

## Computational investigation of the OH initiated oxidation of C6 unsaturated alcohols

Natália Aparecida Rocha Pinto (GR), Stella Maris Resende (PQ)

*Laboratório de Química Atmosférica Teórica (LAQAT)*

*Departamento de Ciências Naturais, Universidade Federal de São João del-Rei (UFSJ)  
São João del-Rei, Minas Gerais, Brazil.*

**Abstract:** An important class of compounds emitted into our atmosphere is the volatile organic compounds (VOCs).[1] The presence of these compounds in the atmosphere has important environmental consequences because their oxidation leads to the formation of organic aerosols, which are involved in the regulation of the planet climate and the physical and chemical properties of the atmosphere.[2] Among oxygenated VOCs, an important group are C6 alcohols, which are emitted when plants are stressed or drying grass.[3] In this work, we investigated the first step of the atmospheric oxidation, initiated by OH radical, of (Z)-hex-3-en-1-ol, (E)-hex-3-en-1-ol, (Z)-hex-4-en-1-ol and (E)-hex-4-en-1-ol alcohols, whose structural aspects have already been determined by us and for which the atmospheric decomposition process has not yet been determined theoretically. Geometry optimizations and harmonic frequencies calculations were conducted at the MP2/cc-pVTZ level of theory. We have considered two possibilities for the first step of the reaction: hydrogen abstraction or OH addition, generating four possible products for each isomer. The values obtained for reaction enthalpy and Gibbs free energy are in Table 1 and in Table 2.

**Table 1.** Reaction enthalpy ( $\Delta H_r$ ) and Gibbs free energy ( $\Delta G_r$ ) for the reaction of OH with (Z)-hex-4-en-1-ol and (E)-hex-4-en-1-ol alcohols, in  $\text{kJ mol}^{-1}$  (298 K and 1 atm).

Compounds	(Z)-hex-4-en-1-ol		(E)-hex-4-en-1-ol	
	$\Delta H_r$	$\Delta G_r$	$\Delta H_r$	$\Delta G_r$
H abstraction in C4	-110.06	-108.62	-115.93	-112.65
H abstraction in C5	-112.00	-110.39	-117.22	-113.83
OH addition in C4	-167.14	-123.46	-179.34	-129.49
OH addition in C5	-168.14	-124.82	-169.22	-126.38

**Table 2.** Reaction enthalpy ( $\Delta H_r$ ) and Gibbs free energy ( $\Delta G_r$ ) for the reaction of OH with (Z)-hex-3-en-1-ol and (E)-hex-3-en-1-ol alcohols, in  $\text{kJ mol}^{-1}$  (298 K and 1 atm).

Compounds	(Z)-hex-3-en-1-ol		(E)-hex-3-en-1-ol	
	$\Delta H_r$	$\Delta G_r$	$\Delta H_r$	$\Delta G_r$
<b>H abstraction in C3</b>	-95.38	-94.29	-91.67	-89.63
<b>H abstraction in C4</b>	-110.47	-110.28	-89.80	-87.85
<b>OH addition in C3</b>	-158.86	-117.95	-165.28	-113.82
<b>OH addition in C4</b>	-167.31	-128.09	-174.66	-130.20

All values obtained for  $\Delta H_r$  and  $\Delta G_r$  are negative, which shows that all reaction possibilities are exothermic and exoergic. In general, hydrogen abstraction and OH addition in (Z)-hex-4-en-1-ol and (E)-hex-4-en-1-ol compounds are more favorable at C5 than C4; in (Z)-hex-3-en-1-ol and (E)-hex-3-en-1-ol, reaction in C4 is more favorable than in C3; OH addition is preferable to the hydrogen abstraction and the reaction with the (E) isomer leads to more favorable products than the reaction with the (Z) isomer. According our knowledge, this is the first determination of these values for this system. Kinetic studies are in progress.

**Key-words:** *ab initio*, thermochemistry, atmospheric chemistry, volatile organic compounds.

**Support:** This work has been support by CNPq, FAPEMIG e Rede Mineira de Química (RQ-MG).

#### References:

- [1] A. Guenther, C. N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. A. Mckay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, P. J. Zimmerman, Geophys. Res. Atmos. 100, 8873 (1995).
- [2] J. H. Seinfeld, S. N. Pandis, "Atmospheric Chemistry and Physics", 2a ed. (2006), WileyInterscience, New York.
- [3] A. C. Heiden, K. Kobel, C. Langebaterls, G. Schuh-Thomas, J. Whildt, J. Atmos. Chem. 45, 143 (2003).