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Could the reactions of formic acid with $CH_3NH_2^+/CH_3NH_3^+$ produce protonated glycine?

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ABSTRACT

A theoretical study of the reactions of $CH_3NH_2^+/CH_3NH_3^+$ with formic acid has been carried out in order to clarify their role in the formation of glycine derivatives under the conditions of the interstellar medium. The possible intermediate species as well as the relevant transition states for these reactions were characterized at the MP2 level with the cc-pVTZ basis set. Energetic data were obtained at the CCSD(T) level employing the aug-cc-pVTZ basis set. Formation of protonated glycine is an exothermic process for the reaction of formic acid with $CH_3NH_2^+$ (−2.5 kcal/mol at the CCSD(T) level) and a quasi-isoenergetic one for its reaction with $CH_3NH_3^+$ (2.9 kcal/mol at the CCSD(T) level). However, in both cases a net activation barrier is found, suggesting that both processes are not allowed under interstellar conditions.

1. Introduction

The list of molecular species identified in space, in interstellar clouds as well as in circumstellar envelopes, is increasing continuously owing to the use of more and more powerful telescopes and interferometer arrays. Among them, a special interest is devoted to carbon and nitrogen based molecules which should be considered as precursors of bio-molecules, particularly interstellar amino acids, basic units of proteins and therefore key elements for the origin of life. This is directly related to the presence of amino acids in the prebiotic chemistry of early Earth [1,2]. One theory that tries to explain this primitive presence establishes that essential material for prebiotic chemistry could have been first originated in the interstellar medium, and was then transported to the Earth by comets and meteorites [3–7]. Even though, this theory is supported by the fact that more than 70 amino acids were detected in meteorites such as Murchison [8–11] and Murray [10], no successful detection of them in interstellar medium has been reported. In this way, extensive searches of the simplest amino acid, glycine, were carried out. However, to date no conclusive identification was made [12–18].

In this context, a central point is the determination of feasible routes for the formation of amino acids under interstellar conditions. Experimental studies have demonstrated that UV photolysis of interstellar ice analogs can produce complex organic molecules as amino acids [19–21]. Theoretical works were also devoted to analyze the viability of different pathways for producing amino acids in astrophysical ices [22,23]. However, these processes are determined by the low expected efficiency of UV photolysis in dark clouds [24]. On the other hand, Elsila et al. [25] pointed out that it is possible that only amino acid precursors are synthesized by the ice photochemistry, whereas amino acids could be formed later on the asteroids or comet surfaces by hydrolysis.

It is well known that gas-phase reactions, mainly ion-molecule ones, are involved in the formation of a great number of interstellar species [26]. Maeda and Ohno [27] based on quantum chemical calculations showed that glycine could be formed via the barrier free reaction of closed-shell species: CO_2 and a higher energy isomer of methylamine CH_2NH_3. Different gas-phase ion-molecule reactions initiated by cosmic and ultraviolet radiation have been considered as possible routes for amino acids synthesis. The feasibility of the gas-phase formation of glycine from formic acid and methylenimine and related cations have been theoretically analyzed by Basiuk and Kobayashy [28]. These processes are exothermic but they have an energetic barrier and competitive formation of side compounds. Recent theoretical and experimental studies carried out by Blagojevic et al. [29,30] show that glycine and β-alanine could be formed in the interstellar medium by the gas-phase reactions of NH_2OH^+/NH_3OH^+ with acetic and propanoic acids, respectively. Selected ion flow tube (SIFT) studies were carried out by Jackson et al. [31,32] for different ion-molecule reactions as possible ways of the formation of amino acids from interstellar species. They conclude that neither reactions of nitrogen containing ions (N^+, N_2^+, NH_2^+, NH_3^+, and $HCNH^+$) with formic

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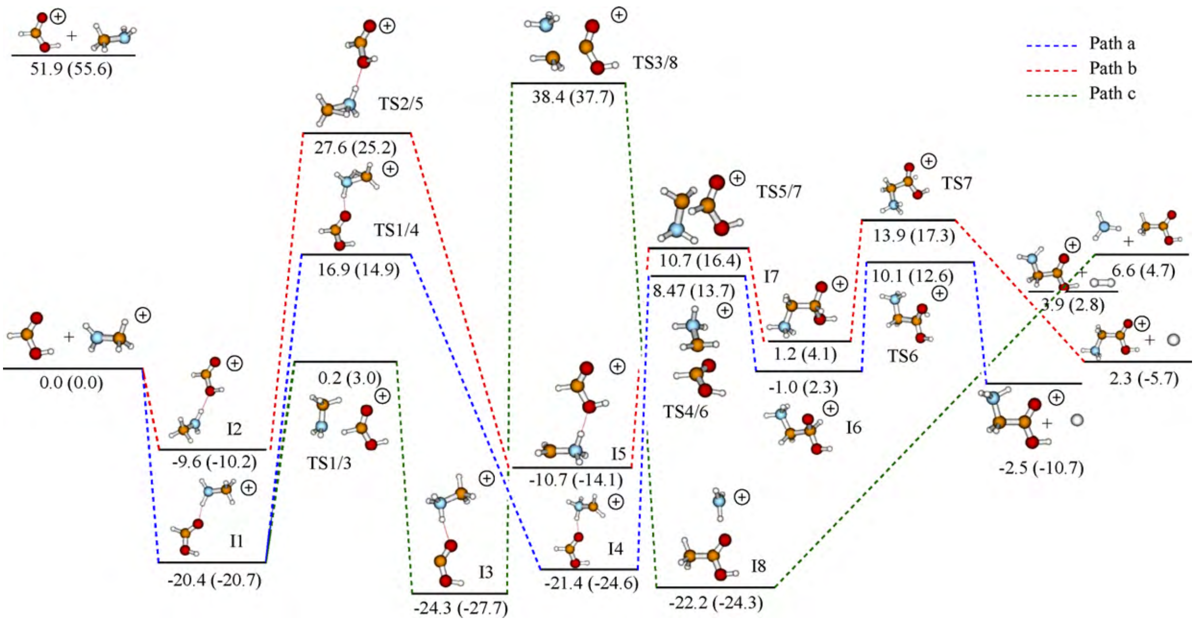

Fig. 1. Energy profile, in kcal/mol, for the reaction of $CH_3NH_2^+$ with HCOOH at the CCSD(T)/aug-cc-pVTZ and MP2/cc-pVTZ (in parentheses) levels. Zero-point vibrational energy differences are included.

acid, acetic acid, and methyl formate [31] nor reactions of amines (CH_3NH_2, and $CH_3CH_2NH_2$) with ions (N^+, N_2^+, CO_2^+, CO^+, O_2^+, $HCOOH_2^+$, $CH_3COOH_2^+$, and $HC(OH)OCH_3^+$) [32] produce interstellar amino acids. We performed theoretical studies on the reactions of acetic acid with NH_2^+ [33] and NH_3^+ [34]. In both cases we found that the formation of ionized and protonated glycine respectively, is viable process under interstellar conditions (exothermic and barrier free). However, we found other more favorable channels, namely hydrogen transfer process and the formation of $NH_3 + CH_2COOH^+$ for the reaction with NH_2^+, and in the case of NH_3^+, the results obtained indicate that the hydrogen transfer process for producing $NH_4^+ + CH_2COOH$ is clearly the dominating path. These theoretical results are in agreement with the experimental evidence [31].

Following our previous theoretical studies on the viability of different ion-molecule processes leading to precursors of glycine in the interstellar medium [33,34], in this work we present the results obtained for the reactions of formic acid with ionized and protonated methylamine. Both, formic acid and methylamine, are present in the interstellar medium [35,36], and ionization and protonation of methylamine under interstellar conditions are possible given its ionization energy (IE = 9.04 eV [37]) and proton affinity (PA = 215.4 kcal/mol [38]). To our knowledge, no experimental data are available for these reactions. From a theoretical point of view, only a prediction of the reaction enthalpy at different theoretical levels for the reaction $HCOOH + CH_3NH_2^+$ has been reported in a preliminary study [39]. The formation of protonated glycine from this reaction is demonstrated to be an exothermic process. For this reaction we report a study of the potential energy surface in order to determine the viability of this process in the conditions reigning in molecular clouds. In addition, a complete analysis of the reaction $HCOOH + CH_3NH_3^+$ is also carried out.

2. Computational methods

As in our previous study on the reaction of NH_3^+ with acetic acid [34], the geometries of the different species involved in the processes studied in this work were optimized at the second-order Moller-Plesset level in conjunction with Dunning's cc-pVTZ basis set [40,41], which has a triple-zeta character and includes polarization functions. For the characterization of the stationary points located on each potential surface as minima or transition states, a vibrational analysis was carried out at the same level, MP2/cc-pVTZ. This also allows us an estimate of the zero-point vibrational energy (ZPVE) correction for each structure. In order to check the connections between transition-state structures and adjacent minima, the intrinsic reaction coordinate (IRC) technique [42,43] was used.

Electronic energies were refined by means of single point calculation at the CCSD(T) level (coupled-cluster single and double excitation model augmented with a non-iterative triple excitation correction) [44], on the MP2/cc-pVTZ optimized geometries. The aug-cc-pVTZ basis set, which also includes diffuse functions, was employed for the energetic calculations.

All calculations reported in this work were carried out with the *Gaussian-98* program package [45].

3. Results and discussion

The possible intermediate species, products, as well as the relevant transition states of the reactions $CH_3NH_2^+ + HCOOH$ (reaction A) and $CH_3NH_3^+ + HCOOH$ (reaction B) have been characterized. The relative energy, taking the reactants as reference, of the possible products and intermediate species characterized for reaction A are reported in Table 1, whereas its energy profile is depicted in Fig. 1. The corresponding information for reaction B is collected in Table 2 and Fig. 2. Optimized geometries of reactants and products for reactions A and B are given as Supplementary material, Figs. S1 and S2, respectively. In addition, optimized geometries for the intermediates and transition states for reaction A and B are also included as Supplementary material in Figs. S3–S5, respectively. According to the multiplicity of the reactants (HCOOH ($^1A'$), $CH_3NH_2^+$ ($^2A'$) and $CH_3NH_3^+$ ($^1A'$)), reaction A should take place on the doublet potential energy surface and reaction B on the singlet one. All transition states located have an imaginary frequency which is associated in each case to the corresponding reaction coordinate. Similar energy profiles are obtained at both MP2/cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels (Figs. 1 and 2).

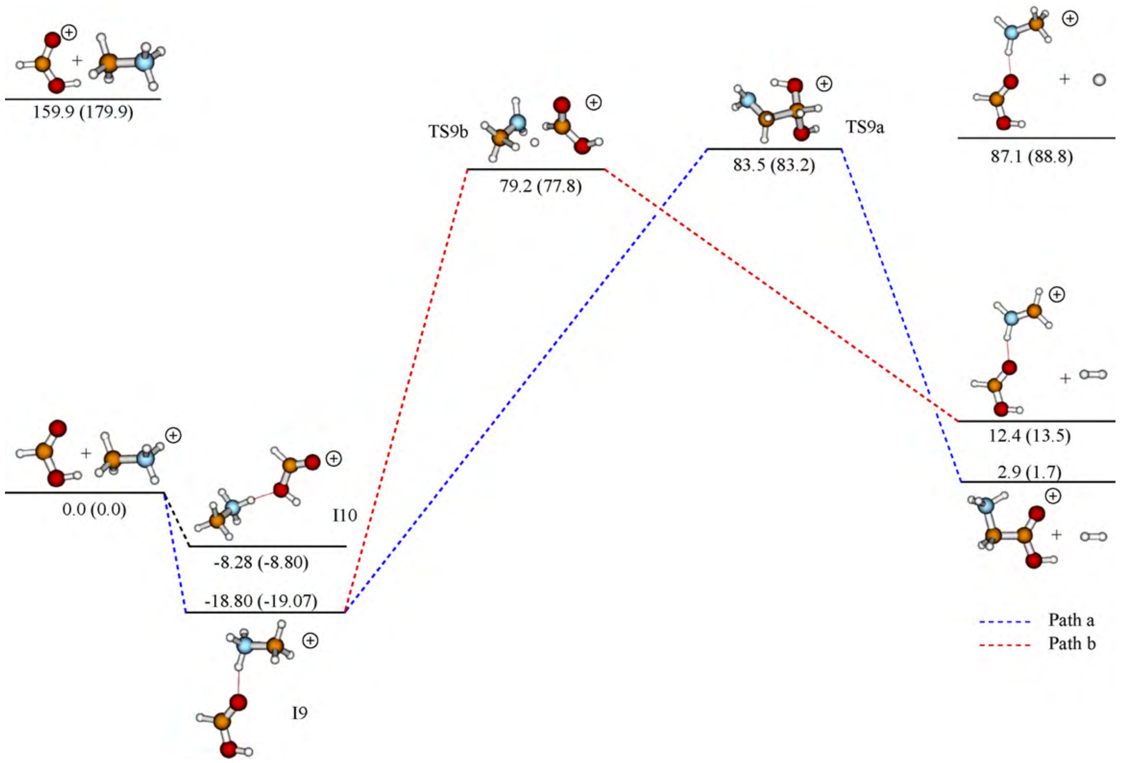

Fig. 2. Energy profile, in kcal/mol, for the reaction of $CH_3NH_3^+$ with HCOOH at the CCSD(T)/aug-cc-pVTZ and MP2/cc-pVTZ (in parentheses) levels. Zero-point vibrational energy differences are included.

3.1. *$CH_3NH_2^+$ + HCOOH reaction*

For the reaction of ionized methylamine with formic acid we have considered different products shown in Table 1. Formation of the most stable conformer of protonated glycine, c1, is an exothermic process whereas obtaining conformer c2 is a quasi-isoenergetic one. On the other hand, getting ionized glycine from this reaction is a slightly endothermic path. Finally, electron transfer and formation of NH_3^+ + CH_3COOH are endothermic processes.

We will briefly analyze the stability of the eight intermediates which take part in the reaction A (Table 1 and Fig. S3). The optimized geometries, given in Fig. S3, show that five of them are produced by the interaction of formic acid with derivatives of methylamine, I1–I5, the rest of them can be associated with derivatives of acetic acid, I6 to I8. The direct interaction of ionized methylamine with amine takes place between a hydrogen of the amine group and the carbonylic/hydroxylic oxygen of formic acid, intermediates I1 and I2, respectively. The most stable isomer located is I3 and is obtained from I1 by means of a hydrogen atom migration from the acid to the amine group. Isomer I8 is also relatively stable. It corresponds to the interaction of the hydrogen atom of the NH_3 group with the carbonylic oxygen of acetic acid. In general, the interaction through the carbonylic oxygen is more favorable than the interaction through the hydroxylic one. This fact is also reflected in the corresponding O–H bond distances, shorter in the case of interaction through carbonylic oxygen. The CCSD(T)/aug-cc-pVTZ level tends to predict lower relative energies than the MP2/cc-pVTZ. The stability order of the different isomers at CCSD(T)/aug-cc-pVTZ level is (>means more stable than):

Table 1
Relative energies for the relevant species in the reaction of $CH_3NH_2^+$ with HCOOH. Zero-point vibrational energy differences have been included.

	ΔE(MP2) (kcal mol^{-1})	ΔE(CCSD(T)) (kcal mol^{-1})
Reactants		
$CH_3NH_2^+$ ($^2A'$) + HCOOH ($^1A'$)	0.0	0.0
Products		
$NH_3CH_2COOH^+$(c1) ($^1A'$) + H	−10.7	−2.5
$NH_3CH_2COOH^+$(c2) ($^1A'$) + H	−5.8	2.3
$NH_2CH_2COOH^+$ ($^2A''$) + H_2	2.8	3.9
NH_3^+ ($^2A_2''$) + CH_3COOH ($^1A'$)	4.7	6.6
CH_3NH_2 ($^1A'$) + $HCOOH^+$ ($^2A'$)	55.6	51.9
Intermediates		
$HCOHOH_2NCH_3^+$ **I1** (^2A)	−20.7	−20.4
$HCOOHH_2NCH_3^+$ **I2** (^2A)	−10.2	−9.6
$COHOH_3NCH_2^+$ **I3** ($^2A'$)	−27.7	−24.3
$HCOHOHNH_2CH_2^+$ **I4** (^2A)	−24.6	−21.4
$HCOOHHNH_2CH_2^+$ **I5** ($^2A'$)	−14.1	−10.7
$NH_3CH_2HCOOH^+$ **I6** (^2A)	2.3	−1.0
$NH_3CH_2HCOOH^+$ **I7** (^2A)	4.1	1.2
$CH_3COHOHNH_2^+$ **I8** ($^2A'$)	−24.3	−22.2

Table 2
Relative energies for the relevant species in the reaction of $CH_3NH_3^+$ with HCOOH. Zero-point vibrational energy differences have been included.

	ΔE(MP2) (kcal mol^{-1})	ΔE(CCSD(T)) (kcal mol^{-1})
Reactants		
$CH_3NH_3^+$ ($^1A'$) + HCOOH ($^1A'$)	0.0	0.0
Products		
$NH_3CH_2COOH^+$(c1) ($^1A'$) + H_2	1.7	2.9
$NH_3CH_2COOH^+$(c2) ($^1A'$) + H_2	6.7	7.8
$HCOHONH_2CH_2^+$($^1A'$) + H_2	13.5	14.4
$HCOHONH_2CH_3^+$(^2A) + H	88.8	87.1
CH_3NH_3 ($^2A'$) + $HCOOH^+$ ($^2A'$)	179.9	159.9
Intermediates		
$HCOHOH_3NCH_3^+$($^1A'$) **I9**	−19.1	−18.8
$HCOOHH_3NCH_3^+$(^1A) **I10**	−8.8	−8.3

I3 > I8 > I4 > I1 > I5 > I2 > I6 > I7

According to the obtained energetic data for reaction A, the main interest from an interstellar point of view is the localization of barrier free paths giving protonated glycine. In this way, a detailed study of the doublet potential surface is carried out and the results are collected in Fig. 1.

The reaction of ionized methylamine with formic acid starts with the formation of isomer I1, which is the result of the direct interaction between the hydrogen of the amine group with the carbonylic oxygen of formic acid. Isomer I1 may evolve through the transition state TS1/4, to produce another intermediate, I4. Transition state TS1/4, as can be seen in Fig. 1 and Fig. S4, corresponds to the migration of a hydrogen atom from carbon to nitrogen in the methylamine group. Structure I4 then isomerizes into structure I6 involving the transition state TS4/6. In this transition state takes place the rupture of the bond between the hydrogen of the amine group with the carbonylic oxygen of formic acid and the formation of a carbon-carbon bond. The subsequent elimination of a hydrogen atom through transition state TS6 leads to conformer c1 of protonated glycine. This process can be summarized as follows:

$$\mathrm{CH_3NH_2}^+ + \mathrm{HCOOH} \rightarrow \mathrm{I1} \rightarrow \mathrm{TS1/4} \rightarrow \mathrm{I4} \rightarrow \mathrm{TS4/6} \rightarrow \mathrm{I6}$$
$$\rightarrow \mathrm{TS6} \rightarrow \mathrm{NH_3CH_2COOH}^+(\mathrm{c1}) + \mathrm{H} \quad \text{path a}$$

As can be seen in Fig. 1, the global process is exothermic, $\Delta E = -2.5$ kcal/mol at the CCSD(T) level, and has a net activation barrier of 16.9 kcal/mol. Therefore it is not feasible under interstellar conditions.

The second most stable conformer of protonated glycine, c2, could be formed through the following path:

$$\mathrm{CH_3NH_2}^+ + \mathrm{HCOOH} \rightarrow \mathrm{I2} \rightarrow \mathrm{TS2/5} \rightarrow \mathrm{I5} \rightarrow \mathrm{TS5/7} \rightarrow \mathrm{I7}$$
$$\rightarrow \mathrm{TS7} \rightarrow \mathrm{NH_3CH_2COOH}^+(\mathrm{c2}) + \mathrm{H} \quad \text{path b}$$

In this case direct interaction of ionized methylamine with formic acid produces the least stable isomer, I2, which evolves, through similar steps as path a, to produce in this case conformer c2 of protonated glycine. From Fig. 1, we can see that the energy profile of path b is quasi-parallel to path a, with all intermediates and transition states higher in energy than those corresponding to path a. Therefore, path b also has a net activation barrier (27.6 kcal/mol at the CCSD(T) level), which prevents the process to take place under interstellar conditions.

We will also consider another channel originated from intermediate I1, path c:

$$\mathrm{CH_3NH_2}^+ + \mathrm{HCOOH} \rightarrow \mathrm{I1} \rightarrow \mathrm{TS1/3} \rightarrow \mathrm{I3} \rightarrow \mathrm{TS3/8} \rightarrow \mathrm{I8}$$
$$\rightarrow \mathrm{NH_3}^+ + \mathrm{CH_3COOH} \quad \text{path c}$$

Once structure I1 is obtained, hydrogen atom migration from carbon to nitrogen through transition state TS1/3, leads to the most stable intermediate, I3. The rupture of the carbon–nitrogen bond and the formation of the carbon–carbon one involving transition state TS3/8, leads to the isomer I8. It should be pointed out that this reaction takes place on the same potential energy surface that the reaction of $\mathrm{NH_3}^+$ with acetic acid [34]. Isomer I8 is also reached from direct interaction between $\mathrm{NH_3}^+$ with acetic acid (isomer I1 in reference [34]). Taking into account our previous results for the reaction of $\mathrm{NH_3}^+$ with acetic acid (Fig. 3 in Ref. [34]), we can see that there are many possibilities of evolution for I8. The most favorable one is the formation of $\mathrm{NH_4}^+ + \mathrm{CH_2COOH}$ (located 17.6 kcal/mol below our reactants, at the CCSD(T) level). In addition, formation of protonated glycine from I8 is also possible (path a.1 in Ref. [34]). We have not included these processes from I8 because formation of this isomer involves the transition state TS3/8 which is clearly located (38.4 kcal/mol at the CCSD(T) level) above the reactants, and therefore none of the subsequent processes is energetically feasible under interstellar conditions.

We will emphasize that we were not able to locate paths to form ionized glycine (slightly endothermic product, see Table 1), since all our attempts led to the formation of protonated glycine.

Our theoretical results on the reaction of $\mathrm{CH_3NH_2}^+$ with formic acid show that this reaction is not a feasible process for the formation of glycine precursors under interstellar conditions.

3.2. $\mathrm{CH_3NH_3}^+ + \mathrm{HCOOH}$ reaction

We will briefly comment the energetic results for the reaction of protonated methylamine with formic acid which are collected in Table 2. The formation of c1 conformer of protonated glycine should be considered as a quasi-isoenergetic process, since it is slightly endothermic (2.9 kcal/mol at the CCSD(T) level). On the other hand, formation of conformer c2 of protonated glycine, $\mathrm{HCOHONH_2CH_2}^+$, and $\mathrm{HCOHONH_2CH_3}^+$ are clearly endothermic processes. In addition, electron transfer reaction is also endothermic.

In Fig. S5 we show the intermediates and transition states, on the $(\mathrm{NO_2C_2H_8})^+$ singlet surface, which are relevant in the reaction of $\mathrm{CH_3NH_3}^+$ with formic acid. According to our results, only the two intermediates obtained by direct interaction between $\mathrm{CH_3NH_3}^+$ and formic acid are involved in this reaction. The interaction of the hydrogen atom of the $\mathrm{NH_3}$ group through the carbonylic oxygen is more favorable than the interaction through the hydroxylic one, and consequently, the intermediate I9 is more stable than I10 (see Table 2). The higher interaction in intermediate I9 is reflected in a shorter hydrogen–oxygen bond distance.

The reaction of protonated methylamine with formic acid, whose results are reported in Fig. 2, shows two possible paths. Path a can be summarized as follows:

$$\mathrm{CH_3NH_3}^+ + \mathrm{HCOOH} \rightarrow \mathrm{I9} \rightarrow \mathrm{TS9a} \rightarrow \mathrm{NH_3CH_2COOH}^+(\mathrm{c1})$$
$$+ H_2 \quad \text{path a}$$

The $\mathrm{CH_3NH_3}^+$ molecule approaches formic acid through the carbonylic oxygen to produce intermediate I9. The subsequent formation of a carbon–carbon bond with elimination of a molecule of hydrogen through the transition state TS9a leads to protonated glycine, $\mathrm{NH_3CH_2COOH}^+$(c1). The normal mode, with imaginary frequency, corresponds to the approach of the two carbon atoms and the simultaneous elimination of $\mathrm{H_2}$ molecule. It can be seen in Fig. 2, that the formation of protonated glycine has a very high activation barrier of 83.5 kcal/mol at the CCSD(T) level, and consequently, this process cannot take place in the interstellar medium.

Intermediate I9 can also evolve through path b. In this case, elimination of molecular hydrogen from protonated methylamine forms $\mathrm{HCOHONH_2CH_2}^+$:

$$\mathrm{CH_3NH_3}^+ + \mathrm{HCOOH} \rightarrow \mathrm{I9} \rightarrow \mathrm{TS9b} \rightarrow \mathrm{HCOHONH_2CH_2}^+$$
$$+ \mathrm{H_2} \quad \text{path b}$$

Fig. 2 shows that this process is not viable in the interstellar medium because it is clearly endothermic (12.4 kcal/mol at the CCSD(T) level) and has a net activation barrier of 79.2 kcal/mol at the CCSD(T) level. A similar process where elimination of a hydrogen atom from methylamine produces $\mathrm{HCOHONH_2CH_3}^+$ is not considered here because it is clearly endothermic and therefore, not relevant in the interstellar context. In this way, formation of conformer c2 of protonated glycine, which would be reached from intermediate I10 through a similar process to path a, has not been included because it is also endothermic (see Table 2).

In their SIFT experiment Jackson et al. [32] show that the reaction of $\mathrm{CH_3NH_2}$ with $\mathrm{HCOOH_2}^+$ reacts to form the proton transfer product $\mathrm{CH_3NH_3}^+$ and HCOOH. Analyzing our previous results we can conclude that the reaction between $CH_3NH_3^+$ and HCOOH is not feasible in the interstellar medium, and therefore does not contribute to the formation of precursors of glycine in this medium.

4. Conclusions

We have carried out a theoretical study of the reactions of protonated and ionized methylamine with formic acid in order to clarify their role in the formation of glycine precursors under the conditions of the interstellar medium. The possible intermediate species, as well as the relevant transition states for these reactions, have been characterized at the MP2/cc-pVTZ level and the energies have been recalculated at the CCSD(T)/aug-cc-pVTZ level.

In general, for intermediates located on $(NO_2C_2H_7)^+$ doublet and $(NO_2C_2H_8)^+$ singlet potential energy surfaces, the interaction through the carbonylic oxygen is more favorable than the interaction through the hydroxylic one. This fact is also reflected in the corresponding O–H bond distances, shorter in the case of carbonylic oxygen.

The analysis of the corresponding potential energy surfaces demonstrates that the formation of protonated glycine is an exothermic process for the reaction of formic acid with $CH_3NH_2^+$ (−2.5 kcal/mol at the CCSD(T) level), whereas for the reaction with $CH_3NH_3^+$ is a quasi-isoenergetic one (2.9 kcal/mol at the CCSD(T) level). However, in both cases a net activation barrier is found, suggesting that both processes are not allowed under interstellar conditions.

We can conclude, based on our theoretical results, that the reactions of $CH_3NH_2^+/CH_3NH_3^+$ with formic acid cannot take place under interstellar conditions, and therefore they are not relevant processes for the synthesis of glycine in space.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2010.06.017.

References

[1] S.L. Miller, Science 117 (1953) 528.
[2] C. De Duve, Origins Life Evol. Biospheres 33 (2003) 559.
[3] G. Winnewisser, E. Herbst, Rep. Prog. Phys. 56 (1993) 1209.
[4] A.G.G.M. Tielens, S.B. Charnley, Origins Life Evol. Biospheres 27 (1997) 23.
[5] F. Combes, N.Q. Rieu, G. Wlodarczak, Astron. Astrophys. 308 (1996) 618.
[6] M.P. Bernstein, J.P. Dworkin, S.A. Sandford, G.W. Cooper, L.J. Allamandola, Nature 416 (2002) 401.
[7] C. Chyba, D. Sagan, Nature 335 (1992) 125.
[8] M.H. Engel, S.A. Macko, Nature 389 (1997) 265–268.
[9] J.R. Cronin, S. Pizzarello, Science 275 (1997) 951–955.
[10] J.R. Cronin, S. Pizzarello, Adv. Space Res. 23 (1999) 293–299.
[11] S. Pizzarello, M. Zolensky, K.A. Turk, Geochim. Cosmochim. Acta 67 (2003) 1589–1595.
[12] C. Ceccarelli, L. Loinard, A. Castets, A. Faure, B. Lefloch, Astron. Astrophys. 362 (2000) 1122.
[13] J.M. Hollis, L.E. Snyder, R.D. Suenram, F.J. Lovas, Astrophys. J. 241 (1980) 1001.
[14] J.M. Hollis, J.A. Pedelty, L.E. Snyder, P.R. Jewell, F.J. Lovas, P. Palmer, S.-Y. Liu, Astrophys. J. 588 (2003) 353.
[15] J.M. Hollis, J.A. Pedelty, D.A. Boboltz, S.-Y. Liu, L.E. Snyder, P. Palmer, F.J. Lovas, P.R. Jewell, Astrophys. J. Lett. 596 (2003) L235.
[16] J.-Y. Kuan, S.B. Charnley, H.-C. Huang, W.-L. Tseng, Z. Kisiel, Astrophys. J. 593 (2003) 848.
[17] L.E. Snyder, J.M. Hollis, R.D. Suenram, F.J. Lovas, L.W. Brown, D. Buhl, Astrophys. J. 268 (1983) 123.
[18] L.E. Snyder, F.J. Lovas, J.M. Hollis, D.N. Friedel, P.R. Jewell, A. Remijan, V.V. Ilyushin, E.A. Alekseev, S.F. Dyubko, Astrophys. J. 619 (2005) 914.
[19] M.P. Bernstein, J.P. Dworkin, S.A. Standford, G.W. Cooper, L.J. Allamandola, Nature 416 (2002) 401–403.
[20] G.M. Muñoz-Caro, U.J. Meierhenrich, W.A. Schutte, B. Barbier, A. ArconesSegovia, H. Rosenbauer, W.H.-P. Thiemann, A. Brack, J.M. Greenberg, Nature 416 (2002) 403–406.
[21] M. Nuevo, G. Auger, D. Blanot, L. Hendecourt, Origin Life Evol. Biosphere 38 (2008) 37–56.
[22] D.E. Woon, J. Phys. Chem. A 105 (2001) 9478.
[23] D.E. Woon, Astrophys. J. 571 (2002) L177.
[24] E.L. Gibb, D.C.B. Whittet, W.A. Schutte, A.C.A. Boogert, J.E. Chiar, P. Ehrenfreund, P.A. Gerakines, J.V. Keane, A.G.G.M. Tielens, E.F. van Dishoeck, O. Kerkhof, Astrophys. J. 536 (2000) 347.
[25] J.E. Elsila, J.P. Dworkin, M.P. Bernstein, M.P. Martin, S.A. Sandford, Astrophys. J. 660 (2007) 911.
[26] E. Herbst, Chem. Soc. Rev. 30 (2001) 168.
[27] S. Maeda, K. Ohno, Astrophys. J. 640 (2006) 823–828.
[28] V.A. Basiuk, K. Kobayashi, Viva Origino 30 (2002) 54–62.
[29] V. Blagojevic, S. Petrie, D.K. Bohme, Mon. Not. R. Astron. Soc. 339 (2003) L7.
[30] J.L. Snow, G. Orlova, V. Blagojevic, D.K. Bohme, J. Am. Chem. Soc. 129 (2007) 9910.
[31] D.M. Jackson, N.J. Stibrich, J.L. McLain, L.D. Fronden, N.G. Adams, L.M. Bacbcock, Int. J. Mass Spectrom. 247 (2005) 55–60.
[32] D.M. Jackson, N.J. Stibrich, N.G. Adams, L.M. Bacbcock, Int. J. Mass Spectrom. 243 (2005) 115–120.
[33] L. Largo, V.M. Rayón, C. Barrientos, A. Largo, P. Redondo, J. Chem. Theory Comp. 4 (2008) 2085.
[34] L. Largo, P. Redondo, V.M. Rayón, A. Largo, C. Barrientos, Astron. Astrophys. (2010), doi:10.1051/0004-6361/201014057.
[35] B. Zuckerman, J.A. Ball, G.A. Gottlieb, Astrophys. J. 163 (1971) L41–L45.
[36] N. Kaifu, M. Morimoto, K. Nagane, K. Akabane, T. Iguchi, K. Takagi, Astrophys. J. 191 (1974) L135–L137.
[37] S.J. Baek, K.-W. Choi, Y.S. Choi, S.K. Kim, J. Chem. Phys. 118 (2003) 11040–11047.
[38] J.E. Szulejko, T.B. McMahon, J. Am. Chem. Soc. 115 (1993) 7839.
[39] A. Largo, P. Redondo, C. Barrientos, Int. J. Quant. Chem. 98 (2004) 355–360.
[40] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[41] D.E. Woon, T.H. Dunning, J. Chem. Phys. 98 (1993) 1358.
[42] C. Gonzalez, H.B. Schlegel, J. Chem. Phys. 90 (1989) 2154–2161.
[43] C. Gonzalez, H.B. Schlegel, J. Phys. Chem. 94 (1990) 5523–5527.
[44] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[45] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millan, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelly, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Gaussian Inc., Pittsburgh, PA, 1998.