Hydroxide Attack on Acetylene: Theoretical Structures and Energies

O. Dolgounitcheva,[†] V. G. Zakrzewski,[†] and J. V. Ortiz*[,†]

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131-1096

Received: September 27, 1996; In Final Form: November 7, 1996[⊗]

Several $C_2H_3O^-$ species resulting from the interaction of acetylene and hydroxide have been characterized with *ab initio* calculations. MP2 geometry optimizations were performed with augmented, correlation-consistent, polarized-valence, double-ζ basis sets. The total energies of the most crucial structures were also recalculated at the QCISD(T) level with MP2-optimized geometries. Nine structures corresponding to local minima have been found at the MP2 level, their stability decreasing in the following order: acetaldehyde enolate anion > acetyl anion ≈ ethynide−water complex > ethenyloxy anion ≈ vinyloxy anion. The ethynide−water complex is either the most stable product of the reaction of hydroxide with acetylene or at least an initial stable intermediate.

Introduction

Nucleophilic additions to acetylenes in so-called superbasic media have been widely used to obtain various products of vinylation and have found some industrial application.[1] The superbasicity of a system is defined by the ability of a solvent to capture cations, thus leaving anions free and increasing their basicities by orders of magnitude. Comprehensive reviews of reactions of alkynes in superbasic media have emphasized that in aprotic, dipolar solvents, the greatly increased nucleophilicities of anions lead to a number of fundamentally different reactions such as vinylation of polyols, pyrroles, and ketoximes, hydration−oligomerization of acetylene, and vinylation of S, Se, and Te derivatives.[1,2] The most recent applications include the formation of substituted vinylphosphines from phosphine and aryl- and heteroarylacetylenes.[3]

One of the most interesting reactions of this type is the oligomerization of acetylene by hydration, where acetylene reacts with water in a medium consisting of MOH (M = K, Na, Li) and an aprotic dipolar solvent such as DMSO or triethylphosphine oxide.[4−6] This reaction is usually performed in an autoclave at temperatures between 80 and 120 °C and at pressures from 12 to 15 atm in an excess of solid alkali metal hydroxide. A number of hydratooligomers have been obtained, and the formation of up to 20% benzene as a byproduct has been observed.[1−6] Two anionic intermediates were considered to be responsible for the unusual products of this reaction: ethenyloxy anion, arising initially from direct nucleophilic addition of hydroxide to acetylene according to

$$\mathrm{HCCH + OH^- \rightarrow HCCHOH^-} \qquad (1)$$

and a subsequently formed acetaldehyde enolate anion (also called vinyloxide anion[1]),

$$\mathrm{HCCHOH^- \rightarrow H_2CCHO^-} \qquad (2)$$

Since hydroxide is a much stronger base than a nucleophile, one might expect the exchange reaction to prevail:

$$\mathrm{HCCH + OH^- \rightarrow HCC^- + H_2O} \qquad (3)$$

Indeed, in a gas-phase reaction between hydroxide and acetylene studied in flowing afterglow experiments, the ethynide anion, C_2H^-, was the only anionic product observed. Equilibrium was obtained at room temperature, and the standard enthalpy change was estimated as −6.2 ± 0.5 kcal/mol.[7]

Nonempirical calculations on exchange reactions between acetylene and hydroxide and on the ethynide complex with water[8−12] have been performed. All of these calculations indicated that the shift reaction (3) and ion−molecular complex formation are highly exothermic processes. *Ab initio* calculations on a model system where hydride attacks linear and bent acetylene[13,14] indicated that direct addition of H^- to one of the carbon atoms is the minimum energy path for this reaction. Of all possible isomers of the general formula $C_2H_3O^-$, only the acetaldehyde−enolate anion and an acetyl anion (H_3CCO^-) have been studied *ab initio*.[15−20] There was, however, a series of semiempirical MNDO calculations where a number of products of eq 1 have been studied together with their interconversion routes.[21] In these studies, four isomers have been found to be stable relative to decomposition to acetylene and hydroxide. All four isomers were found to be much lower in energy than the ethynide−water complex. The latter species was also described as a nonrigid moiety with two preferred orientations of the water molecule around ethynide: mono- and bidentate. The complex formation energy was estimated to be −9.3 kcal/mol.[21] It also has been shown that the formation of vinyloxy anions either via direct addition of OH^- to acetylene or through rearrangement of an ethynide−water complex would demand some harsher than normal conditions, while the formation of an enolate anion or an acetyl anion would be very unlikely due to the high barriers to any rearrangement. A number of side reactions, such as benzene formation and oligomerization of C_2H_2 into *trans*- and *cis*-vinylacetylide and divinylacetylide anions, with low activation energies were predicted by MNDO calculations.[22,23] Easy formation of divinyl sulfide from C_2H_2 and KSH (or H_2S) in the presence of OH^- also has been explained.[23] In all these reactions, C_2H^- was considered to be a necessary intermediate.

To obtain accurate structural and energetic information pertinent to this chemistry, we undertook *ab initio* calculations on isomers of $C_2H_3O^-$. Basis sets and correlation methods that are equal to this task have been employed.

Methods

All calculations have been performed with the Gaussian 94 set of programs.[24] As is well-known, anions can be adequately

---

[†] Current address: Department of Chemistry, Kansas State University, Manhattan, KS 66506-3701.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

S1089-5639(96)02984-2 CCC: $14.00

described by *ab initio* methods only when basis sets with diffuse functions are employed. We have utilized two basis sets; the smaller, 6-31+G**,[25] was used for preliminary geometry optimizations at the SCF level. The augmented, correlation-consistent, polarized-valence, double-ζ basis set[26] (aug-cc-pvdz) was used for frozen core MP2[27] optimization of all stationary points found at the SCF/6-31+G** level and for subsequent calculation of harmonic frequencies.[28] The optimizations were performed using the redundant internal coordinates procedure.[29] Higher order correlation effects were studied at three levels: partial fourth-order many-body perturbation theory (MBPT)[30] with single, double, and quadruple excitation terms (MP4SDQ); quadratic configuration interaction with single and double substitutions (QCISD) and with certain triple substitution terms.[31,32] The latter approximation, also known as QCISD(T), contains all terms included in full fourth-order MBPT and is the most complete correlation method. Single-point calculations were performed with these methods for some of the structures at their MP2/aug-cc-pvdz-optimized geometries. The energies for shift reaction (3) were also estimated at the QCISD(T) level with the augmented, correlation-consistent, polarized-valence, triple-ζ basis set (aug-cc-pvtz).[26]

Results and Discussion

Structures and Energies. The following $C_2H_3O^-$ structures (Figure 1) proved to be local minima in the MP2/aug-cc-pvdz potential energy surface: ethynide−water complex (**1**), acetaldehyde enolate anion (**2**), acetyl anion (**3**), *cis*-1-oxy-*trans*-ethenyl anion (**4**), *trans*-1-oxy-*trans*-ethenyl anion (**5**), *cis*-1-oxy-*cis*-ethenyl anion (**6**), *trans*-1-oxy-*cis*-ethenyl anion (**7**), *trans*-2-oxyvinyl anion (**8**), and *cis*-2-oxyvinyl anion (**9**).

The total energies and relative energies obtained at the MP2/aug-cc-pvdz level and with higher order correlation methods are presented in Tables 1[33] and 2. Tables 3 and 4 display the OH^- and CCH^- proton affinities and reaction heats, respectively. Data pertaining to the optimization of complex **1** and other structures are given in the supporting information.

All structures are stable with respect to decomposition to acetylene and hydroxide, though this stability is decreased when the zero-point-energy (ZPE) vibrational correction is included (Table 1). Structures **1**−**4**, **6**, **8**, and **9** are stable with respect to decomposition to ethynide and water. Anions **5** and **7** become unstable upon accounting for ZPE corrections.

The ethynide−water complex's energy is compared to other $C_2H_3O^-$ isomers in the ΔE_3 column of Table 1 and in Table 2. The last column of Table 2 is an additive estimate of relative energies in which the ZPE corrections of Table 1 are applied to the ΔQCISD(T) results.

Molecular Anions. Species **2** and **3** are the lowest energy structures among molecular anions **2**−**9**. The total energy differences between **2** and all the other structures are large (*ca.* 27−52 kcal/mol), thus making acetaldehyde enolate the thermodynamically preferrable product of reactions 1 and 2. QCISD(T) calculations have only a minor effect (less than 0.1 kcal/mol) on the relative energies of **1** and **2**.

Optimized geometry parameters for **2** and **3** can be found in the supporting information. In both cases, the bond lengths are systematically larger when calculated at the MP2 level with aug-cc-pvdz. The bond angles are less dependent on the basis sets and correlation, with differences not exceeding 0.7° in the case of **2** and 1.6° in the case of **3**. The acetaldehyde enolate anion is essentially planar, and the eclipsed CH−CO structure is the minimum for the acetyl anion. Two transition states also have been found: one corresponding to rotation of the CH_2 group in **2** (TS1), and another resembling deprotonated ethylene oxide (TS2). Both transition structures lie much higher than **2**: 36.2 kcal/mol for TS1 and 102.2 kcal/mol for TS2.

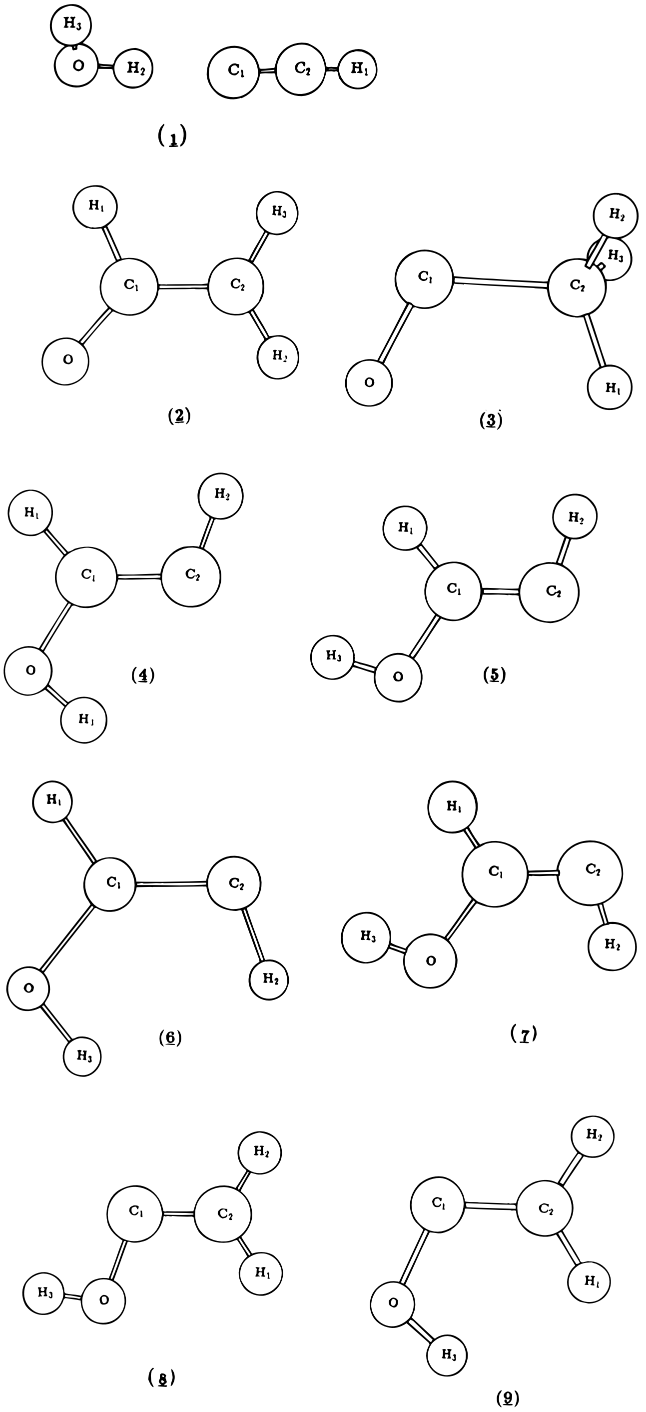

Figure 1.

Proton Affinities. In order to verify the reliability of the relative energies, we have calculated the proton affinities (PAs) of C_2H^- and OH^- and compared them with available experimental and theoretical data (Table 3). The agreement of our calculated PAs with experimental data is rather good for the MP2/aug-cc-pvdz level. ZPE corrections lower the PAs slightly. All higher order correlation treatments produce higher PAs than MP2. The same is also true for single-point calculations in the triple-ζ basis set. The best estimates are formed by adding the latter corrections to the MP2 ZPE results and are within 2 kcal/mol of experimental values.

Proton-Exchange and Complex Formation. The results of our calculations on reaction 3 and ethynide−water complex

TABLE 1: MP2/aug-cc-pvdz Total Energies (E in au) and Relative Energies[a] (ΔE in kcal/mol)

	$E + 152$	$E + \mathrm{ZPE} + 152$	ΔE_1	ΔE_2	ΔE_3	$\Delta E_3'$ [b]	ΔE_4
1	−0.77901	−0.74165	−30.5 (−27.5)	−18.6 (−17.1)	0 (0)	0	30.8 (27.9)
2	−0.82811	−0.78611	−61.7 (−55.4)	−49.4 (−45.0)	−30.8 (−27.9)	−30.8	0 (0)
3	−0.78314	−0.74255	−33.3 (−28.0)	−21.2 (−17.7)	−2.6 (−0.6)	−4.9	28.2 (27.3)
4	−0.76317	−0.72143	−20.8 (−14.8)	−8.6 (−4.4)	9.9 (12.7)	11.6	40.7 (40.6)
5	−0.74842	−0.70372	−11.5 (−3.7)	−0.6 (6.7)	19.2 (23.8)		50.0 (51.7)
6	−0.75704	−0.71570	−17.0 (−11.2)	−4.8 (−0.8)	13.8 (16.3)	16.1	44.6 (44.2)
7	−0.74925	−0.70861	−12.1 (−6.7)	−0.1 (3.6)	18.7 (20.7)		49.5 (48.6)
8	−0.76108	−0.71928	−19.5 (−13.4)	−7.3 (−3.1)	11.2 (14.0)	9.5	42.1 (41.9)
9	−0.76018	−0.71931	−18.9 (−13.5)	−6.8 (−3.1)	11.8 (14.0)	10.9	42.6 (41.9)

[a] Values in parentheses refer to ZPE--corrected total energy differences; $\Delta E_1 = E - E(C_2H_2) - E(OH^-)$;[33] $\Delta E_2 = E - E(C_2H^-) - E(H_2O)$;[33] ΔE_3 is the relative energy with respect to **1**; ΔE_4 is the relative energy with respect to **2**. [b] Relative energies obtained at the SCF level with the 6-31+G** basis set.

TABLE 2: Total Energies (E in au) and Relative Energies (ΔE in kcal/mol)

	MP4SDQ		QCISD		QCISD(T)		best est
	$E + 152$	ΔE	$E + 152$	ΔE	$E + 152$	ΔE	ΔE
1	−0.79646	0	−0.79786	0	−0.81904	0	0
2	−0.84755	−32.0	−0.84809	−0.31.5	−0.86804	−30.7	−27.8
3	−0.80818	−7.4	−0.81066	−8.0	−0.82930	−6.4	−4.4
4	−0.78422	7.7	−0.78568	7.6	−0.80648	7.9	10.7
8	−0.78407	7.8	−0.78556	7.6	−0.80580	8.3	11.1

TABLE 3: Proton Affinities (kcal/mol)

method	PA(OH^-)	PA(C_2H^-)
SCF/6-31G*[11]	−429.3	−402.8
SCF/6-31+G*[a,11]	−402.5	−380.6
MP2/6-31+G*[a,11]	−389.4	−380.6
CEPA[b,9]	−400.2	−384.4
SCF/6-31+G**	−406.2	−385.9
SCF/6-31+G** + ZPE	−391.6	−378.4
MP2/aug-cc-pvdz	−391.5	−379.3
MP2/aug-cc-pvdz + ZPE	−383.5	−372.0
MP4SDQ/aug-cc-pvdz[c]	−395.5	−381.4
QCISD/aug-cc-pvdz[c]	−396.1	−381.4
QCISD(T)/aug-cc-pvdz[c]	−395.0	−379.8
MP4SDQ/aug-cc-pvtz[c]	−398.0	−385.3
QCISD/aug-cc-pvtz[c]	−398.7	−385.5
QCISD(T)/aug-cc-pvtz[c]	−396.8	−383.6
best estimate	−388.8	−376.3
exp	−390.7[c]	−375.4[d]

[a] Single-point calculations with 6-31G*-optimized geometries. [b] Double-ζ-plus polarization plus diffuse s and p basis. [c] MP2/aug-cc-pvdz-optimized geometries were used. [d] References cited in ref 11.

TABLE 4: $C_2H_2 + OH^-$ Reaction Energies (kcal/mol)

method, basis	$\Delta E'$ [a]	$\Delta E''$ [a]	$\Delta E'''$ [a]
SCF, 4-31G[10]	−17.7	−44.8	−25.1
SCF, 4-31+G[10]	−9.0	−28.9	−17.9
SCF 6-31G*[11]	−26.5	−47.2	−20.7
SCF 6-31+G*//6-31G*[11]	−17.9	−33.4	−15.5
MP2/6-31+G*//6-31G*[11]	−8.8	−27.2	−18.4
CEPA[9]	−15.8		
MP2/6-311++G**[12]			−17.4
MNDO[21]	−8.2	−17.5	−9.3
SCF/6-31+G**	−20.3	−35.8	−15.6
MP2/aug-cc-pvdz	−12.1	−30.7	−18.6
MP2/aug-cc-pvdz + ZPE	−10.3	−27.5	−17.1
MP4SDQ/aug-cc-pvdz[d]	−14.1	−31.6	−17.5
QCISD/aug-cc-pvdz[d]	−14.5	−31.9	−17.4
QCISD(T)/aug-cc-pvdz[d]	−15.2	−33.1	−17.9
MP4SDQ/aug-cc-pvtz[d]	−12.7		
QCISD/aug-cc-pvtz[d]	−13.2		
QCISD(T)/aug-cc-pvtz[d]	−13.2		
additive est	−13.4	−29.9	−16.4
counterpoise est			−15.0
exp	−6.2[b]		−16.2 ± 2.0[c]

[a] $\Delta E' = E_{total}(C_2H_2) + E_{total}(OH^-) - E_{total}(C_2H^-) - E_{total}(H_2O)$. $\Delta E'' = E_{total}(\mathbf{1}) - (E_{total}(C_2H_2) + E_{total}(OH^-))$. $\Delta E''' = E_{total}(\mathbf{1}) - (E_{total}(C_2H^-) + E_{total}(H_2O))$. [b] ΔH°_{298} from ref 7. [c] See ref 34. [d] Geometry optimized with MP2/aug-cc-pvdz was used in these calculations.

formation are summarized in Table 4 together with data available from the literature. The energies of reaction 3, $\Delta E'$, calculated with various methods ranged from −26 to −8 kcal/mol. All $\Delta E''$ results predict exothermic formation of complex **1** from acetylene and hydroxide. At the MP2/aug-cc-pvdz level, the energy of ethynide−water complex formation from its fragments, $\Delta E'''$, is −18.6 kcal/mol. ZPE corrections lead to a rather small decrease of the interaction energy, 1.5 kcal/mol. Further correlation corrections differ little from each other and do not exceed 1.2 kcal/mol.

Gas-phase measurements of solvation enthalpies, performed with pulsed, high-pressure mass spectrometry, obtain −16.2 kcal/mol for the ethynide−water complex.[34] A preliminary approximation, called *additive estimate* in Table 4, was obtained from the MP2/aug-cc-pvdz total energies with ZPE corrections and estimates of higher order correlation effects from QCISD(T) results. A final estimate includes counterpoise corrections.[35] The latter require additional MP2/aug-cc-pvdz total energies for CCH^- and H_2O with and without ghost basis functions at their geometries in the ethynide−water complex. The counterpoise corrections reduce the complex formation energy by 1.4 kcal/mol. Application of correlation (0.7 kcal/mol) and counterpoise (1.4 kcal/mol) corrections to the MP2 + ZPE result (−17.1 kcal/mol) yields an estimate of −15.0 kcal/mol for the energy of complex formation, $\Delta E'''$, that is in excellent agreement with experimental estimates.[34]

Optimization of the ethynide−water complex's structure required some special measures. Initially, this complex was subject to complete optimization in redundant internal coordinates,[29] as were all other species in this study. Convergence problems were severe, and even the "tight" mode of optimization with analytically calculated second derivatives at every step did not lead to an optimized structure. In order to estimate the potential energy surface features in the vicinity of the minimum, we performed SCF calculations (first with 6-31+G**) with some geometry restrictions:

1. The bond angles in the HCC···H fragment were fixed so as to keep this fragment linear while all interatomic distances and HOH and CHO angles were optimized as well.
2. The position of H_2O around C_2H^- was changed and fixed at CCH angles of 150° and 120°. An optimization of other parameters (except for the HCC angle, which was kept at 180°) was performed. Each optimization routine was followed by a vibrational frequency calculation.

The results shown in the supporting information show that the potential energy surface in the vicinity of the minimum is rather flat: a change of 60° in the CCH angle produced only a 2.26 kcal/mol increase in the HF/6-31+G** relative energy. There were almost no changes either in structural parameters or in the total energy of the system when the CCH bond angle changed from 180° to 150°. Even the frequencies do not seem to be sensitive to this change, for they all remain positive at the CCH value of 150°. The same conclusions are obtained for the MP2/aug-cc-pvdz optimization. Poor convergence in the optimization of the complex is caused by the shallowness of the potential energy surface. It should be mentioned, however, that the total energy and structural parameters obtained for the fixed linear arrangement of HCC···H are virtually the same as those reached via complete optimization, though the frequencies differ slightly. In this case, convergence was finally reached while adopting a slightly asymmetrical initial arrangement.

Earlier calculations[10] on $C_2H_2 + OH^-$ with 4-31G and 4-31+G basis sets gave significantly different reaction profiles. The smaller basis gave only one minimum, that of an ethynide−water complex, and a flat region for HO^-···HCCH. A second minimum (acetylene−hydroxide complex) was obtained with the 4−31+G basis. The barrier between the two minima was rather small (1.7 kcal/mol) and could result from the imposition of linearity in the optimization. The same qualitative picture was obtained in the MNDO calculations,[21] where the barrier between the two hydrogen-bonded structures was 1.9 kcal/mol. Preliminary searches carried out at the HF/6-31+G** level did encounter an acetylene−hydroxide minimum. A transition state for proton transfer was only 0.015 kcal/mol above this minimum. No minimum with an acetylene−hydroxide structure was found at the MP2/aug-cc-pvdz level. It is likely that formation of the ethynide−water complex from acetylene and hydroxide has either no barrier or a very small one.

Optimized structural parameters for complex **1** are compiled in the supporting information together with data obtained from the literature. The obvious differences between our MP2/aug-cc-pvdz results and those obtained at the SCF level in various basis sets are systematic elongation of the CC, CH, and OH bonds and sharp contraction in the C···H hydrogen bond. The latter effect is accompanied by a small increase in the energy of complex formation, 3.0 kcal/mol (see Table 4).

All calculations indicate that the formation of the ethynide−water complex as a result of interaction between acetylene and hydroxide is highly exothermic. The exothermicity of this reaction may lead to a number of fast processes in superbasic media discussed in the Introduction, unless water is added to the reaction mixtures. (This is always the case, according to refs 4−6 and references therein.) The release of energy may also enable further rearrangements of the reaction intermediates.

Ethenyloxy and Vinyloxy Anions. Isomers **4**−**7** of the ethenyloxy anion and two isomers of the vinyloxy anion, **8** and **9**, are local minima of $C_2H_3O^-$ at the MP2/aug-cc-pvdz level.

Ethenyloxy anions **4**−**7** can be considered to be possible reaction intermediates resulting from direct nucleophilic addition of hydroxide to acetylene. Two pairs of rotamers, **4**−**5** and **6**−**7**, have been considered. Both **5** and **7** are transition states for internal rotation about the CO bond at the SCF/6−31+G** level. Optimized structural parameters for ethenyloxy anions obtained with the MP2/aug-cc-pvdz and SCF/6-31+G** total energies are compiled in the supporting information.

Vinyloxy anions **8** and **9** are rotamers of almost identical stability (Table 1). The major difference between the two is the CO bond length, which is larger for rotamer **8**. (See supporting information.) It is likely that neither of these isomers can be obtained via direct nucleophilic addition of OH^- to acetylene, unless one considers the rather improbable formation of vinylidene from acetylene as the initial step. The best estimated energy difference shown in Table 2 between **8** and **4** is 0.4 kcal/mol.

The most unexpected result arising from the present SCF and MP2 calculations on various isomers of $C_2H_3O^-$ is that all possible ethenyl and vinyloxy anions are higher in energy than the ethynide−water complex **1**. The closest isomer, anion **4**, is 10.7 kcal/mol (see Table 2) higher than the ethynide−water complex. This result contradicts earlier MNDO data[21] where the least stable ethenyloxy anion was 26.4 kcal/mol lower in energy than the ethynide−water complex. It also predicts that no D scrambling via **4** takes place when D_2O is combined with C_2H^-, in agreement with the conclusions of a flowing afterglow study.[36]

As was noted above, we do not expect the barrier to formation of the ethynide−water complex to be higher than 2−3 kcal/mol. Our efforts to locate a transition state for reaction 1 at the SCF/6-31+G** level proved to be fruitless: all optimization procedures led to the ethynide−water complex instead. This could be an indication of the absence of any route consistent with reaction 1 in the gas phase. Thus, both thermodynamic and kinetic factors indicate that the ethynide−water complex is the most likely initial product of reaction between acetylene and hydroxide and the formation of different oligomers observed in “superbasic media” cannot be explained on the basis of direct nucleophilic addition.

Conclusions

A variety of low-energy isomers of $C_2H_3O^-$ were studied within the SCF/6-31+G** and MP2/aug-cc-pvdz approximations. Nine structures corresponding to local minima in the potential energy surface were found to be stable with respect to decomposition into acetylene plus hydroxide. Both methods gave the following order of relative stabilities for the isomers: acetaldehyde enolate anion > acetyl anion ≈ ethynide−water complex > ethynyloxy anions ≈ vinyloxy anions. This result agrees well with gas-phase flowing afterglow data on the reaction between acetylene and hydroxide where ethynide has been observed as the only product.[7] The results obtained provide the basis for a different view of nucleophilic addition to acetylene: both thermodynamic and kinetic factors seem to favor the formation of an ethynide−water complex rather than ethynyloxy anions.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-9321434, the Petroleum Research Fund, administered by the American Chemical Society, Gaussian, Inc., and the Maui High Performance Computing Center. We thank Dr. F. Dubnikova of the Hebrew University, Jerusalem, for providing her MNDO results.

Supporting Information Available: Results of geometry optimizations on **1**−**9** (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Trofimov, B. A.; Shainyan, B. A. In *Chemistry of Sulphur-Containing Groups*; Patai, S., Rappoport, Z., *Eds.*; J. Wiley and Sons, Inc.: New York, 1993. Trofimov, B. A. *Chem. Heterocycl. Comp.* **1992**, *48*, 131. Trofimov, B. A. *Russ. Chem. Rev.* **1981**, *50*, 138.

(2) Trofimov, B. A. *Z. Chem.* **1986** *26*, 41.

(3) Trofimov, B. A.; Gusarova, N. K.; Malysheva, S. F.; den Besten, R.; Brandsma, L. *Synthesis* **1995**, *4*, 387. Semenzin, D.; Etemad-Moghamad, G.; Albouy, D.; Koenig, M. *Tetrahedron Lett.* **1994**, *35*, 3297.

(4) Trofimov, B. A.; Amosova, S. V. *Russ. J. Org. Chem.* **1972**, *8*, 2664.

(5) Trofimov, B. A.; Amosova, S. V.; Alpert, M. L.; Tarasova, O. A. *Russ. J. Org. Chem.* **1977**, *13*, 2081.

(6) Trofimov, B. A. *Heteroatomic derivatives of acetylene*, Nauka: Moscow, 1981.

(7) Bohme, D. K.; MacKay, G. I.; Schiff, H. I.; Hemsworth, R. S. *J. Chem. Phys.* **1974**, *61*, 2175.

(8) Čarsky, P.; Zahradnik, R.; Kozák, I. *Chem. Phys. Lett.* **1976**, *41*, 165.

(9) Lischka, H.; Čarsky, P.; Zahradnik, R. *Chem. Phys.* **1977**, *25*, 19.

(10) Cao, H. Z.; Allavena, M.; Tapia, O.; Evleth, E. M. *J. Phys. Chem.* **1985**, *89*, 1581.

(11) Gao, J.; Garner, D. S.; Jorgensen, W. N. *J. Am. Chem. Soc.* **1986**, *108*, 4784.

(12) Pudzianowski, A. T. *J. Chem. Phys.* **1995**, *102*, 8029.

(13) Dykstra, C. E.; Arduengo, A. J.; Fukunaga, T. *J. Am. Chem. Soc.* **1978**, *100*, 6007.

(14) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.

(15) O'Neal, D.; Simons, J. *J. Phys. Chem.* **1989**, *93*, 58.

(16) Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61.

(17) Lambert, C.; Wu, Y.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1993**, 255.

(18) Nimlos, M. R.; Soderquist, J. A.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 7675.

(19) Saunders, W. H. *J. Am. Chem. Soc.* **1994**, *116*, 5400.

(20) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 5405.

(21) Vitkovskaya, N. M.; Dolgunicheva, O. Yu.; Dubnikova, F. S.; Trofimov, B. A. *Bull. Acad. Sci. USSR, Chem. Engl.* **1988**, 1173. Vitkovskaya, N. M.; Dolgunicheva, O. Yu.; Dubnikova, F. S.; Trofimov, B. A. *Ibid*. **1988**, 1177.

(22) Dolgunicheva, O. Yu.; Vitkovskaya, N. M.; Dubnikova, F. S.; Trofimov, B. A. *Bull. Acad. Sci. USSR, Chem. Engl.* **1989**, 1645.

(23) Dubnikova, F. S. Ph.D. Thesis, Irkutsk, 1989.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(25) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294.

(26) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796. Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(27) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503. Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275. Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281.

(28) Head-Gordon, M.; Head-Gordon, T. *Chem. Phys. Lett.* **1994**, *220*, 122.

(29) Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49.

(30) Bartlett, R. J. *Ann. Rev. Phys. Chem.* **1981**, *32*, 359 and references therein.

(31) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(32) Ragavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(33) Total energies and ZPE-corrected energies (in parentheses) in au: C_2H_2, −77.093 00 (−77.067 66); C_2H^-, −76.488 46 (−76.474 77); H_2O, −76.260 91 (−76.239 58); OH^-, −75.637 02 (−75.628 44).

(34) Meot--Ner, M. *J. Am. Chem. Soc.* **1988**, *110*, 3858.

(35) Emsley, J.; Hoyte, O. P. A.; Overill, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 3303 and references therein.

(36) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565.