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A Quantum Chemical Study of the Generation of a Potential Prebiotic Compound, Cyanoacetaldehyde, and Related Sulfur Containing Species

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Cyanoacetaldehyde ($N{\equiv}CCH_2CHO$), which may have played a role in the prebiotic formation of the pyrimidine bases cytosine and uracil, is formed in water solutions by addition of water to cyanoacetylene ($H{-}C{\equiv}C{-}C{\equiv}N$), a compound that exists in interstellar space, in comets, and planetary atmospheres. A gas-phase model of the uncatalyzed addition of water to cyanoacetylene is explored by ab initio calculations at the MP2/6-311++G** level of theory. A reaction path consisting of several steps was found in these calculations, but the activation energy of the first step is relatively high, which makes it unlikely that cyanoacetaldehyde is formed in an uncatalyzed reaction. Similar calculations were also performed for the uncatalyzed reaction of water to protonated cyanoacetylene ($H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$), a component of the interstellar medium, forming protonated cyanoacetaldehyde ($H{-}N{\equiv}CCH_2CHO^+$), but a high activation energy was found for this reaction as well. Moreover, the corresponding addition reactions of hydrogen sulfide (H_2S) to $H{-}C{\equiv}C{-}C{\equiv}N$, as well as to $H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$, have been explored with similar results.

Introduction

The fundamental question whether a prebiotic synthesis of the pyrimidines cytosine and uracil exists has interested researchers for a long time. The fact that pyrimidines have been found in the carbonaceous meteorites[1] suggests that an efficient prebiotic synthesis of these compounds indeed takes place, but it is by no means clear how they were formed. One possibility is that cyanoacetylene ($H{-}C{\equiv}C{-}C{\equiv}N$) and its hydrolysis product, cyanoacetaldehyde ($N{\equiv}CCH_2CHO$), are involved in the prebiotic synthesis of pyrimidines. Interestingly, cyanoacetylene is formed in a spark discharge reaction in a methane−nitrogen mixture[2] and is also found in the interstellar medium,[3] in comets,[4] and in Titan's atmosphere.[5]

In 1968, Ferris et al.[6] reported that cytosine is formed in 4.8% yield from an aqueous solution of 1 M cyanoacetylene and 1 M urea, a well-established prebiotic compound.[7,8] The reaction between cyanoacetylene and cyanate, a plausible prebiotic molecule,[6] also yields cytosine. Six years later, Ferris and coworkers[9] found that cyanoacetaldehyde condenses with guanidine, a likely prebiotic compound,[8,9] in dilute aqueous solutions to form 2,4-diaminopyrimidine, which in turn is hydrolyzed to cytosine and uracil. Robertson and Miller[10] showed that in concentrated solutions of urea, which may have been formed in drying lagoons, cyanoacetaldehyde reacts to form cytosine in 30−50% yield. They also pointed out that the cyanoacetylene reaction of Ferris et al.[6] might have gone through cyanoacetaldehyde.[11] Shapiro[12,13] has, however, vigorously challenged Robertson and Miller's[10] suggestion.

More recent studies have revealed that cyanoacetaldehyde reacts with guanidine hydrochloride to give high yields of 2,4-diaminopyrimidine under concentrated conditions of a drying

SCHEME 1: Suggested Reactions for the Synthesis of Pyrimidines from Cyanoacetaldehyde and Urea or Guanidine

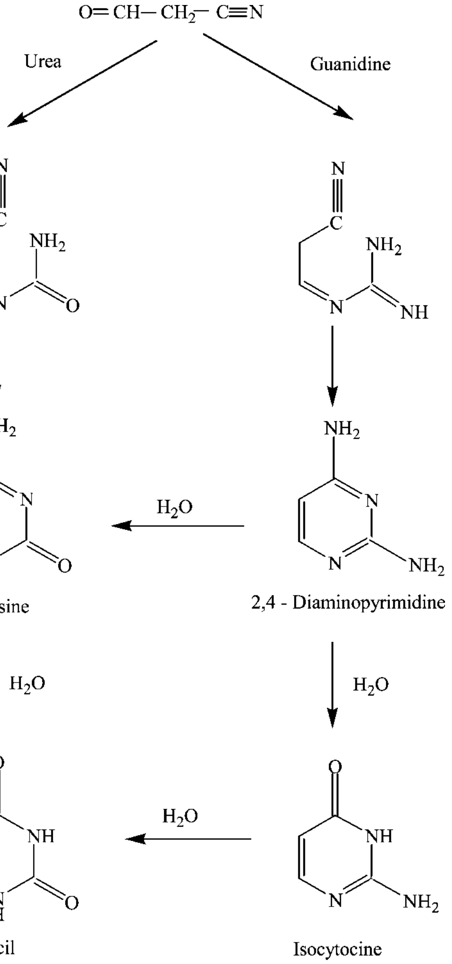

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TABLE 1: Total Energies[a] (in Hartrees) and Relative Energies (in kJ/mol, Parentheses) for the Stationary Forms and Their Interconversion

Addition of Water to H—C≡C—C≡N

H_2O + HCCCN	complex	TS1	*trans*-HOCH═CHCN	TS2	*cis*-HOCH═CHCN	TS3	$CH_2(CN)CHO$
−245.375877	−245.382227	−245.293770	−245.412943	−245.318872	−245.416447	−245.326314	−245.422596
(0)	(−16.7)	(215.6)	(−97.3)	(149.7)	(−106.5)	(130.1)	(−122.7)

Addition of Water to H—C≡C—C≡N—H^+

H_2O + $HCCCNH^+$	complex	TS4	*trans*-HOCH═$CHCNH^+$	TS5	*cis*-HOCH═$CHCN^+$	TS6	$HNCCH_2CHO^+$
−245.656988	−245.676816	−245.613725	−245.716195	−245.659498	−245.710301	−245.633665	−245.710624
(0)	(−52.1)	(113.6)	(−155.4)	(−6.6)	(−140.0)	(61.3)	(−140.8)

Addition of Hydrogen Sulfide to H—C≡C—C≡N

H_2S + HCCCN	complex	TS7	*trans*-HSCH═CHCN	TS8	*cis*-HSCH═CHCN	
	−567.954678	−567.958297	−567.877479	−568.002442	−567.890426	−568.005702
	(0)	(−9.5)	(202.7)	(−125.4)	(168.7)	(−134.0)

Addition of Hydrogen Sulfide to H—C≡C—C≡N—H^+

H_2S + $HCCCNH^+$	complex	TS9	*trans*-HSCH═$CHCNH^+$	TS10	*cis*-HSCH═$CHCNH^+$
−568.235789	−568.24611	−568.209355	−568.307354	−568.250577	−568.302817
(0)	(−27.1)	(69.4)	(−187.9)	(38.8)	(−176.0)

[a] Zero-point vibrational energies included.

lagoon model of prebiotic synthesis,[14] and with thiourea to produce 2-thiocytosine, which hydrolyzes to thiouracil, cytosine, and then uracil. Another study of cyanoacetaldehyde and urea under dry-down conditions at 100 °C and in solution at 4 and −20 °C, showed that cytosine is produced more effectively at low temperatures than calculated using the Arrhenius extrapolation from higher temperatures.[15] Recently,[16] it was shown that even dilute solutions of cyanoacetaldehyde and urea or guanidine under eutectic freezing conditions allows the formation of cytosine and uracil. Cold environments may therefore have allowed the synthesis of all of the RNA bases even from low organic yielding atmospheres, such as those on early Earth, Mars, Titan, and Europa.[16] The reactions suggested for the synthesis of the pyrimidines from cyanoacetaldehyde and urea or guanidine are summarized in Scheme 1.

The formation of cyanoacetaldehyde by the addition of water to cyanoacetylene is a crucial step in the suggested syntheses[9−11,14−16] of the pyrimidines, and this motivated the current study by quantum chemical methods of the mechanism of this addition reaction. The present calculations mimic uncatalyzed gas-phase reactions such as those that take place in the interstellar medium where the temperature is a few K, and the extremely low pressure indicates that reactions in this medium are generally not in thermodynamic equilibrium. The results should also be of some relevance for reactions in planetary atmospheres and in water solutions. The calculated energies are presumably accurate to within ±20 kJ/mol.

It is well-known that reactions between neutral molecules and cations often have lower activation energies than reactions between neutrals. Protonated cyanoacetylene, H—C≡C—C≡N—H^+, exists in interstellar space.[17] Calculations for the addition reaction of water to H—C≡C—C≡N—H^+ with the formation of protonated cyanoacetaldehyde H—N≡C—CH_2CHO^+ have therefore been performed. Cyanoacetaldehyde may then be produced by an electron recombination reaction between protonated cyanoacetaldehyde and an electron (H—N≡CCH_2CHO^+ + e^- → H + N≡CCH_2CHO + $h\nu$).

The analogous reactions between H_2S, a well-known interstellar molecule,[18] and a constituent of planetary atmospheres, with both cyanoacetylene and protonated cyanoacetylene, H—C≡C—C≡N—H^+, have also been explored by quantum chemical methods in the current study. A quantum chemical study of the similar addition of ammonia to cyanoacetylene and to protonated cyanoacetylene, respectively, has recently been reported.[19]

Computational Methods

All calculations were performed using the Gaussian03 program package[20] running on the Titan cluster of the University of Oslo. The geometries of all the reactants, products, intermediates, and transition states were optimized using the Møller−Plesset second order perturbation theory[21] in conjunction with the 6-311++G** basis set, which is of triple-ζ quality and includes both diffuse and polarized functions. Frequency calculations were performed at the same level to check whether the obtained species is a minimum (with all real frequencies) or a transition state (with one and only one imaginary frequency). The species were not conformationally optimized because conformational energy differences are normally relatively small (a few kJ/mol). Intrinsic reaction coordinate (IRC)[22,23] calculations were performed to confirm that the transition state connects the designated intermediates. The results are collected in Table 1, in which the electronic energies corrected for zero-point vibrational contributions are listed.

Under the temperature and pressure conditions prevailing in interstellar space, the energy differences (ΔE) calculated from the entries of Table 1 will practically be the same as the corresponding enthalpy differences (ΔH) and the Gibbs energy differences (ΔG). ΔE values relative to the reactants, which have been assigned a value of zero, are also given in Table 1 in parenthesis.

H_2O and H—C≡C—C≡N. The structures of the reactants, intermediates, transition states, and products of the reaction between water and cyanoacetylene are shown in Figure 1, and

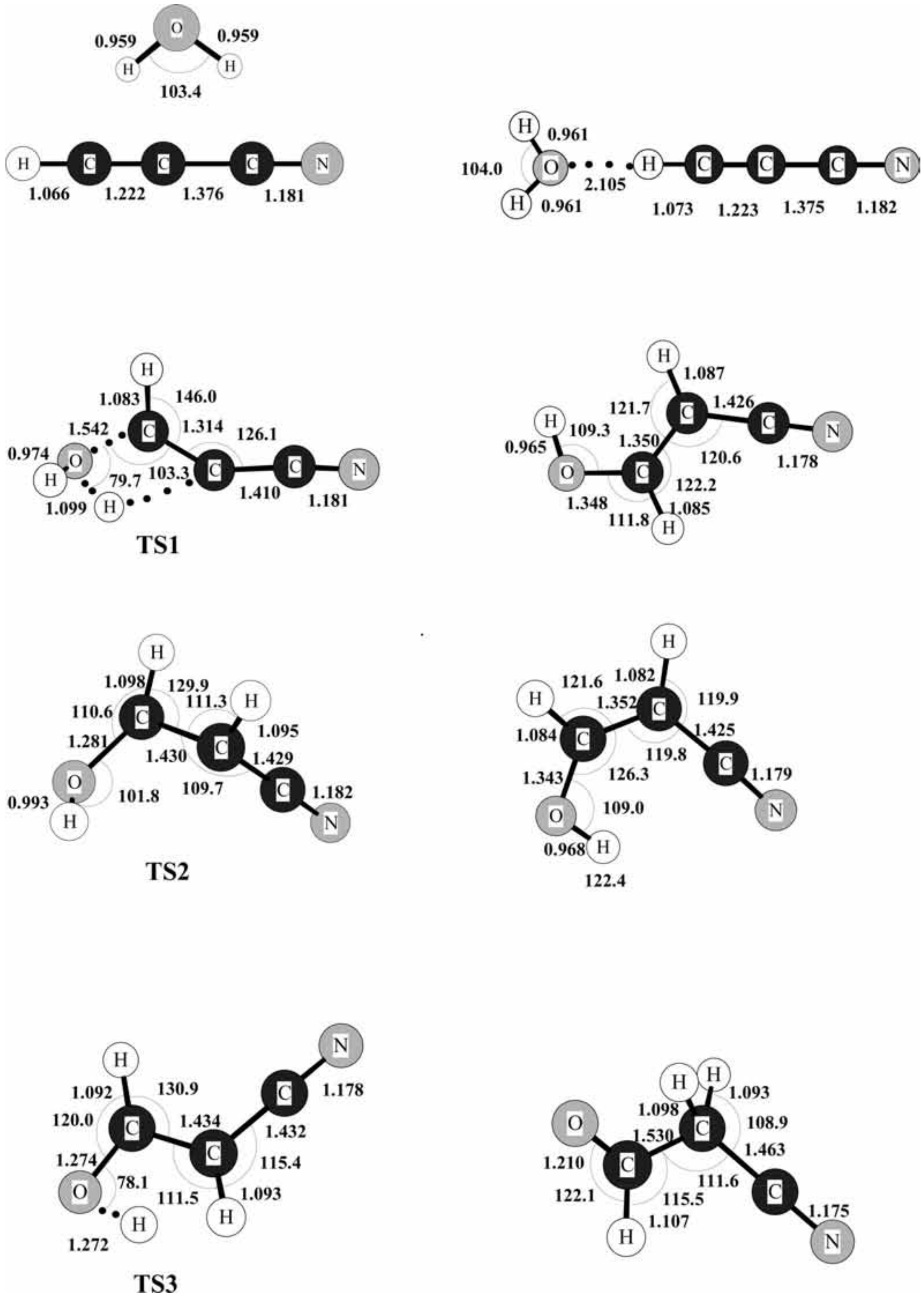

Figure 1. Optimized structures (distances in angstroms and angles in degrees) of the reactants, intermediates, and products of the addition of water to H—C≡C—C≡N. The dots shown on two of these figures indicate interactions or unusual bond lengths.

the potential-energy surface (PES) of this reaction is sketched in Figure 2. Miniature molecular model figures of the stationary states without atom labeling are shown in Figure 2 to facilitate their identification.

The combined energies of water and cyanoacetylene have been assigned a value of zero in Figure 2. A hydrogen-bonded complex with 16.7 kJ/mol lower energy than the reactants is assumed to occur as the first step in this reaction. The microwave spectrum of this complex is known.[24] The transition state (TS1; Figure 1) for the addition of water, which is the next step, is located 215.6 kJ/mol above the energies of the reactants. The following intermediate has a trans arrangement for the HOCH═CHCN link of atoms and is 97.3 kJ/mol lower in energy than the reactants. This trans form has to pass over a new transitions state (TS2) with a relative energy of 149.7 kJ/mol to reach the cis HOCH═CHCN form, which is more stable by 106.5 kJ/mol than the starting species. This cis form is in a tautomeric equilibrium with cyanoacetaldehyde, which is the global minimum (−122.7 kJ/mol relative to the energies of H_2O and HC≡C—C≡N). The transition state (TS3) for the tautomeric transformation has an energy that is 130.1 kJ/mol higher that the sum of the energies of the starting species.

The PES of this reaction (Figure 2) warrants comments. The critical step in the formation of cyanoacetaldehyde from water and

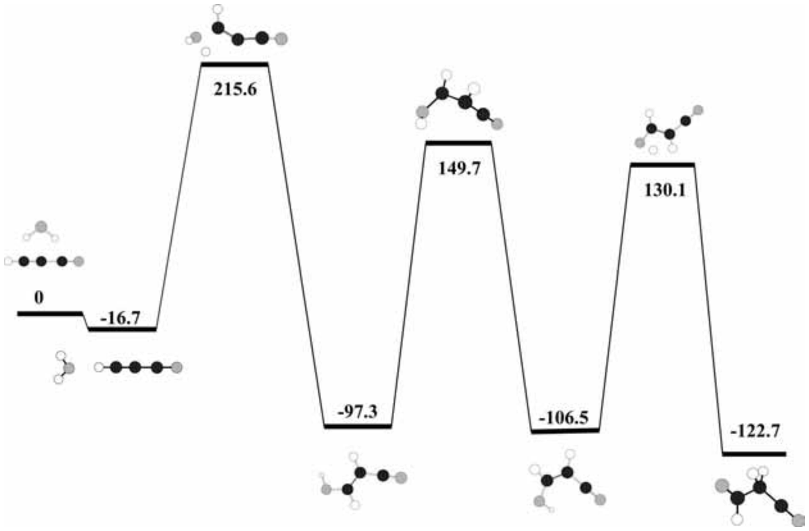

Figure 2. The PES for the addition of H_2O to $H{-}C{\equiv}C{-}C{\equiv}N$ and the formation of $CH_2(CN)CHO$. Energies are electronic energies corrected for zero-point vibrational energies and are in kJ/mol.

cyanoacetylene is the high activation energy of 215.6 kJ/mol relative to the combined energy of the reactants. The energy of TS1 represents the maximum in the PES. A complex with sufficiently high energy to pass this energy barrier would therefore have sufficient energy to ultimately form cyanoacetaldehyde.

The fact that the cis form of $HOCH{=}CHCN$ is about 9.2 kJ/mol $[(-106.5 - (-97.3))$ kJ/mol; Figure 2] more stable than the trans form, seems plausible because intramolecular interaction, presumably intramolecular hydrogen bonding, may occur between the hydroxyl and cyano group in the cis form, which is similar to the findings for the amino analogue, 3-amino-2-propenenitrile ($H_2NCH{=}CHCN$), where B3LYP/6-311+G(3df,2p) and G2 calculations yielded an energy difference of 8.0 kJ/mol for the trans−cis energy difference,[25] and the infrared spectrum indicated that the equilibrium mixture of cis/trans ≈ 20.[25] A barrier height of $[149.7 - (-97.3)]$ kJ/mol $= 247.0$ kJ/mol for the cis to trans transformation seems reasonable. Likewise, the prediction that the aldehyde form ($CH_2(CN)CHO$) is more stable than the cis enol form (*cis*-$HOCH{=}CHCN$) is in accord with recent G3B3 calculations.[26] The enol-aldehyde barrier of 252.8 kJ/mol seems reasonable and is in good agreement with ab initio calculations of Su et al.[27]

The high initial barrier of 215.6 kJ/mol indicates that this reaction is unlikely to occur in the gas phase at low temperatures. This is in accord with the fact that no cyanoacetaldehyde is formed when water vapor and gaseous cyanoacetylene are mixed at room temperature.[28] However, cyanoacetaldehyde is formed in water solutions,[6,9,28] and this formation occurs especially readily in basic solutions,[6,9,28] indicating that this is actually a catalyzed reaction, where the hydroxyl ion (OH^-) may play a role. Cyanoacetylene trapped in water ice and subject to UV irradiation with wavelengths larger than 120 nm shows great photoreactivity with the formation of several products, but cyanoacetaldehyde appears not to be formed in this manner.[29]

Interestingly, the barrier height of the addition of ammonia to cyanoacetylene to form a mixture of *cis*- and *trans*-$H_2NCH{=}CHCN$ is significantly lower than the addition of water, being 128.9 kJ/mol according to G3 calculations.[19] The addition of gaseous ammonia to gaseous cyanoacetylene proceeds readily at room temperature[28] in spite of a high barrier of about 128.9 kJ/mol. Guillemin et al.[28] expressed reservation about whether they were seeing a true gas-phase reaction or something occurring on the walls of their cell. A barrier height of 128.9 kJ/mol would seem to preclude the two-body gas reaction at room temperature.

H_2O and $H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$. The structures of the species of relevance to this reaction are depicted in Figure 3, and the corresponding PES is shown in Figure 4. This reaction follows essentially the same steps as the previous reaction, but the energy barriers are generally lower. Interestingly, *trans*-$HOCH{=}CHCN$-H^+ is calculated to be the global minimum, about 15 kJ/mol more stable than the analogous cis isomer as well as the aldehyde tautomer ($HNCCH_2CHO^+$). Cyanoacetaldehyde and atomic hydrogen are then thought to be formed by an electron recombination reaction with $HNCCH_2CHO^+$, where the excess energy has either to be radiated or go into the kinetic energy of translation of the products, because the pressure in interstellar space is extremely low.

The fact that the crucial step, the formation of the transition state TS4, has an energy as high as 113.6 kJ/mol relative to the energy of the reactants indicates that it is unlikely that cyanoacetaldehyde would be formed in the gas phase at low temperatures and pressure solely by this mechanism. This is different from what was found in the model calculations of the analogous reaction between NH_3 and $H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$, which has a low initial barrier of just a few kJ/mol[19] and is therefore considered to be a possible candidate for a gas-phase addition reaction.

H_2S and $H{-}C{\equiv}C{-}C{\equiv}N$. A weak H-bonded complex (Figure 5) with a stabilization energy of 9.5 kJ/mol is first formed in this case, followed by a transition state, TS7 (Figure 6), with an energy as high as 202.7 kJ/mol relative to the energy of the reactants. The *trans*-$HSCH{=}CHCN$ compound is stabilized by 125.4 kJ/mol relative to the combined energies of H_2S and $HC{\equiv}C{-}C{\equiv}N$. A barrier of 168.7 kJ/mol has to be surmounted to reach *cis*-$HSCH{=}CHCN$, which has been prepared by flash vacuum pyrolysis at 800 °C of 3-(*tert*-butylthio)-2-propenenitrile[30] and whose microwave spectrum has been reported.[30] The MP2/6-311++G** trans−cis energy difference of 8.6 kJ/mol compares favorably with a difference of 10.4 kJ/mol found in MP2/aug-cc-pVTZ calculations[30] and the G3 value of 7.5 kJ/mol for this difference.[30]

Addition of hydrogen sulfide to cyanoacetylene is unlikely to occur in the gas phase because of the high barrier of 202.7 kJ/mol, which is rather similar to the barrier of the water addition to cyanoacetylene (215.6 kJ/mol) discussed above. However,

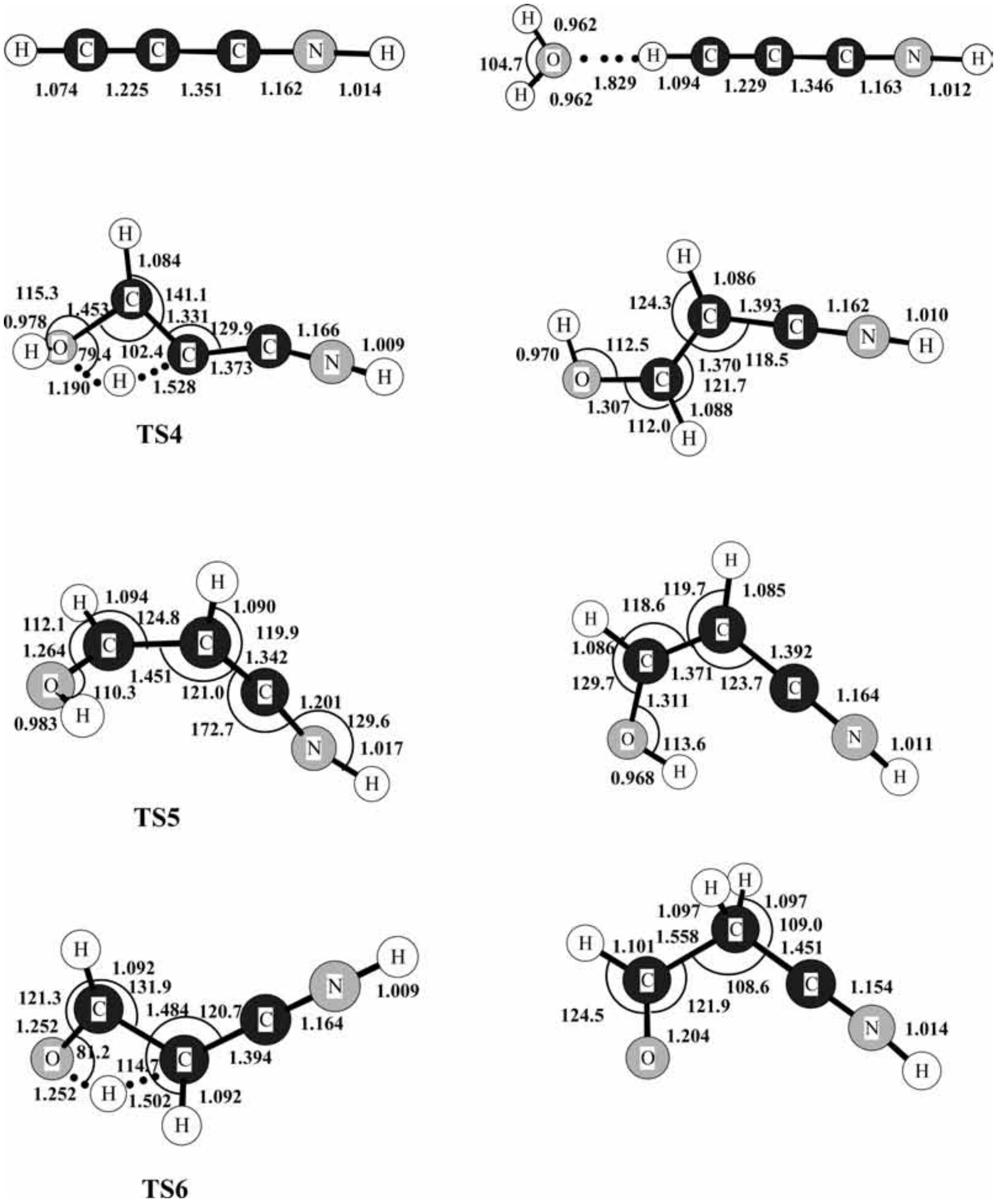

Figure 3. Optimized structures (distances in angstroms and angles in degrees) of the reactants, intermediates, and products of the addition of water to H—C≡C—C≡N—H$^+$.

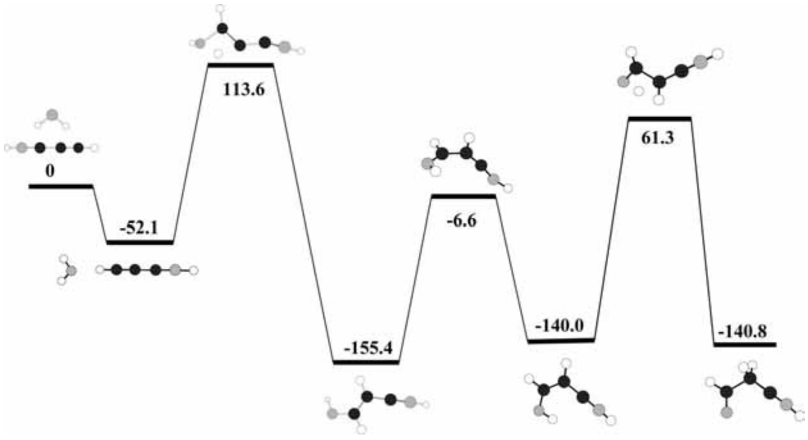

Figure 4. The PES for the addition of H_2O to H—C≡C—C≡N—H$^+$ and the formation of $HNCCH_2CHO^+$. Energies are electronic energies corrected for zero-point vibrational energies and are in kJ/mol.

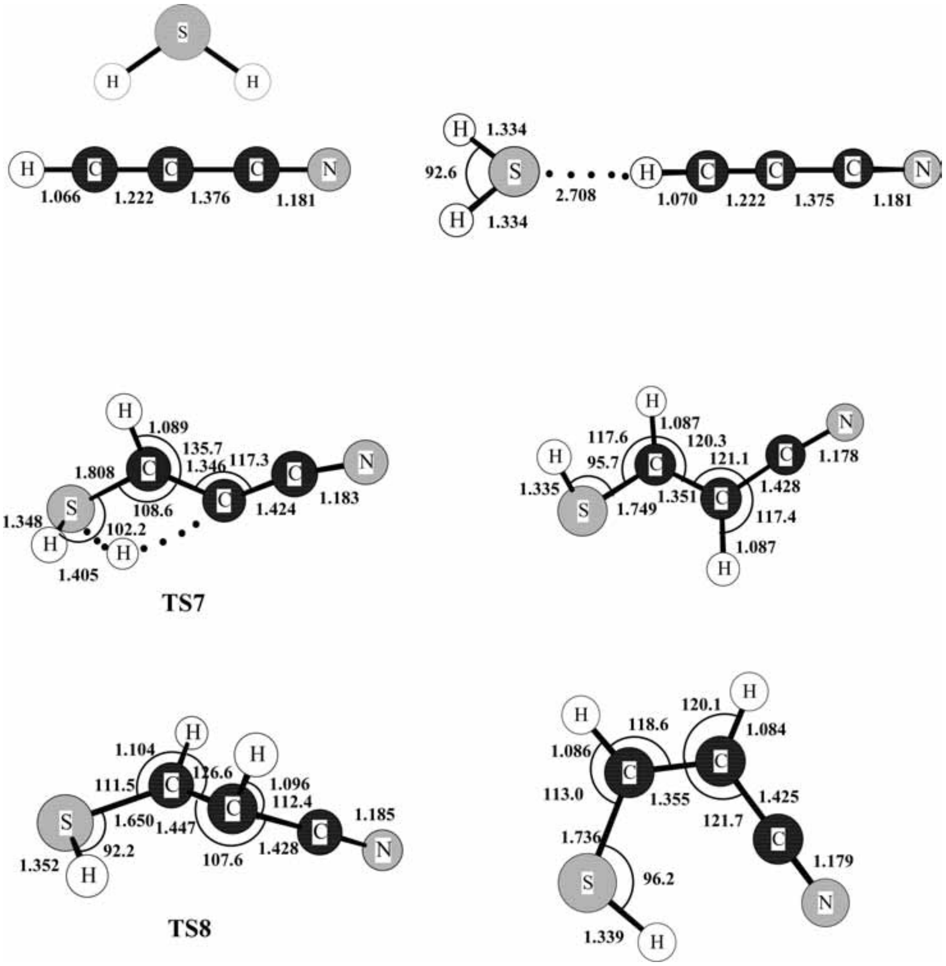

Figure 5. Optimized structures (distances in angstroms and angles in degrees) of the reactants, intermediates, and products of the addition of H_2S to H−C≡C−C≡N.

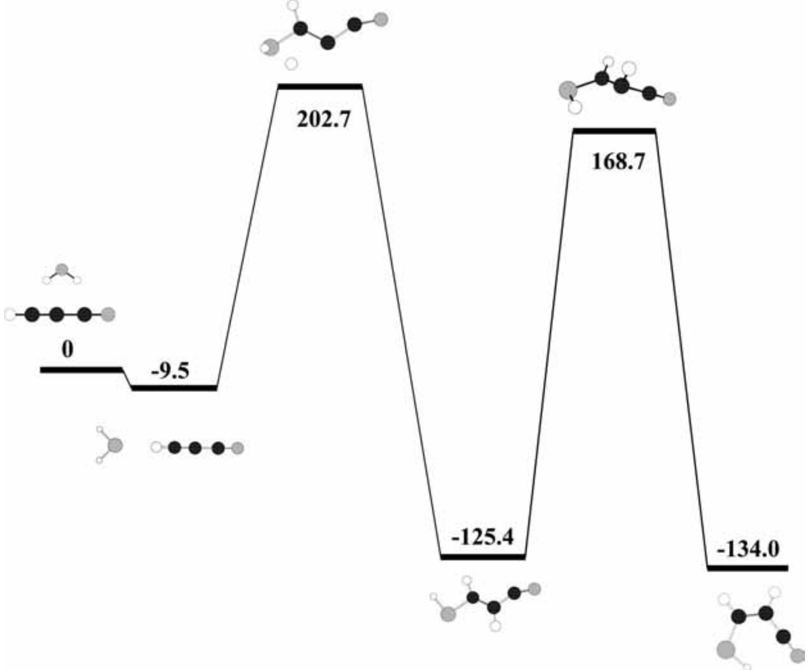

Figure 6. The PES for the addition of H_2S to H−C≡C−C≡N and the formation of *cis*-HSCH=CHCN. Energies are electronic energies corrected for zero-point vibrational energies and are in kJ/mol.

when gaseous H_2S and H−C≡C−C≡N are mixed at room temperature and subject to photolysis ($\lambda = 254$ nm), *cis*,*cis*-bis-acrylonitrile sulfide (NCCH=CHSCH=CHCN) is generated instead.[28] The same result is obtained when a catalytic amount

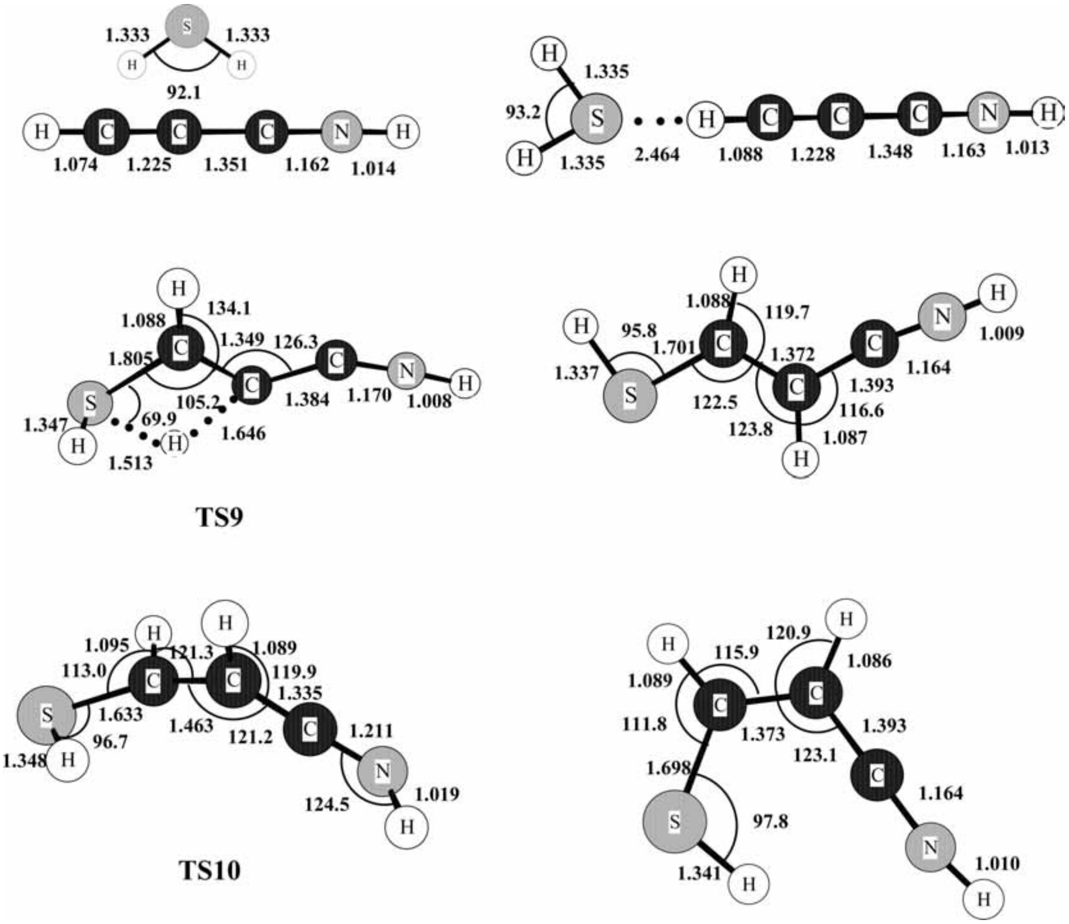

Figure 7. Optimized structures (distances in angstroms and angles in degrees) of the reactants, intermediates, and products of the addition of H_2S to $H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$.

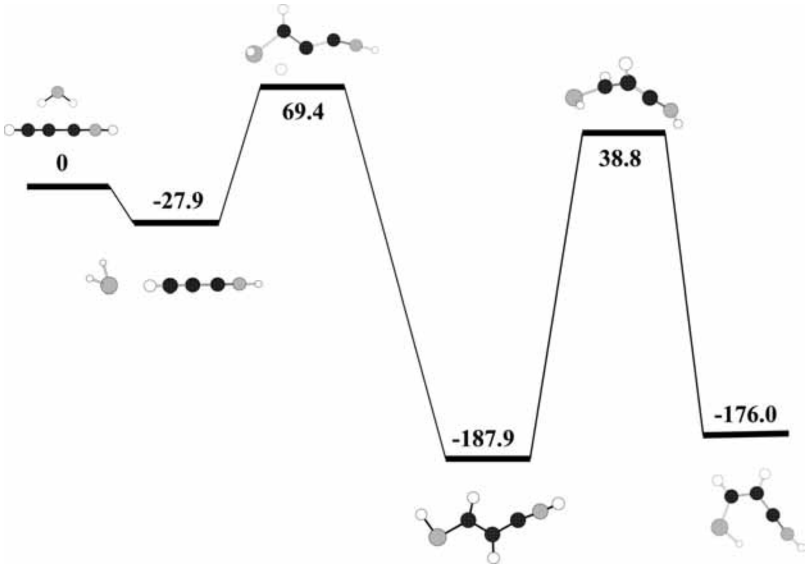

Figure 8. The PES for the addition of H_2S to $H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$. Energies are electronic energies corrected for zero-point vibrational energies and are in kJ/mol.

of a base is added to the gaseous mixture of the two compounds.[28] No *cis*-HSCH═CHCN was formed in these two cases.[28]

H_2S and $H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$. The various species of this reaction sequence are depicted in Figure 7, and its PES is shown in Figure 8. The first barrier of 69.4 kJ/mol is still so high that it is unlikely that a gas-phase reaction at low temperatures would result in protonated 3-mercapto-2-propenenitrile (HSCH═CHCN-H$^+$), which might yield HSCH═CHCN upon electron recombination.

Interestingly, the trans form of HSCH═CHCNH$^+$ is predicted to be more stable than the cis form by 11.9 kJ/mol, just the opposite of what was found for unprotonated 3-mercapto-2-propenenitrile discussed in the previous paragraph.

Conclusions

The addition reactions of gaseous H_2O, H_2S, and NH_3 to gaseous cyanoacetylene ($H{-}C{\equiv}C{-}C{\equiv}N$) are all characterized by relatively high barrier of more than 100 kJ/mol according to quantum chemical calculations. This effectively prevents the formation of the addition products in the gas phase at low temperatures and pressures.

However, the presence of a base seems to be essential to catalyze reactions between water, hydrogen sulfide, and ammonia on the one side with cyanoacetylene on the other.[28] Gaseous NH_3 is added to gaseous $H{-}C{\equiv}C{-}C{\equiv}N$,[28] possibly because ammonia acts both as a reactant and as a catalyst, and H_2O and $H{-}C{\equiv}C{-}C{\equiv}N$ forms $N{\equiv}CCH_2CHO$ in a basic solution of water. The reaction between H_2S and $H{-}C{\equiv}C{-}C{\equiv}N$ to form *cis*,*cis*-bis-acrylonitrile sulfide ($NCCH{=}CHSCH{=}CHCN$) is also catalyzed by the presence of a base.[28]

Protonated cyanoacetylene ($H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$) is known to exist in the interstellar space.[17] The addition of H_2O, H_2S, and NH_3 to this species is characterized by significantly lower activation energies than the corresponding reactions with neutral cyanoacetylene. However, the barriers preventing the addition of H_2O and H_2S are still significant, whereas the addition of NH_3 to $H{-}C{\equiv}C{-}C{\equiv}N{-}H^+$ under conditions of low temperature and pressure is considered to be possible.[19]

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