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Research paper

A theoretical study of the formation of glycine via hydantoin intermediate in outer space environment

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ABSTRACT

As a possible formation mechanism of glycine in astrophysical environments, a reaction path via aminoacetonitrile and hydantoin (2,4-imidazolidinedione), which have been detected in an interstellar cloud and meteorites, respectively, were analyzed using the density functional theory. The formation of hydantoin from aminoacetonitrile via the Bücherer-Bergs reaction and the hydrolysis of hydantoin were investigated. The results showed that the catalytic water molecules significantly lower the reaction barriers for the formation of hydantoin. Although the highest barrier is still too high that the pathway is inactive in an interstellar medium, this reaction would proceed during the heating of the meteorite parent body.

1. Introduction

Currently, more than 150 molecular species have been detected in interstellar clouds, including many organic molecules [1]. To understand the evolution of these organic molecules in space [2], especially, the possible formation of prebiotic molecules, such as amino acids and nucleobases, elaborate observations and laboratory experiments have been conducted [3]. Although no amino acid has been detected in interstellar space, several amino acids and their precursors have been detected in meteorites such as the Murchison meteorite [4], and quite recently, glycine, the simplest amino acid, has been found in a comet 67P/Churyumov-Gerasimenko [5]. Many laboratory experiments have shown that amino acids can be formed under astrophysical conditions [6–8], for example, the proton irradiation [9] and the ultraviolet (UV) irradiation [10,11] of interstellar ice analogues.

Several theoretical studies using quantum chemistry calculations have reported the possible reaction paths for the formation of glycine. Basiuk examined the gas phase reactions of the formation of amino acid precursors, glycine amide and glycine amide radical, from methylenimine ($NHCH_2$), HCN, CN radical, H_2O, and OH radical via aminoacetonitrile (NH_2CH_2CN) and aminoacetonitrile radical (NH_2CHCN) intermediates and showed that glycine amide radical formation, which involves CN and OH radicals, might be plausible [12]. The hydrolyses of glycine amide with H_2O molecule and OH radical were also analyzed by Basiuk et al., and it was revealed that the activation barrier was significantly lowered in the latter case, though they concluded that this reaction is hardly possible under the cold space condition [13]. Rimola et al. analyzed the so-called Strecker-type reactions ($CH_2O + NH_3 + H_2O + HCN \rightarrow NHCH_2 + 2H_2O + HCN \rightarrow NH_2CH_2CN$ (aminoacetonitrile) $+ 2H_2O \rightarrow NH_2CH_2COOH + NH_3$) and showed that the formation of aminoacetonitrile would be possible when $NHCH_2$ is generated by radical-radical reaction ($HCN + 2H$) though the hydrolysis of aminoacetonitrile could not occur at cryogenic temperatures [14]. The formation of aminoacetonirtile (NH_2CH_2CN), the precursor of glycine in the above reaction mechanisms, from CH_2NH and HNC in the gas phase and on a model icy grain surface was studied by Koch et al., and they showed that the reaction is feasible on the icy grain surface [15].

Woon investigated a variety of reactions involving HCOOH and CH_2NH and showed that the formation of glycine by the direct reaction between these molecules is very unfavorable [16]. Maeda et al. proposed a barrier-less reaction between CO_2 and ammonium ylide, CH_2NH_3, which can be produced by the radiative association reaction of NH_3 and CH_3^+ followed by the dissociative recombination, i.e., $CH_3NH_3^+ + e^- \rightarrow CH_3NH_2 + H$ [17]. Rimola et al. analyzed the reactions between COOH radical and $NHCH_2$ or $NH_2CH_2^+$, which generate glycine radical, [18] on water ice models. Singh et al. investigated the radical-radical and radical-molecule reactions ($NH_2 + CH_2 + CO + OH \rightarrow NH_2CH_2 + CO + OH \rightarrow NH_2CH_2CO + OH \rightarrow NH_2CH_2COOH$, $NH_2 + CH + CO + OH + H \rightarrow NH_2CH + CO + OH + H \rightarrow$

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$NH_2CHCO + OH + H \rightarrow NH_2CHCOOH + H \rightarrow NH_2CH_2COOH$, and $NH_2 + CH_2 + CO + OH \rightarrow NH_2 + CH_2CO + OH \rightarrow NH_2 + CH_2COOH \rightarrow NH_2CH_2COOH$) [19]. Lee et al. studied the formation of glycine from HCN and H_2O via the amino malononitrile monoamide ($NH_2CH(CN)CONH_2$) intermediate [20].

Using a three-phase chemical model, Garrod has proposed the radical-addition mechanisms for the formation of glycine ($NH_2 + -CH_2COOH \rightarrow NH_2CH_2COOH$, $NH_2CH_2 + HOCO \rightarrow NH_2CH_2COOH$, and $NH_2CH_2CO + OH \rightarrow NH_2CH_2COOH$) [21].

Among the various possible precursors of glycine, aminoacetonitrile, which is an intermediate of the Strecker reaction, is of particular interest, since aminoacetonitrile has been observed in Sagittarius B2 [22], and has a much longer lifetime under UV photolysis than the corresponding acid, i.e., glycine [23]. Another important precursor is hydantoin (2,4-imidazolidinedione), which generates glycine after hydrolysis. Hydantoin and 5-substituted hydantoins have been found in Murchison and Yamato-791198 meteorites [24,25]. It has been shown that 5-substituted hydantoins are more stable under γ-ray irradiation compared to the corresponding amino acid [26] and generate hydantoin after photolysis by UV irradiation [27]. However, the formation process of glycine via hydantoin has not yet been fully understood. In the present study, we theoretically investigated a possible mechanism for the formation of glycine; the generation of hydantoin from aminoacetonitrile by the Bücherer-Bergs reaction [28–30] followed by the hydrolysis of hydantoin using quantum chemistry calculations because Bücherer-Bergs reaction is recently considered as a prebiotically relevant reaction [30]. Since complex organic molecules are considered to form on icy mantles of interstellar dust, the effects of catalytic water molecules on the series of the formation processes were investigated. Finally, we gave careful consideration to the reactions in an outer space environment and its timescale from an astrophysical view point.

2. Computational details

The structures of the intermediates and the transition states of the formation mechanism of hydantoin from aminoacetonitrile (the Bücherer-Bergs reaction) and the hydrolysis reaction of hydantoin to generate glycine were optimized by the density functional theory (DFT) with B3LYP functional using 6-31G* basis sets. To confirm whether the structures were true energy minima or transition states, vibrational analyses were performed for all the optimized structures. Intrinsic reaction coordinate (IRC) calculations were carried out for each transition state to verify that the transition states surely connect the expected reactant to the product. The zero point energy (ZPE) correction was considered in the reaction. We investigated the energy profiles without any catalytic water molecules and with one or two catalytic water molecules (three catalytic water molecules are also considered for some reaction steps) to model the reactions in the gas phase and on the interstellar ice surface (or in the liquid water when a high-temperature environment is considered as discussed in Section 3.3), respectively. The calculations were performed using Gaussian 09 quantum chemistry software [31].

3. Results and discussion

3.1. Formation of hydantoin by Bücherer-Bergs reaction

- In the Bücherer-Bergs reaction, aminoacetonitrile (**1**) reacts with CO_2 on the amino group to generate an intermediate

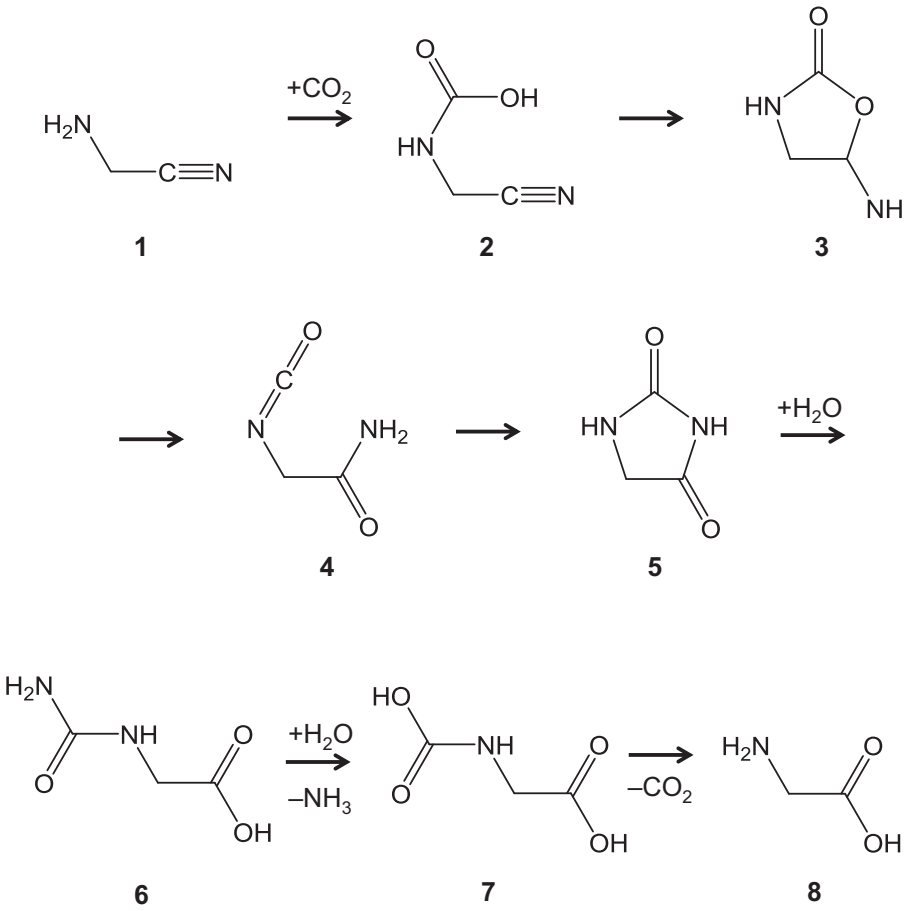

Fig. 1. Reaction mechanism of the formation of hydantoin (**5**) from aminoacetonitrile (**1**) and the hydrolysis of hydantoin to generate glycine (**8**).