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Molecular Orbital Theory of the Electronic Structure of Molecules. 36. A Theoretical Study of Several α -Substituted Vinyl Cations^{1a}

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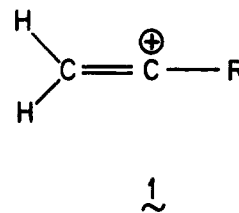
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The α -ethynylvinyl (4), α -ethenylvinyl (5), α -cyclopropylvinyl (6), and α -phenylvinyl (7) cations have been investigated by SCF-MO ab initio methods, using both the STO-3G and the 4-31G basis sets. The cations 5, 6, and 7 are more stable in perpendicular conformations (5a, 6a, and 7a, respectively) where the interaction between the "empty" cationic orbital and the HOMO of the substituent is maximized. The calculated rotation barriers around the C⁺-substituent bonds are 22.2, 15.8, and 24.7 kcal/mol for 5, 6, and 7, respectively, approximately half the barrier in the corresponding primary alkyl cations. The efficiency of the α substituent in stabilizing the vinyl cation follows the order $C_6H_5 > c-C_3H_5 \approx HC=CH_2 \gg C\equiv CH \approx CH_3 \gg H$. The ability of the substituents to donate electrons to the empty cationic orbital follows the order $C_6H_5 > CH=CH_2 > C\equiv CH > c-C_3H_5 > CH_3 > H$. No correlation is found between the total charge at the cationic center or the corresponding populations of the formally empty p orbital and the stability of the cation. The cations vinyl (2), α -methylvinyl (3), and 6 have stabilities which are intermediate between those of the corresponding primary and secondary alkyl cations. However, the π -stabilized cations 4, 5, and 7 are of comparable stability to the corresponding primary alkyl cations. Corresponding substituted ethyl cations are 12–17 kcal/mol more stable than the vinyl cations, suggesting that, for the groups examined here, substituent effects are inherently similar for alkenyl and for alkyl cations. The proton affinities of substituted acetylenes and olefins are comparable, with the olefins being 1–5 kcal/mol more basic.

Vinyl cations are by now well-established reaction intermediates in solvolytic reactions.² Despite active research in the field over the last 10 years, very little is known about their inherent stabilities, their structures, or their charge distributions. The use of solvolysis rates to deduce the relative stability of resulting cations is complicated by ground state and solvation effects.² Observation of stable vinyl cations in superacid media has been claimed but not fully substantiated.^{3a,b} Related experimental data in the gas phase are rare, although some heats of formation are known. These are for the parent vinyl cation (2),^{3c} the propenyl cation (3),^{3c-e} and $C_4H_3^+$ and $C_4H_5^+$ cations of unknown structure.^{3b}

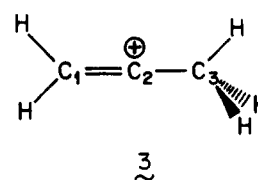
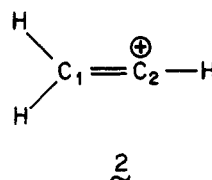
Extensive research has established that ab initio molecular orbital calculations even with minimal basis sets are a powerful, accurate, and inexpensive tool for the study of organic molecules.⁴ Many theoretical studies of carbocations have been made,⁵ but the vinylic cation family has received only little attention, with most of the emphasis devoted to the structure of the parent, 2.^{5a,6} The only other α -substituted vinylic cation which has been investigated in detail by ab initio methods is the 2-propenyl cation 3.^{7a} The energies of several other alkyl-substituted vinyl cations (1, R = Et, *i*-Pr, *t*-Bu) have been reported but not discussed in detail.^{7b} We reported recently a systematic study of α -substituted vinyl cations 1 where R is varied along the whole series of first short period substituents, Li, BeH, BH₂, CH₃, NH₂, OH, and F.⁸ In the present paper we use standard MO-SCF ab initio procedures to study the effect of substituents which are frequently used in solvolysis reactions (i.e., 1, R = ethynyl, vinyl, phenyl, and cyclopropyl).²



- | | |
|------------------------|--|
| 2, R = H | 5, R = CH=CH ₂ |
| 3, R = CH ₃ | 6, R = <i>c</i> -C ₃ H ₅ (cyclopropyl) |
| 4, R = C≡CH | 7, R = C ₆ H ₅ |

Method, Geometrical Models, and Results

Calculations were carried out at the restricted Hartree-Fock (RHF) level using the ab initio SCF-MO Gaussian 70 series of programs.⁹ The structures were fully or partially optimized using the minimal basis RHF/STO-3G method,^{10a} followed by single-point calculations at the split-valence basis RHF/4-31G level.^{10b} This procedure has been used previously for 2^{6d} and 3.^{7a}



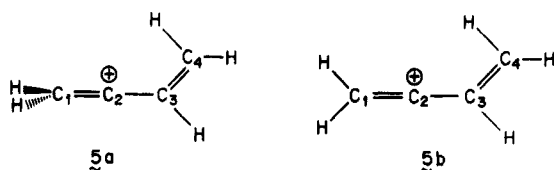
The structure of 4 was fully optimized (Figure 1). In the

Table I. Optimized Geometrical Parameters of Several α -Substituted Vinyl Cations (1)^{a,b}

R	Structure and symmetry	C ₁ -C ₂ , Å	C ₂ -C ₃ , Å	C ₃ -C ₄ , Å	C ₄ -C ₅ , Å
CH=CH ₂	5a , C _s	1.285	1.379	1.366	
c-C ₃ H ₅	6a , C _s	1.281 ^c	1.424	1.551	1.488
c-C ₃ H ₅	6b , C _s	1.281 ^c	1.468	1.521	1.511
C ₆ H ₅	7a , C _{2v}	1.281 ^c	1.380	<i>d</i>	<i>d</i>
C ₆ H ₅	7b , C _{2v}	1.281 ^c	1.450	<i>d</i>	<i>d</i>

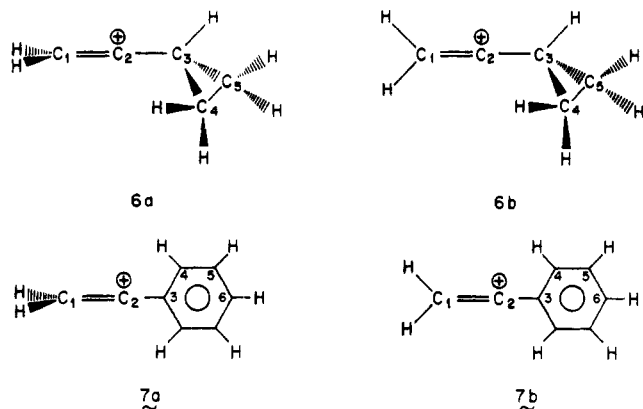
^a At RHF/STO-3G. For a detailed discussion of the parameters optimized and those held constant see text. ^b Numbering of atoms according to structures 5, 6, 7. ^c Vinyl cation value without reoptimization. ^d Standard value used, see text.

remaining cations, only the parameters that are expected to affect the energy considerably were optimized. **5** was examined most fully in the nonplanar form **5a** which is expected to be



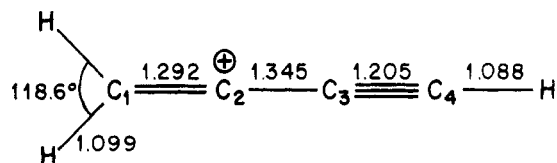
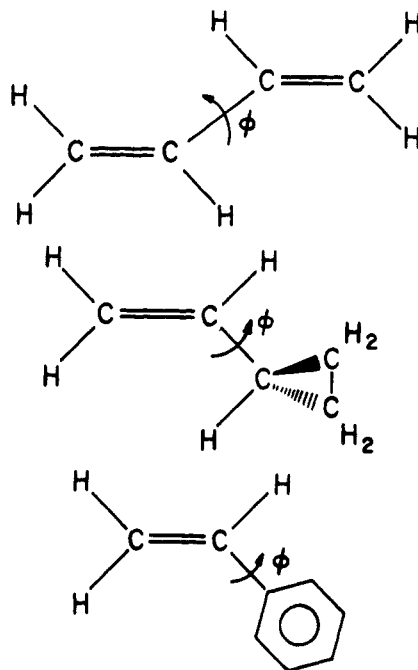
most stable. All CC bond lengths were optimized but CH bond lengths were kept at the standard value (1.08 Å).¹¹ All bond angles were fixed at standard values (120° at C₁, C₃, C₄, and 180° at C₂). Only one structure of **5b** was examined, obtained from **5a** by 90° rigid rotation about the C₁C₂ bond.

In **6** and **7**, the vinyl cation moiety was assumed to have

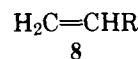


standard CH lengths (1.08 Å) and angles (120° at C₁, 180° at C₂) and a fixed C=C⁺ length of 1.281 Å, taken from the RHF/STO-3G optimized structure of **2**.^{6d,12} In **6**, both the C⁺-R bond and the CC bonds of the cyclopropyl ring were optimized, while keeping the CH lengths and the HCH and HCC⁺ angles as in cyclopropane.¹³ The HCH and HCC⁺ planes were taken to bisect the ring CC angles. In **7**, only optimization of C⁺-R was carried out with standard geometry for the phenyl ring. To investigate rotation about the C⁺-R bond, these geometrical optimizations were carried out for the conformers **6a**, **6b** of the α -cyclopropylvinyl cation and **7a**, **7b** of the α -phenylvinyl cation. The resulting parameters are listed in Table I.

For the neutral substituted ethylenes (**9**–**14**), two conformations differing by 90° rotation about the substituent bond were examined where appropriate (**12a**, **12b**, **13a**, **13b**, **14a**, **14b**). Fully optimized RHF/STO-3G geometries⁴ were used for **9**–**11** and **12b**. Rigid rotation about the single bond was used for **12a**. In cyclopropylethylene (**13a** and **13b**), standard

**Figure 1.** RHF/STO-3G structure of α -ethynylvinyl cation (**4**).

geometry was used for CH₂=CH- and the cyclopropyl ring was taken to be identical with that calculated for cyclopropane.¹³ Standard geometry was used for styrene (**14a** and **14b**).



- | | |
|---------------------------------|--|
| 9 , R = H | 12 , R = CH=CH ₂ |
| 10 , R = CH ₃ | 13 , R = c-C ₃ H ₅
(cyclopropyl) |
| 11 , R = C≡CH | 14 , R = phenyl |

12a, $\phi = 90^\circ$; **b**, $\phi = 0^\circ$

13a, $\phi = 90^\circ$; **b**, $\phi = 0^\circ$

14a, $\phi = 90^\circ$; **b**, $\phi = 0^\circ$

The calculated total energies of the cations (**1**) and of the corresponding neutral molecules (**8**) are presented in Table II.

Discussion

The isodesmic^{14a} hydride-transfer reaction 1 compares the stabilities of different vinyl cations **1** with that of the 2-propenyl cation **2**. The energies of reaction 1, derived from Table II using the most stable conformations for all species, are listed in Table III. A positive energy indicates a greater stabilization by the substituent (relative to methyl) in the cation than in the corresponding neutral molecule. Previous experience shows that the energies of such isodesmic reactions are well described even at the RHF/STO-3G level, and the estimated error limit is of the order of 2–5 kcal/mol.^{4,14}

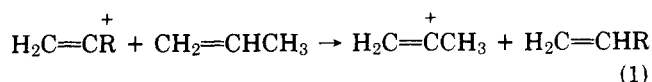


Table II. Total Energies (hartrees) of α -Substituted Vinyl Cations 1 and the Corresponding Neutral Molecules 8

Substituent	Structures		Cations (1)		Neutral Molecules (8)	
	1	8	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
H	2	9	-76.16540 ^{a,b}	-76.97753 ^{a,b}	-77.07396 ^{a,b}	-77.92188 ^{a,b}
CH ₃	3	10	-114.79296 ^{a,c}	-116.00048 ^{a,c}	-115.66030 ^{a,d}	-116.90459 ^{a,d}
HC≡C	4	11	-150.94215 ^a	-152.58574 ^a	-151.80626 ^{a,e}	-153.48995 ^{a,e}
H ₂ C=CH perpendicular	5a	12a	-152.17709 ^f	-153.81767 ^f	-153.00592 ^{g,h}	
H ₂ C=CH planar	5b	12b	-152.13931 ⁱ	-153.78234 ⁱ	-153.02036 ^{a,e,j}	-154.69906 ^{a,e}
c-C ₃ H ₅ perpendicular	6a	13a	-190.76019 ^f	-192.77680 ^f	-191.59801 ^k	
c-C ₃ H ₅ bisected	6b	13b	-190.73856 ^f	-192.75155 ^f	-191.60234 ^{k,o}	-193.65341 ^p
C ₆ H ₅ perpendicular	7a	14a	-303.01200 ^f		-303.82176 ^{k,l,m}	
C ₆ H ₅ planar	7b	14b	-302.97268 ^f		-303.82479 ^{k,m,n}	

^a Fully optimized RHF/STO-3G geometry. ^b From ref 12. ^c From ref 7a. ^d From ref 17. ^e From ref 4. ^f Partially optimized; see text for specification of the parameters optimized. ^g Rigid rotation of 12b (standard geometry). ^h From L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970). ⁱ Rigid rotation of 5a. ^j With the standard geometry the energy is -153.01661 hartrees (2.35 kcal/mol higher). ^k Standard geometry. ^l Optimization of the CCC angle lowers the energy by 0.62 kcal/mol. ^m From ref 28. ⁿ Optimization of the CCC angle lowers the energy by 3.14 kcal/mol. ^o Reference 27a gives -191.60520 for a slightly different geometry. ^p From Ref 27a.

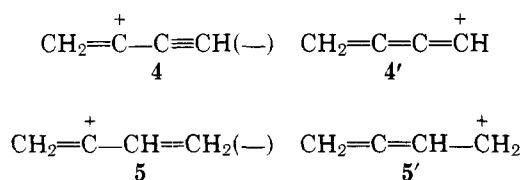
Table III. Calculated Energies^a (kcal/mol) for Reaction 1^b

Substituent	RHF/STO-3G	RHF/4-31G
H	-25.9	-25.2
CH ₃	0.0	0.0
C≡CH	2.0	-0.1
CH=CH ₂	15.1	14.3
c-C ₃ H ₅	15.8	17.3
C ₆ H ₅	34.2	

^a Using the total energies from Table II. ^b For each substituent the most stable conformation of both the cation 1 and the olefin 8 was used.

The results of Table III show that effectiveness of the substituents in stabilizing the vinyl cation follows the order C₆H₅ >> c-C₃H₅ ≈ HC=CH₂ >> C≡CH ≈ CH₃ >> H. Our results are, of course, pertinent only to the isolated cations in the gas phase where unfortunately little experimental data are available. Comparison with available solvolytic data should be done with circumspection, keeping in mind that solvation reduces the magnitude of electronic and polarization effects, and may change the relative stabilities of cations which have different sizes and charge distributions.¹⁵ The RHF/4-31G results should be more reliable for energy comparisons. For cations 5-7 where geometry optimization is not complete, further optimization should produce only small changes in the energies of reaction 1.¹⁶

α -Ethenyl and α -Ethylnyl Substituents. Both ethenyl and ethynyl substituents possess π electrons which can stabilize the cationic center by allylic-type conjugation, as represented by the resonance forms 4 \leftrightarrow 4' and 5 \leftrightarrow 5' below.



This conjugation is reflected in both the structures and the charge distributions of these cations. The calculated bond lengths (Figure 1 and Table I) of 4 and 5a lie between those expected for the contributing resonance structures. The C₂C₃ bond length has an intermediate value between those of a single C₂C₃ bond (1.288 Å in 1,3-butadiene and 1.459 Å in but-1-yn-3-ene⁴) and a C₂C₃ double bond (1.288 Å in allene¹⁷ and 1.257 Å in butatriene⁴). As expected, the C₃C₄ bonds are

longer in the cations than in the corresponding hydrocarbons (1.171 Å in but-1-yn-3-ene and 1.313 Å in 1,3-butadiene), but the changes are smaller than in the C₂C₃ bonds. Similar bond lengths to 4 and 5a were found in the analogous propargyl¹⁸ and allyl cations.^{7a} The calculated charge distributions (which are discussed in detail below) show that the positive charge is shared by C₂ and C₄ as expected if p- π conjugation is important. The allylic conjugation in 5 is possible only if the two double bonds are perpendicular; conformation 5a is indeed 22.2 kcal/mol more stable than the planar conformer 5b (RHF/4-31G, rigid rotation around the C₂C₃ bond). The lower stability of planar conformations of systems related to 5 was shown experimentally by Grob and Pfaendler.^{19a}

An α -ethenyl substituent stabilizes the vinyl cation by 14.3 kcal/mol (RHF/4-31G) more than a methyl group (Table III). This is in agreement with the experimental result that 2-butadienyl derivatives solvolyze (in 80% EtOH) roughly 2000^{19b,20} times faster (corresponding to a free-energy difference of 4.5 kcal/mol) than 2-propenyl derivatives. A larger substituent effect is expected in the gas phase than in solution.¹⁵

Ground-state effects, such as the energy associated with the π conjugation of butadiene, are included in reaction 1 as the neutral molecules are considered in their preferred conformation. As the preferred conformations of butadiene (12b) and of the butadienyl cation (5a) are different, a higher energy for reaction 1 results if perpendicular butadiene (12a) is used as the basis for comparison. The rotational barrier in butadiene (roughly 12b vs. 12a) is 6.7 kcal/mol at RHF/STO-3G^{21a} (5.0 kcal/mol experimentally^{21b}). The solvolysis of butadienylic systems where the double bonds are constrained in nonplanar conformations is indeed faster than normal.^{19a} In addition, as the leaving group in 8 is a hydrogen, no account is taken of energy effects involving the double bond and other leaving groups, such as halogens or sulfonic esters.^{7a}

In contrast to the large stabilizing effect of the conjugated α -double bond in 5a, the triple bond in 4 provides stabilization which is only comparable to that of a methyl group. The failure of a triple bond to provide higher stabilization does not arise from ineffective charge delocalization, as the charge in the "empty" orbital on C₂ is almost the same in both cations (see Table VII and latter discussion). The low stabilization probably reflects cancellation between a stabilizing π conjugation and a destabilizing σ withdrawal by the acetylenic group, as previously suggested for the propargyl cation.¹⁸ Derivatives of 4 have not yet been solvolyzed and our results suggest (assuming that solvation and leaving-group effects are similar for both cations) that their reactivity should be comparable to that of 2-propenyl derivatives.

α -Phenyl and α -Cyclopropyl Substituents. The ability of phenyl and cyclopropyl rings to stabilize an adjacent carbenium center is well known,²² but the question of their relative efficiencies has been in dispute. Solvolysis rates^{23a} and fluorine shielding constants^{23b} suggest that an α -cyclopropyl is superior, while the ¹³C shielding constants of the cation point to the opposite conclusion.²⁴ Taft, Hehre, and their co-workers²⁵ have recently applied ICR and ab initio computational techniques to this problem and showed that in the gas phase a phenyl substituent is superior to cyclopropyl in stabilizing both primary and secondary carbenium ions.

The results in Table III show that this is also the case for the vinyl cation, where the phenyl group is 18.4 kcal/mol more stabilizing than the α -cyclopropyl group (RHF/STO-3G). The excellent agreement between the corresponding calculations and the ICR measurements of Taft and Hehre²⁵ suggest that our results also should be close to experimental values. The 18.4 kcal/mol difference in the stabilizing abilities of phenyl and cyclopropyl is close to that in the corresponding primary saturated cations.²⁵ A much lower difference was observed by Taft and Hehre²⁵ for the saturated secondary cations, and both groups have comparable stabilizing effects on a tertiary carbenium ion. As in the saturated analogues,²³ α -cyclopropylvinyl derivatives solvolyze roughly 500 times faster than α -phenylvinyl derivatives.²⁶ The discrepancy between the gas-phase and solvolysis data probably results from preferential solvation of the smaller and less polarizable cation **6**.^{15,25} Very large solvation effects (up to 10²⁵ in equilibrium constants) were recently reported for proton-transfer reactions between small, highly solvated cations and large electron-delocalized cations.^{15c} The gap between the gas phase and the solution results is much larger in the vinylic than in the corresponding alkyl cations. Thus, while the α -cyclopropyl/ α -phenyl solvolysis rate ratio is 500 in both families,^{23,26} the calculated energy difference between the corresponding cations is only 2.4 kcal/mol (phenyl favored) for the alkyl tertiary cations²⁵ compared to 18.4 kcal/mol for the vinylic cations. This points to differential solvation effects.

α -Cyclopropylethylene (**13**) and styrene (**14**) are included in reaction 1 in their most stable conformations, i.e., bisected (**13b**) for the first and planar (**14b**) for the second. The preference of a bisected conformation (**13b**) for **13**, in which the antisymmetric Walsh orbital of cyclopropane can interact with the π double bond, is analogous to the preferred planar arrangement for butadiene.²⁷ The conformation of the substituent relative to the double bond is reversed in the neutral molecule and in the cation (see below), and the double-bond conjugation of both **13b** and **14b** is therefore lost on ionization. The rotation barriers in **13** and **14** (2.7 and 4.4²⁸ kcal/mol, respectively) are good estimates of this conjugation energy.

The high stabilizing effect of the phenyl and cyclopropyl substituents arises mainly from the interaction between the empty cationic 2p (C⁺) orbital and the highest occupied molecular orbital (HOMO) of the ring. For this interaction to be effective, the ring must be oriented appropriately. Similar effects have been discussed previously for benzyl^{5b} and cyclopropylcarbinyl cations.^{5b,29} Using the axes shown in Figure 2, the HOMO of the rings should have a node in the xz plane for effective stabilization. Thus, for α -phenylvinyl (**7**), 2p (C⁺)– π (ring) overlap is possible only when the vinyl fragment and the phenyl ring are perpendicular; conformation **7a** is therefore most stable. Similarly, the perpendicular³⁰ conformation (**6a**), where interaction with the antisymmetric Walsh orbital of cyclopropane²⁹ takes place, is preferred in the α -cyclopropylvinyl cation **6**.

The 2p–HOMO interactions (Figure 2) are reflected in the cationic structures. The transfer of electrons from the ring to the empty 2p (C⁺) orbital produces a shortening of the C₂C₃ bond by 0.044 and 0.070 Å (Table I) in **6a** and **7a**, respectively,

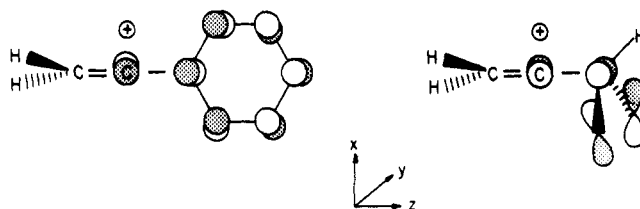
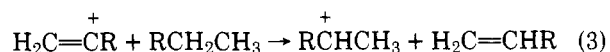


Figure 2. Formally vacant 2p_x (C⁺) orbital of a vinyl cation interacting with the HOMO of phenyl (**7a**) and cyclopropyl (**6a**) substituents.

relative to the bond lengths in **6b** and **7b**. Similar, but even larger, results were reported for the benzyl and cyclopropyl carbinyl cations.^{5b,29b} In **6a**, electrons are withdrawn from the antisymmetric Walsh orbital of the cyclopropyl ring, resulting in elongation of the C₃C₄ and the C₃C₅ bonds (1.551 Å) and shortening of the C₄C₅ bond (1.488 Å) relative to cyclopropane (1.50 Å).¹³ Much weaker interactions are expected in the bisected conformation **6b** and the resulting geometrical changes (elongation of all the cyclopropyl ring bonds) are small (Table I).

Another consequence of the interaction between the cationic 2p orbital and the ring HOMO (Figure 2) is the high rotation barrier around the C₂C₃ bonds, 24.7 kcal/mol (RHF/STO-3G) in the α -phenylvinyl cation (**7**) and 13.6 (RHF/STO-3G) and 15.8 kcal/mol (RHF/4-31G) in the α -cyclopropylvinyl cation (**6**).³¹ A similar relationship with even higher rotation barriers was found for the benzyl and cyclopropylcarbinyl cations,^{5b,29b} respectively. Both **6b** and **7b** are stabilized by conjugation between the double bond and the cyclopropyl or the phenyl rings. A part of the higher rotation barriers in the saturated cations is therefore due to the absence of such stabilization in the perpendicular benzyl or cyclopropylvinyl cations.

Comparison with Alkyl Cations. The stability of the vinylic cations (**1**) may be compared to that of the corresponding primary or secondary alkyl cations by means of reactions 2 and 3, respectively (Table IV). These reactions provide a direct comparison of the stabilities of the cations, uncomplicated by ground-state and solvation effects as are the relative solvolysis rates of vinyl and alkyl derivatives.^{2,7a}



Comparing the RHF/STO-3G and RHF/4-31G results in Table IV, one finds that the minimal basis set gives larger estimates of stability of the vinyl cations by 3–9 kcal/mol. RHF/4-31G results for reactions 2 and 3 (R = H, CH₃) were found earlier to be in good agreement with both experimental and theoretical results using a more extensive basis set (RHF/6-31G*).^{7a} The RHF/4-31G energies can therefore be used with some confidence and, when not available (for **6** and **7**), 3–9 kcal/mol should probably be subtracted from the RHF/STO-3G energies.

The parent vinyl cation is 14.7 kcal/mol less stable than the ethyl cation, but 15.1 kcal/mol more stable than the methyl cation^{7a} (Table IV). Similarly, the stability of the 2-propenyl cation (**3**) is intermediate between those of the ethyl (+10.5 kcal/mol) and propyl (–12.0 kcal/mol) cations. The preference of the vinylic cation over the primary alkyl cation (reaction 2) is, however, much smaller (or disappears) with the other substituents. Thus, the allyl cation is calculated to be 1.2 kcal/mol more stable than **5**, and the propargyl, cyclopropylcarbinyl, and benzyl cations are only slightly less stable than **4**, **6a**, and **7a**. (The STO-3G value for **7a** should be even

Table IV. Calculated Energies (kcal/mol) for Reactions 2 and 3^{a,b}

Substituent	ΔE for reaction 2		ΔE for reaction 3	
	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
H	24.4 ^c	15.1 ^c	-6.6 ^c	-14.7 ^c
CH ₃	19.3 ^c	10.5 ^c	-5.4 ^c	-12.0 ^c
C≡CH	13.1 ^d	3.9 ^d	-12.1	-13.5
CH=CH ₂	4.7 ^f	-1.2 ^f	-13.3 ^g	-17.2 ^g
c-C ₃ H ₅	7.2 ^g	3.9 ^g	-8.7	^e
C ₆ H ₅	5.5 ^h		-13.0 ^h	

^a For each substituent the most stable conformation of both the cation and the hydrocarbon was used. ^b For the vinylic compounds the total energies from Table I were used. ^c From ref 7a. ^d Energies for the substituted alkanes and alkyl cations are taken from ref 17 and 18, respectively. ^e Energies for the saturated molecules are not available. ^f Energies for the substituted alkanes and alkyl cations are from ref 17 and 7a, respectively. ^g Energies for the substituted alkanes and alkyl cations from ref 4, 5a, and W. J. Hehre, unpublished results. ^h Energies for the saturated hydrocarbons and cations from W. J. Hehre, unpublished results, and from ref 45b, respectively.

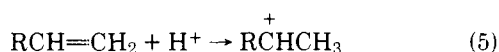
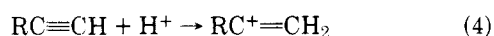
Table V. Calculated Energies (kcal/mol) for Reactions 6, 7, and 8, and of the Relative Proton Affinities (PA) of Acetylenes and Ethylenes^{a,b}

Substituent R	Reaction 6		Reaction 7		Reaction 8		Relative PAs ^c	
	RHF/ STO-3G	RHF/ 4-31G	RHF/ STO-3G	RHF/ 4-31G	RHF/ STO-3G	RHF/ 4-31G	RHF/ STO-3G	RHF/ 4-31G
H	15.6 ^d	3.5 ^{d,e}	0.0	0.0	0.0	0.0	5.0 ⁱ	5.0 ⁱ
CH ₃	14.7 ^d	2.1 ^{d,f}	21.8	20.9 ^g	20.8	19.4 ^h	4.0	3.5 ^j
C≡CH	13.2	2.3	23.4	21.6	21.0	20.4	2.6	3.4
CH=CH ₂	15.3	0.1	38.7	37.8	38.4	34.3	4.7	1.5
c-C ₃ H ₅	17.4		38.2		39.9		6.7	
C ₆ H ₅	15.1		52.2		48.5		1.2	

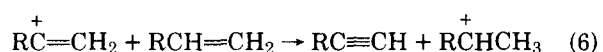
^a For each substituent the most stable conformation of both the cation and the hydrocarbon was used. ^b The total energies for the vinylic hydrocarbons and cations are taken from Table II, those for the acetylenes from ref 12, 17, and 45b, and for the saturated cations from the corresponding footnotes in Table IV. ^c Based on the difference between the calculated energies of reaction 7 and 8 and the experimental^{3d} relative PA of acetylene and ethylene. ^d From ref 7a. ^e 4.1 kcal/mol at RHF/6-31G*. ^f 3.3 kcal/mol at RHF/6-31G*. ^g 19.8 kcal/mol at RHF/6-31G*. ^h 18.9 kcal/mol at RHF/6-31G*. ⁱ Experimental value, see ref 7a and references therein. ^j 4.1 kcal/mol at RHF/6-31G*.

smaller at 4-31G.) However, the values given by reaction 2 are influenced by the change in the relative sizes (polarizabilities) of the methyl and vinyl systems. A more representative comparison of substituent effects is provided by eq 3, where both vinyl and ethyl systems have the same number of carbon atoms. The values (12–17 kcal/mol, RHF/4-31G) are almost constant,³³ suggesting that substituent effects for the groups examined here are inherently similar for alkenyl and for alkyl cations. This is not general behavior, however. In a comparable study of a range of α substituents of widely differing electronegativity, it was found that σ donors, like lithium, preferentially stabilize the vinyl cation, but σ acceptors, like fluorine, favor the ethyl cation.⁸

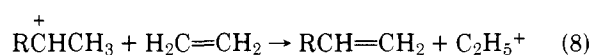
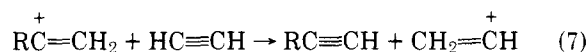
Proton Affinities (PA) of Several Acetylenes and Ethylenes. The proton affinities (PA) of acetylenes and ethylenes are defined as the negative of the standard enthalpy change in reactions 4 and 5, respectively.



These reactions, however, are not isodesmic^{14a} and the theoretical energies are, therefore, subject to greater error.^{5a,34} Thus, the PA of both acetylene and ethylene are overestimated by 10–13 kcal/mol even when the 6-31G* basis set is used.³⁵ The difference, however (reaction 6, R = H), is reasonably well reproduced with the 4-31G basis set (3.5 kcal/mol compared to the experimental value of 5.0 kcal/mol^{3d}). The RHF/STO-3G energy difference (15.6 kcal/mol) is, however, far too high.



Only RHF/STO-3G energies are available for some of the molecules discussed here, and we therefore use the isodesmic reactions 7 and 8, which compare the proton affinities of substituted acetylenes and ethylenes with those of acetylene and ethylene respectively.



The calculated energies for reactions 6, 7 and 8 are presented in Table V. The RHF/STO-3G and RHF/4-31G energies for reactions 7 and 8 are indeed very similar. If R is CH₃, the RHF/6-31G* and the RHF/STO-3G results differ by only 2 kcal/mol, supporting the reliability of the minimal basis set for obtaining energies of these isodesmic reactions. Furthermore, the experimental PA of propene is 19 kcal/mol higher than that of ethylene^{35c} in excellent agreement with the calculations.

The proton affinities of acetylene and ethylene increase markedly upon substitution. Thus, phenylacetylene and styrene are ~50 kcal/mol more basic than their parent hydrocarbons, acetylene and ethylene, and have comparable proton affinities to ammonia.^{15a} As expected, the order parallels that of the stabilizing effect of R on the corresponding cations.

The relative PA of the substituted acetylenes and ethylenes are given directly by the RHF/4-31G energies of reaction 6, or can be computed from the energies of reaction 7 and 8 and the experimentally known relative PA of acetylene and ethylene (see Table V).³⁶ The PA of ethylene is only 5 kcal/mol^{3d,35c} higher than that of acetylene, while the difference

Table VI. Mulliken Atomic Charges (RHF/STO-3G) for Vinylic Cations 2-7^a

Substituent	Structure	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	H (C ₁)	H (C ₂)	H (C ₃)	H (C ₄)	H (C ₅)	H (C ₆)
H	2	-0.060	+0.283					+0.250	+0.277				
CH ₃	3	-0.096	+0.320	-0.193				+0.226		+0.172			
C \equiv CH	4	-0.056	+0.262	-0.008	+0.149			+0.214			+0.225		
CH=C-	5a	-0.101	+0.235 ^b	-0.092	+0.073			+0.196		+0.152	+0.171		
H ₂													
c-C ₃ H ₅	6a	-0.107	+0.276 ^c	-0.113	-0.079	-0.079		+0.206		+0.150	+0.134		
C ₆ H ₅	7a	-0.107	+0.213 ^d	-0.038	-0.023	-0.054	+0.028	+0.183			+0.121	+0.114	+0.130

^a The carbon numbering according to structures 2-7. Hydrogen charges are averaged over all hydrogens attached to the same carbon.^b +0.336 in 5b. ^c +0.328 in 6b. ^d +0.326 in 7b.Table VII. Mulliken Gross Orbital Populations (RHF/STO-3G) in the Vinylic Cations 2-7^a

Substituent	Structure	p _x (2) ^b	p _x (3)	p _x (4)	p _x (5)	p _x (6)	p _y (1)	p _y (2)	p _y (3)	p _y (4)
H	2	0.136					0.788	1.212		
CH ₃	3	0.211					0.862	1.157		
C \equiv CH	4	0.295	1.151	0.550			0.816	1.177	0.941	1.066
CH=CH ₂	5a	0.427 ^c	1.116	0.546			0.886	1.122		
c-C ₃ H ₅	6a	0.334 ^d					0.885	1.130		
C ₆ H ₅	7a	0.474 ^e	1.133	0.838	1.005	0.791	0.910	1.039		

^a The numbering of the atoms and the specification of the axes are given in Figure 2 and structures 2-7. ^b The p_x orbital of carbon 2, etc. ^c The population is 0.206 in 5b. ^d The population is 0.208 in 6b. ^e The population is 0.192 in 7b.

in the stabilities of the ethyl and vinyl cations is 15 kcal/mol. This apparent inconsistency is clarified if one remembers that acetylenes are more "strained" than olefins,³⁷ compensating for the lower stability of the vinyl cation.^{7a} The relative PA are lower for all the substituted derivatives (except for cyclopropyl) than for the parent hydrocarbons (Table V), so that, in general, additions of protons to double and triple bonds should be comparably easy. The data in solution, although solvent dependent, also point to comparable rates of protonic additions to a variety of substituted ethylenes and acetylenes.^{38,39}

The available experimental data in the gas phase are generally in good agreement with our calculations. Thus, propene and styrene are 19^{35c} and 3.6 kcal/mol^{15a,25} more basic than ethylene and cyclopropylethylene, respectively (calculated: 19.4 and 8.6 kcal/mol, respectively; Table V). A considerable discrepancy exists, however, between the experimental^{3d} and calculated values for the relative PAs of propene and propyne, e.g., ~9 and 4.1 kcal/mol, respectively.

Charge Distributions. The calculated total atomic charges and the gross populations⁴⁰ in orbitals of particular interest in the cations 2-7 are reported in Tables VI and VII respectively. The data for the p_x(2) orbital (Table VII) show that the relative efficiency of the different substituents in donating electrons to the formally empty 2p (C⁺) orbital follows the order C₆H₅ > CH=CH₂ > c-C₃H₅ > C \equiv CH > CH₃ > H. All the π donors investigated are therefore superior to the π -type cyclopropyl MOs in delocalizing the positive charge. In particular, a phenyl substituent donates 0.140 electron more than a cyclopropyl ring to the 2p (C⁺) orbital. From the ¹³C chemical shifts of phenyl- and cyclopropyl-substituted cations Olah^{24b} concluded that: "Phenyl and cyclopropyl groups can show comparable ability to conjugatively delocalize positive charge, and steric interactions within a particular system may determine the relative order". Other workers have concluded from the fluorine chemical shifts of several cations that a cyclopropyl ring delocalizes the positive charge better than a phenyl.^{23b} Our results suggest that, at least for the vinyl cation, phenyl is superior to cyclopropyl. A similar conclusion has been reached for the corresponding substituted alkyl cations (i.e., the benzyl and the cyclopropylcarbinyl cations), although the superiority of phenyl is smaller (0.137 electrons).²⁵ Among

the π donors, phenyl delocalizes the charge better than a double bond in contrast with Olah's conclusions for alkyl cations;²⁴ the triple bond is the poorest π donor. The positive charge in 4 and 5 is divided between the p_x(2) and p_x(4) orbitals, pointing to almost equal contributions from the resonance structures 4 \leftrightarrow 4' and 5 \leftrightarrow 5'. On the basis of ¹³C chemical shifts it was argued that in the analogous alkynoyl cation (HC \equiv CC⁺=O) charge delocalization by the triple bond is unimportant.^{41a} This conclusion was recently questioned by Pittman et al. who found considerable charge in the δ position of several alkynoyl cations by INDO calculations.^{41b} The substantial delocalization by the triple bond in 4 supports Pittman's results.^{41b} In 7a the charge is delocalized mostly to the para (+0.209) and ortho (+0.162) positions, while some negative π charge (-0.005) is found in the meta position.

An α -methyl substituent can supply electrons to the 2p (C⁺) orbital by hyperconjugation. The p- π (CH₃) hyperconjugation is however less effective than p- π or p-cyclopropane conjugation and the 2p (C⁺) orbital in 3 is less populated than in 4, 5a, 6a, or 7a. In 5b, 6b, and 7b, however, where conjugation with the substituent is excluded, the 2p (C⁺) charge is similar to that in 3 (Table VII). The fact that alkyl groups are the poorest π -electron donors is well established.^{5,24} The population is the lowest in the parent vinyl cation (2) and only 0.14 electron is transferred to the 2p (C⁺) orbital by hyperconjugation with the two β -hydrogens.

An interesting result (see the p_y orbitals in Table VII) is the considerable polarization of the vinylic double bond (the C₁C₂ bond). In the extreme case (cation 2), 1.2 of the vinylic π double-bond electrons are located at the α carbon and only 0.8 at the β carbon, pointing to a contribution from the resonance form H₂C⁺=CH.⁴² The polarization is smaller for the other cations, although significant (0.1 electron) even in the phenylvinyl cation (7a). Thus, although the cationic 2p (C⁺) orbital and the C₁C₂ π electrons occupy two perpendicular planes and cannot interact directly, they are strongly coupled through polarization effects. An analogous interaction between the π and the σ frameworks was found for phenyl cation systems.⁴³

The total charges in Table VI reflect both the inductive effect and π donation by the substituent. The total charge on C₂ parallels (except for methyl) the charge in the 2p (C⁺) or-

bital, although the variations are smaller. Exclusion of the conjugation (by rotation) between the 2p (C^+) orbital and the substituent causes a sharp increase in the total charge at C_2 in **5**, **6**, and **7** (Table VI). The C_2 charge in **5b**, **6b**, and **7b** is higher than in **2**, reflecting the inductive electron-withdrawing nature (relative to hydrogen) of a double bond, a cyclopropyl group, or a phenyl group. An interesting result is that the total charge at C_2 is significantly more positive in the 2-propenyl cation (**3**) than in the vinyl cation (**2**), even though the 2p (C^+) orbital in the latter has a lower population. This suggests that relative to hydrogen a methyl group withdraws electrons inductively from an sp-hybridized carbon. Olah recently reached a similar conclusion regarding trigonal sp^2 cationic centers.⁴⁴

In all the cations most of the unit positive charge is transferred to the hydrogens, with a relatively small fraction remaining on the cationic and the conjugating carbons. Some charge alteration is found in both the total (Table VI) and π charges (Table VII), a phenomenon well documented for both cationic and neutral species.^{44,45}

Charge Distribution and Stability. It is often assumed that electron donation to a cationic center is of benefit energetically and that, in conjugated systems, better charge dispersal (or additional resonance structures) leads to a more stable cation.⁴⁶ It was shown recently, however, that the charge in the 2p (C^+) orbital, which correlates with the measured ^{13}C chemical shifts,^{25,44b,47} does not necessarily reflect the stability of the cation.^{25,48} Our study, which includes both σ and π donors and which covers cations of a wide range of stabilities, is suitable for the evaluation of this assumption.⁴⁶

Neither the charge in the 2p (C^+) orbital (Table VII) nor the total charge (Table VI) at the cationic center correlates well with the stabilization provided by the substituents (Table III). Vinyl and cyclopropyl substituents, for example, stabilize the cation to a comparable degree but the 2p (C^+) population in the two cations (+0.43 in **5a** and +0.33 in **6a**) differ considerably. Similarly, α triple bond and methyl substituents have comparable stabilizing effects (Table III), but the triple bond is more efficient in delocalizing the positive charge (Table VI). The 2-propenyl cation (**3**) is 25.2 kcal/mol (RHF/4-31G, Table III) more stable than the parent vinyl cation (**2**), but the total charge at C_2 in **3** is higher than **2**. When only the π donors are compared, a gradual decrease in the 2p (C^+) charge with increasing stability of the cation is found, suggesting that with closely related substituents a correlation between charge and stability may exist. We conclude that it might be misleading to deduce the stability of cations from their charge densities (or from their NMR shielding constants^{25,44b,47,48}) especially when comparing cations with substituents of different types (such as π or σ donors).

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