Theoretical study of oxidation of acetonitrile with nitrogen trioxide and formation of secondary organic aerosol

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ABSTRACT

This theoretical study investigated the oxidation reaction mechanism of acetonitrile as a volatile organic compound by nitrogen trioxide in formation of secondary organic aerosol. The B3LYP level with 6-311++G (3df, 3pd) basis set was used to optimize geometries of reactants, products, and transition states. One product was obtained and the reaction pathway of the product was discussed and potential energy surface was plotted. The rate constant calculated at atmospheric pressure over the temperature range 300-2500 K. Finally formation of secondary organic aerosol has been discussed.

Keywords: VOC; SOA; acetonitrile; nitrogen trioxide; potential energy surface.

1. Introduction

Secondary organic aerosol, (SOA), is tiny particulate matter that is created from chemical transformation of atmospheric organic compounds [1]. Experiments indicate that large amount of total organic particulate mass is because of SOA. As a result, understanding SOA formation mechanisms is important in atmospheric chemistry [2]. Studies have proven that oxidation of volatile organic compounds (VOCs), is the major mechanism of formation of SOA. Volatile organic compounds are chemical compounds that can evaporate in temperature

and pressure of atmospheric conditions [3] and have two major sources: natural (primary) and chemical reactions (secondary) in the atmosphere [4]. They can impact on air quality by producing atmospheric pollutants, ozone, and organic aerosol.

Acetonitrile (CH_3CN, methyl cyanide), is one of the volatile organic compounds which has gained much attention in recent years because of its importance in atmospheric chemistry [5]. There are various sources of acetonitrile to the atmosphere that the major source is biomass burning [6].

To our knowledge no study has been done over reaction of acetonitrile with nitrogen trioxide. On the other hand no research has been done over the role of acetonitrile in the formation of SOA. Therefore, in this paper we first aim to study reaction pathways of acetonitrile with NO_3. Then, we focus on the potential of adducts of this reaction in producing secondary organic aerosol.

2. Experimental

All of the calculations were carried out with the GAUSSIAN 03 program. Therefore geometries of reactants, products (denoted as P), and transition states (denoted as TS) were optimized using B3LYP [7] with 6-311++G (3df, 3pd) basis set. Connections between transition states, and products are confirmed by the intrinsic reaction coordinate (IRC) [8] analysis at the B3LYP level of theory. All these calculations are done at a temperature of 298.15 K and under atmospheric pressure. Finally rate constant have been calculated by transition state theory (TST) [9] with GPOP program.

3. Results and discussion

The optimized geometries of the reactants, transition states, and products at the B3LYP level and 6-311++G (3df, 3pd) are shown in Fig. 1. The relative energies and zero point energy corrections have been listed in Table 1 for the B3LYP level. To simplify our discussion, the energy of reactant (CH_3CN+NO_3) is set to be zero as reference. The thermodynamic and atmospheric pressure are tabulated in Table 2.
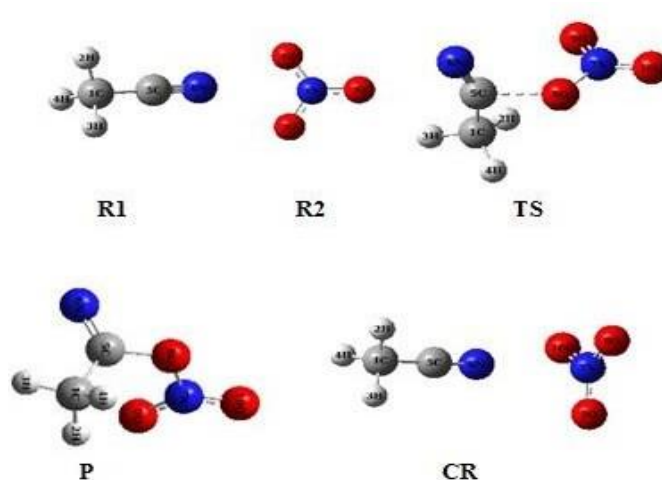

Fig. 1. Geometries of reactants, transition states, and products optimized at B3LYP level.

Then, by means of the transition states and their connected products, the PES profile has been plotted at the B3LYP level in Fig. 2. Finally the rate constant k for the reaction pathway of P is plotted in Fig. 3 and rate constant values over the range 200-2500 K and atmospheric pressure are listed in Table 3.

Table1. The relative energies of the reactants and product in the CH_3CN+NO_3 reaction.

Species	B3LYP
CH_3CN+NO_3	0.00
CR	-1.5456
TS	14.2575
P	2.2453

3.1. Reaction pathway

The pathway initiated from one pre-reactive complex, CR that has been found between reactants CH_3CN and NO_3 on PES.
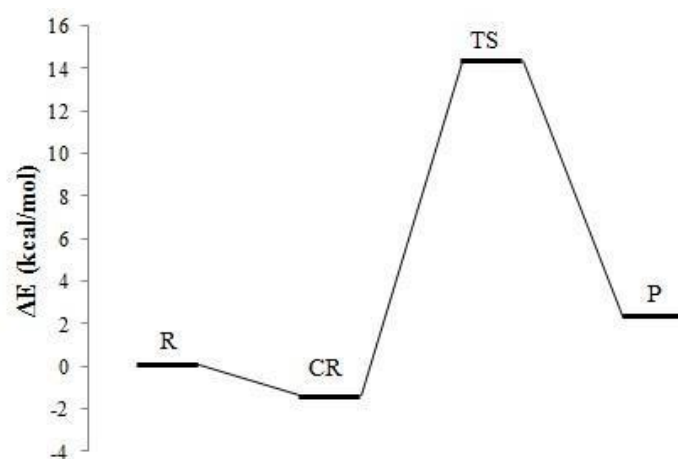

Fig. 2. The potential energy profile of the CH_3CN+NO_3 reaction at the b3lyp/6-311++G (3df, 3pd) level.

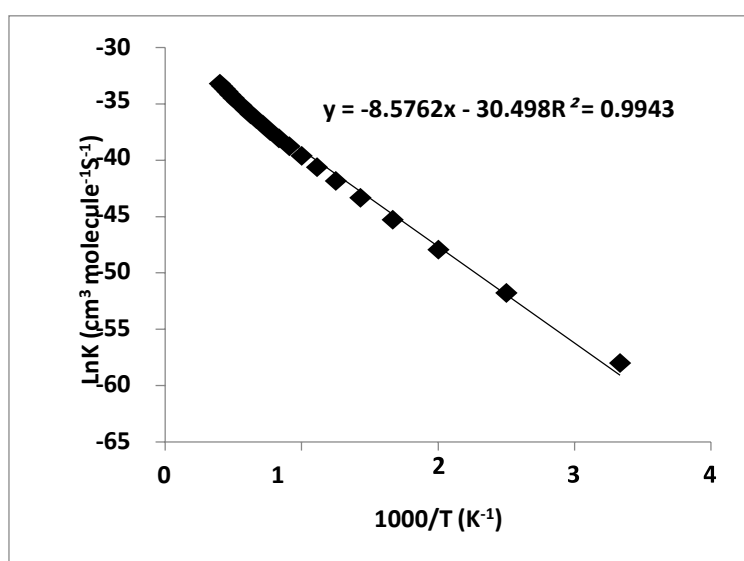**Fig. 3.** Arrhenius plot for the k rate constant.

The complex lies -1.545 kcal/mol below the original reactant (CH_3CN+NO_3) at the B3LYP level. In this path CR converts to P via TS with energy barrier of 15.803 kcal/mol and one imaginary frequency at - 499i cm^{-1} at the B3LYP level.

Thermodynamic data shows that the overall process is endothermic with the reaction enthalpy of 1.34 kcal/mol and nonspontaneous in gas phase with 13.67 kcal/mol Gibbs free energy.

Table 2. The reaction energies, enthalpies, and Gibbs free energies, and entropies (kcal/mol).

Reaction	ΔE°	ΔH°	ΔG°	$T\Delta S^{\circ}$
$CH_3CN + NO_3 \rightarrow CH_3C(N)ONO_2$	1.93	1.34	13.67	-12.33

3.2. Calculation of rate constant

The rate constant has been calculated for this pathway by the transition state theory (TST) implemented in the GPOP program. As shown in Fig. 2 the pathway P includes only one transition state, TS. The overall rate constant values of the CH_3CN+NO_3 reaction through path P have been listed in Table 3 at the temperature range of 300-2500K.

Table3. Rate constants k (cm^{-1} molecule^{-1} s^{-1}) at the temperature range of 300-2500 K.

T	K	T	K	T	K
300	6.33E-26	1100	1.46E-17	1900	7.76E-16
400	3.22E-23	1200	3.01E-17	2000	1.06E-15
500	1.52E-21	1300	5.66E-17	2100	1.42E-15
600	2.14E-20	1400	9.89E-17	2200	1.86E-15
700	1.51E-19	1500	1.63E-16	2300	2.40E-15
800	6.83E-19	1600	2.54E-16	2400	3.04E-15
900	2.30E-18	1700	3.81E-16	2500	3.80E-15
1000	6.25E-18	1800	5.52E-16		

Figure 3, also shows the Arrhenius plot for the k rate constant. Arrhenius parameters for the k rate constant are as follows:

$$k= 5.69\times10^{-14} \exp (-71.30 \text{ kj mol}^{-1}/RT)$$

3.3. SOA Formation

One of the important factors that control secondary organic aerosol formation of organic compounds in the atmosphere is volatility. Organic species in oxidation reactions can lower volatility by adding functional groups or increase volatility by breaking C-C bonds. On the other hand, formation of species with high molecular weight can also affect volatility. Therefore, oxidation reactions of volatile organic compounds (VOCs), are determinant in formation of SOA [1]. In term of volatility, polarity and size are two key functions that determining the vapor pressure of a molecule. The more polarity is, the less volatility will become. As a result, oxidation reactions which increase polarity or size of a molecule can play important role in formation of SOA [10]. Nitrogen trioxide is one of the main oxidants in the atmosphere that as a polar functional group can be added to carbon skeleton and facilitate formation of SOA [11]. This product will have decrease in volatility because of the addition of polar nitrogen trioxide. Moreover they can react with oxygen molecules and new formed products can lead to much decrease in volatility. Therefore, they have potential to produce SOA. An alternative mechanism that is likely is non-oxidative reaction in the condensed phase. Because there is a reverse relation between vapor pressure and every two carbon added by order of magnitude, these reactions can form low volatile products and hence help yielding the SOA [12].

4. Conclusions

In this work, the mechanism for the reaction of CH_3CN+NO_3 was studied at B3LYP level with 6-311++G (3df, 3pd) basis set. The potential energy profile was drawn and thermodynamic data was calculated. Then the rate constant values for the P production pathway has been calculated using TST theory at atmospheric pressure and temperature range of 300-2500 K. Finally, formation of secondary organic aerosol from given adducts was

studied. This research reveals that oxidation of acetonitrile by NO_3 can result in formation of secondary organic aerosol.

References

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