nitrogen-to-nitrogen proton transfer. [k] Structure **68** is the complex between carbon dioxide and **67**, and **69** is the corresponding oxygen-to-oxygen proton-transfer ts. [l] Structure **70** is the internal oxygen-to-oxygen proton shift within **67**. [m] Structure **83** is the ts for identity proton transfer between **78** and **80**.

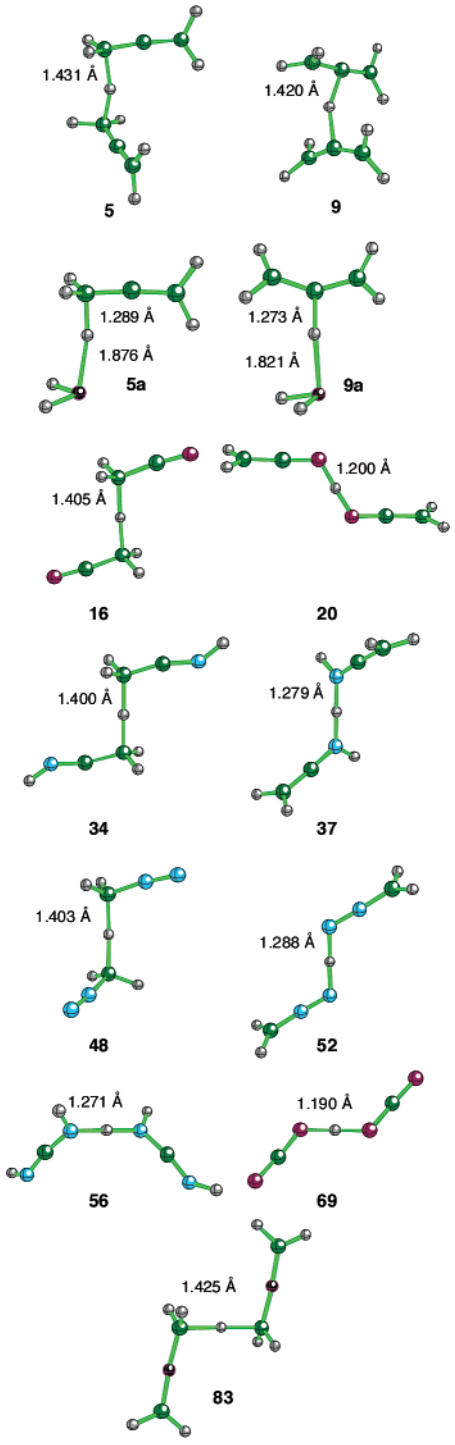


FIGURE 3. MP2/6-311+G** transition structures for identity end-to-end proton transfers, for proton transfer from H_3S^+ to allene, and a hypothetical model structure, **9**, for a center-to-center transition state formed from allene and allyl cation. For the transfers between heteroatoms, the structures represent the preferred geometries for the symmetrically proton-bound ion−molecule complexes on their electronic energy surfaces. Color coding: carbon is green, hydrogen is gray, oxygen is red, boron is black, sulfur is black, and nitrogen is blue.

is a second-order saddle point rather than a true transition state. Comparison with the end-to-end proton transfer of the allene/2-propenyl cation system (with the same C−H bond constraint) shows that $\Delta H^\ddagger$ for end-to-end proton transfer in the allene system (allene/2-propenyl cation) is preferred by about 22 kcal/mol over the center-to-center transfer (allene/allyl cation). The geometry of structure **9** is noteworthy for the fact that the two three-carbon halves are not linear and are somewhat twisted.

Loss of stability in the allene fragment is therefore also a factor contributing to the large barrier. A full 90° twist converts the allene structure to a planar geometry, and is very costly, requiring 41 to 50 kcal/mol, depending upon whether the three-

(20) The two imaginary frequencies (HF) correspond to the proton transfer coordinate, $i\nu = 1126$ cm^{-1}, and to torsion about all four C−C bonds, $i\nu = 269$ cm^{-1}. The HF and MP2 structures are geometrically very similar.

TABLE 4. Results Pertinent to Positional Exchange in the Allyl Cation

species	$\Delta H^\circ = (H^\circ - H^\circ_6)$,[a] kcal/mol	
	MP2//MP2	MP2//HF
6 allyl$^+$	0	0
7‡ rotational ts	NA	35.1
8‡ hydride shift ts	28.2	29.2
4 2-propenyl$^+$	10.0	10.1
10‡ cyclopropenyl$^+$	34.5	33.5

[a] Enthalpy relative to allyl cation, **6**. MP2//MP2 signifies values obtained by using optimized MP2/6-311+G** structures, and MP2//HF indicates results of MP2/6-311+G** single-point calculations with HF/6-311+G** structures. ZPVE values were scaled by 0.9135 as recommended by Scott and Radom; see: Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. The "‡" symbol denotes a transition state, hence ($H^\circ - H^\circ_6$) becomes an activation enthalpy.

carbon skeleton is linear or bent.[21] Thus, structure **9** has lost some of the stabilizing attributes of both precursors.

More accurate information about the contrast between center and end protonation of allene was obtained by using H_3S^+ as the proton donor. Here we were successful in finding first-order saddle point structures for protonation at both C1 and C2 (see structures **5a** and **9a** in Table 3 and Figure 3). The activation enthalpies differ by 9.9 kcal/mol, favoring protonation at C1, despite the fact that thermodynamically, protonation at C2 is more favorable by 10 kcal/mol. Since electrophilic addition to allene is well-known to give products arising from the 2-propenyl cation intermediate rather than from the allyl cation,[2] we infer that protonation at the central carbon occurs through a ts that does not much resemble the allyl cation, but is much like a primary carbenium ion with an attached, destabilizing, almost orthogonal vinylic group as in "allyl cation (perp)", compound **7**. In ts structure **9a** the planes of the CH_2 fragments have twisted, but only slightly, from a 90° dihedral in allene to about 75°. The twisting motion coupled with proton transfer comprise the reaction coordinate. Although allylic conjugation has begun, it is far from optimal at the ts. This description is qualitatively the same as that suggested by Aue and co-workers.[2e] By extension, protonation at the central atoms of the heteroallenes passes through transition states resembling primary carbenium, oxenium, or nitrenium ions with almost orthogonal heterovinylic groups attached. The total penalty for lack of the planarity displayed by allyl cation (perp) is large: 35 kcal/mol relative to the authentic allyl cation at MP2/6-311+G**//HF/6-311+G**, see Table 4. This compares well with a value of 33 kcal/mol calculated by Wiberg and co-workers.[17]

Entries in Table 3 also show that end-to-end proton transfer between heteroatoms is, as expected,[9a] more facile than that between carbons, even when the C-protonated cation is more stable. As noted above, proton transfers between heteroatoms in these systems have no intrinsic barriers in the gas phase. Although transition states were found on the electronic potential energy surface in several cases, the inclusion of zero-point vibrational energy pushed the transition structure's energy below that of the ion/molecule complex leading to its formation. The only exception to this generalization is a trivial one, the intramolecular oxygen-to-oxygen transfer within ion **67**, $OCOH^+ \rightarrow HOCO^+$, which has a barrier of 83 kcal/mol. This proton transfer passes through ts **70**, a highly strained structure with unusually long (1.69 Å) partial O−H bonds.

The Allyl Cation: Positional Exchange. Rotational isomerization within the allyl cation, **6**, leading to positional exchange of the hydrogens, has been studied both experimentally and computationally. A 1970 NMR study of the 1,1,3,3-tetramethylallyl cation concluded that rotation about the partial C=C bonds within the allyl moiety, presumably via a "perpendicular" (C_s) transition state structure such as **7**, is the preferred pathway; see eq 1.[22] In a later high level computational study Foresman et al. noted that such a path would be enhanced by the attached methyl groups, and therefore had not been proved for the parent allyl cation.[23] In that study the preferred pathway was computed to be partial rotation and rearrangement by hydride shift through transition state **8** to the 2-propenyl cation, **4**, after which rotation about the C2-methyl bond occurs followed by a return hydride shift; see eq 2.

$$\underset{\mathbf{6}}{\text{allyl}^+} \rightarrow [\underset{\mathbf{7}}{\text{allyl}^+ \text{ (perp)}}]^‡ \rightarrow \underset{\mathbf{6'}}{\text{allyl}^+} \quad (1)$$

$$\underset{\mathbf{6}}{\text{allyl}^+} \rightarrow \underset{\mathbf{8}}{[\text{ts}]^‡} \rightarrow \underset{\mathbf{4}}{\text{2-propenyl}^+} \rightarrow \underset{\mathbf{8}}{[\text{ts}]^‡} \rightarrow \underset{\mathbf{6'}}{\text{allyl}^+} \quad (2)$$

A 1969 study of the disrotatory, ring-opening heterolyses of the three diastereomeric 1-chloro-2, 3-dimethylcyclopropanes and subsequent isomerization of the three stereoisomeric 1,3-dimethylallyl cations showed a third pathway in which disrotatory ring closure to a cationic cyclopropyl species, followed by a disrotatory opening in the opposite sense, eq 3, is *not* operative in those systems.[24] Again the methyl substitution might bias these carbocations toward a path like eq 1.

$$\underset{\mathbf{6}}{\text{allyl}^+} \rightarrow [\underset{\mathbf{10}}{\text{cyclopropyl}^+}]^‡ \rightarrow \underset{\mathbf{6'}}{\text{allyl}^+} \quad (3)$$

We have examined these three pathways using the 6-311+G** basis set. In pathway 2 an intrinsic reaction coordinate (irc) calculation showed that transition state **8** does indeed connect the allyl cation with the 2-propenyl cation. In pathway 3 the cyclopropyl cation (**10**) was found to have one imaginary frequency at both the HF and MP2 levels. The motion corresponds to movement of all five hydrogens: a C−H bending motion at the trigonal carbon and twisting about the CH_2-CH_2 bond. An irc calculation showed that this state leads to disrotatory ring opening in both manners, leading to the allyl cation, and thus providing a pathway for hydrogen exchange. We were unable to find **7** (pathway 1), the "perpendicular" allyl cation, at the MP2/6-311+G** level.[17]

In Table 4 we report ΔH° values calculated at the MP2/6-311+G** and MP2/6-311+G**//HF6−311+G** levels for conversion of the allyl cation to the other pertinent cations and transition states in this section. No corrections were made for the number of equivalent ways each pathway can reach the transition state: four for paths 1 and 2, and two for path 3. The results show, in agreement with Foresman and co-workers,[23] that the hydride shift pathway is superior to the C=C rotation

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pathway. The advantage is 5.9 kcal/mol at the MP2//HF level. Moreover it is superior to the ring-closure/ring-opening path by 6.3 kcal/mol at the MP2//HF level and by 4.3 kcal/mol with use of optimized MP2/6-311+G** energies.

Under experimental conditions cations are often generated in the gas phase with internal energies exceeding that of the ground state. Thus, under some conditions, an excited allyl cation might undergo rotational isomerization using all three pathways. Likewise, using data from Table 2, we can estimate that protonation of allene, initially giving the 2-propenyl cation, needs about18 kcal/mol of extra energy to rearrange to the allyl cation.[2e] Therefore, protonation at the terminal carbon followed by rearrangement to the allyl cation is viable for energetic proton transfers to allene. The data in Table 1 show that the experimental and calculated $\Delta H°_{protonation}$ values for allene are in better agreement taking the allyl cation as the conjugate acid at equilibrium. Under equilibrium conditions, the allyl cation could be formed from allene by either direct protonation at the central carbon (kinetically unfavorable) or rearrangement of the 2-propenyl cation (kinetically favored) within the ion−molecule complex, presumably facilitated by the partner in the complex.

Conclusions

The major conclusions of this work are the following.

(1) *Equilibrium* protonation of the X = Y = Z structures in this study strongly favors protonation at one of the ends of the structure. If one of the ends is CH_2 that is the favored site. The only exception is allene for which protonation at the central carbon gives the allyl cation, favored computationally by 10 kcal/mol over end protonation, which gives the 2-propenyl cation.

(2) Protonation at the central atom can give "open" structures which can rearrange to end-protonated cations, add to their neutral precursors, or cyclize leading to isomeric, three-membered ring cations. The cyclic or bridged species are more stable than the open forms by large amounts except for center-protonated allene (allyl cation).

(3) *Kinetic* protonation, studied by use of identity, bimolecular proton transfers, occurs most rapidly at one or the other end of the X = Y = Z triad. When a heteroatom occupies a terminal position, X or Z, proton transfer is barrier-free. Protonation at C1 of allene by H_3S^+ is kinetically favored over protonation at C2 by 9.9 kcal/mol but is thermodynamically disfavored by 10 kcal/mol. The ts for protonation at C2 shows that proton transfer is coupled with a slight (15°) twisting of the allenic skeleton.

(4) The lowest energy path for positional exchange of the hydrogen atoms in allyl cation occurs by hydride shift to the 2-propenyl cation, partial rotation about the C−CH_3 bond, and a return hydride shift to the allyl cation as in eq 2, a conclusion reached earlier by Foresman and co-workers.[23] Under experimental gas-phase conditions rotation about a C=C bond and disrotatory cyclization to the cyclopropyl cation followed by disrotatory opening in the opposite sense could provide alternate, but higher energy, pathways.

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Supporting Information Available: Tables S1, S2, S3, and S4 containing electronic energies, zero-point vibrational energies for all structures, imaginary frequencies for transition state structures, Cartesian coordinates, selected geometric features, and point group assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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