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The Atmospherically Important Reaction of Hydroxyl Radicals with Methyl Nitrate: A Theoretical Study involving the Calculation of Reaction Mechanisms, Enthalpies, Activation Energies and Rate Coefficients.

by

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Abstract

A theoretical study, involving the calculation of reaction enthalpies and activation energies, mechanisms and rate coefficients, has been made of the reaction of hydroxyl radicals with methyl nitrate, an important process for methyl nitrate removal in the earth's atmosphere.

Four reaction channels were considered:- formation of $H_2O + CH_2ONO_2$, $CH_3OOH + NO_2$, $CH_3OH + NO_3$, and $CH_3O + HNO_3$. For all channels, geometry optimization and frequency calculations were carried out at the M06-2X/6-31+G** level, while relative energies were improved at the UCCSD(T*)-F12/CBS level. The major channel is found to be the H abstraction channel, to give the products $H_2O + CH_2ONO_2$. The reaction enthalpy (ΔH_{298K}^{RX}) of this channel is computed as -17.90 kcal.mol^{-1}. Although the other reaction channels are also exothermic, their reaction barriers are high (> 24 kcal.mol^{-1}) and therefore these reactions do not contribute to the overall rate coefficient in the temperature range considered (200-400 K). Pathways via three transition states have been identified for the H abstraction channel. Rate coefficients were calculated for these pathways at various levels of variational transition state theory (VTST) including tunneling. The results obtained are used to distinguish between two sets of experimental rate coefficients, measured in the temperature range 200-400K, one of which is approximately an order of magnitude greater than the other. This comparison, as well as the temperature dependence of the computed rate coefficients, shows that the lower experimental values are favoured. The implications of the results to atmospheric chemistry are discussed.

Introduction

Alkyl nitrates act as temporary reservoirs of nitrogen oxide radicals in the lower atmosphere (the troposphere) as they have relatively long atmospheric lifetimes, of the order of days to weeks [1,2]. This enables them to undergo long-range transport to remote areas where they can release NO_x (defined here as NO + NO_2 + NO_3) that can give rise to ozone formation. As a result, alkyl nitrates play an important role in contributing to the concentration of O_3 in the troposphere. Methyl nitrate (CH_3ONO_2) and ethyl nitrate ($C_2H_5ONO_2$) are present in the troposphere mainly from marine emissions [3-6] whereas larger alkyl nitrates are predominantly produced through atmospheric oxidation of hydrocarbons in the presence of NO_x (*e.g.* in urban or polluted areas) [1-7]. CH_3ONO_2 and $C_2H_5ONO_2$ account for 20-40% of the light ($C_n \leq 5$) alkyl nitrates in the troposphere with concentrations of 1-43 pptv and 1-50 pptv respectively having been measured [3,6,8]. For the heavier alkyl nitrates, with 4 or more carbon atoms, the association reaction of NO with RO_2 becomes a significant alkyl nitrate source i.e. $RO_2 + NO + M \rightarrow RONO_2 + M$ (M is a third body), whereas for $C_n \leq 4$ the major product channel from the RO_2 + NO reaction is RO + NO_2.

A number of recent regional and global model studies have demonstrated that key kinetic and photolytic parameters for alkyl nitrates are missing, preventing chemical models from describing their atmospheric oxidation chemistry adequately and hence obtaining their atmospheric lifetimes (9,10). These parameters include their loss rate via reaction with OH and O_3, and whether NO_x is released in these reactions. Also, how much NO_x (photochemically reactive nitrogen oxide) and how much HNO_3 (photochemically non-reactive nitrogen oxide) are eventually formed from organic nitrate reactions is important in understanding the contribution of alkyl nitrates to the oxidizing capacity of the troposphere [8]. In a recent study of the mechanism of the atmospherically relevant reaction of chlorine atoms with methyl nitrate and calculation of the rate coefficient of this reaction at temperatures relevant to the troposphere [11], we noted that the lifetime of methyl nitrate in the troposphere is determined by loss through photolysis, reaction with OH and reaction with Cl atoms. This is because methyl nitrate is thermally stable in the troposphere in the temperature range 200-300 K and heterogeneous removal is slow because its solubility in and reactivity with water is low. The photolysis rate of CH_3ONO_2 in the atmosphere has been determined on a number of occasions [12,13] and the rate coefficient (k) of the Cl + CH_3ONO_2 reaction is now reliably known in the temperature range 200-300 K [11]. However, the rate coefficient of the OH +

CH_3ONO_2 reaction in this temperature range is not well established. Available experimental rate coefficients at 298 K occur in two groups which differ by an order of magnitude, a lower group at ~$3x10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} [14-17] and a higher group at ~$3x10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} [18,19]. There is also uncertainty over the temperature dependence of this rate coefficient. Nielsen et al. [18] report a value of (3.2 ± 0.5) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K and a negative temperature dependence of *k* in the region 298-393 K, whereas Shallcross et al.[15] and Talukdar et al.[14] report 298 K values of (2.33 ± 0.14) x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} and (4.7 ± 1.0) x 10^{-14} cm^3 $molecule^{-1}$ s^{-1} respectively and a positive temperature dependence in the region 220-420 K. Also, Talukdar et al. [14] suggest that the OH + CH_3ONO_2 reaction proceeds via H abstraction, based on the fact that the measured rate coefficient was independent of gas composition, the observed trend of rate coefficients as the size of the alkyl group is increased and the large observed primary kinetic isotope effect (as seen in the ratio of the *k*'s measured for OH + CH_3ONO_2 vs OH + CD_3ONO_2). However, the mechanism of the reaction is not well established

In this work, the following reaction channels were considered

H abstraction: $OH + CH_3ONO_2 \rightarrow H_2O + CH_2ONO_2$ ----------(1)

NO_2 formation: $OH + CH_3ONO_2 \rightarrow CH_3OOH + NO_2$ ----------(2)

NO_3 formation: $OH + CH_3ONO_2 \rightarrow CH_3OH + NO_3$ ----------(3)

HNO_3 formation: $OH + CH_3ONO_2 \rightarrow CH_3O + HNO_3$ ----------(4)

Using available heats of formation ($\Delta H_{f,298K}$) of the respective reactants/products, the enthalpies of these reactions, ΔH_{298K}^{RX}, were evaluated as ΔH_1 = -17.72 kcal.mol^{-1}, ΔH_2 = -2.41 kcal.mol^{-1}, ΔH_3 = -9.83 kcal.mol^{-1}, ΔH_4 = -7.22 kcal.mol^{-1} (see Tables 1, 2, 4-7; *vide infra*).

CH_3ONO_2 has a C_s structure with the methyl group staggered with respect to the cis oxygen of the NO_2 group [20]. The methyl V_3 rotational barrier is 811 cm^{-1}. In the CH_3 group, one hydrogen atom is in the plane of the heavy atoms, trans to the O-N bond of the C-O-N unit, while the other two hydrogen atoms lie above and below the plane respectively.

The aim of this work is to use state-of-the-art wavefunction and DFT methods to investigate the reaction mechanisms of these OH + CH_3ONO_2 reactions and to compute reaction rate coefficients in the 200-400 K region which should be valuable to test the available experimental values and to decide which experimental values are the more reliable.

Theoretical considerations and computational details

Ab initio and DFT calculations

Geometry optimization, transition state (TS) search, intrinsic reaction coordinate (IRC) and vibrational frequency calculations were carried out using the M06-2X functional [21] and the 6-31+G** basis set with the Gaussian 09 suite of programs [22]. The M06-2X functional was chosen because it has been shown to perform particularly well for TS structures and reaction barrier heights in some recent benchmark studies [23-26]. It is a highly parameterised hybrid meta functional which allows for mid-range interactions but not dispersion. It is recommended in refs (23-26) for calculations of main group thermochemistry, kinetics and non-covalent interactions. In the IRC calculations, using the Hessian-based predictor-corrector (HPC) reaction path following method [27-29], 15 points from the TS in each direction towards the reactants and products were computed with a step size of 0.1 bohr, and gradients and Hessians were calculated analytically at every IRC point. The computed IRC paths of all the reaction channels cover reaction coordinates of up to *ca.* s = ±1.50 bohr.

Electronic energies of the reactants, products, TSs, reactant complexes (RCs) and product complexes (PCs) were improved by performing single-point energy calculations with the explicitly correlated UCCSD(T*)-F12x (where x = a or b) methods [30,31] on the geometries optimized at the M06-2X/6-31+G** level using the MOLPRO suite of programs [32,33]. The VTZ-F12 and VQZ-F12 basis sets [34] were employed for the atomic orbital (AO) basis sets. The corresponding AVXZ/MP2FIT [35] basis sets (X = T or Q) were used to compute the F12 integrals by density fitting (DF) while the VXZ-F12/OPTRI [34] basis sets were used to compute the many electron integrals by the resolution of identity (RI) method. The computed UCCSD(T*)-F12x/VTZ-F12 and UCCSD(T*)-F12x/VQZ-F12 relative electronic energies, with respect to the separate reactants, were extrapolated to the complete basis set (CBS) limit employing two schemes. In the first scheme, the two-point $1/X^3$ formula of Helgaker et al. [36,37] was used to extrapolate the relative electronic energies computed at the UCCSD(T*)-F12x/VTZ-F12 and UCCSD(T*)-F12x/VQZ-F12 levels, and the extrapolated relative electronic energies are denoted as CBS1. In the other scheme, the relative electronic energies computed at the UCCSD(T*)-F12x/VTZ-F12 and UCCSD(T*)-F12x/VQZ-F12 levels were extrapolated to the CBS limit by the generalized formula of Schwenke [38], with the CBS coefficients optimized by Hill et al. [39] for CCSD-F12b energies with the VTZ-F12/VQZ-F12 basis set combination. The extrapolated relative electronic energies thus obtained are denoted as CBS2. The averages of the computed UCCSD(T*)-F12a/CBS1//M06-2X/6-31+G**,

UCCSD(T*)-F12b/CBS1//M06-2X/6-31+G**, UCCSD(T*)-F12a/CBS2//M06-2X/6-31+G** and UCCSD(T*)-F12b/CBS2//M06-2X/6-31+G** relative electronic energies, labelled as UCCSD(T*)-F12ave/CBSave//M06-2X, are considered to be the best theoretical estimates in the present study. The choice of the average value as the best theoretical estimate is mainly because the values obtained by the various extrapolation schemes described above are very close to each other (vide infra).

In the $^2\Pi$ state of OH, the spin-orbit (SO) splitting of 139.6 cm^{-1} results in an energy lowering of the unperturbed $^2\Pi$ state to the $^2\Pi_{3/2}$ state of 0.20 kcal mol^{-1} [40]. Therefore, all the computed relative energies, namely, reaction enthalpies (ΔH_{298K}^{RX}), reaction energies (ΔE^{RX}) and activation energies ($\Delta E^{\ddagger}$), were increased by 0.20 kcal mol^{-1} to allow for this. This correction has also been applied to the relative energy of the RCs and PCs, notably for reaction 1. Also, the electronic partition functions of both the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states of OH, together with the appropriate energies and degeneracies, were included in the subsequent rate coefficient calculations.

For reactions (1)-(4), the transition states that were located in the M06-2X calculations can be labelled as follows (*vide infra)*:-

H abstraction: $OH + CH_3ONO_2 \rightarrow TS_{1a} / TS_{1b} / TS_{1c} \rightarrow H_2O + CH_2ONO_2$ ----(1′)

NO_2 formation: $OH + CH_3ONO_2 \rightarrow TS_2 \rightarrow CH_3OOH + NO_2$ ----(2′)

NO_3 formation: $OH + CH_3ONO_2 \rightarrow TS_3 \rightarrow CH_3OH + NO_3$ ----(3′)

HNO_3 formation: $OH + CH_3ONO_2 \rightarrow TS_{4a} \rightarrow CH_3O + HNO_3$ ----(4′)

$OH + CH_3ONO_2 \rightarrow TS_{4b} \rightarrow CH_3O(OH)NO_2$ conformer 1

$\rightarrow TS_{rot} \rightarrow CH_3O(OH)NO_2$ conformer 2 $\rightarrow TS_{4c} \rightarrow CH_3O + HNO_3$

Rate coefficient calculations

Reaction rate coefficients were computed for the H abstraction channel {channel (1)} at various TST levels in single-level and improved single-level direct dynamics calculations at temperatures in the region 200-400 K using the POLYRATE 2010-A program [41]. The rate coefficients obtained correspond to rate coefficients obtained in the high pressure limit. As the computed barrier heights of channels (2), (3) and (4) are considerably higher than that of channel (1), only channel (1) was considered in the rate coefficient calculations. In addition, for channel (1), the computed energies of TS_{1b} and TS_{1c} relative to the reactants are higher than that of TS_{1a} by *ca.* 2-3 kcal mol^{-1} and therefore it is expected that TS_{1a} would contribute

the most to the total rate coefficient of channel (1).

The geometries of the reactants, reactant complex (RC), TS, product complex (PC), products and the 30 non-stationary points on the IRC path obtained at the M06-2X/6-31+G** level, together with the corresponding analytical gradients and Hessians, were used in the single-level direct dynamics calculations. All the methyl torsional modes (in CH_3ONO_2 and the RC) were treated as hindered internal rotations within the hindered-internal-rotator (HIR) approximation [42] using the full Chuang-Truhlar (CT) method [43,44]. The V_{MEP} curves were obtained by interpolation/extrapolation in the range of s = ±0.86 Å using the Euler-steepest-descents (ESD) method [45] with a Hessian step size of 2.39 x 10^{-3} Å, which is nine times larger than the gradient step size of 2.65 x 10^{-4} Å. In the generalized normal mode analysis, curvilinear internal coordinates [46] were used instead of the redundant internal coordinates [47] because it was found in the present study that the redundant internal coordinates gave extra imaginary vibrational frequencies, which indicate unphysical descriptions of the vibrational motions of the molecules. With curvilinear internal coordinates, no extra imaginary vibrational frequency was found along the minimum energy path (MEP). Rate coefficients were calculated at different TST levels, namely, conventional transition state theory (TST), canonical variational transition state theory (CVT) and improved canonical variational transition state theory (ICVT), with different tunneling methods, including zero-curvature tunneling (ZCT) and small-curvature tunneling (SCT) corrections.

Improved single-level direct dynamics calculations [48] were carried out, with the M06-2X/6-31+G** V_{MEP} curve as the lower level (LL) and the higher-level (HL) V_{MEP} curve obtained by using the computed HL energies of five stationary points. These are the separated reactants, RC, TS, PC and the separated products computed at the UCCSD(T*)-F12ave/CBSave level (the average of the four CBS values). More IRC points on the HL V_{MEP} were obtained by the following scaling expression devised by us previously (equation (5),[49]).

$$E_s^{HL} = (E_s^{LL} - E_{RC}^{LL}) .\{(E_{TS}^{HL} - E_{RC}^{HL})/(E_{TS}^{LL} - E_{RC}^{LL})\} + E_{RC}^{HL} \quad \text{---------- (5)}$$

With this expression, an improved HL energy (E_s^{HL}) at a certain s along the LL IRC can be evaluated using the LL energy (E_s^{LL}) and the ratio between the computed HL and LL barriers. Together with the HL energies of the five stationary points, the additional HL IRC energies obtained from this scaling expression were used in improved single-level rate coefficient calculations with the geometries and vibrational frequencies at the lower level. This scaling formula gave almost identical rate coefficients as those obtained with the dual-level mapping method of POLYRATE [48] (more detail is given in the Supplementary Information section SI1).

Results and discussion

Ab initio and DFT results

From the results of the *ab initio* and DFT calculations, channels (2), (3) and (4) were found to have considerably higher barrier heights (> 20 kcal mol^{-1}) than channel (1). As a result, channel (1) is the dominant pathway of the OH + CH_3ONO_2 reaction and will be considered, after channels (2), (3) and (4) have been discussed. The contributions of channels (2), (3) and (4) to the total rate coefficient of the OH + CH_3ONO_2 reaction are expected to be negligibly small and hence they were neglected in the subsequent rate coefficient calculations.

Inspection of the results of UCCSD(T*)-F12x calculations shows that the effects of basis set size on the computed ΔE_e^{RX} and $\Delta E_e^{\ddagger}$ (the reaction energy and activation energy respectively calculated using only electronic energies), the energy differences between the F12a and F12b results, and those between the two CBS extrapolation schemes (CBS1 and CBS2) are small in all channels, as the energy differences are within chemical accuracy (1 kcal. mol^{-1}). The geometries of the TSs in all channels (equations 1′-4′), optimized at the M06-2X/6-31+G** level, are shown in Figure 1, while those of the adduct conformers in channel (4) and those of the RC and PC in channel (1) are shown in Figure 2. Furthermore, the ΔE_{0K} values computed at the UCCSD(T*)-F12ave/CBSave//M06-2X level are summarized in the energy profile in Figure 3.

NO_2 formation: OH + CH_3ONO_2 → CH_3OOH + NO_2 --- Channel (2)

The geometry of the TS in channel (2′), TS_2, optimized at the M06-2X/6-31+G** level is shown in Figure 1. The computed imaginary vibrational frequency of TS_2, 988i cm^{-1}, corresponds to the asymmetric O…O…N stretching mode, indicating that TS_2 undergoes O-N bond breaking and O-O bond formation via a S_N2 mechanism to release NO_2, when the O atom of the OH radical attacks the O atom next to the methyl group. In TS_2, the breaking C-N bond is elongated by 33% while the forming O-O bond is longer than that in CH_3OOH by 22%. Hence, it is not obvious whether TS_2 is reactant-like or product-like, as the elongations of the breaking C-N bond and the forming O-O bond are comparable. The computed reaction energies (ΔE_e^{RX}) and activation energies ($\Delta E_e^{\ddagger}$) of channel (2) at various levels of theory are summarized in Table 1. The best computed ΔE_e^{RX} and $\Delta E_e^{\ddagger}$ values (labelled as F12ave/CBSave) are -1.72 ± 0.01 and 24.08 ± 0.17 kcal mol^{-1}. Including the zero-point

energy (ZPE) correction and the spin-orbit correction for OH, the best computed ΔE_{0K}^{RX} and $\Delta E_{0K}^{\ddagger}$ values of -1.21 and 24.56 kcal mol^{-1} are obtained. This indicates that channel (2) has a high activation barrier and, therefore, its contribution to the total rate coefficient of the OH + CH_3ONO_2 reaction is negligible (more detail is given in the Supplementary Information section SI2).

NO_3 formation: OH + CH_3ONO_2 → CH_3OH + NO_3 --- Channel (3)

The geometry of the TS in channel (3′), TS_3, optimized at the M06-2X/6-31+G** level is shown in Figure 1. The imaginary vibrational frequency of 1251i cm^{-1} corresponds to the asymmetric O…C…O stretching mode, which shows that TS_3 undergoes O-C bond breaking and C-O bond forming via a S_N2 mechanism to release NO_3 when the O atom in the OH radical attacks the C atom in the methyl group. The breaking O-C bond in TS_3 is elongated by 29% while the forming C-O bond is longer than the equilibrium value of 1.41 Å in CH_3OH by 25%, and so the TS_3 is not reactant-like or product-like. The computed ΔE_e^{RX} and $\Delta E_e^{\ddagger}$ values at various levels of theory are summarized in Table 2. The best computed ΔE_e^{RX} and $\Delta E_e^{\ddagger}$ values at the F12ave/CBSave level are -7.99 ± 0.12 and 36.07 ± 0.11 kcal mol^{-1} respectively, and the corresponding best computed ΔE_{0K}^{RX} and $\Delta E_{0K}^{\ddagger}$ values are -7.73 and 37.09 kcal mol^{-1}. Although the computed ΔH_{298K}^{RX} value of -8.01 kcal mol^{-1} indicates that channel (3) is exothermic, the large reaction barrier height of 37.09 kcal mol^{-1} means that this reaction will only make an extremely small contribution to the overall OH + CH_3ONO_2 rate coefficient. As a result, channel (3) was also not considered in the rate coefficient calculations (more detail is given in the Supplementary Information section SI3).

HNO_3 formation: OH + CH_3ONO_2 → CH_3O + HNO_3 --- Channel (4)

The reaction leading to HNO_3 formation can take place through a concerted mechanism, in which the reactants proceed to the products via a transition state, or through a stepwise mechanism involving adduct formation (see equation 4′). Both pathways are calculated to have high activation energies (> 28 kcal.mol^{-1}) and therefore this channel is not expected to contribute to the overall reaction rate coefficient (more detail is given in the Supplementary Information section SI4).

H abstraction: OH + CH_3ONO_2 → H_2O + CH_2ONO_2 --- Channel (1)

In channel (1), a H atom of the methyl group of CH_3ONO_2 is abstracted by the OH

radical to give H_2O and CH_2ONO_2. As shown in equation (1′), three TS's have been located and their optimized geometries at the M06-2X/6-31+G** level are shown in Figure 1. Some major geometrical parameters, the imaginary vibrational frequencies, the ΔE_e and ΔE_{0K} values as well as the ZPE corrections of the three TS's are summarized in Table 6. In TS_{1a} and TS_{1b}, the OH radical abstracts the out-of-plane H atom, with the O-H bond in the OH radical nearly parallel to the C_s plane of CH_3ONO_2. The geometry of TS_{1a} is similar to that of TS_{1b}, except that in TS_{1a} the H atom in the OH radical points towards the O atom in the nitrate group and this results in a O---H hydrogen bond-like interaction with a distance of 2.34 Å between the O and H atoms. In TS_{1c}, the OH radical abstracting the in-plane H atom is in the C_s plane of CH_3ONO_2, and the O-H bond in the OH radical is almost parallel to the C-O bond. TS_{1a}, TS_{1b} and TS_{1c} have imaginary vibrational frequencies of 1294i, 1135i and 1486i cm^{-1} respectively (see Table 6), which correspond to the asymmetric C···H···O stretching mode. The *L* parameters determined from the ratio of the elongation of the breaking C-H bond to that of the forming H-O bond {$L = \Delta$(C-H)/Δ(H-O)} are 0.39, 0.25 and 0.39 for TS_{1a}, TS_{1b} and TS_{1c} respectively, indicating that all the three TS's are reactant-like because their *L* parameters are smaller than 1. It can be seen that both the ΔE_e and the ΔE_{0K} values of the TS's are in the order $TS_{1c} > TS_{1b} > TS_{1a}$. TS_{1a} has the lowest energy of the three TS's, as expected, due to the presence of the hydrogen bond-like interaction, which stabilizes TS_{1a} by *ca*. 1.5 to 2 kcal mol^{-1}. The best computed activation energies (ΔE_e without ZPE and OH spin-orbit corrections) to the transition states TS_{1a}, TS_{1b} and TS_{1c}, at the F12ave/CBSave level, are 4.02, 5.52 and 7.05 kcal mol^{-1} respectively. They are within 1 kcal.mol^{-1} of the corresponding M06-2X values (3.01, 5.10 and 6.23 kcal.mol^{-1}), suggesting that the M06-2X functional performs well for barrier heights of this channel, especially for TS_{1b} where the energy difference between the M06-2X and the F12ave/CBSave levels is 0.42 kcal mol^{-1}. With the ZPE and spin-orbit corrections, the best computed activation energies (ΔE_{0K}) associated with TS_{1a}, TS_{1b} and TS_{1c} are 2.76, 4.02 and 5.04 kcal mol^{-1} respectively, showing that channel (1) has the lowest barrier height of all channels and hence is the dominant pathway of the OH + CH_3ONO_2 reaction. This supports the conclusion of the study of Talukdar *et al.*[14] that the OH + alkyl nitrate reaction proceeds via simple H abstraction, rather than OH addition suggested by He *et al*. [8].

Regarding the out-of-plane OH + $CH_3ONO_2 \rightarrow H_2O + CH_2ONO_2$ channel via TS_{1a}, a RC and a PC (labelled as RC_{1a} and PC_{1a} respectively) have been located in the entrance and exit channels respectively. The geometries of the RC_{1a} and PC_{1a} optimized at the M06-2X/6-

31+G** level are shown in Figure 2. In the seven-membered ring RC_{1a}, there is an interaction between the H atom of the OH radical and the O atom in the nitrate group with a O---H distance of 2.51 Å. In PC_{1a}, the two H atoms in H_2O are oriented to enable interactions with the two O atoms in the nitrate group with O---H distances of 2.96 Å and 3.25 Å. The computed ΔE_e, ΔE_{0K} and ΔH_{298K} values of the RC_{1a} and PC_{1a}, together with those of TS_{1a} and the separate products, obtained at various UCCSD(T*)-F12x//M06-2X/6-31+G** levels are summarized in Table 7. These values were used in the rate coefficient calculations with POLYRATE. The energies of the RC_{1a} and PC_{1a} are lower than the separate reactants and products, respectively, by *ca*. 3 kcal mol^{-1}. The best computed ΔE_e values of the RC_{1a}, TS_{1a}, PC_{1a} and the separate products at the F12ave/CBSave level are -3.01 ± 0.01, 4.02 ± 0.05, -20.51 ± 0.07 and -17.23 ± 0.08 kcal mol^{-1} respectively. The estimated uncertainties are within 0.1 kcal mol^{-1}, which are negligibly small, for all the species. It was found that the M06-2X functional performs reasonably well for the ΔE_e values of TS_{1a} and PC_{1a}, and fairly well for the ΔE_e values of RC_{1a} and the separate products, as the differences between the M06-2X and the F12ave/CBSave values for RC_{1a}, TS_{1a}, PC_{1a} and separate products are 2.41, 1.03, 0.20 and 2.64 kcal mol^{-1} respectively. The best computed ΔH_{298K}^{RX} value (including the spin-orbit correction) for channel (1) is -17.90 kcal mol^{-1}, which is lower than the ΔH_{298K}^{RX} of -13.92 kcal mol^{-1} evaluated from the available $\Delta H_{f,298K}$ values of CH_3ONO_2 [50], OH [51], CH_2ONO_2 [50], and H_2O [52] by *ca*. 4 kcal mol^{-1}. However, it agrees very well with the ΔH_{298K}^{RX} value of -17.72 kcal mol^{-1} determined using these $\Delta H_{f,298K}$ values but with the $\Delta H_{f,298K}$ values for CH_3ONO_2 and CH_2ONO_2, obtained from the tabulation of Burcat et al. [50], replaced by -29.71 and 19.30 kcal mol^{-1} respectively, computed in our previous study [11].

Rate coefficients of the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 channel

Computed rate coefficients at the M06-2X single level

The reaction paths, including the V_{MEP}, ΔZPE and V_a^G curves, obtained at the M06-2X/6-31+G** level for the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 C-H out-of-plane channel via TS_{1a} are shown in Figure 4 (upper panel). There is a dip of ~ 3 kcal mol^{-1} in the ΔZPE curve near the saddle point region (s = 0), which leads to a shift of the maximum of the V_a^G curve to s = -0.16 Å. The computed rate coefficients for this channel (k_{1a}), obtained at different VTST levels using the M06-2X IRC, plotted against temperature are shown in Figure 5. The available experimental values [14-19] determined in the temperature range of 200-423 K are also included in the lower part of this figure ($\log_{10}k$ vs 1000/T). It should be noted

that all the k_{1a} computed rate coefficients have been multiplied by two to account for the two possible C-H out-of-plane H abstraction sites, which are equivalent. The higher sets of experimental values from Nielsen et al. [18] and Kerr et al. [19] are not shown in the upper part of Figure 5, the k vs T plot, as they are considerably larger than the other values. They are however shown in the lower part of Figure 5 where $\log_{10}$k is the vertical axis. As expected, the computed TST rate coefficients, k^{TST}, at a given temperature are larger than all the VTST computed values. They are larger than the CVT and ICVT values by an order of magnitude, indicating that the variational effect is significant. The tunneling effects, whether with ZCT or SCT, are small when T > 360 K, as the transmission coefficients are close to unity. However, the tunneling effects become more significant as temperature decreases. The transmission coefficients with ZCT and SCT at 200 K are 4.56 and 9.64 respectively; thus the SCT correction at this temperature can increase the computed rate coefficients by nearly an order of magnitude. The classical adiabatic ground-state (CAG) correction [53-55] accounts for the fact that the generalized transition state (GTS) at the CVT level is not located at the maximum of the V_a^G curve. The CAG factor at the CVT level ($\kappa^{CVT/CAG}$) is close to unity in the range 200-400 K, indicating that the CAG correction with CVT is insignificant, because the maximum of the ΔG curve is located at $s \approx$ -0.15 Å, which is near to the maximum of the V_a^G curve (s = -0.16 Å). (ΔG is the change in free energy of the reaction system relative to the reactants). Considering the computed rate coefficients at the highest ICVT/SCT level ($k^{ICVT/SCT}$), they are closer to the lower sets of experimental values of Gaffney et al. [16], Talukdar et al. [14], Kakesu et al. [17] and Shallcross et al. [15], than the higher values of Nielsen et al. [18] and Kerr et al. [19], but are lower than the lower group of experimental values by an order of magnitude. In addition, the computed $k^{ICVT/SCT}$ values show a positive temperature dependence which is observed in the lower set of experimental values but not in the higher group, indicating that the computed $k^{ICVT/SCT}$ values, derived from the computed M06-2X reaction paths, favour the lower set of experimental values.

Computed rate coefficients at the UCCSD(T*)-F12ave/CBSave//M06-2X/6-31+G dual level**

The V_{MEP}, ΔZPE and V_a^G curves obtained at the UCCSD(T*)-F12ave/CBSave//M06-2X/6-31+G** level for the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 C-H out-of-plane channel via TS_{1a} are shown in Figure 4 (lower panel). As shown in Table 7, $\Delta E_e^{\ddagger}$ obtained at the UCCSD(T*)-F12ave/CBSave//M06-2X/6-31+G** level is 4.02 kcal.mol^{-1} compared with 3.01 kcal.mol^{-1} at the M06-2X/6-31+G** level (both values are without correction for OH

spin-orbit splitting which would increase them both by 0.20 kcal.mol^{-1}).The HL V_{MEP} and V_a^G curves are shown in the lower half of Figure 4. These were obtained using HL energies of the reactants, RC_{1a}, TS_{1a}, PC_{1a} and products, as well as extra HL IRC points calculated by the expression devised by us previously (equation (5) and ref.(49)). The HL F12ave/CBSave V_{MEP} curve follows the shape of the M06-2X V_{MEP} curve and has a maximum of 4.22 kcal mol^{-1} at s = 0. The plots of the rate coefficients computed at various VTST levels for this channel (1(a)) with the HL F12ave/CBSave//M06-2X/6-31+G** IRC in the temperature range between 200 K and 400 K are shown in Figure 6. The spread and the order of the F12ave/CBSave k values at different VTST levels are similar to those of the M06-2X k values. However, the F12ave/CBSave k values are smaller than the corresponding M06-2X values by an order of magnitude, as the F12ave/CBSave $\Delta E^{\ddagger}$ is higher than the M06-2X $\Delta E^{\ddagger}$ by *ca*. 1 kcal mol^{-1}. Computed ICVT/SCT rate coefficients of reactions (1a), (1b) and (1c) in the temperature range between 200 K and 400 K, as well as the total rate coefficients of the hydrogen atom abstraction reaction, obtained with the HL F12ave/CBSave//M06-2X/6-31+G** IRC, are shown in Figure 7 (see also Tables SI5 and SI6 in the Supplementary Information (SI)). The total rate coefficient has been obtained from $k_{total} = 2k_{1a} + 2k_{1b} + k_{1c}$, as there are two hydrogen atoms in CH_3ONO_2 that could be removed in channels 1a and 1b (the out-of-plane H atoms), but only one that could be removed in channel 1c (the in-plane H atom). This figure shows that k_{1a} is the main contribution to the overall rate coefficient in the temperature range 200-300K, with k_{1b} also becoming significant above 300 K. k_{1c} is significantly lower than k_{1a} by at least an order of magnitude at all temperatures considered, and hence its contribution to k(total) is very small. As can be seen from Figure 7, k_{1b} becomes comparable with k_{1a} at temperatures higher than 280 K, and k_{1b} becomes higher than k_{1a} at temperatures greater than 334K ($1000/T$ = 2.99 K^{-1}) . This is somewhat surprising as channel 1b has a higher barrier than channel 1a ($\Delta E_e^{\ddagger}$ values 4.22 (1a) and 5.72 (1b) kcal.mol^{-1} respectively). This arises because the entropy term ($\Delta S^{\ddagger}$) in the rate coefficient ($\Delta S^{\ddagger}$ is negative in both cases) makes a larger contribution to k_{1b} than k_{1a} in the temperature range 340-400 K, such that $\Delta G^{\ddagger}$ is more positive for channel 1a than 1b in the temperature range 340-400 K, whereas $\Delta G^{\ddagger}$ is less positive for channel 1a than 1b in the temperature range 200-340 K

The computed $k^{ICVT/SCT}$ values of channel 1 (k_{total}) at the F12ave/CBSave level fall below the experimental values, indicating that the F12ave/CBSave $\Delta E_e^{\ddagger}$ for TS_{1a} of 4.22 kcal mol^{-1} and $\Delta E_e^{\ddagger}$ for TS_{1b} of 5.72 kcal mol^{-1} (with spin-orbit correction of OH) are too high (see

Table 8; the $k^{ICVT/SCT}$ values are shown in column 3). In order to obtain an improved match between theory and experiment, calculations were carried out with reduced barrier heights for channels 1(a), 1(b) and 1(c). A reduction of the barrier heights of channels 1(a), 1(b) and 1(c) of 2.5 kcal mol^{-1} has been made, to give $\Delta E_e^{\ddagger}$ values of 1.72, 3.22 and 4.75 kcal mol^{-1} for these channels, and rate coefficient calculations were carried out with the corresponding HL F12ave/CBSave IRC. This lowering of 2.5 kcal.mol^{-1} in the $\Delta E_e^{\ddagger}$ values made for channels 1(a), 1(b) and 1(c) is similar to the downward correction we had to make in related studies of the Cl + $CH_3C(O)OCH_3$ [49] and Cl + HCOOH [56] reactions of 2.2 and 2.7 kcal.mol^{-1} respectively. k_{total} ICVT/SCT values obtained at different temperatures with this correction are shown in column 2 of Table 8. As can be seen from this table, the experimental rate coefficients fall into two groups. A lower set, where the experimental values of Talukdar [14] and Shallcross [15] show a positive temperature dependence in the temperature range 220-420 K, and a higher group, where the experimental values of Nielsen [18] show a negative temperature dependence in the temperature range 298-393 K. At 300 K, the computed $k^{ICVT/SCT}$ value with the HL F12ave/CBSave IRC is ~ 30 times lower than the 300 K values of Talukdar [14] and Shallcross [15]. However, a 2.5 kcal.mol^{-1} reduction of the $\Delta E_e^{\ddagger}$ values for channels 1(a), 1(b) and 1(c) increases the 300 K $k^{ICVT/SCT}$ value, to give good agreemnt with the 300 K values of Talukdar [14] and Shallcross [15]. These computed $k^{ICVT/SCT}$ values also show a positive temperature dependence, as observed in the work of Talukdar and Shallcross (see Figure 8). To increase the computed $k^{ICVT/SCT}$ 300 K value to agree with the higher value of Nielsen [18], requires a reduction in barrier heights $\Delta E_e^{\ddagger}$ of at least 3.5 kcal.mol^{-1}. With such a reduction a positive temperature dependence of $k^{ICVT/SCT}$ is still computed, not a negative temperaure dependence as observed by Nielsen [18]. Also, a reduction of $\Delta E_e^{\ddagger}$ of 3.5 kcal.mol^{-1} is larger than we have had to apply to calculations at the same level on related reactions [49,56] to give acceptable agreement with experimental values. Therefore, considering all the evidence it is concluded that the lower set of experimental rate coefficients, with a positive temperature dependence, are to be preferred. As has been noted previously [49.56], the main reason for the difference between the experimental and computed rate coefficients is because the equilibrium geometries and vibrational frequencies of the stationary points on the reaction surface, and the entropy term used in the calculation of the rate coefficient come from the lower level calculations (M06-2X/6-31+G** in this case) whereas the higher level calculations give the enthalpy term used in the calculation of the rate coefficient. This is discussed further in the Concluding Remarks.

Atmospheric Implications

Both the M06-2X/6-31+G** single level and UCCSD(T*)F12ave/CBSave//M06-2X/6-31+G** improved single level electronic structure / rate coefficient calculations performed in this work favour the lower set of experimental rate coefficients [14-17] over the higher group [18,19]. They also support the positive temperature dependence of the rate coefficient in the temperature range 200-400 K observed in the work of refs (14) and (15) rather than the negative temperature dependence observed in ref.(18).

It is valuable to compare the results of this present work on the OH + CH_3ONO_2 reaction with those obtained in our earlier work on the Cl + CH_3ONO_2 reaction[11]. Both proceed via a hydrogen abstraction reaction. For the Cl + CH_3ONO_2 reaction, the recommended values for the reaction barrier ($\Delta E_e^{\ddagger}$) and reaction enthalpy (ΔH_{298K}^{RX}) are 0.17 and -2.30 kcal.mol^{-1}, values obtained at the UCCSD(T*)-F12/CBS//M06-2X/6-31+G** level, whereas the corresponding recommended values in this work for the OH + CH_3ONO_2 case are 1.72 (1a) and -17.72 kcal.mol^{-1}. The reaction barrier ($\Delta E_e^{\ddagger}$) is lower in the Cl + CH_3ONO_2 case than in the OH + CH_3ONO_2 reaction, and the Cl + CH_3ONO_2 rate coefficients are higher, in the temperature range 200-400 K. The Cl + CH_3ONO_2 reaction rate coefficient shows a positive temperature dependence as is now established for the OH + CH_3ONO_2 case. For the OH + CH_3ONO_2 reaction, as shown in Figure 1, TS_{1a} has a structure with a hydrogen bond between the O of the O-H and an H of the CH_3 group, and a longer hydrogen bond between the H of the O-H and an O of the -NO_2 group. In the Cl + CH_3ONO_2 case, this hydrogen bonding is obviously not possible and the transition state structure is similar to that shown for TS_{1b} and TS_{1c} in Figure 1.

As was noted in the Introduction, the lifetime of methyl nitrate in the troposphere is controlled by photolysis, reaction with Cl atoms and reaction with OH. The photolysis lifetime of methyl nitrate in the troposphere (0-15 km above ground level) has been determined to be in the region of 1-5 days [1,12,13]. In the troposphere the temperature typically drops from 288 K at ground level to 216 K at 15 km, and hence the rate coefficients shown in Table 8 in the temperature range 200-300 K are the most relevant to the troposphere. In our earlier work on Cl + CH_3ONO_2 [11], we calculated that for [Cl] = 10^3 atom.cm^{-3}, the estimated day-time global average in the marine boundary layer [57], the methyl nitrate lifetime with respect to this reaction is 3.68x10^4 days at 300 K and 2.49x10^5 days at 200 K, using the now well established Cl + CH_3ONO_2 rate coefficients [11]. For the OH + CH_3ONO_2 reaction, the work of Talukdar et al. [14] is the only study in which rate coefficients have been measured in

the range 200-300 K. The 298 K rate coefficient of ref.(14) is in the lower group. Also, the rate coefficients determined by these authors in the higher temperature region 300-423 K agree reasonably well with previously determined values in this temperature range by Shallcross et al. [15]. The experimental rate coefficients of Talukdar et al. [14] were therefore assumed as a reliable reference for the purposes of calculating the lifetime of methyl nitrate with respect to reaction with OH. This can be calculated at a particular temperature as $1/(k_{OH}$ [OH]), if [OH] and k_{OH} , the OH + CH_3ONO_2 rate coefficient, are known at that temperature. Using OH = $1x10^6$ molecule.cm^{-3}, the estimated average day-time concentration of OH [58], with the rate coefficients from Talukdar et al. [14] (see Table 8), the methyl nitrate lifetime with respect to reaction with OH is calculated as 422 (300K) and 2320 (200K) days respectively. Therefore, under normal atmospheric conditions in the troposphere the methyl nitrate lifetimes are in the order

$$\text{Photolysis} < \text{OH}_{\text{reaction}} < \text{Cl}_{\text{reaction}}$$

Concluding remarks

The reaction mechanism of the OH + CH_3ONO_3 reaction has been investigated by carrying out *ab initio*/DFT calculations on four possible reaction channels:- hydrogen atom abstraction, NO_2 production, NO_3 production and HNO_3 production. All reaction channels are exothermic but the H abstraction channel has a much lower activation energy compared with the other channels. This means that the H abstraction channel will have the highest rate coefficients and is therefore kinetically the most important while NO_2, NO_3 and HNO_3 formation will be minor. The H abstraction channel was found to proceed via three possible pathways involving transition states TS_{1a}, TS_{1b} and TS_{1c} (see Figure 1-3). The pathway via TS_{1a}, a hydrogen bonded transition state, has the lowest activation energy.

ICVT/SCT rate coefficients obtained with the UCCSD(T*)-F12ave/CBSave//M06-2X IRC for the H abstraction reaction (reaction 1) via the three transition states, TS_{1a}, TS_{1b} and TS_{1c}, show that k_{1a} and k_{1b} are the main contributors to the overall rate coefficient ($k_{total} = 2k_{1a} + 2k_{1b} + k_{1c}$) in the temperature range 200-400 K. k_{1c} makes a negligible contribution. k_{1a} is greater than k_{1b} in the atmospherically important temperature range 200-300K in the troposphere with k_{1b} becoming greater than k_{1c} at $T > 334$ K. A reduction in the barrier heights ($\Delta E_e^{\ddagger}$) of TS_{1a} , TS_{1b} and TS_{1c} by 2.5 kcal.mol^{-1} brings the computed k_{total} values in reasonably good agreement with the experimental values over the range 200-400 K. k_{1a}, k_{1b} and k_{1c} all increase with increasing temperature. This behaviour as well as the fact that the

k_{total} is less than the lower group of experimental rate coefficients favours the lower experimental rate coefficients over the higher group. The relative importance of the methyl nitrate loss processes (photolysis, reaction with OH and reaction with Cl atoms) in the troposphere is discussed and the methyl nitrate lifetimes with respect to these processes is shown to be in the order

$$\text{Photolysis} < \text{OH}_{\text{reaction}} < \text{Cl}_{\text{reaction}} .$$

In summary, the rate coefficients computed at the highest level favour the lower set of experimental rate coefficients, which show a positive temperature dependence. However, the computed lower level (M06-2X/6-31+G**) rate coefficients agree better with these experimental values than the rate coefficients computed at the higher level (UCCSD(T*)F12ave/CBSave//M06-2X/6-31+G**). This type of discrepancy has been noted before [59]. At present, with wavefunction methods, one can carry out systematic improvements in the computation of relative electronic barriers, with the geometries of the reactants, RC, TS, PC and products obtained at a lower level (M06-2X/6-31+G** in this case). In this connection, there is little more that we can do to improve the enthalpy of activation as UCCSD(T*)-F12-CBS is at present at the state-of-the-art level. (It should also be noted that it is inappropriate to compare computed activation energies with experimentally derived activation energies; see our previous work [11,49,56]). Regarding geometrical structures and vibrational frequencies, a method with analytical first and second derivatives is required. We have previously shown that using different functionals for the lower level, for geometries and frequencies, with the same higher level barrier height can lead to computed rate coefficients which differ by one order of magnitude as the entropic contribution to the free energy of activation will be different with different functionals [11,49,56]. In summary, one should bear in mind that the uncertainties associated with the entropic and/or enthalpic contributions can lead to computed uncertainties in the computed rate coefficients. Further theoretical and experimental investigations are required to bring theory closer to experiment for this reaction, with the evidence from the present work clearly favouring the lower set of experimental rate coefficients.

Contents of Supporting Information

SI1. A note on calculation of improved single-level V_{MEP} curves
SI12 Extra information on NO_2 formation:

$OH + CH_3ONO_2 \rightarrow CH_3OOH + NO_2$ --- Channel (2)

SI3 Extra information on NO_3 formation:

$OH + CH_3ONO_2 \rightarrow CH_3OH + NO_3$ --- Channel (3)

SI4 Extra information on HNO_3 formation:

$OH + CH_3ONO_2 \rightarrow CH_3O + HNO_3$ --- Channel (4)

SI5. Table SI1**.** $k^{ICVT/SCT}$ values obtained with the HL UCCSD(T*)-F12ave/CBSave//M06-2X IRC for $2k_{1a}$, $2k_{1b}$ and k_{1c} from barrier heights ($\Delta E_e^{\ddagger}$) of 4.22, 5.72 and 7.25 kcal mol^{-1} respectively.

SI6. Table SI2. $k^{ICVT/SCT}$ values obtained with the HL UCCSD(T*)-F12ave/CBSave//M06-2X IRC for $2k_{1a}$, $2k_{1b}$ and k_{1c} from barrier heights ($\Delta E_e^{\ddagger}$) of 1.72, 3.22 and 4.75 kcal mol^{-1} respectively. $\Delta E_e^{\ddagger}$ values for 1a, 1b and 1c are reduced by 2.5 $kcal.mol^{-1}$ from those used in SI5 (see text).

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Table 1. Computed reaction (ΔE_e^{RX}) and activation ($\Delta E_e^{\ddagger}$) energies (in kcal mol^{-1}) of the OH + CH_3ONO_2 → TS_2 → CH_3OOH + NO_2 channel at various UCCSD(T*)-F12x//M06-2X/6-31+G** levels of calculation.

Methods	ΔE_e^{RX}			$\Delta E_e^{\ddagger}$		
	F12a	F12b	(other)	F12a	F12b	(other)
(M06-2X/6-31+G**)			(0.28)			(29.86)
UCCSD(T*)-F12x/VTZ-F12	-1.81	-1.75		23.38	23.56	
UCCSD(T*)-F12x/VQZ-F12	-1.76	-1.72		23.82	23.90	
$1/X^3$ CBS1	-1.72	-1.71		24.14	24.15	
Schwenke CBS2	-1.74	-1.72		23.98	24.03	
Average ΔE_e (CBS1 and CBS2)	-1.73	-1.71		24.06	24.09	
Best ΔE_e (F12ave/CBSave)[a]			-1.72(1)			24.08(17)
ΔE_{0K} (CBSave)	-1.42	-1.40		24.35	24.38	
ΔE_{0K} (include SO of OH)	-1.22	-1.20		24.55	24.58	
Best ΔE_{0K} (F12ave/CBSave)[a]			-1.21			24.56
ΔH_{298K}	-1.36	-1.35				
ΔH_{298K} (including SO of OH)	-1.16	-1.15				
Best ΔH_{298K} (F12ave/CBSave)[a]			-1.16			
ΔH_{298K} (from available $\Delta H_{f,298K}$)			-2.96[b] -2.41[c]			

[a] The average of four CBS values (uncertainties w.r.t. F12b/VQZ-F12 values).

[b] Using $\Delta H_{f,298K}$ values of CH_3ONO_2, -29.16 kcal mol^{-1};[50] OH, 8.93 kcal mol^{-1};[51] CH_3OOH, -31.31 kcal mol^{-1};[60] NO_2, 8.12 kcal mol^{-1}.[51,61]

[c] Using the $\Delta H_{f,298K}$ value of -29.71 kcal mol^{-1}, which was computed in our previous study,[11] for CH_3ONO_2 instead of the value from Burcat[50] given in footnote (b).

Table 2. Computed reaction (ΔE_e^{RX}) and activation ($\Delta E_e^{\ddagger}$) energies (in kcal mol^{-1}) of the OH + CH_3ONO_2 → TS_3 → CH_3OH + NO_3 channel at various UCCSD(T*)-F12x//M06-2X/6-31+G** levels of calculation.

Methods	ΔE_e^{RX}			$\Delta E_e^{\ddagger}$		
	F12a	F12b	(other)	F12a	F12b	(other)
(M06-2X/6-31+G**)			(-2.21)			(37.71)
UCCSD(T*)-F12x/VTZ-F12	-8.31	-8.33		35.64	35.76	
UCCSD(T*)-F12x/VQZ-F12	-8.11	-8.11		35.91	35.97	
$1/X^3$ CBS1	-7.96	-7.95		36.11	36.12	
Schwenke CBS2	-8.03	-8.03		36.01	36.04	
Average ΔE_e (CBS1 and CBS2)	-7.99	-7.99		36.06	36.08	
Best ΔE_e (F12ave/CBSave)[a]			-7.99(12)			36.07(11)
ΔE_{0K} (CBSave)	-7.93	-7.93		36.88	36.90	
ΔE_{0K} (include SO of OH)	-7.73	-7.73		37.08	37.10	
Best ΔE_{0K} (F12ave/CBSave)[a]			-7.73			37.09
ΔH_{298K}	-8.21	-8.21				
ΔH_{298K} (including SO of OH)	-8.01	-8.01				
Best ΔH_{298K} (F12ave/CBSave)[a]			-8.01			
ΔH_{298K} (from available $\Delta H_{f,298K}$)			-11.77[b] -11.22[c] -9.83[c,d]			

[a] The average of four CBS values (uncertainties w.r.t. F12b/VQZ-F12 values).

[b] Using $\Delta H_{f,298K}$ values of CH_3ONO_2, -29.16 kcal mol^{-1};[50] OH, 8.93 kcal mol^{-1};[51] CH_3OH, -49.0 kcal mol^{-1}(average of nine values);[62-67] NO_3, 17.0 kcal mol^{-1}.[68]

[c] Using the $\Delta H_{f,298K}$ value of -29.71 kcal mol^{-1}, which was computed in our previous study,[11] for CH_3ONO_2 instead of the value from Burcat[50] given in footnote (b).

[d] Using the $\Delta H_{f,298K}$ value of -47.61 kcal mol^{-1}, which was computed in the present study, for CH_3OH instead of the average of nine values given in footnote (b).

Table 3. Computed reaction energies (ΔE_e^{RX}; in kcal mol^{-1}) obtained at different levels of calculation for the $CH_3OH \rightarrow CO + 2H_2$ reaction, and the derived $\Delta H_{f,298K}$ value for CH_3OH.

ΔE_e^{RX}	UCCSD(T*)-F12a	UCCSD(T*)-F12b
VTZ-F12	34.11	34.03
VQZ-F12	34.40	34.36
$1/X^3$ CBS1	34.61	34.60
Schwenke CBS2	34.50	34.48
Best estimate (F12ave/CBSave)[a]		34.55
ΔE_{0K}^{RX} (ΔZPE = -16.90 kcal mol^{-1})		17.65
ΔH_{298K}^{RX} [b]		21.20
$\Delta H_{f,298K}(CH_3OH)$[c]		-47.61
Experimental $\Delta H_{f,298K}(CH_3OH)$		-48.0,[d] -47.94,[e] -48.1 ± 1.2,[f] -48.21,[g] -48.33 ± 0.05,[h] -48.07 ± 0.05,[i] -50.86,[j] -50.98 ± 0.48,[k] -51.1 ± 1.2[l]

[a] The average of the four UCCSD(T*)-F12x/CBS values.

[b] ΔZPE + ΔE_v^{298K} + 6.5RT = -13.35 kcal mol^{-1}.

[c] Using $\Delta H_{f,298K}(CO)$ = -26.417 ± 0.041 kcal mol^{-1} and the computed best F12ave/CBSave ΔH_{298K}^{RX} of 21.20 kcal mol^{-1}.

[d] From Ref. [62].

[e] Value computed using $\Delta H_{f,liquid}°$ of -238.4 kJ mol^{-1} from Ref. [63] and $\Delta H_{vap}°$ of 37.8 kJ mol^{-1} from Ref. [65].

[f] Value computed using $\Delta H_{f,liquid}°$ of -238.4 kJ mol^{-1} from Ref. [63] and $\Delta H_{vap}°$ of 8.91 kcal mol^{-1} from Ref. [71].

[g] Value computed using $\Delta H_{f,liquid}°$ of -239.5 ± 0.2 kJ mol^{-1} from Ref. [64] and $\Delta H_{vap}°$ of 37.8 kJ mol^{-1} from Ref. [65].

[h] Value computed using $\Delta H_{f,liquid}°$ of -238.4 kJ mol^{-1} from Ref. [64] and $\Delta H_{vap}°$ of 8.91 kcal mol^{-1} from Ref. [71].

[i] From Ref. [65].

[j] Value computed using $\Delta H_{f,liquid}°$ of -250.6 kJ mol^{-1} from Ref. [66] and $\Delta H_{vap}°$ of 37.8 kJ mol^{-1} from Ref. [65].

[k] Value computed using $\Delta H_{f,liquid}°$ of -250.6 kJ mol^{-1} from Ref. [66] and $\Delta H_{vap}°$ of 8.91 kcal mol^{-1} from Ref. [71].

[l] Value computed using $\Delta H_{f,liquid}°$ from Ref. [67] and $\Delta H_{vap}°$ of 8.91 kcal mol^{-1} from Ref.

[71].

Table 4. Computed reaction (ΔE_e^{RX}) and activation ($\Delta E_e^{\ddagger}$) energies (in kcal mol^{-1}) of the OH + CH_3ONO_2 → TS_{4a} → CH_3O + HNO_3 channel at various UCCSD(T*)-F12x//M06-2X/6-31+G** levels of calculation.

Methods	ΔE_e^{RX}			$\Delta E_e^{\ddagger}$		
	F12a	F12b	(other)	F12a	F12b	(other)
(M06-2X/6-31+G**)			(-7.32)			(31.88)
UCCSD(T*)-F12x/VTZ-F12	-6.47	-6.51		26.48	26.63	
UCCSD(T*)-F12x/VQZ-F12	-6.54	-6.56		27.01	27.06	
$1/X^3$ CBS1	-6.60	-6.59		27.39	27.37	
Schwenke CBS2	-6.57	-6.57		27.20	27.21	
Average ΔE_e (CBS1 and CBS2)	-6.58	-6.58		27.29	27.29	
Best ΔE_e (F12ave/CBSave)[a]			-6.58(3)			27.29(17)
ΔE_{0K} (CBSave)	-6.53	-6.53		28.62	28.62	
ΔE_{0K} (include SO of OH)	-6.33	-6.33		28.82	28.82	
Best ΔE_{0K} (F12ave/CBSave)[a]			-6.33			28.82
ΔH_{298K}	-6.98	-6.98				
ΔH_{298K} (including SO of OH)	-6.78	-6.78				
Best ΔH_{298K} (F12ave/CBSave)[a]			-6.78			
ΔH_{298K} (from available $\Delta H_{f,298K}$)			-7.77[b] -7.22[c]			

[a] The average of four CBS values (uncertainties w.r.t. F12b/VQZ-F12 values).

[b] Using $\Delta H_{f,298K}$ values of CH_3ONO_2, -29.16 kcal mol^{-1};[50] OH, 8.93 kcal mol^{-1};[51] CH_3O, 4.1 kcal mol^{-1};[70] HNO_3, -32.101 kcal mol^{-1}.[68]

[c] Using the $\Delta H_{f,298K}$ value of -29.71 kcal mol^{-1}, which was computed in our previous study,[11] for CH_3ONO_2 instead of the value from Burcat[50] given in footnote (b).

Table 5. Computed ΔE_e, ΔE_{0K} and ΔH_{298K} (w.r.t. separate reactants; in kcal mol^{-1}) of various species in the OH + CH_3ONO_2 → TS_{4b} → $CH_3O(OH)NO_2$ conformer 1 → TS_{rot} → $CH_3O(OH)NO_2$ conformer 2 → TS_{4c} → CH_3O + HNO_3 channel obtained at various UCCSD(T*)-F12x//M06-2X/6-31+G** levels of calculation.

ΔE_e (in kcal mol^{-1})	**TS_{4b}**	**$CH_3O(OH)NO_2$ conformer 1**	**TS_{rot}**	**$CH_3O(OH)NO_2$ conformer 2**	**TS_{4c}**	**Δ(RX)**
M06-2X/6-31+G**	30.86	21.67	23.53	20.16	28.48	-7.32
UCCSD(T*)-F12a/VTZ-F12	31.95	25.56	27.22	23.74	30.44	-6.47
UCCSD(T*)-F12b/VTZ-F12	32.06	25.68	27.35	23.86	30.54	-6.51
UCCSD(T*)-F12a/VQZ-F12	32.15	25.58	27.24	23.74	30.58	-6.54
UCCSD(T*)-F12b/VQZ-F12	32.18	25.62	27.29	23.78	30.61	-6.56
UCCSD(T*)-F12a/CBS1	32.30	25.59	27.26	23.75	30.69	-6.60
UCCSD(T*)-F12b/CBS1	32.27	25.57	27.24	23.73	30.66	-6.59
UCCSD(T*)-F12a/CBS2	32.22	25.58	27.25	23.74	30.64	-6.57
UCCSD(T*)-F12b/CBS2	32.23	25.60	27.26	23.76	30.64	-6.57
Best ΔE_e (F12ave/CBSave)[a]	32.25(7)	25.59(3)	27.25(3)	23.74(4)	30.66(5)	-6.58(3)
Δ(ZPE)	1.97	3.09	3.04	3.21	1.77	0.06
ΔE_{0K} (= best ΔE_e + ΔZPE)	34.22	28.68	30.30	26.95	32.42	-6.53
ΔE_{0K} (include SO of OH)	34.42	28.88	30.50	27.15	32.62	-6.33
ΔH_{298K}		27.44		25.76		-6.98
ΔH_{298K} (include SO of OH)		27.64		25.96		-6.78
ΔH_{298K} (using $\Delta H_{f,298K}$ values)[b]						-7.77

[a] The average of four CBS values (uncertainties w.r.t. F12b/VQZ-F12 values).

[b] Using $\Delta H_{f,298K}$ values of CH_3ONO_2, -29.16 kcal mol^{-1};[50] OH, 8.93 kcal mol^{-1};[51] CH_3O, 4.1 kcal mol^{-1};[70] HNO_3, -32.101 kcal mol^{-1}.[68]

Table 6. Some major geometrical parameters (bond distance; in Å), the imaginary vibrational frequencies (ω_i; in cm^{-1}), the ΔE_e, ΔE_{0K} (w.r.t. separate reactants; in kcal mol^{-1}) and the zero-point energy correction {Δ(ZPE); in kcal mol^{-1}} of the three TS's in the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 channel.

ΔE_e (in kcal mol^{-1})	TS_{1a}	TS_{1b}	TS_{1c}
ω_i[a]	1294i	1135i	1486i
C···H bond distance	1.20	1.19	1.22
H···O bond distance	1.33	1.36	1.29
L = Δ(C-H)/Δ(H-O)	0.39	0.25	0.39
M06-2X/6-31+G**	3.01	5.10	6.23
UCCSD(T*)-F12a/VTZ-F12	3.88	5.39	6.94
UCCSD(T*)-F12b/VTZ-F12	3.88	5.39	6.93
UCCSD(T*)-F12a/VQZ-F12	3.98	5.48	7.01
UCCSD(T*)-F12b/VQZ-F12	3.97	5.47	7.00
UCCSD(T*)-F12a/CBS1	4.04	5.55	7.06
UCCSD(T*)-F12b/CBS1	4.03	5.53	7.05
UCCSD(T*)-F12a/CBS2	4.01	5.51	7.04
UCCSD(T*)-F12b/CBS2	4.00	5.50	7.03
Best ΔE_e (F12ave/CBSave)[b]	4.02	5.52	7.05
Δ(ZPE)[c]	-1.46	-1.70	-2.20
ΔE_{0K} (= best ΔE_e + ΔZPE)	2.56	3.82	4.84
ΔE_{0K} (include SO of OH)[d]	2.76	4.02	5.04

[a] Computed at the M06-2X/6-31+G** geometries.

[b] The average of four CBS values (uncertainties w.r.t. F12b/VQZ-F12 values).

[c] Using computed M06-2X/6-31+G** harmonic frequencies.

[d] Including spin-orbit splitting in OH (0.40 kcal mol^{-1} = 0.0006 Hartree), the $^2\Pi_{3/2}$ SO state of OH is lower than the unperturbed $^2\Pi$ state by 0.20 kcal mol^{-1}.

Table 7. Computed ΔE_e, ΔE_{0K} and ΔH_{298K} (w.r.t. separate reactants; in kcal mol^{-1}) of various species in the out-of-plane OH + CH_3ONO_2 → H_2O + CH_2ONO_2 channel 1(a) obtained at various UCCSD(T*)-F12x//M06-2X/6-31+G** levels of calculations.

ΔE_e (in kcal mol^{-1})	RC_{1a}	TS_{1a}	PC_{1a}	Δ(RX)
M06-2X/6-31+G**	-5.41	3.01	-20.34	-14.63
UCCSD(T*)-F12a/**VTZ-F12**	-3.05	3.88	-20.34	-17.02
UCCSD(T*)-F12b	-3.03	3.88	-20.34	-17.02
UCCSD(T*)-F12a/**VQZ-F12**	-3.02	3.98	-20.46	-17.16
UCCSD(T*)-F12b	-3.02	3.97	-20.45	-17.15
UCCSD(T*)-F12a/CBS1[a]	-3.00	4.04	-20.54	-17.27
UCCSD(T*)-F12b/CBS1[a]	-3.01	4.03	-20.53	-17.24
UCCSD(T*)-F12a/CBS2[b]	-3.01	4.01	-20.50	-17.21
UCCSD(T*)-F12b/CBS2[b]	-3.02	4.00	-20.49	-17.20
Best ΔE_e (F12ave/CBSave)[c]	-3.01(1)	4.02(5)	-20.51(7)	-17.23(8)
Δ(ZPE)[d]	1.11	-1.46	-0.03	-1.31
ΔE_{0K} (= best ΔE_e + ΔZPE)	-1.91	2.56	-20.54	-18.54
ΔE_{0K} (include SO of OH)[e]	-1.71	2.76	-20.34	-18.34
Experimentally derived $\Delta E^{\ddagger}$		1.20[f] 2.03[g]		
ΔH_{298K}	-1.94	1.62	-20.00	-18.10
ΔH_{298K} (include SO of OH)[e]	-1.74	1.82	-19.80	-17.90
ΔH_{298K} (using $\Delta H_{f,298K}$ values)				-13.92,[h] -17.72[i]

[a] Using the $1/X^3$ CBS extrapolation of the ΔE_e at the UCCSD(T*)-F12/VTZ-F12 and UCCSD(T*)-F12/VQZ-F12 levels.

[b] Using the generalized two point CBS expression of Schwencke [38] {$E_{CBS}=(E_{large}-E_{small})F+E_{small}$, with F = 1.363388 from Hill et al.[39]} with the UCCSD(T*)-F12/VTZ-F12 and VQZ-F12 values.

[c] The best CBS estimate is the average of all the four CBS values and the estimated uncertainties are the differences between the best estimates and the UCCSD(T*)-F12b/VQZ-F12 values.

[d] Using computed M06-2X/6-31+G** harmonic frequencies.

[e] Including spin-orbit splitting in OH (0.40 kcal mol^{-1} = 0.0006 Hartree), the $^2\Pi_{3/2}$ SO state of

OH is lower than the unperturbed $^2\Pi$ state by 0.20 kcal mol^{-1}.

[f] Determined experimentally in Ref. [15].

[g] Determined experimentally in Ref. [14].

[h] Using $\Delta H_{f,298K}$ values of CH_3ONO_2, -29.16 kcal mol^{-1};[50] OH, 8.93 kcal mol^{-1};[51] CH_2ONO_2, 23.65 kcal mol^{-1};[50] H_2O, -57.7978 kcal mol^{-1}.[52]

[i] Using the $\Delta H_{f,298K}$ values of -29.71 and 19.30 kcal mol^{-1} for CH_3ONO_2 and CH_2ONO_2 respectively, which were computed in our previous study,[11] instead of the values from Burcat[50] given in footnote (f).

Table 8.

Comparison of computed $k^{ICVT/SCT}$ values {cm^3 $molecule^{-1}$ s^{-1}; $k^{ICVT/SCT} = 2k(1a) + 2k(1b) + k(1c)$} of the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 reaction (column 2 and 3) at different temperatures obtained with the HL UCCSD(T*)-F12ave/CBSave//M06-2X IRC and available experimental values. Column 3 obtained with $\Delta E_e^{\ddagger}$ values 4.22 (1a), 5.72 (1b) and 7.25 (1c) kcal.mol^{-1} and column 2 obtained with these values reduced by 2.5 kcal.mol^{-1} (see text).

T (K)	$k_{ICVT/SCT}$	$k_{ICVT/SCT}$	Nielsen[a]	Kerr[b]	Gaffney[c]	Talukdar[d]	Kakesu[e]	Shallcross[f]
200	9.98E-15	9.07E-17						
220	1.38E-14	1.70E-16						
221						8.12E-15		
225						8.81E-15		
240	1.88E-14	3.04E-16						
250						1.39E-14		
260	2.52E-14	5.20E-16						
275						2.01E-14		
280	3.32E-14	8.55E-16						
290								
298	4.19E-14	1.29E-15	2.99E-13		3.40E-14			5.40E-14
300	4.29E-14	1.35E-15	2.93E-13			2.74E-14		5.48E-14
303				3.70E-13				
304							3.00E-14	
320	5.47E-14	2.06E-15						
325			2.23E-13			3.56E-14		6.39E-14
340	6.87E-14	3.06E-15						
350			1.77E-13			4.45E-14		7.30E-14
358								
360	8.52E-14	4.40E-15						
375			1.45E-13			5.40E-14		8.19E-14
380	1.04E-13	6.17E-15						
393			1.28E-13					
400	1.26E-13	8.47E-15				6.41E-14		9.06E-14
414						6.98E-14		
423								9.84E-14

[a] From Ref. [18]; rate coeffs. calculated from Arrhenius expression provided

[b] From Ref. [19].

[c] From Ref. [16].

[d] From Ref. [14]; rate coeffs. calculated from Arrhenius expression provided

[e] From Ref. [17];

[f] From Ref. [15]; rate coeffs. calculated from Arrhenius expression provided

Figure 1. Optimized geometries of the TS's at the M06-2X/6-31+G** level.

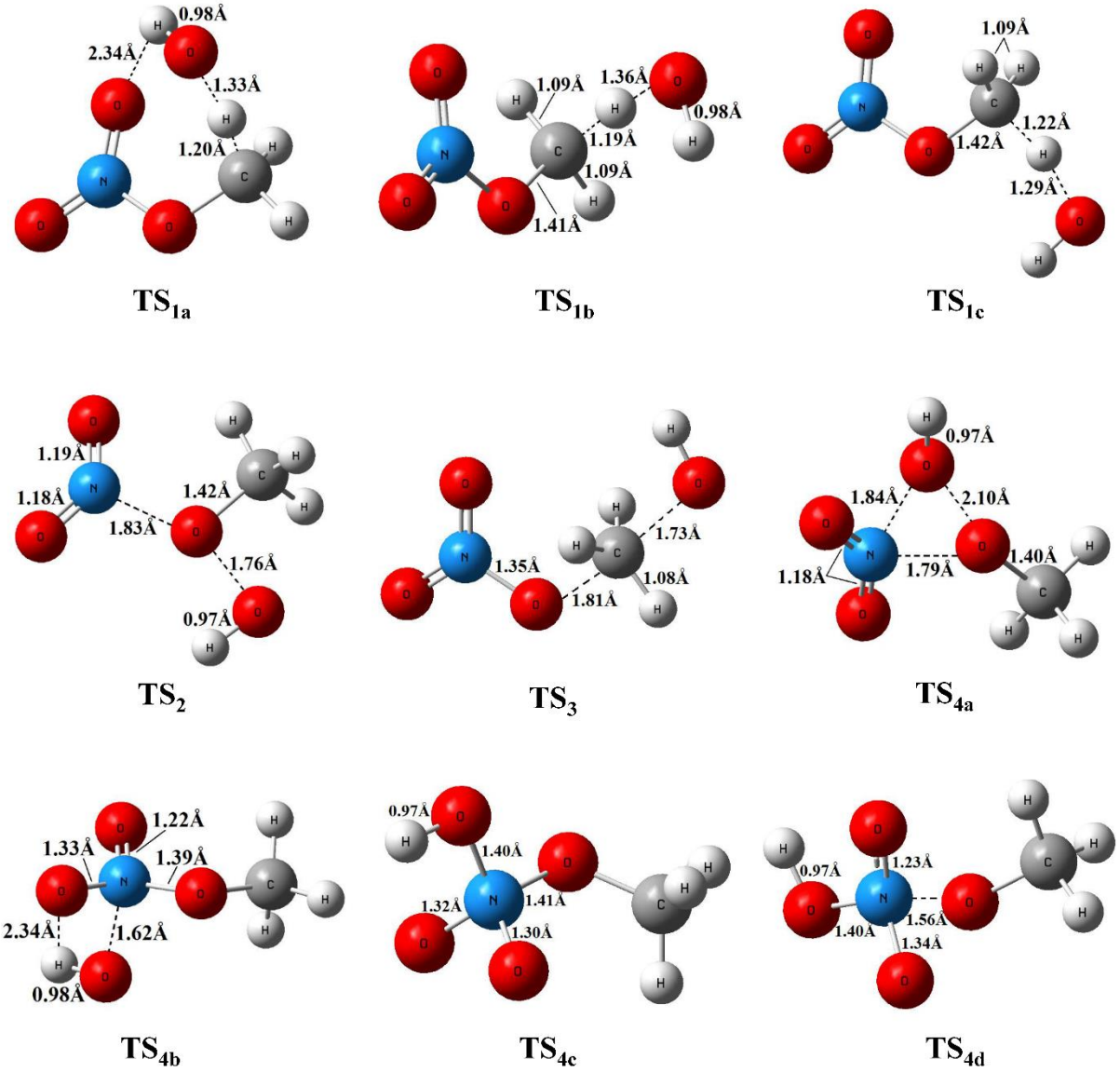


Figure 2. Optimized geometries of the adduct conformers in channel (4) and the complexes associated with TS_{1a} in channel (1) at the M06-2X/6-31+G** level. The reaction complexes through TS_{1a}, TS_{1b} and TS_{1c} have been optimised for reaction 1 and were considered in the rate coefficient calculations. Reactions 1a and 1b share the same reaction complex. For clarity only the reaction complex (RC_{1a}) is shown in this figure.

TheT

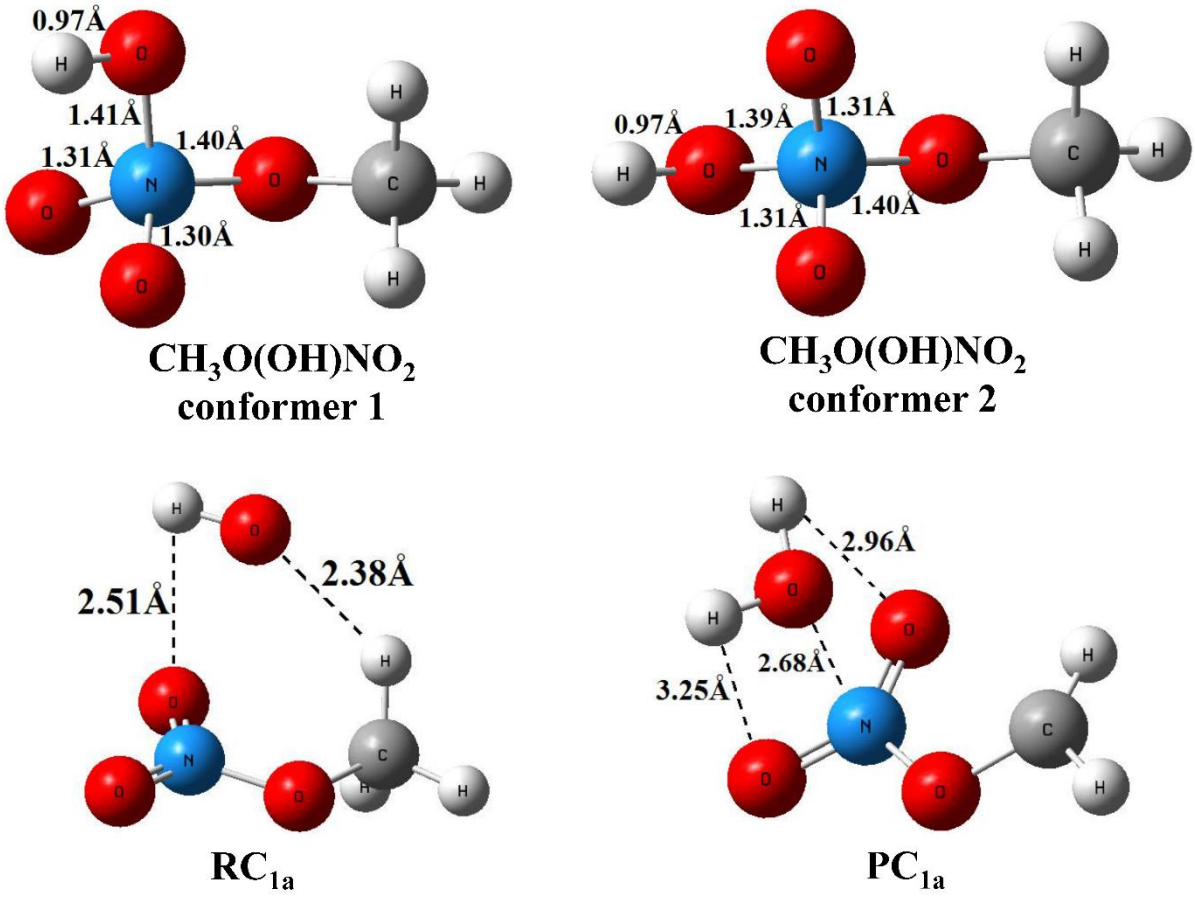


Figure 3. A schematic potential energy surface of the OH + CH_3ONO_2 reaction at the UCCSD(T*)-F12ave/CBSave//M06-2X level, including the ZPE and the SO corrections.

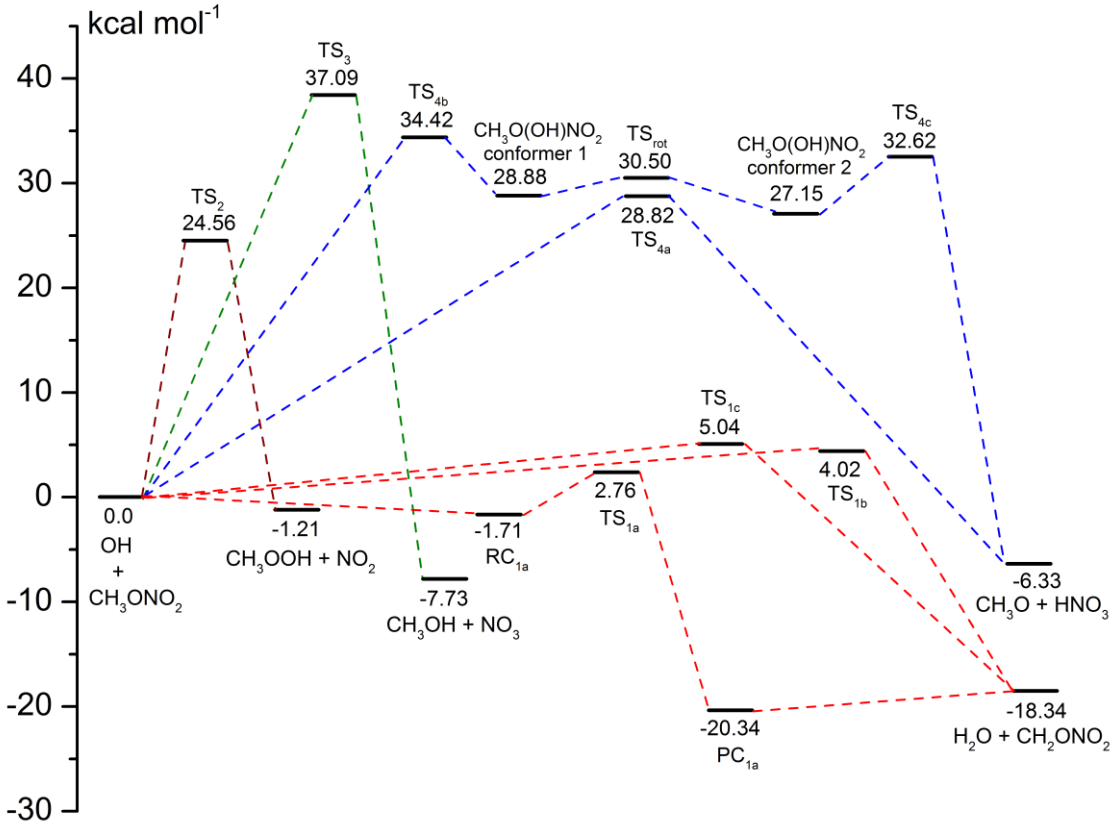


Figure 4. V_{MEP}, ΔZPE and V_a^G curves of the M06-2X/6-31+G** level (top) and the F12ave/CBSave//M06-2X level (bottom) for the out-of-plane OH + CH_3ONO_2 → H_2O + CH_2ONO_2 channel via TS_{1a}. The higher level (HL) V_{MEP} and V_a^G curves (bottom) were obtained by using the HL energies of the reactants, RC_{1a}, TS_{1a}, PC_{1a} and products, with more HL IRC points calculated by the expression devised by us previously (see text).[49]

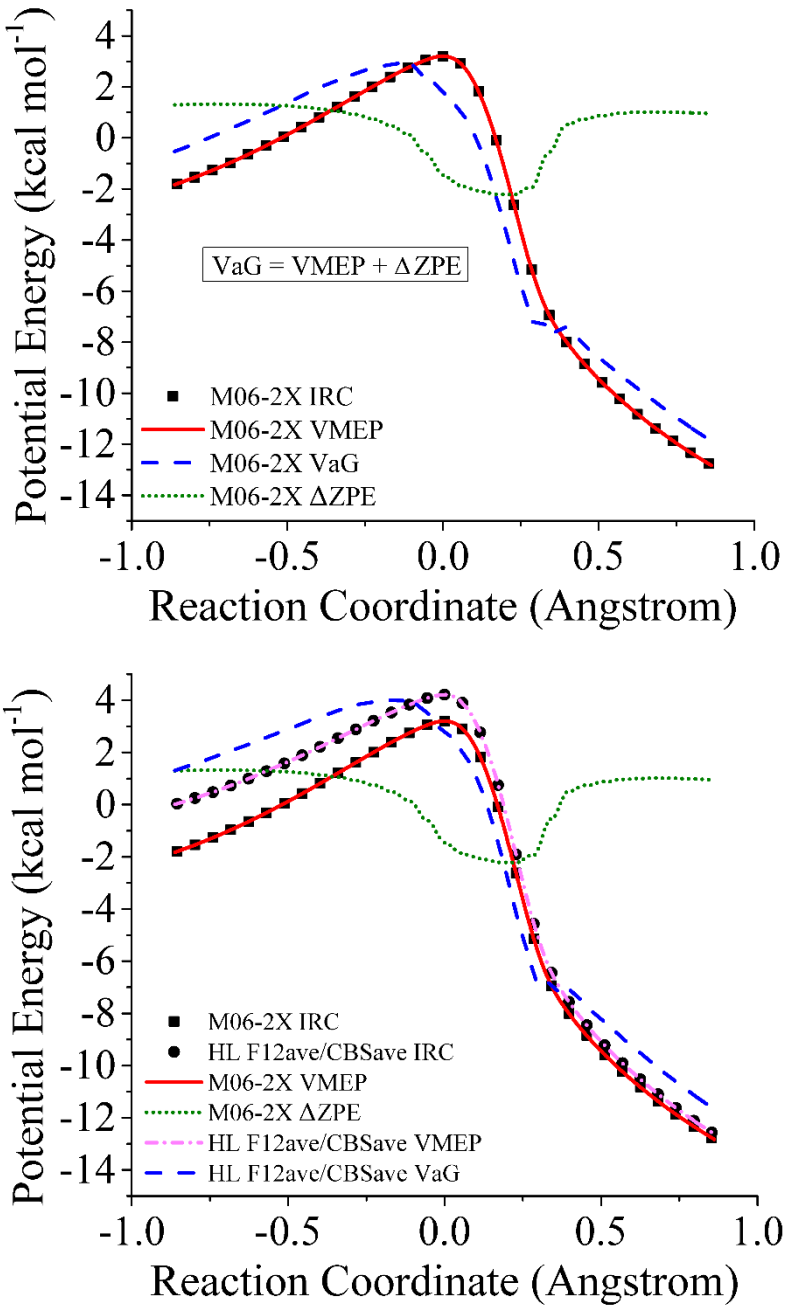


Figure 5. Computed rate coefficients (k; in cm^3 $molecule^{-1}$ s^{-1}) for the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 reaction (channel 1(a)) at different temperatures (T) obtained at different VTST levels using the M06-2X/6-31+G** IRC (computed k values have been multiplied by two to account for two out-of-plane H abstraction sites with hydrogen bond-like interaction).

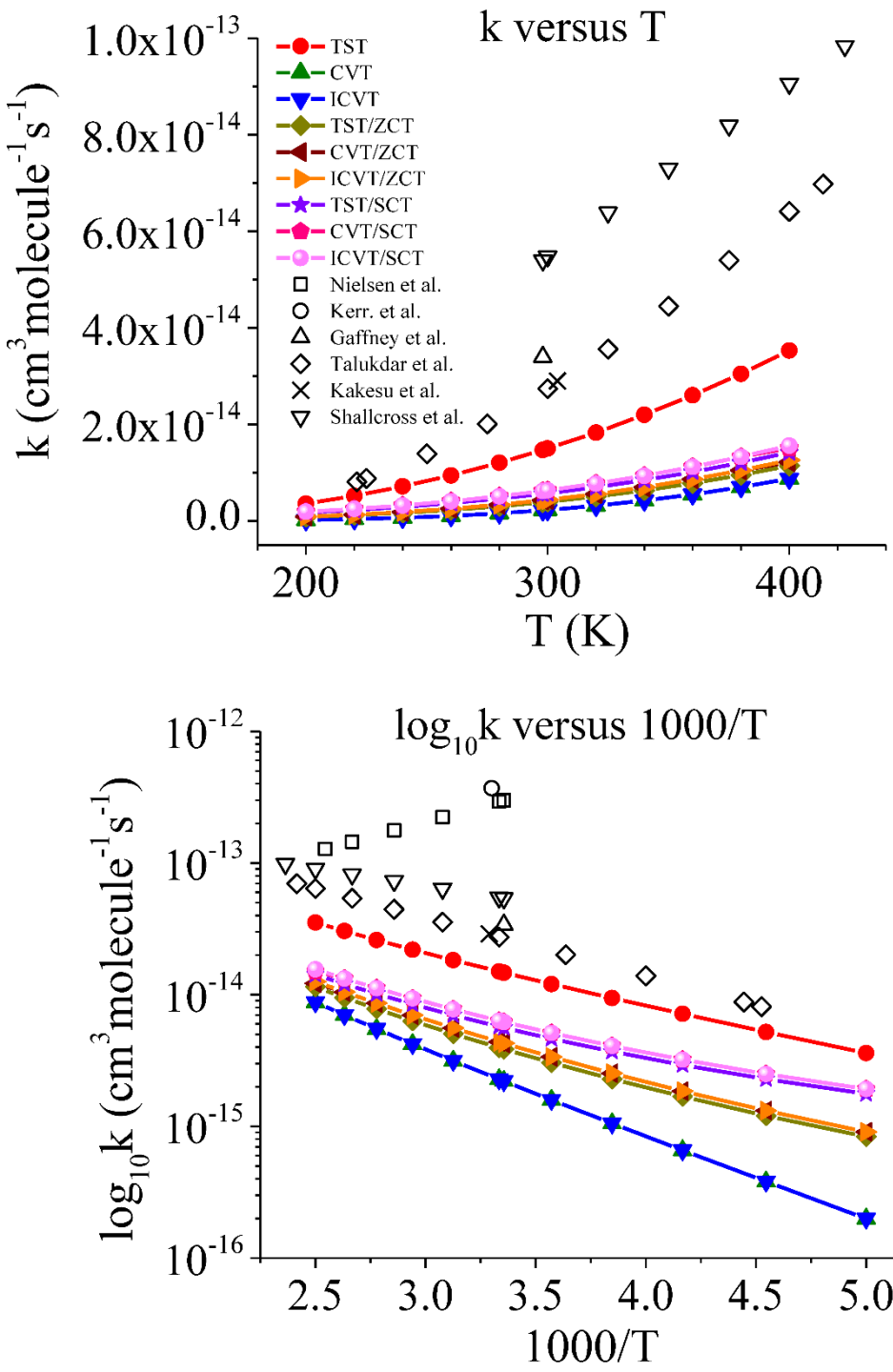


Figure 6. Rate coefficients (k; in cm^3 $molecule^{-1}$ s^{-1}) computed at different VTST levels for the $OH + CH_3ONO_2 \rightarrow H_2O + CH_2ONO_2$ reaction (reaction 1(a)) with the HL F12ave/CBSave//M06-2X/6-31+G** IRC in the temperature range between 200 K and 400 K (computed k values have been multiplied by two to account for two H abstraction sites with hydrogen bond).

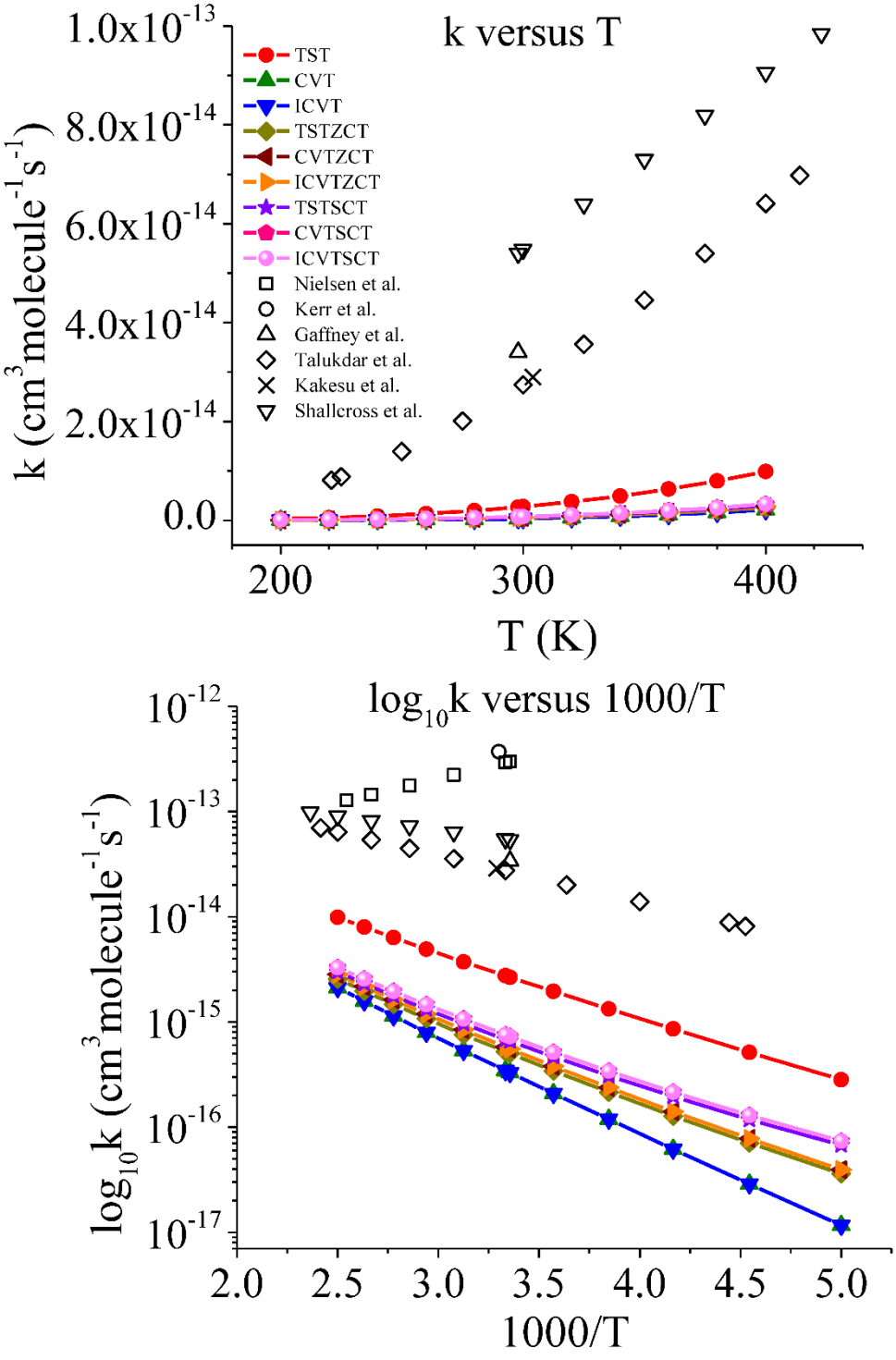


Figure 7. Computed ICVT/SCT rate coefficients (k; in cm^3 $molecule^{-1}$ s^{-1}) of reactions (1a), (1b) and (1c), as well as the total rate coefficients of the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 reaction with the HL F12ave/CBSave//M06-2X/6-31+G** IRC in the temperature range between 200 K and 400 K {k(total) = 2k(1a) + 2k(1b) + k(1c)}.

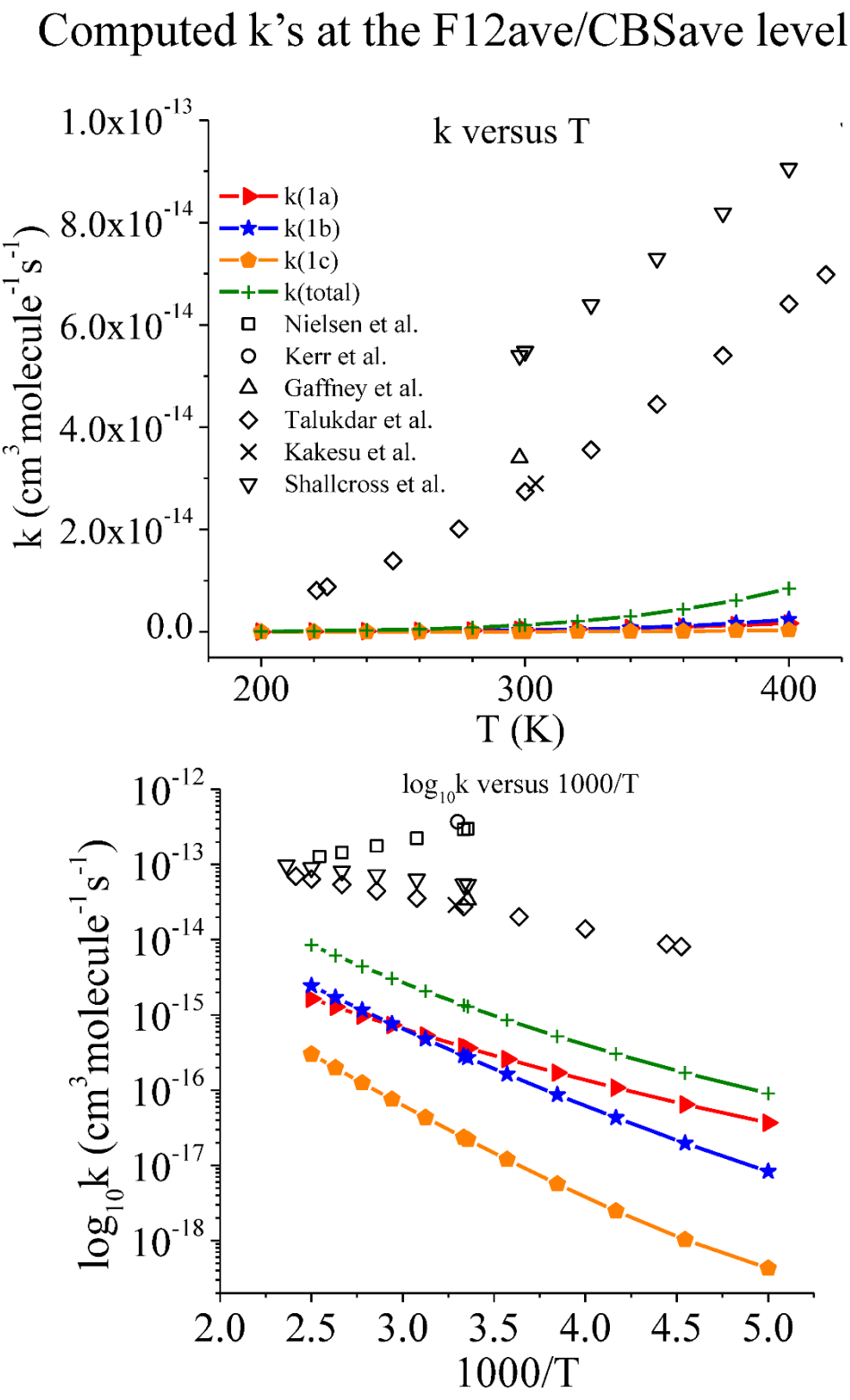
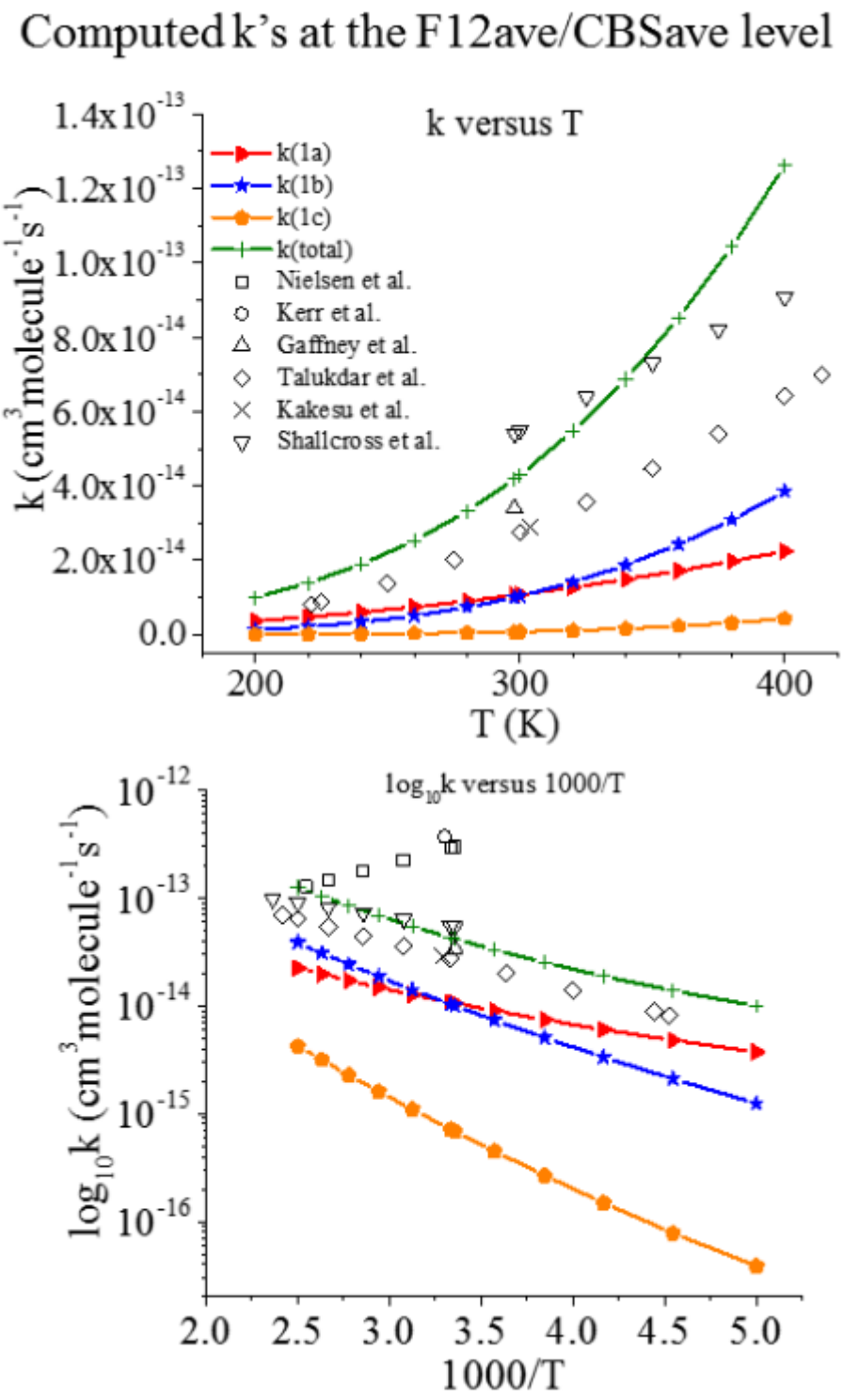
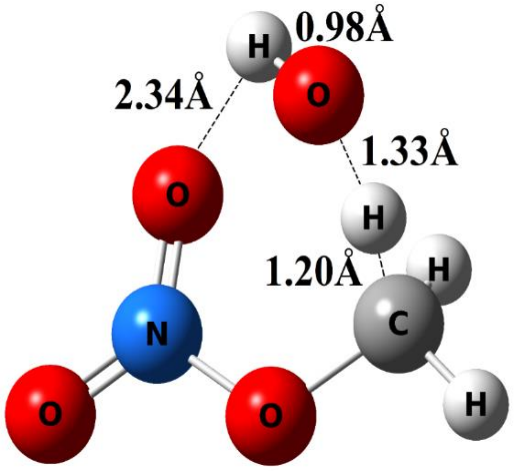
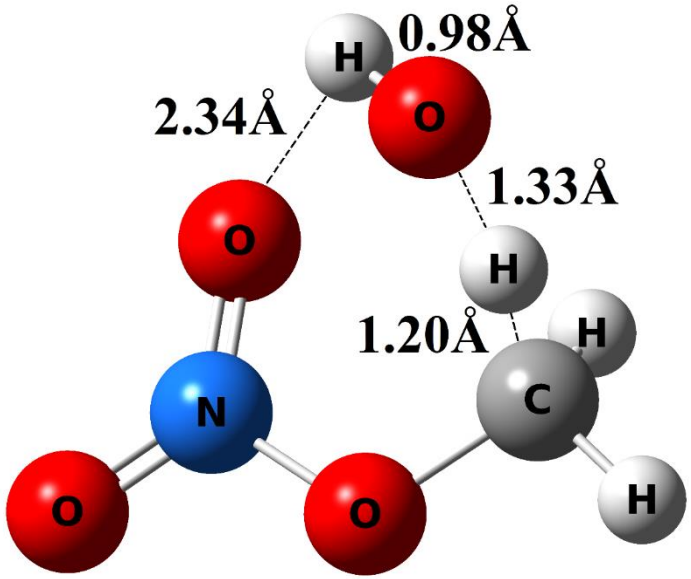


Figure 8 Computed ICVT/SCT rate coefficients (k; in cm^3 $molecule^{-1}$ s^{-1}) of reactions (1a), (1b) and (1c), as well as the total rate coefficients of the OH + CH_3ONO_2 → H_2O + CH_2ONO_2 reaction with the HL F12ave/CBSave//M06-2X/6-31+G** IRC in the temperature range between 200 K and 400 K {k(total) = 2k(1a) + 2k(1b) + k(1c)}, with the HL F12ave/CBSave//M06-2X/6-31+G** barrier heights for channels 1(a), 1(b) and 1(c) reduced by 2.5 $kcal.mol^{-1}$ (see text).


Computed k's at the F12ave/CBSave level
k versus T
k(1a)
k(1b)
k(1c)
k(total)
Nielsen et al.
Kerr et al.
Gaffney et al.
Talukdar et al.
Kakesu et al.
Shallcross et al.
k (cm3molecule-1s-1)
T (K)
log10k versus 1000/T
log10k (cm3molecule-1s-1)
1000/T

TOC GRAPHIC





OH + CH_3ONO_2 TS