Water Catalysis of the Reaction between Methanol and OH at 294 K and the Atmospheric Implications

Rafael A. Jara-Toro, Federico J. Hernández, Raúl A. Taccone, Silvia I. Lane, and Gustavo A. Pino*

Abstract: *The rate coefficient for the reaction CH$_3$OH + OH was determined by means of a relative method in a simulation chamber under quasi-real atmospheric conditions (294 K, 1 atm of air) and variable humidity or water concentration. Under these conditions, a quadratic dependence of the rate coefficient for the reaction CH$_3$OH + OH on the water concentration was found. Thus the catalytic effect of water is not only important at low temperatures, but also at room temperature. The detailed mechanism responsible of the reaction acceleration is still unknown. However, this dependence should be included in the atmospheric global models since it is expected to be important in humid regions as in the tropics. Additionally, it could explain several differences regarding the global and local atmospheric concentration of methanol in tropical areas, for which many speculations about the sinks and sources of methanol have been reported.*

$\mathbf{W}$ater is ubiquitous in the Earth's atmosphere, reaching concentrations up to 8×10^{17} molecules cm^{-3} at 298 K and 100% relative humidity (% H$_R$) in the lower troposphere.[1] Water can form hydrogen bonded (H-bonded) complexes with many molecules and radicals in the atmosphere, affecting their absorption cross-sections and vibrational frequencies as well as their reactivity. Even very low concentrations of these H-bonded complexes can have significant effects on the atmospheric chemistry as well as in the global warming process.[1–4]
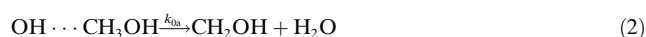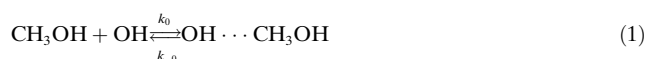
The role of a water molecule as catalyst in the oxidation reactions of oxygenated volatile organic compounds (OVOCs) and simple atmospheric compounds by OH radicals has been the subject of several studies during the last years.[1,4] Recently, experimental evidence were found for single water molecule catalysis in the oxidation reaction of acetaldehyde (CH$_3$CHO) at very low temperatures (< 120 K).[5] Theoretical calculations showed that one water molecule forms an H-bonded complex with CH$_3$CHO lowering the energy barrier for the reaction with OH. However, while the catalytic effect does take place at low temperatures, its relevance to

atmospheric chemistry was questioned since the tropospheric concentration of the OH···CH$_3$CHO···H$_2$O complex is expected to be very low to have a detectable effect on the global reaction rate.[6,7]

Since then, many theoretical works have been devoted to study the possible acceleration of the reactions between OVOCs and OH by one water molecule,[8–13] and most of them[9–13] have also concluded that the OH···OVOC···H$_2$O complexes concentration in the troposphere is very low to reveal any effect on the reaction rate. All these works invite new experiments on other systems and especially under more realistic atmospheric conditions, such as room temperature and atmospheric pressure, to disentangle the role of water in the tropospheric oxidation of OVOCs.

Methanol is one of the simplest and most abundant OVOCs in the atmosphere. It is emitted from biogenic and anthropogenic sources.[14] The atmospheric oxidation of methanol proceeds mainly through reaction with the OH radical. This reaction has been extensively studied and it shows a non-Arrhenius behavior in the temperature range 56–870 K.[15–19] The reaction rate coefficient, at room temperature (298 K) in absence of water, was determined to be $k_0 = 9.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[15]

The reaction CH$_3$OH + OH proceeds by abstraction of a hydrogen atom by the OH radical at either the methyl or the hydroxyl site of CH$_3$OH, assisted by the formation of a pre-reactive complex, that has been recently isolated in a He nanodroplet (Equations (1), (2), and (3)):[20]

$$CH_3OH + OH \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} OH \cdots CH_3OH \tag{1}$$

$$OH \cdots CH_3OH \xrightarrow{k_{0a}} CH_2OH + H_2O \tag{2}$$

$$OH \cdots CH_3OH \xrightarrow{k_{0b}} CH_3O + H_2O \tag{3}$$

Very recently, an enhancement of the reaction rate coefficient at temperatures below 200 K was reported, as a consequence of the fact that at these temperatures the pre-reactive H-bonded complex is sufficiently long-lived to undergo tunneling to form products.[16–19] While Eq. (2) is predominant at room temperature, a relative enhancement of Eq. (3) is observed at lower temperatures (< 200 K). Hereafter, we will consider the total fate of CH$_3$OH and OH leading to products [see Eqs (2) and (3)] with a global rate coefficient k_0.

We present herein a study of the effect of the % H$_R$ on the rate coefficient for the reaction of CH$_3$OH with OH performed in an atmospheric simulation chamber, in air, at 294 K. The rate coefficient of the title reaction was deter-

[*] R. A. Jara-Toro, F. J. Hernández, Prof. R. A. Taccone, Prof. S. I. Lane, Prof. G. A. Pino
INFIQC (CONICET–UNC). Dpto. de Fisicoquímica—Facultad de Ciencias Químicas—Centro Láser de Ciencias Moleculares—Universidad Nacional de Córdoba
Ciudad Universitaria, X5000HUA Córdoba (Argentina)
E-mail: gpino@fcq.unc.edu.ar

mined relative to that of the reaction of OH with a reference compound (C_5H_{12}), which was chosen to preclude the formation of H-bonded complexes with the OH radical and/or water molecules. All experiments were carried out in an 80 L collapsible Teflon bag at (294 ± 2) K and atmospheric pressure (750 ± 10) torr of synthetic air, using the photolysis of H_2O_2 at 254 nm as the source of OH radicals. The variation of the concentration of CH_3OH and C_5H_{12} in time was monitored by gas chromatography. The global rate coefficient of the reaction was obtained from the slope of plots of $\ln([CH_3OH]_0/[CH_3OH]_t)$ versus $\ln([C_5H_{12}]_0/[C_5H_{12}]_t)$ at different % H_R. More details about the experimental method and supplementary experimental results are given in the Supporting Information.

The rate coefficients derived from this analysis are plotted as a function of the added % H_R in Figure 1 a. The error bars represent the uncertainty in the determination of the rate constants, which is explained in more detail in the Supporting Information. This plot clearly shows an unexpected dependence of the reaction rate coefficient on the water vapor pressure.

This dependence could be due to an enhancement of the wall-loss rate of CH_3OH on the moist surface of the bag, which is not expected for C_5H_{12}. However, this was dismissed on the basis of the experimental results shown in the Supporting Information. Therefore, suggesting that this is a catalytic effect on the reaction.

This effect was probably missed in previous publications because the % H_R in those works was much lower than 50 % (< 11.5 torr of H_2O), where the effect is almost negligible as shown in Figure 1.

The curvature in Figure 1 a shows that the reaction is not first order in water vapor as expected by a single water molecule catalysis. This plot can be satisfactory fitted by a second order function ($k_{obs} = (1.34 \pm 0.2) \times 10^{-16}$ % $H_R^2 + (0.86 \pm 0.06) \times 10^{-12}$), the intercept $(8.6 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, is in very good agreement with the rate coefficient previously reported $(9.3 \pm 0.7) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and determined under dry conditions.[15] Remarkably, the linear coefficient is negligible within the fitting error, indicating that the catalysis by a single water molecule is insignificant.

Figure 1 b shows the linear dependence between k_{obs} and $[H_2O]^2$ at 294 K whose intercept is $(8.3 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and the slope is $(4.1 \pm 0.9) \times 10^{-48}$ cm^9 molecule^{-3} s^{-1}. These data indicate that two water molecules are required to induce an enhancement in the reaction rate constant.

The quadratic dependence of reaction rate coefficient on the water concentration has been previously observed in the hydrolysis reaction of SO_3 to produce H_2SO_4,[21,22] and more recently in the reaction of the simplest Criegee intermediate with water vapor.[23,24] However, in both cases the detailed mechanism still remains controversial.

Water dimer $(H_2O)_2$ is present in the atmosphere at appreciable concentrations (10^{14}–10^{15} molecules cm^{-3}) which makes it as abundant as methane under certain conditions. It has been suggested that, although this concentration only represents 0.1–0.2 % of the total water in the atmosphere, it
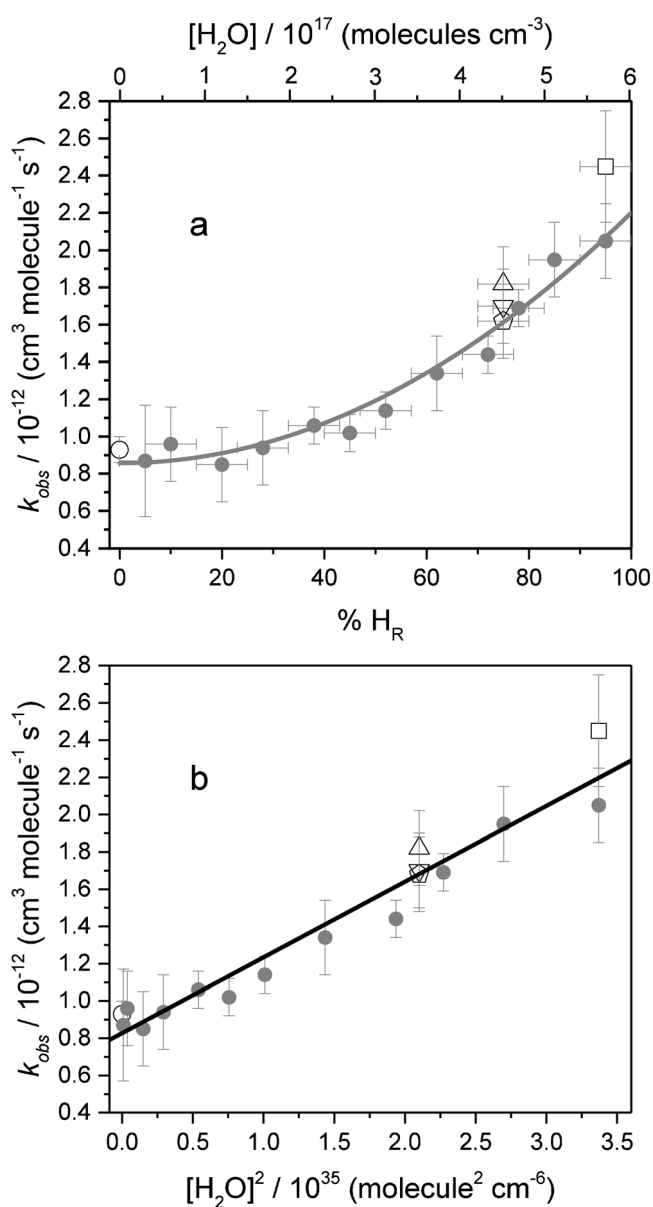
Figure 1. Dependence of the global rate coefficient (k_{obs}) at 294 K for the reaction $CH_3OH + OH$ on a) humidity (% H_R) and b) water concentration to the second power. Rate coefficient determined relative to rate coefficient for the reaction $C_5H_{12} + OH$ in 1 atm of air and at different initial concentrations of H_2O_2 ($\times 10^{17}$ molecules cm^{-3}), OH ($\times 10^8$ radicals cm^{-3}), and CH_3OH ($\times 10^{14}$ molecules cm^{-3}), with $[C_5H_{12}] = (9.8 \pm 0.4) \times 10^{14}$ molecules cm^{-3} in all cases: gray ● $[H_2O_2] = 3.2 \pm 0.2$, $[OH] = 2.3 \pm 0.2$, $[CH_3OH] = 9.2 \pm 0.2$; pentagon $[H_2O_2] = 3.2 \pm 0.2$, $[OH] = 1.4 \pm 0.2$, $[CH_3OH] = 9.2 \pm 0.2$; △ $[H_2O_2] = 3.2 \pm 0.2$, $[OH] = 2.3 \pm 0.2$, $[CH_3OH] = 4.7 \pm 0.4$; ▽ $[H_2O_2] = 3.2 \pm 0.2$, $[OH] = 2.3 \pm 0.2$, $[CH_3OH] = 92 \pm 2$; □ $[H_2O_2] = 0.16 \pm 0.01$, $[OH] = 0.34 \pm 0.05$, $[CH_3OH] = 9.2 \pm 0.4$. Rate coefficient determined under dry condition by others.[15]

could have important implications in the above mentioned reactions.[2,25]

On the other hand, it has been speculated that the presence of $OH(H_2O)_n$ clusters in the troposphere could have significant effects on the solar absorption balance and the

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reactivity of hydroxyl radical, but theoretical calculations predicted that these clusters are not abundant.[4,26] Nevertheless, the $OH(D_2O)_{n=1,2}$ have been stabilized in He-nanodroplets and characterized spectroscopically.[27] Furthermore, $CH_3OH(H_2O)$ complexes are also expected to exist in the troposphere (Supporting Information, Table S1). Therefore, we suggest two likely mechanisms that can account for the experimental observations; one involving $OH(H_2O)$ and $CH_3OH(H_2O)$ complexes and the other considering the $(H_2O)_2$ dimer.

One possibility (Mechanism 1) is to consider a real catalytic mechanism in which the potential energy surface (PES) for the reaction is modified by the presence of water, due to the formation of H-bonded complexes between this molecule and one or both reactants as in the case of the $CH_3CHO + OH$ reaction.[5] Therefore, calculations of the equilibrium constant (K_{eq}) for the formation of the complexes $(H_2O)_2$, $OH(H_2O)$, $OH(H_2O)_2$, $CH_3OH(H_2O)$, CH_3OH-$(H_2O)_2$ were performed at the MP2/aug-cc-pVDZ level with the Gaussian09 program.[28] The results are shown in the Supporting Information, Table S1.

We suggest that the reaction of $OH(H_2O)$ with CH_3OH-(H_2O) could be responsible for the observed behavior, considering that these are the most abundant complexes of OH and CH_3OH with water (Supporting Information, Table S1) and the fact that the dipolar moments of OH ($\mu_{OH} = 1.67$ D)[29] and CH_3OH ($\mu_{CH_3OH} = 1.68$ D)[30] are enhanced upon complexation with one water molecule $OH(H_2O)$ ($\mu_{OH(H_2O)} = 3.75$ D)[27] and $CH_3OH(H_2O)$ ($\mu_{CH_3OH(H_2O)} = 2.72$ D) (Supporting Information, Table S2), which could induce longer range interactions and therefore an enhanced reaction cross-section.

To obtain more insight into this mechanism, the relevant stationary points on the PES were calculated at the uCCSD-(T)/aug-cc-pVDZ//uMP2/aug-cc-p-VDZ level for the dry reaction and for the reaction with one ($OH + CH_3OH(H_2O)$ or $OH(H_2O) + CH_3OH$) and two water molecules (OH-$(H_2O) + CH_3OH(H_2O)$) considering the above argument. The PESs are shown in Figure 2. The optimized structures and the relative energies of all the equilibrium complexes of

the reactants (C), the pre-reactive complexes (CR), the transition states (TS), and the product complexes (CP) are shown in the Supporting Information, Tables S3–S6.

The PES calculated for the dry reaction is the same as in previous works.[12,16,19,31,32] The PES for the reaction with one water molecule shows that the energy barriers for the reactions $OH + CH_3OH(H_2O)$ or $OH(H_2O) + CH_3OH$ do not change very much, as compare to those of the dry reaction (Supporting Information, Tables S4, S5). Therefore, the catalytic effect for one water molecule is expected to be negligible.

However, the PES for the $OH(H_2O) + CH_3OH(H_2O)$ reaction shows that the energy of these reactants is about 1 kcal mol^{-1} above the highest energy barrier for Eq. (3) and 9 kcal mol^{-1} above the lowest energy barrier for Eq. (2). This would allow the unimolecular reaction rate coefficient for the decomposition of the pre-reactive complex $OH \cdots CH_3OH(H_2O)_2$ (CR-a,b-WW) to product to be larger than the unimolecular rate coefficient for the re-dissociation back to the reactants $OH(H_2O) + CH_3OH(H_2O)$. Therefore, it leads to an enhancement on the global reaction rate constant.

The other possibility (Mechanism 2) is to consider that $(H_2O)_2$ acts as a third body on the PES of the dry reaction, whose role is to stabilize CR, removing the excess energy above its potential energy well (4–5 kcal mol^{-1}), and then been trapped below the energy threshold for the re-dissociation back to the reactants. Therefore, it can only decompose to product through tunneling the energy barrier.

This amount of energy can be efficiently removed by $(H_2O)_2$ since the energy transferred from CR in a single collision can be dissipated by dissociating the intermolecular H-bond of the water dimer ($E_{HB} = 3.15$ kcal mol^{-1}).[33] This is unlikely in the case of a single water molecule for which many collisions are required to remove that amount of energy, (usually $\Delta E \approx 100$–350 cm^{-1} per collision). Then, as the lifetime of the excited CR complex is too short, it will decompose back to reactants before the complete stabilization takes place and the catalysis by one water molecule would be inefficient.
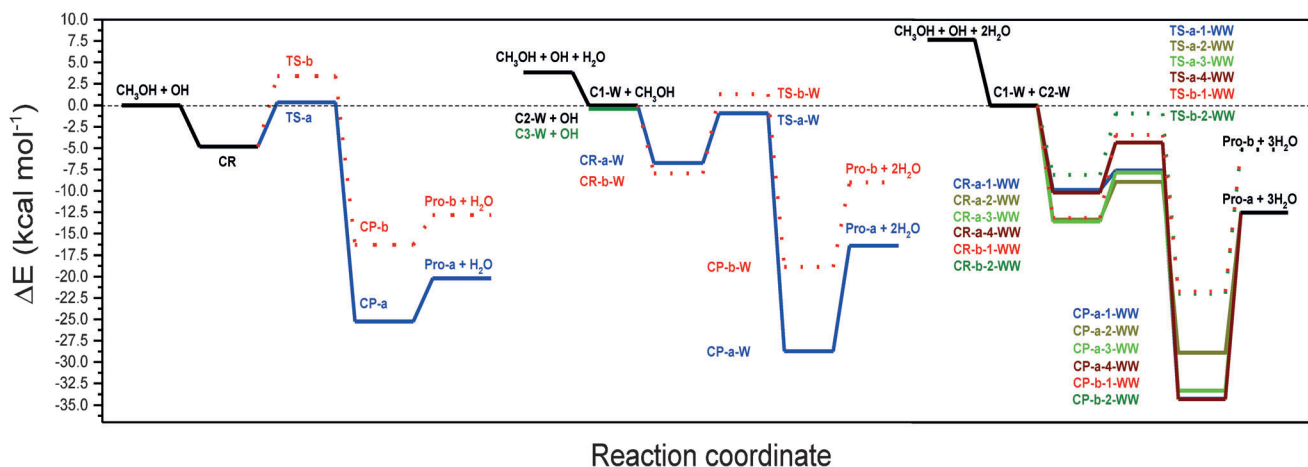
Figure 2. Relative energies [kcal mol^{-1}], including ZPE correction, of the stationary points calculated at the uCCSD(T)/aug-cc-pVDZ//uMP2/aug-cc-pVDZ level of theory for the reaction between OH radicals and CH_3OH without or with one or two molecules of water.

Although CR can be thermalized at 294 K by collisions with O_2/N_2, only the highest energy tail of the Boltzmann distribution could have enough energy to overcome the barrier to reactants.

From the available information we cannot distinguish whether the observed enhancement is due to direct effect of the water dimer or reactions of water complexes with OH and/or CH_3OH in one or different steps. But, in any case and regardless the mechanism responsible for the acceleration of the reaction, the rate coefficient at 294 K and 1 atm for the reaction $CH_3OH + OH$ changes up to a factor of two with % H_R.

Therefore, this result is relevant not only for laboratory, but also for the atmospheric chemistry, indicating for example that in the tropical regions or during humid days methanol should be oxidized faster than expected, reducing its atmospheric lifetime.

The global atmospheric methanol budget is uncertain with estimates of global sources ranging from 123 to 343 Tg yr^{-1}.[34–37] In a seminal work,[34] the oxidation of methanol by OH was suggested to account for the 63 % of the total atmospheric sink of this compound, rendering a tropospheric lifetime of 10–13 days, under dry conditions, while the other sinks are dry deposition to land 26 %, wet deposition 6 %, uptake by the ocean 5 %, and aqueous-phase oxidation in clouds less than 1 %.

It has been observed that global models using the latter values[34] underestimate the concentration of methanol in the South Pacific as compared to those determined by PEM-Tropics B in 1999.[34,35] In this sense, it was suggested that the self-reaction of CH_3O_2 radicals or with other organic peroxy radicals (RO_2) to produce CH_3OH could account for this discrepancy.[35] More recently, the reaction $CH_3O_2 + OH$ has also been postulated as a feasible source of CH_3OH in the South Pacific.[38,39]

However, in other cases, global 3D atmospheric models tend to overestimate the concentration of methanol. Therefore, to improve the models, the emission rates from different sources of methanol are modified as well as its sinks.

Previous analysis of the global methanol budget in different works suggested that the overall atmospheric lifetime ranges from 4.7 to 12 days.[34–37] These values are adjusted by the models in order to fit the experimental data. However, the variation in the global lifetime observed in most of the published work can be also accounted for by considering the dependence of the reaction rate coefficient with the OH radical on the % H_R reported in this work, as shown in Figure 3. For this reason, we suggest that the atmospheric chemical models should include this dependence to fit the global methanol budget.

In this aspect, the concentrations of methanol in the ocean mixed layer (OML) determined by aircraft and surface measurements were overestimated by the GEOS-Chem transport model.[35] To fit the methanol concentrations, the authors suggested an enhanced ocean uptake accounting for 41 % of the total sink, then becoming this process a major global sink, comparable in magnitude to oxidation by OH (35 %). This is in contrast with a previous report[34] in which the ocean uptake was suggested to account only for 5 % of the
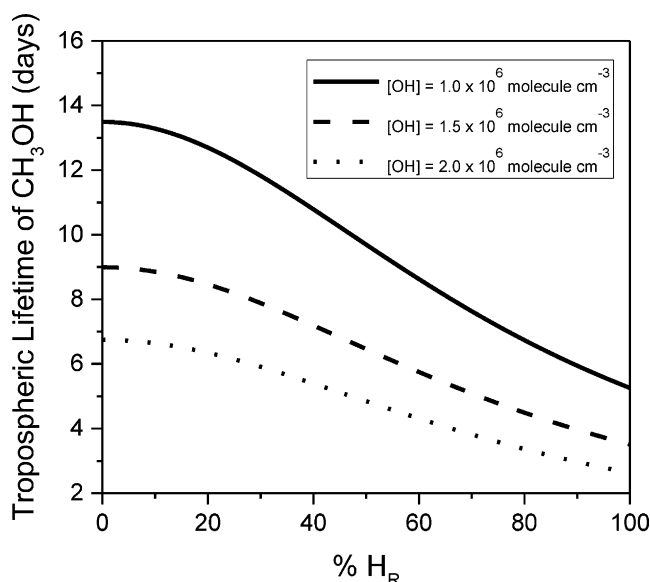
Figure 3. Dependence of the tropospheric lifetime of CH_3OH due to the homogeneous reaction with OH, on the relative humidity. Considering different [OH]: (——) 1.0×10^6 radicals cm^{-3}, (-----) 1.5×10^6 radicals cm^{-3}, (•••••) 2.0×10^6 radicals cm^{-3}.

total atmospheric sink of this species and the oxidation by the OH radical accounts for 63 %. The concentration of methanol could be reduced considering the dependence of its lifetime on the % H_R and this will probably render a more realistic value for the ocean uptake rate. Furthermore, these authors suggested a reduction of terrestrial biogenic sources of methanol, which improves the simulated concentrations.[35] However, even the best model estimation, renders higher concentrations of methanol by a factor of 1.5–1.7 over the tropical areas, for example Surinam and Brazil (Amazonia and Rondonia). This is consistent with an enhancement in the oxidation rate constant at higher humidities.

Recent spaceborne determinations by the thermal infrared sensor IASI aboard the MetOp satellite were compared with concentrations derived by the IMAGESv2 model.[36] The new model optimizes the emission sources and sinks and it shows great improvements as compared with the model of Jacob et al.[34] However, yet the best simulations using the optimized model, overestimates the monthly concentration of methanol in some places, for example Sumatra, Borneo, North Australia, South Atlantic, the North Indian Ocean and the South Pacific.[36] This is another example in which models fail to simulate tropical areas.

More recently, it was reported that the concentration of methanol in Reunion Island, situated in the Indian Ocean with a very high average humidity (70 %), is overestimated by the IMAGESv2 standard model by about 40 %.[37] The authors suggest that this difference is due to the fact that the biogenic emissions of methanol are lower than predicted by the model. However, our determinations show that the rate coefficient for the oxidation reaction of CH_3OH by OH radicals at % $H_R = 70$ % ($k_{70\%} = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) is 50 % higher than the rate coefficient under dry conditions, and therefore this could be another reason for the discrepancy

between the experimental and modeled concentration of methanol in Reunion Island.

The goal of this work is not to stand that the rate coefficient dependence on the % H_R will give de final answer to the disagreements between models and field determinations, but just another variable to be considered that could help to improve the models. Due to the large variation of humidity along the whole planet, it turns out reasonable to include this dependence to build a more realistic model and evaluate whether it is important or not on the global and local budgets of methanol. Finally, the acceleration effect of water is likely to be expected in the oxidation reactions of other OVOCs with OH radical and this work is in progress.

Conflict of interest

The authors declare no conflict of interest.

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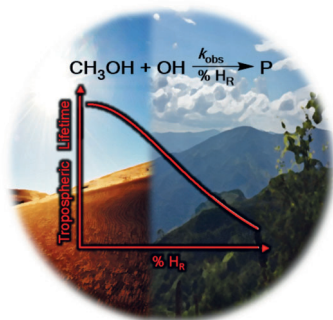
Communications

Atmospheric Chemistry

R. A. Jara-Toro, F. J. Hernández,
R. A. Taccone, S. I. Lane,
G. A. Pino* —————— ▮▮▮–▮▮▮

Water Catalysis of the Reaction between
Methanol and OH at 294 K and the
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$$CH_3OH + OH \xrightarrow[\% H_R]{k_{obs}} P$$

The rate coefficient of the oxidation reaction of CH_3OH by the OH radical depends quadratically on the humidity. This dependence affects the tropospheric lifetime of CH_3OH ranging from 14 days in dry regions as deserts to 4 days in humid areas as the tropics.

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