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Do the Vinyl Isomers of $C_2H_2Cl^+$ and $C_2H_2Br^+$ Exist?

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Abstract: Five stationary points on the potential energy hypersurfaces for the $C_2H_2Cl^+$ and $C_2H_2Br^+$ cations are found at various levels of ab initio quantum-mechanical theory. At lower levels of theory, the vinyl-like cations are minima on the potential energy surface. Upon improvement of the wave function to include polarization functions and electron correlation, the structures corresponding to the classical 2-halovinyl cations become shallow minima or transition states. It is clear that both the halogen-bridged structure and the H_2CCX^+ isomer are stable minima that are lower in energy than $HCCHX^+$, a fact not evident from low-level theory. This emphasizes that comparisons made between unsophisticated ab initio studies and experimental solution chemistry should be made with caution. Stabilization energies are evaluated for comparison with previous studies.

Introduction

The study of vinyl cations as reactive intermediates has grown in the past two decades, with an entire volume dedicated to the subject.[1] These cationic species participate in the solvolysis of vinyl halides and vinyl triflates and are involved in electrophilic additions to acetylenes. In general, the addition of chlorine and bromine to double bonds is much faster than addition to triple bonds, especially in solvents with low dielectric constants.[2] The addition of halogens to alkynes generates "vinyl cations" with either bridged or open structures. Given the importance of these cations in organic reaction mechanisms, it is of interest to know the inherent stabilities of the unsubstituted ions and the factors that affect the relative energies in the absence of solvent effects and alkyl or aryl substituents. Lucchini and Modena point out that the relative stability of bridged vs open ions is different between the saturated and unsaturated analogues.[3] The isomers containing three-membered rings are more viable in the saturated cases, although there is experimental evidence for halogen-bridged intermediates in dialkylacetylenes[2] or diarylacetylenes.[4]

Past theoretical studies have primarily focused on the parent vinyl cation, $C_2H_3^+$, at high levels of theory (see ref 5 and references therein). Naturally, the most studied system in the halogen series is the $C_2H_2F^+$ potential energy surface, but these studies have been performed only with small basis sets and without the inclusion of electron correlation[6-9] or by semiempirical methods.[10] Similarly, $C_2H_2Cl^+$ has been investigated by low-level ab initio theory[9,11,12] and by MNDO.[13] Details from these papers will be covered when the corresponding topic arises under Results and Discussion. No experimental or theoretical papers on $C_2H_2Br^+$ have appeared in the literature.

This article reports on ab initio studies of the potential energy surfaces for $C_2H_2Cl^+$ and $C_2H_2Br^+$, with emphasis on the existence and relative energies of the 1-halovinyl (H_2CCX^+), 2-halovinyl ($HCCHX^+$), and bridged (halenium) ions. The basis sets used are more complete than in previous studies, and electron correlation will be accounted for by large-scale configuration interaction (CI) wave functions. The influence of inductive effects, back-donation from halogen lone pairs, and hyperconjugation is addressed, and the stabilization of the vinyl cation by Cl or Br (relative to H) is also discussed.

Theoretical Methodology

The wave functions utilized throughout were the Hartree–Fock self-consistent-field (SCF) and CI with single- and double-substitution (CISD) wave functions. The core orbitals were kept frozen (1s on C; 1s, 2s, 2p on Cl; 1s, 2s, 2p, 3s, 3p, 3d on Br), as were virtual orbitals lying above 20 hartrees. The resulting numbers of frozen orbitals are given in Tables I and II. The approximate effect of quadruple excitations was incorporated by utilizing the Davidson correction.[14] Geometry optimizations were performed by using analytic gradients for both SCF[15] and CISD[16] levels of theory. The location of transition states was accelerated by using the eigenvector-following routine of Baker.[17] The stationary points on the SCF potential energy surfaces were characterized as minima or transition states by harmonic vibrational frequency analyses based on analytically computed second derivatives.[18] Likewise, IR intensities were obtained from analytic dipole moment derivatives.

Three levels of basis set quality were used, namely double-ζ (DZ), DZ with a set of polarization d functions on each heavy atom (DZ+d), and triple-ζ with two sets of polarization functions of heavy atoms combined with a set of p polarization functions appended to the hydrogen DZ basis. The last basis will be referred to as TZ2P for brevity, even though it is of only DZP quality on the hydrogen atoms. All of the d function sets were five-component spherical harmonics.

The DZ basis consisted of the standard contracted set from Huzinaga and Dunning for carbon (9s5p/4s2p) and hydrogen (4s/2s),[19,20] the (11s7p/6s4p) Huzinaga–Dunning set for Cl,[21] and the Br (15s12p5d/8s6p2d) set from Dunning that was tabulated in ref 22. The exponents of the polarization d functions were $\alpha_d(C) = 0.75$, $\alpha_d(Cl) = 0.75$, and $\alpha_d(Br) = 0.40$ in the DZ+d basis. The sp part of the TZ2P basis consisted of the Huzinaga–Dunning (10s6p/5s3p) set for carbon,[19,20] the McLean–Chandler (12s9p/6s5p) contracted Gaussians for Cl,[23] and the

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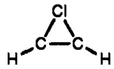
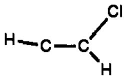
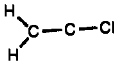
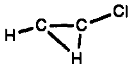
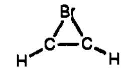
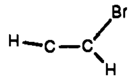
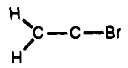
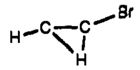
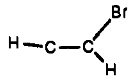
Table I. Absolute Energies (+535.0) in hartrees and Relative Energies in kJ/mol (in Parentheses) for $C_2H_2Cl^+$

	DZ SCF	DZ+d SCF	TZ2P SCF	DZ+d CISD[a]	DZ+d CISD(+-Q)	TZ2P CISD[a]	TZ2P CISD(+Q)
	−0.876 649 (103.3) ts[b] 377*i*	−0.947 067 (112.0) ts 102*i*	−1.012 166 (95.7) min	−1.306 228 (100.1)	−1.349 463 (97.9)	−1.409 146 (86.9)	−1.460 069 (84.2)
	−0.896 657 (50.7) min	−0.957 067 (85.7) min	−1.015 544 (86.9) min	−1.300 404 (115.4)	−1.341 176 (119.7)	−1.399 586 (112.0)	−1.447 655 (116.9)
	−0.915 978 (0.0) min	−0.989 723 (0.0) min	−1.048 616 (0.0) min	−1.344 340 (0.0)	−1.386 758 (0.0)	−1.442 225 (0.0)	−1.492 155 (0.0)
	−0.871 491 (116.8) ts 805*i*	−0.951 796 (99.6) ts 389*i*	−1.011 650 (97.1) ts 369*i*				

[a] Seven frozen core orbitals and three frozen virtuals. [b] Transition states are characterized by their imaginary vibrational frequency.

Table II. Absolute Energies (+2648.0) in hartrees and Relative Energies in kJ/mol (in Parentheses) for $C_2H_2Br^+$

	DZ SCF	DZ+d SCF	TZ2P SCF	DZ+d CISD[a]	DZ+d CISD(+Q)
	−0.764 428 (93.9) ts[b] 327*i*	−0.857 135 (70.3) min	−0.884 746 (73.3) min	−1.200 394 (59.1)	−1.242 723 (57.9)
	−0.778 571 (56.8) min	−0.855 536 (74.5) min		−1.184 169 (101.7)	−1.224 274 (106.3)
	−0.800 211 (0.0) min	−0.883 903 (0.0) min	−0.912 653 (0.0) min	−1.222 919 (0.0)	−1.264 779 (0.0)
	−0.755 494 (117.4) ts 775*i*	−0.848 910 (91.9) ts 363*i*	−0.879 581 (86.8) ts 349*i*		
		−0.855 522 (74.5) ts 64*i*			

[a] Sixteen frozen core orbitals and seven frozen virtuals. [b] Transition states are characterized by their imaginary vibrational frequency.

TZ contraction of the Br 15s12p primitive set given above [to (15s12p/10s8p)] with the contraction coefficients given in ref 24. The polarization function exponents for the TZ2P set were specified as α_d(C) = 1.5, 0.375; α_d(Cl) = 1.5, 0.375; α_d(Br) = 0.54, 0.19; and α_p(H) = 0.75.

Results and Discussion

Energetics. $C_2H_2Cl^+$. Previous studies on the $C_2H_2Cl^+$ ion primarily focused on the relative energies of the chlorenium and the 2-chlorovinyl structures, with the conclusion that the open 2-chlorovinyl isomer is preferred. The STO-3G SCF difference is 18.4 kJ/mol on the basis of partially optimized geometries,[12] and from DZ-quality SCF computations, these differences range from 42 to 54 kJ/mol.[3,9,11,12] MNDO places the chlorovinyl cation 35.6 kJ/mol above the chlorenium ion.[13] The 1-chlorovinyl global minimum, which would result directly from Markovnikov protonation of chloroacetylene, is found to be so in all theoretical studies. Predictions of the energy difference between the 1- and 2-chlorovinyl cations are less variable, from 49 to 57 kJ/mol for MNDO, STO-3G SCF, and DZ-quality SCF.

The above results (see Table I) are consistent with those from our DZ SCF predictions. The vibrational frequencies reveal that the bridged ion is a transition state for the motion of the Cl atom between equivalent 2-chlorovinyl cations, with a 52.6 kJ/mol classical energy barrier. The 2-chlorovinyl cation is a minimum at this level of theory, as is the 1-chlorovinyl ion. A transition state for the interconversion of $HCCHCl^+$ and H_2CCCl^+ is located on the potential energy surface in a region that indicates that an H atom and the Cl atom are simultaneously moving (see Figure 1). This is reminiscent of the $C_2H_3^+$ surface, in which a similar motion occurs with a much smaller barrier.[26] This latter stationary point is the highest energy point of major interest on the DZ SCF hypersurface.

The situation dramatically changes even upon adding polarization functions on the heavy atoms. While the stationary points retain their minimum or saddle point character, the 2-chlorovinyl cation increases in energy with reference to the global minimum. The two transition states are stabilized and destabilized until the chlorine-bridged transition state is the highest point on the surface. With our largest basis set, the chlorenium ion becomes a minimum at the SCF level of theory. Searches to find the saddle points connecting the ring isomer of $C_2H_2Cl^+$ to the neighboring minima at the TZ2P SCF level of theory were unsuccessful.

Upon inclusion of electron correlation into the wave function, only three stationary points were found. In spite of the lack of harmonic vibrational frequencies for these stationary points, we are convinced that the ring and 1-chlorovinyl structures are definitely minima and that the 2-chloro isomer is probably a higher energy minimum. The CISD and CISD(+Q) energies reveal that electron correlation preferentially stabilizes the bridged isomer by about 12 kJ/mol, not an unexpected result. This effect should be sufficient to change the DZ+d SCF transition state to a DZ+d CISD minimum. There is no question that the 1-chlorovinyl cation is a minimum, whereas the potential energy hypersurface around the 2-chlorovinyl cation was probed by finite displacements of the C–C–Cl and C–C–H bends. At the TZ2P CISD level, the finite displacement of the C–C–Cl angle by ±0.001 rad increases the energy by 3.3 × 10^{-7} hartree, and the simultaneous displacement of the C–C–Cl and C–C–H angles by ±0.001 rad increases the energy by 2.1 × 10^{-7} hartree. The latter displacements at the DZ+d CISD level increase the energy relative to the DZ+d CISD

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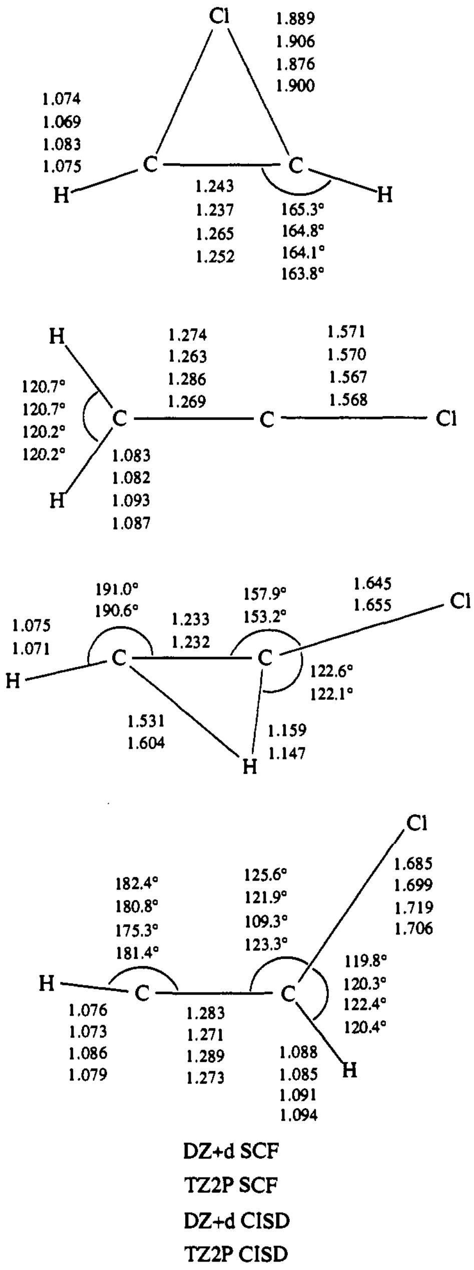

Figure 1. Optimized geometries for the structural isomers of $C_2H_2Cl^+$ investigated in this paper. Bond lengths are in angstroms. The level of theory at which the parameters are optimized follows the order given at the bottom of the figure. For example, if two bond lengths are given for a structure, they are DZ+d SCF and TZ2P SCF optimized distances.

stationary point by 3.5×10^{-7} hartree. This procedure of using finite displacements along probable transition vectors in no way guarantees that the 2-chlorovinyl structure is a minimum. The apparently increasing flatness of the potential energy surface does suggest that the 2-chlorovinyl cation is less favored at higher levels of theory. In fact, the chlorine-bridged ion is clearly lower in energy than the 2-chlorovinyl ion, with the best estimate of the energy difference being 33 kJ/mol in favor of the nonclassical ion. Thus the situation has been completely reversed from the DZ SCF level of theory.

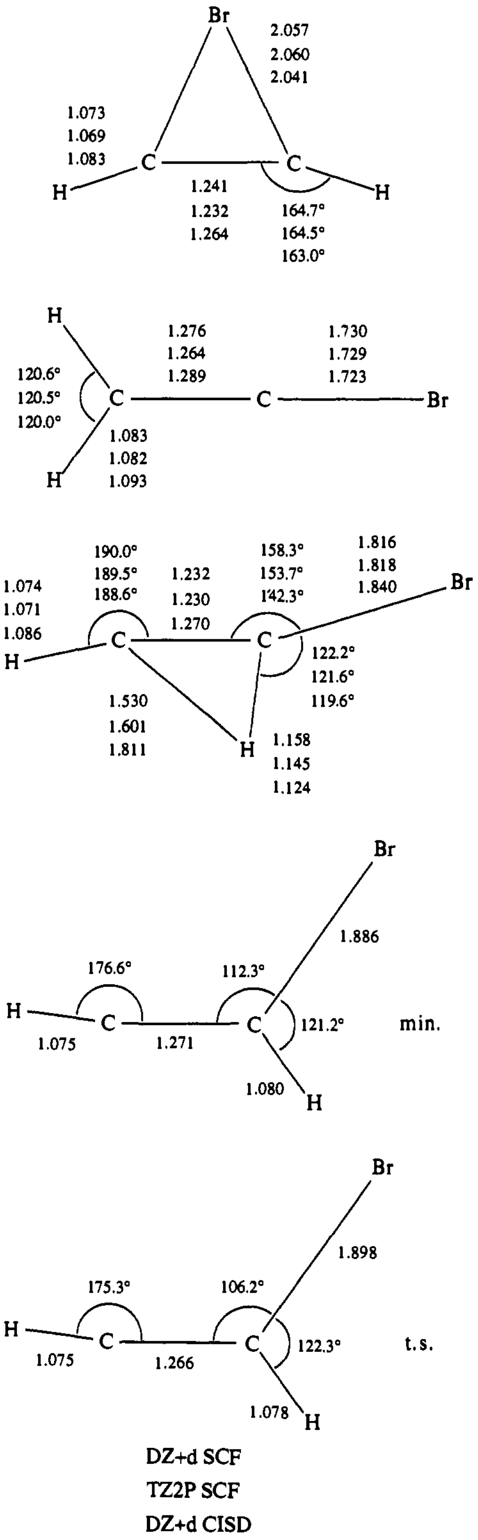

Figure 2. Geometrical parameters for the optimized geometries of the structural isomers of $C_2H_2Br^+$ found in this work. Bond lengths are in angstroms. The levels of theory at which the structural parameters are optimized are given at the bottom of the figure. For example, if two bond lengths are given for a structure, they are DZ+d SCF and TZ2P SCF optimized distances.

$C_2H_2Br^+$. For $C_2H_2Br^+$, SCF theory with small basis sets is again found to be inadequate. At the DZ SCF level, $C_2H_2Br^+$ is seen to be much like $C_2H_2Cl^+$ in its energetic properties (see Table II), with a slightly more stable bridged structure that remains a transition state. The addition of d functions to heavy atoms even more radically affects the energy than for $C_2H_2Cl^+$. The bromenium ion is already a minimum at the DZ+d SCF level of theory, lower than the 2-bromovinyl cation, which is located in an extremely shallow potential well. Upon the improvement of the basis set to TZ2P, no stationary point could be found that resembles a 2-bromovinyl cation. Thus it is possible that there are only the three stationary points on the potential energy surface for in-plane motion of the H and Br atoms about the C–C backbone.

Treatment of electron correlation with a DZ+d basis set leads to three stationary points for $C_2H_2Br^+$ that resemble those for $C_2H_2Cl^+$ (see Figure 2), except that the Br–bridged ion is only

58 kJ/mol above the global minimum, whereas the 2-bromovinyl cation is now 49 kJ/mol above the cyclic structure! The energy of the nonclassical ion relative to the open isomers is lower for the brominated forms than for the Cl-substituted isomers, a trend that is seen in halogen additions to alkenes and alkynes (see ref 1, p 483, and ref 25); i.e., bridged ions are more likely to be intermediates for addition of heavier halogens. The 2-bromovinyl cation also appears to be a CISD minimum from simultaneous finite displacements of the C–C–Br and C–C–H angles by ±0.001 rad to give energy increases of 7.5×10^{-8} hartree, an indication of a shallower minimum than that found for the 2-chlorovinyl cation.

Comparison to $C_2H_3^+$, $C_2H_2F^+$, and $C_2H_4Br^+$. Comparisons with $C_2H_2F^+$ are difficult to make, since the highest level theory in the literature to date is of DZ SCF quality. The ordering of the structural isomers from previous theoretical work gives the 1-fluorovinyl cation as the global minimum, the 2-fluorovinyl cation 67 kJ/mol higher,[9] and the three-membered ring at 151 kJ/mol.[3,8] It is clear that more advanced ab initio computations will lower the energy of the cyclic structure, but probably not to the point that it becomes a minimum or lower than that of either fluorovinyl form.

Examinations of the parent $C_2H_3^+$ potential surface have been made at high levels of theory, so we can estimate the qualitative effect of better wave functions. Incorporation of higher level excitations improves the relative energy of the nonclassical ion by 3 kJ/mol, and enlarging the basis set also lowers the relative energy of the bridged ion slightly.[27] Basis sets need to be more complete for the heavier atoms, so the effect will be somewhat larger for the halenium ions. These high-level studies on $C_2H_3^+$ have also obtained the transition state for the motion of the H atoms around the C=C bond.[26] This movement is much more facile in the $C_2H_3^+$ system than in the corresponding halovinyl systems, since all of the $C_2H_3^+$ stationary points are within 19 kJ/mol of each other.

The behavior of $C_2H_2Br^+$ (and presumably $C_2H_2Cl^+$) is markedly different from that of the corresponding halonium ion system, $C_2H_4Br^+$. The bromonium ion is the global minimum with the 1-bromoethyl cation only 11 kJ/mol higher in energy.[28] It is well-known that halonium ions form more easily than bridged intermediates from halogen addition to alkynes and that reaction rates for halogen addition to alkenes are usually orders of magnitude faster.[2] The formation of the 2-bromoethyl cation, which is the saturated analogue of the 2-bromovinyl cation, is so unfavorable that it takes less energy to undergo a 1,2 hydrogen shift to create the 1-bromoethyl cation.

Stabilization Energies. The stabilization of a carbocation by a substituent X (relative to H) can be taken as the negative of the energy for the reaction

$$C_2H_3X + C_2H_3^+ \rightarrow C_2H_2X^+ + C_2H_4 \qquad (1)$$

Of course, the most stable structure is used in computing this quantity, so the vinyl cations $C_2H_3^+$ and $C_2H_2X^+$ have classical structures at the levels of theory employed. Using SCF energies with the DZ+d basis set, we obtain stabilization energies of 17 kJ/mol for Cl and 33 kJ/mol for Br; i.e., the right-hand side of eq 1 is favored. Upon an increase of the basis set size to TZ2P, the SCF stabilization energies change to 20 and 35 kJ/mol for Cl and Br, respectively. Therefore, increasing the basis set further will probably have little effect. The effect of electron correlation was determined with the DZ+d basis by using a supermolecule approach (the CISD energies of the two fragments on either side of eq 1 are computed by using a supermolecular system of the two fragments separated by 10000 au) because of the well-known size-consistency errors in truncated CI. The stabilization energies increase to 30 kJ/mol for Cl and 52 kJ/mol for Br when electron correlation is included. The most reliable values arise from utilizing the Davidson-corrected CISD energies to obtain stabilization energies of 35 and 59 kJ/mol for Cl and Br, respectively. These results are contrary to those expected on the basis of the *negative* stabilization energies for F and Cl from early studies.[7,12] Therefore, the stabilization energy for F is probably not as negative as previously thought.

Geometries. The structural parameters for the optimized geometries are shown in Figures 1 and 2. The three-membered-ring structures of $C_2H_2Cl^+$ and $C_2H_2Br^+$ are very similar. They resemble strong π complexes in that the acetylene-derived portion is slightly bent away from the halogen and the C–C bond is lengthened from that of acetylene by 0.05 Å (DZP CISD gives a C–C bond distance of 1.213 Å for C_2H_2[29]). The C–Br distance is about 0.015 Å longer in the bromenium ion than in the bromonium ion (DZ+d CISD C–Br distance of 2.025 Å[28]), an indication of weaker bonding for bridged $C_2H_2X^+$ when compared to $C_2H_4X^+$. The difference in carbon–halogen bond distance from that of a single bond is greater for cyclic $C_2H_2Cl^+$ than for cyclic $C_2H_2Br^+$, which is consistent with the idea that the Cl atom is repelled more by the out-of-plane π bond since the Cl atom must get closer to carbon to form a bond.

The 1-halovinyl cation geometries also share common features, except for the C–X bond of course. The C–C bond is longer than in the cyclic arrangement discussed above, as it in no way can be viewed as a complexed acetylene. The DZ+d SCF C–Br bond is 0.21 Å shorter than the typical single-bond length of 1.94 Å. A small part of this difference is the usual tendency of SCF theory to give bond lengths too short if reasonable basis sets are used, but most of it results from the use of sp hybrid orbitals by the carbon to which the Br is bonded and from π back-donation of lone-pair electron density into the empty p orbital on carbon. The DZ+d SCF C–Cl bond distance is 0.20 Å shorter than the typical C–Cl length of 1.77 Å, for identical reasons. The C–H bond distances are increased because some of the C–H bond density is used to stabilized the empty p orbital through hyperconjugation.

The hydrogen-bridged stuctures are transition states and are hence more variable. The only exception is the inclusion of the DZ+d CISD 2-bromovinyl cation, which appears to be a shallow minimum from finite displacements. Its likeness to the transition state leads us to conjecture that the 2-bromovinyl isomer may actually become a transition state at high levels of theory or from interactions with solvent. These hydrogen-bridged $C_2H_2X^+$ geometries resemble protons complexed to haloacetylenes. The π cloud is polarized toward the halogen, so the H atom is mostly on that side. This is not to maintain that proton addition will result in anti-Markovnikov addition, however. Most of the shortening of the C–X bond lengths is due to sp–sp^3 orbital overlap, since π bonding involving halogen is not feasible.

The geometries that bear a likeness to 2-bromovinyl cations are found only at the DZ+d SCF level, both a minimum and a transition state. Given their extreme closeness in energy, their structural similarities make sense. Of the 2-chlorovinyl structures (all apparently minima) the DZ+d CISD structure seems anomalously different from the others. However, the H–C–Cl angle is consistent with the others. The H–C–X angle seems to hold at about 120° for all of the 2-halovinyl and the hydrogen-bridging geometries. A final note to make on the 2-halovinyl isomers is that the C–H bond to the carbocation center is significantly shorter than the other C–H bond, which is expected to stabilize the cation via hyperconjugation. This hyperconjugation and the variation in hybridization account for the differences.

Frequencies. Harmonic vibrational frequencies for the minima found at the TZ2P SCF level of theory are presented in Table III. The halenium ions are very similar, both in their vibrational frequencies and in the more sensitive IR intensities. The only modes that can be used to easily distinguish the two are the lower frequency modes involving halogen motion. The predicted IR intensities are large enough to warrant optimism about observing them (keeping in mind that SCF vibrational frequencies are typically 10% too high). The symmetric C–Cl stretch is at a higher

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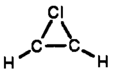
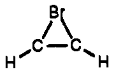
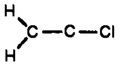
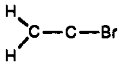
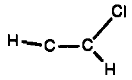
Table III. TZ2P SCF Harmonic Vibrational Frequencies in cm^{-1} and IR Intensities in km/mol (in Parentheses) for the TZ2P SCF Minima of $C_2H_2Cl^+$ and $C_2H_2Br^+$

							
sym CH	3501 (29)	3504 (38)	asym CH	3322 (115)	3320 (106)	CH str	3421 (259)
asym CH	3412 (334)	3416 (331)	sym CH	3223 (181)	3222 (190)	CH str	3237 (122)
CC str	1956 (13)	1961 (18)	CC str	1969 (183)	1932 (139)	CC str	1770 (3)
asym rock	1002 (16)	952 (23)	CH_2 scissor	1422 (15)	1416 (17)	CH rock	1233 (4)
sym rock	991 (7)	954 (6)	CH_2 wag	1006 (55)	1013 (52)	CH rock	1037 (20)
trans wag	817 (0)	801 (0)	CH_2 rock	892 (6)	864 (3)	CH wag	880 (31)
cis wag	807 (108)	810 (105)	CX str	815 (80)	648 (61)	CX str	794 (14)
sym CX	598 (54)	468 (32)	CCX bend oop	364 (6)	326 (7)	CH wag	565 (104)
asym CX	63 (25)	187 (24)	CCX bend ip	356 (1)	331 (1)	CCX bend	180 (12)

frequency than the C–Br stretch, but the asymmetric C–Cl stretch (essentially opening the three-membered ring) vibrates at a lower frequency. This is yet another sign of the bromenium ion being more stable than chlorenium, because the bromenium ion's higher asymmetric C–X stretching frequency reflects a deeper potential well, especially when the greater mass of Br is considered. If one is interested in detecting shifts in acetylene vibrational frequencies upon halenium ion formation, comparisons of Table III values with literature TZ2P SCF values for acetylene[30] reveal that C–H stretching frequencies should decrease by 180 cm^{-1}, the C–C stretch should be lowered by 250 cm^{-1}, and the C–H rocking modes should increase by 130–170 cm^{-1} for chlorenium or 80–120 cm^{-1} for bromenium. The C–H wagging vibrations produce little repulsion, so it is no surprise that those frequencies are shifted upward only slightly from acetylene bending modes.

The vibrational frequencies of the 1-halovinyl cations also resemble each other except for modes involving significant halogen motions. The C–X stretches have reasonable IR intensities and, hence, should be detectable at about 730 cm^{-1} for C–Cl and 590 cm^{-1} for C–Br. The vibrational frequencies for the normal modes that do not contain much halogen motion bear similarities to ethene vibrations. The following DZP SCF ethylene vibrations[31] can be compared to the 1-halo frequencies in Table III: 3400 and 3100 cm^{-1} for average C–H stretches, 1817 cm^{-1} for C–C stretching, 1471 cm^{-1} for the CH_2 scissors mode, 1080 cm^{-1} for the averaged CH_2 wag, and 887 cm^{-1} for the appropriate rocking vibration.

The 2-chlorovinyl cation is a minimum on the TZ2P SCF surface, but the 2-bromovinyl ion is not. The 2-chlorovinyl cation is lower in energy than the chlorenium ion; therefore it is to be expected that the C–C–Cl bending frequency is higher; i.e., the local minimum for the classical structure is deeper than the one for the nonclassical ion. The C–H rocking modes are in the range found above in the chlorenium and 1-chlorovinyl cation, and the C–Cl stretch is similar to that of the 1-chlorovinyl structure. The C–H stretching modes are separated by 200 cm^{-1}, which correlates with the difference in TZ2P SCF bond lengths of 0.012 Å. The wagging vibrations are decoupled, with the low-frequency wag involving the carbocation center. This difference in wagging frequencies is consistent with the idea that a favorable hyperconjugative stabilization of the carbocation center will be lost if the C–H bond partly responsible is bent out of the molecular plane. Surprisingly, the C–C stretch is 200 cm^{-1} lower than for the other two $C_2H_2Cl^+$ minima! This correlates with the TZ2P SCF bond lengths; the actual C–C stretching frequencies for the $C_2H_2Cl^+$ isomers will not be so different, judging from the smaller gap between CISD values for C–C bond lengths, based upon Badger's rule.

Conclusions

The 1-halovinyl isomers of $C_2H_2Cl^+$ and $C_2H_2Br^+$ are the global minima, which is not surprising, since significant π donation can occur to stabilize the empty p orbital on the carbocation center. What is unexpected is that the halenium ion is preferred over the 2-halovinyl cation for X = Cl and Br. This is only evident at more advanced levels of ab initio theory, however. It may be possible that very high level theory or certain experimental conditions may cause the minimum for the 2-bromovinyl cation to disappear. The barrier between the bridged ion and the 1-halovinyl ion is significant, so either form should be isolable. The presence of the double bond in bromenium destabilizes the cyclic ion relative to the 1-bromo structure by 70 kJ/mol, when compared to energy differences in $C_2H_4Br^+$. The stabilization energies for Cl and Br and 36 and 55 kJ/mol, respectively. Given that the stabilization energy is negative for Cl at low levels of theory, it is demonstrated that the stabilization energy for F is not as negative as previously supposed, either. Harmonic vibrational frequencies are presented (along with IR intensities) with the hope that they will be measured by experiment.

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Registry No. 1-Chlorovinyl cation, 66202-71-9; 1-bromovinyl cation, 135257-59-9; 2-chlorovinyl cation, 57847-84-4; 2-bromovinyl cation, 135257-60-2.

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