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A computational chemistry investigation of the intermolecular interaction between ozone and isothiocyanic acid (HNCS)

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ABSTRACT

The binding energy and geometrical structure of all the possible dimeric systems of isothiocyanic acid (HNCS) with ozone have been investigated in the gas phase, theoretically. Six minima located on the singlet potential energy surface of the HNCS–ozone system at the MP2 level with binding energies (corrected with ZPE and BSSE) in the range 492.29–531.40 kcal/mol. All intermolecular interactions in the HNCS–ozone system are significant interactions with remarkable E_I values.

Keywords: computational; isothiocyanic acid; ozone; interaction; MP2

INTRODUCTION

Ozone is a considerable part of the atmosphere and has exuded to play a significant role in the Earth's global climate change [1]. Head ozone density is in the stratosphere at 20 km-25 km altitude. Since 1985, it has been reduced in the stratosphere and southern mid latitudes such that people began to pay consideration to its evacuation phenomena [2]. The global mean total column ozone condensation from 1997 to 2001 was approximately 3% below the ozone mean amounts before 1980 [3]. Global ozone in the upper stratosphere decreased between 1979 and 1995, with the largest decrement between 10 and 15% near 40 km over mid-latitudes [4,5]. According to ozone's role as a defensive layer opposite UV radiation and its essential role for life on the earth, the scanning and controlling the quantity of pollutants in the atmosphere are of great importance in modern society [6-8].

The isothiocyanic acid (HNCS) is a sulfur analog of the famous isocyanic acid HNCO [9,10]. Because the mentioned kinds acts a significant role in both atmospheric and combustion processes, it has attracted remarkable consideration [11–16]. At the same time HNCS and its derived free radical NCS are also significant intermediates of sulfur-containing fuel combustion proceeding, they can take part in the process of elimination the toxic NO_4 compounds from rapid combustion exhaust gas too [9,14]. Theoretical investigation of the reaction mechanism for small molecules with HNCS is a hot topic in recent years [17–19].

Since the latter species play a significant

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role in the earth's atmosphere, it is important to receive atmospheric information about their behaviors. In the present study, we explore the dimers involving intermolecular interactions of HNCS with the ozone molecule to prepare a precise examination of the stability and property of the HNCS–ozone system.

COMPUTATIONAL METHODS

Ab initio calculations are performed using the Gaussian 03 programs [20]. The geometries of ozone and isothiocyanic acid monomers and all the dimers are fully optimized by employing the Moller–Plesset second-order perturbation (MP2) method [21] with Dunning's correlation consistent basis set, cc-pVDZ [22]. The interaction energy *(E_I)* was calculated as the difference between the total energy of the dimer and the sum of total energies of the ozone and isothiocyanic acid monomers. The dimers possess no imaginary frequencies. Also, the calculation of the vibrational frequencies leads to the evaluation of zeropoint energies (ZPEs). The counterpoise (CP) method [23] has been used to take into account the basis set superposition error (BSSE) in the calculation of the energies and presents the energies without any BSSEs.

RESULTS AND DISCUSSION

The electronic structures of the isolated ozone and isothiocyanic acid monomers were used to generate a set of dimers. The symbol S shows the dimers of the HNCS–ozone system. The binding energies are corrected with BSSE and ZPE at the MP2/cc-pVDZ level. The optimized geometries of all the dimer systems and their ranking are shown in Figures 1 and 2, respectively. Also, the calculated binding energies and interaction data for different dimer systems at the MP2 level were listed in Tables 1 and 2, respectively.

The association of the HNCS and the ozone monomers causes to the organization of six minima, S1 to S6. The binding energies of the HNCS–ozone dimers involving BSSE and ZPE corrections lie in the range of -492.29 to -531.40 kcal/mol at the MP2/ccpVDZ level.

Table 1. Binding energies (kcal/mol) of dimers obtained in the HNCS–ozone system at the cc-pVDZ level

System	**Optimization MP2/cc-pVDZ E_I**	**E_I + BSSE**	**E_I + BSSE + ZPE**
S1	-530.25	-530.25	-530.22
S2	-531.43	-531.43	-531.40
S3	-529.96	-529.96	-529.93
S4	-527.59	-527.59	-527.62
S5	-529.83	-529.83	-529.80
S6	-492.25	-492.25	-492.22

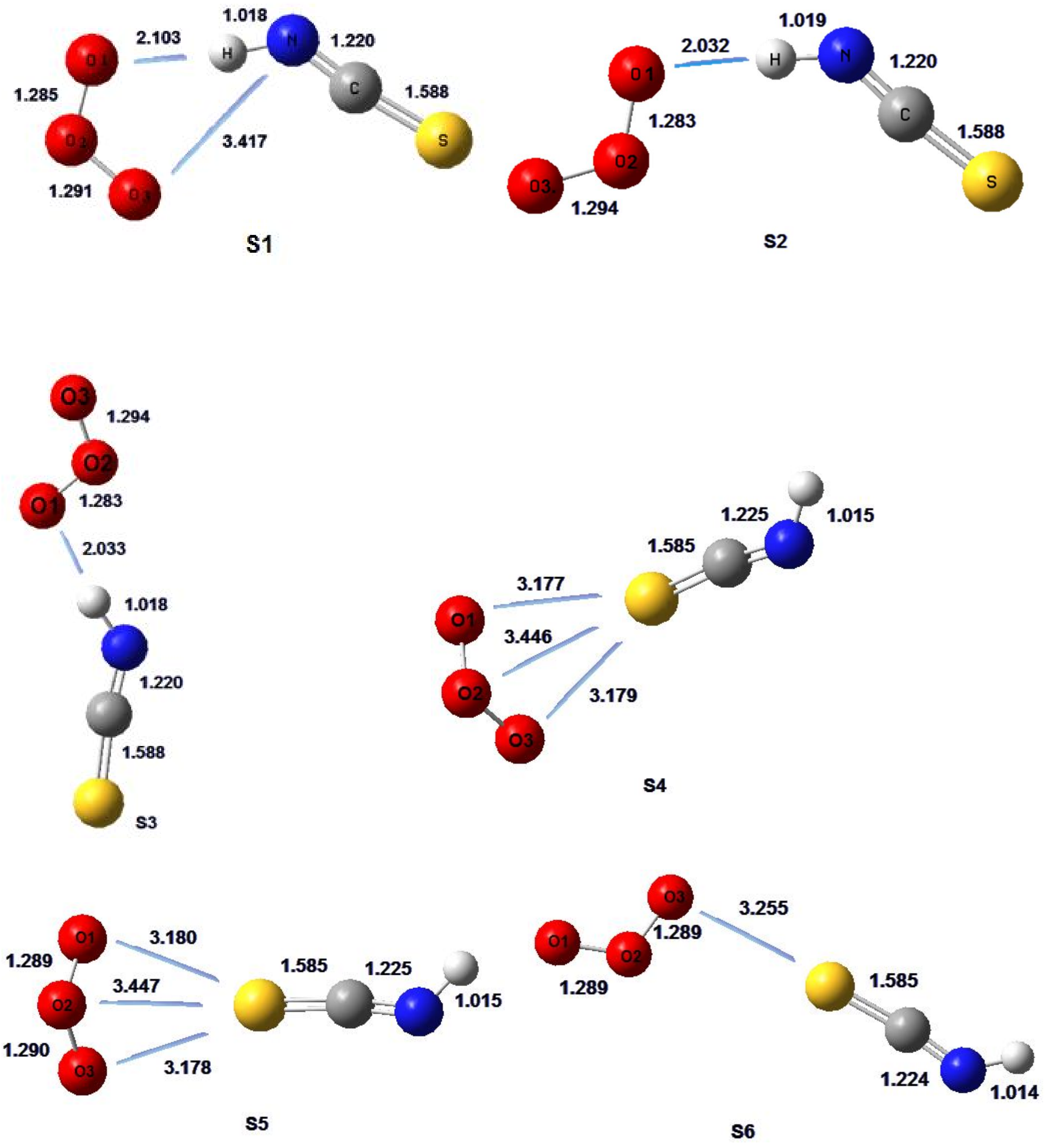

Fig. 1. Optimized geometries of all the HNCS–ozone systems at the MP2/cc-pVDZ level (the bond lengths are in angstrom).

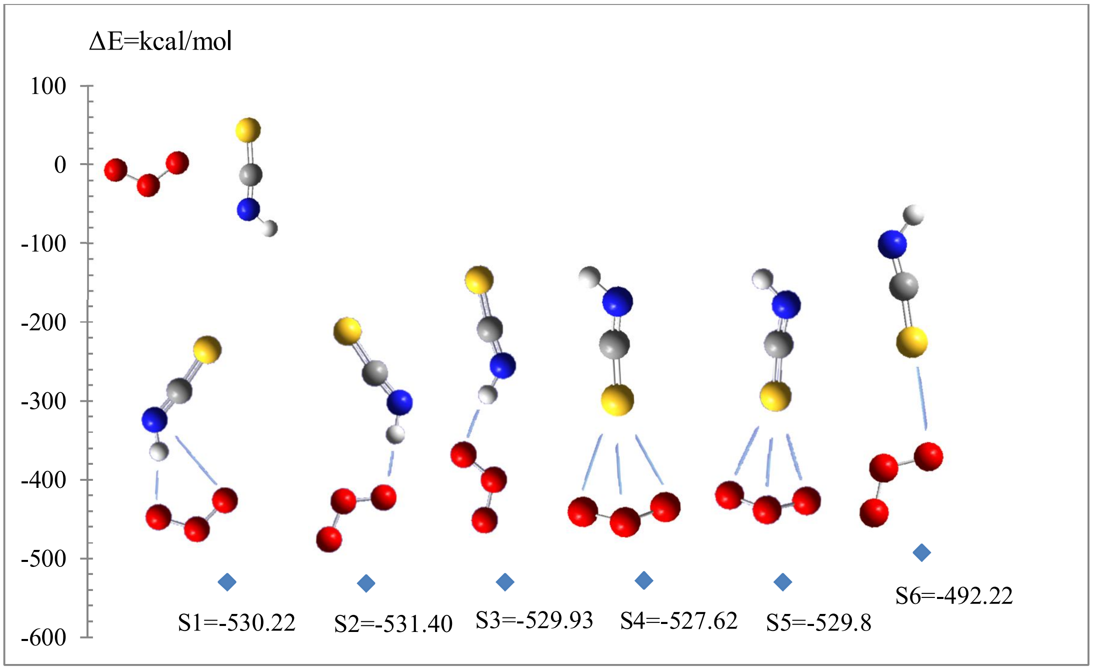

Fig. 2: The E_I levels for possible dimmers obtained in the HNCS–ozone system in terms of E_I + BSSE + ZPE at the MP2/cc-pVDZ level.

Table 2. Interatomic distances (Å) calculated for possible dimmers at the MP2/cc-pVDZ level

System	Interaction	Interatomic dictance
S1	O1…H	2.103
	O3…N	3.417
S2	O1…H	2.032
S3	O1…H	2.033
S4	O1…S	3.177
	O2…S	3.446
	O3…S	3.179
S5	O1…S	3.180
	O2…S	3.447
	O3…S	3.178
S6	O3…S	3.255

It is obvious that S2 is the most stable dimer of the HNCS–ozone system with a binding energy 531.4 kcal/mol after corrections of BSSE and ZPE at the MP2/cc-pVDZ level. Figure 1 presents that the system of S2 establishes when O1 and O3-atoms of the ozone monomer attack H- and N-atoms of the HNCS monomer to develop the interactions of O1…H and O3…N, respectively. The interactions of O1…H and O3…N are 2.103 and 3.417 Å at the MP2/cc-pVDZ level, respectively. As presented in Table 2, the binding energy of the S1 system is 1.18 kcal/mol less than that of the S2 system at the MP2/cc-pVDZ level. Figure 1 shows that in the S1 system, the imtermolecular interaction is O1…H with 2.032 Å at the

MP2/cc-pVDZ level. As shown in the figure 1, the atomic connectivity of the S2 system is similar to the S3 which both of them contain intermolecular interaction of O1…H. Their main difference is the position of the ozone molecule around the HNCS molecule. It shows that the spatial position of the ozone molecule and resulting interaction in the S2 system leads a more stable system of the S2. S4 system contains three interactions between the ozone and the HNCS molecule. In the S4 system, S-atom of the HNCS molecule approaches threes O-atom of ozone molecule to form S…O interactions with bond length 3.177, 3.446 and 3.179 Å. This system has binding energy 527.62 kcal/mol (corrected with BSSE and ZPE) at MP2/cc-pVDZ level. S5 system has the fourth stability order among six systems captured for the HNCS–ozone system. It lies 529.80 kcal/mol below the initial molecules of the HNCS and the ozone. As shown the figure 1, three interactions of S…O with interaction distance 3.180, 3.447 and 3.178 have been detected in the S5 system. The comparison between S4 and S5 systems demonstrates that atomic connectivity of them is equal. In S4 and S5 systems, the S-atom of the HNCS molecule reacts with the three O-atoms of the ozone monomer to produce the S…O interactions. It is obvious that, in spite of similar atomic connectivity, the S5 system (527.80.24 kcal/mol) is 2.18 kcal/mol stable than 4 (529.80 kcal/mol) at the MP2/ccpVDZ level. The atomic connectivity of the S6 system shows only one interaction between S in HNCS molecule and O3 in the ozone. The binding energy of the S6 is 429.22 kcal/mol at the MP2/cc-pVDZ level. S6 system is the least stable system of the HNCS–ozone dimer. In S6 sytem, the attack of the S atm in the HNCS on O3-atom of the ozone molecule causes to the O3…S interaction with the bond length 3.255 Å. Vessally et al., [24] investigated the intermolecular interactions of the HNCS–SSO system at the MP2/aug-cc-pVTZ level. They have shown nine stable complexes for the HNCS–SSO system. Our study demonstrates obvious results in comparsion of the Vessally's investigation. The binding energy of the most stable system (S2) of the HNCS–ozone system corrected with only BSSE and ZPE (531.40 kcal/mol) is much more than that of the most stable HNCS–SSO system (19.12 kcal/mol). This means that the HNCS– ozone system has much more important effect than the HNCS–SSO system in the atmosphere. Wierzejewska and Wieczorek [25] explored the intermolecular interactions of the HNCS–N_2 and HNCS–Xe systems at the MP2 level. The most stable systems acquired for two systems of the HNCS–N_2 and the HNCS–Xe [25] contain an interaction from HN group of the HNCS molecule with either the Xe (in the HNCS–Xe system) or N_2 molecule (in the HNCS–N_2 system). It is in good agreement with our study which shows intermolecular interactions for the S2 systems as the most stable dimer of the HNCS–ozone system. In this study, we can see all the possible intermolecular interactions in the HNCS–ozone system except O..C interaction. It means that none of the HNCS–ozone systems contain an interaction between either the atoms of the ozone and the C-atom of the HNCS molecule.

CONCLUSION

The interaction of ozone molecule toward HNCS molecule was studied by using MP2 calculations at the cc-pVDZ level of theory. It was found that the HNCS-ozone dimer system show considerable changes after interatomic interactions with E_I= -531.40 kcal/mol after BSSE and ZPE corrections. Therefore, it is obvious that the dimer systems in this study are so much stable than that of Vessally's investigation for HNCS-SSO dimeric system or Wierzejewska and Wieczorek investigation for HNCS–Xe and HNCS–N_2 system.

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