A theoretical study on the acid catalysed hydration of excited state acetylene

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That significant modification in the acid/base behavior of aromatic molecules can be induced by electronic excitation is common knowledge. A recent application of this phenomenon is the acid catalyzed photohydration of aromatic acetylenes: ArCCH. The energetics of proton transfer and subsequent hydration of acetylene, as indicated by *ab initio* MO methods, suggests that this property of enhanced excited state basicity is not uniquely characteristic of the Ar substituent.

Key words: *Ab-initio* — Acid catalysed hydration — Excited state acetylene.

1. Introduction

The specific changes in acid/base equilibria accompanying electronic excitation can be illustrated [1] by considering the simple indicator equilibrium,

$$BH^+ = B + H^+,$$
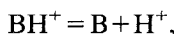
where $K_a = 1$. If for example BH^+ absorbs light of higher frequency than B (blue shift), then upon excitation BH^{+*} will be shifted to a higher energy relative to B^*, resulting in a stronger tendency for the deprotonation reaction. Hence B has become a stronger acid. On the other hand if BH^+ absorbs at lower frequency than B (red shift), the B^* will be displaced toward higher energy than BH^{+*}, thereby favoring the reverse reaction, thus increasing the basic properties of B.

It is well-known that the thermal hydration of substituted phenyl acetylenes to produce acetophenones,

$$ArCCH \xrightarrow[\text{slow}]{\text{conc } H^+} ArCOCH_3,$$

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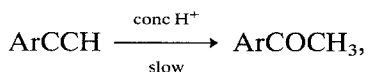
exhibits general acid catalysis (plots of k_{obs} vs. pH being linear) in concentrated acid solution [2]. Moreover the reaction involves a rate determining proton transfer to produce a vinyl cation [2] as indicated by a solvent isotope effect (k_{H_2O}/k_{D_2O}) of 2.5.

It was later realized that the rate could be greatly accelerated if the thermal reaction in concentrated acid was replaced by a photochemical reaction in dilute acid. The suggested mechanism involves photoexcitation to low lying excited states, of enhanced basicity relative to the ground state (S_0), followed by rate limiting Markovnikov (M) protonation to give the vinyl cation which rapidly collapses with H_2O to form the enol [3]. Recently a more in depth study was made of this process. For aromatic alkynes the reaction was found to proceed through S_1 which are postulated to be of the form

$$\overset{+}{Ar} = C = \bar{C}H \;\; \leftrightarrow \;\; Ar - \overset{+}{C} = \bar{C}H,$$

hence facilitating M protonation in the rate determining step [4]. It is not known whether or not this addition is adiabatic over the whole reaction coordinate. Since there were no theoretical studies in the literature reporting these phenomena it was decided to investigate the intrinsic acid/base behavior of a simpler analog; the acid catalyzed photohydration of acetylene. The acid/base properties of a gaseous molecule can be rationalized in terms of the energy of proton transfer (E_{PT}) in the gas phase,

$$H_3O^+ + B = H_2O + BH^+,$$
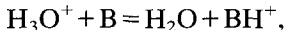
where

$$E_{PT} = E(H_2O) + E(BH^+) - E(H_3O^+) - E(B).$$

The LCAO-MO-SCF calculations of this study provide an estimate of E_{PT} as follows

$$E_{PT} \cong E_{SCF}(H_2O) + E_{SCF}(BH^+) - E_{SCF}(H_3O^+) - E_{SCF}(B).$$

2. Computational details

Ab initio LCAO-MO-SCF determinations were performed utilizing the program MONSTERGAUSS [5] in conjunction with a SEL 32/75 minicomputer. The minimal STO-3G [6], split valent 3-21G [7] and the split valent with double polarization 6–31**G [8] constitute the three basis sets employed in this study. For both closed [9] and open [10] shell systems the RHF method was used exclusively. The geometry of S_0 and the lowest excited states S_1 and T_1 for all molecules under consideration were energy optimized, by the optimally conditioned [11] technique, excluding 6-31**G determinations which were performed on best 3-21G geometries. All gradient optimizations were terminated when the gradient length $|g|$

$$|g| = [\sum (\delta E/\delta q_i)^2/N^{1/2}$$

where the q_i are the internal coordinates and the sum is over the N optimized coordinates, was reduced below 0.0005 mdyne. This criterion generally yields structures within 0.01 pm or 0.01° of the true theoretical optimum values and energies stable below the μ hartree level. Initial S_0 geometries were taken as those predicted by the Valence Shell Electron Pair Repulsion Theory (VSEPR) [12]. Bond lengths were obtained from standard tables [13]. Both S_1 and T_1 were assumed to arise from $\pi - \pi^*$ excitation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In the case of acetylene it is known that S_1 is trans bent.

3. Results and discussion

The total SCF energies (E_{SCF}) for acetylene, vinyl cation and hydrated vinyl cation in S_0, S_1 and T_1 and for the hydronium ion and water molecule in S_0 are given in Table 1 and displayed graphically to form the reaction coordinate in Fig. 1. The energy of proton transfer (E_{PT}) and hydration (E_H) for the appropriate species are given in Table 2.

From the results it is immediately obvious that the energy differences between the ground and excited states are red shifted for the vinyl cation relative to acetylene. In other words, acetylene becomes more basic in the excited state. Also note that the energies of the acetylene-hydronium ion reactants and the corresponding vinyl cation-water molecular products are situated such that proton transfer is endothermic in S_0 and exothermic in each of S_1 and T_1. As far as hydration is concerned the vinyl cation exhibits reduced excited state acidity in Lewis sense in that the formation of hydrated vinyl cation is more exothermic in S_1 and T_1 than in S_0. Aside from the fact that hydration becomes progressively

Table 1. Total energies $(E_{SCF})^a$

Molecule	State	STO-3G^b	E_{SCF} 3-21G^b	6-31**G^c
HCCH	S_0	−75.8562	−76.3960	−76.8218
HCCH	T_1	−75.7457	−76.2887	−76.7208
HCCH	S_1	−75.6586	−76.2156	−76.6575
HCCH$_2^+$	S_0	−76.1654	−76.6558	−77.0930
HCCH$_2^+$	T_1	−76.1489	−76.6217	−77.0649
HCCH$_2^+$	S_1	−76.1143	−76.5902	−77.0344
H$_2$OHCCH$_2^+$	S_0	−151.2872	−152.3496	−153.1921
H$_2$OHCCH$_2^+$	T_1	−151.2266	−152.2771	−153.1199
H$_2$OHCCH$_2^+$	S_1	−151.2240	−152.2731	−153.1157
H$_3$O$^+$	S_0	−75.3284	−75.8912	−76.3077
H$_2$O	S_0	−74.9659	−75.5859	−76.0228

^{a} Energies in Hartrees.
^{b} Energy optimized geometries.
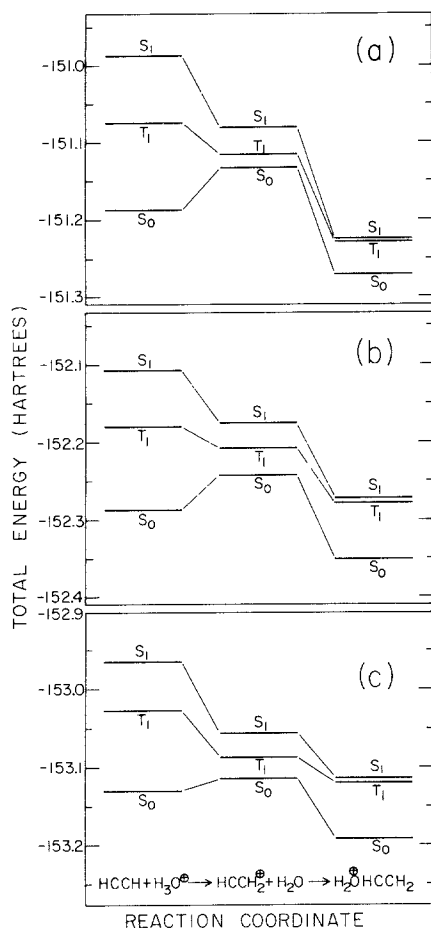^{c} 3-21G energy optimized geometries.

Fig. 1. Total energy (E_{SCF}) as a function of the reaction coordinate for proton transfer and subsequent hydration of acetylene in the ground (S_0), lowest lying singlet (S_1) and triplet (T_1). (**a**) STO-3G; (**b**) 3-21G; (**c**) 6-31**G

Table 2. Energies[a] of proton transfer (E_{PT})[b] and hydration (E_H)[c]

Molecule	State		E_{PT}	
		STO-3G	3-21G	6-31**G
HCCH	S_0	+0.0533	+0.0455	+0.0137
HCCH	T_1	−0.0407	−0.0277	−0.0592
HCCH	S_1	−0.0932	−0.0693	−0.0920
			E_H	
		STO-3G	3-21G	6-31**G
$HCCH_2^+$	S_0	−0.1559	−0.1079	−0.0763
$HCCH_2^+$	T_1	−0.1118	−0.0695	−0.0322
$HCCH_2^+$	S_1	−0.1438	−0.0970	−0.0585

[a] Energies in Hartrees.
[b] $B + H_3O^+ \rightarrow BH^+ + H_2O$, $\Delta E = E_{PT}$.
[c] $A + H_2O \rightarrow A(H_2O)$, $\Delta E = E_H$.

less exothermic in each of S_0, T_1 and S_1 little was achieved by way of the more extensive basis sets.

Of the transition energies obtainable from Table 1 the only one that has been measured with any certainty is the acetylene transition $S_0(^1\Sigma_g) \to S_1(^1A_u)$ of 5.23 eV [14]. These calculations predict 103% (STO-3G), 94% (3-21G) and 85% (6-31**G) of this energy respectively. Despite the error incurred by the neglect of correlation energy associated with electron unpairing it is worth noting that the excitation energy does not converge monotonically with the improvement in basis sets.

Comparing the calculated energies with the experimental value ($E_{exp} = -77.365$) for HCCH S_0 98.0% STO-3G), 98.8% (3-21G) and 99.3% (6-31**G) of the latter is obtained [15]. As far as the Hartree–Fock limit is concerned ($E_{HF} = -76.8540$) the present results yield 98.7% (STO-3G), 99.4% (3-21G) and 99.9% (6-31**G) of this quantity [16]. Confidence in both the STO-3G and 3-21G basis sets is established when it is realized that the predicted geometry is in good agreement with that experimentally determined for each of HCCH S_0 and S_1 [17, 18] (see Table 3). Stabilization of S_1 and T_1 by bending has been demonstrated via a Walsh diagram obtained by mapping the changes in the HOMO and LUMO as a function of HCC bending, from which it was determined that the two degenerate LUMO (π^*) are split into a σ^* and π^* component, the σ^* of which is more stable for both *cis* and *trans* bending. On the other hand the two degenerate HOMO (π) are split into a σ and π component, the σ component of which is more stable for *trans* bending and vise versa [19]. A qualitative explanation assumes that if the molecule retains its shape upon π-π^* excitation then the repulsion between the electron in the π^* MO and the pair of electrons forming the C-H bond causes the "sp hybridization" governing the nuclear framework to assume "sp^2 hydridization" so that it resembles an ethylene

Table 3. Theoretical and experimental bond lengths[a] and angles [b] of HCCH S_0, S_1 and T_1

Molecule	Parameter	STO-3G	3-21G	Expt.
HCCH S_0 (linear)				
	r_{H-C}	1.065	1.051	1.061
	r_{C-C}	1.168	1.187	1.203
HCCH S_1 (*trans* bent)				
	r_{H-C}	1.102	1.080	—
	r_{C-C}	1.374	1.362	1.388
	HCC	120.8	125.5	120
HCCH T_1 (*cis* bent)				
	r_{H-C}	1.092	1.076	—
	r_{C-C}	1.313	1.318	—
	HCC	126.3	128.5	—

[a] Bond lengths in Å.
[b] Bond angles in degrees.

molecule devoid of two H atoms [20]. Replacing the two H atoms are two "sp^2 atomic orbitals", each capable of holding up to two unshared electrons, which to a first approximation are nonbonding molecular orbitals of identical energy. Realizing the energy associated with a nonbonding orbital (NBO) is expected to lie between that of an antibonding orbital (ABO) and a bonding orbital (BO) it is reasonable to expect the linear Frank–Condon state to be stabilized by planar bending. However whether the *cis* or *trans* mode is lowest for a given state cannot be predicted by qualitative arguments. It turns out that S_1 is *trans* bent and T_1 *cis* bent.

By replacing the canonical MO's with localized hybrid orbitals (neglecting angular discrepancies) a simple pictorial representation of S_1 [20] and T_1 can be given. In both cases the nuclear framework is represented by "sp^2 hybridization" however for T_1 the π bond is doubly occupied as opposed to S_1 in which it is
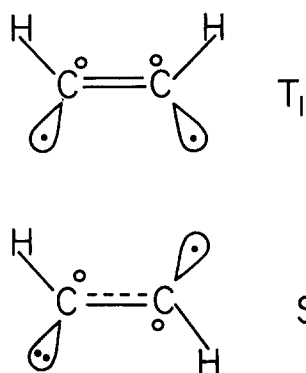

Fig. 2. VSEPR representations of HCCH S_1 and T_1. All carbon atoms are of sp^2 hybridization

Table 4. Theoretical bond lengths [a] and angles[b] of $HCCH_2^+$ S_0, S_1 and T_1[c]

Parameter	STO-3G					3-21G
	S_0	T_1	S_1	S_0	T_1	S_1
$r_{C_1-C_2}$	1.281	1.423	1.436	1.260	1.390	1.396
$r_{H_1-C_2}$	1.106	1.106	1.096	1.086	1.076	1.074
$r_{H_2-C_2}$	1.106	1.106	1.098	1.086	1.078	1.077
$r_{H_3-C_1}$	1.106	1.107	1.118	1.068	1.073	1.075
$H_1C_2C_1$	120.7	120.2	119.8	120.9	120.2	120.3
$H_2C_2C_1$	120.7	121.3	119.7	120.9	121.1	120.1
$H_3C_1C_2$	180.0	130.6	136.8	180.0	133.9	139.3

[a] Bond lengths in Å.
[b] Bond angles in degrees.
[c] Bond lengths and bond angles are specified for the following structure

$$
\begin{array}{c}
H_1 \\
\diagup \\
C_1-C_2 \\
\diagup \qquad \diagdown \\
H_3 \qquad\quad H_2
\end{array}
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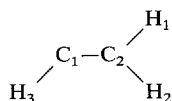
singly occupied. The two remaining nonbonding "sp^2 hybrid orbitals" are then occupied with the remaining electrons. Thus, although feasible to regard T_1 as a "*cis*-vinyl biradical" it is a common misconception that portrays S_1 as a "*trans*-vinyl biradical" (refer to Fig. 2).

The *cis* model for T_1 closely mirrors the calculated geometry; the C-C bond length being just slightly shorter than that of a C—C double bond. However for S_1 the calculated bond length is not indicative of a sytem in which the bond length is intermediate between 1.54 Å (—C—C—) and 1.34 Å (—C=C—). The reason can be attributed to the fact that the two "sp^2 orbitals" are not really NBO but actually interact to form a weak BO. This is in fact suggested by the Walsh diagram study where the sum of the σ and σ^* orbital energies are less than zero.

Regarding the vinyl cation, there is at present little direct experimental evidence for either its geometry or energy [21]. The present calculation yields 98.8% (STO-3G), 99.5% (3-21G) and 99.9% (6-31**G) of the most accurate calculation ($E_{SCF} = -77.1039$) to date [22]. The structure as predicted by VSEPR is fairly consistent with the calculated facts. According to the MO scheme the LUMO of $HCCH_2^+ S_0$ is almost completely localized as the $2p$ atomic orbital of the unprotonated carbon lying perpendicular to the π system (HOMO). Both
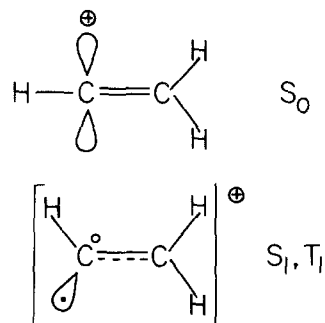

Fig. 3. VSEPR representations of $HCCH_2^+$ S_0, S_1 and T_1. All carbon atoms are of sp^2 hybridization, excluding the unprotonated carbon of S_0 which is of sp hybridization
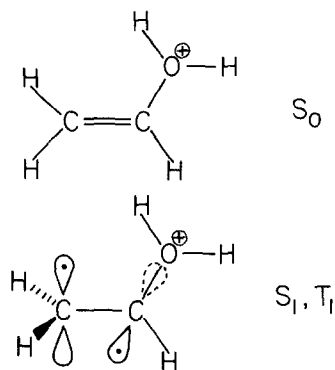

Fig. 4. VSEPR representations of $H_2OHCCH_2^+$ S_0, S_1 and T_1. All heavy atoms are of sp^2 hybridization

Table 5. Theoretical bond lengths[a] and angles[b] of $H_2OHCCH_2^+S_0$[c]

Parameter	STO-3G	3-21G
$r_{C_1-C_2}$	1.305	1.298
$r_{O_1-C_2}$	1.459	1.500
$r_{H_1-C_2}$	1.088	1.065
$r_{H_2-C_1}$	1.087	1.072
$r_{H_3-C_1}$	1.087	1.072
$r_{H_4-O_1}$	0.983	0.975
$r_{H_5-O_1}$	0.984	0.975
$O_1C_2C_1$	119.6	119.0
$H_1C_2C_1$	130.9	132.5
$H_2C_1C_2$	118.7	118.5
$H_3C_1C_2$	123.9	124.3
$H_4O_1C_2$	121.5	121.1
$H_5O_1C_2$	122.0	121.8

[a] Bond lengths in Å.
[b] Bond angles in degrees.
[c] Bond lengths and bond angles are specified for the following structure.

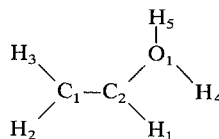**Table 6.** Theoretical bond lengths[a] and angles[b] of $H_2OHCCH_2^+ S_1$ and T_1[c]

Parameter	STO-3G		3-21G	
	S_1	T_1	S_1	T_1
$r_{C_1-C_2}$	1.489	1.482	1.460	1.449
$r_{O_1-C_2}$	1.458	1.460	1.500	1.511
$r_{H_1-C_2}$	1.090	1.090	1.065	1.065
$r_{H_2-O_1}$	0.984	0.984	0.976	0.975
$r_{H_3-O_1}$	0.984	0.984	0.976	0.976
$r_{H_4-C_1}$	1.086	1.086	1.072	1.073
$r_{H_5-C_1}$	1.086	1.086	1.072	1.073
$O_1C_2C_1$	1115.5	115.6	114.3	114.9
$H_1C_2C_1$	133.4	133.5	135.5	135.5
$H_2O_1C_2$	122.2	122.2	122.1	122.1
$H_3O_1C_2$	121.4	121.5	120.3	120.5
$H_4C_1C_2$	118.5	118.6	119.7	120.1
$H_5C_1C_2$	118.5	118.6	119.7	120.1
$H_4C_1C_2O_1$	101.7	101.6	94.9	92.4
$H_5C_1C_2O_1$	258.3	258.4	265.1	267.6

[a] Bond lengths in Å.
[b] Bond angles in degrees.
[c] Bond lengths and bond angles are specified for the following structure
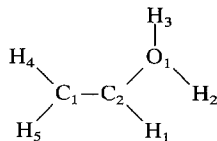
S_1 and T_1 were derived by removing an electron from the π MO and singly occupying this virtual orbital. When the geometries were energy optimized it was found that again the molecule stabilized itself by bending in the plane. Again neglecting angular discrepancies about the unprotonated carbon stabilization is achieved by "rehybridization of sp to sp^2". The resulting model for both protonated S_1 and T_1 predict $C-C$ bond lengths intermediate between $1.54\,\text{Å}$ ($-C-C-$) and $1.34\,\text{Å}$ ($-C=C-$) and this in fact is born out by the optimized geometry (Table 4; Fig. 3).

The last intermediate on the reaction coordinate considered is the hydrated vinyl cation. The calculations indicate a planar structure in close agreement with the VSEPR prediction. The much extended C–O bond is perhaps reflective of the electron-electron repulsion between the filled π system (HOMO) and the remaining oxygen lone pair. As before stabilization upon π-π^* excitation requires structural alteration, which in this instance is achieved by conformation change to the staggered rotomer, resulting in the destruction of the π system characteristic of the planar eclipsed ground state. Refer to Fig. 4 and Tables 5 and 6.

In summary, the present calculations indicate that the enhanced basicity of excited acetylene is an inherent characteristic of the acetylenic functional group itself. Therefore in conclusion acetylene may be classified with those compounds (indicators) that exhibit such a red shift upon protonation. Further calculations are in progress to determine the effect of substituents on this phenomena.

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