Theoretical Studies of Amino Acid Formation in the Interstellar Medium: Reactions of Formic Acid with Methylenimine and Related Cations

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Abstract

To evaluate feasibility of the gas-phase formation of glycine in dense interstellar clouds from formic acid, methylenimine and related cations, main stationary points for the reactions $HN{=}CH_2 + HCOOH \rightarrow H_2N{-}CH_2{-}COOH$, $HN^+CH + HCOOH \rightarrow HN^+{-}CH_2{-}COOH$ and $H_2N^+{=}CH_2 + HCOOH \rightarrow H_2N^+{-}CH_2{-}COOH$ have been computed at the B3LYP/6-31++G(d,p) level of theory. Although all the reactions are exothermic, they are prohibited due to the presence of transition states with positive relative energies of >40 kcal mol^{-1} and the possibility of competitive formation of side products.

Key Words: Amino acids, glycine, interstellar, gas phase, methylenimine, formic acid

Introduction

A discovery of amino acids in the interstellar medium would be of great importance for our understanding of possible pathways of the chemical evolution and the origins of Life in the Universe. Nevertheless, even after more than two decades of systematic efforts of radioastronomers, no convincing detection of even the simplest representative, glycine, has been reported [1-7]. Among more than 120 interstellar species (neutral molecules, as well as ions and radicals) identified in the interstellar clouds and circumstellar envelopes (for a review of the known interstellar organic species, see for example [5-7]), various closed and open-shell species can be envisioned as possible building blocks for amino acids. One of the best candidates is methylenimine $HN{=}CH_2$, since its molecule has a C—N bond and a high degree of hydrogenation, having much in common with amino acids. Thus it is quite understandable why soon after its identification in several Galactic objects [8-10], interstellar chemistry of methylenimine became a subject of theoretical (but not experimental yet) studies with an emphasis on the possible ways of amino acid formation [11,12]. In particular, to evaluate feasibility of the gas-phase formation of amino acid precursors (nitriles and amides) in dense interstellar clouds starting from methylenimine, we studied theoretically four reactions with the participation of HCN, CN radical, water, and OH radical [11]. Although some of them pass through positive-energy transition states, the radical reactions were found to be generally feasible, producing complex chemical species, which can be considered as precursors not only for glycine, but also for other α-amino acids of biological importance.

One has to remember, however, that the earliest suggestion by Hoyle and Wickramasinghe [13] was that the complementary building block to form glycine from methylenimine is formic acid, according to the following reaction:

$$HN{=}CH_2 + HCOOH \rightarrow H_2N{-}CH_2{-}COOH \qquad (1)$$

Indeed, the compounds were found together in different circumstellar objects with comparable (although rather low, ca. 10^{-10} relative to H_2) abundances [9,10]. Thus the main goal of the present work was to verify whether the reaction 1 is energetically feasible in the gas phase, by means of quantum chemical calculations. Since it was known, that the protonation of nitrogen-containing interstellar species can increase their reactivity in condensation reactions (see, for example [12,14]) we additionally considered two other reactions with the participation of methylenimine-related cations HN^+CH and $H_2N^+{=}CH_2$, namely

$$HN^+CH + HCOOH \rightarrow HN^+{-}CH_2{-}COOH \qquad (2)$$

$$H_2N^+{=}CH_2 + HCOOH \rightarrow H_2N^+{-}CH_2{-}COOH \qquad (3)$$

(The first of them was observed in many molecular clouds, and is considered as a very important intermediate in the interstellar organic chemistry [10,15-18]).

Computational Method

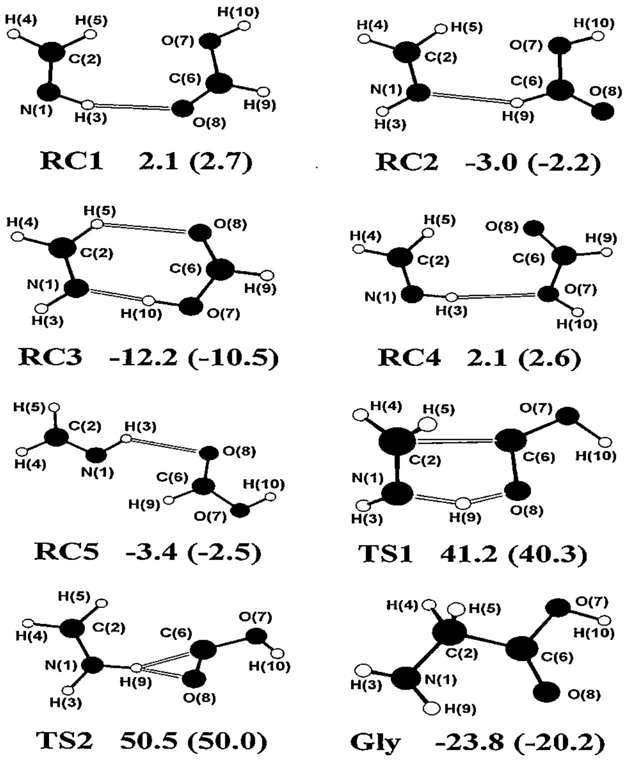
The Gaussian 98W suite of programs [19] was used. All the computations were performed with Becke's three-parameter hybrid method [20] and the exchange functional of Lee, Yang and Parr [21] (B3LYP) included in the program package, using the 6-31G(d) and 6-31++G(d,p) basis sets [22-24]. (The former was used for rough searches for stationary points; the latter, for their refinement. As it was demonstrated in our recent benchmark study [25], further extending the basis set does not influence significantly neither geometric nor energetic parameters for this type of reactions.) The choice of the B3LYP functional was due to its cost efficiency along with sufficient precision to provide valuable information on the mechanisms and energetics of interstellar reactions [26-30]. The search for transition states was carried out using the QST2 and QST3 procedures when possible (this ensures transition states found to relate unambiguously to given reaction complexes and products), with only a limited use of the TS procedure. The stationary point geometries were fully optimized and characterized as minima (0 imaginary frequencies) or first-order saddle points (1 imaginary frequency) by calculations of vibrational frequencies. Zero-point energies (ZPEs) were retrieved from the vibration frequency calculations. The features of the potential energy surfaces obtained were not affected by the ZPE-corrections. All the optimizations met the default convergence criteria set in Gaussian 98W.

Results and Discussion

Quantum mechanical studies involving polyatomic molecules of the present level of complexity is not an easy case. Building an explicit potential energy surface is hardly accomplishable due to a large number of possible competitive processes, which are difficult to account for. For this reason we limited our study to the search of most important stationary points and estimates of energetic feasibility for the reactions 1-3 (although do mention some possible undesirable pathways, if their existence directly follows from the stationary points found).

Also, the reaction complexes (or van der Waals complexes; RCs) can considerable vary in spatial structure (geometry) and energy, depending on how the initial structure for geometry optimization was built. For example, Figure 1 shows as many as five different reaction complexes possible for the reaction 1. [Geometry optimization with the 6-31G(d) basis set reveals even more, but some of them disappear with 6-31++G(d,p), when additional polarization and diffuse functions are added to enhance true van der Waals interactions.] Two of them, RC1 and RC4, appear energetically unfavorable, lying above the reactant level by more than 2 kcal mol^{-1} (see also a simplified energy profile for this reaction in Figure 4a). A feature they have in common is weak hydrogen bonds, with the interatomic distance N(1)-H(3)$\cdots$O(8) of 2.314 Å for RC1, and N(1)-H(3)$\cdots$O(7) of 2.457 Å for RC4 (bond distances and angles are listed in Table 1; the contacts longer than 2.5 Å are not shown). The H-bond N(1)-H(3)$\cdots$O(8) of 2.366 Å can be found also in RC5, which along with RC2 lays next below RC1 and RC4 (at ca. –3 kcal mol^{-1}). Finally, the most energetically favorable is the complex RC3: its energy is –12.2 (-10.5 ZPE-corrected) kcal mol^{-1} relative to the level of separated reactants. Its main difference from the other four reaction complexes is the presence of two close contacts qualified as hydrogen bonds: a very short O(7)-H(10)$\cdots$N(1) of 1.715 Å, and C(2)-H(5)$\cdots$O(8) of 2.407 Å.

When considering which of the five reaction complexes shown in Figure 1 is the most plausible for the conversion into glycine (Gly), we were looking for a structure with the shortest distances between the atoms N(1) and H(9), as well as between C(2) and C(6). In turn, priority was given to the former, since the transfer of H(9) means not only the formation of amino group, but also considerably reduces spatial obstructions for the atoms C(2) and C(6) to approach. RC2 best satisfies this criterion. Besides that, it well matches spatial orientation of the atoms in one of stable conformations of glycine itself (Gly in Figure 1). Thus, based on these two structures, we performed a QST2 search for transition state. As a result, we obtained a first-order saddle point with a high positive relative energy of 41.2 (40.3 ZPE-corrected) kcal mol^{-1}; the corresponding structure TS1 is shown in Figure 1. In TS1, H(9) atom is almost in the middle between N(1) and O(8) (the distances H(9)-N(1) and H(9)-O(8) are 1.319 and 1.182 Å, respectively), and the atoms C(2) and C(6) approached at 2.434 Å. We would like to stress once again, that the use of the QST2 and QST3 procedures for search of transition states is highly preferable to TS, since the potential energy surface is very complicated, and some first-order saddle points found by TS can be irrelevant to a given reaction pathway. Apparently, this can be exemplified by another transition state TS2 found by the latter option. It cannot lead to glycine, first of all since the atoms C(2) and C(6) are too far from each other. Neither it can directly produce other covalent bonds between heavy atoms, for the same reason; but we cannot give any definite suggestion on the side product structure. To conclude on the reaction 1, although its exothermicity is high enough, -23.8 (-20.2 ZPE-corrected) kcal mol^{-1}, and glycine has much lower energy than any of the complexes between methylenimine and formic acid, the reaction has to pass through a very high activation barrier (Figure 4a).



RC1 2.1 (2.7) **RC2 -3.0 (-2.2)**

RC3 -12.2 (-10.5) **RC4 2.1 (2.6)**

RC5 -3.4 (-2.5) **TS1 41.2 (40.3)**

TS2 50.5 (50.0) **Gly -23.8 (-20.2)**

Figure 1. Optimized structures with atom numbering and relative energies (kcal mol^{-1}; in parenthesis, ZPE-corrected values) for the most important stationary points for the gas-phase reaction $HN{=}CH_2 + HCOOH \rightarrow H_2N{-}CH_2{-}COOH$ (1) computed at the B3LYP/6-31++G(d,p) level of theory.

Another interstellar species, close generically to methylenimine, observed in many molecular clouds, and considered an important intermediate in the interstellar organic chemistry [10,15-18], is $HN^{+}CH$ cation. Ion-neutral reactions contribute very significantly into the chemistry of dense interstellar clouds, and we expected that involving this species into the gas-phase reaction with formic acid (that is, the reaction 2) will produce glycine (or more exactly, its cation HN^{+}—CH_2—COOH) more easily than through the previous process. However, this is not the case. $HN^{+}CH$ is closely related not only to methylenimine, but also to hydrogen cyanide HCN, and is believed to form through protonation of the latter. It has a linear structure, as HCN has, and loses the proton readily, so that the behavior of $HN^{+}CH$ turns to be totally distinct from that of methylenimine. At the B3LYP/6-31++G(d,p) level of theory, any starting geometry, with any mutual orientation of the reactant molecules, ends up with one of two reaction complexes shown in Figure 2. In both of them, one of the hydrogen atoms of $HN^{+}CH$ is transferred to O(6) of formic acid. In RC1, the H-transfer is partial, and H(4) remains approximately in between C(2) and O(6): the distances C(2)-H(4) and O(6)-H(4) are 1.271 and 1.310 Å, respectively (Table 1). In RC2, the distance O(6)-H(4) shortens to 1.063 Å, comparable with a normal OH bond (for example, O(7)-H(9) of 0.975 Å), whereas N(1)-H(3) elongates to 1.478 Å. It is evident that none of these two complexes possess a geometry favorable for the conversion into HN^{+}—CH_2—COOH (P in Figure 2).

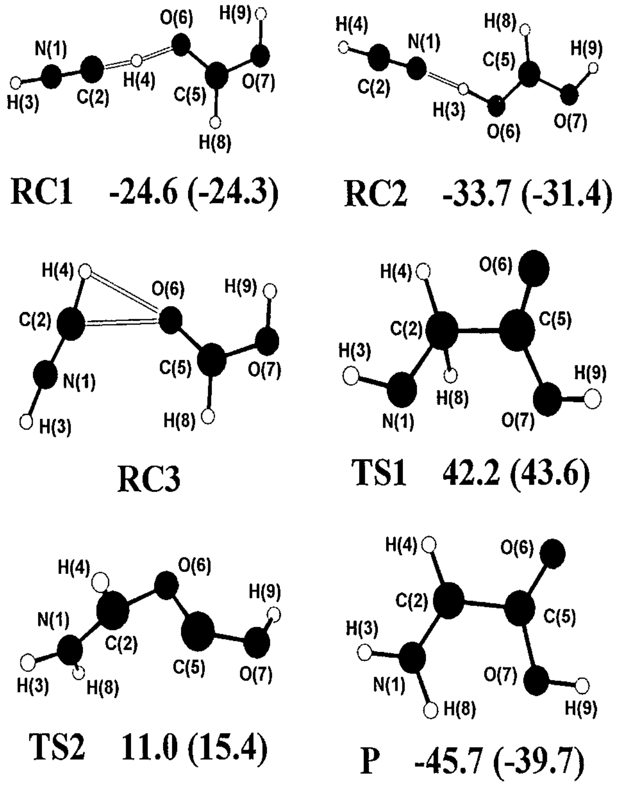


Figure 2. Optimized structures with atom numbering and relative energies (kcal mol^{-1}; in parenthesis, ZPE-corrected values) for the most important stationary points for the gas-phase reaction $HN^{+}CH$ + HCOOH → HN^{+}—CH_2—COOH (2) computed at the B3LYP/6-31++G(d,p) level of theory (RC3 geometry was obtained with the 6-31G(d) basis set).

As we mentioned, the only two complexes obtained with the 6-31++G(d,p) basis set are RC1 and RC2. At the lower theoretical level (i.e., with the 6-31G(d) basis set), one more stationary point has been found, RC3 (Figure 2, Table 1). Here the HCOOH molecule is generally closer to the C-terminus of $HN^{+}CH$, but slipping further to the H(4)-C(2)-N(1)-H(3) axis does not happen so far, due to a simultaneous interaction of the O(6) atom with H(4) and C(2) [O(6)-H(4) and O(6)-C(2) are 2.181 and 2.300 Å, respectively]. We used the 6-31G(d) geometries of RC3 [31] and P (along with a guess for transition state, otherwise calculations stopped) as input structures for the QST3 search, and found a first-order saddle point. After its refinement with 6-31++G(d,p) basis set (the geometry changed insignificantly), we obtained TS1, again with a very high positive energy, of 42.2 (43.6 ZPE-corrected) kcal mol^{-1} (see also Figure 4b). Like in the case of the reaction 1, there are other first-order saddle points corresponding to side reactions: one of them is designated as TS2 in Figure 2. The sequence of heavy atoms (N-C-O-C-O) has nothing to do with that in amino acids. Its relative energy, though remaining positive, is much lower (by ca. 30 kcal mol^{-1}) as compared to that of TS1, so that this reaction channel is much more energetically favorable than the one passing through TS1 (Figure 4b).

As was demonstrated recently [12,14], an efficient way to decrease activation barrier in interstellar reactions might be the protonation of nitrogen-containing reactants. As a matter of fact, we bore in mind essentially the same motivation changing methylenimine to $HN^{+}CH$, although it actually originates from HCN. But a more direct solution is adding proton to methylenimine molecule. The resulting species $H_2N^{+}=CH_2$, likewise methylenimine itself, offers several possibilities for the formation of complexes with HCOOH (Figure 3; for bond lengths and angles, see Table 1). The lowest-energy complex is RC1 (for a simplified energy profile for this reaction, se Figure 4c), of –19.3 (-18.4 ZPE-corrected) kcal mol^{-1}, in which the two reactants lay in the same plain. The H(10) atom, which is to be transferred to N(1), is turned outwards, thus making RC1 less suitable for the conversion into H_2N^{+}—CH_2—COOH than RC2 and RC3 are. The main difference between the latter two is orientation of the hydroxyl group O(8)-H(11) with respect to $H_2N^{+}=CH_2$. In RC2, the hydroxyl is oriented towards the carbon terminus of $H_2N^{+}=CH_2$. All the contacts are relatively long: C(2)···O(8) 2.643 Å, O(8)···H(5)= O(8)···H(6) 2.640 Å, and N(1)···H(10) 3.906 Å. In RC3, the atom closest to $H_2N^{+}=CH_2$ is the carbonyl atom O(9), with the contact distances C(2)···O(9) 2.404 Å, O(9)···H(5)= O(9)···H(6) 2.420 Å, and N(1)···H(10) 4.173 Å. We would like to point to the fact that in both cases an interesting feature can be observed: the oxygen atom forms an almost ideal pyramid with the atoms of CH_2 group, that apparently stabilizes the complexes.

An orientation of the carboxylic moiety matching the geometry RC2 and RC3, can be found in two different conformations of the product: P1 and P2 in Figure 3. Correspondingly, we performed a QST search for transition state between RC2 and P1, RC3 and P2. While for the first pair reactant—product we obtained an

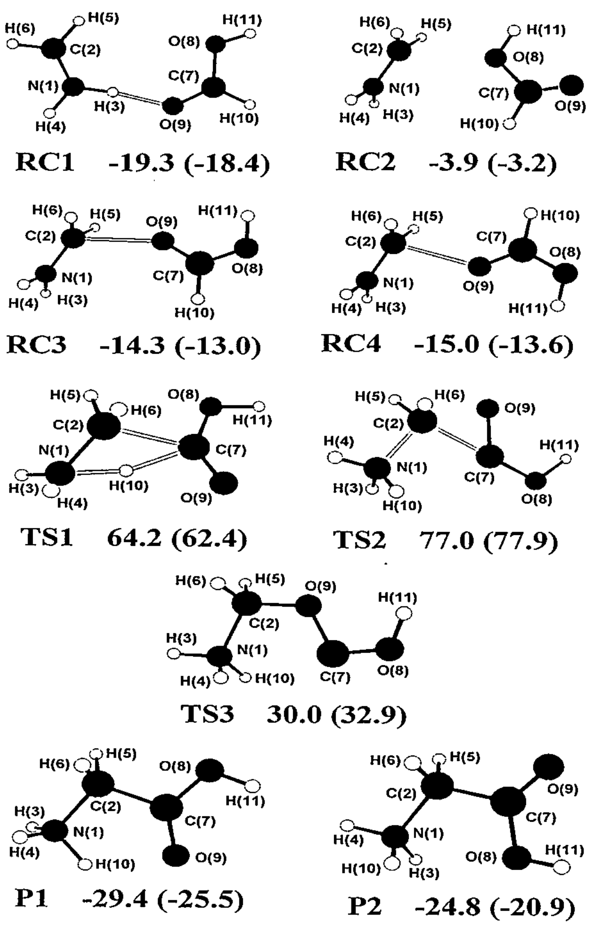


Figure 3. Optimized structures with atom numbering and relative energies (kcal mol^{-1}; in parenthesis, ZPE-corrected values) for the most important stationary points for the gas-phase reaction $H_2N^+{=}CH_2$ + HCOOH → $H_2N^+{-}CH_2{-}COOH$ (3) computed at the B3LYP/6-31++G(d,p) level of theory.

expected first-order saddle-point structure TS1, in the second case the QST2 search produced a "wrong" transition state TS3, with a N-C-O-C-O sequence of heavy atoms similar to that already observed for the reaction 2 (TS2 in Figure 2). We made another attempt to find more reasonable transition state geometry, now by moving some atoms and utilizing the TS procedure [32]. We found one (TS2 in Figure 3) with C(2)···C(7) distance of 1.834 Å, however simultaneously N(1)-C(2) stretches to 1.650 Å: this system would disrupt rather than form an amino acid backbone. We believe that neither TS1 can give rise to the protonated glycine P1, for the following reason: while being transferred to the N(1)-direction, the hydrogen atom H(10) approaches too close the carbon atom C(2) (at 1.260 Å – vs. N(1)···H(10) of 1.425 Å), so that the formation of methyl amine seems much more plausible. In any event, for all three saddle points, the relative energies are again positive, being especially high for TS1 and TS2: 64.2 (62.4 ZPE-corrected) and 77.8 (77.9 ZPE-corrected) kcal mol^{-1}, respectively (Figure 4c). Apparently, overriding such long C(2)···C(7) distances as 3.774 (RC2) and 3.503 Å (RC3) is impossible in the system under the study.

In conclusion, none of the reactions 1-3 turn to be energetically feasible in the gas phase under the interstellar conditions. Furthermore, since protonation of the nitrogen reactants is associated with the condensed-phase chemistry as well (namely with the reactions in interstellar ices [12,14]), it would be true to say that the reactions 2 and 3 reflect some features of the ice-bound chemistry [33]. Thus, the interaction of formic acid with methylenimine or related protonated species HN^+CH and $H_2N^+{=}CH_2$ can hardly produce glycine species in most interstellar environments, unless very specific catalytic reactions are involved (for example, on the surface of silicate dust particles [34,35]).

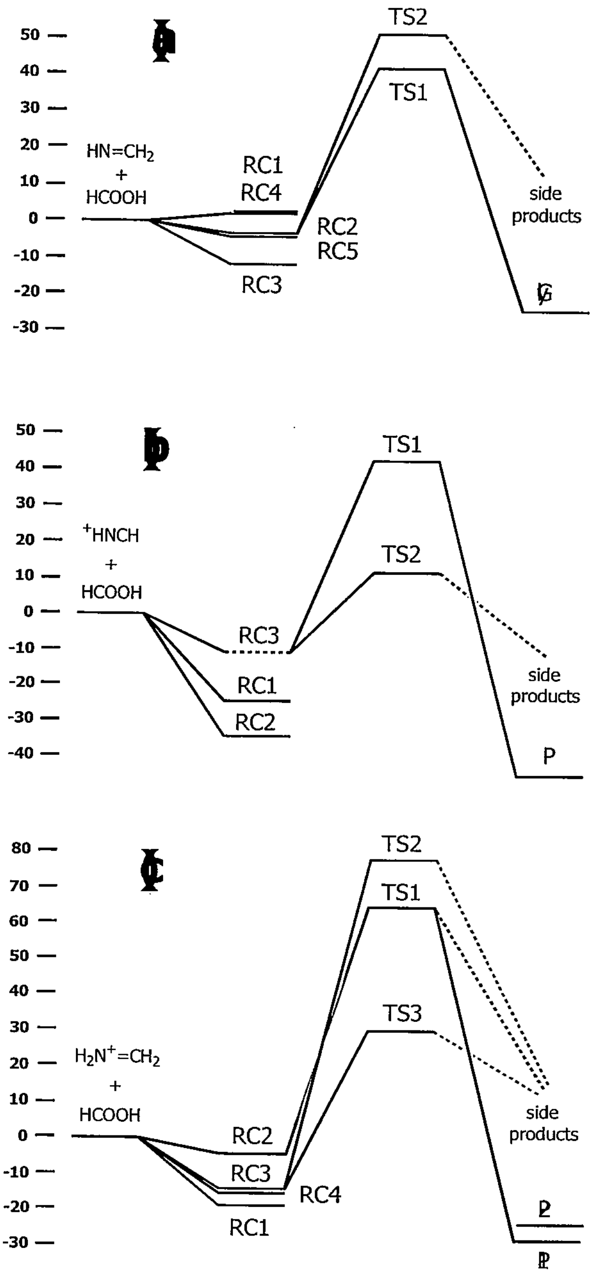


Figure 4. Simplified energy profiles for the reactions 1-3 (a-c, respectively), including reaction complexes (RC), transition states (TS) and products (P and Gly) discussed in the paper and shown in Figures 1-3. For convenience, scale is kept the same for all reactions (in kcal mol^{-1}). Dashed lines denote uncertain species (side products) and/or energetic level.

Table 1. Bond lengths and angles for reaction complexes (RC), transition states (TS) and products (P) in the reactions 1-3. For the structures with atomic numbering, see Figures 1-3.

Interatomic distances (Å)		Angles (°)	
Reaction 1			
RC1			
N(1)-C(2)	1.272	C(2)-N(1)-H(3)	110.0
N(1)-H(3)	1.026	N(1)-C(2)-H(4)	119.1
C(2)-H(4)	1.094	N(1)-C(2)-H(5)	124.4
C(2)-H(5)	1.098	H(4)-C(2)-H(5)	116.5
C(6)-O(7)	1.352	O(7)-C(6)-O(8)	122.1
C(6)-O(8)	1.202	O(7)-C(6)-H(9)	114.2
C(6)-H(9)	1.104	O(8)-C(6)-H(9)	123.6
O(7)-H(10)	0.969	C(6)-O(7)-H(10)	110.6
H(3)-O(8)	2.314	H(3)-O(8)-C(6)	135.2
		N(1)-H(3)-O(8)	159.7
RC2			
N(1)-C(2)	1.273	C(2)-N(1)-H(3)	111.5
N(1)-H(3)	1.024	C(2)-N(1)-H(9)	110.0
N(1)-H(9)	2.363	H(3)-N(1)-H(9)	138.6
C(2)-H(4)	1.097	N(1)-C(2)-H(4)	124.6
C(2)-H(5)	1.092	N(1)-C(2)-H(5)	118.6
C(6)-O(7)	1.356	H(4)-C(2)-H(5)	116.8
C(6)-O(8)	1.209	O(7)-C(6)-O(8)	123.7
C(6)-H(9)	1.099	O(7)-C(6)-H(9)	109.8
O(7)-H(10)	0.974	O(8)-C(6)-H(9)	126.5
		C(6)-O(7)-H(10)	107.4
		N(1)-H(9)-C(6)	151.8
RC3			
N(1)-C(2)	1.274	C(2)-N(1)-H(3)	113.5
N(1)-H(3)	1.022	C(2)-N(1)-H(10)	118.1
N(1)-H(10)	1.715	H(3)-N(1)-H(10)	128.5
C(2)-H(4)	1.095	N(1)-C(2)-H(4)	123.5
C(2)-H(5)	1.091	N(1)-C(2)-H(5)	117.9
C(6)-O(7)	1.326	H(4)-C(2)-H(5)	118.6
C(6)-O(8)	1.218	O(7)-C(6)-O(8)	126.1
C(6)-H(9)	1.101	O(7)-C(6)-H(9)	110.9
O(7)-H(10)	1.013	O(8)-C(6)-H(9)	123.0
H(5)-O(8)	2.407	C(6)-O(7)-H(10)	110.5
		H(5)-O(8)-C(6)	120.0
		N(1)-H(10)-O(7)	177.1
		C(2)-H(5)-O(8)	130.5
RC4			
N(1)-C(2)	1.273	C(2)-N(1)-H(3)	110.1
N(1)-H(3)	1.025	N(1)-C(2)-H(4)	118.8
C(2)-H(4)	1.093	N(1)-C(2)-H(5)	124.3
C(2)-H(5)	1.097	H(4)-C(2)-H(5)	117.0
C(6)-O(7)	1.354	O(7)-C(6)-O(8)	121.9
C(6)-O(8)	1.201	O(7)-C(6)-H(9)	114.1
C(6)-H(9)	1.104	O(8)-C(6)-H(9)	124.0
O(7)-H(10)	0.969	C(6)-O(7)-H(10)	111.0
H(3)-O(7)	2.457	H(3)-O(7)-C(6)	110.3
		H(3)-O(7)-H(10)	138.6
		N(1)-H(3)-O(7)	171.4
RC5			
N(1)-C(2)	1.271	C(2)-N(1)-H(3)	111.8
N(1)-H(3)	1.026	N(1)-C(2)-H(4)	119.1
C(2)-H(4)	1.093	N(1)-C(2)-H(5)	124.6
C(2)-H(5)	1.098	H(4)-C(2)-H(5)	116.3
C(6)-O(7)	1.345	O(7)-C(6)-O(8)	124.3
C(6)-O(8)	1.212	O(7)-C(6)-H(9)	111.2
C(6)-H(9)	1.097	O(8)-C(6)-H(9)	124.5
O(7)-H(10)	0.974	C(6)-O(7)-H(10)	107.9
H(3)-O(8)	2.366	H(3)-O(8)-C(6)	96.2
		N(1)-H(3)-O(8)	130.1
TS1			
N(1)-C(2)	1.308	C(2)-N(1)-H(3)	112.2
N(1)-H(3)	1.020	C(2)-N(1)-H(9)	102.1
N(1)-H(9)	1.319	H(3)-N(1)-H(9)	110.9
C(2)-C(6)	2.434	N(1)-C(2)-C(6)	87.6
C(2)-H(4)	1.090	N(1)-C(2)-H(4)	123.3
C(2)-H(5)	1.084	N(1)-C(2)-H(5)	119.1
C(6)-O(7)	1.330	H(4)-C(2)-C(6)	109.2
C(6)-O(8)	1.273	H(4)-C(2)-H(5)	116.6
O(7)-H(10)	0.982	H(5)-C(2)-C(6)	83.1
O(8)-H(9)	1.182	C(2)-C(6)-O(7)	153.5
		C(2)-C(6)-O(8)	91.1
		C(6)-O(7)-H(10)	110.2
		C(6)-O(8)-H(9)	103.1
		N(1)-H(9)-O(8)	151.9
TS2			
N(1)-C(2)	1.281	C(2)-N(1)-H(3)	121.7
N(1)-H(3)	1.016	C(2)-N(1)-H(9)	117.9
N(1)-H(9)	1.064	H(3)-N(1)-H(9)	120.2
C(2)-H(4)	1.086	N(1)-C(2)-H(4)	121.3
C(2)-H(5)	1.088	N(1)-C(2)-H(5)	116.4
C(6)-O(7)	1.363	H(4)-C(2)-H(5)	122.3
C(6)-O(8)	1.251	O(7)-C(6)-O(8)	116.1
C(6)-H(9)	1.771	O(7)-C(6)-H(9)	171.3
O(7)-H(10)	0.984	O(8)-C(6)-H(9)	68.9
O(8)-H(9)	1.763	C(6)-O(7)-H(10)	107.2
		C(6)-O(8)-H(9)	69.6
		N(1)-H(9)-C(6)	155.0
		N(1)-H(9)-O(8)	149.2
		C(6)-H(9)-O(8)	41.5
Gly			
N(1)-C(2)	1.455	C(2)-N(1)-H(3)	111.5
N(1)-H(3)	1.014	C(2)-N(1)-H(9)	110.5
N(1)-H(9)	1.016	H(3)-N(1)-H(9)	109.0
C(2)-C(6)	1.513	N(1)-C(2)-C(6)	110.3
C(2)-H(4)	1.095	N(1)-C(2)-H(4)	110.7
C(2)-H(5)	1.105	N(1)-C(2)-H(5)	115.1
C(6)-O(7)	1.354	H(4)-C(2)-C(6)	108.6
C(6)-O(8)	1.213	H(4)-C(2)-H(5)	106.5
O(7)-H(10)	0.973	H(5)-C(2)-C(6)	105.3
		C(2)-C(6)-O(7)	111.9
		C(2)-C(6)-O(8)	125.1
		O(7)-C(6)-O(8)	122.9
		C(6)-O(7)-H(10)	107.3

Interatomic distances (Å)		Angles (°)	
Reaction 2			
RC1			
N(1)-C(2)	1.151	C(2)-N(1)-H(3)	179.5
N(1)-H(3)	1.010	N(1)-C(2)-H(4)	179.4
C(2)-H(4)	1.271	O(6)-C(5)-O(7)	123.2
C(5)-O(6)	1.240	O(6)-C(5)-H(8)	124.0
C(5)-O(7)	1.299	O(7)-C(5)-H(8)	112.7
C(5)-H(8)	1.094	H(4)-O(6)-C(5)	127.3
O(7)-H(9)	0.978	C(5)-O(7)-H(9)	111.8
H(4)-O(6)	1.310	C(2)-H(4)-O(6)	172.5
RC2			
N(1)-C(2)	1.150	C(2)-N(1)-H(3)	173.9
N(1)-H(3)	1.478	N(1)-C(2)-H(4)	179.7
C(2)-H(4)	1.076	O(6)-C(5)-O(7)	117.7
C(5)-O(6)	1.250	O(6)-C(5)-H(8)	122.1
C(5)-O(7)	1.287	O(7)-C(5)-H(8)	120.2
C(5)-H(8)	1.095	H(3)-O(6)-C(5)	117.3
O(7)-H(9)	0.975	C(5)-O(7)-H(9)	113.9
H(3)-O(6)	1.063	N(1)-H(3)-O(6)	175.9
RC3			
N(1)-C(2)	1.146	C(2)-N(1)-H(3)	174.4
N(1)-H(3)	1.011	N(1)-C(2)-O(6)	122.4
C(2)-O(6)	2.300	N(1)-C(2)-H(4)	167.6
C(2)-H(4)	1.078	H(4)-C(2)-O(6)	70.0
C(5)-O(6)	1.226	O(6)-C(5)-O(7)	124.7
C(5)-O(7)	1.314	O(6)-C(5)-H(8)	124.4
C(5)-H(8)	1.096	O(7)-C(5)-H(8)	110.9
O(7)-H(9)	0.980	C(2)-O(6)-C(5)	139.0
H(4)-O(6)	2.181	H(4)-O(6)-C(5)	166.7
		C(5)-O(7)-H(9)	110.1
TS1			
N(1)-C(2)	1.334	C(2)-N(1)-H(3)	112.4
N(1)-H(3)	1.038	N(1)-C(2)-C(5)	117.0
C(2)-C(5)	1.585	N(1)-C(2)-H(4)	123.2
C(2)-H(4)	1.095	N(1)-C(2)-H(8)	80.6
C(2)-H(8)	1.182	C(5)-C(2)-H(8)	98.4
C(5)-O(6)	1.195	H(4)-C(2)-C(5)	113.9
C(5)-O(7)	1.311	H(4)-C(2)-H(8)	115.2
O(7)-H(9)	0.979	C(2)-C(5)-O(6)	114.6
		C(2)-C(5)-O(7)	112.9
		O(6)-C(5)-O(7)	132.5
		C(5)-O(7)-H(9)	111.8
TS2			
N(1)-C(2)	1.304	C(2)-N(1)-H(3)	120.1
N(1)-H(3)	1.016	C(2)-N(1)-H(8)	122.0
N(1)-H(8)	1.017	H(3)-N(1)-H(8)	117.7
C(2)-O(6)	1.402	N(1)-C(2)-O(6)	118.6
C(2)-H(4)	1.084	N(1)-C(2)-H(4)	120.3
C(5)-O(6)	1.338	H(4)-C(2)-O(6)	118.2
C(5)-O(7)	1.274	O(6)-C(5)-O(7)	117.3
O(7)-H(9)	0.987	C(2)-O(6)-C(5)	84.2
		C(5)-O(7)-H(9)	115.1
P			
N(1)-C(2)	1.281	C(2)-N(1)-H(3)	122.1
N(1)-H(3)	1.021	C(2)-N(1)-H(8)	120.3
N(1)-H(8)	1.024	H(3)-N(1)-H(8)	117.7
C(2)-C(5)	1.515	N(1)-C(2)-C(5)	121.8
C(2)-H(4)	1.089	N(1)-C(2)-H(4)	120.5
C(5)-O(6)	1.201	H(4)-C(2)-C(5)	117.7
C(5)-O(7)	1.334	C(2)-C(5)-O(6)	120.1
O(7)-H(9)	0.976	C(2)-C(5)-O(7)	110.6
		O(6)-C(5)-O(7)	129.4
		C(5)-O(7)-H(9)	111.1
Reaction 3			
RC1			
N(1)-C(2)	1.276	C(2)-N(1)-H(3)	122.2
N(1)-H(3)	1.060	C(2)-N(1)-H(4)	120.5
N(1)-H(4)	1.020	H(3)-N(1)-H(4)	117.3
C(2)-H(5)	1.088	N(1)-C(2)-H(5)	119.1
C(2)-H(6)	1.087	N(1)-C(2)-H(6)	120.7
C(7)-O(8)	1.329	H(5)-C(2)-H(6)	120.2
C(7)-O(9)	1.218	O(8)-C(7)-O(9)	121.1
C(7)-H(10)	1.098	O(8)-C(7)-H(10)	116.7
O(8)-H(11)	0.972	O(9)-C(7)-H(10)	122.1
H(3)-O(9)	1.619	C(7)-O(8)-H(11)	112.3
		H(3)-O(9)-C(7)	136.1
		N(1)-H(3)-O(9)	173.9
RC2			
N(1)-C(2)	1.283	C(2)-N(1)-H(3)	121.8
N(1)-H(3)	1.019	C(2)-N(1)-H(4)	121.8
N(1)-H(4)	1.019	H(3)-N(1)-H(4)	116.5
C(2)-H(5)	1.085	N(1)-C(2)-H(5)	119.6
C(2)-H(6)	1.085	N(1)-C(2)-H(6)	119.6
C(7)-O(8)	1.380	H(5)-C(2)-H(6)	120.7
C(7)-O(9)	1.195	O(8)-C(7)-O(9)	123.3
C(7)-H(10)	1.097	O(8)-C(7)-H(10)	110.2
O(8)-H(11)	0.977	O(9)-C(7)-H(10)	126.5
		C(7)-O(8)-H(11)	106.2
RC3			
N(1)-C(2)	1.286	C(2)-N(1)-H(3)	121.7
N(1)-H(3)	1.018	C(2)-N(1)-H(4)	121.7
N(1)-H(4)	1.018	H(3)-N(1)-H(4)	116.5
C(2)-O(9)	2.404	N(1)-C(2)-O(9)	119.7
C(2)-H(5)	1.084	N(1)-C(2)-H(5)	119.8
C(2)-H(6)	1.084	N(1)-C(2)-H(6)	119.8
C(7)-O(8)	1.319	H(5)-C(2)-O(9)	77.9
C(7)-O(9)	1.225	H(5)-C(2)-H(6)	120.1
C(7)-H(10)	1.096	H(6)-C(2)-O(9)	77.8
O(8)-H(11)	0.976	O(8)-C(7)-O(9)	124.7
		O(8)-C(7)-H(10)	110.9
		O(9)-C(7)-H(10)	124.4
		C(7)-O(8)-H(11)	110.6
		C(2)-O(9)-C(7)	148.0

Interatomic distances (Å)		Angles (°)	
RC4			
N(1)-C(2)	1.287	C(2)-N(1)-H(3)	121.6
N(1)-H(3)	1.017	C(2)-N(1)-H(4)	121.7
N(1)-H(4)	1.017	H(3)-N(1)-H(4)	116.6
C(2)-O(9)	2.347	N(1)-C(2)-O(9)	103.8
C(2)-H(5)	1.083	N(1)-C(2)-H(5)	119.5
C(2)-H(6)	1.083	N(1)-C(2)-H(6)	119.5
C(7)-O(8)	1.317	H(5)-C(2)-O(9)	86.2
C(7)-O(9)	1.227	H(5)-C(2)-H(6)	120.5
C(7)-H(10)	1.096	H(6)-C(2)-O(9)	86.5
O(8)-H(11)	0.976	O(8)-C(7)-O(9)	124.5
		O(8)-C(7)-H(10)	111.1
		O(9)-C(7)-H(10)	124.4
		C(7)-O(8)-H(11)	110.8
		C(2)-O(9)-C(7)	139.1
TS1			
N(1)-C(2)	1.451	C(2)-N(1)-H(3)	117.4
N(1)-H(3)	1.014	C(2)-N(1)-H(4)	118.0
N(1)-H(4)	1.014	C(2)-N(1)-H(10)	51.9
N(1)-H(10)	1.425	H(3)-N(1)-H(4)	116.2
C(2)-C(7)	1.932	H(3)-N(1)-H(10)	117.7
C(2)-H(5)	1.086	H(4)-N(1)-H(10)	120.3
C(2)-H(6)	1.089	N(1)-C(2)-C(7)	111.3
C(7)-O(8)	1.309	N(1)-C(2)-H(5)	115.3
C(7)-O(9)	1.189	N(1)-C(2)-H(6)	115.1
C(7)-H(10)	1.468	H(5)-C(2)-C(7)	103.0
O(8)-H(11)	0.981	H(5)-C(2)-H(6)	115.8
		H(6)-C(2)-C(7)	93.2
		C(2)-C(7)-O(8)	101.0
		C(2)-C(7)-O(9)	123.5
		C(2)-C(7)-H(10)	40.7
		O(8)-C(7)-O(9)	134.6
		O(8)-C(7)-H(10)	122.5
		O(9)-C(7)-H(10)	99.4
		C(7)-O(8)-H(11)	111.4
		N(1)-H(10)-C(7)	151.8
TS2			
N(1)-C(2)	1.650	C(2)-N(1)-H(3)	110.0
N(1)-H(3)	1.024	C(2)-N(1)-H(4)	111.8
N(1)-H(4)	1.030	C(2)-N(1)-H(10)	109.2
N(1)-H(10)	1.024	H(3)-N(1)-H(4)	108.6
C(2)-C(7)	1.834	H(3)-N(1)-H(10)	107.4
C(2)-H(5)	1.090	H(4)-N(1)-H(10)	109.6
C(2)-H(6)	1.086	N(1)-C(2)-C(7)	97.4
C(7)-O(8)	1.292	N(1)-C(2)-H(5)	99.8
C(7)-O(9)	1.290	N(1)-C(2)-H(6)	101.6
O(8)-H(11)	0.988	H(5)-C(2)-C(7)	124.3
		H(5)-C(2)-H(6)	115.2
		H(6)-C(2)-C(7)	112.3
		C(2)-C(7)-O(8)	174.6
		C(2)-C(7)-O(9)	59.0
		O(8)-C(7)-O(9)	119.4
		C(7)-O(8)-H(11)	112.2
TS3			
N(1)-C(2)	1.519	C(2)-N(1)-H(3)	110.2
N(1)-H(3)	1.027	C(2)-N(1)-H(4)	110.9
N(1)-H(4)	1.028	C(2)-N(1)-H(10)	110.9
N(1)-H(10)	1.028	H(3)-N(1)-H(4)	109.9
C(2)-O(9)	1.407	H(3)-N(1)-H(10)	109.9
C(2)-H(5)	1.092	H(4)-N(1)-H(10)	104.9
C(2)-H(6)	1.092	N(1)-C(2)-O(9)	111.6
C(7)-O(8)	1.288	N(1)-C(2)-H(5)	107.5
C(7)-O(9)	1.361	N(1)-C(2)-H(6)	107.5
O(8)-H(11)	0.985	H(5)-C(2)-O(9)	109.6
		H(5)-C(2)-H(6)	111.1
		H(6)-C(2)-O(9)	109.6
		O(8)-C(7)-O(9)	109.1
		C(7)-O(8)-H(11)	115.2
		C(2)-O(9)-C(7)	117.2
P1			
N(1)-C(2)	1.510	C(2)-N(1)-H(3)	112.9
N(1)-H(3)	1.024	C(2)-N(1)-H(4)	112.9
N(1)-H(4)	1.024	C(2)-N(1)-H(10)	105.1
N(1)-H(10)	1.046	H(3)-N(1)-H(4)	108.0
C(2)-C(7)	1.531	H(3)-N(1)-H(10)	108.9
C(2)-H(5)	1.092	H(4)-N(1)-H(10)	108.9
C(2)-H(6)	1.092	N(1)-C(2)-C(7)	105.6
C(7)-O(8)	1.318	N(1)-C(2)-H(5)	110.1
C(7)-O(9)	1.215	N(1)-C(2)-H(6)	110.1
O(8)-H(11)	0.976	H(5)-C(2)-C(7)	111.1
		H(5)-C(2)-H(6)	108.9
		H(6)-C(2)-C(7)	111.1
		C(2)-C(7)-O(8)	111.8
		C(2)-C(7)-O(9)	120.6
		O(8)-C(7)-O(9)	127.6
		C(7)-O(8)-H(11)	110.7
P2			
N(1)-C(2)	1.516	C(2)-N(1)-H(3)	111.1
N(1)-H(3)	1.027	C(2)-N(1)-H(4)	111.5
N(1)-H(4)	1.027	C(2)-N(1)-H(10)	111.1
N(1)-H(10)	1.027	H(3)-N(1)-H(4)	108.3
C(2)-C(7)	1.528	H(3)-N(1)-H(10)	106.3
C(2)-H(5)	1.092	H(4)-N(1)-H(10)	108.4
C(2)-H(6)	1.092	N(1)-C(2)-C(7)	112.3
C(7)-O(8)	1.351	N(1)-C(2)-H(5)	108.2
C(7)-O(9)	1.197	N(1)-C(2)-H(6)	108.2
O(8)-H(11)	0.976	H(5)-C(2)-C(7)	109.6
		H(5)-C(2)-H(6)	108.9
		H(6)-C(2)-C(7)	109.6
		C(2)-C(7)-O(8)	111.0
		C(2)-C(7)-O(9)	122.1
		O(8)-C(7)-O(9)	126.9
		C(7)-O(8)-H(11)	109.9

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31. RC3 was found only with the 6-31G(d) basis set, and disappeared with the 6-31++G(d,p) basis set. All the energies presented in the paper are relative to the reactant energy calculated with 6-31++G(d,p), which is inapplicable to RC3. According to rough estimates, RC3 energy is negative and low.
32. Although introducing or changing the geometry guess seems a forced solution, sometimes it is the only way to find a relevant transition state and to characterize the system as fully as possible. One of the most reliable procedures for finding saddle points, that is QST3 (implemented in the Gaussian package), necessarily includes such a guess. Regardless of how a particular TS was found, it is always a first-order saddle point, which is the shortest way connecting some reaction complex with some products. But it is to the researcher's judgement, whether this "some" is "the one".
33. In the condensed-phase, optimized conformations and relative energies of reaction complexes, transition states and products should be different from those in the gas-phase. Nevertheless, all the molecules and cations mentioned remain closed-shell species, which are very inert reactants.
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