

Supplementary material

CLEPS: A NEW PROTOCOL FOR CLOUD AQUEOUS PHASE OXIDATION OF VOC MECHANISMS

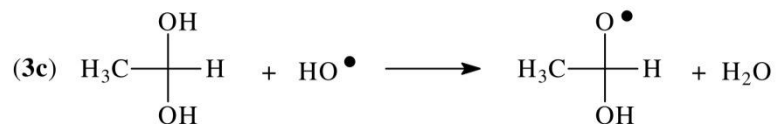
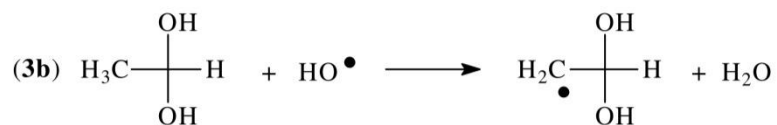
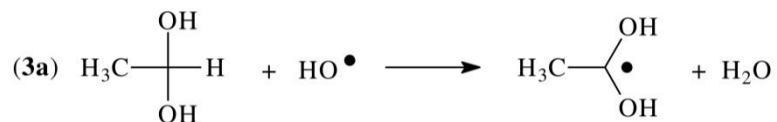
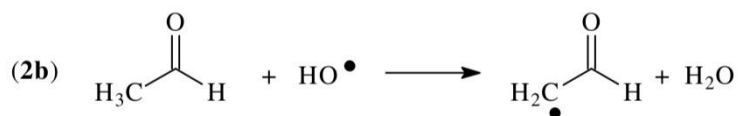
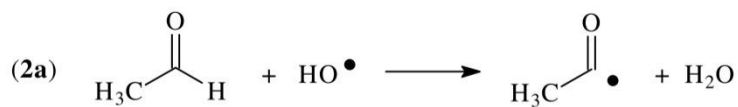
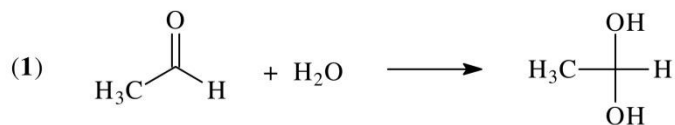
SM1: Computational method

All geometries [1] have been optimized and characterized by vibrational analysis at the DFT level [2] with the M06-2X[3] functional and the 6-311+G(d,p) basis set. [4] Then energies have been recalculated by single-point calculation with the 6-311++G(3df,2pd) [4,5] basis set. Finally, these values are combined with the enthalpy and entropy contributions calculated at room temperature with the 6-311+G(d,p) basis set to get the final reaction energies and free energies. The latter have been converted from the gas phase to the 1M standard state at 1 atm and 298.15 K.[6] Solvent effects were introduced both in geometry optimization -and single point calculation- by the Polarized Continuum Method (PCM) [7] within the universal Solvation Model Density (SMD). [8] All calculations have been performed by program Gaussian 09. [9]

- [1] Reaction enthalpies and free energies were computed as outlined, for instance, in: (a) J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Inc., Pittsburgh, PA (USA), 1996, p. 166-168. (b) D. A. McQuarrie, *Statistical Thermodynamics*, Harper and Row, New York, 1973.
- [2] Jensen W. *Introduction to Computational Chemistry*, Wiley; Chichester, 1999, Chap. 6 ISBN 0-471-98425-6.
- [3] Y. Zhao, DG. Truhlar, *Theor. Chem. Account* 2008; 120: 215. (b) Y. Zhao, DG. Truhlar, *Acc. Chem. Res.* 2008; 41: 157.
- [4] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* 1980, 72, 5639; (b) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comp. Chem.* 1983, 4, 294.
- [5] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* 1984, 80, 3265.
- [6] R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* 2011, 115, 14556.
- [7] (a) V. Barone, M. Cossi, *J. Phys. Chem. A* 1998, 102, 1995; (b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Chem. Phys.* 2001, 114, 5691; (c) M. T. Cancas, B. Mennucci, J. Tomasi, *J. Chem. Phys.* 1997, 107, 3032; (d) M. Cossi, V. Barone, B. Mennucci, J. Tomasi; *Chem. Phys. Lett.* 1998, 286, 253; (e) B. Mennucci, J. Tomasi, *J. Chem. Phys.* 1997, 106, 5151.
- [8] (a) A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* 2009, 113, 6378. (b) A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* 2009, 113, 4538.
- [9] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian, Inc., Wallingford CT, 2009.

SM2: Calculated Reaction Enthalpies & Free Energies (298 K, 1 atm)

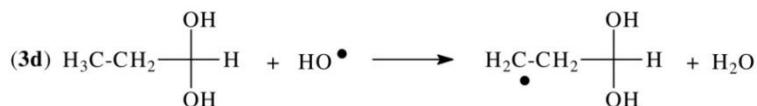
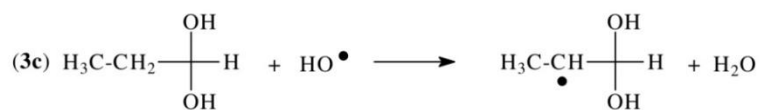
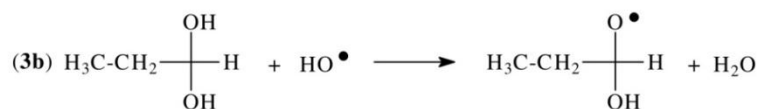
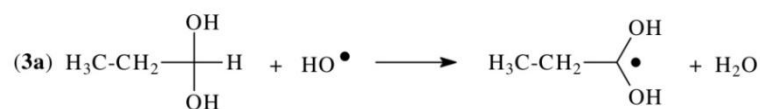
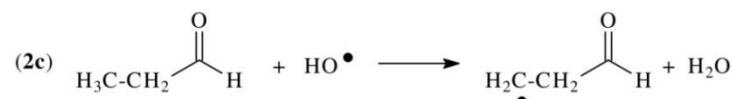
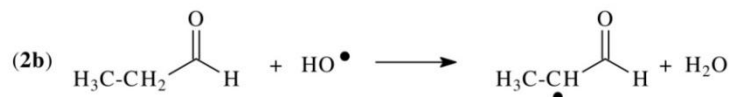
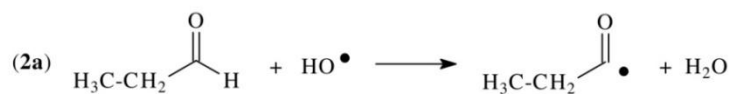
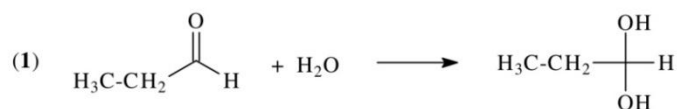
Acetaldehyde



	ΔH	ΔG
1 Idration	-7.0	2.99
2a RHT from CHO	-28.1	-28.7
2b RHT from CH₃	-25.5	-25.5
3a RHT from CH	-24.5	-26.0
3b RHT from CH₃	-16.5	-17.9
3c RHT from OH	-13.7	-14.7

For hydration (reaction 1), the calculated K_h is 0.36. The “preferred value”^a is 1.2. The estimated error in the calculated ΔG is +0.7 Kcal mol⁻¹.

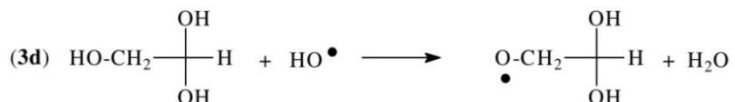
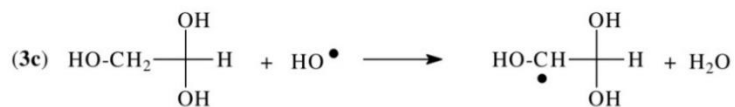
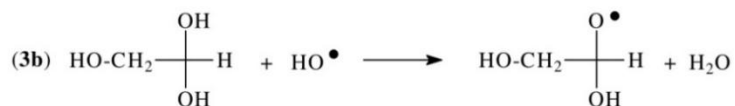
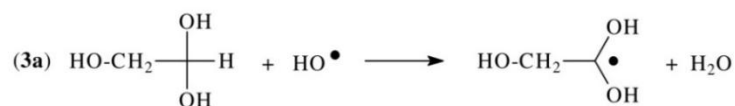
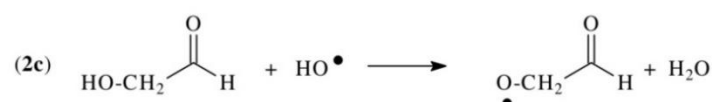
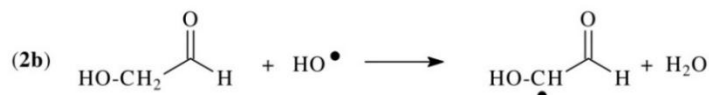
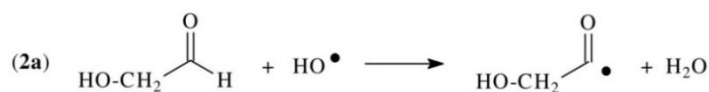
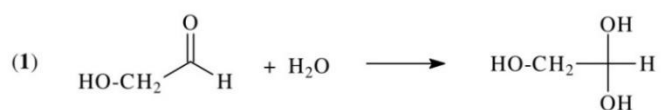
Propionaldehyde



	ΔH	ΔG
1 Hydration^a	-7.6	2.1
2a RHT from CHO	-28.8	-30.0
2b RHT from CH₂	-33.1	-33.8
2c RHT from CH₃	-18.8	-20.1
3a RHT from CH	-25.1	-27.0
3b RHT from OH	-14.2	-15.1
3c RHT from CH₂	-20.7	-23.0
3d RHT from CH₃	-19.2	-20.9

^a For hydration (reaction 1), the calculated K_h is 1.8. The “preferred value”¹ is 0.9. The estimated error in the calculated ΔG is -0.5 Kcal mol⁻¹.

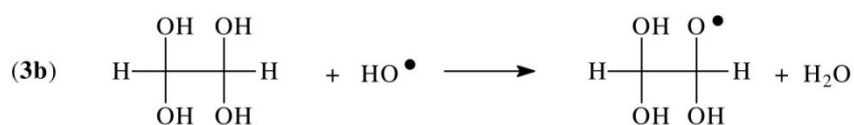
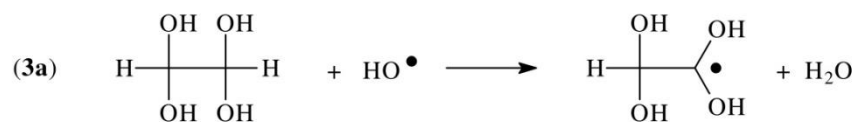
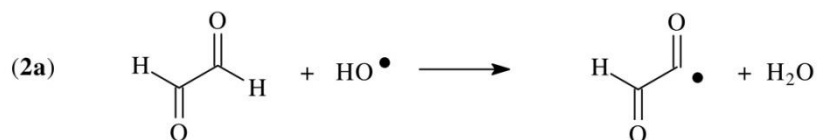
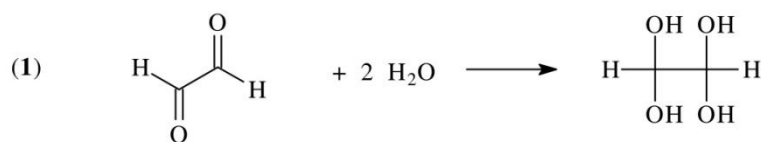
Glyceraldehyde



	ΔH	ΔG
1 Hydration^a	-8.9	0.6
2a RHT from CHO	-28.5	-29.2
2b RHT from CH₂	-41.6	-41.6
2c RHT from <i>w</i>-OH	-13.7	-14.2
3a RHT from CH	-25.5	-26.5
3b RHT from OH	-15.4	-16.1
3c RHT from CH₂	-25.3	-26.2
3d RHT from <i>w</i>-OH	-14.9	-15.5

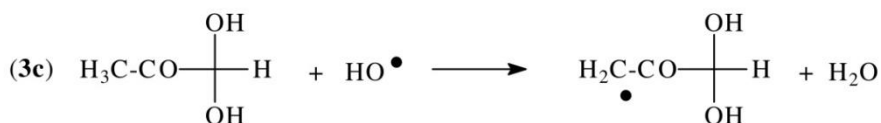
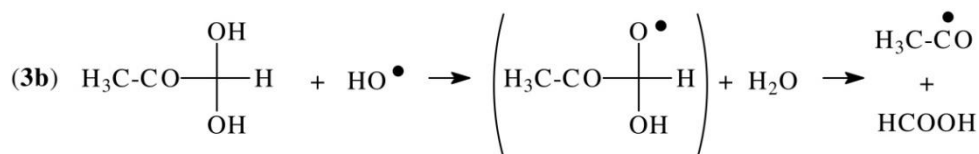
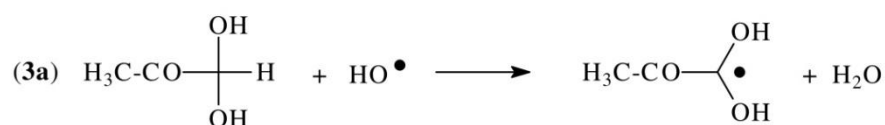
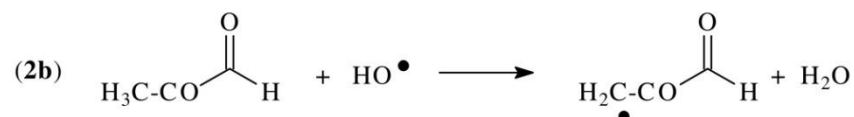
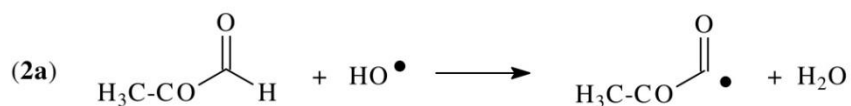
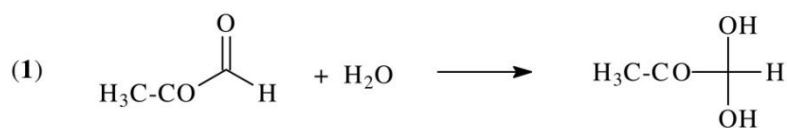
^a For hydration (reaction 1), the calculated K_h is 20. The “preferred value”¹ is 16. The estimated error in the calculated ΔG is -0.1 Kcal mol⁻¹.

Glyoxal



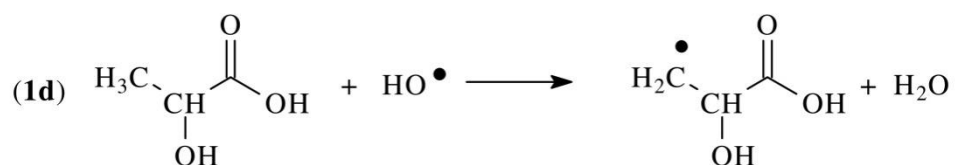
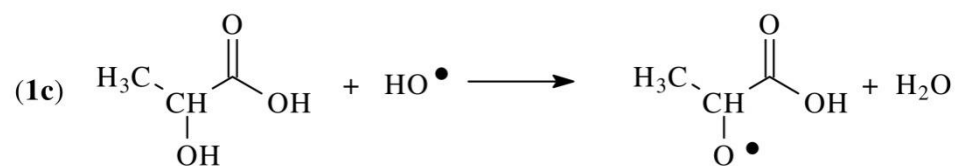
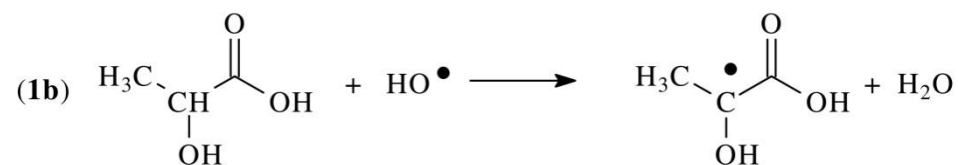
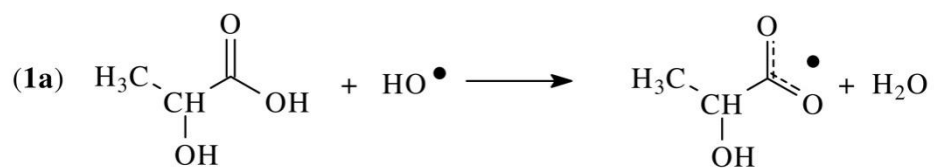
	ΔH	ΔG
1 Hydration^a	-22.8	-5.0
2a RHT from CHO	-26.6	-27.3
3a RHT from CH	-25.2	-26.5
3b RHT from OH	-13.5	-15.1

^a For hydration (reaction 1), the calculated K_h is $2 \cdot 10^5$. The “preferred value”¹ is $4 \cdot 10^6$. The estimated error in the calculated ΔG is $+1.6 \text{ Kcal mol}^{-1}$.

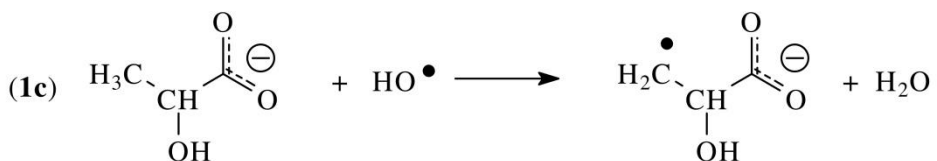
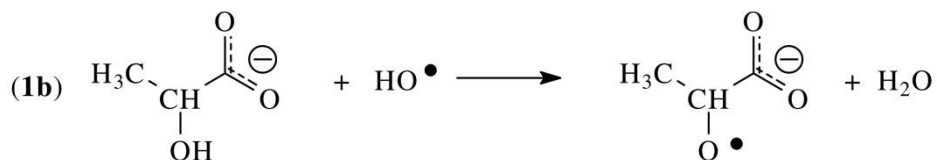
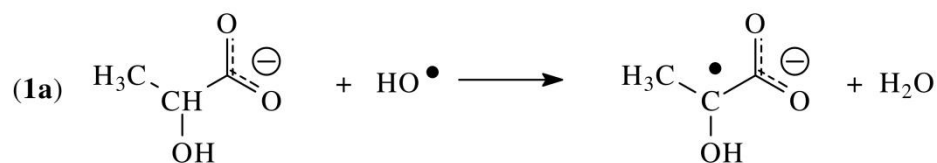


	ΔH	ΔG
1 Hydration^a	-10.2	-1.1
2a RHT from CHO	-32.6	-33.4
2b RHT from CH₃	-25.9	-26.1
3a RHT from CH	-47.3	-47.2
3b RHT from OH^b	-27.2	-31.3
3c RHT from CH₃	-25.2	-25.9

^a For hydration (reaction 1), the calculated K_h is 4×10^2 . The “preferred value” ¹ is 2×10^3 . The estimated error in the calculated ΔG is $+1.0 \text{ Kcal mol}^{-1}$. ^b Radical $\text{CH}_3\text{-CO-CH(OH)O}^\bullet$ is not stable and spontaneously breaks in formic acid and acetyl radical. Data are referred to the complex between these two species.



	ΔH	ΔG
1a RHT from COOH	-24.3	-28.8
1b RHT from CH	-39.5	-40.5
1c RHT from OH	-11.9	-12.9

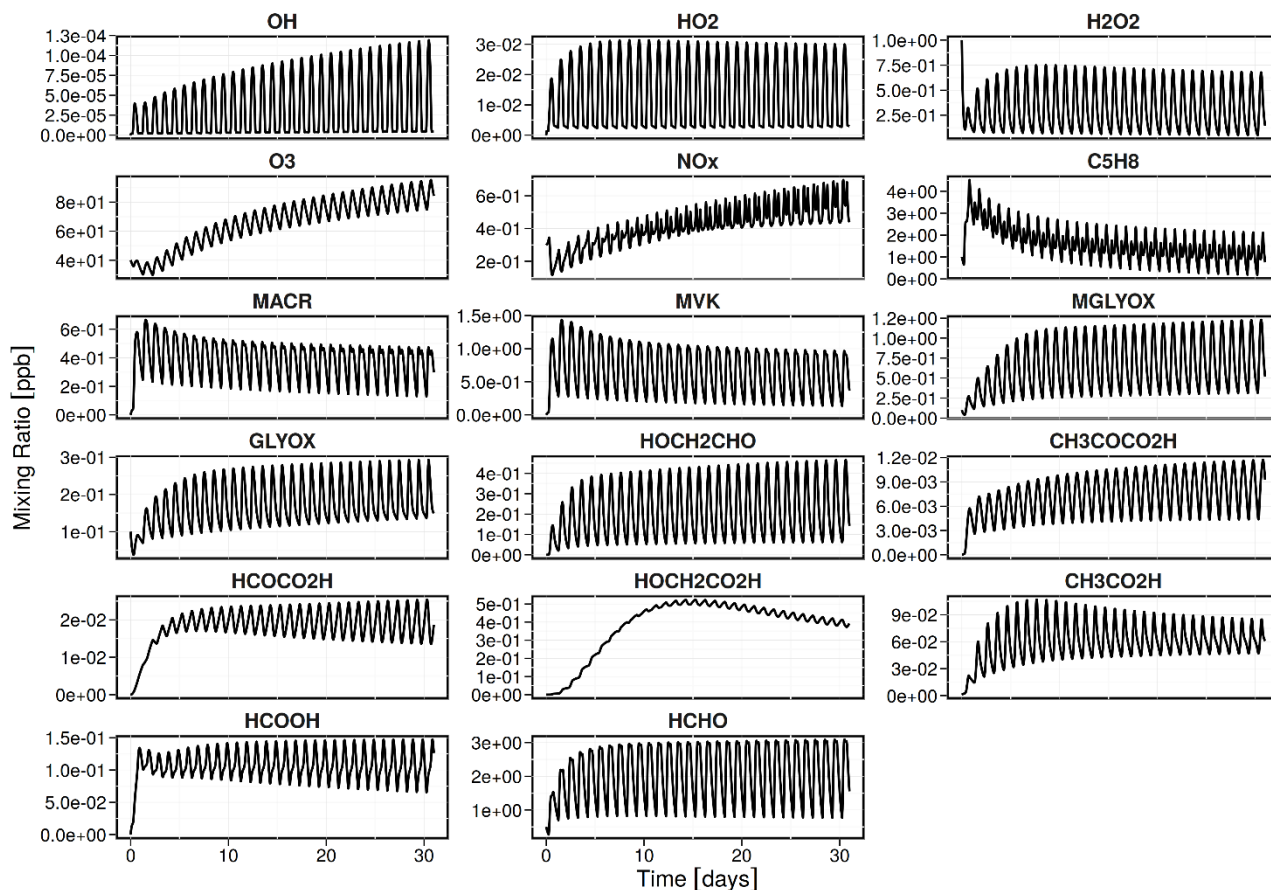


	ΔH	ΔG
1a RHT from CH	-35.3	-36.5
1b RHT from OH	-17.4	-19.0
1c RHT from CH₃	-18.5	-20.2

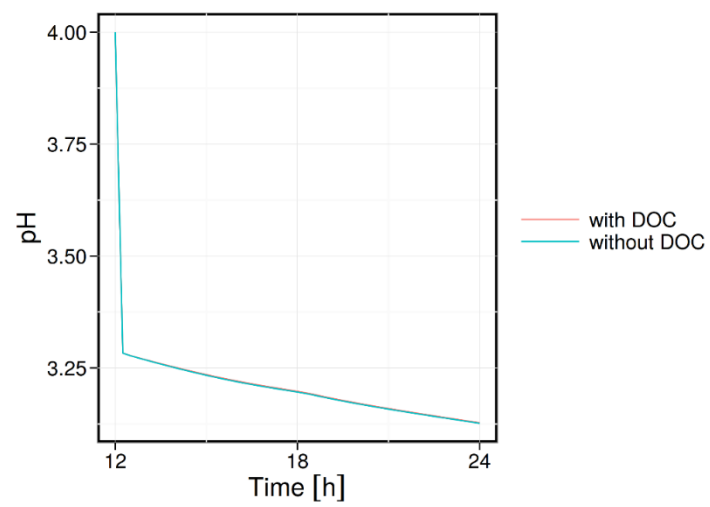
^a Doussin, J.-F. and Monod, A.: Structure–activity relationship for the estimation of OH-oxidation rate constants of carbonyl compounds in the aqueous phase, *Atmos. Chem. Phys.*, 13, 11625-11641, doi:10.5194/acp-13-11625-2013, 2013.

SM3: Gas chemistry simulation (31 days)

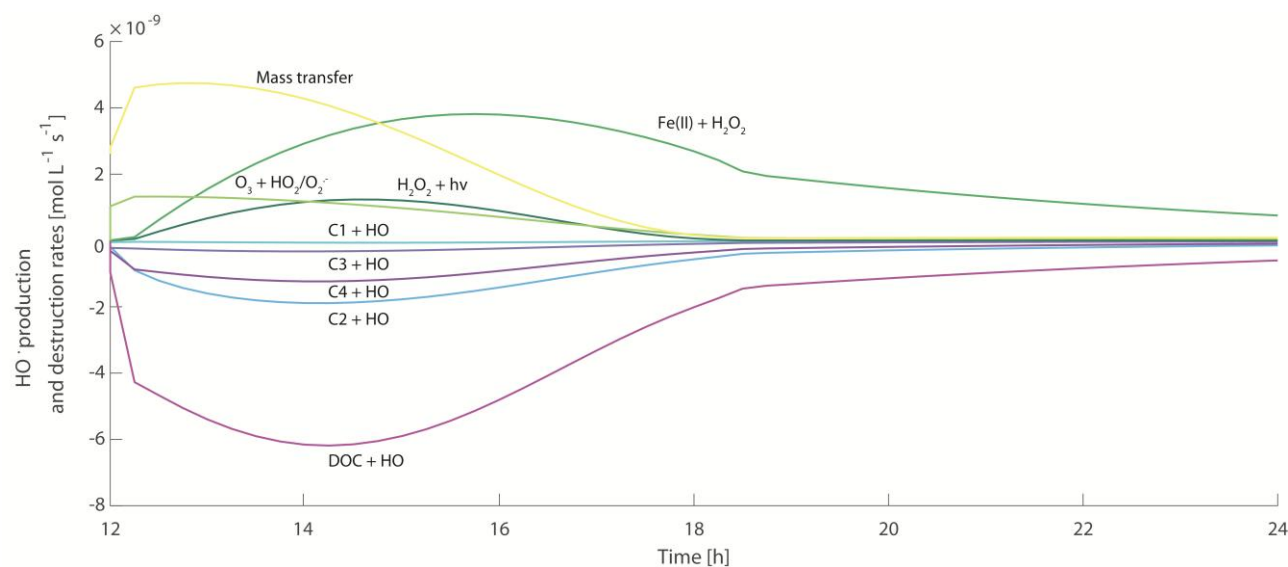
The model was run with initial and environmental conditions adapted from the low- NO_x situation described by McNeill et al. (2012). Information about emissions, deposition and initial concentrations of chemical species are provided in Table 4. Temperature is constant (290K) during the simulations. Under these chemical conditions, a gas chemistry simulation has been run for 31 days starting 21st June 2000. The figure below shows the time evolution of targeted gas species in MCM V3.3.1.



SM4: pH time evolution



SM5: Time evolution of sources and sinks of HO[•] radicals over the cloud period



Average relative contributions of the main production and destruction pathways of HO[•] over the cloud period

	Relative contributions (%)
Destruction pathways	
C ₁ + HO [•]	1%
C ₂ + HO [•]	18%
C ₃ + HO [•]	4%
C ₄ + HO [•]	12%
DOC + HO [•]	64%
Production pathways	
H ₂ O ₂ + Fe(II) (Fenton)	63%
Mass transfer	22%
O ₃ + HO ₂ /O ₂ ^{•-} / H ₂ O ₂ + hv	13%

SM6: List of 267 dissolved MCM species without a reactive equivalent in CLEPS

CH ₃ COCH(OOH)CH ₂ (OOH)	CH ₃ COCO(OONO ₂)
CH ₂ (OH)CH(ONO ₂)C(ONO ₂)(CH ₂ (OH))CHO	CH ₃ C(CH ₂ (OH))=CHCO(OOH)
CH ₃ CH(OOH)CH ₂ (OH)	CH ₃ C(OOH)(CH ₂ (OOH))CHO
CH ₂ (ONO ₂)CH(OH)C(ONO ₂)(CH ₃)CO(OOH)	CH ₃ COCH ₂ (ONO ₂)
CH ₃ C(OH)(CO(OONO ₂))CHO	CH ₃ CH(OH)CO(OONO ₂)
CH ₂ (OH)CH ₂ CO(OONO ₂)	CH ₃ C(CH ₂ (ONO ₂))=CHCH ₂ (OOH)
CH ₃ CH(ONO ₂)CH ₃	CH ₂ (OH)COCH(OH)CH ₂ (OOH)
CH ₃ C(OOH)(CH ₂ (OH))CH ₂ CHO	CH ₃ C(OOH)(CO(OH))CH(OH)CH ₂ (ONO ₂)
CH ₃ C(ONO ₂)(CH ₂ (OH))CH=CH ₂	CH ₂ (OH)CH(OH)C(ONO ₂)(CH ₃)CO(OONO ₂)
CH ₃ C(ONO ₂)(CO(OH))CH(OH)CHO	CO(OOH)CH ₂ C(CH ₃)=CH ₂
CH ₃ C(OH)(CH ₂ (ONO ₂))COCHO	CH ₂ (OOH)CH(OH)CHO
CH ₂ (OH)CH(ONO ₂)C(OOH)(CH ₃)CO(OONO ₂)	CO(OONO ₂)CH=C(CH ₃)CHO
CH ₂ (OH)CH(OH)C(CH ₂ (OH))=CH ₂	CO(OOH)CH=CH ₂
CH ₃ C(ONO ₂)(CH ₂ (OH))CH(OH)CO(OH)	CH ₃ C(ONO ₂)(CH ₂ (OH))CH(OOH)CO(OOH)
CH ₃ C(OOH)(CH ₂ (OH))CH=CH ₂	CH ₃ C(CH ₂ (OH))=CHCO(OH)
CO(OOH)CHO	CH ₃ C(ONO ₂)(CH ₂ (OH))CH(ONO ₂)CHO
CO(OH)CH=CH ₂	CH ₃ C(CH ₂ (OH))=CHCO(OONO ₂)
CH ₃ C(ONO ₂)(CO(OOH))CH(OH)CHO	CH ₃ COCH(ONO ₂)CO(OOH)
CH ₃ C(ONO ₂)(CH ₂ (OH))CH(OOH)CH ₂ (OH)	CH ₂ (OH)COC(OOH)(CH ₃)CHO
CH ₃ CH(ONO ₂)CO(OOH)	CH ₃ C(ONO ₂)(CH ₂ (OH))CH(OOH)CO(OONO ₂)
CH ₃ CH ₃	CH ₃ C(OH)(CHO)CH(OH)CHO
CH ₃ COCOCH ₂ (OOH)	CH ₂ (OH)CH(ONO ₂)C(CH ₃)=CH ₂
CH ₃ C(ONO ₂)(CH ₂ (OH))CH(ONO ₂)CO(OONO ₂)	CH ₂ (OH)CH ₂ (OOH)
CO(OH)CH=C(CH ₃)CH ₂ (ONO ₂)	CH ₃ C(CH ₂ (ONO ₂))=CHCH ₂ (ONO ₂)
CH ₃ C(ONO ₂)(CH ₂ (OH))CHO	CH ₂ (OH)CH(OOH)C(CH ₃)=CH ₂
CH ₂ (OH)C(OH)(CH ₂ (OH))CHO	CH ₂ (ONO ₂)CH(OH)C(OOH)(CH ₃)CHO
CH ₃ C(OOH)(CH ₂ (OH))CH(OH)CHO	CH ₃ C(ONO ₂)(CH ₂ (OH))CH(OH)CH ₂ (OH)
CH ₃ C(CH ₂ (OOH))=CHCHO	CH ₃ C(ONO ₂)(CH ₂ (OH))CO(OH)
CH ₂ (OH)CH=CH ₂	CH ₃ COCH(ONO ₂)CO(OONO ₂)
CH ₂ (OH)C(OOH)(CH ₂ (OH))CHO	CH ₃ CH ₂ CH ₃
CH ₂ (OH)COC(OOH)(CH ₂ (OH))CH ₂ (OH)	CH ₂ (OH)CH(OOH)C(OH)(CH ₃)CH ₂ (ONO ₂)
CO(OONO ₂)CH(OH)CHO	CH ₂ (ONO ₂)COC(ONO ₂)(CH ₃)CO(OONO ₂)
CH ₃ C(ONO ₂)(CH ₂ (OH))CH(OH)CHO	CH ₂ (OH)CH=C(CH ₃)CH ₂ (OOH)
CH ₂ (OH)CH ₂ CH ₂ (OOH)	CH ₃ C(OOH)(CH ₂ (OOH))CH(OH)CO(OOH)
CH ₂ (OH)CH(OOH)CHO	CH ₂ =CHC(CH ₃)=CH ₂
CH ₂ (OOH)CH=CH ₂	CH ₃ C(OH)(CO(OH))CH ₂ (ONO ₂)
CH ₂ (ONO ₂)COCHO	CH ₂ (OH)COCH(OH)CO(OONO ₂)
CH ₃ C(OH)(CH ₂ (ONO ₂))CH(ONO ₂)CHO	CH ₂ (OH)COC(CH ₃)=CH ₂
CH ₂ (ONO ₂)CO(OOH)	CH ₃ C(CO(OONO ₂))=CHCHO
CH ₃ CH=CH ₂	CH ₂ (OH)CH(OOH)C(OOH)(CH ₃)CHO
CH ₃ COCH ₂ CH(OH)CH ₂ (OH)	CH ₃ C(OH)(CH ₂ (OH))CHO
CH ₂ (ONO ₂)CH(OH)C(OOH)(CH ₃)CO(OONO ₂)	CH ₃ C(OH)(CO(OH))CH ₂ (ONO ₂)
CH ₃ CH(OH)CH ₂ (ONO ₂)	CH ₂ (OH)CH(OH)CO(OONO ₂)
CH ₃ CH(OOH)CH ₂ (ONO ₂)	CH ₃ COCH ₂ CH=CH ₂
CH ₂ (OH)CH(OH)C(ONO ₂)(CH ₃)CHO	CH ₂ (ONO ₂)CH(OH)CHO
CH ₃ C(CH ₂ (OH))=CHCHO	CH ₃ COCOCH ₂ (ONO ₂)
CH ₃ COCH ₂ CH(ONO ₂)CH ₂ (OH)	CH ₃ C(ONO ₂)(CHO)CHO
CH ₃ C(OH)(CH ₂ (OH))CH=CH ₂	CH ₃ C(OH)(CH ₂ (ONO ₂))CHO
CH ₃ C(ONO ₂)(CO(OH))CHO	CH ₃ C(ONO ₂)(CO(OH))CH(OH)CH ₂ (ONO ₂)

CH3C(CH2(ONO2))=CHCO(OOH)
CH3CH(ONO2)CO(OONO2)
CH3C(OH)(CH2(OH))CH(OH)CH2(ONO2)
CH3COCO(OOH)
CH2(OH)COC(OH)(CH3)CH2(ONO2)
CH3C(ONO2)(CH2(OH))CO(OOH)
CH2(ONO2)CH(OH)C(ONO2)(CH3)CHO
CO(OOH)CH(OH)C(CH3)=CH2
CH3CO(OONO2)
CH3C(OH)(CH3)CO(OOH)
CH2(OH)CH(OH)CH2(OOH)
CO(OOH)CH(OH)C(ONO2)(CH3)CHO
CH2(ONO2)CH2(OOH)
CH2(OH)CH(OOH)C(CH2(OH))=CH2
CH3C(OH)(CHO)CHO
CH3COCH2COCHO
CH3C(CO(OOH))=CHCHO
CH3C(ONO2)(CO(OOH))CHO
CO(OONO2)CH=CH2
CH2(OOH)CH(OH)C(CH3)=CH2
CH3C(ONO2)(CO(OH))COCH2(ONO2)
CH3C(OH)(CO(OOH))CHO
CH2(OH)CH(ONO2)C(ONO2)(CH3)CO(OH)
CH3C(ONO2)(CH2(OH))CH(ONO2)CH2(OH)
CH2(OH)CH2CO(OOH)
CH2(OH)CH(OH)C(CH3)=CH2
CH2(OH)COC(CH2(OH))=CH2
CH3C(ONO2)(CH2(OH))CH(OH)CO(OOH)
CH2(OH)CH(ONO2)C(ONO2)(CH3)CO(OOH)
CH2(OH)C(CO(OH))=CH2
CH3C(OH)(CH3)CO(OONO2)
CO(OONO2)CH(OH)C(ONO2)(CH3)CHO
CH2(OH)CH(ONO2)C(ONO2)(CH3)CO(OONO2)
CH3C(OH)(CH2(ONO2))CH(ONO2)CO(OONO2)
CH3COCH2(OOH)
CH3C(OOH)(CH2(OH))COCH2(OH)
CO(OH)CH(OH)C(ONO2)(CH3)CHO
CH2(OH)COCH(OH)CO(OOH)
CO(OOH)CH(OH)C(OOH)(CH3)CHO
CH3C(OOH)(CHO)CHO
CH3C(ONO2)(CH2(OH))CH(ONO2)CO(OH)
CH3COCH2CO(OH)
CH3C(OH)(CH2(OH))CH(ONO2)CH2(OH)
CH2(OH)CH(ONO2)C(OH)(CH3)CHO
CH3COCH(OH)CH2(OOH)
CH3COCH(OH)CH2(ONO2)
CH2(OH)CH(OH)C(OH)(CH3)CHO
CH3C(OH)(CH3)CHO
CH3C(ONO2)(CH2(OH))CH(ONO2)CO(OOH)
CH2(OH)C(CO(OOH))=CH2
CO(OOH)CH=C(CH3)CHO
CH3COCH(OOH)CH2(OH)

CH₂(OH)CH(OH)C(ONO₂)(CH₃)CO(OH)
CH₂(OH)CH(OH)C(OH)(CH₃)CH₂(ONO₂)
CH₃C(CH₂(OH))=CHCH₂(OH)
CH₂(OH)C(OH)(CH₂(OH))CH(OOH)CHO
CHOCH(OH)C(CH₃)=CH₂
CH₂(OH)CH(OH)C(OOH)(CH₃)CHO
CH₃C(CH₂(ONO₂))=CHCO(OONO₂)
CH₂(OH)CH(OH)C(OOH)(CH₂(OH))CHO
CH₂(OH)CH(ONO₂)C(OH)(CH₂(OH))CHO
CH₂=CH₂
CH₂(ONO₂)CHO
CH₂(ONO₂)CH(OH)C(OH)(CH₃)CO(OONO₂)
CH₃COCH(OH)CO(OOH)
CH₂(OH)CH(OOH)C(OH)(CH₃)CHO
CH₂(ONO₂)CH(OH)C(OH)(CH₃)CO(OOH)
CH₂(OH)CH(ONO₂)C(OOH)(CH₂(OH))CHO
CH₃C(OOH)(CH₂(OOH))CH(OOH)CHO
CH₃C(CHO)=CHCHO
CH₂(OH)CH=C(CH₃)CO(OH)
CH₃CH(OH)CO(OOH)
CH₃C(OH)(CH₂(OH))CH(OOH)CHO
CH₂(OH)CH(ONO₂)C(OOH)(CH₂(OH))CH₂(OH)
CH₂(OH)CH(ONO₂)C(CH₂(OH))=CH₂
CH₃CH(OH)CH₂(OOH)
CH₃COCH(ONO₂)CHO
CH₃CH₂CO(OONO₂)
CH₂(OH)CH₂CH₂(ONO₂)
CH₂(ONO₂)CH(OH)C(OH)(CH₃)CHO
CH₃C(OH)(CH₃)CO(OH)
CH₂(OH)CH(ONO₂)C(OH)(CH₂(OH))CH₂(OH)
CH₂(OH)CH(ONO₂)C(OOH)(CH₃)CHO
CH₃C(CH₂(OOH))=CH₂
CH₃C(OOH)(CO(OOH))CH(OH)CHO

CH₂(OH)CH(OH)C(ONO₂)(CH₃)CO(OOH)
CH₂(OH)CH=C(CH₃)CH₂(ONO₂)
CH₃C(CH₂(OH))=CHCH₂(ONO₂)
CH₃C(CH₂(ONO₂))=CHCHO
CH₂(OOH)COCH=CH₂
CH₂(OH)CH=C(CH₃)CHO
CH₂(OH)CH(ONO₂)C(OOH)(CH₃)CO(OOH)
CH₂(OH)CH(ONO₂)C(ONO₂)(CH₂(OH))CH₂(OH)
CH₃C(ONO₂)(CO(OONO₂))CH(OH)CHO
CH₂(OH)COCH(OH)CH₂(ONO₂)
CH₃C(ONO₂)(CHO)CH(OH)CHO
CH₃C(ONO₂)(CH₂(OH))CH(OH)CH₂(OOH)
CH₃C(CO(OONO₂))=CH₂
CH₂(OH)CH(OH)CO(OOH)
CH₃CH₂CH₂(OOH)
CH₃CH₂CH₂(ONO₂)
CH₃C(ONO₂)(CH₂(OH))CH(OOH)CHO
CH₃COCH₂CO(OOH)
CO(OH)CH(ONO₂)C(OH)(CH₃)CH₂(ONO₂)
CH₃C(ONO₂)(CH₂(OH))COCH₂(OH)
CHOCOCH=CH₂
CHOCH₂C(CH₃)=CH₂
CH₃C(OH)(CH₂(ONO₂))CH(ONO₂)CO(OOH)
CH₃CH(ONO₂)CH₂(OOH)
CH₃COCH(OOH)CHO
CH₃C(OH)(CH₂(ONO₂))CO(OONO₂)
CH₂(OH)CH=C(CH₃)CO(OOH)
CH₂(OH)CH(ONO₂)COCHO
CH₃C(OOH)(CHO)CH(OH)CHO
CH₂(ONO₂)CH(OH)C(ONO₂)(CH₃)CO(OONO₂)
CH₃C(ONO₂)(CO(OONO₂))CHO
CH₂(OOH)CH(OOH)C(OOH)(CH₃)CHO

SM7: Time evolution of the sum of organic acids in the gas and the aqueous phase during the cloud event

