Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2018

Supporting Information

Water Catalysis of the Reaction Between the Hydroxyl Radicals and Linear Saturated Alcohols (ethanol and n-propanol) at 294 K

Rafael A. Jara-Toro,[a,b,c] Federico J. Hernández,[a,b,c] María de los A. Garavagno,[a,b,c] Raúl A. Taccone[a,b,c] and Gustavo A. Pino[a,b,c,*]

a) INFIQC (CONICET – UNC) - Ciudad Universitaria, X5000HUA Córdoba, Argentina.

b) Dpto. de Fisicoquímica – Facultad de Ciencias Químicas – Universidad Nacional de Córdoba, - Ciudad Universitaria, X5000HUA Córdoba, Argentina.

c) Centro Láser de Ciencias Moleculares – Universidad Nacional de Córdoba, - Ciudad Universitaria, X5000HUA Córdoba, Argentina.

Table S.1: Independent rate constants plotted in Figure 4.

$\%H_R$	$[H_2O]^2 / 10^{35}$ (molecules^2 cm^{-6})	$k_{obs}/ 10^{-12}$ (cm^3 molecule^{-1}s^{-1})
Reported coefficient		
0	<<0.09	3.35 ± 0.17[a]
Air		
28 ± 5	0.28	3.6± 0.1
46 ± 5	0.77	3.8 ± 0.2
62 ± 5	1.40	4.6 ± 0.4
70 ± 5	1.78	5.3 ± 0.3
90 ± 5	2.94	5.8 ± 0.3
95 ± 5	3.28	6.4 ± 0.2[b]
100 ± 5	3.63	7.1 ± 0.4
N_2ultra pure		
5 ± 5	0.09	3.5 ± 0.1
26 ± 5	0.25	3.7 ± 0.1
40 ± 5	0.58	4.2 ± 0.2
60 ± 5	1.31	4.3 ± 0.1
70 ± 5	1.78	4.8± 0.2
79 ± 5	2.27	5.5 ± 0.4
100 ± 5	3.63	7.2± 0.2

a) Ref. 1
b)Determined in a different reaction chamber(60 L collapsible Teflon bag)

Table S.2: Independent rate constants plotted in Figure 5.

% H_R	$[H_2O]^2$/ 10^{35} (molecules^2 cm^{-6})	k_{obs}/ 10^{-12} (cm^3 molecule^{-1}s^{-1})
Reported coefficient		
0	<< 0.09	5.9 ± 0.6[a]
Air		
5 ± 5	0.09	6.1 ± 0.2[b]
25 ± 5	0.23	7.0 ± 0.4[b]
25 ± 5	0.23	7.2 ± 0.3[c]
40 ± 5	0.58	6.7 ± 0.2[c]
60 ± 5	1.31	8.8 ± 0.4[c]
75 ± 5	2.04	9.9 ± 0.2[c]
95 ± 5	3.28	11.5 ± 0.3[c]
100 ± 5	3.63	12.5 ± 0.4[c]
100 ± 5	3.63	13.2 ± 0.6[b]
N_2ultra pure		
5 ± 5	0.09	6.2 ± 0.2[c]
60 ± 5	1.31	9.1 ± 0.3[c]
70 ± 5	1.78	10.4 ± 0.3[c]
85 ± 5	2.62	11.9 ± 0.3[c]
95 ± 5	3.28	10.8 ± 0.3[c]

a) Ref.2
b) Reference reaction: C_5H_{12} + OH
c) Reference reaction: C_7H_{16} + OH

All the computational results presented below have been calculated at the uCCSD(T)/aug-cc-pVDZ//uMP2/aug-cc-pVDZ level of theory, using the Gaussian 09 program package.[3]

Table S.3: Structures and dipolar moments (μ) for the ROH conformers.

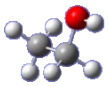
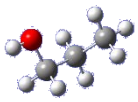
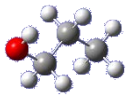
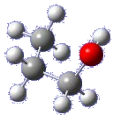
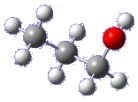
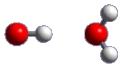
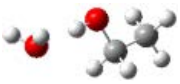
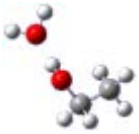
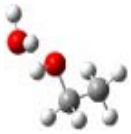
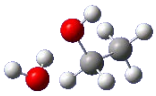
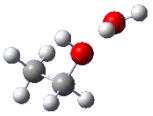
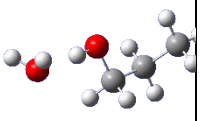
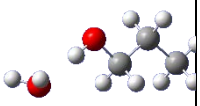
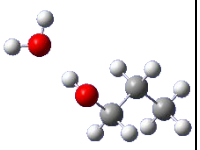
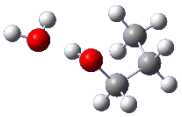
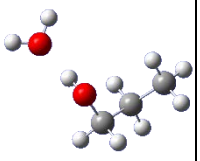
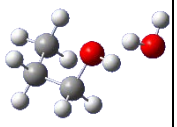
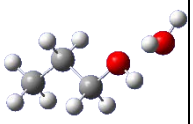
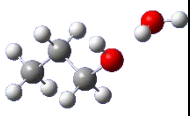
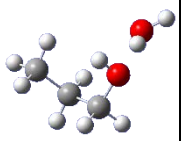
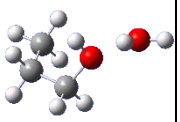
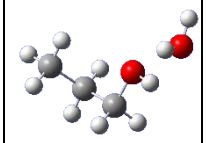
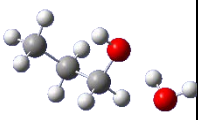
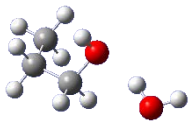
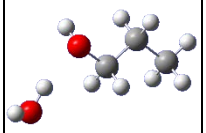
Conformers	**Structure**	**μ (D) MP2**
C_2H_5OH		
C_2H_5OH-1		1.74
C_2H_5OH-2		1.87
C_3H_7OH		
C_3H_7OH-1		1.66
C_3H_7OH-2		1.65
C_3H_7OH-3		1.92
C_3H_7OH-4		1,90
C_3H_7OH-5		1,83

Table S.4: Relative energy including ZPE correction (Δ(E+ZPE), relative Gibbs free energy ($\Delta G°_{294K}$), the corresponding equilibrium constants (K_{294K}) and dipolar moments (μ) of the ROH(H_2O) and OH(H_2O) complexes.The available literature values are also reported in red, forcomparison.

Complexes	**Structure**	**Δ(E+ZPE)** (kcal mol^{-1})	**ΔG°** (kcal mol^{-1}) ± 1 kcal/mol	$K_{eq\text{-}294K}$ (cm^3 $molecule^{-1}$)	$K^{max}_{eq\text{-}294K}$ – $K^{min}_{eq\text{-}294K}$ (cm^3 $molecule^{-1}$)*	**μ (D) MP2**
$OH(H_2O)$		-3.83	1.59 1.14 [a]	2.6×10^{-21} 5.7×10^{-21} [a]	1.5×10^{-20} - 4.8×10^{-22}	4.20 (3.75) [b]
C_2H_5OH						
$[C_2H_5OH(H_2O)]_1$		-3.96	2.28	8.0×10^{-22}	4.4×10^{-21} - 1.4×10^{-22}	2.80
$[C_2H_5OH(H_2O)]_2$		-3.93	2.52	5.4×10^{-22}	3.0×10^{-21} - 9.7×10^{-23}	2.94
$[C_2H_5OH(H_2O)]_3$		-4.89	2.24	8.7×10^{-22}	4.8×10^{-21} - 1.6×10^{-22}	1.95
$[C_2H_5OH(H_2O)]_4$		-4.50	2.25	8.6×10^{-22}	4.7×10^{-21} - 1.5×10^{-22}	2.21
$[C_2H_5OH(H_2O)]_5$		-4.93	2.55	5.1×10^{-22}	2.8×10^{-21} - 9.2×10^{-23}	2.09
C_3H_7OH						
$[C_3H_7OH(H_2O)]_1$		-4.07	2.17	9.8×10^{-22}	5.4×10^{-21} - 1.8×10^{-22}	2.91

$[C_3H_7OH(H_2O)]_2$		-4.05	2.22	8.9×10^{-22}	4.9×10^{-21} - 1.6×10^{-22}	2.77
$[C_3H_7OH(H_2O)]_3$		-4.05	2.18	9.5×10^{-22}	5.3×10^{-21} - 1.7×10^{-22}	3.01
$[C_3H_7OH(H_2O)]_4$		-4.05	2.13	1.0×10^{-21}	5.8×10^{-21} - 1.9×10^{-22}	3.27
$[C_3H_7OH(H_2O)]_5$		-4.05	2.16	1.0×10^{-21}	5.5×10^{-21} - 1.8×10^{-22}	3.05
$[C_3H_7OH(H_2O)]_6$		-4.05	2.29	7.9×10^{-22}	4.4×10^{-21} - 1.4×10^{-22}	1.53
$[C_3H_7OH(H_2O)]_7$		-4.89	2.35	7.1×10^{-22}	3.9×10^{-21} - 1.3×10^{-22}	1.81
$[C_3H_7OH(H_2O)]_8$		-5.04	2.16	9.9×10^{-22}	5.5×10^{-21} - 1.8×10^{-22}	2.06
$[C_3H_7OH(H_2O)]_9$		-5.03	2.47	5.9×10^{-22}	3.2×10^{-21} - 1.1×10^{-22}	2.72
$[C_3H_7OH(H_2O)]_{10}$		-4.05	2.16	1.0×10^{-21}	5.5×10^{-21} - 1.8×10^{-22}	2.04

$[C_3H_7OH(H_2O)]_{11}$		-4.05	2.29	7.9×10^{-22}	4.4×10^{-21} - 1.4×10^{-22}	2.00
$[C_3H_7OH(H_2O)]_{12}$		-4.05	2.18	9.6×10^{-22}	5.3×10^{-21} - 1.7×10^{-22}	2.38
$[C_3H_7OH(H_2O)]_{13}$		-4.05	2.13	1.0×10^{-21}	5.8×10^{-21} - 1.9×10^{-22}	2.34
$[C_3H_7OH(H_2O)]_{14}$		-4.05	2.16	1.0×10^{-21}	5.5×10^{-21} - 1.8×10^{-21}	2.27

a) Theoretical values from ref. 4
b) Experimental value from ref. 5

*The values of $K^{max}_{eq\text{-}294K}$ and $K^{min}_{eq\text{-}294K}$ were obtained assuming a minimum error of ± 1 kcal/mol in the values of $\Delta G°$. Therefore, $K^{max}_{eq\text{-}294K}$ corresponds to the values obtained using $(\Delta G° - 1)$ kcal/mol and $K^{min}_{eq\text{-}294K}$corresponds to the values obtained using $(\Delta G° + 1)$ kcal/mol. The goal of this values is to get some estimation of the lowest error on the $K_{eq\text{-}294\ K}$.

Table S.5: Relative energies (Δ(E+ZPE), in kcal mol^{-1}) of the stationary points for the reaction OH + C_2H_5OH underdry conditions.

Reactants	CR_j	TS_j	CP_j
OH + C_2H_5OH-1 (0.0)	$CR_{\alpha,\beta,o}$ -5.23	$TS_{\alpha1}$ -1.18	$CP_{\alpha1}$ -24.13
		$TS_{\beta1}$ 3.74	$CP_{\beta1}$ -18.98
		TS_{o1} 3.07	CP_{o1} -16.60
	$CR_{\beta2}$ -0.88	$TS_{\beta2}$ 0.60	$CP_{\beta2}$ -15.49
OH + C_2H_5OH-2 (0.0)	$CR_{\alpha2}$ -5.14	$TS_{\alpha2}$ -1.91	$CP_{\alpha2}$ -25.90
		$TS_{\alpha3}$ -1.45	$CP_{\alpha3}$ -25.90
	$CR_{\beta,o}$ -5.27	$TS_{\beta3}$ -1.44	$CP_{\beta3}$ -20.02
		$TS_{\beta4}$ 2.66	$CP_{\beta4}$ -16.70
		TS_{o2} 2.55	CP_{o2} -16.34

Table S.6: Relative energies (Δ(E+ZPE), in kcal mol^{-1}) of the stationary points for the reaction OH + C_2H_5OH including one water molecule.

Reactants	CR_j-W	TS_j-W	CP_j-W
$OH(H_2O) + C_2H_5OH$-1 (0.0)	CR_{α}-W -7.81	$CR_{\alpha1}$-W -2.83	$CR_{\alpha1}$-W -25.94
		$CR_{\alpha2}$-W -4.66	$CR_{\alpha2}$-W -30.07
	$CR_{\beta1}$-W -6.96	$TS_{\beta1}$-W -1.54	$CP_{\beta1}$-W -21.77
	$CR_{\beta2}$-W -11.84	$TS_{\beta2}$-W 0.22	$CP_{\beta2}$-W -23.60
	$CR_{\beta3}$-W -12.96	$TS_{\beta3}$-W 2.55	$CP_{\beta3}$-W -23.64
	CR_{o1}-W -8.36	TS_{o1}-W 0.87	CP_{o1}-W -19.18
$OH(H_2O) + C_2H_5OH$-2 (0.0)	$CR_{\alpha1}$-W -7.10	$TS_{\alpha1}$-W -4.42	$CP_{\alpha1}$-W -29.65
	$CR_{\alpha2}$-W -3.39	$TS_{\alpha2}$-W -2.59	$CP_{\alpha2}$-W -25.89
	$CR_{\alpha3}$-W -7.43	$TS_{\alpha3}$-W -2.36	$CP_{\alpha3}$-W -29.96

	$CR_{\beta 4}$-W -7.43	$TS_{\beta 4}$-W -1.41	$CP_{\beta 4}$-W -22.19
	$CR_{\beta 5}$-W -8.64	$TS_{\beta 5}$-W -2.05	$CP_{\beta 5}$-W -23.51
	CR_{o2}-W -8.22	TS_{o2}-W 0.41	CP_{o2}-W -19.20
	CR_{o3}-W -8.45	TS_{o3}-W 0.15	CP_{o3}-W -19.18

Table S.7: Relative energies (Δ(E+ZPE), in kcal mol^{-1}) of the stationary points for the reaction OH + C_2H_5OH including two water molecules.

Reactants	CR_j-WW	TS_j-WW	CP_j-WW
$OH(H_2O) + [C_2H_5OH(H_2O)]_1$ (0.0)	$CR_{\alpha1}$-WW -10.15	$CR_{\alpha1}$-WW -9.55	$CR_{\alpha1}$-WW -34.24
	$CR_{\alpha2}$-WW -14.05	$CR_{\alpha2}$-WW -11.11	$CR_{\alpha2}$-WW -35.39
	$CR_{\alpha3}$-WW -13.95	$CR_{\alpha3}$-WW -9.42	$CR_{\alpha3}$-WW -34.75
	$CR_{\alpha4}$-WW -10.66	$CR_{\alpha4}$-WW -6.07	$CR_{\alpha4}$-WW -29.36
	$CR_{\beta1}$-WW -13.95	$TS_{\beta1}$-WW -6.96	$CP_{\beta1}$-WW -28.89
	$CR_{\beta2}$-WW -10.66	$TS_{\beta2}$-WW -4.45	$CP_{\beta2}$-WW -29.60
	CR_{o1}-WW -13.52	TS_{o1}-WW -3.50	CP_{o1}-WW -21.00
$OH(H_2O) + [C_2H_5OH(H_2O)]_2$ (0.0)	$CR_{\alpha5}$-WW -9.88	$TS_{\alpha5}$-WW -9.51	$CP_{\alpha5}$-WW -34.04
	$CR_{\alpha6}$-WW -14.08	$TS_{\alpha6}$-WW -10.96	$CP_{\alpha6}$-WW -35.23

	$CR_{\alpha 7}$-WW -13.92	$TS_{\alpha 7}$-WW -9.29	$CP_{\alpha 7}$-WW -34.63
	$CR_{\alpha 8}$-WW -10.58	$TS_{\alpha 8}$-WW -6.24	$CP_{\alpha 8}$-WW -34.00
	$CR_{\beta 3}$-WW -14.15	$TS_{\beta 3}$-WW -7.72	$CP_{\beta 3}$-WW -28.72
	CR_{o2}-WW -8.65	TS_{o2}-WW 5.7	CP_{o2}-WW -21.84

Table S.8: Relative energies (Δ(E+ZPE), in kcal mol^{-1}) of the stationary points for the reaction OH + C_3H_7OH-1 under dry conditions.

Reactants	CR_j	TS_j	CP_j
OH + C_3H_7OH-1 (0.0)	$CR_{\alpha,\beta,\gamma,o}$ -5.46	$TS_{\alpha1}$ -1.43	$CP_{\alpha1}$ -23.88
		$TS_{\alpha2}$ -1.68	$CP_{\alpha2}$ -24.10
		$TS_{\beta1}$ 0.52	$CP_{\beta1}$ -19.04
		$TS_{\beta2}$ 1.06	$CP_{\beta2}$ -21.72
		$TS_{\gamma1}$ -0.22	$CP_{\gamma1}$ -20.35
		TS_{o1} 2.95	CP_{o1} -16.89
		$TS_{\beta3}$ -1.44	$CP_{\beta3}$ -20.02
		$TS_{\beta4}$ 2.66	$CP_{\beta4}$ -16.70
		TS_{o2} 2.55	CP_{o2} -16.34

Table S.9: Relative energies (Δ(E+ZPE), in kcal mol^{-1}) of the stationary points for the reaction OH + C_3H_7OH-1including one water molecule.

Reactants	CR_j-W	TS_j-W	CP_j-W
$OH(H_2O)$ + C_3H_7OH-1 (0.0)	$CR_{\alpha1}$-W -3.16	$TS_{\alpha1}$-W -3.07	$CP_{\alpha1}$-W -25.77
	$CR_{\beta1}$-W -1.60	$TS_{\beta1}$-W 0.14	$CP_{\beta1}$-W -19.35
	$CR_{\beta2}$-W -10.8	$TS_{\beta2}$-W -1.04	$CP_{\beta2}$-W -21.21
	$CR_{\beta3}$-W -12.18	$TS_{\beta3}$-W -2.07	$CP_{\beta3}$-W -25.96
	CR_{o1}-W -8.48	TS_{o1}-W 0.73	CP_{o1}-W -19.54

Table S.10: Relative energies (Δ(E+ZPE), in kcal mol^{-1}) of the stationary points for the reaction OH + C_3H_7OH-1 including two water molecules as catalyst.

Reactants	CR_j-WW	TS_j-WW	CP_j-WW
$OH(H_2O)$ + $[C_3H_7OH(H_2O)]_1$ (0.0)	$CR_{\alpha1}$-WW -14.12	$TS_{\alpha1}$-WW -9.89	$CP_{\alpha1}$-WW -34.30
	$CR_{\alpha2}$-WW -14.12	$TS_{\alpha2}$-WW -11.41	$CP_{\alpha2}$-WW -35.18
	$CR_{\alpha3}$-WW -14.10	$TS_{\alpha3}$-WW -9.78	$CP_{\alpha3}$-WW -34.00
	$CR_{\alpha4}$-WW -10.69	$TS_{\alpha4}$-WW -6.63	$CP_{\alpha4}$-WW -35.60
	CR_{o1}-WW -17.27	TS_{o1}-WW -4.42	CP_{o1}-WW -22.86

Bibliography

1 T. J. Dillon, D. Hölscher, V. Sivakumaran, a Horowitz and J. N. Crowley, *Phys. Chem. Chem. Phys.*, 2005, **7**, 349–55.

2 B. Rajakumar, D. C. McCabe, R. K. Talukdar and A. R. Ravishankara, *Int. J. Chem. Kinet.*, 2010, **42**, 10–24.

3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. M. Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian09 (Revision D.01),Gaussian Inc. Wallingford, CT. 2009.

4 M. A. Allodi, M. E. Dunn, J. Livada, K. N. Kirschner and G. C. Shields, *J. Phys. Chem. A*, 2006, **110**, 13283–13289.

5 F. J. Hernandez, J. T. Brice, C. M. Leavitt, T. Liang, P. L. Raston, G. A. Pino and G. E. Douberly, *J. Chem. Phys.*, 2015, **143**, 164304.