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Theoretical Study of Monosubstituted Propargyl and Cyclopropenyl Cations, $C_3H_2X^+$, and the Reaction of C_3H^+ with HX

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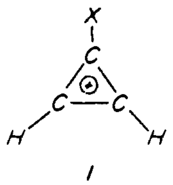
Abstract: Ab initio molecular orbital calculations using gradient optimization procedures with the 6-31G* basis set have been used to optimize structures for cyclopropenyl cations c-$C_3H_2X^+$, α-substituted propargyl cations $XHC^+C{\equiv}CH$, and γ-substituted propargyl cations $H_2C^+C{\equiv}CX$, where X is H, CH_3, NH_2, OH and F. Ions with X=CN and NC were optimized at the 3-21G level followed by single-point calculations at the 6-31G*//3-21G level. Comparison of the relative energies of the isomeric cyclopropenyl and propargyl cations by using 3-21G//3-21G, CI/3-21G//3-21G and 6-31G*//6-31G* levels of theory showed that inclusion of correlation energy usually improves the propargyl cations (by 1–3 kcal/mol) but that inclusion of polarization functions has a larger effect, improving the cyclic ions (by 16–24 kcal/mol). On all surfaces at the 6-31G*//6-31G* level the cyclopropenyl cations are lowest in energy, with the γ-substituted propargyl ions being next lowest except when X is OH and NC. As in other carbenium ions the amino group is the most stabilizing substituent. Despite the inherent stability of the Huckel 2 π-system, the amino, hydroxy, and methyl groups stabilize the cyclopropenyl cations by π-donation, while F, CN, and NC are destabilizing. The structure of the open-chain $C_3H_3^+$ ion is intermediate between that of the propargyl cation (**2a**) and the allenyl cation (**2b**). Substitution at the α-position produces a more propargyl-like structure, while substitution at the γ-position results in a more allenyl-like structure. All the $C_3H_2X^+$ ions are lower in energy than the gas-phase reactants C_3H^+ + HX and also are lower than the gas-phase products CX^+ + H_2C_2. Examination of the profile to interconversion of the propargyl and cyclopropenyl cations yielded an additional structure $H\ddot{C}CH{=}C^+H$ (**6**) in a shallow minimum ~82 kcal/mol above the propargyl cation, and the transition structure for conversion of **6** to the propargyl cation is 104 kcal/mol above the propargyl cation. The barrier to conversion of **6** into the cyclopropenyl cation is 3 kcal/mol at the HF level but disappears at the CI/3-21G//3-21G level.

The cyclopropenyl cation, (**1**) (X = H) is the smallest aromatic molecule, and, despite the large strain energy inherent in the small unsaturated ring system, this ion is stable both in the form of salts, e.g., $C_3H_3^+{\cdot}SbCl_6^-$, and also in polar solvents.[1] The open-chain isomers of the X-cyclopropenyl ions, the alkynylcarbenium ions (**2a** and **3a**), have also been characterized in solution,[2,3] but only ions that are triply substituted are sufficiently stable to have been characterized by NMR.[4] These open-chain ions can be represented by other resonance structures, the allenyl cations[5] **2b** and **3b** and, when X has a lone pair of electrons or a double bond, structures **2c** and **3c**. For methyl- and phenyl-substituted ions analysis of the UV and NMR data has led to the conclusion that both the alkynyl and allenyl structures contribute extensively to the total ion structure.[4]



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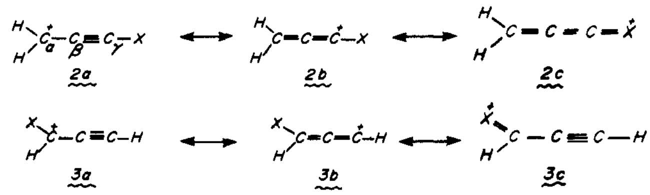
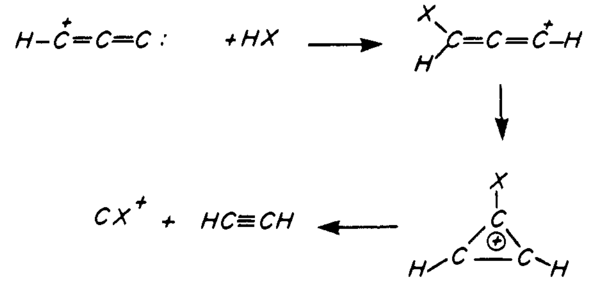


Scheme I



Recently the products of the gas-phase reaction between C_3H^+ and molecules HX have been explained in terms of carbene insertion into the HX bond to give **3b**, followed by rearrangement to the X-cyclopropenyl cation and subsequent decomposition to give acetylene and CX^+ (Scheme I).[6] Ions CX^+ have the largest substituent stabilization energies of all carbocations,[7] and for substituents X = CH_3 and OH, where heats of formation are available,[8-11] the overall reaction in Scheme I is exothermic. However, for the parent system, where the heats of formation of all the species in the scheme are known,[8,9,11,12] the overall reaction

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Table I. Total Energy of Cyclopropenyl Cations at 6-31G*//6-31G* and Relative Energies of α- and γ-Substituted Propargyl Cations at Different Levels of Theory

		energies relative[b] to c-$XC_3H_2^+$					
		$XHC^+C\equiv C^+H$			$H_2C^+C\equiv CX$		
substituent	tot energy[a] c-$XC_3H_2^+$ at 6-31G*//6-31G*	3-21G// 3-21G	CI/3-21G// 3-21G	6-31G*// 6-31G*	3-21G// 3-21G	CI/3-21G// 3-21G	6-31G*// 6-31G*
H	−115.00702	12.6	10.0	35.1	12.6	10.0	35.1
CH_3	−154.06793	11.6	9.3	33.3	8.3	6.7	30.1
NH_2	−170.07988	−6.7	1.5	10.4	−2.6	−4.9	20.1
OH	−189.87555	0.0	11.7	17.9	6.7	4.5	29.3
F	−213.83610	7.3	3.4	23.7	16.1	13.9	38.1
CN	−206.70360[c]	11.8		32.3[c]	7.2	−0.8	29.5[c]
NC	−206.69111[c]	8.8		25.7[c]	4.0	3.1	27.7[c]

[a] Energy in hartrees. [b] Relative energies in kcal/mol. [c] Calculations at 6-31G*//3-21G level.

is endothermic and the observed product $C_3H_3^+$ is probably the cyclopropenyl cation.

We now report an ab initio molecular orbital investigation of the surface for this reaction using 6-31G* level calculations and with X taken to be H, CH_3, NH_2, OH, F, CN, and NC. In particular we were interested in the structures and relative energies of the intermediate cations (**1** and **2**) and in the barrier to their interconversion. We compare our results with a previous ab initio study[13] at the STO-3G level on some of the alkynylcarbenium ions.

Methods

Standard closed-shell ab initio molecular orbital calculations were carried out with the MONSTERGAUSS program.[14] Complete geometry optimizations using gradient optimization procedures[15,16] were performed on ions with X = H, CH_3, NH_2, OH, and F with a 6-31G* basis set.[17] For ions containing the cyano and isocyano groups the size of the ions required that we perform optimizations at the 3-21G level,[18] followed by single-point calculations at the 6-31G* level (denoted 6-31G*//3-21G). In order to assess the inaccuracies arising from using 6-31G* level calculations at 3-21G level geometries for the cyano- and isocyano-substituted compounds, we examined the fluoro-substituted ions at both the 6-31G*//6-31G* and 6-31G*//3-21G levels and found the total energies at the former level of theory for structures I, II, and III (X = F) to be better by 0.9, 1.5, and 1.1 kcal/mol, respectively. These improvements in energy are small and as most of our work involves energy differences that are fairly large we conclude that there is little accuracy sacrificed by using geometries from the 3-21G level. In all cases the criterion for optimization was that the norm of the gradient vector was less than 5×10^{-4} mdyn at convergence, a condition that generally gives bond lengths and angles within 0.0001 Å and 0.1°, respectively, of their true optimum values.

Transition-state structures were optimized with the VA05AD sum of squares optimization technique.[19] Single-point calculations on optimized structures were performed with a CI program using the direct CI method[20] and including all single and double excitations from the valence shell to all the virtual orbitals.

In all calculations involving cyano and isocyano groups the substituent was taken to be linear, following the procedure adopted in earlier studies.[21,22]

Results and Discussion

1. Molecular Structures. (a) X-Cyclopropenyl Cations. For the parent cyclopropenyl cation the 6-31G* optimized carbon–carbon bond length is 1.349 Å (Figure 1), and this compares with an experimental value of 1.373 Å found for the *sym*-triphenylcyclopropenyl cation.[23] Initial studies at lower levels of theory showed all the substituents to lie in the plane of the cyclopropenyl ring, and all substituted ions were optimized with either C_{2v} or C_s symmetry. Comparison of the C–X distance with those in two other classes of carbenium ions, the 1-substituted allyl cations, in which the substituent is attached to an sp^2 carbon in an unsaturated ion, and the α-X-isopropyl cations, in which the substituent is attached to an sp^2 carbon bonded to two saturated carbons, shows the C–X distance to be shortest in X-cyclopropenyl cations for all substituents except when X is CH_3 and NH_2. Furthermore, for the cyclopropenyl ring the vicinal bonds are longer than the distal bond for all substituents except when X = F, indicating that the substituents are electron donors. The calculated net charges on the substituents from a Mulliken population analysis are given in Figure 2, along with their π- and σ-components. All the substituents are π-donors, with the amino group being strongest, but for substituents containing more electronegative elements than carbon σ-withdrawal is dominant and the net charges on the substituents are negative. For all substituents there is less π-donation and the net negative charge is larger than in the isomeric alkynylcarbenium ions **2** and **3**. Nevertheless, as a result of the intrinsic stability of the Hückel 2 π-electron system the X-cyclopropenyl cations are lower in energy than the α- and γ-substituted propargyl cations (Table I). When X = H, the cyclopropenyl cation is lower in energy than the propargyl cation by 35 kcal/mol (experimental value 25 kcal/mol), but substitution reduces the energy difference and the γ-aminopropargyl cation is only 10.4 kcal/mol higher in energy than the aminocyclopropenyl cation.

Inclusion of polarization functions is particularly important for an adequate description of small ring compounds. At the 3-21G//3-21G level ions **2** are close in energy to the cyclopropenyl cation **1** (Table I), but at the 6-31G*//6-31G* level the difference between **1** and **2** increased by between 21 and 24 kcal/mol. Increasing the basis set also improved **1** relative to **3**, but here the improvement is over a wider range (16–23 kcal/mol). Inclusion of correlation energy has a much smaller effect on the relative energies of isomers **1**, **2**, and **3**. At the CI/3-21G//3-21G level the energies of cations **2** relative to **1** were decreased by less than 3 kcal/mol with the exception of X = CN (decreased by 8 kcal/mol). Also at the CI level for ions **3** where X = CH_3 and F there were similar small decreases in energy relative to **1**, but when X = NH_2 and OH inclusion of correlation energy increased the relative energy of **3** by 8.2 and 11.7 kcal/mol, respectively. Finally at the higher CI/6-31G*//6-31G* level the parent cyclopropenyl cation is lower in energy than the propargyl cation

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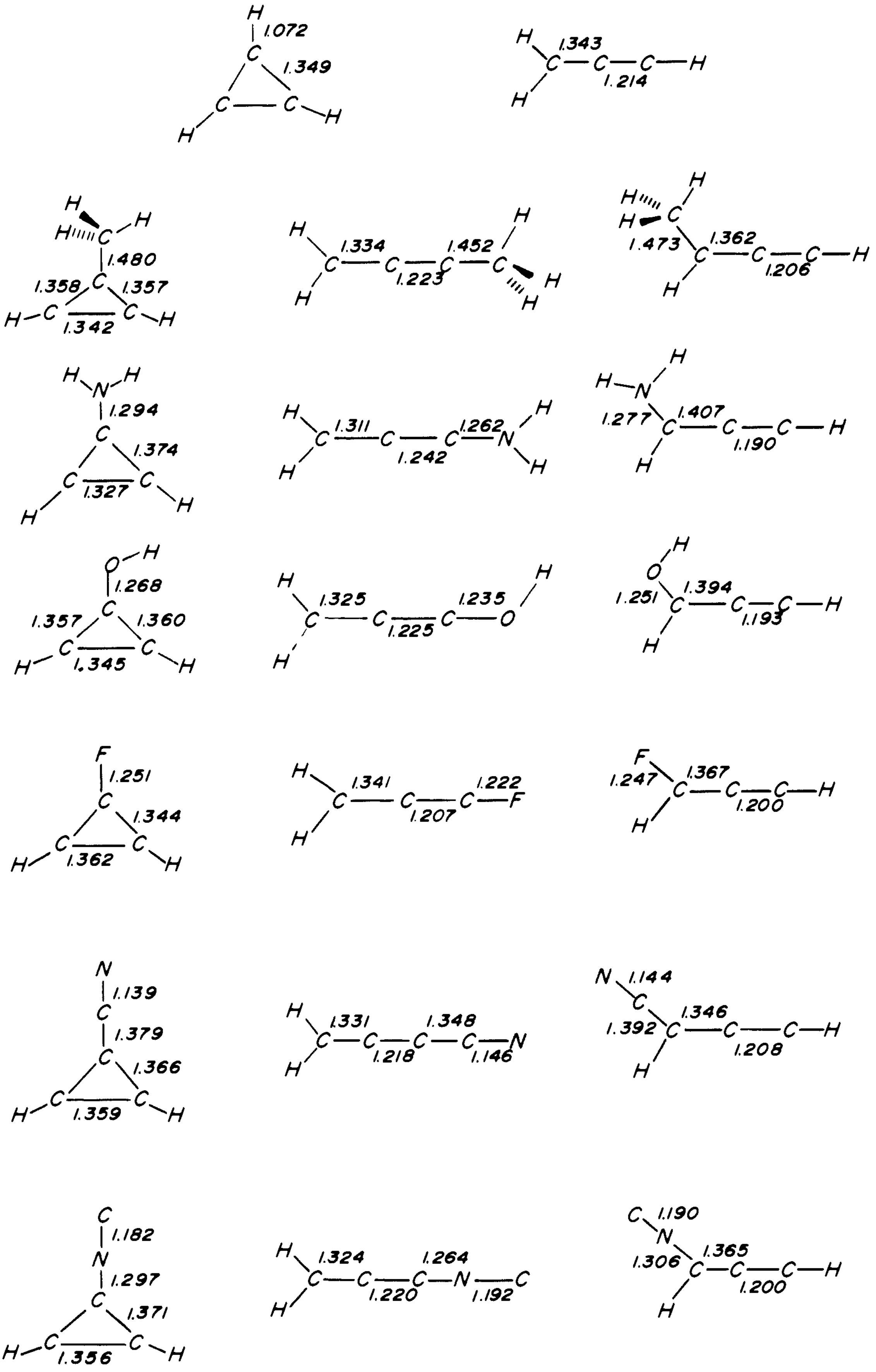


Figure 1. Bond lengths (in angstroms) for bonds between heavy atoms as optimized at the 6-31G* level. Ions containing CN and NC were optimized at the 3-21G level.

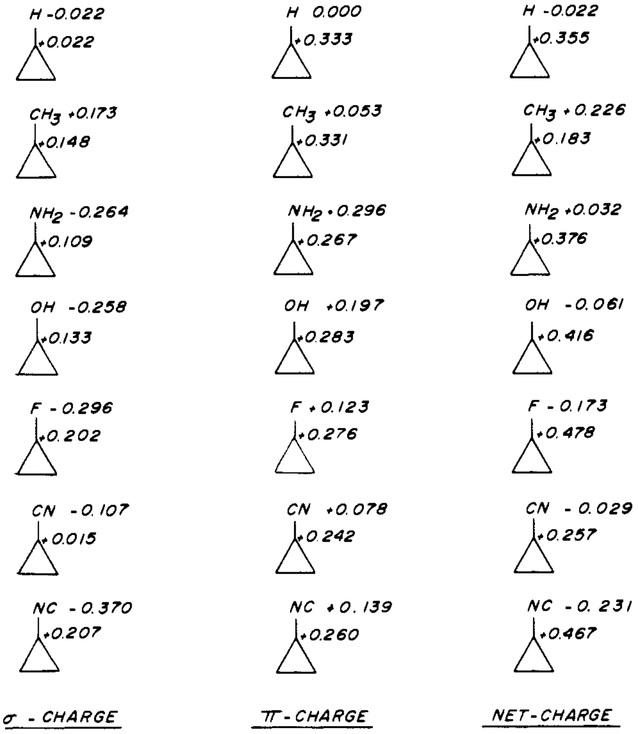


Figure 2. σ, π, and net charges on substituents and cationic carbons.

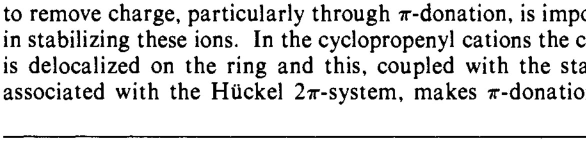
by 33.8 kcal/mol, compared with a difference of 35.1 kcal/mol at the 6-31G*//6-31G* level.

(b) Alkynyl Cations. The carbon–carbon bond lengths (1.343 and 1.214 Å) in the propargyl cation (**2**, **3**, X = H) are close to, but slightly longer than, the average values for a double and a triple bond (1.31 and 1.20 Å, respectively).[24] These parameters indicate that the structure is intermediate between the two resonance structures **2a** and**2b** and the π-charge distribution of +0.584 on the α-carbon and +0.565 on the γ-carbon supports this conclusion.

Introduction of a substituent at the γ-position stabilizes charge at this position. The bond angle at the substituent is almost 180°, with the largest deviation being 176.4° when X is OH. The C_α–C_β distance is shortened and the C_β–C_γ distance, lengthened making the structure closer to that of the allenyl cation (structure **2b**). In these γ-substituted ions the C–X distances are all shorter than in the 1-X-allyl cations,[25] indicating a large substituent–ion interaction.

In the α-substituted ions the C_α–C_β bond is longer than in the parent propargyl cation while C_β–C_γ is shorter. These changes are the opposite of those produced by γ-substitution and are consistent with a more propargyl-like structure, i.e., resonance structure **3a**. The C–X bonds in the α-substituted ions are longer than in the γ-substituted ions, but π-donation in **3** is larger than in ions **1** and **2**, all consistent with the propargyl structure.

2. Stabilization of the X-Cyclopropenyl Cations by Substituents. The relative effect of substituents on the stabilities of the α-X-cyclopropyl and X-cyclopropenyl cations can be assessed by using eq 1. In the cyclopropyl cations the positive charge is largely


(1)

localized at the carbocation center and the ability of the substituent to remove charge, particularly through π-donation, is important in stabilizing these ions. In the cyclopropenyl cations the charge is delocalized on the ring and this, coupled with the stability associated with the Hückel 2π-system, makes π-donation less important. The reaction described by eq 1 then is exothermic (Table II), with the strongest donor, NH_2, having the largest effect.

Table II. Calculated ΔE^a for Isodesmic Reactions To Calculate Substituent Effects

X	eq 1	eq 6
CH_3	-7.0	-11.2 (-8)^b
NH_2	-33.4	-56.1
OH	-22.3	-37.9
F	-12.7	-20.2
CN	-7.6	-0.4
NC	-15.9	-16.4

^{a} In kcal/mol. ^{b} Experimental heat of reaction using heats of formation from ref 9 and Bowers, M. T. *Gas Phase Ion Chemistry*; Academic: New York, 1979; Vol. 2.

Table III. Substituent Stabilization Energies^a in Cyclopropenyl Cations

substituent	eq 4	eq 5	eq 7 and stabilizn energies for 2-X-allyl cations^{b,c}
CH_3	14.9	14.6	8.7, 8.3, 6.9
NH_2	31.8	30.7	22.0, 28.9, 29.9
OH	13.3	7.9	15.2, 12.2, 6.3
F	-10.8	-19.3	-3.5, -8.0, -8.3
CN	-24.7	-25.7	-24.6, -27.1, -28.2
NC	-12.6	-16.3	-14.0, -15.9, -17.0

^{a} In kcal/mol. ^{b} Reference 25. ^{c} The approximation made here that the α-X-cyclopropyl and the α-X-isopropyl cations have the same substituent stabilization energy can be corrected by *adding* the energies given in ref 28.

Previously we have used eq 2 to estimate the large substituent


(2)

stabilization energy of the α-X-cyclopropyl cation relative to the effect in a similarly substituted cyclopropane.[26] Clark et al.[27] have recently shown by use of eq 3 that substituent stabilization energies in cyclopropanes are relatively small (ΔE values are CH_3,

$$CH_3X + c\text{-}C_3H_6 \longrightarrow c\text{-}C_3H_5X + CH_4 \quad (3)$$

-3.1 kcal/mol; NH_2, -6.6 kcal/mol; OH, -3.6 kcal/mol, and F, -5.3 kcal/mol at the 4-31G//4-31G level), and if we therefore neglect any stabilization by X in cyclopropane we can combine eq 1 and 2 to give eq 4, which provides an estimate of the sta-


(4)

bilizing effect of X in the cyclopropenyl cation. For example for NH_2 using this approach we combine ΔE values of -33.4 kcal/mol from eq 1 with 65.2 kcal/mol from eq 2 to obtain a value of 31.8 kcal/mol for the stabilization of the amino group in the cyclopropenyl cation. This is considerably smaller than the stabilizations by the α-amino group in alkyl cations ($CH_2NH_2^+$, 87.4 kcal/mol; $CH_3CHNH_2^+$, 63.4 kcal/mol; $(CH_3)_2CNH_2^+$, 63.4 kcal/mol),[26] and in the 1-substituted allyl cation (values estimated from 54 to 45 kcal/mol).[25]

Combination of the stabilization energies for α-X-cyclopropyl cations[26] with the energies from eq 1, as previously described for the amino group, gives the cyclopropenyl cation substituent stabilization energies given in Table III (first column). Here the

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(28) α-X-cyclopropyl cations have a slightly higher substituent stabilization energy than α-X-isopropyl cations. At the 6-31G*//3-21G level the differences in stabilization energies (kcal/mol) are CH_3, 6.6; NH_2, 1.8; OH, 1.1; F, -2.8; CN, 2.4; NC, 3.7 (data taken from ref 26). Addition of these numbers to column 3 in Table III eliminates the approximation made in calculating ΔE for eq 7.

Table IV. Energies[a] of Intermediate Cyclopropenyl Cations (c-$C_3H_2X^+$) and Products ($CX^+ + C_2H_2$) Relative to Reactions ($C_3H^+ + HX$)

substituent, X	c-$C_3H_2X^+$ 3-21G//3-21G	c-$C_3H_2X^+$ CI/3-21G//3-21G	c-$C_3H_2X^+$ 6-31G*//6-31G*	HC≡CH + CX^{+b} 3-21G//3-21G	HC≡CH + CX^{+b} CI/3-21G//3-21G	HC≡CH + CX^{+b} 6-31G*//6-31G*	exptl[d]
H	−118.3	−109.2	−141.4	41.3	43.4	42.8	58
CH_3	−113.1	−101.0	−136.8	−35.6 (6.7)	−42.2 (4.6)	−34.2 (+7.1)	−45
NH_2	−138.6	−131.1	−151.1	−94.9 (−52.4)	−114.7 (−60.3)	−86.5 (−44.9)	
OH	−114.7	−107.8	−131.8	−71.0 (−50.6)	−95.0 (−34.8)	−74.1 (−41.8)	−78
F	−93.9	−88.8	−111.9	4.4	−11.7	−4.9	+5
CN	−90.8	−65.3	−109.0	4.8 (52.3)	17.9 (49.0)	12.3 (+58.3)	
NC	−95.1	−74.3	−113.6	−4.2	1.4	0.1	

[a] In kcal/mol. [b] Numbers in parentheses use the high-energy forms of CX^+, i.e., H_3CC^+, $H_2N^+{=}C$, $C{=}OH^+$ and $CC^+{\equiv}N$, all assumed to be singlets. [c] At the CI/6-31G*//6-31G* (5d) level energies relative to ($C_3H^+ + H_2$) are −138.3 kcal/mol for c-$C_3H_3^+$ and 43.1 kcal/mol for (HC≡CH + CX^+). [d] Using heats of formation from ref 8–11.

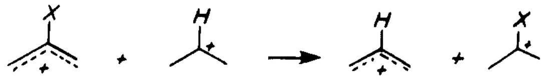
CH_3,NH_2 and OH groups are stabilizing and –CN is destabilizing, as in all previously examined α-X-carbocations. However, all the stabilization energies are small and F and –NC, which normally stabilize carbenium ions,[26] are destabilizing in the cyclopropenyl cation.

An alternate way of assessing substituent stabilization energies is to use the hydride-transfer reaction given in eq 5. The exo-


(5)

thermicity of the reaction is a measure of the ability of substituent X to stabilize the cyclopropenyl cation relative to the stabilization in cyclopropene. We have optimized structures for the cyclopropenes at the 3-21G level and have used the energies from the 6-31G*//3-21G level to obtain the stabilization energies given in Table III (second column). As with the previous method of estimating stabilization energies, CH_3, NH_2, and OH are stabilizing and F, NC, and CN are destabilizing in the cyclopropenyl cation. There is reasonably good agreement between the two sets of stabilization energies, with the largest discrepancy being for the α-fluoro substituent (8.5 kcal/mol).

The analogous open-chain reaction to eq 1 compares the effect of substituents in the 2-X-allyl cations with those in the α-X-isopropyl cations (eq 6). In the delocalized allyl cations sub-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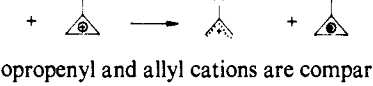
stitution by CH_3, NH_2, and OH at the 2-position has little effect while substitution by F, CN, and NC is destabilizing by 15–20 kcal/mol.[25] The isopropyl cation is strongly stabilized by strong π-donors like NH_2 and OH and less so by CH_3 and F and is destabilized by the cyano group (by 19.5 kcal/mol).[26] The reaction described by eq 6, then, is exothermic for all substituents except CN, for which is is thermoneutral. More importantly in the current context the reaction in eq 6 is more exothermic than that in eq 1, again with the exception of when X = CN. If the effect of α-substituents in the isopropyl and cyclopropyl cations are taken to be equal,[26] then subtraction of eq 6 from eq 1 gives eq 7, in


(7)

which the cyclopropenyl and allyl cations are compared. However, we have previously used several reactions to calculate substituent effects in 2-X-allyl cations, and in conjunction with eq 7 these can be used to calculate substituent effects in the cyclopropenyl cations. For example, for the amino substituent the effect in the 2-X-allyl cation is 6.2, 7.2, and −0.7 kcal/mol, depending upon the reaction used for the calculation, and combining these with Δ*E* for eq 7 (+22.7 kcal/mol) gives values of 28.9, 29.9, and 22.0 kcal/mol for the stabilization of the cyclopropenyl cation by the amino group. With this method of estimating substituent effects in cyclopropenyl cations, CH_3, NH_2, and OH are again found to be stabilizing. Here the methyl group is predicted to be less stabilizing than by the other methods, but the approximation of equating the substituent stabilization of the isopropyl and cyclopropyl cations is least satisfactory for the methyl group, and addition of the actual difference (6.6 kcal/mol) to the numbers in column 3 of Table III makes agreement with the other two methods more satisfactory. The fluoro group is less destabilizing by this method of estimation, while there is good agreement on the destabilization afforded by the cyano and isocyano groups.

3. Reaction of C_3H^+ with HX. The overall reaction to form the products CX^+ and C_2H_2 from reactants C_3H^+ and HX, as outlined in scheme I, is endothermic for X = H and CN and is thermoneutral for X = NC and F (Table IV). For the other substituents the reaction is exothermic, assuming that CH_3C^+, H_2NC^+, and HOC^+ all rearrange by 1,2-hydride shifts to form the lower energy $H_2C{=}CH^+$, $CH{\equiv}NH^+$, and HCO^+ isomers. Experimental heats of reaction calculated from heats of formation show the overall reaction to be exothermic for X = CH_3 and OH, endothermic for X = H, and close to thermoneutral for X = F, in fair agreement with theory. Furthermore in the gas-phase reaction of C_3H^+ with H_2 only the addition product, $C_3H_3^+$, is formed, while with methane the dissociation product, $C_2H_3^+$, is the major product. In the reaction of C_3H^+ with water the products are HCO^+, postulated to be formed by dissociation of the hydroxycyclopropenyl cation, and $C_2H_3^+$, resulting from proton transfer from HCO^+ to the neutral fragment of dissociation, acetylene. For X = H, OH, and CH_3 then theory and experiment agree on the overall product of the reaction between HX and C_3H^+.

For the reaction of C_3H^+ with HX to form C_2H_2 and CX^+ the largest exothermicities are for substituents (X = NH_2 and OH) that strongly stabilize the product CX^+ ions.[7] The exothermicity of this overall reaction is largely independent of the basis set used in Hartree-Fock calculations, but for X = CH_3, NH_2, and OH, where the products formally contain more bonds than the reactants, inclusion of correlation energy increases the exothermicity of the reaction.

For the reaction sequence in scheme I the intermediate α-substituted propargyl and X-cyclopropenyl cations are much lower in energy than the reactants and products at all levels of theory (Table IV). Inclusion of polarization functions is important in the description of small-ring compounds, and stabilization of the X-cyclopropenyl cations is largest at the 6-31G*//6-31G* level. Inclusion of correlation energy at the 3-21G//3-21G level has the opposite effect, slightly decreasing the energies of the cyclopropenyl cations relative to the reactants C_3H^+ and HX. Formation of the X-cyclopropenyl cations from the α-X-propargyl ions requires either X or H to undergo a 1,2-shift and also for the unsaturated carbon atom chain to distort from the linear arrangement found in the propargyl ions.

We have examined the profile to rearrangement of the parent propargyl ion (X = H) to the cyclopropenyl cation and in the course of this work have discovered two additional minima and three transition states. In preliminary work at the 3-21G level our initial guess for the transition-state structure, a structure obtained in a previous point-by-point study,[29] led to a transi-

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[29] Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. So.* **1976**, *98*, 10.

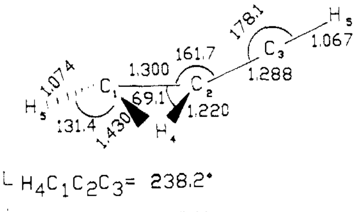
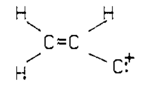


Figure 3. Geometry of transition-state structure (6-31G*//6-31G* level) for conversion of cyclopropenyl cation into propargyl cation.

tion-state structure with ∠CCC of 70° and with two hydrogens attached to the same carbon atom. Slight distortions of this structure caused it to collapse into the prop-2-en-1-yl-3-ylidene ion, **4**, an ion previously[29] found to be the third lowest in energy on the $C_3H_3^+$ surface. At the 6-31G*//6-31G* level we find **4** to be 69.3 kcal/mol above the cyclopropenyl cation.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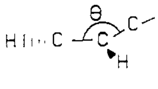
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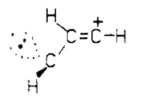
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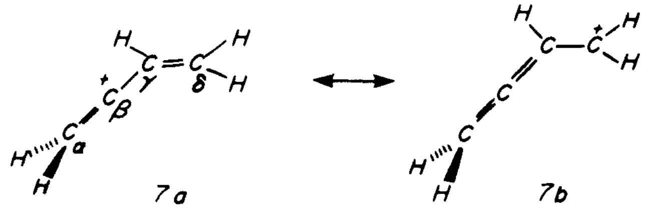
We then reexamined the profile to ring opening of the cyclopropenyl cation using fixed values of θ (see structure **5**) and optimizing the geometric parameters associated with the migrating hydrogen atom and also the C–C distances varying one parameter at a time. This procedure led us to a maximum on the surface at ∠CCC ≈ 120°. Subsequent geometry optimizations at both the 3-21G and 6-31G* levels using the VA05AD method produced a transition-state structure 103.8 and 120.6 kcal/mol, respectively, above the cyclopropenyl cation. Calculations with the OC method at both SCF levels using the transition-state structure with a slightly decreased ∠CCC resulted in collapse to the cyclopropenyl cation, but when the angle was increased a new minimum with ∠CCC around 135° was found. This ion, which was not discussed in an earlier extensive molecular orbital study[29] of $C_3H_3^+$, is best represented by a structure with a carbene at one terminal carbon and a vinyl cation at the other (structure **6**). Structure **6** was only 3.0 kcal/mol at 3-21G//3-21G and 3.5 kcal/mol at 6-31G*//6-31G* below the transition state leading to formation of the cyclopropenyl cation and therefore has little physical significance. Furthermore when CI/3-21G//3-21G calculations were performed on **6** and on the transition state the latter was lower in energy, suggesting that the existence of **6** as a minimum on the surface may be an artifact of Hartree-Fock level calculations.

Further increasing θ at the 3-21G level indicated a higher maximum when $\theta \approx 160°$, and a subsequent optimization at the 6-31G* level using the VAO5AD method produced a transition-state structure 139 kcal/mol above the cyclopropenyl cation. The motion leading to collapse of this structure (Figure 3) is mainly associated with the migrating hydrogen, and slight distortions of the structure followed by optimization with the OC method resulted in formation of **2** and **6**.

The conversion of the propargyl cation into the cyclopropenyl cation by the pathway described above then involves a transition state ~110 kcal/mol above the propargyl cation (113.8 kcal/mol at 3-21G//6-31G*, 104 kcal/mol at 3-31G*//6-31G*, and 114.1 kcal/mol at CI/3-21G//6-31G*) in which the hydrogen is well on its way to the central carbon atom while ∠CCC is only bent about 20° from the linear. The energy of $C_3H^+ + H_2$ is calculated to be 106 kcal/mol (at the 6-31G*//6-31G* level) and is estimated experimentally to be 97 kcal/mol above that of the propargyl cation. It appears then that rearrangement of the propargyl cation to the cyclopropenyl cation by the above pathway is just possible under the reaction conditions in the flowing-afterglow experiment.[6]

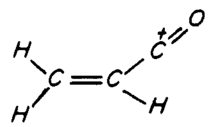
4. Other Isomers of Ions $C_3H_2X^+$. We have examined other plausible structures for several of the ions and find that when X is H, CH_3, and F the cyclopropenyl ions are the lowest in energy. However, for the methylcyclopropenyl cation another isomer, **7**,



7a 7b

is only 0.1 kcal/mol higher in energy at the 3-21G//3-21G level. This ion, which was previously examined at the 4-31G//STO-3G level of theory,[32] has bond lengths for C–C and C–C of 1.366 and 1.359 Å, respectively, showing a large amount of double bond character in both bonds; i.e., the structure is best represented by the delocalized allyl cation intermediate between resonance structures **7a** and **7b**.

We have studied the $C_3H_3O^+$ surface in considerable detail at the 6-31G*//6-31G* level and find that of the 11 structures (Table V, Supplementary Material) we considered, the acylium ion **8** is the global minimum, 22 kcal/mol lower in energy than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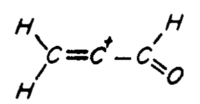
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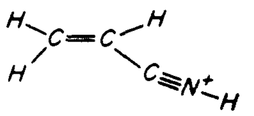
the hydroxycyclopropenyl cation. Formation of **8** from the α-hydroxypropargyl ion (**2**), requires a hydride shift from oxygen to the terminal carbon atom to give the vinyl cation **9** (27 kcal/mol above **2**), followed by a 1,2-hydride shift to produce **8**. Dissociation of **8** yields CO and $C_2H_3^+$, and the latter is one of the products observed in the gas-phase reaction of C_3H^+ with H_2O.[6]

Of 17 structures (Tables VI and VII, Supplementary Material) examined on the $C_3NH_4^+$ surface, only **10** and **11** are of similar energies to the aminocyclopropenyl ion (**1**, X = NH_2). The nitrogen analogue of **8** is protonated acrylonitrile, **10**, and this is the global minimum, 1.7 kcal/mol below **1**. The protonated isonitrile **11** is 9.9 kcal/mol above **1**.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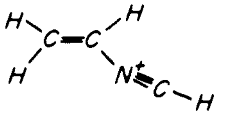
11

On the $C_4NH_2^+$ surface the nitrenium ion $(HC{\equiv}C)_2N^+$ is higher in energy than all the six cyano- and isocyano-substituted compounds given in Table I, and of the limited number of structures examined here the cyanocyclopropenyl cation has the lowest energy. In alkenes[22] and alkanes[21,33] cyano substitution results in molecules that are lower in energy than the isomeric isocyano-substituted molecules by 17–20 kcal/mol. In alkyl carbanions an α-cyano group removes negative charge by π-withdrawal and is even more stabilizing than the isocyano group (by 30–40 kcal mol[33]). However, in carbenium ions cyano is destabilizing and isocyano is weakly stabilizing with the result that the isocyano-substituted isomers are the more stable by 2–7 kcal/mol.[21] In the unsaturated carbenium ions in the current study there is less substituent dependence and the cyano-substituted carbenium ions are lower in energy by 4.7 kcal/mol for **1**, by 1.2

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kcal/mol for **2**, and by 4.7 kcal/mol for **3**.

Summary

The X-cyclopropenyl cations for all substituents (X = H, CH_3, NH_2, OH, F, CN, and NC) are lower in energy than the isomeric α-X- and γ-X-substituted propargyl cations by at least 17 kcal/mol. This preference for the strained cyclic system results from the stabilization inherent in the Hückel 2π-system. Despite the stability of the 2π-electron system all the substituents continue to function as π-donors as in other carbenium ions, and in two of the X-cyclopropenyl cations (X = NH_2 and OH) this results in a further stabilization.

The overall reaction for conversion of C_3H^+ and HX into CX^+ and C_2H_2 is exothermic for all substituents except X = H and CN, and the X-cyclopropenyl cations, if formed, will have such a large excess of energy that they should easily undergo the orbital symmetry-forbidden dissociation into CX^+ and C_2H_2. On the $C_3H_3^+$ energy hypersurface transition-structure calculations show the barrier to formation of the cyclopropenyl cation from the propargyl cation via intermediate **6** to be ~104 kcal/mol at the 6-31G*//6-31G* level. The transition structure for this rearrangement has almost the same energy as the initial reactants (H_2 and C_3H^+ are 106 kcal/mol above the propargyl ion), and given that C_3H^+ may have some excess kinetic energy it therefore seems likely that the cyclopropenyl cation is formed under experimental conditions.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support, York University Computer Centre for generous allotments of computer time, Professor D. K. Bohme for bringing this problem to our attention, and the referees for constructive comments.

Registry No. c-$C_3H_3^+$, 26810-74-2; c-$MeC_3H_2^+$, 60824-24-0; c-$NH_2C_3H_2^+$, 101671-87-8; c-$OHC_3H_2^+$, 49598-05-2; c-$FC_3H_2^+$, 72247-93-9; c-$CNC_3H_2^+$, 101671-88-9; c-$NCC_3H_2^+$, 101671-89-0; $HC{\equiv}C{-}CH_2^+$, 21540-27-2; $HC{\equiv}CCHCH_3^+$, 72183-36-9; $HC{\equiv}CCH{=}NH{\cdot}H^+$, 101671-80-1; $HC{\equiv}CCHO{\cdot}H^+$, 101671-81-2; $HC{\equiv}CCHF^+$, 72188-22-8; $HC{\equiv}CCHCN^+$, 101671-82-3; $HC{\equiv}CCHNC^+$, 101671-83-4; $MeC{\equiv}CCH_2^+$, 64235-83-2; $H_2C{=}C{=}C{=}NH{\cdot}H^+$, 101695-35-6; $H_2C{=}C{=}C{=}O{\cdot}H^+$, 101671-84-5; $FC{\equiv}CCH_2^+$, 57376-53-1; $CNC{\equiv}CCH_2^+$, 101671-85-6; $NCC{\equiv}CCH_2^+$, 101671-86-7; H_2, 1333-74-0; CH_4, 74-82-8; NH_3, 7664-41-7; H_2O, 7732-18-5; HF, 7664-39-3; HCN, 74-90-8; HNC, 75-13-8.

Supplementary Material Available: Tables V, VI, and VII, giving some structural detailed (bonds and angles involving only heavy atoms) and total energies for isomers on $C_3H_3O^+$ and $C_3H_4N^+$ surfaces (5 pages). Ordering information is given on any current masthead page.

Nitrous Oxide in Gas-Phase Ion–Molecule Chemistry: A Versatile Reagent for the Determination of Carbanion Structure

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Abstract: Nitrous oxide has been found to undergo a wide variety of reactions with anions in the gas phase. The products of these reactions are highly characteristic of the ion's structure and, therefore, this reagent (N_2O) is especially useful in distinguishing between different types of ions. In general, primary carbanions react to produce diazo anions as the major products, secondary carbanions dehydrogenate, and tertiary carbanions afford adducts, oxygen atom transfer, and cleavage products. However, novel reaction channels can be brought about by modifying the reactant ion's structures. For example, deprotonation of methylene cyclopropane produces a strained allylic anion which reacts with N_2O to afford cyanide and the 2-nitrosoallyl anion, while removal of a proton from furan, which has a good α-leaving group, generates the nitrogen atom transfer product, 3-cyanoacrolein radical anion, upon reaction with N_2O. It was observed that proton abstraction from cyclopentene, cyclohexene, and internal olefins without allylic methyl groups does not afford M − 1 ions in the flowing afterglow.

Instrumental methods for studying gas-phase ion chemistry continue to improve, with the most recent additions being the Fourier transform technique for ion cyclotron resonance spectrometry[1] (FT-MS) and the selected ion flow tube[2] (SIFT) and the triple quadrupole[3] versions for the flowing afterglow (FA). These improvements have led to a broader range of reactions which can be studied and a deeper understanding of gas-phase ion chemistry, particularly that of carbanions. Despite these technical advances, methods for the determination of ion structure remain a central problem, especially as experimenters study more complex molecules in which the number of possible isomeric ions increases dramatically. In our work[4-7] we have emphasized chemical methods for ion structure determination; among the useful reagents we have investigated are D_2O, O_2, CS_2, COS, and N_2O. All of these reagents are volatile, readily available, and often highly diagnostic of ion structure.

No neutral reagent in gas-phase anion-molecule chemistry shows the variety of reactions that nitrous oxide, N_2O, does. This simple reagent continues to amaze by the sheer diversity of the

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