

On the possible catalytic role of a single water molecule in the acetone + OH gas phase reaction: a theoretical pseudo-second-order kinetics study

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Abstract In this work, we have revisited the mechanism of the acetone + OH radical reaction assisted by a single water molecule simulating atmospheric conditions. Density functional methods are employed in conjunction with CCSD(T) and large basis sets to explore the potential energy surface of this radical-molecule reaction. Computational kinetics calculations in a pseudo-second order mechanism have been performed, taking into account average atmospheric water concentrations and temperatures. We have used this method recently to study the single-water molecule-assisted H-abstraction in acetaldehyde (Iuga et al. in *J Phys Chem Lett* 1:3112, 2010) and in glyoxal (Iuga et al. in *Chem Phys Lett* 501:11, 2010) by OH radicals, and we showed that the initial water complexation step is essential in the rate constant calculation.

In both cases, the amount of complex formed is only about 0.01% of the total organic molecule concentration, and as a consequence, water does not accelerate the reaction. In the acetone reaction with OH radicals under atmospheric conditions, we also find that the water–acetone complex concentration is much too small to be relevant, and thus, the rate constant of the water-assisted mechanism is orders of magnitude smaller than the water-free corresponding value.

Keywords VOC-water complexation · Water-assisted · Atmospheric oxidation · Pseudo-second order · Kinetics · Water catalysis

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1 Introduction

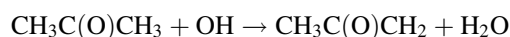
The possible catalytic role of a single water molecule in reactions of OH radicals with volatile organic compounds (VOC) [3–7] has been considered in recent experimental and theoretical publications. Several articles have been published describing how the formation of hydrogen bonds between the VOC, the OH radical, and a water molecule lowers the transition states energy, thus suggesting a possible enhancement of the rate constant [3–7]. Indeed, it is known that water forms complexes with tropospheric-active species such as free radicals as well as with many different VOCs [8–23]. Complexation could affect radical-molecule reactions and change their atmospheric relevance. Hence, two important matters need to be considered: (i) the concentration of the complex under atmospheric conditions and (ii) the possible effect of complexation on reactivity.

Acetone is reported to be the dominant non-methane organic atmospheric pollutant [24]. Its lifetime of about 15 days is sufficiently long to allow it to reach the upper

troposphere and lower stratosphere, where it is believed to be a very important source of HO_x radicals [24–26]. Its average concentration of ≈ 0.5 ppbv makes it one of the most abundant organic compounds in clean air [24–29]. It is well accepted that the atmospheric loss of acetone by reaction with OH dominates at low altitudes, while photolysis is the major degradation process in the upper troposphere [30].

From kinetic data, it has been observed that the carbonyl group has little effect on the reactivities of $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$ groups in ketones, which are quite similar to their reactivities in alkanes [31, 32]. This result is explained in terms of bond dissociation energies, since C–H bond strengths in the R position of ketones are approximately equal to those for the analogous groups in alkanes [33]. However, the carbonyl group is strongly electron withdrawing, and hence, reaction of the electrophilic OH radical with a ketone at the R position could be expected to be less favored than in alkanes.

The experimentally determined rate constant [34, 35] in the gas phase at 300 K is $2.23 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Below room temperature, the rate constant of the overall reaction shows a strong non-Arrhenius behavior [36, 37]. It has generally been assumed that the reaction of OH radicals with acetone leads to the formation of the $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ radical and proceeds via H-atom abstraction:



The gas phase OH + acetone reaction has been studied theoretically by several authors [38, 39]. Theoretical work has also been carried out on the acetone + OH reaction in the presence of a single water molecule [40], to study its possible catalytic effect. However, in recent work on the acetaldehyde + OH reaction [1] and on the glyoxal + OH reaction [2], we have shown that, although in the water-assisted model the transition state barrier is considerably lowered by hydrogen bonds involving the water molecule, it is not correct to calculate the effective rate constant as a bimolecular rate. Indeed, the initial water complexation step is essential, since the amount of complex formed, relative to the amount of VOC, is only about 0.01% [1, 2]. Thus, the rate constant should be calculated in a pseudo-second-order mechanism, taking into account average atmospheric water concentrations and temperatures.

In this work, we have revisited the mechanism of the acetone + OH radical reaction assisted by a single water molecule. We have used ab initio and density functional methods in conjunction with large basis sets to explore the potential energy surface of this radical-molecule reaction. Computational kinetics calculations in a pseudo-second order mechanism have been performed, taking into account average atmospheric water concentrations and temperatures.

2 Computational methodology

Electronic structure calculations are performed with the Gaussian 09 [41] program using the CCSD(T)/6-311++G(d,p)//BHandHLYP/6-311++G(d,p) standard quantum chemistry method. Unrestricted calculations are used for open shell systems. Zero-point energies (ZPE) and thermal corrections to the energy (TCE) are included in the determination of energy barriers. Frequency calculations are performed for all stationary points at the same level of theory as the geometry optimization. Local minima have only real frequencies, while transition states are identified by the presence of a single imaginary frequency that corresponds to the expected motion along the reaction coordinate.

Based on our previous experience [38–45] (Reference [38] concerning the study of the reaction of OH with several ketones including acetone), the use of the CCSD(T)//BHandHLYP approach accurately describes the energetic and kinetics features of VOCs + ·OH hydrogen abstraction reactions. In addition, for this kind of reactions, it has been proven that the differences in geometries between BHandHLYP compared with those of CCSD and QCISD are minimal and smaller than with any other tested methodology [46]. Specifically, for the acetone + OH reaction in the absence of water, this methodology yields rate constants that match the experimental values, and results that explain the observed non-Arrhenius behavior. We have not corrected interaction energies for BSSE because as it has been recently demonstrated it worsens the results [47, 48]. Energy values, partition functions, and thermodynamic data are taken from the quantum mechanical calculations.

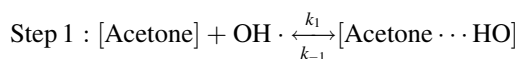
The rate coefficients (k) are computed using conventional transition state theory (TST) [49–51] as implemented in The Rate program [52] at the Computational Science and Engineering Online website (<http://www.cseo.net>) [53]. Tunneling effects are accounted for using the Eckart method [54].

Under pseudo-first-order conditions, the relative equilibrium concentrations depend strongly on the concentration of the excess reactant, i.e., water. As in our previous work on the water-assisted acetaldehyde + OH and glyoxal + OH reactions [1, 2], the pseudo-second-order rate constant is calculated using the maximum possible water concentration at each temperature (i. e., 100% humidity). It corresponds to $7.95 \times 10^{17} \text{ molecules cm}^{-3}$ at 298 K. This methodology has been successfully used previously in theoretical work on water–VOC complexes [55].

3 Results and discussion

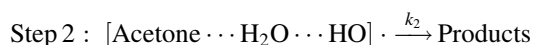
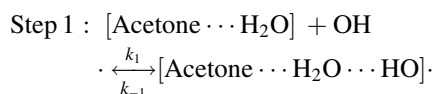
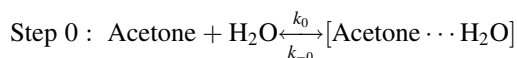
All stationary points on the potential energy surface of the water-free and water-assisted acetone + OH· reaction have been characterized.

In the water-free reaction, the elementary steps in the mechanism are:



where Step 1 is the formation of the pre-reactive complex (RC) in equilibrium with the reactants (R) and Step 2 is the irreversible formation of the products.

To examine the possible catalytic effect of water vapor on the acetone + OH gas phase reaction, we have explored the potential energy surface and the mechanisms involved in the addition of one H₂O molecule to the system. Since the simultaneous collision of three molecules is very improbable, in the water-assisted reaction, the termolecular mechanism is ruled out. Hence, the most probable mechanism consists of two consecutive bimolecular elementary steps, possibly followed by unimolecular steps. In the water-assisted acetone + OH reaction, the following three steps have been considered:



Step 0 is the reversible formation of a complex between acetone and a water molecule; in Step 1, the termolecular water–acetone–OH pre-reactive complex is formed reversibly; the last step is the irreversible formation of the products. The water–acetone intermolecular complex structure (Fig. 1) adopts a six-member ring-like configuration in which the water oxygen atom binds to a methyl H atom, while one of the water hydrogens binds to the

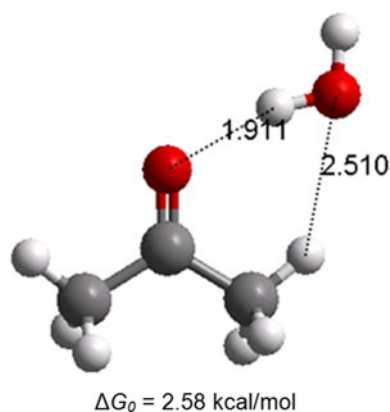


Fig. 1 Water–acetone complex structure

carbonyl oxygen. The complex geometry found in this work is in agreement with previous calculations [55, 56].

No experimental data are available for the amount of acetone–water complex formed under tropospheric conditions, but it can be estimated theoretically using the following expression:

$$[\text{complex}] = K_C [\text{acetone}] [\text{water}] \quad (1)$$

where K_C is calculated from quantum chemistry results. The concentration of water in the gas phase is heavily dependent on the temperature of the atmosphere. The amount of water vapor also generally decreases with increasing altitude. Thus, different possible atmospheric water concentrations were used depending on temperature, in order to estimate the effect of the relative air humidity on the concentration of the acetone–water complex. The acetone concentration was taken to be 1.5×10^{10} molecules cm^{-3} , which is reasonable in a polluted environment [57].

The calculated equilibrium constant K_C , in molecules⁻¹ cm^{-3} , and the corresponding relative concentration of the water–acetone complex, are reported in Table 1. It can be seen that acetone–water complexes always represent less than 0.3% of the original acetone concentration. It is interesting to rationalize the behavior of K_C at different temperatures. Since K_C depends exponentially on $-\Delta G/RT$, and ΔG is positive for the complexation process, an increase in K_C with temperature could be expected to occur. However, using $K_C = \exp(-\Delta H/RT - \Delta S/R)$ shows that actually the temperature dependence involves ΔH , which is negative; therefore, K_C will actually decrease with temperature.

3.1 Water-free structures and energies

Two pathways have been considered for the water-free gas phase reaction of acetone with OH radicals: (i) abstraction of one of the methyl H atoms and (ii) OH radical addition to the carbonyl double bond. For the H-abstraction reaction, there are two possibilities: abstraction of the methyl H atom lying in the C–C(O)–C plane (*in-plane* H-abstraction) and abstraction of one of the methyl H atoms lying above and below of the C–C(O)–C plane (*off-plane* H-abstraction). In the *in-plane* transition state, the dihedral angle between the hydrogen to be abstracted and the oxygen atom in the carbonyl group is about 90°, and this orientation prevents the OH radical from interacting with the >C=O group. In the *off-plane* transition state, an attractive interaction is possible between the H atom in the OH radical and the O atom in the >C=O group. The *in-plane* transition state is stabilized by hydrogen bonds forming six-member rings, and hence, the deactivating inductive effect of the carbonyl group is offset to some extent by the

Table 1 Calculated equilibrium constant K_c , in molecules⁻¹ cm³, and corresponding relative concentration of the water–acetone complex as a function of relative air humidity (%H) and temperature (K)

T (K)	K_c	Complex concentration					
		%H = 100	%H = 90	%H = 80	%H = 70	%H = 60	%H = 50
220	4.09×10^{-21}	4.88×10^7	4.39×10^7	3.90×10^7	3.41×10^7	2.93×10^7	2.44×10^7
240	1.68×10^{-21}	2.00×10^7	1.80×10^7	1.60×10^7	1.40×10^7	1.20×10^7	1.00×10^7
260	8.00×10^{-22}	9.54×10^6	8.58×10^6	7.63×10^6	6.67×10^6	5.72×10^6	4.76×10^6
280	4.28×10^{-22}	5.11×10^6	4.59×10^6	4.09×10^6	3.57×10^6	3.06×10^6	2.55×10^6
300	2.52×10^{-22}	3.00×10^6	2.70×10^6	2.40×10^6	2.10×10^6	1.80×10^6	1.50×10^6
320	1.59×10^{-22}	1.90×10^6	1.71×10^6	1.52×10^6	1.33×10^6	1.14×10^6	9.49×10^5
340	1.08×10^{-22}	1.28×10^6	1.15×10^6	1.03×10^6	8.97×10^5	7.69×10^5	6.40×10^5

Acetone concentration = 1.5×10^{10} molecules/cm³

stabilizing effect of hydrogen bonding. The *off-plane* transition state does not present a cyclic hydrogen-bonded structure. However, the rate constant for the *off-plane* configuration is slightly favored. For the addition path (ii), the energy barrier is considerably higher.

3.2 Water-assisted structures and energies

For the water-assisted reaction mechanism, the potential energy surface was carefully searched, and all stationary structures were identified. Two types of pre-reactive complexes were obtained, depending on whether the OH radical hydrogen atom approaches the water oxygen (*type a*) or the acetone oxygen atom (*type b*) (Fig. 2).

Starting from these pre-reactive complexes, we have identified three mechanisms: (i) a *hydrogen atom abstraction*, (ii) an *OH-addition* pathway, and (iii) a *multiple proton transfer* mechanism.

The multiple proton transfer (iii) originates from the type b pre-reactive complexes, in which the OH hydrogen atom approaches the acetone carbonyl oxygen. It involves the breaking of a bond in the original water molecule, and it leads to the formation of $\text{CH}_3\text{C}(\text{OH})\text{CH}_2 + \text{OH} + \text{H}_2\text{O}$ (keto/enol transformation). In this process, the OH radical and the water molecule in the products are not the original ones (Fig. 3). The barrier involved is very large, the process is endergonic, and this mechanism can be ruled out.

For the abstraction mechanism (i), two paths are identified, corresponding to the *in-plane* and *off-plane* positions of the OH radical and the water molecule. The OH radical hydrogen atom approaches the water oxygen, while the radical oxygen is oriented toward one of the methyl hydrogens. The *off-plane* pre-reactive complex is slightly more stable than the *in-plane* RC by $0.78 \text{ kcal mol}^{-1}$. However, both pre-reactive complexes lead to the same transition structure, which is oriented *off-plane*.

The addition path (ii) is found to originate from the same termolecular pre-reactive complex as the *off-plane*

abstraction. In this mechanism, the OH radical oxygen atom approaches the $>\text{C}=\text{O}$ double bond, and eventually, it binds to the carbon atom. The transition vector corresponds to the vertical movement of the OH group in the direction of the carbon site. The $-\text{CH}_3$ groups attached to the carbon atom involved in forming the new bond fold back slightly to accommodate the incoming OH radical.

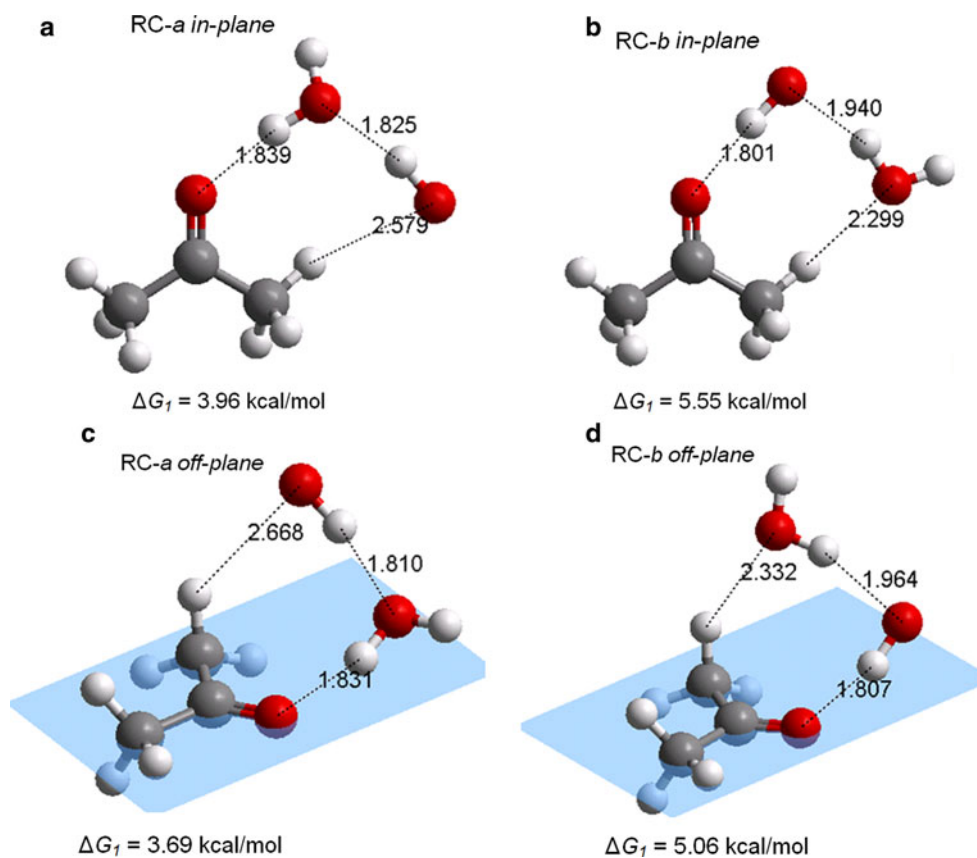
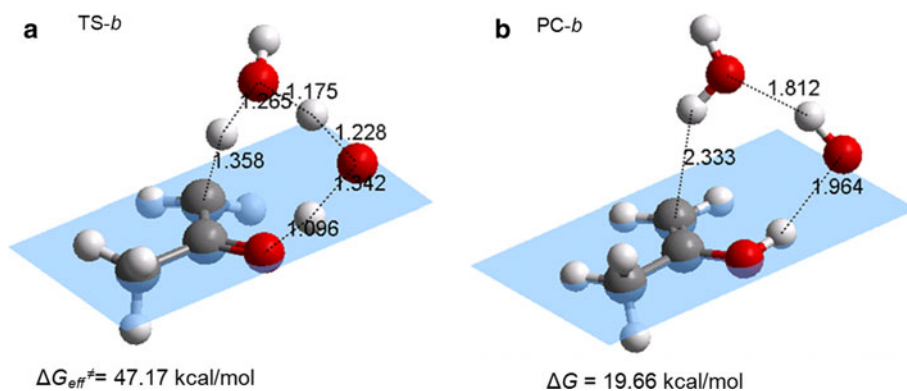
Relative energies are calculated with respect to the sum of the separated reactants, i. e., acetone, OH radical, and water, at 0 K, and they are reported in Table 2. ΔE_0 is the binding energy between acetone and a water molecule; ΔE_1 ($\Delta E_1 = E^{\text{RC}} - E^{\text{R}}$) is the pre-reactive complex stabilization energy, which also represents the barrier height for the unimolecular elementary reaction in the first step of the complex mechanism. $\Delta E_{\text{eff}}^{\ddagger}$ is the effective activation energy ($\Delta E_{\text{eff}}^{\ddagger} = E^{\text{TS}} - E^{\text{R}}$), and ΔE is the reaction energy ($\Delta E = E^{\text{P}} - E^{\text{R}}$). The complexation energies, ΔE_0 and ΔG_0 , are calculated as:

$$\Delta E_0 = E_{\text{complex}} - (E_{\text{acetone}} + E_{\text{water}}) + \Delta(\text{ZPE})$$

$$\Delta G_0 = G_{\text{complex}} - (G_{\text{acetone}} + G_{\text{water}})$$

It can be observed that in both water-free and water-assisted reactions, the abstraction channel is thermodynamically favored with respect to addition. In terms of Gibbs free energy, the difference is more than 5 kcal mol^{-1} , indicating a large difference between the corresponding rate constants.

The fully optimized structures of the stationary points involved in the water-assisted H-abstraction and OH-addition pathways (pre-reactive complexes, transition states and corresponding product complexes) are presented in Fig. 4, with the corresponding free energy profiles. Since the rate coefficient analysis includes the influence of entropic factors on the reactivity, we consider that ΔG profiles provide a more complete approach to chemical reactions than mere energetic considerations. The entropy changes, as well as the tunneling effect, could lead to a site reactivity different than the one expected by taking into account only ZPE-corrected energy barriers. For

Fig. 2 Pre-reactive complexes**Fig. 3** Multiple proton transfer mechanism**Table 2** Relative electronic energies (including ZPE) and Gibbs free energies at 298 K (including TCE), in kcal/mol, in the water-free and water-assisted acetone + OH reactions, calculated at the CCSD(T)//BHandHLYP level

	ΔE_0	ΔE_I	$\Delta E_{\text{eff}}^{\ddagger}$	ΔE	ΔG_0	ΔG_I	$\Delta G_{\text{eff}}^{\ddagger}$	ΔG
Water-free reactions								
In-plane H-abstraction	–	–4.81	3.61	–19.00	–	2.31	11.98	–19.38
Off-plane H-abstraction	–	–4.81	3.48	–19.00	–	2.31	11.60	–19.38
OH-addition	–	–4.81	6.94	–13.82	–	2.31	16.68	–3.72
Water-assisted reaction								
In-plane H-abstraction	–4.79	–10.78	–5.15	–19.00	2.58	3.69	12.21	–19.38
Off-plane H-abstraction	–4.79	–11.56	–5.15	–19.00	2.58	3.96	12.21	–19.38
OH-addition	–4.79	–11.56	–0.41	–13.82	2.58	3.96	18.08	–3.72

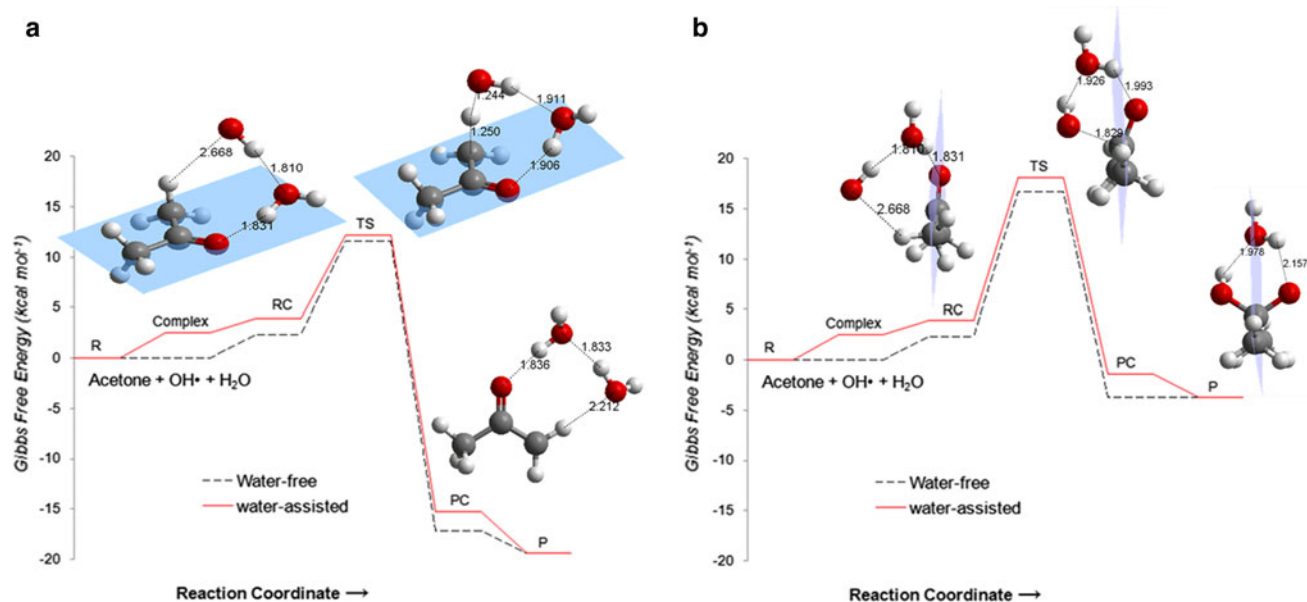


Fig. 4 Gibbs free energy profiles in the water-free and water-assisted **a** H-abstraction and **b** OH-addition reactions (*R* reactants, *RC* pre-reactive complex, *TS* transition state, *PC* product complex, *P* products)

abstraction, we have represented the *off-plane* configuration as the starting point for the H-abstraction path.

3.3 Reaction kinetics

The rate constants for the water-free and water-assisted acetone + OH reactions have been determined using transition state theory. For the water-free reaction, assuming that the pre-reactive concentration is stationary, the effective rate constant $k_{\text{water-free}}^{\text{eff}}$ is calculated as [58–66]:

$$k_{\text{water-free}}^{\text{eff}} = \sigma K_{\text{eq}1} \kappa k_2,$$

where κ is the tunneling correction, σ is the reaction path degeneracy, $K_{\text{eq}1}$ is the equilibrium constant for Step 1, and k_2 is the rate constant for Step 2.

In the water-assisted reaction, an additional elementary step, Step 0, has to be included, and the effective rate constant is:

$$k_{\text{water-assisted}}^{\text{eff}} = \sigma K_{\text{eq}0} K_{\text{eq}1} \kappa k_2 [\text{water}]$$

where $K_{\text{eq}0}$ is equal to the equilibrium constant K_C for the formation of the acetone–water complex (Eq. 1).

Results are presented in Table 3. The water concentration is taken to be 7.95×10^{17} molecules cm^{-3} , which corresponds to 100% humidity at 298 K and 1 atm.

If all the reaction paths are taken into account, it is possible to write the overall rate constants as the sum of the individual rate constants. Thus, the overall water-free and water-assisted rate constants are 1.78×10^{-13} and 9.57×10^{-16} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Table 3 Calculated equilibrium constants (in $\text{molecules}^{-1} \text{cm}^3$), rate constants k^{eff} (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and tunneling corrections (κ) at 298 K, in the water-free and water-assisted acetone + OH reactions

	σ	$K_{\text{eq}0}$	$K_{\text{eq}1}$	κ	k_2	k^{eff}
Water-free reactions						
in-plane H-abstraction	2	—	8.30×10^{-22}	89.7	4.98×10^5	7.41×10^{-14}
off-plane H-abstraction	4	—	8.30×10^{-22}	32.6	9.58×10^5	1.04×10^{-13}
OH-addition	2	—	8.30×10^{-22}	1.7	1.81×10^2	5.07×10^{-19}
Water-assisted reactions						
in-plane H-abstraction	2	2.64×10^{-22}	6.18×10^{-21}	29.0	3.52×10^6	2.65×10^{-16}
off-plane H-abstraction	4	2.64×10^{-22}	3.98×10^{-21}	37.9	5.46×10^6	6.92×10^{-16}
OH-addition	2	2.64×10^{-22}	3.98×10^{-21}	1.73	2.72×10^2	7.88×10^{-22}

Water concentration = 7.95×10^{17} molecules cm^{-3}

Table 4 Rate constants k^{eff} (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at different temperatures (K) at 100% relative air humidity (%H) in the water-free and water-assisted acetone + OH H-abstraction reactions

T (K)	$k_{\text{water-free}}$	$k_{\text{water-assisted}}$
220	6.94×10^{-13}	4.45×10^{-13}
240	4.02×10^{-13}	5.97×10^{-14}
260	2.72×10^{-13}	1.15×10^{-14}
280	2.08×10^{-13}	2.95×10^{-15}
300	1.75×10^{-13}	9.48×10^{-16}
320	1.58×10^{-13}	3.65×10^{-16}
340	1.51×10^{-13}	1.63×10^{-16}

From Eq. 1, the quantity $K_{\text{eq0}} [\text{water}]$ is equal to the fraction: $X_{\text{complex}} = [\text{complex}]/[\text{acetone}]$. According to the results in Table 1, this fraction is equal to 0.0002 at 100% humidity and 300 K (water concentration = 7.95×10^{17} molecules cm^{-3}). Thus, if Step 0 is not taken into account, reaction of the acetone–water complex with OH is approximately 26 times faster than the corresponding reaction for free acetone + OH. However, multiplying by the Step 0 factor greatly overcomes the catalytic factor. Rate constants for the addition path are negligible in comparison with abstraction and even more so in the water-assisted case.

An alternative, but exactly equivalent, way to determine the effective overall rate constant in the presence of water vapor is to add the contributions, to the effective rate constants, of free acetone and the water complex. Then, the effective overall rate constant can be written as:

$$k_{\text{overall}}^{\text{eff}} = \left[\sigma K_{\text{eq1}} \kappa k_2 \right]_{\text{water-free}} (1 - X_{\text{complex}}) + \left[\sigma K_{\text{eq1}} \kappa k_2 \right]_{\text{water-assisted}} X_{\text{complex}}$$

Since X_{complex} is very small (0.0002 at 300 K), the contribution of the water-assisted pathway is totally irrelevant under atmospheric conditions, and it is not measurable. The latter approach allows us to make a direct comparison between the present result and similar calculations in which Step 0 was ignored.

We have also calculated the variation of the rate constants with the relative air humidity (%H) at 298.15 K (Table S1). As expected, the rate constant is directly proportional to the relative air humidity: a smaller initial water concentration leads to less water complex and to a smaller rate constant.

Additionally, the rate constant variation with temperature has been analyzed in the 220–340 K range (Table 4), at 100% relative air humidity. At very low atmospheric temperatures, the water-free and water-assisted rate constants could be equivalent, assuming that water vapor exists in any detectable amount, which is not the case below 273 K.

4 Conclusions

In conclusion, we show that water does not accelerate the reaction between acetone and OH radicals under atmospheric conditions.

The importance of Step 0 cannot be overemphasized for the reaction in tropospheric conditions. Ignoring Step 0 is equivalent to assuming that all the acetone is complexed with water, which is absolutely not true. Actually, it is clear that there is a very small amount of water–acetone complex to begin with. At very low temperatures, K_C is larger than at room temperature, and most of the acetone could then be in the form of the complex. However, in this case, the water vapor pressure would be so low that the rate constant would still be very small.

This work introduces a new and important perspective pertaining to the, so-called, single-water molecule catalysis under atmospheric reactions. It is now possible to generalize our findings with the acetaldehyde + OH, glyoxal + OH, and acetone + OH reactions to atmospheric radical–molecule reactions. In any reaction between a VOC and an OH radical, if the concentration of the VOC–water complex formed in Step 0 is very low, as is the case for almost all VOC–water complexes with the exception, perhaps, of some strong acids and the OOH radical [55], the lowering of the step 2 barrier is not expected to be large enough to produce a noticeable rate increase, i.e., a catalytic effect. In addition, it is interesting to point out that, according to Ref [55], acetone is one of the VOCs that exists in a relatively large concentration.

Therefore, the rule is that a single water molecule does not catalyze the reaction of OH radicals with volatile organic compounds. If there is an exception to this rule, it still remains to be found. As pointed out by an anonymous referee, such reactions may still occur in molecular complexes consisting of several water molecules. These molecular complexes are known to be abundant prior to atmospheric aerosol nucleation events [67] and have been shown to catalyze organic (including glyoxal) reactions in nanoparticles [68, 69]. The study of these very interesting reactions is, however, outside the scope of the present work.

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