New Reactions for the Formation of Organic Nitrate in the Atmosphere

Gang-Biao Li, Shao-Hong Cai, and Bo Long*

ABSTRACT: Organic nitrates make an important contribution to the formation of secondary organic aerosols, but the formation mechanisms of organic nitrates are not fully understood at the molecular level. In the present work, we explore a new route for the formation of organic nitrates in the reaction of formaldehyde (HCHO) with nitric acid (HNO$_3$) catalyzed by water (H$_2$O), ammonia (NH$_3$), and dimethylamine ((CH$_3$)$_2$NH) using theoretical methods. The present results using CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S unravel that dimethylamine has a stronger catalytic ability in the reaction of HCHO with HNO$_3$, reducing the barrier by 21.97 kcal/mol, while water and ammonia only decrease the energy barrier by 7.35 and 13.56 kcal/mol, respectively. In addition, the calculated kinetics combined with the corresponding concentrations of these species show that the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction can compete well with the naked HCHO + HNO$_3$ reaction at 200–240 K, which may make certain contributions to the formation of organic nitrates under some atmospheric conditions.

1. INTRODUCTION

Secondary organic aerosols (SOAs) have important impacts on the global atmosphere by affecting the global radiation balance, which can produce direct or indirect radiative forcing on the climate, thereby affecting the global climate system, the ecosystem, and human health.$^{3,6}$ SOAs are produced by synthetic or naturally occurring semivolatile organic compounds (SVOCs) or volatile organic compounds (VOCs) through atmospheric oxidation processes, leading to the formation of low volatile organic precursors floating in the atmosphere.$^{7-9}$ Although the atmospheric oxidation processes of VOCs and SVOCs have been considered to be the main route for the formation of important nucleation precursors to lead to the formation of SOAs,$^7$ the molecular-level formation mechanism of the nucleation precursors is still unclear.

Organic nitrates (RONO$_2$) are a type of typical nitrogen-containing organics, containing −ONO$_2$ groups, which are an important component of SOAs and account for 5–44% of SOAs.$^{10-13}$ Due to the importance of organic nitrates in the formation of secondary organic aerosols, the formation of organic nitrates has been extensively investigated both experimentally and theoretically. In general, two main routes have been suggested in the formation of organic nitrates. For example, hydrocarbons are oxidized in the presence of hydroxyl radicals and nitrogen oxides during the daytime.$^{14-16}$ Nitrate-free radicals initiate the oxidation of olefins at night.$^{17,18}$ In these two main routes, the yield of organic nitrates is high at night, while the yield of organic nitrates formed during the daytime is very low.$^{19,20}$ For example, the yield of alkyl nitrates is 2.9%.$^{21}$ Pye et al., through Community Multiscale Air Quality (CMAQ) model research, found that the source of particle-phase organic nitrates during the daytime is lacking.$^{22}$ It is pointed out that the mechanism of NO$_3$ + biogenic volatile organic compounds (BVOCs) to form RONO$_2$ is still unclear,$^{24}$ and that the understanding of the gas-phase mechanism of organic nitrate aerosols lacks completeness.$^{25}$ Therefore, it is required to further understand the formation mechanism of organic nitrates at the molecular level.

Here, we propose a new route to form an organic nitrate (H$_2$C(OH)ONO$_2$) by the reaction of formaldehyde and nitric acid. We have studied the reaction rate and energy barrier of formaldehyde and nitric acid, as well as catalysts, to understand the important role of these reactions in the atmosphere and to better understand the formation of SOAs. This is of great importance for understanding the formation mechanism of

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SOAs at the molecular level and the reaction of acids and aldehydes in the atmosphere.

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\text{HCHO} + \text{HNO}_3 \rightarrow \text{H}_2\text{C(OH)ONO}_2 \quad \text{(R1)}
\]

\[
\text{HCHO} + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C(OH)ONO}_2 + \text{H}_2\text{O} \quad \text{(R2)}
\]

\[
\text{HCHO} + \text{HNO}_3 + \text{NH}_3 \rightarrow \text{H}_2\text{C(OH)ONO}_2 + \text{NH}_3 \quad \text{(R3)}
\]

\[
\text{HCHO} + \text{HNO}_3 + (\text{CH}_2)_2\text{NH} \rightarrow \text{H}_2\text{C(OH)ONO}_2 + (\text{CH}_2)_2\text{NH} \quad \text{(R4)}
\]

Nitric acid and formaldehyde react to form an organic nitrate (H\(_2\)C(OH)ONO\(_2\)), which is catalyzed by water, ammonia, and dimethylamine in R\(_2\)-R\(_4\). The reason why formaldehyde and nitric acid are chosen in the present investigation is that their concentration is relatively high in the atmosphere.\(^{26-29}\) It is found that all of the three catalysts have certain catalytic ability with dimethylamine having a higher value. The new formation mechanism of organic nitrates proposed here has a certain significance for understanding the formation of SOAs.

2. COMPUTATIONAL METHODS

The geometric structures of all reactants, prereaction complexes, transition states, postreaction complexes, and products were optimized using the M06-2X\(^{30}\) functional with the MG3S\(^{31}\) basis set. Previous studies have shown that M06-2X is reliable in the calculation of atmospheric clusters.\(^{32}\) The frequency calculations of all optimized structures were carried out using the same method. As a result, the reactants, prereaction complexes, postreaction complexes, and products have positive frequencies, while the transition state has only one imaginary frequency with all other frequencies positive. In addition, intrinsic reaction coordinate (IRC)\(^{33,34}\) calculations were used to determine the reaction path from the prereaction complexes to the postreaction complexes. The results for IRC calculations are provided in Figures S1−S4. A scale factor of 0.970 was used to scale zero-point vibrational energies of M06-2X/MG3S to improve the zero-point vibrational energies by including anharmonicity and systematic error correction for high frequencies.\(^{35}\)

To obtain reliable relative energies, based on the optimized geometric structure of M06-2X/MG3S, the CCSD(T)-F12a\(^{36,37}\) theoretical method and the cc-pVTZ-F12\(^{38,39}\) basis set were used to calculate the single-point energies of each species investigated here. Our previous investigations have shown that the CCSD(T)-F12a/cc-pVTZ-F12 method can reach the accuracy of CCSD(T)/CBS.\(^{40-42}\) Moreover, to estimate the multireference features for the stationary points, T\(_1\) diagnostic values are given in Table A1 (Supporting Information). T\(_1\) diagnostic values of all species do not exceed the upper limit of 0.02 for the close-shell systems in Table A1; this shows that the CCSD wave functions for the stationary points are reliable.\(^{43}\) The rate calculations of all reactions were conducted using conventional transition-state theory (CTST)\(^{44}\) with Eckart tunneling,\(^{45}\) which was done by the TheRate code.\(^{46}\) Gaussian 16 software package version A03\(^{47}\) was used for density functional calculation (DFT) and Molpro 2019.2\(^{48}\) was used for single-point energy calculation.

3. RESULTS AND DISCUSSION

3.1. Reaction of Formaldehyde with Nitric Acid. The reaction of formaldehyde with nitric acid is shown in Figure 1,

![Figure 1. Calculated potential energy profile for the HCHO + HNO\(_3\) → H\(_2\)C(OH)ONO\(_2\) reaction with zero-point vibrational energies corrected at the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S level (in kcal/mol). Optimized geometries at the M06-2X/MG3S level. Bond distances are in Angstroms and the experimental values are in brackets.\(^{49,50}\)](https://doi.org/10.1021/acsomega.2c03321)
energy barriers are very close to each other. However, the energy barrier of HCHO + HNO\(_3\) (8.80 kcal/mol) is much higher (at least 5 kcal/mol) than those of the HCHO + H\(_2\)SO\(_4\) reaction (3.5−6.1 kcal/mol) at the W2X//QCISD/cc-pVTZ level,\(^{53}\) the HCHO + OH reaction (−0.12 kcal/mol) at the CCSD(T)/aug-cc-pVTZ level,\(^{57}\) the HCHO + HO\(_2\) reaction (−1.03 kcal/mol) at the MW3X-L//CCSD(T)-F12a/cc-pVTZ-F12 level,\(^{58}\) the HCHO + CH\(_3\)OO reaction (−5.26 kcal/mol) at the W3X-L//CCSD(T)-F12a/cc-pVTZ-F12 level,\(^{50}\) and the HCHO + HIO\(_3\) reaction (2.96 kcal/mol) at the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/aug-cc-pVTZ level.\(^{59}\) It is noted that these reactions mentioned above were carried out using different theoretical methods; this can cause some different error bars for different theoretical methods. However, we also note that the error bars of these theoretical methods could be 1−2 kcal/mol in the HCHO + HNO\(_3\)/H\(_2\)SO\(_4\)/OH/HO\(_2\)/CH\(_3\)OO/HIO\(_3\) reactions. Therefore, we conclude qualitatively that the HCHO + HNO\(_3\) reaction is less likely to occur than the HCHO + H\(_2\)SO\(_4\)/OH/HO\(_2\)/CH\(_3\)OO/HIO\(_3\) reactions from the energetic point of view.

Taking into account the Gibbs free energy barrier of 20.02 kcal/mol for TS1 at 298 K, it is shown that HCHO + HNO\(_3\) is quite slow under atmospheric conditions. However, the reaction of HCHO + HNO\(_3\) in solution is considered to be the formation of HNO\(_2\) and HCOOH.\(^{60}\) In addition, the reaction enthalpy calculated at the CCSD(T)-F12a/cc-pVTZ-F12/M06-2X/MG3S level of theory is −14.34 kcal/mol for HCHO + HNO\(_3\), which reveals that the reaction is exothermic.

3.2. Reaction of Formaldehyde with Nitric Acid Catalyzed by Water. When a single water molecule is introduced into the HCHO + HNO\(_3\) reaction, they are trimolecular reaction systems. There are three possible entrance channels in the reaction of HCHO + HNO\(_3\) + H\(_2\)O → H\(_2\)C(OH)ONO\(_2\) + H\(_2\)O, namely, HCHO···HNO\(_3\) + H\(_2\)O, HCHO···H\(_2\)O + HNO\(_3\), and HNO\(_3\)···H\(_2\)O + HCHO. From the perspective of spatial structure, HNO\(_3\)···H\(_2\)O is easily reactive, and the binding energies of the HCHO···HNO\(_3\) (−8.67 kcal/mol) and HNO\(_3\)···H\(_2\)O (−8.31 kcal/mol) complexes are lower than that of HCHO···H\(_2\)O (−3.41 kcal/mol) (see Table S1). Therefore, the HNO\(_3\)···H\(_2\)O + HCHO entrance channel is considered here, where HNO\(_3\) and H\(_2\)O collide to form a binary complex (HNO\(_3\)···H\(_2\)O), further colliding with formaldehyde to form ternary C2 (HNO\(_3\)···H\(_2\)O + HCHO) from the steric point of view, as shown in Figure 2.

The HCHO + HNO\(_3\) + H\(_2\)O reaction starts with the formation of the prereaction C2 complex and proceeds through the corresponding transition state TS2 responsible for the formation of the postreaction C2P complex, as listed in Figure 2. The C2 complex is an eight-membered ring structure with one van der Waals interaction and two hydrogen bond interactions. This catalytic reaction is still a concerted reaction mechanism in which the hydrogen atom (H5) of the OH group in nitric acid is transferred to the oxygen atom (O10) in H\(_2\)O. The hydrogen atom (H11) of the OH group in H\(_2\)O is migrated to the oxygen atom (O9) of the C6=O9 group in formaldehyde, and simultaneously, the oxygen atom (O3) in nitric acid is added to the carbon atom (C6) of the C6=O9 group in formaldehyde to form the postreaction C2P complex. From C2 to TS2, the O4−H5 bond in nitric acid is lengthened from 1.015 to 1.373 Å, and the O10−H11 bond is increased from 0.975 to 1.163 Å. Furthermore, the bond distance between the carbon atom (C6) of the C6=O9 group in HCHO and the oxygen atom (O3) of HNO\(_3\) is shortened to 2.045 Å (TS2) from 3.024 Å in C2. As a result, it is obvious that H\(_2\)O acts both as a proton donor and an acceptor.

The binding energy of the C2 (HCHO···HNO\(_3\)···H\(_2\)O) complex is −15.44 kcal/mol, which is in good agreement with the value of −15.34 kcal/mol of CR1-4 at the CCSD(T)-F12a/cc-pVTZ-F12/M06-2X/6-311++G(d,p) level.\(^{52}\) In particular, compared with the HCHO + HNO\(_3\) reaction, the reaction barrier is only reduced by 7.35 kcal/mol, which shows that a single water molecule has a certain catalytic ability on the HCHO + HNO\(_3\) reaction. However, the catalytic ability of a single water molecule in the HCHO + HNO\(_3\) reaction is much weaker than that in other reactions as previous literature. For example, when a single water molecule is introduced as a catalyst, the energy barriers of the CH\(_3\)CHO + H\(_2\)O + (CH\(_3\)\(_2\)NH\(_3\) \(^{63}\)) CF\(_2\)CHO + H\(_2\)O + (CH\(_3\)\(_2\)NH\(_3\)) \(^{64}\) and H\(_2\)CO + H\(_2\)O + (CH\(_3\)\(_2\)NH\(_3\)) \(^{65}\) reactions are decreased by 24.76, 24.15, and 26 kcal/mol at the CCSD(T)-F12a/cc-pVTZ-F12/M06-2X/6-311++G(d,p), CCSD(T)-F12a/jun-cc-pVTZ/M06-2X/6-311++G(3df,3pd), and CCSD(T)/6-311++G-

![Figure 2. Calculated potential energy profile for the HCHO + HNO\(_3\) + H\(_2\)O reaction with zero-point vibrational energies corrected at the CCSD(T)-F12a/cc-pVTZ-F12/M06-2X/MG3S level (in kcal/mol). Optimized geometries at the M06-2X/MG3S level. Bond distances are in Angstroms and the experimental values are in brackets.\(^{61}\)](https://pubs.acs.org/doi/10.1021/acsomega.2c03321)
(3df,3pd)//MP2(Full)/6-311++G(3df,3pd) levels, respectively.

3.3. Reaction of Formaldehyde with Nitric Acid Catalyzed by Ammonia. The HCHO + HNO₃ + NH₃ reaction starts with the prereaction C3 complex with an eight-membered ring structure undergoing a unimolecular isomerization through TS3, where the hydrogen atom (H5) of the OH group in HNO₃ is transferred to the nitrogen atom (N10) in ammonia, the hydrogen atom (H11) in ammonia is transferred to the oxygen atom (O9) of the C6=O9 group in formaldehyde, and meanwhile, the oxygen atom (O3) of the C6=O9 group in nitric acid is added to the carbon atom (C6) of the C6=O9 group in HCHO, resulting in the formation of the corresponding postreaction C3P complex, as depicted in Figure 3. The HNO₃···NH₃ complex contains a hydrogen bond H5···N10, and the bond length is 1.616 Å (see Figure 3), which slightly differs from the experimental value by 0.058 Å.⁶⁶ The O4−H5 bond length is increased from 1.060 Å in C3 to 1.780 Å in TS3, and the bond distance between C6 and O3 is shortened from 2.673 Å in C3 to 1.866 Å in TS3.

In Figure 3, the binding energy of the HNO₃···NH₃ complex is −11.57 kcal/mol, which is not much different from −12.25 kcal/mol after zero-point energy correction at the MP2/6-311++G(d,p) level.⁶⁶,⁶⁷ Due to the catalysis of ammonia, the reaction energy barrier is reduced by 13.56 kcal/mol, which is 6.21 kcal/mol lower than that of water catalysis, indicating that the catalytic ability of ammonia is greater than that of water. However, the catalytic effects of ammonia on the HCHO + HNO₃ reaction are also much weaker than those on the ammonia-catalyzed HCHO + H₂SO₄ reaction, as the energy barrier is decreased by 16−21 kcal/mol in the reaction of HCHO + H₂SO₄ catalyzed by NH₃ at the M08-SO/maug-cc-pVTZ level.⁵³

3.4. Reaction of Formaldehyde with Nitric Acid Catalyzed by Dimethylamine. This reaction is similar to the R2 and R3 reactions (see Figure 4), where the H5 atom of the OH group in nitric acid is transferred to the N10 atom in dimethylamine, and the H11 atom in dimethylamine is transferred to the O9 atom of the O9=O9 group in formaldehyde. At the same time, the O3 atom in nitric acid is added to the C6 atom of the carbonyl group in formaldehyde. It can be seen that dimethylamine acts as a bridge for hydrogen atom transfer.

Figure 3. Calculated potential energy profile for the HCHO + HNO₃ + NH₃ reaction with zero-point vibrational energies corrected at the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S level (in kcal/mol). Optimized geometries at the M06-2X/MG3S level. Bond distances are in Angstroms and the experimental values are in brackets.⁶⁶

Figure 4. Calculated potential energy profile for the HCHO + HNO₃ + (CH₃)₂NH reaction with zero-point vibrational energies corrected at the CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/MG3S level (in kcal/mol). Optimized geometries at the M06-2X/MG3S level. Bond distances are in Angstroms.

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In the HNO$_3$·(CH$_3$)$_2$NH complex, there are two hydrogen bonds H5···N10 and H11···O2 between nitric acid and dimethylamine, and the bond lengths are 1.493 and 2.688 Å, respectively. The bond distance between O4 and H5 is lengthened from 1.492 Å in C4 to 2.056 Å in TS4. In addition, the N10···H11 bond in dimethylamine is increased from 1.024 Å in C4 to 1.098 Å in TS4, and the C6···O3 bond distance is decreased from 2.740 Å in C4 to 1.985 Å in TS4. The binding energy of HNO$_3$···(CH$_3$)$_2$NH is $-15.12$ kcal/mol, which is close to the value of $-16.11$ kcal/mol at the CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p) level and $-16.6$ kcal/mol at the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level.

The energy barrier of the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction is reduced by 21.97 kcal/mol compared with the HCHO + HNO$_3$ reaction, which is 14.62 and 8.41 kcal/mol lower than those of water- and ammonia-catalyzed HCHO + HNO$_3$ reactions, respectively, showing that dimethylamine has a stronger catalytic ability. The catalytic effects of dimethylamine on the HCHO + HNO$_3$ reaction are much weaker than those of the formation of 2-methyl-6-nitrophenol catalyzed by dimethylamine, as the energy barrier is 49.40 kcal/mol lower than that without dimethylamine.

However, the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction is more feasible because the energy barrier of the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction is 7.77 kcal/mol lower than that of HCHO + H$_2$O + (CH$_3$)$_2$NH.

3.5. Kinetics. The rate constants for the four reactions in R1–R4 were calculated here at the temperature range from 200 to 298 K. The reaction rate expressions of the reactions R1–R4 are provided in eqs (1) to (4), respectively, in the Supporting Information.

The detailed expression of the trimolecules is provided by the reaction pathway HNO$_3$··H$_2$O + HCHO as an example in the Supporting Information, and this reaction is similar to our previous studies in the HFCO + H$_2$O + H$_2$SO$_4$ and HCHO + H$_2$SO$_4$ + HCOOH reactions.

Table 1 lists the calculated results. In Table 1, $K_{eq1}$, $K_{eq2}$, and $K_{eq3}$ represent the equilibrium constants of the complexes HNO$_3$··H$_2$O, HNO$_3$··NH$_3$, and HNO$_3$··(CH$_3$)$_2$NH, respectively. $k_1$, $k_2$, $k_3$, and $k_4$ denote the bimolecular rate constants of the HCHO + HNO$_3$, HNO$_3$··H$_2$O + HCHO, HNO$_3$··NH$_3$ + HCHO, and HNO$_3$··(CH$_3$)$_2$NH + HCHO reactions, respectively. Here, we consider the concentrations of HCHO, HNO$_3$, H$_2$O, NH$_3$, and (CH$_3$)$_2$NH in the atmosphere, which are $10^1$, $10^2$, $10^3$, $10^4$, and $10^5$ molecules cm$^{-3}$, respectively.

The rate constant $k_1$ of the HCHO + HNO$_3$ reaction is $2.09 \times 10^{-23}$ to $3.50 \times 10^{-21}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 200–298 K, as shown in Table 1 and Figure 5, which shows a positive temperature dependence. Moreover, the calculated rate constant of formaldehyde and nitric acid is consistent with the experimental value of $2.5 \times 10^{-21}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 290 K. However, the calculated results show that the values of the rate constant $k_1$ are so small that the HCHO + HNO$_3$ reaction is insignificant in the atmosphere. At 298 K, the rate constants $k_2$, $k_3$, and $k_4$ in the entrance channel of the reactions R2–R4 are $4.75 \times 10^{-22}$, $7.04 \times 10^{-21}$, and $6.35 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, as listed in Table 1. In addition, $k_2$, $k_3$, and $k_4$ also show positive temperature dependence, as shown in Table 1 and Figure 5.
### 3.6. Atmospheric Implications

To compare with the effects of catalysis, the following rate ratio expressions are obtained in equations (5)–(7) in the Supporting Information. These calculation results are shown in Table 1. From Table 1, the rate ratio between HCHO + HNO$_3$ + H$_2$O and HCHO + HNO$_3$ ($v_f/v_i$) is from $5.80 \times 10^{-3}$ to $2.12 \times 10^{-3}$, the rate ratio between HCHO + HNO$_3$ + NH$_3$ and HCHO + HNO$_3$ ($v_f/v_i$) is from $4.30 \times 10^{-3}$ to $3.16 \times 10^{-3}$, and the rate ratio between HCHO + HNO$_3$ + (CH$_3$)$_2$NH and HCHO + HNO$_3$ ($v_f/v_i$) is from $4.30 \times 10^{-3}$ to $6.75 \times 10^{-3}$ at the temperature range of 200–298 K. The rate ratios show that the HCHO + HNO$_3$ + H$_2$O/NH$_3$ reactions could not compete well with the naked HCHO + HNO$_3$ reaction at 200–298 K. However, this also shows that the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction could only dominate over the HCHO + HNO$_3$ reaction at 200–240 K.

In the atmosphere, the reaction of HCHO + OH is the main sink of formaldehyde. Therefore, it is important to compare the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction with the HCHO + OH reaction. The rate ratio is as shown in eq 8 in the Supporting Information. $k_{HCHO+OH}$ represents the rate constant of the reaction of HCHO + OH → HCO + H$_2$O in the atmosphere, and the value is $5.40 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. When [OH] = $1 \times 10^9$ molecules cm$^{-3}$, [HNO$_3$] = $1.16 \times 10^{10}$ molecules cm$^{-3}$, and [(CH$_3$)$_2$NH] = $3.2 \times 10^9$ molecules cm$^{-3}$, the value of rate ratio of HCHO + HNO$_3$ + (CH$_3$)$_2$NH and HCHO + OH ($v_f/v_i_{HCHO+OH}$) is $1.93 \times 10^{-3}$ to $5.07 \times 10^{-8}$ in the temperature range of 200–298 K (see Table S2), showing that the reaction of HCHO + OH in the atmosphere is still the main sink of formaldehyde degradation in the atmosphere.

In addition, nitric acid is an important species in the troposphere and stratosphere. The removal of nitric acid is also very important, which is of great significance by comparing the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction with the HNO$_3$ + OH reaction. The rate ratio is as written in eq (9) in the Supporting Information. $k_{HNO_3+OH}$ represents the rate constant of the HNO$_3$ + OH reaction, and the value is $8.50 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. When [HCHO], [OH], and [(CH$_3$)$_2$NH] are $1 \times 10^{11}$, $1 \times 10^9$, and $3.2 \times 10^9$ molecules cm$^{-3}$, respectively, the range of the rate ratio $v_f/v_i_{HNO_3+OH}$ is 1.06 to 2.78 $\times 10^{-5}$ in the range of 200–298 K. However, the concentration of hydroxyl radical (OH) is quite low, which is varied between 0 and 2 $\times 10^9$ molecules cm$^{-3}$ at nighttime and an average of 1.5 $\times 10^9$ molecules cm$^{-3}$ at daytime. When the OH concentration is $1 \times 10^8$ molecules cm$^{-3}$ and the temperature is 200 K, the ratio is 1.06 (Table S3). Moreover, when the OH concentration is reduced to $10^7$ molecules cm$^{-3}$, the (CH$_3$)$_2$NH-catalyzed reaction of HCHO + HNO$_3$ can compete well with the corresponding OH radical below 240 K. However, it is noted that nitric acid is removed from further gas-phase atmospheric processes predominantly via wet deposition and acid rains. Therefore, the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction cannot contribute to the sink of nitric acid. The HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction may play an important role in the formation of secondary organic aerosols (SOAs), as previous studies have shown that nitric acid can react with amine at the surface of air–water to form gas-phase particles. In addition, the present results show that dimethylamine has a stronger catalytic effect on the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction, where dimethylamine acts as a bridge for hydrogen shift compared with water and ammonia in the HCHO + HNO$_3$ + H$_2$O/NH$_3$ reactions. Moreover, dimethylamine has been shown to have remarkable catalytic effects on the hydrolysis of IO$_3^-$ for the nucleation process in polluted coastal regions and the hydrolysis of sulfur dioxide. Therefore, the catalytic ability of dimethylamine is also expected to be found in other hydrogen shift reactions.

### 4. CONCLUSIONS

In this work, we have studied the reactions HCHO + HNO$_3$ → H$_2$C(OH)ONO$_2$ and HCHO + HNO$_3$ catalyzed by water, ammonia, and dimethylamine using quantum chemical methods and conventional transition-state theory. We have found that dimethylamine as a catalyst can significantly reduce the energy barrier of HCHO + HNO$_3$. In addition, the calculated rate ratio shows that the main sink of formaldehyde is still the HCHO + OH reaction in the atmosphere. Moreover, we also found that the HCHO + HNO$_3$ reaction catalyzed by dimethylamine can produce organic nitrate under certain atmospheric conditions. Therefore, the HCHO + HNO$_3$ + (CH$_3$)$_2$NH reaction may play a key role in the formation of SOA precursors and consequently may enhance our understanding of the chemistry of atmospheric aerosols.

### ASSOCIATED CONTENT

#### Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03321.

Binding energies ($\Delta E$, 0 K) of each binary complex with zero-point correction (ZPE) at the CCSD(T)-F12a/cc-pVTZ-F12/M06-2X/MG3S level (in kcal/mol) (Table S1); rate ratios of the HCHO + HNO$_3$ + (CH$_3$)$_2$NH and HCHO + OH reactions at different OH concentrations and the temperature range of 200–298 K (Table S2); rate ratios of the HCHO + HNO$_3$ + (CH$_3$)$_2$NH and HNO$_3$ + OH reactions at different OH concentrations and the temperature range of 200–298 K (Table S3); molecular coordinate and frequency information (Table S4); $T_1$ diagnostic values (Table A1); enthalpies ($\Delta H$) and free energies ($\Delta G$) for the HCHO + HNO$_3$ reaction at the CCSD(T)-F12a/cc-pVTZ-F12/M062X/MG3S level with zero-point correction at 298 K (Table A2); intrinsic reaction coordinate results of TS (Figures S1–S4) (PDF)

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#### Notes

The authors declare no competing financial interest.
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