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# Theoretical investigation on atmospheric reaction of atomic O($^3$P) with acrylonitrile

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ABSTRACT

The theoretical study has been performed on the mechanisms and kinetics for the O($^3$P) + $CH_2{=}CHCN$ reaction. The reaction mechanism indicates that O($^3$P) addition to C=C double bond to form the activated adducts IM1($OCH_2{-}CHCN$) and c2-IM1($CH_2{-}CHOCN$) over the low barriers of TS1 and c2-TS1. Additionally, direct hydrogen abstraction and O($^3$P) atom addition to C atom of —CN group have been found. Multichannel Rice–Ramsperger–Kassel–Marcus theory are employed to calculate the overall and individual rate constants over a wide range of temperatures and pressures. The branching ratios indicate that P1(H + CHOCHCN) is the major product at 200–3000 K.

## 1. Introduction

Unsaturated nitriles are widely used in industry [1]. As a consequence of the widespread use of these unsaturated nitriles, they would release into the atmosphere during their manufacture. Biomass combustion is an additional important emission source of many unsaturated nitriles to the atmosphere [2]. Acrylonitrile has been widely used in the production of plastics, nitrile rubbers, nitrile barrier resins, adiponitrile, and acrylamide. And acrylonitrile will release into atmosphere to contribute the formation of poisonous gas like hydrogen cyanide which will lead to environmental pollution [3]. In addition, the oxygen atom is one of the most cosmically abundant atomic species under atmospheric condition. In order to assess the oxidation progress of acrylonitrile, we study the mechanism and kinetics of the O($^3$P) + $CH_2{=}CHCN$ reaction.

The reaction of acrylonitrile with O($^3$P) was only previously studied by Upadhyaya et al. using the fast-flow technique in 1997 [4]. Rate constants was $(4.9 \pm 1.0) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at the pressure of 1.2–1.7 Torr and 298 K. In their work, the O($^3$P) atom addition to C=C was investigated simply using the semi-empirical MNDO method and HF/STO-3G level. The major channel was thought to be the formation of a biradical($O{-}CH_2{-}CHCN$).

There is no specific theoretical study for the reaction of O($^3$P) with acrylonitrile till now. Based on our previous works about the reactions of O($^3$P) with saturated nitriles RCN(R = $C_2H_5$, $CH_3$, $CF_3$) and OH with $CH_2{=}CHCN$ [5–8], how is the mechanisms and kinetics of O($^3$P) with $CH_2{=}CHCN$? We present detail quantum calculations for potential energy surface (PES). Moreover, multichannel RRKM theory [9] has been employed to calculate the rate constants over a broad range of temperatures and pressures.

## 2. Computational methods

All the electronic structure calculations are carried out using the GAUSSIAN 09 suits of programs [10]. Geometry optimizations and frequency calculations are performed using BHandHLYP [11,12] and M05-2X [13] functional with triple-$\zeta$ 6-311++G(d,p) basis set. Herein, BHandHLYP and M05-2X method show much better to describe the interaction reactions and have been proved effectiveness [14–17]. All stationary points are characterized by harmonic vibrational frequency analysis (number of imaginary frequencies, NIMAG, 0 for minima and 1 for transition states). The intrinsic reaction coordinate (IRC) method is used to construct the minimum energy paths from transition state structures to the corresponding local minima [18]. The energies for the PES were refined by the single point calculations using the BMC-CCSD methods [19]. It has been shown that the BMC-CCSD method gives accurate energies

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for the reactions of nitriles with free radicals [5–8].To ensure that all stationary points were well treated with a single-reference-based wave function, the $T_1$-diagnostic value was evaluated for important transition states and intermediates using the CCSD(T)/cc-pVTZ method. The $T_1$ diagnostic value gives a qualitative assessment of the significance of nondynamic correction. For closed-shell systems, values exceeding 0.02 are suspect. However, Lee and Taylor [20] suggested that $T_1$-diagnostic values for open-shell systems may be larger. A number of studies have shown that the multireference wave function is significant if the $T_1$ diagnostic value calculated is greater than 0.045 [20–23]. The largest $T_1$ value is 0.047 for c-TS1, while the others are less than 0.045.

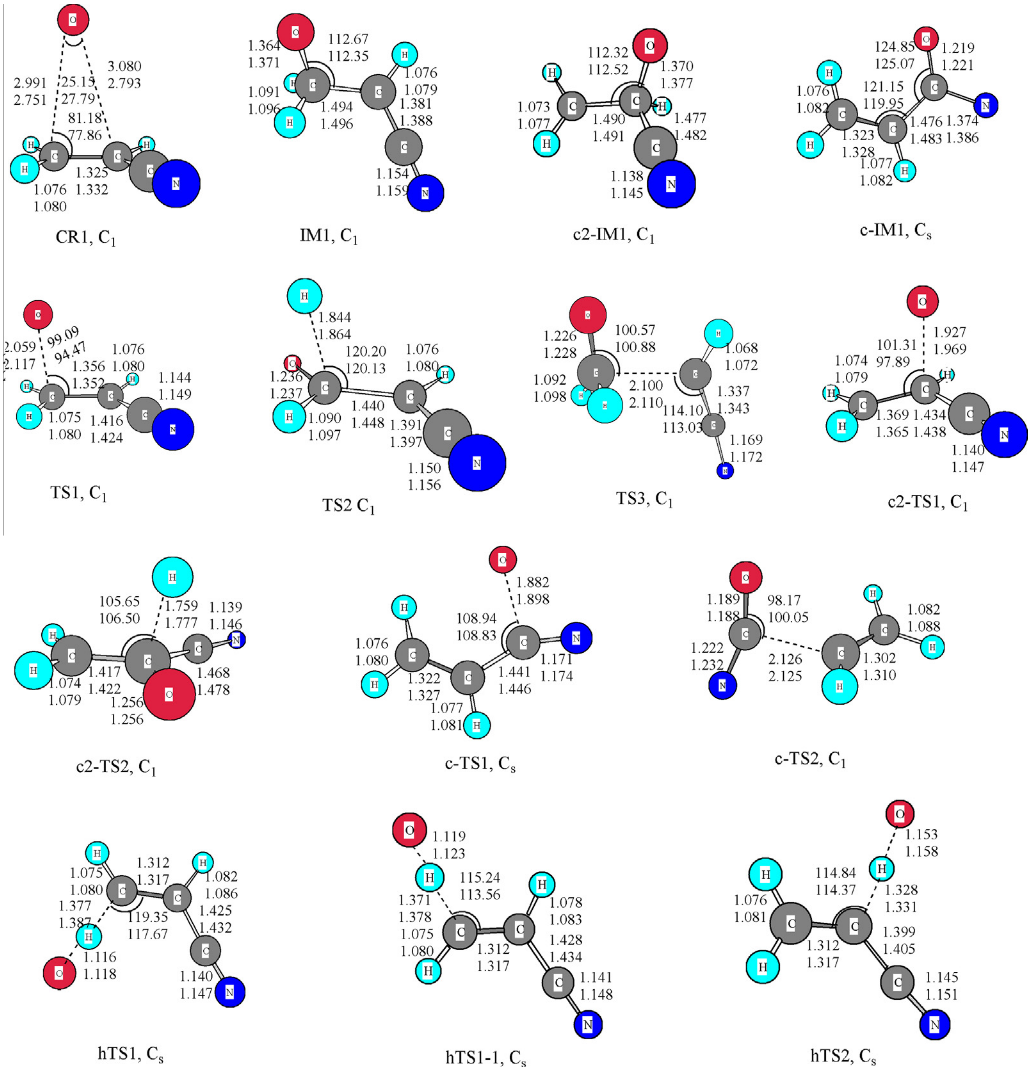
Rate constants for the important product channels have been calculated statistically using multichannel RRKM theory that had been successfully used to deal with some complex reactions [24–26].

## 3. Results and discussion

### 3.1. The comparisons with different calculation methods

In order to test the reliability of BHandHLYP and M05-2X, the critical intermediates and transition states are also optimized using MP2 [27,28] and B3LYP [29,12] methods on the same basis set. It appears that neither B3LYP nor MP2 is appropriate for these calculations because (1) B3LYP gives transition states that are too early and activation energies that are too low, even worse, some important species cannot be located, for example, pre-reactive complex (CR1) and entrance transition state (TS1); (2) MP2 method shows significant spin contamination for the wave-function of transition states, for example, the spin contamination of the most important entrance transition state TS1 is 2.04. However, the BHandHLYP and M05-2X functional show much better to describe this reaction. For the species $CH_2{=}CHCN$, OH, $CH_2O$, $CH_2CO$, HNC, HCN, $C_2H_3$, $CH_2$ and $C_2H_2$ in the supporting information, the calculated bond lengths and angles by BHandHLYP and M05-2Xmethods with 6-311++G(d,p) basis set are in good agreement with the experimental values [30], with the largest deviations being 0.015 Å for C=C bond and 0.1° for CCC angle in $CH_2CHCN$ at the BHandHLYP/6-311++G(d,p) level. Comparison with the experimental heats of reaction, BMC-CCSD energies appear to be quantitatively accurate. For example, the reaction enthalpy of c2-P4 is −33.28 kcal/mol in good agreement with the experimental value −34.59 kcal/mol.

Thus, in the following discussion, BHandHLYP/6-311++G(d,p) optimized geometric parameters and BMC-CCSD + ZPE energies are used unless otherwise stated.



CR1, $C_1$ IM1, $C_1$ c2-IM1, $C_1$ c-IM1, $C_s$

TS1, $C_1$ TS2 $C_1$ TS3, $C_1$ c2-TS1, $C_1$

c2-TS2, $C_1$ c-TS1, $C_s$ c-TS2, $C_1$

hTS1, $C_s$ hTS1-1, $C_s$ hTS2, $C_s$

**Fig. 1.** Optimized geometries (length in Å and angle in degree) of some important intermediates and transition states. The values from top to down correspond to the values obtained at the BHandHLYP and M05-2X level using 6-311++G(d,p) basis set.