

GAS-PHASE SYNTHESIS OF PRECURSORS OF INTERSTELLAR GLYCINE: A COMPUTATIONAL STUDY OF THE REACTIONS OF ACETIC ACID WITH HYDROXYLAMINE AND ITS IONIZED AND PROTONATED DERIVATIVES

CARMEN BARRIENTOS, PILAR REDONDO, LAURA LARGO, VÍCTOR M. RAYÓN, AND ANTONIO LARGO

Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain; alargo@qf.uva.es

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ABSTRACT

A computational study of the reactions of hydroxylamine and its ionized and protonated derivatives with acetic acid is provided. The reaction of neutral hydroxylamine with acetic acid, despite being clearly exothermic, involves a very large energy barrier. The reaction of ionized hydroxylamine with acetic acid is also clearly exothermic, but again a significant energy barrier is found (around 24 kcal mol^{-1} at the CCSD(T) level). The reaction of the most stable protonated isomer of hydroxylamine, NH_3OH^+ , with acetic acid also involves a high barrier (more than 27 kcal mol^{-1} at the CCSD(T) level). Only the higher energy isomer, NH_2OH_2^+ , leads to a sensibly lower energy barrier (about $2.3 \text{ kcal mol}^{-1}$ at the CCSD(T) level). Nevertheless, an estimate of the reaction coefficient at low temperatures such as those reigning in the interstellar medium gives very low values. Therefore, it seems that precursors of interstellar glycine could not be efficiently produced from the reactions of hydroxylamine-derived ions with acetic acid.

Key words: astrobiology – astrochemistry – ISM: molecules – molecular processes

Online-only material: color figures, machine-readable table

1. INTRODUCTION

One of the most interesting debates in interstellar chemistry concerns the possibility of finding bio-molecules in astronomical sources. In particular the search for interstellar glycine, the simplest amino acid, has been a recurrent subject in recent years (Hollis et al. 1980; Snyder et al. 1983, 2005; Ceccarelli et al. 2000; Hollis et al. 2003a, 2003b; Kuan et al. 2003; Jones et al. 2007; Cunningham et al. 2007). Despite several radioastronomical searches, no conclusive identification of glycine has been possible. Nevertheless, it should be pointed out that there are several intrinsic difficulties for a possible detection of glycine in space. In first place, the rotational spectrum of glycine has relatively weak lines (Irvine 1998), due to its large molecular partition function. Therefore it is likely that detection of the target transitions would be hindered by the emission of other molecules. Second, amino acids have limited photostability since they are highly susceptible to UV photo destruction (Ehrenfreund et al. 2001). Consequently, they would survive only in shielded environments. However, the development of new instruments with higher resolution, as well as the recent detection in space of related molecules such as amino acetonitrile (Belloche et al. 2008), has prompted the search for interstellar glycine.

Within this context physico-chemical studies can be valuable to ascertain whether there are plausible and efficient synthetic routes toward interstellar glycine. Both laboratory and theoretical studies have been performed in recent years with this purpose. Basically we can distinguish two types of synthetic mechanisms: reactions on the surface of interstellar grains and gas-phase reactions.

Amino acids have been successfully produced from ultraviolet photolysis of interstellar ice analogs (Bernstein et al. 2002; Muñoz-Caro et al. 2002). In these experiments ice mixtures containing interstellar molecules such as methanol, ammonia, or hydrogen cyanide were employed. One of the most important results of these experiments is the evidence that at least part of

the amino acids observed in meteorites might have an extraterrestrial origin. From the theoretical side Woon (2001, 2002a, 2002b) has carried out computational studies of different reactions which could take place on astrophysical ices leading to precursors of glycine. For example, radical–radical reactions (Woon 2002a) involving species such as t-HOCO and CH_2NH_2 could produce glycine. More recently other experimental studies (Holtom et al. 2005; Elsila et al. 2007) of ice mixtures containing these and related species have been carried out.

Formation of glycine precursors through gas-phase chemistry has also been considered. Some of these studies are inspired by the Miller experiment (Miller 1953), where amino acids were produced from simple organic molecules. For example, Maeda & Ohno (2004a) proposed a two-step route to glycine starting from neutral closed-shell molecules (CO_2 , NH_3 , CH_2) and involving the reaction of CO_2 with CH_2NH_3 , a higher energy isomer of methylamine. Even though this pathway was shown to be barrier-free, it seems that this route should not be very efficient under interstellar conditions since CH_2NH_3 could be destroyed by water molecules. The same authors have also proposed other gas-phase reactions from neutral molecules as possible synthetic routes toward glycine (Maeda & Ohno 2004b, 2006). Other proposals (Hoyle & Wickramasinghe 1976) for glycine synthesis from neutral–neutral processes include reactions involving methanimine, HNCH_2 , also present in the interstellar medium. However, Basiuk & Bogillo (2000) and Basiuk (2001) have carried out theoretical studies of reactions leading to amino acids from methanimine and methanimine-related species, concluding that they are not feasible under interstellar conditions. It has also been suggested that glycine could be formed through neutral–neutral reactions from amino acetonitrile (Basiuk & Kobayashi 2004; Andreatza et al. 2006), a molecule observed in space.

Gas-phase ion chemistry plays a crucial role in interstellar chemistry, and the possibility of synthesizing amino acids through ion–molecule reactions has been suggested by Herbst (2001). Jackson et al. (2005a, 2005b) carried out selected-ion

flow tube (SIFT) experiments on the reactions of ammonia-related cations with neutral species such as formic and acetic acids, as well as for the reactions of different cations with neutral amine species (CH_3NH_2 and $\text{CH}_3\text{CH}_2\text{NH}_2$). Theoretical studies for some of these ion–molecule processes have also been carried out (Largo et al. 2004, 2008, 2010). It was found that some of these pathways leading to precursors of glycine have significant energy barriers, whereas others are exothermic and barrier free but are less favorable than other channels not rendering glycine precursors.

Bohme et al. (Blagojevic et al. 2003; Snow et al. 2007) carried out SIFT studies of the reactions of hydroxylamine-derived ions (NH_2OH^+ , NH_3OH^+) with acetic acid. These studies are very interesting, since the formation of precursors of glycine was reported. Whereas acetic acid has been detected in space, hydroxylamine has not yet been observed in the interstellar medium. However, hydroxylamine is a plausible interstellar molecule. Furthermore, the ultraviolet laser irradiation of ice mixtures simulating interstellar grains produced hydroxylamine (Nishi et al. 1984). More recently, formation of hydroxylamine was observed in electron-irradiated ammonia-water ices at temperatures of 10 and 50 K (Zheng & Kaiser 2010). Bohme et al. (Snow et al. 2007) also carried out an exploration of the potential surface for the reaction initiated by protonated hydroxylamine, NH_3OH^+ . Given the promising results obtained in the studies by Bohme et al. (Blagojevic et al. 2003; Snow et al. 2007), in the present work we provide a computational study of the reactions of ionized and protonated hydroxylamine with acetic acid. In addition, we will also provide a theoretical study of the neutral reaction between hydroxylamine and acetic acid. This will allow a discussion of the factors which favor this kind of process upon ionization or protonation.

2. COMPUTATIONAL METHODS

The geometries of the different species reported in this work have been obtained at the second-order Moller–Plesset level. In these optimizations the cc-pVTZ (correlation-consistent polarized valence triple-zeta) basis set developed by Dunning (1989; Kendall et al. 1992) has been employed. The different optimized structures were verified to be a stationary point or a transition state (TS) by vibrational analysis carried out at the same level (MP2/cc-pVTZ).

In order to compute more accurate relative energies CCSD(T) calculations (coupled-cluster single and double excitation model augmented with a non-iterative triple excitation correction; Raghavachari et al. 1989) have been carried out on the MP2/cc-pVTZ geometries. The aug-cc-pVTZ basis set, which also includes diffuse functions, has been employed for the energetic calculations. Zero-point vibrational energy corrections were included at the MP2/cc-pVTZ level.

All calculations reported in this work were carried out with the *Gaussian-09* program package (Frisch et al. 2009).

3. RESULTS AND DISCUSSION

In their pioneering work on the reaction of protonated hydroxylamine with acetic acid, Bohme et al. (Snow et al. 2007) provided a theoretical study of the possible mechanism for this reaction. One of the main conclusions of their work is that in order for the process to be feasible under interstellar medium, the reaction should be initiated from a high-lying isomer of protonated hydroxylamine, NH_2OH_2^+ . In their experiments, Bohme et al. (Snow et al. 2007) generated protonated hydroxylamine

Table 1
Cartesian Coordinates for the Intermediates and Transition States

Species	Element	X	Y	Z
PRC1	C	−0.36007	−0.02306	1.383578
PRC1	O	−0.72669	−0.06803	2.684125
PRC1	O	0.804921	−0.03704	1.045986
PRC1	C	−1.54586	0.044802	0.475571
PRC1	H	−2.12164	0.938129	0.707782
PRC1	H	−1.2209	0.06282	−0.55886
PRC1	N	1.425663	0.086529	−2.02241
PRC1	H	1.314171	0.001379	−1.01493
PRC1	H	1.805896	1.014846	−2.17263
PRC1	O	0.063282	0.208494	−2.49847

(This table is available in its entirety in a machine-readable form in the online journal. A portion is shown here for guidance regarding its form and content.)

from CH_5^+ as protonating agent. According to their calculations both isomers, NH_3OH^+ (the most stable one) and NH_2OH_2^+ , can be formed in the protonation process. Furthermore, we have concluded in a previous work (Largo et al. 2009) that both isomers do not react with H_2 under interstellar conditions, and therefore both species, if present in the interstellar medium, should be able to react with other species, such as acetic acid.

There is a key point in the reaction of protonated hydroxylamine with acetic acid concerning the existence of a barrier which could hinder its progress in the interstellar medium. Therefore, we have carried out a computational study of such a process. Despite extensive exploration of the corresponding potential surface, we have not found any favorable path apart from the one considered by Bohme et al. (Snow et al. 2007). We will focus our interest in both determining if this process has a barrier and estimating its reaction coefficient. In addition, we have considered the reaction of ionized hydroxylamine with acetic acid. In this case we have found a mechanism similar to that for the reaction with protonated hydroxylamine, as well as an alternative path. Finally, we have studied the process that could be termed as “parent reaction,” which is the reaction of neutral hydroxylamine with acetic acid. In order to make comparisons more easily the similar paths for the three reactions will be presented in a common figure. In what follows we discuss the three reactions of acetic acid with protonated, ionized, and neutral hydroxylamine.

3.1. Reaction of Protonated Hydroxylamine with Acetic Acid

In Figure 1, we have depicted the energy profile for the reaction of protonated hydroxylamine with acetic acid, along with the corresponding reactions of neutral and ionized hydroxylamine. The energy of the reactants is taken as a reference and the notation is similar to that employed by Bohme et al. (Snow et al. 2007). We have used the notation PRC1 and PRC2 for intermediates and TS1 and TS2 for transition states in the case of the neutral reaction (hydroxylamine with acetic acid). The corresponding species for the reaction initiated by ionized hydroxylamine are denoted adding a “+” superscript (PRC1⁺, PRC2⁺, TS1⁺, TS2⁺), whereas in the case of the reaction of protonated hydroxylamine with acetic acid the species are denoted adding “H⁺” to the notation employed in the neutral reaction (PRC1H⁺, PRC2H⁺, TS1H⁺, TS2H⁺). The schematic representation of the intermediates and TSs is given in Figure 2. The detailed structures are provided in Table 1 in the online journal.

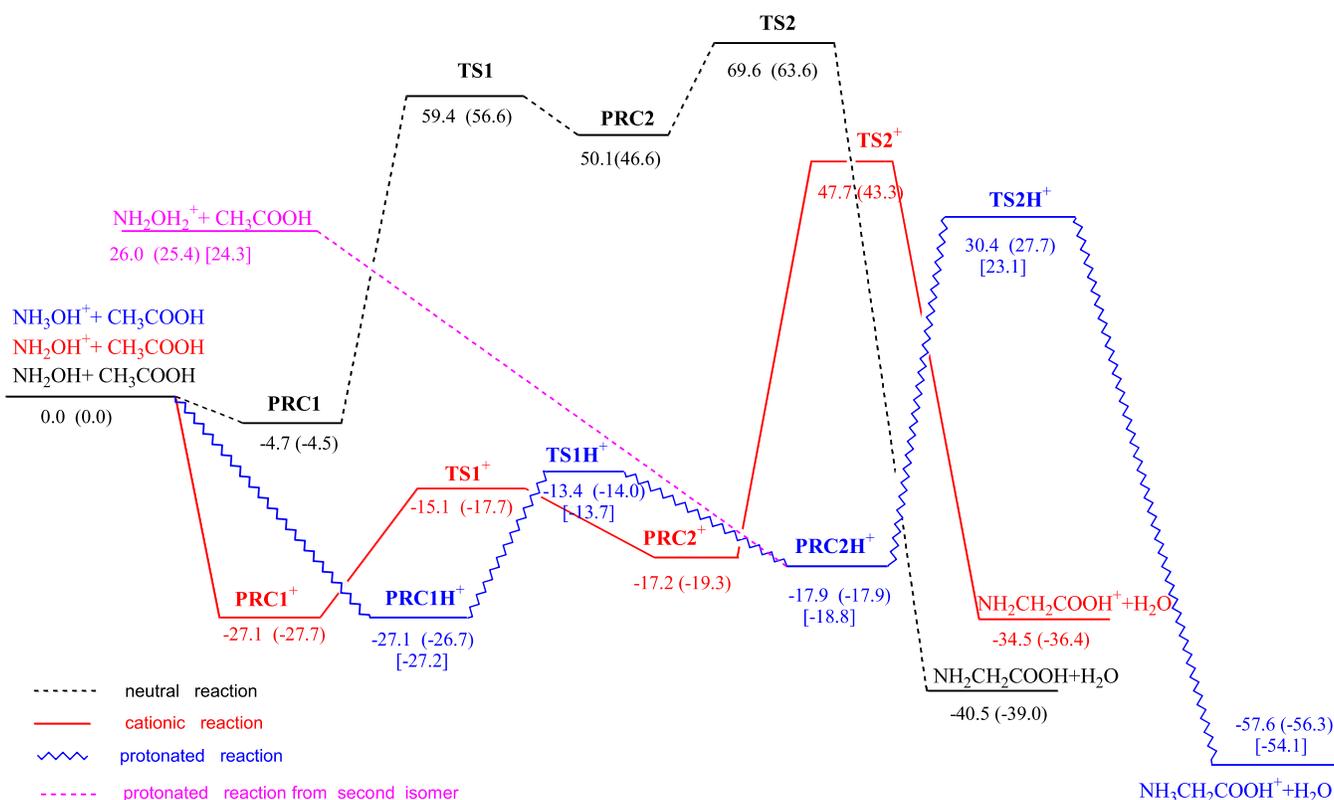


Figure 1. Energy profile, in kcal mol^{-1} , for the reactions of neutral, ionized, and protonated hydroxylamine with acetic acid obtained at the MP2/cc-pVTZ and CCSD(T)/aug-cc-pVT (in parentheses) levels including zero-point vibrational energy differences computed at the MP2/cc-pVTZ level. In the case of the reaction of protonated hydroxylamine B3LYP/6-311++G(df,pd) values are given in brackets and are taken from Snow et al. (2007).

(A color version of this figure is available in the online journal.)

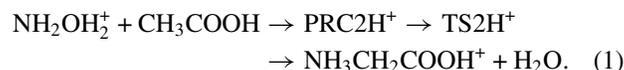
As established by Bohme et al. (Snow et al. 2007), the mechanism for the reaction of protonated glycine with acetic acid starts with the formation of a prereaction complex PRC1H⁺, which implies the interaction of the NH₃ group with the carbonyl oxygen of acetic acid. Then, the 1,2-proton shift from the nitrogen to the oxygen atom takes place through the transition state TS1H⁺ and produces a second intermediate, PRC2H⁺. Finally, the insertion of the NH₂ group into a C-H bond and N-O bond cleavage produces protonated glycine and the elimination of a water molecule.

Our MP2 profile for the reaction of protonated hydroxylamine with acetic acid is rather similar to the B3LYP profile reported by Bohme et al. (Snow et al. 2007). From this energy profile it seems clear that production of protonated glycine from the lowest-lying isomer of protonated hydroxylamine involves a large energy barrier, since TS2H⁺ lies clearly higher in energy than the NH₃OH⁺ + CH₃COOH limit (27.7 kcal mol⁻¹ at the CCSD(T) level).

Therefore, as suggested by Bohme et al. (Snow et al. 2007), only the reaction initiated from the higher energy isomer of protonated hydroxylamine could eventually lead to protonated glycine. However, there is an important discrepancy between the MP2 and B3LYP results concerning the relative energy of TS2H⁺, since the difference between the values obtained at both levels is about 7 kcal mol⁻¹. This discrepancy is qualitatively very important, since at the B3LYP level TS2H⁺ is placed below the NH₂OH₂⁺ + CH₃COOH limit, and therefore that means that there should be no net barrier for the production of protonated glycine from the higher energy isomer of protonated hydroxylamine. On the other hand, the MP2 level predicts

an effective barrier of 4.4 kcal mol⁻¹. This barrier is slightly dropped to 2.3 kcal mol⁻¹ at the CCSD(T) level. Therefore, our theoretical calculations suggest that there should be a small but non-negligible barrier associated with the process of production of protonated glycine from the reaction of NH₂OH₂⁺ with acetic acid.

In order to explore the consequences of the existence of such barrier, we have carried out a simplified computational kinetic treatment applying the statistical kinetic theories. We have just considered the following pathway:



For the kinetic calculations concerning the formation of the initial intermediate, PRC2H⁺, we adopted the microcanonical variational transition state theory in its vibrator formulation (Garrett & Truhlar 1979; Hu & Hase 1991). The potential energy path was first scanned. Subsequently, at each point of the scan, the Hessian matrices describing the modes orthogonal to the reaction path were evaluated according to the standard procedure of Miller et al. (1980), and then the sum of states was minimized to obtain the location of the loose TS. For the unimolecular process involving the pass from the intermediate to the final products through TS2H⁺, the microcanonical rate coefficients have been calculated employing the RRKM theory (Robinson & Holbrook 1973; Baer & Hase 1996). The density and sum of states were estimated through the Forst algorithm (Forst 1973) using the corresponding frequencies and moments of inertia.

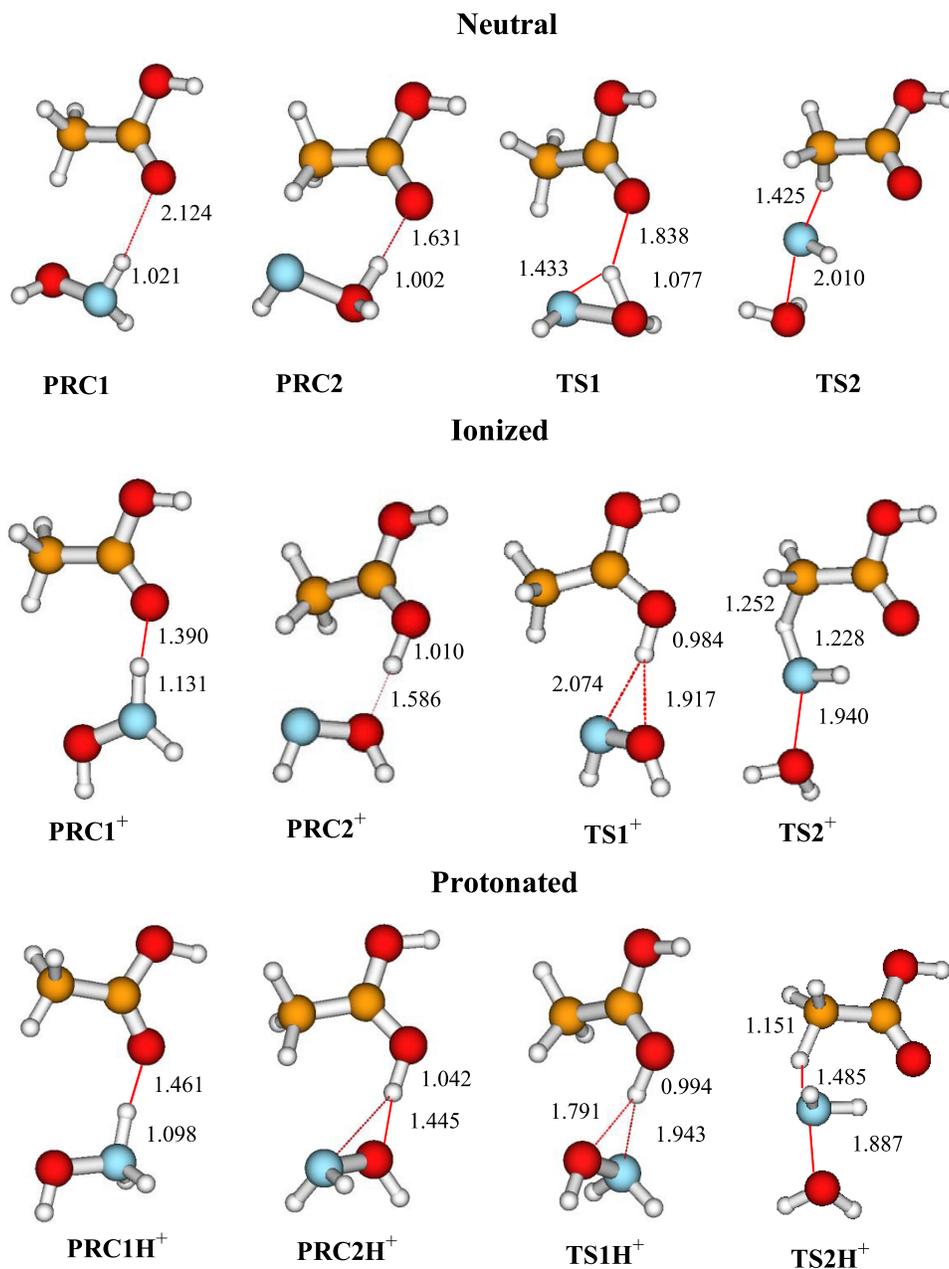


Figure 2. Schematic representation of the intermediates and transition states for the reactions of neutral, ionized, and protonated hydroxylamine with acetic acid. Detailed geometries are given in Table 1 in the online journal.

(A color version of this figure is available in the online journal.)

As we mentioned above, the reaction starting from NH_2OH_2^+ involves a small but non-negligible barrier ($2.3 \text{ kcal mol}^{-1}$; CCSD(T) level). Even though this is indeed a rather small barrier, it could have significant effects at very low temperatures, such as in interstellar clouds. An estimate employing the statistical kinetic theories in the simplified kinetic scheme (1) results in a reaction coefficient of about $6.5 \times 10^{-27} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ at 40 K. This value suggests that at temperatures relevant in the interstellar medium the reaction of NH_2OH_2^+ with acetic acid would not produce significant amounts of protonated glycine. Therefore, it seems that the laboratory experiments conducted at room temperature reporting the formation of protonated glycine from the reaction of acetic acid with protonated hydroxylamine should not be directly extrapolated to the interstellar medium, since our theoretical calculations suggest that this process should not be rather efficient.

3.2. Reaction of Ionized Hydroxylamine with Acetic Acid

The energy profile of the analogous mechanism for the reaction of ionized hydroxylamine with acetic acid is also shown in Figure 1. Essentially this energy profile is very similar to that observed for the reaction initiated by protonated hydroxylamine. Both intermediates, PRC1^+ and PRC2^+ , have relative energies which are very close to their counterparts in the protonated reaction, PRC1H^+ and PRC2H^+ . The transition state for the 1,2-hydrogen shift, TS1^+ , also has a similar relative energy to TS1H^+ . The main differences are found for the relative energies of the reaction products and of the second transition state, TS2^+ . The exothermicity of the reaction initiated by protonated hydroxylamine, $-56.3 \text{ kcal mol}^{-1}$ at the CCSD(T) level, is about $19.9 \text{ kcal mol}^{-1}$ higher than the exothermicity of the reaction of ionized hydroxylamine with acetic acid,

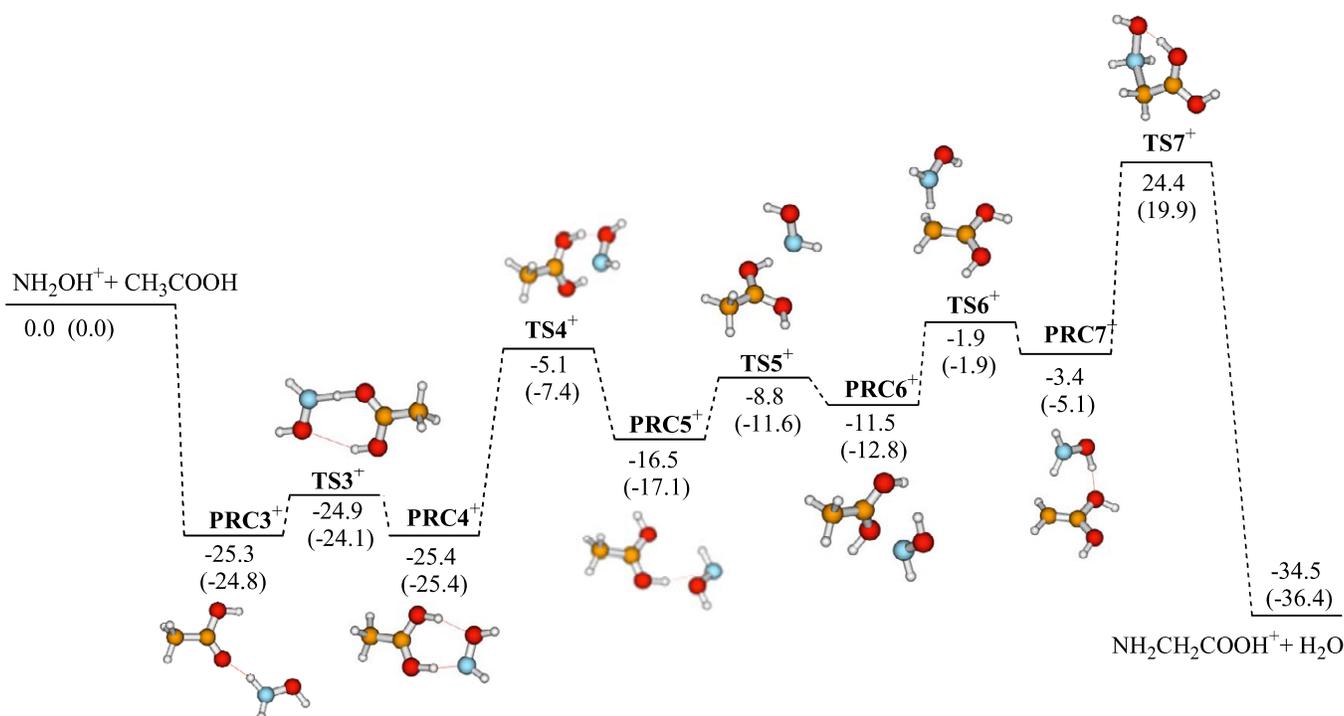


Figure 3. Energy profile, in kcal mol⁻¹, for the alternative mechanism of the reaction of ionized hydroxylamine with acetic acid obtained at the MP2/cc-pVTZ and CCSD(T)/aug-cc-pVT (in parentheses) levels including zero-point vibrational energy differences computed at the MP2/cc-pVTZ level.

(A color version of this figure is available in the online journal.)

namely, -36.4 kcal mol⁻¹ at the same level of theory. This energy difference between the reaction enthalpies is close to the difference between TS2⁺ and TS2H⁺, namely, 15.6 kcal mol⁻¹ at the CCSD(T) level. The immediate consequence is that the studied path for the reaction of NH₂OH⁺ with acetic acid involves a large energy barrier, which at the CCSD(T) level takes a value of 43.3 kcal mol⁻¹. This barrier clearly precludes this mechanism from taking place in the interstellar medium. Furthermore, in the NH₂OH⁺ + CH₃COOH reaction there is no alternative high-lying NH₂OH⁺ isomer which could initiate the reaction, as in the case of protonated hydroxylamine.

We have explored other possible reaction mechanisms for the NH₂OH⁺ + CH₃COOH reaction. The only competitive pathway found in our explorations is schematically depicted in Figure 3. The mechanism starts with the formation of a pre-reaction complex, PRC3⁺, which is similar to PRC1⁺ since the interaction takes place through the NH₂ group, which is bonded to the carbonyl oxygen via a hydrogen bridge. The difference is that in PRC3⁺ the OH group of ionized hydroxylamine points in the opposite direction to the CH₃ group of acetic acid. Then PRC4⁺ is formed upon hydrogen atom transfer to the carbonyl oxygen, a process involving transition state TS3⁺. Subsequent migration of the NHOH moiety from the carboxyl group toward the CH₃ group takes place through intermediates PRC5⁺ and PRC6⁺ (involving transition states TS4⁺ and TS5⁺). Hydrogen atom donation from the CH₃ group to NHOH implies transition state TS6⁺ and results in PRC7⁺, an intermediate corresponding to the interaction of NH₂OH⁺ with CH₂COHOH. Finally, N-O cleavage and water molecule formation takes place through transition state TS7⁺, leading to the final products NH₂CH₂COOH⁺. The stability of the different intermediates along this path is progressively reduced. Nevertheless, all intermediates and most TSs lie in energy below the reactants. However, TS7⁺ lies quite high in energy and implies an energy barrier of about 24 kcal mol⁻¹

at the CCSD(T) level. Therefore, this second mechanism also involves a significant energy barrier to be feasible under interstellar conditions.

3.3. Reaction of Hydroxylamine with Acetic Acid

The energy profile for the reaction of neutral hydroxylamine with acetic acid is also shown in Figure 1. These kind of neutral reactions have usually large energy barriers, and therefore the main purpose of this part of the work is to make a comparison with the reactions of acetic acid with ionized and protonated hydroxylamine in order to obtain useful information to understand the factors which favor this kind of process upon ionization or protonation. For reasons of brevity we will refer to *neutral*, *ionized*, and *protonated* reactions for the reactions of acetic acid with neutral, ionized, and protonated hydroxylamine, respectively.

We will focus on the analogous mechanism for all three reactions, which is shown in Figure 1, even though there are other possible pathways that could be even more competitive. The neutral reaction starts with the formation of an intermediate, PRC1, much less stable than its ionized and protonated counterparts (-4.5 kcal mol⁻¹ at the CCSD(T) level). The 1,2-hydrogen shift from the nitrogen to the oxygen atom produces the intermediate PRC2, which lies much higher in energy (46.6 kcal mol⁻¹ above the reactants at the CCSD(T) level) and involves a large energy barrier (56.6 kcal mol⁻¹). Finally TS2 implies an energy barrier of 63.6 kcal mol⁻¹. Therefore, based on the energy profile shown in Figure 1 for the reaction of neutral hydroxylamine with acetic acid, it is clear that this reaction is not feasible in the interstellar medium, despite its relatively high exothermicity (-39.0 kcal mol⁻¹ at the CCSD(T) level). In fact, the neutral products have similar stability to their ionized and protonated counterparts. The exothermicity is higher for the protonated

reaction, but the neutral products are slightly more stable than in the case of the ionized reaction.

The geometrical parameters of the involved species shown in Figure 2 also give some clues to rationalize the energy profile. The initial prereaction complex PRC1 has a relatively long H-O distance (2.124 Å) since it corresponds to a neutral-neutral interaction and consequently a rather low stability. On the other hand, both PRC1⁺ and PRC1H⁺ have much shorter H-O distances (1.390 and 1.461 Å, respectively) due to the ion-molecule interaction. Both charged prereaction complexes have similar relative stabilities, about 27 kcal mol⁻¹. The subsequent intermediates, PRC2⁺ and PRC2H⁺, also exhibit very similar stabilities, as well as the associated transition states TS1⁺ and TS1H⁺. The corresponding neutral species, PRC2 and TS1, are much less stable. This important difference in stability is due to the possibility of proton transfer to the carbonyl oxygen atom of the acetic acid in the charged reactions, which could be considered a sort of acid catalysis.

Finally, the insertion of a nitrogen atom into one of the C-H bonds of the methyl group accompanied by N-O bond cleavage leads to the final products. This process involves transition states TS2, TS2⁺, and TS2H⁺ for the neutral, ionized, and protonated reactions, respectively. TS2 lies only about 17 kcal mol⁻¹ higher in energy than PRC2, since PRC2 is already rather high in energy. On the other hand, the energy barriers from PRC2⁺ and PRC2H⁺ to give the final products are much higher, about 62 and 45 kcal mol⁻¹, respectively, at the CCSD(T) level. Therefore, the last step in the mechanism is not efficiently favored in the ionized and protonated reactions compared with the neutral one. In fact, both ionized and protonated reactions, as a consequence of the high-lying transition state (TS2⁺ or TS2H⁺), have relatively high energy barriers compared with the respective ground state reactants. Only in the case of the protonated reaction starting from the NH₂OH₂⁺ isomer is the barrier small enough to be a potentially viable process.

4. CONCLUSIONS

A computational study of the reactions of hydroxylamine and its ionized and protonated derivatives with acetic acid has been carried out. The formation of neutral glycine from the reaction of neutral hydroxylamine with acetic acid is clearly exothermic, but, as expected, involves a very large energy barrier (63.6 kcal mol⁻¹ at the CCSD(T) level). This barrier rules out the possibility of producing glycine from neutral hydroxylamine. The reaction of ionized hydroxylamine with acetic acid is also clearly exothermic, but again a significant energy barrier is found (around 19.9 kcal mol⁻¹ at the CCSD(T) level) even in the energetically most favorable pathway. A similar situation is found for the reaction of the most stable protonated isomer of hydroxylamine, NH₃OH⁺, with acetic acid. Only when the higher energy isomer, NH₂OH₂⁺, is considered is the involved energy barrier substantially lower (about 2.3 kcal mol⁻¹ at the CCSD(T) level). However, an estimate of the reaction coefficient at low temperatures such as those reigning in the interstellar medium gives very low values.

Therefore, there are three factors that might suggest that the reaction of protonated hydroxylamine with acetic acid would not constitute an efficient way of synthesizing protonated glycine in the interstellar medium: (1) hydroxylamine has not yet been observed in the interstellar medium (although it seems that it could be synthesized through reactions on the surface of interstellar grains); (2) the most stable isomer of protonated hydroxylamine does not seem to be an adequate reactant, since

it leads to a high energy barrier; (3) only the higher energy isomer of protonated hydroxylamine involves a reduced barrier, but even in this case its efficiency at low temperatures should be rather limited.

In summary, even though laboratory experiments conducted at room temperature have reported the formation of protonated glycine from the reaction of acetic acid with protonated hydroxylamine, our theoretical calculations suggest that this should not be an efficient process under interstellar conditions.

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