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# Study On addition Reaction Mechanism between Acetone and Organic Amine Catalyzed by Monomolecular Water using Quantum Chemistry Calculation Method

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## Abstract

We have used density functional theory and conventional transition state theory to study the reaction mechanism of  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}/\text{CH}_3\text{NH}_2$  reactions catalyzed a single water molecule from the aspects of energetics and kinetics, respectively. The energy barrier of  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH} + \text{H}_2\text{O}$  is lower than that of  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  by 25.31 kcal/mol, similar reaction with methylamine is also reduced by 24.55 kcal/mol, and the reaction energy barrier of dimethylamine is lower. The rate calculation results show that water catalysis can significantly accelerate the reaction rate. Both in energetics and kinetics,  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  reaction involving water catalyzed are all more competitive. The mechanism of these of reactions may be used to help explain the formation of alkanolamines in the atmosphere and the formation mechanism of secondary aerosols.

## Keywords

Acetone; Methylamine; Dimethylamine; Reaction Mechanism.

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## 1. Introduction

Organic amines are one of the most abundant substances in the atmosphere[1,2]. The most common are 24 species of methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA) [3]. Sources of organic amines include natural and artificial sources. Natural sources mainly come from biodegradation, metabolism, and biomass burning, human activities contribute more emissions, including factory emissions, automobile exhaust, and animal husbandry excretion[3–6]. Organic amines not only have a low olfactory threshold, and are prone to olfactory aversion, but also can harm human health when they reach a certain concentration in the air, including respiratory diseases, central nervous system and cardiovascular damage, and even induce canceration[7]. Therefore, it has long attracted widespread attention and research[8,9].

Although the concentration is much lower than that of  $\text{NH}_3$ , benefit from its stronger alkalinity, it can react with atmospheric nitric acid, sulfuric acid, etc. to form low volatile organic amine salts. Studies also have shown that organic amines can react with  $\text{OH}^-$ ,  $\text{NO}_3^-$ , and  $\text{O}_3$  to form secondary aerosols (SOA) and contribute significantly to the growth of particulates[10,11]. In recent years, the reaction of aldehydes and organic amines has also attracted the attention of researchers, either theoretical or experimental studies, which react mainly form imines, enamines, and finally evolve into aerosols[12–16]. Further experiments also have confirmed the presence of macromolecular ammonium salts in aerosols[17]. Sinha et al. calculated the reaction of formaldehyde with organic amines to show that this type of reaction may contribute to the formation and growth of aerosols in the

atmosphere[18]. However, the mechanism for the formation secondary aerosols is still not fully explained. Given that acetone is one of the most abundant carbonyl compounds[19], and Water is the most commonly effective catalyst in the atmosphere[20–22], we examine the reaction of dimethylamine and methylamine with  $\text{CH}_3\text{COCH}_3$  involving a single water molecules and water-free catalysis.

In the current work, we first examined all reactions from the perspective of energetics and compared the energy barriers of water-catalyzed reaction of  $\text{CH}_3\text{COCH}_3 + \text{DMA/MA}$ . The reaction rate of  $\text{CH}_3\text{COCH}_3 + \text{DMA/MA} + \text{H}_2\text{O}$  was investigated in terms of kinetics, and also compared the reaction rate of  $\text{CH}_3\text{COCH}_3 + \text{OH}$ , discuss the possible contribution of the reaction mechanism in the atmosphere.

## 2. Calculation Method

Using density functional theory with M06-2X functional[23], based on Gauss 09 program package[24], geometric configurations of all reactants, intermediates, transition states, and products were completed at the 6-311++G(d,P) basis group level. Moreover, the vibration frequency of each stagnation point was also calculated at this level, confirming that the transition state has only one imaginary frequency, and the other stable points are all positive frequencies. The lowest energy path of the linked reactants and products was determined by intrinsic reaction coordinate (IRC) calculations. To obtain more accurate energy information, a higher level single-point CCSD(T)-F12 method was carried out with JUN-cc-pVTZ basis set. Finally, conventional transition state theory with Echart tunneling [25,26] was used to calculate rate constants for each reaction studied here[27], while rate constant calculations have executed using TheRate code[28].

## 3. Results and Discussions

### 3.1 Energetics Analysis

Previous literature reports have pointed out that the reaction of carbonyl compounds with amines needs to overcome certain energy barriers[18]. We first discuss the reaction of dimethylamine addition to acetone from energetics. Figure 1 shows the potential energy surface of the  $\text{CH}_3\text{COCH}_3 + \text{NH}(\text{CH}_3)_2$  reaction. It can be seen from the figure that acetone and DMA react first at the initial stage of the reaction to form a pre-complex (RC1) and then undergo a transition state (TS1) to form the final product  $(\text{CH}_3)_2\text{NC}(\text{CH}_3)_2\text{OH}$  alkanolamine, with a energy barrier height up to 27 Kcal/mol relate to the separate  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  reactants. The specific reaction mechanism is the cleavage of the carbonyl group on the acetone, while the N-H bond on the DMA is broken and the protons are transferred to the acetone molecule's C=O to form the alkanolamine. In contrast, when a single water molecules were introduced into the  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  reaction, a quick look at the structures shown in Figure 2, the energy barrier at TS2 is as low as 2.06 kcal/mol, compared to the reaction energy barrier for  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  alone the difference is 25.31 kcal/mol, apparently the presence of water molecules can greatly reduce the energy barrier of the reaction and accelerate the reaction. This is mainly due to the greater tension of the six-membered ring formed between water molecules, dimethylamine and acetone. For the reaction of  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH} + \text{H}_2\text{O}$ , according to the classical collision theory, the probability of simultaneous reaction of three molecules is extremely low, so we consider the collision reaction of two molecules and then react further with the third molecule. Thus only the two reactions  $\text{DMA}\cdots\text{H}_2\text{O} + \text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{COCH}_3\cdots\text{H}_2\text{O} + \text{DMA}$  may take into account. Further, Previous studies indicated that the  $\text{DMA}\cdots\text{H}_2\text{O}$  complex will greatly limit the reaction site of subsequent addition reaction[18,29], so we only consider  $\text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$  to form  $\text{CH}_3\text{COCH}_3\cdots\text{H}_2\text{O}$  reaction path.

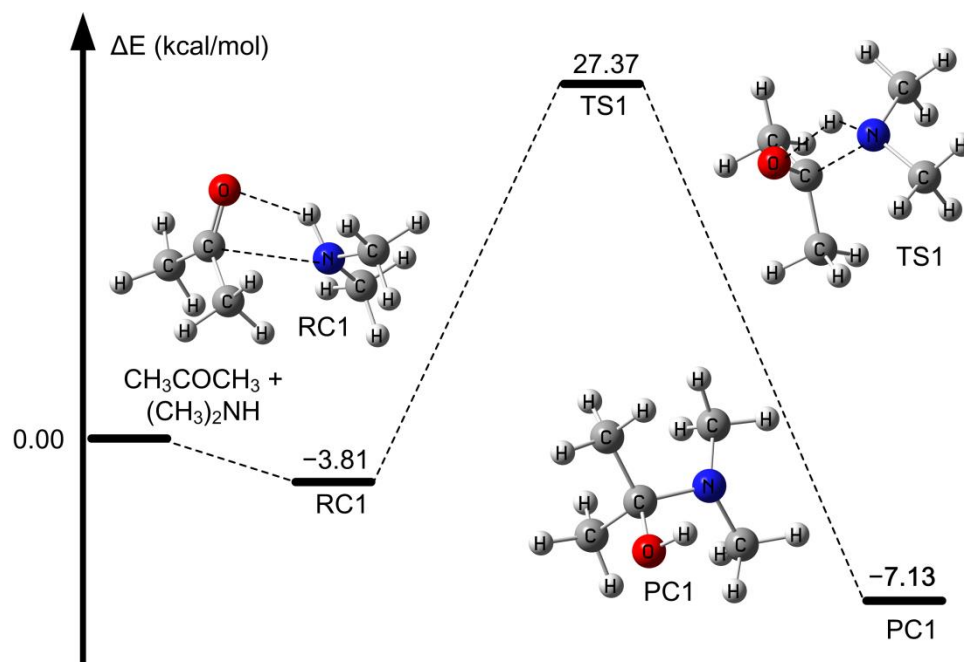


Fig 1. The potential energy profile for the  $\text{CH}_3\text{COCH}_3 + \text{NH}(\text{CH}_3)_2$  reaction at the CCSD (T)-F12a/JUN-cc-pit //M06-2X/6-311++G (d, p) level

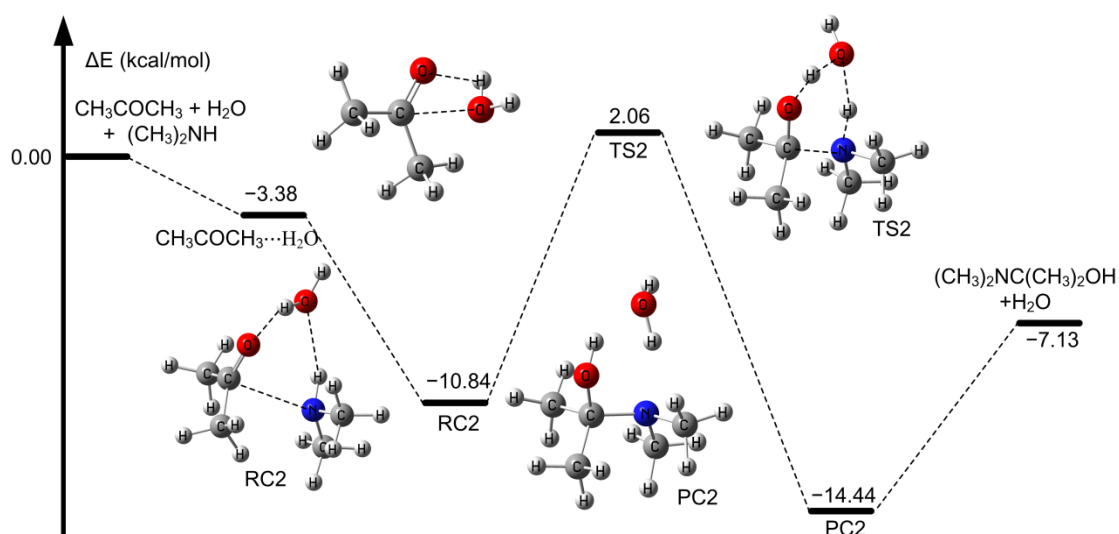


Fig 2. The potential energy profile for the  $\text{CH}_3\text{COCH}_3 + \text{NH}(\text{CH}_3)_2 + \text{H}_2\text{O}$  reaction at the CCSD (T)-F12a/JUN-cc-pit //M06-2X/6-311++G (d, p) level

Considering the prominent role of water molecules in reducing the reaction energy barrier, we further investigated the reaction of  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{NH}_2$  with water and water deficit catalysis. Similar to the discussion of dimethylamine, the schematic diagram of the potential energy surface for  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{NH}_2$  reaction is shown in Figure 3. The reaction energy barrier of  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{NH}_2$  is 29.54 kcal/mol, which is even higher than that of acetone and dimethylamine. Similarly, when the water molecules are introduced into the reaction, the reaction energy barrier height is reduced to 4.44 kcal/mol. Thus a single water molecules can significantly reduce the reaction energy barrier of similar reactions. We can also find that Dimethylamine is more easily reacted with acetone than methylamine. Comparing the results of  $\text{HCHO} + \text{H}_2\text{O} + \text{DMA/MA}$  calculated by Francisco et al. at the CCSD(T)/6-311++G(3df,3dp)//MP2/6-311++G(3df,3dp) level, the reaction energy barriers are -5.4 kcal/mol and -1.5 kcal/mol, respectively. The reaction of acetone with methylamine and dimethylamine needs to overcome higher energy barriers, This is mainly due to the larger steric hindrance of acetone. However, It is extremely obvious that the presence of water molecules helps to

reduce the reaction energy barrier, accelerate the reaction process, and is consistent with the results reported in the literature[20–22].

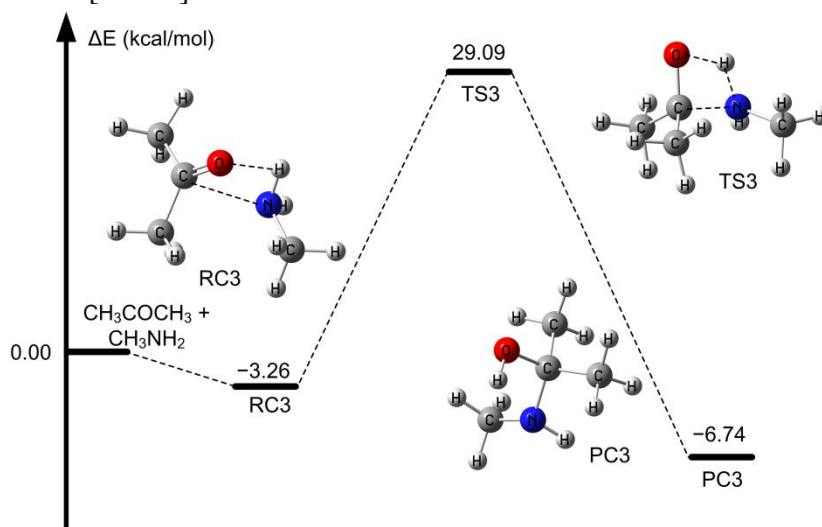


Fig 3. The potential energy profile for the  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$  reaction at the CCSD (T)-F12a/JUN-cc-pit //M06-2X/6-311++G (d, p) level

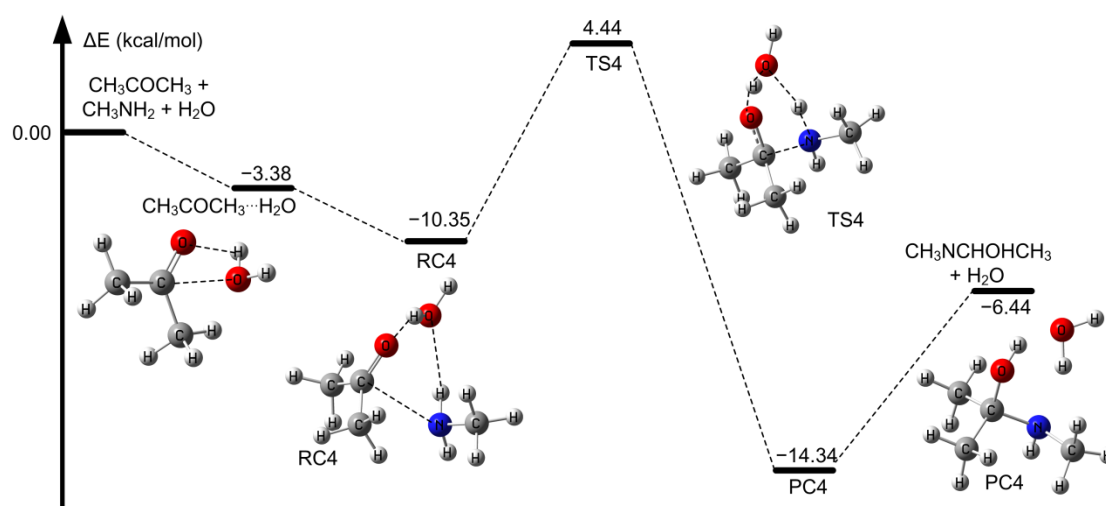
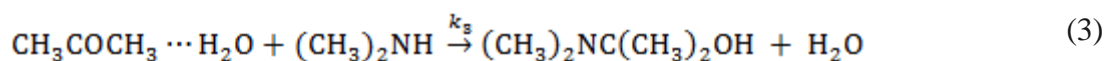
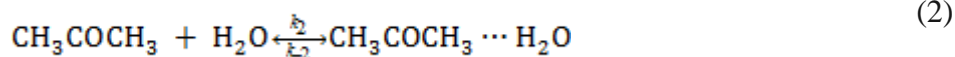
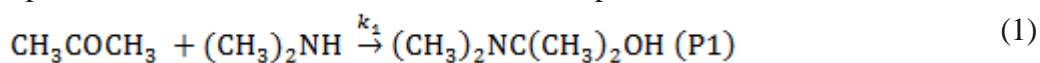


Fig 4. The potential energy profile for the  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$  reaction at the CCSD (T)-F12a/JUN-cc-pit //M06-2X/6-311++G(dip) level

### 3.2 Kinetic Analysis

Due to the important role of aldehydes and ketones in the conversion and transfer of atmospheric substances. To further confirm the effect of  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  reaction on the atmospheric environment and SOA formation, we compared the rate of reaction of  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH} + \text{H}_2\text{O}$  and  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  in the atmosphere by means of rate constant calculations. Moreover, for the purpose of comparison, we also calculate the rate constant of  $\text{CH}_3\text{COCH}_3 + \text{OH}$ . The main reaction steps of DMA with acetone in the absence and presence of water are as follows:



$$v_1 = \frac{d[\text{P1}]}{dt} = k_1[\text{CH}_3\text{COCH}_3][(\text{CH}_3)_2\text{NH}] \quad (4)$$

$$v_2 = \frac{d[P1]}{dt} = K_{eq} k_3 [CH_3COCH_3][H_2O][(CH_3)_2NH] \quad (5)$$

$$v_1/v_2 = \frac{K_{eq} k_3 [CH_3COCH_3][H_2O][(CH_3)_2NH]}{k_1 [CH_3COCH_3][(CH_3)_2NH]} = \frac{K_{eq} k_3 [H_2O]}{k_1} \quad (6)$$

In the above equation,  $K_{eq}$  means the equilibrium constant of the eq.2.  $k_1$  and  $k_3$  represent the rate constants of the bimolecular reactions of  $CH_3CHO + (CH_3)_2NH$  and  $CH_3CHO \cdots H_2O + (CH_3)_2NH$ , respectively. Additionally,  $v_1/v_2$  is the rate constant ratio between eq.4 and eq.5. At the same time, consulting the literature shows that the concentration of water molecules in the atmosphere is about  $3.9 \times 10^{17}$  molecules/cm<sup>3</sup>. The kinetic calculation results are shown in Table 1:

Table 1. Equilibrium constant ( $K_{eq}$ , molecules/cm<sup>3</sup>), the rate constants (cm<sup>3</sup>·molecules<sup>-1</sup>·s<sup>-1</sup>), and the rate ratio between 298 and 350 K.

T	$k_1^a$	$K_{eq}^b$	$k_2^c$	$k_3^d$	$k_4^e$	$v_2/v_1^f$	$v_4/v_3^g$
298K	$4.26 \times 10^{-36}$	$8.43 \times 10^{-28}$	$8.74 \times 10^{-23}$	$1.81 \times 10^{-41}$	$6.60 \times 10^{-24}$	$6.75 \times 10^{+03}$	$1.20 \times 10^{+08}$
310 K	$2.24 \times 10^{-35}$	$1.08 \times 10^{-27}$	$1.06 \times 10^{-22}$	$1.25 \times 10^{-40}$	$9.08 \times 10^{-24}$	$1.99 \times 10^{+03}$	$3.06 \times 10^{+07}$
320 K	$8.16 \times 10^{-35}$	$1.32 \times 10^{-27}$	$1.23 \times 10^{-22}$	$5.87 \times 10^{-40}$	$1.17 \times 10^{-23}$	$7.74 \times 10^{+02}$	$1.02 \times 10^{+07}$
330 K	$2.75 \times 10^{-34}$	$1.59 \times 10^{-27}$	$1.42 \times 10^{-22}$	$2.58 \times 10^{-39}$	$1.48 \times 10^{-23}$	$3.20 \times 10^{+02}$	$3.56 \times 10^{+06}$
340 K	$8.65 \times 10^{-34}$	$1.90 \times 10^{-27}$	$1.63 \times 10^{-22}$	$1.06 \times 10^{-38}$	$1.86 \times 10^{-23}$	$1.40 \times 10^{+02}$	$1.29 \times 10^{+06}$
350 K	$2.55 \times 10^{-33}$	$2.25 \times 10^{-27}$	$1.86 \times 10^{-22}$	$4.10 \times 10^{-38}$	$2.30 \times 10^{-23}$	$6.39 \times 10^{+01}$	$4.93 \times 10^{+05}$

a The rate constant of the  $(CH_3)_2NH + CH_3COCH_3$  reaction, b The equilibrium constant of  $CH_3COCH_3 + H_2O$  reaction to form  $CH_3COCH_3 \cdots H_2O$  complex, c The rate constant of the  $CH_3COCH_3 \cdots H_2O + (CH_3)_2NH$  reaction, d The rate constant of the  $CH_3COCH_3 + CH_3NH_2$  reaction, e The rate constant of the  $CH_3COCH_3 \cdots H_2O + CH_3NH_2$  reaction, f The reaction rate ratio between  $CH_3COCH_3 + (CH_3)_2NH + H_2O$  and  $CH_3COCH_3 + (CH_3)_2NH$ , g The reaction rate ratio between  $CH_3COCH_3 + CH_3NH_2 + H_2O$  and  $CH_3COCH_3 + CH_3NH_2$

It can be clearly seen from Table 1 that all the bare reactions and the reactions catalyzed by a single water molecule show a good positive dependence on the temperature. Under the same conditions, the reaction rate of  $CH_3COCH_3 + (CH_3)_2NH + H_2O$  is 1-3 orders of magnitude faster than that of  $CH_3COCH_3 + (CH_3)_2NH$ , and similarly the reaction of methylamine is even 5-8 orders of magnitude faster. Further, compared with the  $CH_3COCH_3 + MA$  reaction, the  $CH_3COCH_3 + (CH_3)_2NH$  reaction has a more pronounced rate advantage. However the reaction rate of methylamine and dimethylamine catalyzed by single molecule water is almost equivalent, It is mainly because when water is used as a catalyst, the rate constants of the two are roughly the same, and the concentration of methylamine in the atmosphere is about three times that of dimethylamine. ( $[(CH_3)_2NH]$   $1.9 \times 10^8$  molecules/cm<sup>3</sup>,  $[CH_3NH_2] \approx 6 \times 10^8$  Molecules/cm<sup>3</sup>).

Given that the importance of the OH reaction in the atmosphere, we also compare the reaction rate between  $CH_3COCH_3 + (CH_3)_2NH + H_2O$  and  $CH_3COCH_3 + OH$ . A similar rate ratio equation can be written in eq.7 :

$$v_2/v_5 = \frac{K_{eq} k_3 [(CH_3)_2NH][H_2O]}{k_{OH}[OH]} \quad (7)$$

In eq.7,  $v_5$  is the rate of OH reaction at room temperature. R. Atkinson et al. reported that the reaction rate constant of  $CH_3COCH_3 + OH$  reaction at room temperature is  $1.8 \times 10^{-13}$  cm<sup>3</sup>·molecules<sup>-1</sup>·s<sup>-1</sup>, and the concentration of OH radicals in the atmosphere is approximately  $1.06 \times 10^8$  molecules/cm<sup>3</sup>. The results show that the OH reaction rate has categorically advantages and occupies an absolute dominant position in the reaction competition in the atmosphere. Therefore, these reactions may have a negligible contribution to SOA formation under gas phase conditions, but it may also play an important role in liquid phase reactions.

## 4. Conclusion

Using the density functional and ab initio methods, the reaction of methylamine and dimethylamine addition to acetone was calculated from energy and kinetic simulations. The calculated results show that a single water molecules can significantly reduce the reaction energy barrier and accelerate the reaction rate; the reaction energy barrier and rate of  $\text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{NH}$  are significantly better than that of  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{NH}_2$  under the same conditions. Compared with the reaction of organic amine addition to formaldehyde, acetone has a slightly higher reaction energy barrier and slower rate due to steric hindrance, but this type of reaction mechanism can still play a positive role in revealing the formation mechanism of SOA.

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