

Computational studies of ion–neutral reactions of astrochemical relevance: Formation of hydrogen peroxide, acetamide, and amino acetonitrile



Zhibo Yang*, Ning Pan

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, United States

ARTICLE INFO

Article history:

Received 5 May 2014

Received in revised form 24 October 2014

Accepted 25 October 2014

Available online 5 November 2014

Keywords:

Astrochemistry
Density functional theory
Ion–neutral reactions
Gas-phase reactions
Surface reactions

ABSTRACT

Aromatic hydrocarbons (AHs) and their derivatives have been suggested as the building blocks of interstellar dust grains and are responsible for the evolution of astrobiological molecules via surface reactions in space. Gas-phase studies of molecules and ions known to exist in space are crucial to understand relevant ion–molecule reactions and the generation of new species. Reactions catalyzed by large species such as AHs remain relatively unexplored. Our computational studies focus on the energetics and reaction mechanisms of the formation of representative molecules (i.e., hydrogen peroxide, acetamide, and amino acetonitrile) that are critical for the origin of water and amino acids in the universe. Calculations have been carried out using Gaussian 09 to obtain the structures, energetics, and reaction mechanisms to investigate the formation of hydrogen peroxide (H_2O_2), acetamide ($\text{CH}_3\text{C}(\text{O})\text{NH}_2$), and amino acetonitrile ($\text{NH}_2\text{CH}_2\text{CN}$). Our results suggest that there are energetically accessible reaction pathways leading to the formation of these molecules through species which have been discovered in the interstellar medium (ISM). Ionized benzene and polycyclic aromatic hydrocarbons (PAHs) can act as catalysts to facilitate the formation of astromolecules. The theoretical studies can enhance our understanding of ion–molecule reactions that are relevant to the formation of important astromolecules in the gas phase, and provide a new way to investigate the formation of polyatomic molecules on surfaces of dust grains such as large PAHs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Ion–molecule reactions play crucial roles in molecular synthesis in our galaxy [1–3]. About 180 distinct molecules have been identified in the interstellar medium (ISM) and the circumstellar envelope. Although the majority of these detected molecules exist as neutral species, the photoionization of neutral species readily occurs in some stellar regions due to the existing radiation (UV, X-ray, γ -ray, etc.) [4]. To date, ~20 distinct ions (e.g., CO^+ , H_2COH^+ , CN^- , and C_3N^-) have been detected, suggesting that ions are involved in astrochemical reactions and that they are critical components for the evolution of the universe. In addition to small ions, larger species such as ionic PAHs likely exist in space and contribute to astrobiological evolution [5]. Polycyclic aromatic hydrocarbons (PAHs), long carbon-chain molecules, and fullerenes, have been suggested as potential carriers of the Diffuse Interstellar

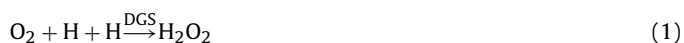
Bands (DIBs), [6,7] but their chemistry remains unexplored. Recent detection of fullerenes (C_{60} and C_{70}) in a young planetary nebula raises great demand for further understanding of their chemistry [8,9]. Among these species, PAHs are believed to be the most abundant free organic molecules in space, and they are the major reservoir of carbon in our galaxy [10].

As the smallest interstellar dust grains, PAHs are suggested to act as the nucleation sites needed for the formation of carbonaceous dust particles [11], and they are likely responsible for the astrobiological evolution of the ISM [5]. Due to the ever-present radiation in the ISM and the low ionization energies of PAHs (~6–10 eV), these species can exist as molecular cations upon removing an electron by radiation. For example, cationic anthracene ($\text{C}_{14}\text{H}_{10}^{+\bullet}$) [12] and Buckminsterfullerene ($\text{C}_{60}^{+\bullet}$) [13] have been detected in the ISM. Therefore, neutral and ionic PAHs are very likely to participate in the subsequent ion–neutral reactions [14–16]. For example, hydrogen atoms diffuse very rapidly in space, whereas they become very efficient reactant on surfaces [2]. Previous experimental and theoretical studies suggest that aromatic hydrocarbons (AHs) cations may play a role as the catalyst in the formation of H_2 through

* Corresponding author. Tel.: +1 405 325 1772; fax: +1 405 325 6111.
E-mail address: zhibo.yang@ou.edu (Z. Yang).

the recombination of H atoms [13–16]; however, similar studies of polyatomic molecules have not been carried out to the best of our knowledge.

Current experimental and theoretical studies have mainly focused on “gas-phase” reactions (i.e., all species in the gas phase) of astrochemistry relevance. However, important “gas-phase” reactions can, and do, occur on particulate surfaces. For example, some molecules (e.g., H₂, hydrogen peroxide, and acetamide) are very likely formed on surfaces [2,14,15,17,18]. Among these molecules, hydrogen peroxide (H₂O₂) was detected in the interstellar space in 2011 [17], and it has been proposed that H₂O₂ is formed on dust grain surfaces (DGS) through reactions involving oxygen molecules and hydrogen atoms (reaction 1), although the mechanism of formation of this molecule is not well understood. Hydrogen peroxide is critical for the generation of H₂O, a key for the life in the universe, through reactions on DGS (reaction 2).



Such surface-modulated processes play very important roles in astrochemistry, but only limited studies have been conducted due to the complex mechanisms of reactions on surfaces.

As the building blocks of large dust grains, PAHs are likely the appropriate model systems to investigate the surface reactions. However, it is surprising that not much PAH-dependent chemistry has been performed. Using carefully designed model systems (*vide infra*) we have performed suitable theoretical calculations to gain fundamental insight into the basic reaction mechanisms on surfaces relevant to astrochemistry. In particular, we focused on three molecular species that have been detected in space (e.g., hydrogen peroxide, acetamide, and amino acetonitrile), which are critical for the production of the essential molecules of life (e.g., water and amino acids). Our computational studies can provide molecular-level understanding of the role of AHs in the molecular synthesis of astromolecules, as well as shed light on our novel approach to investigate surface reactions through gas-phase studies. Our studies are classified into two major research themes:

- (1) Studies of the relevance of benzene to astrochemistry. These studies will include benzene radical cation (C₆H₆^{+•}) and a number of neutral molecules observed in the ISM, and the corresponding reactions are expected to produce hydrogen peroxide and acetamide. Hydrogen peroxide is critical for the generation of water in the universe [17], whereas acetamide is regarded as a precursor of amino acids [19–21].
- (2) Approaches of surface synthesis of amino acetonitrile, a precursor of amino acids [19–21], through the gas-phase reactions involving PAH species (i.e., naphthalene). These reactions in the gas-phase are expected to exhibit as model systems to investigate surface reactions.

Studying the synthetic mechanisms and reactivities of these and related astromolecules will significantly contribute to the unraveling, in a broader sense, of the complex astrochemistry related to the origin of life in the universe.

2. Theoretical calculations

Theoretical calculations are usually employed to provide insight into the reaction mechanisms at the molecular level. Gaussian 09[22] is currently accessed through the Supercomputing Center for Education & Research (OSCE) at the University of Oklahoma. Density functional theory (DFT) methods, such as B3LYP, have been extensively utilized to calculate large systems such as PAHs. All

calculations have been carried out at the B3LYP/aug-cc-pVDZ level of theory for geometry optimization and frequency analysis. These calculations provide us with information on the structures, energetics, and reaction mechanisms to enhance our understanding of relevant experiments in the future.

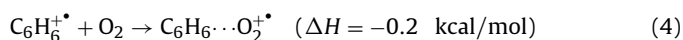
3. Results and discussion

3.1. Relevance of benzene to astrochemistry

Benzene, the simplest aromatic hydrocarbon, has been detected in the proto-planetary nebula [23]. Due to its low ionization energy (9.24 eV), it is very likely that the molecular cation of benzene (C₆H₆^{+•}) can be directly generated from neutral benzene by intermediate UV fluxes in space. Previous experimental and theoretical studies of benzene and small PAHs indicate that a variety of species, including the molecular cations and fragments, are formed through UV photoionization and dissociation under vacuum [24,25]. Therefore, it is very likely that C₆H₆^{+•} exists in certain regions in the ISM and participates in ion–neutral reactions near the molecular clouds. Similarly, the charged carbonaceous dust grains (e.g., large PAHs) are likely to be produced by UV photoionization and responsible for surface reactions. Studying reactions involving C₆H₆^{+•} will unravel its role in ion–molecule reactions, and provide a starting point for surface reactions on larger PAHs and carbonaceous dust grains.

3.1.1. Formation of hydrogen peroxide

It has been suggested H₂O₂ is formed on dust grain surfaces (DGS) (reaction 1) [17,18], but a direct study of the reaction mechanisms remains a great challenge. In contrast, the related gas-phase reactions occur in a simpler environment, and the relevant studies of appropriate model systems can provide the framework for a more complete understanding of the real reaction mechanisms on surfaces. Our computational studies utilize benzene radical cation (C₆H₆^{+•}) and its derivatives, which may play important roles as the reaction media or catalysts in ion–neutral reactions in space. The diatomic oxygen molecule has been detected in space, and the oxygen atom is the most abundant atomic species after H and He [1–3]. In dense molecular clouds, oxygen exists as discrete diatomic molecules, whereas in diffuse clouds it mainly appears as single O-atoms [26]. Ion–neutral reactions are likely to occur in the boundary regions between dense and diffuse clouds [1]. For example, benzene radical cation (C₆H₆^{+•}) can be generated upon UV radiation in space (reaction 3), and its sequential ion–neutral reaction with ground state (triplet) oxygen (O₂) is expected to form the complex C₆H₆··O₂^{+•} (reaction 4).



According to our calculations performed at the B3LYP/aug-cc-pVDZ level of theory, reaction 4 is a barrierless exothermic association reaction ($\Delta H = -0.2$ kcal/mol). We have also carried out calculations at the CCSD(T)/aug-cc-pVDZ level of theory, and obtained a slightly higher binding energy in the C₆H₆··O₂^{+•} complex ($\Delta H = -1.7$ kcal/mol, reaction 4). Nevertheless, this is a weak interaction, such that the formation of the C₆H₆··O₂^{+•} complex is disfavored at higher temperatures due to the reduced free energies of binding. However, the van der Waals dispersion is expected to play an important role in stabilizing the ion–molecule complexes involving larger PAHs. Therefore, large PAH cations are very likely to absorb O₂ under typical temperatures (15–20 K) in the dense clouds, which are largely composed of molecular species, in the ISM.[1]

In the following exothermic association reaction ($\Delta H = -75.8$ kcal/mol), a hydrogen atom can be added to a

Download English Version:

<https://daneshyari.com/en/article/1192117>

Download Persian Version:

<https://daneshyari.com/article/1192117>

[Daneshyari.com](https://daneshyari.com)