The $C_2H_3^+$ Cation and Its Interaction with HF

An *ab initio* Study

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The structure and stability of classical and bridged $C_2H_3^+$ is reinvestigated. The SCF and CEPA-PNO computations performed with flexible s and p basis sets including two d-sets on carbon confirm our previous results. We find the protonated acetylene structure to be more stable than the vinyl cation by 3.5–4 kcal/mol. The energy barrier for the interconversion of these two structures is at most a few tenths of a kcal/mol. The equilibrium SCF geometries of Weber *et al.* [15] are affected insignificantly by further optimization at the CEPA-PNO level.

Several structures for the interaction of $C_2H_3^+$ with HF have been investigated at the SCF level. With our largest basis set which includes a complete set of polarization functions we find a remarkable levelling of the stabilities of most of the structures. In these cases the stabilization energy ΔE ranges from -10 to -13 kcal/mol.

Key words: Interaction of $C_2H_3^+$ with HF

1. Introduction

Experimental evidence for solvation of carbocations in superacid media has accumulated during the last few years [1–4]. For example, heats of ionization have been obtained by Arnett and Petro [4] for a series of alkyl chlorides in solvents of low nucleophilicity. The solvolysis of adamantane derivatives has been studied by Schleyer and coworkers [1]. All these investigations indicate a relatively small influence of the solvent on the order of stability of carbocations, even if compared to the gas phase.

A number of quantum chemical investigations on the solvation of cations have been published [5–7]. However, most of these calculations have been restricted to

the interaction with atomic cations. Recently, Jorgensen has studied in a series of papers [8–13] the interaction of carbocations with dipolar molecules (HF and HCl) which should serve as a crude model for the solvent effects in a superacid medium. The *ab initio* calculations [12] have been performed with relatively small basis sets (STO-3G and 4-31G) and for a very limited number of structures only.

In this work we want to concentrate in a more systematic way on the most simple model system – the interaction between $C_2H_3^+$ and HF. We are not only interested in the most stable structures but also in arrangements for which the approach of the HF molecule is less favourable. Such structures may not be of interest if one considers the dimer only. But since the HF molecules shall act as a model compound for a solvent and solvent molecules are distributed all around the solute knowledge of intermolecular potentials for a wide range of structures is necessary. Since we are actually computing dimer interactions only it is not our aim to compare directly our calculated stabilization energies with experimental data from solution. What we can get is an idea of the energy profile when moving the HF molecule around the $C_2H_3^+$ system. Our data may help to construct a potential energy surface which could serve as input for statistical Monte Carlo type or molecular dynamics calculations.

Before discussing the interaction $C_2H_3^+$/HF we report a continuation of our previous investigation on the $C_2H_3^+$ system itself [14]. In this latter work we have found that using the SCF geometries of Weber *et al.* [15] the energy barrier between the classical and non-classical structures of $C_2H_3^+$ is relatively small (~ 0.4 kcal/mol). In the original work of Weber *et al.* a somewhat larger value (~ 1.6 kcal/mol) has been observed. Moreover, we have found the relative stability of protonated acetylene enhanced in comparison to the results of Ref. [15]. These relatively small but nevertheless significant discrepancies prompted us to perform calculations with still larger basis sets and to investigate the influence of electron correlation on the computed geometries.

2. Computational Details

The computational procedures are essentially the same as in Ref. [14]. The valence shell correlation energy is computed from localized orbitals [16] within the CEPA-PNO scheme [17, 18]. The basis sets are collected in Table 1. Basis sets 1–4 refer to our calculations on isolated $C_2H_3^+$. Basis sets 5–8 have been used for the calculations on $C_2H_3^+$/HF. In the latter case the geometry optimization has been performed with a gradient program developed by Pulay [19].

3. Results and Discussions

3.1. $C_2H_3^+$

As already mentioned in the introduction we have performed further investigations on $C_2H_3^+$ concerning basis set dependence and geometry optimization. Total energies and relative stabilities obtained with different basis sets are compared in

Table 1. Basis sets

Basis set no.	Atom	Primitive set[d]	Polarization function[e]
1[a]	C	7s3p	1d (1.0)
	H	3s	1p (0.65)
2[a]	C	7s3p	2d (1.4, 0.4)
	H	4s	1p (0.65)
3[a]	C	8s4p	1d (1.0)
	H	4s	1p (0.65)
4[a]	C	9s5p	1d (1.0)
	H	4s	1p (0.65)
5	F	4-21G[b]	
	C	STO-3G[c]	
	H	STO-3G[c]	
6[a]	F	8s4p	
	C	7s3p	
	H	3s	
7[a]	F	8s4p	1d (1.5)
	C	7s3p	1d (1.0)
	H	3s	
8[a]	F	8s4p	1d (1.5)
	C	7s3p	1d (1.0)
	H	3s	1p (0.65)

[a] S. Huzinaga, "Approximate Atomic Functions I", University of Alberta, Canada 1971.

[b] Ref. [20]. [c] Ref. [21].

[d] The 7s3p, the 8s4p, and the 9s5p sets were contracted to [4111/21], [41111/211], and [51111/2111], respectively. The orbital exponents of the 2s and 4s sets on hydrogen were scaled with $\eta^2 = 1.44$ and contracted to [21] and [211], respectively. The p and d functions were constructed from lobes [22].

[e] Orbital exponents are given in parentheses.

vinyl cation

protonated acetylene
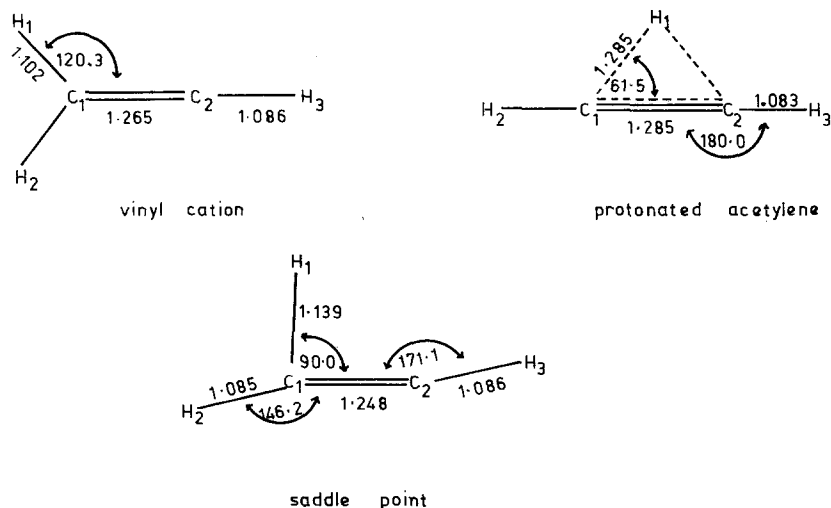
saddle point

Fig. 1. CEPA-PNO geometries for different structures of the $C_2H_3^+$ system. The saddle point structure has not been optimized separately. Instead, this geometry has been obtained by linear interpolation based on the results of Ref. [15]

Table 2. *Ab initio* energies (a.u.) of the different structures for $C_2H_3^+$ (geometries from Weber, Yoshimine and McLean [15])

Cation	$-E_{SCF}$					$-E^a_{CEPA}$				$-E_{CI}$
	Basis set no. 1	Basis set no. 2	Basis set no. 3	Basis set no. 4	[15]	Basis set no. 1	Basis set no. 2	Basis set no. 3	Basis set no. 4	[15]
Vinyl cation	77.03405	77.04665	77.09297	77.10401	77.10391	77.28851	77.31566	77.35534	77.36921	77.34492
Protonated acetylene	77.02659	77.04007	77.08694	77.09830	77.09536	77.29237	77.31848	77.36163	77.37566	77.34491
Saddle point[b] structure	77.02730	77.04110	77.08711	77.09853	77.09740	77.28655	77.31396	77.35466	77.36909	77.3424

[a] The π molecular orbital is not included in the localization process.
[b] Structure B ($\alpha = 90.8°$) in Ref. [15].

Table 3. Relative stabilities (kcal/mol)[a] of the different structures for $C_2H_3^+$ with respect to vinyl cation

Cation	ΔE_{SCF}					ΔE_{CEPA}				ΔE_{CI}
	Basis set no. 1	Basis set no. 2	Basis set no. 3	Basis set no. 4	[15]	Basis set no. 1	Basis set no. 2	Basis set no. 3	Basis set no. 4	[15]
Vinyl cation	0	0	0	0	0	0	0	0	0	0
Protonated acetylene	4.68	4.13	3.79	3.58	5.37	-2.43	-1.77	-3.95	-4.05	0.01
Saddle point[b] structure	4.24	3.48	3.68	3.44	4.09	1.23	1.07	0.43	0.08	1.58

[a] 1 a.u. = 627.73 kcal/mol.
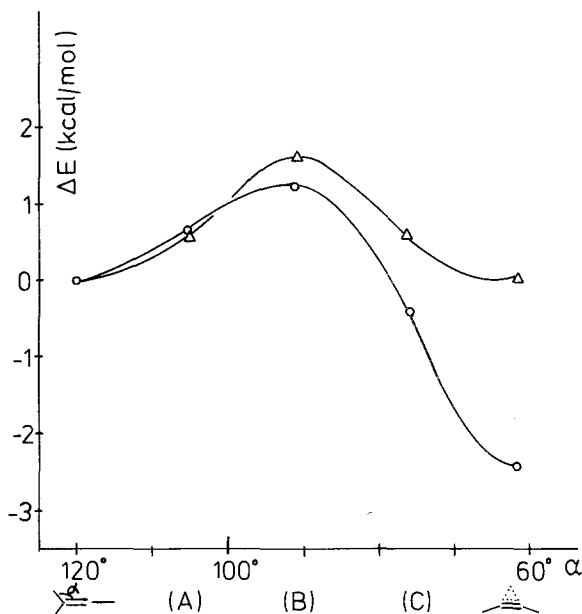[b] Structure B ($\alpha = 90.8°$) in Ref. [15].

Fig. 2. Energy profile for the interconversion of the vinyl cation into protonated acetylene. Geometries and notations are taken from Ref. [15]. —△— Ref. [15]. —○— this work

Tables 2 and 3. In these calculations the SCF geometries of Weber *et al.* [15] have been used (for a characterization of the individual structures see Fig. 1) and σ-π separation of the localized orbitals has been maintained. Let us look first at the energy difference between the vinyl cation and the protonated acetylene. Since basis set 1 is already relatively flexible further effects are small. Nevertheless, addition of a second *d*-set (compare basis sets 1 and 2) and enlargement of the *s* and *p* basis (basis sets 1, 3 and 4) diminishes ΔE_{SCF}. If we assume that the effects of adding *d*-functions and improving the *s* and *p* sets are approximately independent of each other we arrive at ΔE_{SCF} of 3.0–3.6 kcal/mol. Weber *et al.* [15] obtain 5.4 kcal/mol. Since the primitive basis functions of basis set 4 are practically equivalent to theirs we think that the discrepancy of ~2 kcal/mol arises from the fact that the primitive set was contracted too strongly by Weber *et al.* (9s5p to [4211/41]) whereas our basis is essentially uncontracted in the valence region. Moreover, since their contraction coefficients were taken from calculations on the neutral carbon atom they might not be quite adequate for a cation for which the orbitals are shrunken in comparison to the neutral system. These discrepancies become even more pronounced in case of correlation energy calculations. If we again combine the change of ΔE_{CEPA} between basis sets 1 and 2 with the results obtained with basis set 4 we arrive at a final negative ΔE of 3.5–4 kcal/mol within our basis sets. In comparison, Weber *et al.* obtain $\Delta E \sim 0$.

The complete energy curve obtained from basis set 1 for the transformation vinyl cation → protonated acetylene is shown in Fig. 2. Near the classical structure our results agree quite well with those of Weber *et al.* whereas the systematic deviations

Table 4. *Ab initio* energies (a.u., basis set no. 1) of the different structures for $C_2H_3^+$ (on the basis of CEPA optimized geometries, see Fig. 1) and relative stabilities (kcal/mol) with respect to the vinyl cation

Cation	$-E_{SCF}$	$-E_{CEPA}^a$	$-E_{CEPA}^b$	ΔE_{SCF}	ΔE_{CEPA}^a	ΔE_{CEPA}^b
Vinyl cation	77.03382	77.28878	77.28529	0	0	0
Protonated acetylene	77.02579	77.29284	77.29066	5.04	−2.55	−3.37
Saddle point structure	77.02679	77.28677	77.28378	4.41	1.26	0.95

[a] The π molecular orbital is not included in the localization process.
[b] Complete localization.

increase as the angle α approaches the value for the bridged structure. Tables 2 and 3 demonstrate the basis set dependence of the saddle point energy. The larger basis sets show that the saddle point structure lies at most a few tenths of a kcal/mol higher in energy than the vinyl cation. This small barrier is thus negligible in comparison to the zero-point energy of the cation.

Starting from the SCF geometry of Weber *et al.* we optimized the vinyl cation and protonated acetylene structures at the CEPA level with basis set 1. As in Ref. [15] very small changes are observed (see also Fig. 1). Because of these small effects we did not perform a search for the saddle point geometry separately but interpolated the geometry changes linearly on the basis of the changes from Ref. [15]. Table 4 shows that the geometry optimization yields practically negligible energy effects as well.

Since our CEPA results are not strictly invariant under unitary transformation of the occupied Hartree–Fock orbitals we performed another CEPA calculation starting from localized orbitals which were obtained from subjecting all of the valence orbitals to the Boys localization procedure. The results indicate (see Table 4) that this type of localization stabilizes the bridged structure even somewhat more. Furthermore, we have calculated the proton affinity of acetylene with respect to its bridged protonated structure. This has been done in two ways:

a) from the SCF geometries of Weber *et al.* [15] for $C_2H_3^+$ and the experimental geometry [23] for acetylene and
b) from STO-3G geometries.

A comparison of these two cases may serve as a first test how good energy differences are obtained from calculations using larger basis sets but STO-3G geometries. The computations were performed with basis set 1 and all valence orbitals have been used for localization ("banana bond" type localization):

case a) ΔE_{SCF}(vinyl cation/prot. acetylene) = 5.0 kcal/mol
$\quad\quad\quad\Delta E_{CEPA}$(vinyl cation/prot. acetylene) = − 3.4 kcal/mol
$\quad\quad\quad\Delta E_{CEPA}(C_2H_3^+ = C_2H_2 + H^+)$ = 162.3 kcal/mol
$\quad\quad\quad$P.A. calc.   = 158.1 kcal/mol
$\quad\quad\quad$P.A. exp. [24]   = 155.5 kcal/mol

case b) ΔE_{SCF}(vinyl cation/prot. acetylene) $= 5.2$ kcal/mol
ΔE_{CEPA}(vinyl cation/prot. acetylene) $= -2.9$ kcal/mol
ΔE_{CEPA}(C$_2$H$_3^+$ $=$ C$_2$H$_2$ $+$ H$^+$) $= 162.7$ kcal/mol
P.A. calc. $= 158.5$ kcal/mol
P.A. exp.[1] $= 155.5$ kcal/mol

In calculating the proton affinity P.A. from ΔE_{CEPA} the zero-point energy- and $\Delta H^0_{298.16} - \Delta H^0_0$ corrections have been computed from MINDO/3 results in the same way as in Refs. [14, 25–27]. The agreement between the results of cases a) and b) is very satisfactory although care has to be taken in generalizing this agreement to more complex molecules.

3.2. The Interaction of C$_2$H$_3^+$ with HF

In Figs. 3 and 4 the structures are depicted which we have chosen for a characterization of the intermolecular complex between C$_2$H$_3^+$ and HF. Since we found it important to perform a complete geometry optimization for each structure we were, of course, strongly limited in the choice of the basis sets. Jorgensen and Cournoyer [12] have shown that the STO-3G basis yields unrealistic geometries. They obtained a covalent C–F bond whereas the more flexible 4-31G calculations resulted in bond distances characteristic for an intermolecular interaction.

It is clear that the largest deficiencies in the STO-3G basis occur at the fluorine atom. Thus we simply replaced in the STO-3G set the basis functions on fluorine by a 4-21G basis developed by Pulay *et al.* [20]. Using this basis set (no. 5 in Table 1) we obtain reasonable C—F bond distances although they are still somewhat too small in comparison to Jorgensen's and Cournoyer's results.

The relative stability of the vinyl cation and the protonated acetylene is completely wrong when computed with basis set no. 5 (see Table 5). Thus it would be impossible

Table 5. Results for the isolated systems C$_2$H$_3^+$ [a] and HF (total energies are given in a.u., energy differences in kcal/mol)

Molecule or cation	Basis set no. 5	$-E_{SCF}$ Basis set no. 6	Basis set no. 7	Basis set no. 8	$-E_{CEPA}$[b] Basis set no. 8
Hydrogen fluoride[c]	99.74674	99.98694	99.99901	100.00871	——
Vinyl cation	76.16539	76.99520	77.02166	77.03262	77.28437
Protonated acetylene	76.13652	76.96120	77.00506	77.02436	77.28896
		ΔE_{SCF}			ΔE_{CEPA}[b]
Vinyl cation	0	0	0	0	0
Protonated acetylene	18.12	21.34	10.42	5.19	-2.88

[a] The STO-3G geometries have been used (see Figs. 3 and 4).
[b] Complete localization.
[c] $r_{HF} = 0.970$ Å (obtained with basis set no. 5).

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[1] Calculated from $\Delta H_f(C_2H_2) = 54.3$ kcal/mol, $\Delta_f(H^+) = 367.2$ kcal/mol and $\Delta H_f(C_2H_3^+) = 266$ kcal/mol; cf. Ref. [24].
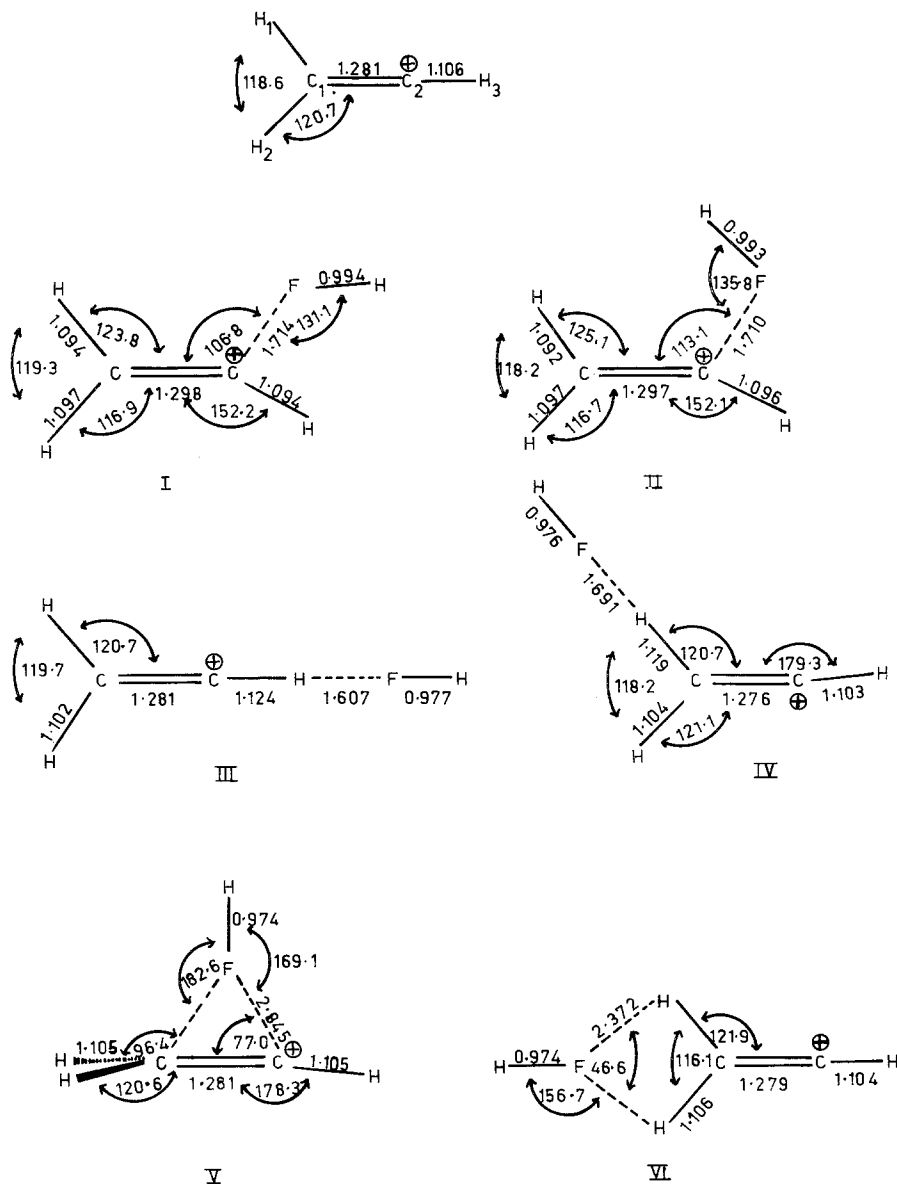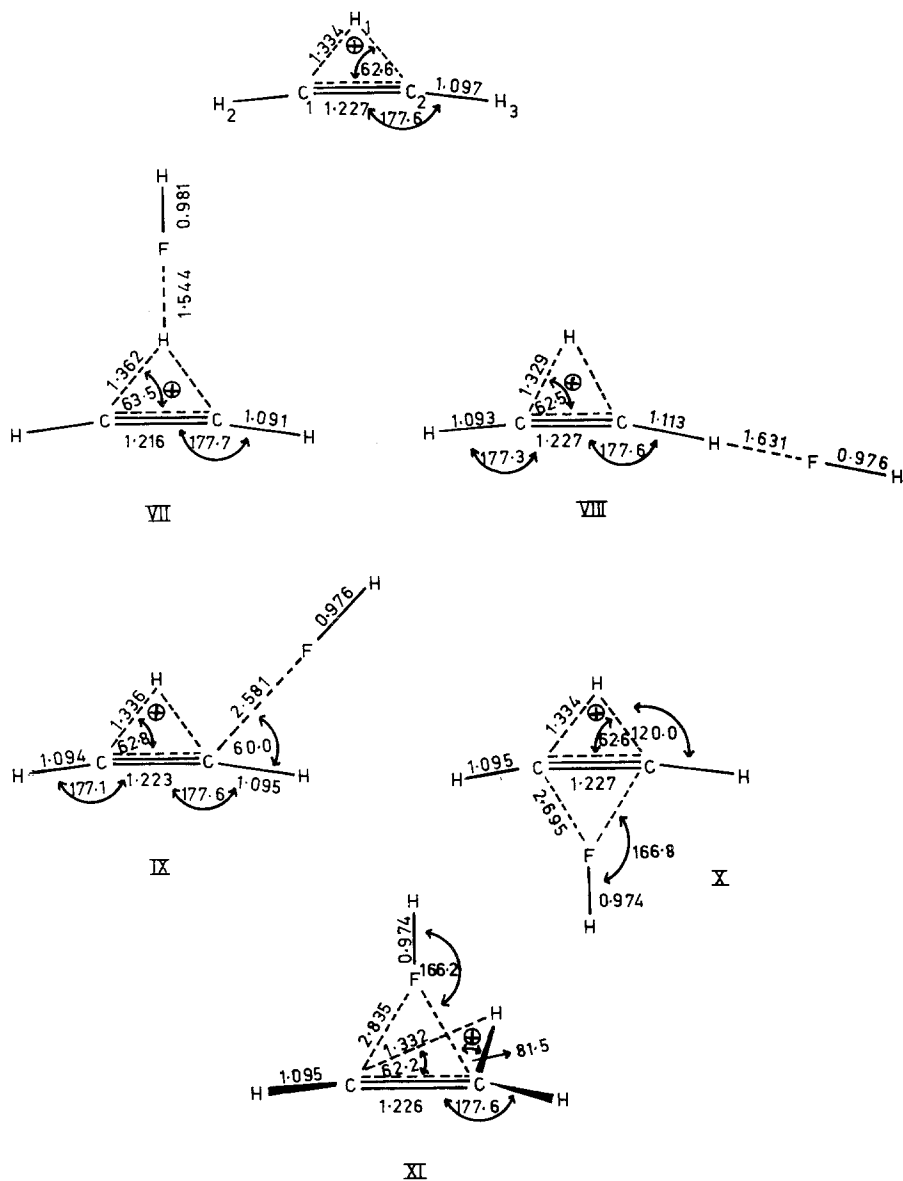
Fig. 3. Vinyl cation/HF interactions. The geometries have been computed with basis set no. 5 (distances are given in Å, angles in degrees)

to study the interaction of the bridged structure with HF without imposing any further constraints. In order to inhibit the transformation of the protonated acetylene to the vinyl cation we kept the optimized angles $H_1C_2C_1$ and $H_1C_1C_2$ equal for the structures shown in Fig. 4. Moreover, in the case of structure IX we had to impose as a further restriction a value of 60° for the FCH angle since otherwise a reorganization of that structure would have occurred. Under these conditions

Fig. 4. Protonated acetylene/HF interactions. The geometries have been computed with basis set no. 5 (distances are given in Å, angles in degrees)

a complete geometry optimization for each of the structures in Figs. 3 and 4 has been performed with basis set no. 5.

Using these geometries SCF calculations with the larger basis sets 6–8 have been performed as well (see Tables 6 and 7). Since the relative stability of the vinyl cation/protonated acetylene system is not satisfactory even at a near Hartree–Fock

Table 6. *Ab initio* energies (a.u.) of the different $C_2H_3^+/HF$ complexes

Complex[a]	$-E_{SCF}$ Basis set no. 5	Basis set no. 6	Basis set no. 7	Basis set no. 8
I	175.95026	177.00625	177.04462	177.06234
II	175.94777	177.00471	177.04290	177.06033
III	175.93763	177.00772	177.04194	177.06066
IV	175.93309	177.00369	177.03834	177.05735
V	175.92725	176.99707	177.03405	177.05372
VI	175.92724	177.00149	177.03774	177.05723
VII	175.91195	176.97517	177.02510	177.05179
VIII	175.90730	176.97297	177.02472	177.05166
IX	175.90414	176.97249	177.02580	177.05336
X	175.89876	176.96708	177.02110	177.04899
XI	175.89873	176.96411	177.01816	177.04606

[a] See Figs. 3 and 4.

level (see Tables 3 and 5) only the relative stabilization energies ΔE of the complex with respect to the corresponding isolated systems are of real interest.

The ΔE values in Table 7 change quite significantly with increasing basis set: not only $|\Delta E|$ decreases generally but also the energy differences between the individual structures are clearly modified.

3.2.1. Vinyl Cation/HF Interactions

Structure II has also been calculated by Jorgensen and Cournoyer [12]. Our basis set 6 is approximately comparable to the 4-31G set. The stabilization energies of

Table 7. Stabilization energies ΔE of $C_2H_3^+/HF$ with respect to the separated systems

	ΔE_{SCF}(kcal/mol) Basis set no. 5	Basis set no. 6	Basis set no. 7	Basis set no. 8
Vinyl cation/HF[a]	0	0	0	0
I	−23.9	−15.1	−15.0	−13.2
II	−22.4	−14.2	−14.0	−11.9
III	−16.0	−16.1	−13.4	−12.1
IV	−13.2	−13.5	−11.1	−10.1
V	−9.5	−9.4	−8.4	−7.8
VI	−9.5	−12.1	−10.7	−10.0
Protonated acetylene/HF[a]	0	0	0	0
VII	−18.0	−17.0	−13.2	−11.8
VIII	−15.1	−15.6	−13.0	−11.7
IX	−13.1	−15.3	−13.6	−12.7
X	−9.7	−11.9	−10.7	−10.0
XI	−9.7	−10.0	−8.8	−8.2

[a] Isolated systems.

14 kcal/mol (Table 7) and 10 kcal/mol [12] agree quite reasonably. However, structure II is not the most stable one. Structure I for which the HF molecule is oriented away from the CC bond is more stable than II by ~1 kcal/mol. With basis set 5 structures I and II are significantly more stable (8 kcal/mol and more) than the others. Thus one could say that the cationic carbon center is preferentially stabilized. This picture changes in case of larger basis sets. The gap in stability to the structures for which the HF molecule approaches towards a hydrogen atom is reduced. Finally, all structures with exception of V lie within a stability range of 3 kcal/mol.

3.2.2. Protonated Acetylene/HF

With basis set no. 5 $|\Delta E|$ is ~6 kcal/mol smaller for structure VII than $|\Delta E|$ for structure I. Thus the vinyl cation is stabilized by the interaction with HF with respect to the protonated acetylene. If one adds this difference to the most realistic stability difference for the isolated isomers (-4.0 kcal/mol) one ends up with the fact that "solvation" (in fact it is only the interaction with a single HF molecule) changes the order of stability between the vinyl cation and protonated acetylene in favour of the former. But comparison with the results of the more elaborate computations shows that these conclusions cannot be maintained. A situation similar to the case vinyl cation/HF is found. A levelling of the ΔE's occurs: all structures with exception of no. XI lie within the range of 3 kcal/mol. The distance in stability to the vinyl cation/HF case has been reduced to 1 kcal/mol only.

4. Conclusions

Our calculations on the isolated C$_2$H$_3^+$ system show the bridged protonated structure to be more stable than the classical vinyl cation by 3.5–4 kcal/mol. Thus we confirm the IEPA results of Zurawski et al. [30] ($\Delta E = -7.4$ kcal/mol) although the stability of the protonated acetylene structure has been over-emphasized by the latter method. Weber et al. [15] obtain equal stability for the classical and non-classical structures. Moreover, they estimate that the bridged structure is lower in energy than the open one by 1–2 kcal/mol. Thus, in comparison to these numbers our calculations show an enhanced trend for the stabilization of the bridged structure. Since we can rely on a series of basis set investigations (see Table 3) we believe that this trend is significant. We have also given arguments in the text why we think that our calculations are the more reliable ones. The barrier between the classical and the nonclassical structures, if it exists at all, is at most a few tenths of a kcal/mol which is a small quantity with respect to the internal energy of the molecule.

Several structures have been chosen to characterize the interaction of HF with C$_2$H$_3^+$. The results obtained from more refined basis sets show a different picture than the STO-3G/4-21G basis set does. Calculations using the former basis sets show that specific energetic interactions between the HF molecule and the cationic carbon center are absent (or at least are very small). Under consideration of all

necessary care which has to be observed in a comparison of such simple systems like $C_2H_3^+$/HF with solution the absence of specific interactions is in good agreement with recent experimental observations [4, 28, 29].

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