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COMMUNICATION

Water does not Catalyze the Reaction of OH Radicals with Ethanol

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Recent experiments suggested that water catalyzes the reaction of OH radicals with alcohols, while another work found the contrary. Here, we resolve this disagreement and show that heterogeneous oxidation systematically biased the work showing the catalytic effect and corroborate that water does not catalyze the reaction of OH with alcohols.

Methanol, CH_3OH, is one of the most abundant oxygenated volatile organic compounds in the atmosphere[1,2]. The major sources are direct emissions, but some oxidation pathways of methane also contribute to its abundance, especially in the remote troposphere[3-5]. Ethanol, C_2H_5OH, is a less abundant volatile organic compound and its major source is also the direct emission into the atmosphere from living and decaying plants, with minor input from anthropogenic production. C_2H_5OH is a precursor for acetaldehyde, peroxyacetyl nitrate and secondary aerosols and has thus some impact on the composition of the atmosphere[6]. The major decay pathway for both alcohols in the troposphere is their reaction with OH radicals. Rate constants for both reactions

$$OH + CH_3OH \rightarrow product + H_2O \qquad (R1)$$

$$OH + C_2H_5OH \rightarrow product + H_2O \qquad (R2)$$

have been measured numerous times and are thought to be well known with the IUPAC committee estimating uncertainties of less than ±20%[7] onto the recommended values for k_1 and k_2.

However, Jara-Toro et al. published recently two papers that showed that for CH_3OH[8] as well as for C_2H_5OH and for the next-larger alcohol, n-propanol[9], the rate constant of their reaction with OH radicals increases with increasing relative humidity (RH). Their experiments showed that the rate constant increased quadratically with RH and was enhanced by

around a factor of 2 when the measurements were carried out under high humidities (RH > 90%), far outside of the current estimated uncertainty of the rate constant. As earlier measurements were always carried out at low RH, such an increase might have escaped in earlier experiments.

However, such an increase of the rate constant with RH would have a significant impact on the lifetime of alcohols in the troposphere, because high RHs are often encountered in tropical regions where the photochemical activity is high. Therefore, we have carried out more recently new experiments to investigate again the influence of water on the rate constant of reaction $(R1)$[10] and did not reproduce experimentally the increase of the rate constant with RH such as observed by Jara-Toro et al.[8,9] We carried out quantum chemical calculations which confirmed that addition of water should not increase the rate constant of $(R1)$: even though it was shown that water stabilizes the reactant complex and thus lowers the barrier, the increase in entropy makes more than up for this, and as a result no impact of water on the rate constant is expected at room temperature. The following table summarizes the different studies and the observation (X) or not (-) of a catalytic effect.

	FAGE	Chamber - CH_3ONO	Chamber - H_2O_2
CH_3OH	- [10]	- [10]	X [8]
C_2H_5OH	- [This work]	- [This work]	X [9, this work]
n-C_3H_7OH			X [9]

Nonetheless, no explanation for the strong disagreement between the experimental results of Jara-Toro et al.[8] and our work[10] could be given. There were several differences between both works: Jara-Toro et al.[8] carried out their experiments in a simulation chamber made of a small Teflon bag (80 l). They determined the rate constant by classical relative rate method, *i.e.* in the Teflon bag they mixed an OH precursor (H_2O_2), CH_3OH and a reference compound (C_5H_{12}) and generated steady-state concentrations of OH radicals by continuous photolysis. The decay of both stable compounds, CH_3OH and C_5H_{12}, was measured by GC, and the slope of a linear

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regression of a plot of the loss of CH_3OH as a function of the loss of C_5H_{12} leads to the ratio of both rate constants:

$$\ln\left(\frac{[CH_3OH]_{t=0}}{[CH_3OH]_t}\right) = \frac{k_{OH+CH_3OH}}{k_{OH+C_5H_{12}}} \times \ln\left(\frac{[C_5H_{12}]_{t=0}}{[C_5H_{12}]_t}\right) \qquad \text{Eq. 1}$$

They observed an increased loss of CH_3OH relative to the loss of C_5H_{12} with increasing RH. From this observation and under the assumption that the reaction of the non-polar C_5H_{12} with OH is not influenced by increased RH, they concluded that the rate constant for the reaction of OH with the polar CH_3OH is increasing. Their subsequent work on C_2H_5OH and n-C_3H_7OH[9] was carried out in the same way, using C_5H_{12} or C_7H_{16} as reference compound.

In our work[10] we used two different methods: we carried out experiments using the same relative method as Jara-Toro, but (a) in a bigger Teflon bag (400 l) and (b) with a different precursor for OH radicals, namely the photolysis of CH_3ONO, a very common precursor for OH radicals in simulation chamber studies.

CH_3ONO + hν → CH_3O + NO   (R3)

CH_3O + O_2 → CH_2O + HO_2   (R4)

HO_2 + NO → OH + NO_2   (R5)
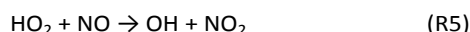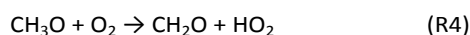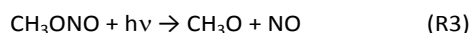
Additionally, we directly measured the rate constant using a laser photolysis reactor coupled to a time-resolved detection of OH radicals by laser induced fluorescence at low pressure (FAGE)[11]. Both series of experiments did not reveal any increase in the rate constant of (R1) with increasing RH.

With the goal of completing the study with another alcohol and resolving the remaining, still unexplained disagreement between both experimental studies, we have carried out new experiments on the impact of the humidity on the rate constant of OH radicals with ethanol, C_2H_5OH. The approach was the same as in our work on the reaction of OH with CH_3OH: (a) the absolute rate constant has been measured using the direct method of laser photolysis coupled to time-resolved OH detection by FAGE and (b) the relative rate constant has been measured relative to the rate constant of OH radicals with n-heptane, C_7H_{16}, in a simulation chamber. However, this time we have used two different precursors in the simulation chamber: the photolysis of CH_3ONO as in our work on CH_3OH, and also the photolysis of H_2O_2, as in the works of Jara-Toro *et al*. In the following, only a brief description of the experimental procedure is given, for more details see Chao *et al*.[10]

Figure 1 shows the absolute rate constant as a function of the relative humidity such as obtained by the measurement of time-resolved OH decays in the presence of different water concentrations, all experiments have been carried out at a total pressure of 740 Torr. OH radicals have been generated at a repetition rate of 1 Hz by pulsed 266nm laser photolysis of O_3 (Quantel, Brillant Easy) in the presence of H_2O, leading to

formation of $O(^1D)$, which subsequently generated OH radicals through its reaction with H_2O. The time-resolved OH decays are then followed by laser induced fluorescence using a dye laser (Sirah, PrecisionScan pumped by Spectra Physics Navigator) at a repetition rate of 5 kHz[12]. Two different methods have been applied: (a) OH decays have been measured for different C_2H_5OH concentrations at fixed RH: a linear regression of a plot of the decay rate as a function of $[C_2H_5OH]$ leads directly to the rate constant of OH + C_2H_5OH, with the intercept expressing the loss of OH radicals through diffusion or reaction with impurities (open squares in Figure 1). (b) OH decays have been measured for different RH with a fixed $[C_2H_5OH]$ (circles in Figure 1). C_2H_5OH has been prepared as diluted mixture in stainless steel canisters by injecting liquid C_2H_5OH with a micro-syringe and filling the canister with N_2 to 2 bar total pressure. Two different mixtures have been used, expressed by the different colors in Figure 1. The mixture is then added to the main flow through a calibrated flowmeter. Figure 1 summarizes the results. While the absolute values obtained with the two different mixtures differ by around 30% due to large uncertainties in the preparation of the mixtures (no special effort for a precise determination of the concentration has been undertaken, as the determination of the absolute rate constant k_2 was not the goal of this work), no increase of the rate constant with increasing relative humidity is observed. This is consistent with our results obtained for methanol[10].
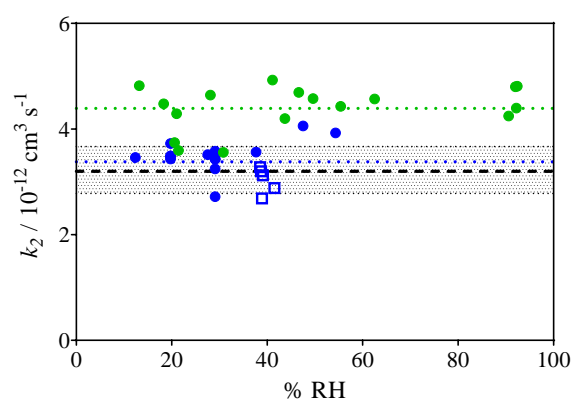

Figure 1: Absolute rate constant of C_2H_5OH + OH as a function of relative humidity, obtained by laser photolysis / FAGE: Blue symbols mixture 1, green symbols mixture 2, dotted lines average value for each mixture. Open squares: k obtained by varying $[C_2H_5OH]$ at constant RH, circles: k obtained at fixed $[C_2H_5OH]$. Black dashed line recommended value for k_2 with shaded area being uncertainty[7]

Next, we have repeated the experiments in the atmospheric simulation chamber in the same way as for CH_3OH, but this time using two different OH precursors. The rate constant for the reaction of the reference compound, C_7H_{16}, with OH is given as[13] k_{ref}= 6.74×10^{-12} $cm^3 s^{-1}$, while the rate constant for (R2) is recommended[7] as k_2= 3.2×10^{-12} $cm^3 s^{-1}$, the expected slope of Eq. 1-type plots is hence 0.47, value indicated by the dotted line in Figure 3.

The upper graph of Figure 2 shows the results obtained with H_2O_2 as precursor (same as Jara-Toro), plotted following Eq. 1 for low (RH = 5%, black symbols) and high (85%, red symbols) humidity. For both humidities, experiments have been carried out with the bag filled with different volumes: completely filled with 200 l (filled symbols) and filled only to half of the maximum volume (100 l, open symbols). The slope of the linear regression is equal to the ratio of the two rate constants. A clear change in the slope can be seen for the different RH experiments. Also, an increase in the slope with decreasing volume (open red versus full red circles in upper graph of Figure 2) can be observed, while the slopes are identical within the experimental uncertainty for the low RH experiments (black open and filled circles).

Next, we have carried out three experiments using CH_3ONO as precursor (same as for our CH_3OH experiments in Chao et al.), shown in the lower graph of Figure 2 a black symbols for low RH and red symbols for high RH (black dots in Figure 3). As for the experiments with CH_3OH[10], instead of an increase as Jara-Toro et al., we observe a small, barely significant, decrease of the ratio of the rate constants with increasing RH (see Table 1). Interestingly, a recent theoretical study on the title reaction[14] is in line with this observation, as it predicts a decrease of the effective rate constant between hydrated or di-hydrated reaction partner.
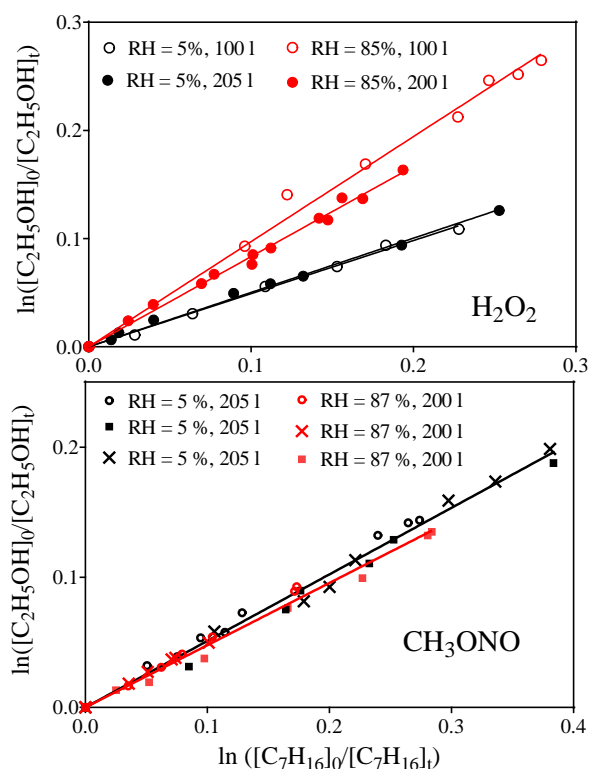

Figure 2: Loss of C_2H_5OH as a function of the loss of the reference compound, C_7H_{16}, black symbols low humidity, red symbols high humidity. Upper graph: H_2O_2 was precursor for OH radicals, open symbols bag filled with 100 l, filled symbols bag filled with 200 l. Lower graph: CH_3ONO was precursor for OH radicals: different symbols show different experiments on different days, all in bags filled with 200 l.

All results have been summarized in Table 1 and plotted in Figure 3 for all experiments, together with the data from Jara-Toro et al. [8,9]

A clear increase in the ratio, i.e. an apparent increase in k_2, can be seen when using H_2O_2 as a precursor (blue symbols in Figure 3) Filled symbols represent experiments in which the Teflon bag was completely filled with around 200 l of gas and the line represents a fit of these data to a quadratic increase of these slopes with RH, consistent with the quadratic increase observed by Jara-Toro et al.

From these results we suspect that the increased oxidation rate of the alcohols with increasing RH is due to an additional oxidation of the alcohols in the liquid film that builds up on the walls of the Teflon bag with increasing RH. Indeed, Jara-Toro et al. have observed that the gas phase concentration of the alcohols decreased by around 15% upon addition of H_2O when increasing RH from dry to 95% (supplementary data of Jara-Toro et al.[8] for CH_3OH and Jara-Toro et al.[9] for C_2H_5OH and C_3H_7OH). However, not only the alcohol, but also some H_2O_2 will dissolve in this film, depending on their Henry constant and when the UV-lamps are turned on, dissolved H_2O_2 can lead to dissolved OH radicals, which oxidizes the dissolved alcohol. The decrease of dissolved alcohol is constantly compensated due to the equilibrium between dissolved and gas phase alcohol, and will hence lead to a faster decay of the alcohol concentration in the gas phase compared to the non-polar, non-dissolved reference compound (C_5H_{10} for Jara-Toro et al. or C_7H_{16} as in this work) which is oxidized solely in the gas phase.

Table 1: Ratios of k_2 / k_{ref}, obtained as slopes from Figure 2

	RH = 5%	RH = 85%
CH_3ONO, 200 l	0.511±0.006	0.478±0.007
H_2O_2, 100 l	0.502±0.008	0.971±0.02
H_2O_2, 200 l	0.491±0.007	0.833±0.01
CH_3OH, 100 l[10]	0.26±0.02	0.21±0.04
CH_3OH, 400 l[10]	0.32±0.05	0.20±0.01

To test for this hypothesis, we have carried out experiments with the Teflon bag filled to different volumes (100, 150 and 200 l), i.e. different surface / volume ratios using H_2O_2 as precursor. This test has also been carried out by Jara-Toro et al.[8,9], but they have varied the volume only in a very small range (60 and 80 l). The results are presented as open symbols in Figure 3: a strong increase in the slope is observed for the high RH experiments when the bag is only filled to half its volume (open squares in Figure 3 and red symbols in Figure 2). At low RH (black symbols in Figure 2) no influence of the surface / volume ratio on the slope could be observed. These results are in line with an increased fraction of C_2H_5OH oxidized in the liquid film with decreasing gas phase volume, and corroborate the above hypothesis.
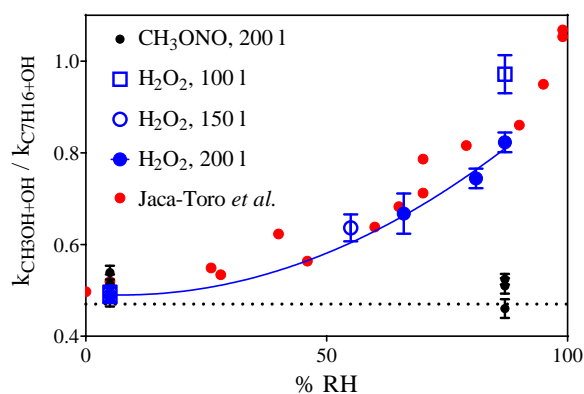
Figure 3: Slope of Eq. 1-type plots as a function of relative humidity. Error bars are statistical only from Figure 2 linear regressions (95% confidence interval). Red dots show values from Jaca-Toro *et al.*

As a conclusion it appears that the unexplained disagreement between two recent experimental results on the influence of water on the rate constant of the reaction of OH radicals with alcohols has been resolved: the experiments carried out by Jara-Toro *et al.*[8,9] in a small Teflon bag at high RH, using the hydrophilic H_2O_2 as OH-precursor, suffered probably from a systematic bias due to a partial, heterogeneous oxidation of the hydrophilic alcohol, in contrary to the hydrophobic reference compound. This led to the apparent increase of the rate constant of OH with alcohols at high RH. The current experiments reinforce again the conclusions from Chao *et al.*[10], drawn from experiments and quantum chemical calculations, that water does not enhance the rate constant of OH radicals with alcohols.

Acknowledgement

Conflicts of interest

There are no conflicts to declare.

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