Understanding the active role of water on laboratory chamber studies of reactions of the OH radical with alcohols of atmospheric relevance

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Section S1. Second-order rate coefficients, k_{obs}, for the cycloalcohols (cROH) and OH radical rection

This section summarises the experimental k_{obs} values for the reaction between the OH radical and cyclobutanol, cButOH (Table S1), cyclopentanol cPenOH (Table S2), and cyclohexanol, cHexOH (Table S3), respectively at variable relative humidity (RH).

The errors, Δk_{obs}, reported for each individual value of k_{obs}, listed in Table S1 to S3, were calculated according to the Equation S1;

$$\Delta k_{obs} = \left(\frac{\Delta S}{S} + \frac{\Delta k_{Ref}}{k_{Ref}}\right) \times k_{obs} \qquad \text{(Eq. S1)}$$

where ΔS is $2_{\sigma n-1}$ of the slope (S) obtained from the least squares fit of $\ln([cROH]_0 /[cROH]_t)$ vs. $\ln([Ref]_0 /[Ref]_t)$ graphs at different RH (Figure 2 in the manuscript). k_{Ref} and Δ_{kRef} stand for the rate coefficient of the reference reaction and its associated uncertainty, respectively.

Table S1: Individual rate constants plotted in Figure 1a in the main manuscript.

RH	k_{obs} / 10^{-12} (cm^3 molecule^{-1} s^{-1})	Experimental concentration (molecules cm^{-3})				bath gas
		[H$_2$O]	[cButOH]	[C$_{10}$H$_{22}$]	[H$_2$O$_2$]	
2 ± 5	7.3 ± 0.2	1.5 x 10^{16}	5.6 x 10^{14}	4.5 x 10^{14}	6.4 x 10^{16}	Air
22 ± 5	7.5 ± 0.1	1.7 x 10^{17}	5.6 x 10^{14}	4.2 x 10^{14}	6.4 x 10^{16}	Air
22 ± 5	7.6 ± 0.1	1.7 x 10^{17}	1.3 x 10^{15}	4.2 x 10^{14}	6.4 x 10^{16}	N$_2$
22 ± 5	7.5 ± 0.1	1.7 x 10^{17}	5.6 x 10^{14}	4.2 x 10^{14}	1.2 x 10^{17}	Air
39 ± 5	7.7 ± 0.1	2.9 x 10^{17}	5.9 x 10^{14}	4.2 x 10^{14}	3.2 x 10^{16}	Air
40 ± 5	7.8 ± 0.1	3 x 10^{17}	5.6 x 10^{14}	4.7 x 10^{14}	6.4 x 10^{16}	Air
55 ± 5	7.9 ± 0.2	4.1 x 10^{17}	7 x 10^{14}	4.2 x 10^{14}	6.4 x 10^{16}	N$_2$
55 ± 5	7.9 ± 0.1	4.1 x 10^{17}	7 x 10^{14}	4.2 x 10^{14}	1.2 x 10^{17}	N$_2$
67 ± 5	8.1 ± 0.1	5 x 10^{17}	5.7 x 10^{14}	4.5 x 10^{14}	6.4 x 10^{16}	Air
83 ± 5	8.3 ± 0.2	6.2 x 10^{17}	5.5 x 10^{14}	3.5 x 10^{14}	6.4 x 10^{16}	Air
83 ± 5	8.3 ± 0.2	6.2 x 10^{17}	5.5 x 10^{14}	3.5 x 10^{14}	1.2 x 10^{17}	Air

Table S2: Individual rate constants plotted in Figure 1b in the main manuscript.

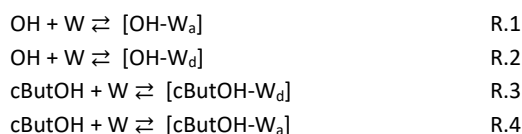| RH	k_{obs} / 10^{-11} (cm^3 molecule^{-1} s^{-1})	Experimental concentration (molecules cm^{-3})		Ref		[H$_2$O$_2$]	bath gas
		[H$_2$O]	[cPenOH]	[C$_7$H$_{16}$]	[C$_{10}$H$_{22}$]		
1 ± 5	1.1 ± 0.1	7.5 x 10^{15}	6.5 x 10^{14}	3.1 x 10^{14}	-	6.4 x 10^{16}	Air
20 ± 5	1.3 ± 0.1	1.5 x 10^{17}	6.5 x 10^{14}	-	6.5 x 10^{14}	1.2 x 10^{17}	Air
23 ± 5	1.3 ± 0.1	1.72 x 10^{17}	6.5 x 10^{14}	4 x 10^{14}	-	6.4 x 10^{16}	N$_2$
30 ± 5	1.4 ± 0.1	2.2 x 10^{17}	6.5 x 10^{14}	3.5 x 10^{14}	-	6.4 x 10^{16}	Air
40 ± 5	1.5 ± 0.1	3 x 10^{17}	6.5 x 10^{14}	-	6.5 x 10^{14}	1.2 x 10^{17}	Air
62 ± 5	1.6 ± 0.1	4.7 x 10^{17}	6.5 x 10^{14}	-	3.1 x 10^{14}	6.4 x 10^{16}	Air
63 ± 5	1.6 ± 0.1	4.72 x 10^{17}	6.5 x 10^{14}	4 x 10^{14}	-	1.2 x 10^{17}	N$_2$
70 ± 5	1.7 ± 0.2	5.2 x 10^{17}	6.5 x 10^{14}	3.1 x 10^{14}	-	6.4 x 10^{16}	Air
71 ± 5	1.7 ± 0.1	5.3 x 10^{17}	6.5 x 10^{14}	4 x 10^{14}	-	6.4 x 10^{16}	N$_2$
88 ± 5	1.8 ± 0.1	6.6 x 10^{17}	6.5 x 10^{14}	-	6.5 x 10^{14}	6.4 x 10^{16}	Air
88 ± 5	1.8 ± 0.2	6.6 x 10^{17}	6.5 x 10^{14}	-	3.1 x 10^{14}	8 x 10^{16}	Air
89 ± 5	1.8 ± 0.1	6.7 x 10^{17}	6.5 x 10^{14}	-	6.5 x 10^{14}	1.2 x 10^{17}	N$_2$

Table S3: Individual rate constants plotted in Figure 1c in the main manuscript.

RH	k_{obs} / 10^{-11} (cm^3 molecule^{-1} s^{-1})	Experimental concentration (molecules cm^{-3})				bath gas
		[H$_2$O]	[cHexOH]	[C$_{10}$H$_{22}$]	[H$_2$O$_2$]	
2 ± 5	1.9 ± 0.1	1.5 x 10^{16}	4 x 10^{14}	3.5 x 10^{14}	6.4 x 10^{16}	Air
24 ± 5	2.0 ± 0.2	1.8 x 10^{17}	3.3 x 10^{14}	3.5 x 10^{14}	3.2 x 10^{16}	N$_2$
66 ± 5	1.9 ± 0.2	5 x 10^{17}	6.0 x 10^{14}	6.3 x 10^{14}	6.4 x 10^{16}	N$_2$
87 ± 5	2.0 ± 0.1	6.5x10^{17}	3.2x10^{14}	3.2 x 10^{14}	6.4 x 10^{16}	Air

Section S2. Computational results

Structure and stability of the equilibrium complexes (EC) between the reactants

Depending on whether the water molecule, W, acts as H donor, W_d, or H acceptor, W_a, of for H-bond formation, four pre-equilibrium complexes, EC, can be proposed between this molecule and the reactants cButOH and OH, R1-4.
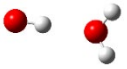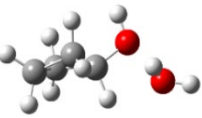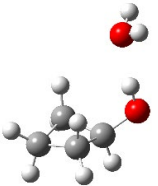
OH + W $\rightleftarrows$ [OH-W_a]   R.1
OH + W $\rightleftarrows$ [OH-W_d]   R.2
cButOH + W $\rightleftarrows$ [cButOH-W_d]   R.3
cButOH + W $\rightleftarrows$ [cButOH-W_a]   R.4

It has been established that a reaction such as R2 is unlikely to occur.[1] Hence, the [OH-W_a] EC was discarded in the proposed reaction mechanism. The abundance of each EC was determined based on their equilibrium constants, K_{EQ}, according to Equation S2.

$$K_{EQ} = e^{\frac{-(G^\circ_{Eq} - G^\circ_{reactans})}{RT}} \qquad \text{(Eq. S2)}$$

where G°_{EQ}, $G^\circ_{Reactans}$, R and T represents the EC standard Gibbs energy, reactants standard Gibbs energy, the molar Boltzmann constant, and the experimental temperature (296 K), respectively.

The calculated concentration of [OH-W], [cButOH-Wd] and [cButOH-Wa] are shown in Table S4. The experimental concentrations of cButOH and W are listed in Table S1. In addition, the photostationary concentration of OH radicals in the experimental setup was determined and found to be $(2.5 \pm 0.7) \times 10^8$ radicals cm^{-3}.

Table S4: Molecular structure, ΔG° (296 K), K_{EQ} (296 k) and their estimated experimental concentrations for each pre-equilibrium complex.

Reaction	Molecular structure	$\Delta G^\circ_{(296\ K)}$ (kcal mol^{-1})	$K_{EQ\ (296\ K)}$ (cm^3 molecule^{-1})	Experimental concentration (Estimate) (molecules cm^{-3})
OH + W $\rightleftarrows$ [OH-W_a]		1.51	2.6 x 10^{-21} [2]	5 x 10^5
cButOH + W $\rightleftarrows$ [cButOH-W_d]		1.88	1.5 x 10^{-21} This work	
cButOH + W $\rightleftarrows$ [cButOH-W_a]		1.95	1.6 x 10^{-21} This work	5 x 10^{11}

Exploring Reaction Pathways between cButOH and OH Radical: Effects of Water Presence

The reaction pathways between cButOH and the OH radical in the absence ("dry reaction") and in the presence ("wet reaction") of the water were explored by computing the stationary points of the potential energy surface (PES). The results shown here were performed with the most stable conformer found for the cButOH molecule (for more details see Ref. 3).

The reaction channels were determined depending on the position of the H atom suffering the abstraction by the OH radical as shown in Figure S1.
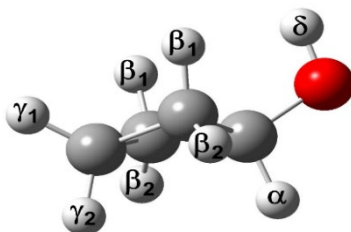

Figure S1: Molecular structures of cButOH

The relative energy for the main stationary points in the PES for the dry reaction will be named according to the following criteria: reactants, pre-reactive complex (CR_i), transition state (TS_i), product complex (PC_i) and radical intermediates (R_i). The subscript "i" is used to specify the abstraction position, denoted as α_n, β_n, γ_n, or δ_n. For the wet reaction, the stationary points will be identified using the same criteria mentioned above and accompanied by the letter W to represent the presence of the water molecule, as follows: pre-reactive complex (CR_i-W), transition state (TS_i-W), product complex (CP_i-W) and product radical (R_i) (the nomenclature of the latter does not change since it is the same regardless of whether it is a wet or dry reaction). A summary of the Gibbs Energy values found for the reaction pathways in both, the dry and the wet reaction is presented in Table S5.

The results suggest that the stabilization of the TS for the wet vs. dry reaction are not significant to associate the increase of the rate coefficient for the wet reaction as a consequence of a homogeneous gas-phase catalysis process.

Table S5: Gibbs Energy, in kcal/mol, for the reaction pathways in the dry (top) and the wet (bottom part) reaction between cButOH and OH radicals.

DRY REACTION				
Reactants	**CR_i**	**TS_i**	**CP_i**	**R +H_2O**
cButOH + OH 0	CR_α **0.90**	TS_α **4.88**	CP_α **18.87**	α-cyclobutyl-ol + H_2O **20.69**
	$CR_{\beta1}$ **0.96**	$TS_{\beta1}$ **6.22**	$CP_{\beta1}$ **-13.78**	β-cyclobutyl-ol + H_2O **- 16.56**
	$CR_{\beta2}$ **0.88**	$TS_{\beta2}$ **7.53**	$CP_{\beta2}$ **-12.73**	
	$CR_{\gamma1}$ **0.87**	$TS_{\gamma1}$ **7.23**	$CP_{\gamma1}$ **-13.67**	γ-cyclobutyl-ol + H_2O **- 16.78**
	$CR_{\gamma2}$ **3.51**	$TS_{\gamma2}$ **7.23**	$CP_{\gamma2}$ **-13.96**	
	CR_δ **0.90**	TS_δ **9.36**	CP_δ **-11.94**	cyclobutoxyde + H_2O **-14.34**
WET REACTION				
Reactants	**EC**	**CR_{xi}-W**	**TS_{xi}-W**	**CP_{xi}-W**	**R + $2H_2O$**

WET REACTION					
Reactants	**EC**	**CR_{xi}-W**	**TS_{xi}-W**	**CP_{xi}-W**	**R + $2H_2O$**
[OH-W] + cButOH 0	[OH-W] + cButOH 1.5	CR_α-W **2.89**	TS_α-W **5.69**	CP_α-W **-18.38**	α-cyclobutyl-ol + $2H_2O$ **-20.68**
		$CR_{\beta1}$-W **5.59**	$TS_{\beta1}$-W **8.46**	$CP_{\beta1}$-W **-13.78**	β-cyclobutyl-ol + $2H_2O$ **-16.59**
		$CR_{\beta2}$-W **2.61**	$TS_{\beta2}$-W **8.56**	$CP_{\beta2}$-W **-10.97**	
		$CR_{\gamma1}$-W **4.49**	$TS_{\gamma1}$-W **11.41**	$CP_{\gamma1}$-W **-9.98**	γ-cyclobutyl-ol + $2H_2O$ **-16.77**
		$CR_{\gamma2}$-W **2.64**	$TS_{\gamma2}$-W **10.23**	$CP_{\gamma2}$-W **- 13.53**	
		CR_δ-W **3.94**	TS_δ-W **11.2**	CP_δ-W **-11.04**	cyclobutoxyde + $2H_2O$ **-14.32**

Section S3. Comparison between the experimental and theoretical value of Henry's Law Solubility constants, K_H

The theoretical values of Henry's constants, K_H^{theo}, were obtained from the United States Environmental Protection Agency, EPA, database (https://comptox.epa.gov/dashboard/).[3] A comparison of several Henry's constants experimental values,[4] K_H^{exp}, and K_H^{theo} for lineal, branched, and cyclic alcohols was plotted, Figure S. From the slope value, a correction factor of 0.99 was obtained. The closeness of this value to the unit clearly shows the excellent agreement between the experimental and the theoretical values. Since the K_H^{exp} values for cyclobutanol and cyclopentanol are unknown, their K_H^{theo} corrected values were used in Figure 4 from the main manuscript.
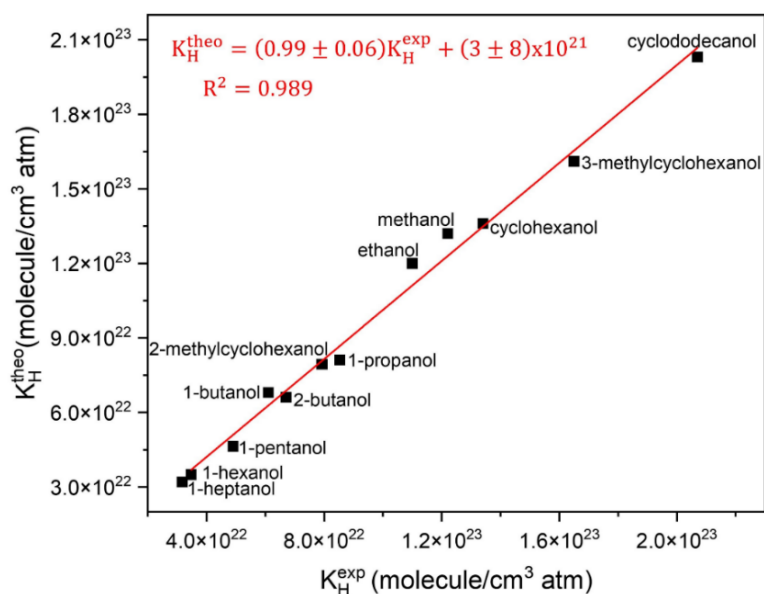

Figure S2: Experimental Henry's constants values,K_H^{exp} [10] vs theoretical values, K_H^{theo} [9] for several linear and cyclic alcohols.

References

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