The Proton Affinities of the Acetylene Molecule, and of the Acetylide and Diacetylide Ions

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Summary Non-empirical LCAO–MO–SCF calculations using Gaussian basis sets were used to predict the geometry of the acetylide ion, proton affinities of 547·5, 391·6, and 166·1 kcal/mole being computed for C_2^{2-}, C_2H^-, and C_2H_2, respectively.

NON-EMPIRICAL LCAO–MO–SCF calculations using extensive basis sets of Gaussian functions predict quite accurately the proton affinities of several small molecules and negative ions.[1,2] Now, employing in part the results of recent molecular orbital studies on the protonation of acetylene[3] and on the heats of formation of small molecules,[4] we are able to report computed proton affinities for C_2^{2-}, C_2H^-, and C_2H_2.

The total electronic energies of the C_2H_n ($n = 0$—3) species containing fourteen electrons, were calculated using a variety of basis sets[1,5] and, with the exception of those for the acetylide ion, are tabulated elsewhere.[3,4] The computations were carried out on an IBM-7094-II computer using an extensively modified POLYATOM system[6] and on an IBM-360-65 computer using an IBMOL-II program[7]. The acetylide ion was assumed to be linear and the bond lengths were optimized using the "large" basis set (7^s3^p functions[8] on carbon, 3^s functions[9] on hydrogen). The optimum C–C and C–H bonds were found to be 1·203 and 1·035 Å, respectively, compared with experimental values of 1·206 and 1·061 Å for *acetylene*.[10] The corresponding computed total energy of the acetylide ion was −76·0480 hartree, and that of the ion with the same geometry but with the larger Double ζ basis set was −76·1678 hartree.

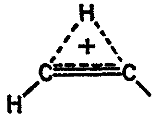
The difference in the total electronic energies of a base B^{n-} and its conjugate acid $BH^{(n-1)-}$ gives ΔE for the reaction

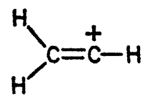
$$B^{n-} + H^+ \rightarrow BH^{(n-1)-}$$

This may be converted into ΔH_{298}^0 by addition of several small correction terms for changes in the translational, rotational and zero-point vibrational energies, and $-RT$ (−0·59 kcal/mole) for changes in the number of molecules.[4] However, the major contribution comes from the change in zero-point energy and this cannot be calculated for the ions in this study due to lack of experimental vibrational frequencies. The total correction for a protonation reaction will be of the order ± 5 kcal/mole[2,4] and should be added to the calculated proton affinities listed in the Table.

The experimental value (897·8 kcal/mole) for the addition of *two* protons to the acetylide ion was calculated from ΔH_f (C_2^{2-}) = 222 kcal/mole,[11] ΔH_f (H^+) = 365 kcal/mole,[12] and ΔH_f (C_2H_2) = 54·19 kcal/mole.[13] The computed value converges on this experimental value as the number of basis functions is increased, in the manner observed previously.[1]

The experimental proton affinity of acetylene was estimated from ΔH_f (H^+),[12] ΔH_f (C_2H_2),[13] and ΔH_f ($C_2H_3^+$) = 269 kcal/mole.[14] The $C_2H_3^+$ ion may have one of two plausible structures: either the π-protonated ion (I) or the vinyl cation (II).


(I)


(II)

Non-empirical molecular orbital calculations[4] have shown that the vinyl cation is the more stable and that there is no energy barrier for conversion of the initially formed π-complex into this ion. The computed proton affinity of acetylene should therefore be based on the σ-protonated

Proton affinities (*kcal/mole*)

Molecule or ion	Minimum[a]	Medium[a]	Large	Double ζ	Experimental value	Values from previous calculations
C_2^{2-} (Monoprotonation)	—	—	559·7	547·5	—	—
C_2^{2-} (Diprotonation)	1453·4	1024·8	946·2[a]	939·1	897·8[b]	—
$H{-}C{\equiv}C^-$	—	—	386·9	391·6	—	—
$H{-}C{\equiv}C{-}H$						
(a) π-Protonation	196·2	133·2	135·0	147·6	150·2[c]	130·8[d]
(b) σ-Protonation (formation of vinyl cation)	211·1	160·9	157·4	166·1		
$H_2C{=}C$	301·8	196·6	194·1	201·7	—	—

[a] Calculations used experimental or estimated geometry.
[b] Calculated from experimental heats of formation.[11–13]
[c] Calculated from experimental heats of formation.[12–14]
[d] Ref. 15.

cation giving a value of 166·1 kcal/mole from the most accurate calculations.

Experimental proton affinities for negative ions are difficult to measure and the computed values for the acetylide and diacetylide ions are the first reported values for these species. The results from the Double ζ basis set calculations are the more reliable and, by comparison with a previous extensive study of the correlation between experimental and computed proton affinities,[1] are expected to overestimate the correct value by between 5 and 10%.

Finally, the computed proton affinities of vinylidenecarbene, an unstable isomer of acetylene, and the conjugate base of the vinyl cation, were included in the Table.

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