The reaction between NH_3^+ and CH_3COOH : a possible process for the formation of glycine precursors in the interstellar medium

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ABSTRACT

Context. The formation of glycine is strongly relevant to our understanding of the interstellar medium and is most accurately studied computationally.

Aims. We carry out a theoretical study of the reactions between the radical cation of ammonia and $\text{CH}_3\text{COOH}/\text{CH}_2\text{COOH}$ as possible processes leading to glycine derivatives.

Methods. The gas-phase reactions were theoretically studied using ab initio methods. We employed the second-order Moller-Plesset level in conjunction with the cc-pVTZ basis set. In addition, the electronic energies were refined by means of single-point calculations at the CCSD(T) level on the MP2/cc-pVTZ geometries with the aug-cc-pVTZ basis set.

Results. We report accurate potential energy surfaces for the reactions considered in this work. The different intermediate species as well as the most relevant transition states for these reactions are characterized.

Conclusions. Formation of protonated glycine from the reaction of NH_3^+ with acetic acid is an exothermic (-9.15 kcal/mol at CCSD(T) level) barrier free process. However, the results obtained indicate that the hydrogen-transfer process forming NH_4^+ and CH_2COOH is clearly the dominating path, in agreement with the experimental evidence. The formation of ionized glycine from the reaction of product CH_2COOH with NH_3^+ is a quasi-isoenergetic (2.03 kcal/mol at CCSD(T) level) barrier free process that leads to a highly stable intermediate: protonated glycine.

Key words. astrochemistry – astrobiology – molecular processes – molecular data – methods: numerical

1. Introduction

There has been an increasing fascination with the complexity of interstellar chemistry and the existence of interstellar molecules of biological interest. In particular, the formation of biomolecules in space constitutes an open question about the origin of life. It has been argued that interstellar amino acid formation could precede the syntheses of more complex systems in space (Wincel et al. 2000). Astrochemical models, laboratory experiments, and theoretical studies have aided in understanding the formation of different organic molecules in interstellar clouds, the regions where stars and planetary systems could be formed. If organic matter were to have been formed in the interstellar regions by gas phase reactions or reactions catalyzed by dust grains, interstellar bodies might have deposited this matter on Earth in the pre-life era which would indicate that these bodies play an essential role in the formation of life. Among the biologically important molecules the amino acids, as key building blocks of proteins and peptides, deserve special attention. The presence of amino acids in the interstellar medium would be of crucial importance to understanding the possible pathways in the origin of life in the Universe. Nevertheless, after more than two decades of continuous searches in space no convincing detection of even the simplest amino acid, glycine, has been reported (Brown et al. 1979; Hollis et al. 1980; Snyder et al. 1983; Combes et al. 1996; Ceccarelli et al. 2000; Kuan et al. 2003; Hollis et al. 2003a,b; Snyder et al. 2005; Guélin et al. 2008).

The observational difficulties associated with the detection of amino acids in line-rich, compact, hot molecular cores can be summarized in two points:

- amino acids have limited photostability (Ehrenfreund et al. 2001). Amino acids in the gas phase will probably be destroyed during the lifetime of a typical interstellar cloud, even when exposed to ultraviolet photons of relatively low energy. However, this does not preclude the amino acids in meteorites having formed in the interstellar medium; it only requires that amino acids be shielded from UV in protected environments, such as dense molecular clouds and hot cores (star-forming regions);
- amino acids constitute relatively large molecules and their rotational spectrum contains weak lines due to large molecular partition functions and contamination of the target transitions by emission from many other molecules in the hot molecular cores and their accompanying extended molecular envelopes (Combes et al. 1996).

Different reaction pathways leading to glycine have been proposed involving relatively abundant interstellar organic molecules. Hoyle & Wickramasinghe (1976) suggested the formation of glycine from the reaction of methanimine (HNCH_2) and formic acid (HCOOH) since these compounds had been observed in dense molecular clouds of comparable abundance. In this context, Basiuk & Bogillo (2000), Basiuk (2001), and Basiuk & Kobayashi (2002) carried out a theoretical study of amino-acid-precursor formation in the interstellar medium

considering different pathways that include the participation of methanimine and methanimine-related cations, HNCH^+ and H_2NCH_2^+ . Their studies demonstrated that although the reactions considered are exothermic they are not feasible under the interstellar conditions because of the high energy transition states and the possibility of competitive formation of side products.

Based on the Miller experiment (Miller 1953), involving the synthesis of amino acids under conditions that simulated primitive Earth's atmosphere from simple organic molecules, Maeda & Ono (2004) considered a two-step synthetic route of glycine with no activation barriers. The route is composed of an addition reaction of ammonia with singlet methylene yielding ammonium ylide ($\text{NH}_3 + \text{CH}_2 \rightarrow \text{H}_2\text{CNH}_3$) followed by carboxylation of the ylide with carbon dioxide ($\text{H}_2\text{CNH}_3 + \text{CO}_2 \rightarrow \text{H}_2\text{NCH}_2\text{COOH}$).

Other authors (Bernstein et al. 2002) have reported a laboratory demonstration that amino acids can be naturally formed from ultraviolet photolysis of icy interstellar grains containing small amounts of materials such as methanol, ammonia, and hydrogen cyanide. The study suggests that at least some meteoritic amino acids are the result of interstellar photochemistry rather than formation in liquid water on an early Solar System body. In addition, different theoretical works (Woon 2001, 2002a,b) have been devoted to the study of the viability of various pathways in forming amino acids in astrophysical ices.

The possibility of synthesizing amino acids from simple interstellar species by means of gas-phase ion-molecule reactions initiated by cosmic and ultraviolet radiation was discussed by Herbst (2001) in his work about the chemistry of interstellar space.

In this context, different synthetic means of producing glycine and alanine have been proposed (Blagojevic et al. 2003; Snow et al. 2007; Jackson et al. 2005a,b) involving the joining of amine and carboxyl functional groups. In particular, theoretical and experimental works (Blagojevic et al. 2003; Snow et al. 2007) have dealt with the study of gas-phase synthesis of amino acids from smaller molecules found in the space. From these studies, the formation of both ionized/protonated glycine and β -alanine in the interstellar medium was inferred to occur by means of the reactions of ionized/protonated hydroxylamine, $\text{NH}_{2,3}\text{OH}^+$ with acetic and propanoic acids, respectively. However, we note that $\text{NH}_{2,3}\text{OH}^+$ has not yet been detected in the interstellar medium.

To seek a viable formation pathway for producing amino acids from interstellar molecules, Jackson et al. (2005a,b) carried out a selected ion flow tube (SIFT) study of two types of ion-molecule reactions: a) reactions between a sequence of ions such as N^+ , N_2^+ , HCOOH_2^+ , $\text{CH}_3\text{COOH}_2^+$... with neutral amine species, CH_3NH_2 and $\text{CH}_3\text{CH}_2\text{NH}_2$ (Jackson et al. 2005a,b); and b) reactions of positively charged ammonia and amine ion fragments, NH_2^+ , NH_3^+ , and HCNH^+ with neutral species, HCOOH , CH_3COOH , and CH_3OCHO (Jackson et al. 2005b).

We performed a preliminary theoretical study of possible ion-molecule reactions leading to precursors of interstellar glycine (Largo et al. 2004), including predictions of their reaction enthalpies at different levels of theory. One of our main conclusions was that the reactions between both NH_2^+ and NH_3^+ with acetic acid were promising because the formation of glycine precursors (ionized and protonated glycine, respectively) were exothermic. For these exothermic processes, and to ascertain whether energetic barriers are present, a full exploration of the potential energy surface was required. To complete our early study, we carried out a theoretical study of the reaction of NH_2^+ with acetic acid considering both the singlet and triplet potential

energy surfaces (Largo et al. 2008). Our work suggests that the formation of ionized glycine from the route considered is a feasible process under interstellar conditions (exothermic and barrier free). However, we found two more favourable channels, namely proton transfer and the formation of $\text{NH}_3 + \text{CH}_2\text{COOH}^+$.

The reaction between the radical cation of ammonia and acetic acid was previously studied by selected ion flow tube experiments (Jackson et al. 2005b). The authors concluded that NH_3^+ reacts with CH_3COOH via H atom abstraction giving $\text{NH}_4^+ + \text{CH}_2\text{COOH}$, this product being more thermodynamically stable than the CH_3COO radical. In this work, we consider whether the radicals generated by the NH_3^+ abstraction reaction, CH_2COOH , play a role in forming interstellar amino acids. On the other hand, Blagojevic et al. (2003) argued that the reaction of NH_3^+ with CH_3COOH does not produce ionized glycine but instead the acetohydroxamic acid cation, $\text{CH}_3\text{CONHOH}^+$.

Following on from our previous studies (Largo et al. 2004, 2008), we focused on the reaction of the radical cation of ammonia with acetic acid as a possible gas-phase reaction that could produce interstellar protonated glycine. In addition, to address previous experimental suggestions (Jackson et al. 2005b), we considered the reaction between NH_3^+ and the CH_2COOH radical. We present estimations of the geometries of the different species involved in both reactions and reaction enthalpies for the possible products. We also carried out a detailed analysis of the corresponding potential energy surfaces. We note that the reactants considered in this study have been identified in the interstellar medium. Acetic acid was detected in one core source within the giant molecular cloud complex Sagittarius B2 (Mehringher et al. 1997) and hot cores are rich in ammonia (Ehrenfreund 2000). Theoretical studies in the field of the interstellar chemistry are especially suitable because the conditions of the molecular clouds are appropriate for the application of theoretical methods.

2. Computational methods

The geometries and harmonic vibrational frequencies of the minima and transition states involved in the reactions of NH_3^+ with CH_3COOH or CH_2COOH were computed at the second-order Moller-Plesset level in conjunction with the cc-pVTZ (correlation-consistent polarized valence triple-zeta) basis set developed by Dunning (1989). The nature of each optimized structure on the corresponding potential surfaces was checked by calculating vibrational frequencies; these computations also allow us to estimate zero-point vibrational energy (ZPVE) corrections.

Electronic energies were refined by means of single-point calculations at the CCSD(T) level (coupled cluster single and double excitation model augmented with a non-iterative treatment of triple excitations) (Raghavachari et al. 1989) on the MP2/cc-pVTZ geometries with the aug-cc-pVTZ basis set, which also includes diffuse functions. In this case, ZPVE corrections were included at the MP2/cc-pVTZ level.

The intrinsic reaction coordinate (IRC) technique (Gonzalez & Schelegel 1989, 1990) was used to check the connections between transition-state structures and adjacent minima.

All calculations were performed with the Gaussian-98 program package (Frisch et al. 1998).

Fig. 1. MP2/cc-pVTZ optimized geometries for the different $(\text{NO}_2\text{C}_2\text{H}_7)^+$ minima. Distances are given in angstroms and angles in degrees.

3. Results and discussion

3.1. Reaction of NH_3^+ with CH_3COOH

Given the multiplicity of the reactants, NH_3^+ ($^2A_2'$), CH_3COOH ($^1A'$), the reaction takes place on the doublet potential energy surface; we therefore characterized the possible intermediate species as well as the relevant transition states in this potential energy surface. For systems involving polyatomic molecules of the present level, building an explicit potential energy surface, is difficult because of a large number of possible competitive processes, which are difficult to account for. Consequently, we limited our study to the search for the most important stationary points and estimates of energetic feasibility for some selected reactions.

Figure 1 depicts the optimized geometrical parameters, at the MP2/cc-pVTZ level of theory, of the $(\text{NO}_2\text{C}_2\text{H}_7)^+$ isomers that are relevant to the reaction of NH_3^+ with CH_3COOH . The relative energies, including zero-point vibrational energy differences (MP2/cc-pVTZ level), at both MP2/cc-pVTZ//MP2/cc-pVTZ and CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ levels, are collected in Table 1. All the intermediates shown in this table present real vibrational frequencies and are therefore true minima on the potential surface.

From the examination of the different structures shown in Fig. 1, it can be inferred that isomer I1 is obtained from the direct approach of the hydrogen atom of the NH_3 group to the carbonylic oxygen of acetic acid. On the other hand, isomer I2 results from the interaction of the hydrogen atom of NH_3^+ with the carbonylic oxygen of CH_3COOH and abstraction of the hydrogen atom of the methyl group to the nitrogen atom. Isomer

Table 1. Relative energies (kcal/mol) for the relevant intermediates.

Isomer		ΔE (MP2)	ΔE (CCSD(T))
$\text{CH}_3\text{COOHNH}_3^+$	I1 ($^2A'$)	20.42	19.37
$\text{CH}_2\text{COOHNH}_4^+$	I2 ($^2A''$)	0.00	0.00
$\text{NH}_3\text{CH}_2\text{COHOH}^+$	I3 (2A)	24.68	23.31
$\text{NH}_3\text{CH}_2\text{COHOH}^+$	I4 (2A)	25.62	24.35
$\text{CH}_3\text{COOHNH}_3^+$	I5 ($^2A'$)	33.28	32.64
$\text{CH}_3\text{COOHNH}_3^+$	I6 (2A)	29.35	26.22
$\text{CH}_3\text{COOHNH}_3^+$	I7 ($^2A'$)	35.36	32.96

I5 is produced by the approach of one hydrogen atom of NH_3^+ to the hydroxylic oxygen of acetic acid. Isomers I6 and I7 correspond to the interaction between the nitrogen atom of NH_3^+ and the carbonylic oxygen of CH_3COOH . Finally, isomers I3 and I4 are produced by the approach of the nitrogen atom of the NH_3^+ ion to the carbon atom of methyl group of acetic acid and abstraction of hydrogen atom of the methyl group to carbonylic oxygen.

Analyzing the optimized geometries from a quantitative viewpoint, we can see that, apart from isomer I2, all intermediates depicted in Fig. 1 have similar C–C bond distances (in the range of 1.486 Å to 1.493 Å), which are typical of carbon-carbon single bonds. The C–C bond distance in isomer I2, 1.445 Å, suggests a certain degree of double character.

In term of energetics, Table 1 shows that the two levels of theory employed predict similar stability order for the different intermediates. The CCSD(T)/aug-cc-pVTZ level tends to predict slightly lower relative energies than the MP2/cc-pVTZ level. At both MP2/cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels of theory, the global minimum is predicted to be clearly isomer I2. The stability order of the different isomers is ($>$ means more stable than)

$$\text{I2} > \text{I1} > \text{I3} > \text{I4} > \text{I6} > \text{I5} > \text{I7}.$$

In principle, acetic acid may react with the radical cation of ammonia to produce protonated glycine, although other different products could be formed:

As we previously mentioned, because of the typical conditions reigning in the interstellar medium (basically low density and low temperature), only reactions that are exothermic and barrier free may play a significant role in interstellar chemistry. Accordingly, we first will calculate the reaction energies for the different processes considered.

In Table 2, we collected the relative energies with respect to reactants, at MP2/cc-pVTZ//MP2/cc-pVTZ and CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ levels of theory, of the possible products that can be formed in the reaction between NH_3^+ and CH_3COOH . Zero-point vibrational energy differences were included (MP2/cc-pVTZ level). In some cases, two possible conformations (referred to as a quasi cis conformer) and t- (a quasi

Table 2. Relative energies (kcal/mol) for the possible products.

Products		ΔE (MP2)	ΔE (CCSD(T))
$\text{NH}_3\text{CH}_2\text{COOH}^+$ (c1) ($^1A'$) + H	[A]	-15.43	-9.15
$\text{NH}_3\text{CH}_2\text{COOH}^+$ (c2) ($^1A'$) + H	[B]	-10.42	-4.27
NH_4^+ (1A) + CH_2COOH (1A)	[C]	-24.35	-24.22
$\text{NH}_2\text{CH}_2\text{COOH}^+$ ($^2A''$) + H_2	[D]	-1.90	-2.69
$\text{c-CH}_3\text{CONHOH}^+$ ($^2A''$) + H_2	[E1]	32.41	31.81
$\text{t-CH}_3\text{CONHOH}^+$ ($^2A''$) + H_2	[E2]	41.93	38.77
$\text{t-CH}_3\text{C(OH)}_2^+$ ($^1A'$) + NH_2	[F1]	3.88	1.42
$\text{c-CH}_3\text{C(OH)}_2^+$ ($^1A'$) + NH_2	[F2]	7.95	5.45
$\text{c-CH}_3\text{COOHNH}_2^+$ ($^1A'$) + H	[G1]	35.68	38.79
$\text{t-CH}_3\text{COOHNH}_2^+$ ($^1A'$) + H	[G2]	43.35	45.67
$\text{c-CH}_3\text{CONH}_2\text{OH}^+$ ($^1A'$) + H	[H1]	44.93	48.62
$\text{t-CH}_3\text{CONH}_2\text{OH}^+$ ($^1A'$) + H	[H2]	47.32	51.07
NH_3 (1A) + CH_3COOH^+ ($^2A'$)	[I]	17.51	10.91
CH_2COOH^+ (1A) + NH_4	[J]	78.34	69.80

trans conformer) are considered. The optimized geometries for reactants and products are given, as Online Material, in Fig. A.1. Examination of the energetics showed in Table 2 allows us to infer that the formation of protonated glycine, through channels A and B, leading, respectively, to the lowest conformation c1 (consisting of an intramolecular hydrogen bond between a hydrogen atom of NH_3 and the carboxylic oxygen) and to the second most stable conformer c2 (where the hydrogen bond is connected to the less basic hydroxilic oxygen) of protonated glycine are exothermic processes. However, the most favorable process, from thermodynamical arguments, is the formation of ammonium cation and CH_2COOH (channel C) in consonance with the SIFT experiments (Jackson et al. 2005b). In this case, we emphasize that the reaction may also form the CH_3COO radical via extraction of the carboxylic H, although this was reported to be less thermodynamically and structurally stable (Schalley et al. 1998; Butkovskaya et al. 2004). Our results for this process are in agreement with this assertion. The relative energy with respect to the reactants for the formation of NH_4^+ + CH_3COO is $\Delta E = -10.91$ kcal/mol at CCSD(T) level and -6.95 kcal/mol at MP2 level. On the other hand, the reaction between NH_3^+ + CH_3COOH to produce ionized glycine (Channel D) is a slightly exothermic process (quasi-isoenergetic). Following the comment of Blagojevic et al. (2003), we also considered the formation of acetohydroxamic acid cation $\text{CH}_3\text{CONHOH}^+$ and $\text{CH}_3\text{CONH}_2\text{OH}^+$ produced by inserting NH_3^+ into the C–OH bond and the subsequent elimination of H_2 or H, respectively (channels E and H). Nevertheless, these reactions clearly seem endothermic at both levels of theory ($\Delta E = 31.81$ kcal/mol and 48.62 kcal/mol respectively at CCSD(T) level). Charge transfer products and the remaining processes studied are endothermic.

The exothermicity is a necessary, but not a sufficient argument for a reaction to be plausible under interstellar conditions. In addition to this energetic requirement, interstellar reactions should be barrier free. We therefore carried out a full exploration of the potential surface, to analyze the feasibility of the reactions studied as a source of precursors of glycine in the interstellar medium.

Figure 2 shows the geometries of the more relevant transition states, whereas the energy profile for the NH_3^+ + CH_3COOH reaction is represented in Fig. 3. As already mentioned, the MP2 and CCSD(T) energetics are in good agreement. Reaction between NH_3^+ and the acetic acid starts with the barrierless approximation of the radical cation of ammonia to the carbonyl oxygen

Fig. 2. MP2/cc-pVTZ optimized geometries for the relevant transition states involved in the reaction of NH_3^+ ($^2A_2''$) with CH_3COOH ($^1A'$). Distances are given in angstroms and angles in degrees.

atom in CH_3COOH giving rise to a rather stable intermediate I1 ($\Delta E = -28.8$ kcal/mol at CCSD(T) level)

The exothermic formation of intermediate I1 produces an energy reservoir that is used as the reaction proceeds toward the products. After forming the intermediate I1, different processes can take place. Intermediate I1 can proceed to the most stable conformer of protonated glycine through an exothermic and barrier free path, a.1:

Once structure I1 is obtained, the hydrogen atom migration from the carbon atom to the nitrogen one, through the transition state TS_{11-12} , leads to the most stable intermediate I2 ($\Delta E = -48.24$ kcal/mol at CCSD(T) level of theory). Intermediate I2 may then form isomer I3 by means of hydrogen abstraction from the NH_4 group to the carbonyl oxygen atom and the subsequent approach of the NH_3 group to the carbon atom. Structure I3 then isomerizes into structure I4 through transition state TS_{13-14} . Finally, intermediates I3 or I4 may form protonated glycine through direct hydrogen elimination. All of these steps do not seem to involve any transition state. We note that we performed a scan for these steps carrying out optimizations at different O–H distances and no sign of transition states were found.

Protonated glycine can also be obtained from other two different paths. One of them, path a.2, involves the approach of

Fig. 3. Energy profile, in kcal/mol, for the reaction of NH_3^+ ($^2A_2'$) with CH_3COOH ($^1A'$) at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ and MP2/cc-pVTZ//MP2/cc-pVTZ (in parentheses) levels (including zero-point vibrational energy differences).

the NH_3 group to the carbon atom and simultaneous H atom elimination from carbon through transition state TS1:

This process has a significant activation barrier (36.64 kcal/mol at CCSD(T) level of theory). The third path (a.3), which also leads to the formation of the most stable conformer of protonated glycine, involves one isomerization process from isomer I1 to I2, also considered in path a.1, followed by hydrogen atom elimination from nitrogen and subsequent migration of NH_3 from oxygen atom to carbon one through transition state TS2:

Again, transition state TS2 is clearly located (56.96 kcal/mol at CCSD(T) level of theory) above the reactants in the potential energy surface. In conclusion, none of the paths a.2 and a.3 is energetically feasible under the interstellar conditions.

The second most stable conformer of protonated glycine, $\text{NH}_3\text{CH}_2\text{COOH}^+(\text{c2})$, could be formed through the following path

The reaction starts with the approach of the ammonia radical cation to the hydroxilic oxygen of acetic acid giving intermediate I5. Once I5 is obtained, the migration of the NH_3 group from oxygen to carbon through the transition state TS3 and the subsequent elimination of a hydrogen atom from carbon, produces protonated glycine (c2). This path has a significant activation barrier (39.14 kcal/mol at CCSD(T) level) and consequently should not be relevant under interstellar conditions.

Finally, we must consider another channel originating from the most stable intermediate, I2, and subsequent fragmentation into ammonium cation and CH_2COOH

As can be seen from Fig. 3, path c constitutes the most favourable process from both thermodynamic and kinetic arguments. Our theoretical calculations are in agreement with the previous results obtained from SIFT experiments for this reaction (Jackson et al. 2005b). As mentioned before, the formation of ionized glycine (channel C) is a slightly exothermic process. However, we were not able to identify paths that form this product, since all our attempts led to the formation of protonated glycine.

3.2. Reaction of NH_3^+ with CH_2COOH

Following the suggestion of Jackson et al. (2005b) and to check whether the radical generated by the NH_3^+ atom abstraction reaction could play a role in forming glycine derivatives, we considered the formation of ionized glycine from the reaction of the most favourable product of the previous reaction (CH_2COOH) with NH_3^+ :

Given the multiplicity of the reactants, NH_3^+ ($^2A_2''$) and CH_2COOH (2A), the reaction should take place on the singlet potential energy surface. The energy profile for this reaction is shown in Fig. 4. We note that the ionization energy of NH_3 is higher than that of CH_2COOH and therefore the reaction of electron transfer ($\text{NH}_3^+ + \text{CH}_2\text{COOH} \rightarrow \text{NH}_3 + \text{CH}_2\text{COOH}^+$) is clearly an exothermic process (−29.09 kcal/mol at CCSD(T) level). The reaction of NH_3^+ with CH_2COOH starts with the barrierless interaction between the nitrogen and the carbon atom of the CH_2 group of the CH_2COOH radical giving rise to the most stable conformer of protonated glycine (c1). This conformer is energetically well below the reactants (−106.51 kcal/mol at CCSD(T) level of theory). From this intermediate stage, the direct elimination of hydrogen leads to ionized glycine. This step does not seem to involve any transition state. We carried out a scan of the process that confirmed our assertion.

From inspection of Fig. 4, we can conclude that the reaction between NH_3^+ and the radical CH_2COOH is a quasi-isoenergetic barrier free process. We note that the high stability of the intermediate of the reaction, protonated glycine, indicates that it could be a long-lived species given its relative energy with respect to the products. This reaction takes place on the same potential energy surface as the previously studied $\text{NH}_2^+ + \text{CH}_3\text{COOH}$ reaction (Largo et al. 2008). It can be seen that the other possible channels are not feasible under interstellar conditions (see Fig. 4 in Largo et al. 2008).

Fig. 4. Energy profile, in kcal/mol, for the reaction of NH_3^+ ($^2A_2'$) with CH_2COOH ($^2A'$) at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ and MP2/cc-pVTZ//MP2/cc-pVTZ (in parentheses) levels (including zero-point vibrational energy differences).

4. Conclusions

We have performed a theoretical study of the reactions between the radical cation of ammonia and $\text{CH}_3\text{COOH}/\text{CH}_2\text{COOH}$ to investigate whether they are processes that can produce glycine derivatives. The different intermediate species and the most relevant transition states for these reactions have been characterized. The second-order Moller-Plesset level with the cc-pVTZ (correlation-consistent polarized valence triple-zeta) basis set was used. Energetic data were refined at the CCSD(T) level (coupled cluster single and double excitation model augmented with a non-iterative treatment of triple excitations) on the MP2/cc-pVTZ geometries with the aug-cc-pVTZ basis set. The two levels of theory employed in the present study provide energy predictions that are in good agreement. The most stable species of the $(\text{NO}_2\text{C}_2\text{H}_7)^+$ system was found to be isomer I2 (-48.24 kcal/mol below reactants at the CCSD(T) level). This species results from the interaction between the hydrogen atom of NH_3^+ and the carbonylic oxygen of CH_3COOH and abstraction of the hydrogen atom of the methyl group to the nitrogen atom. The analysis of the potential energy surface corresponding to the reaction between NH_3^+ and acetic acid suggests that path a.1 leading to protonated glycine is a feasible process in the interstellar medium (exothermic and barrier free). However, the dominating path is clearly the hydrogen transfer process giving NH_4^+ and CH_2COOH in agreement with the experimental evidence. In considering whether the formation of the acetohydroxamic acid cation from the reaction of NH_3^+ with CH_3COOH is possible, our theoretical study shows that this process is by far endothermic and therefore not be viable under interstellar conditions. The formation of ionized glycine from the subsequent reaction of the CH_2COOH radical with NH_3^+ , is a quasi-isoenergetic (2.03 kcal/mol at CCSD(T) level) barrier free process, which leads to a highly stable intermediate, protonated glycine. Our results suggest that the reaction between the radical cation of ammonia and both CH_3COOH and CH_2COOH leading to glycine derivatives could take place under interstellar conditions but there are other competitive channels that are more favorable. Our theoretical study provides a reasonable interpretation of the experiments that have been performed to date.

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Appendix A

Fig. A.1. MP2/cc-pVTZ optimized geometries for the reactants and products involved in the reaction of NH_3^+ (²A₂) with CH_3COOH (¹A₁). Distances are given in angstroms and angles in degrees.

Fig. A.1. continued.