

Supplementary Material

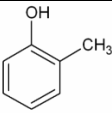
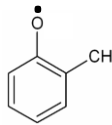
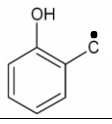
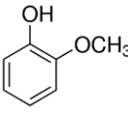
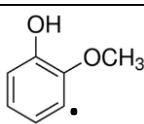
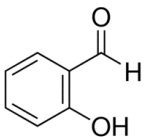
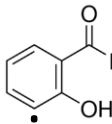
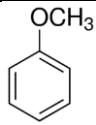
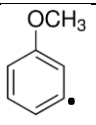
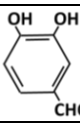
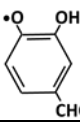
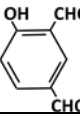
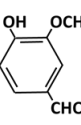
Detailed kinetics of pyrolysis and oxidation of substituted phenolic species.

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Table S1: Nomenclature of primary species of relevance in the pyrolysis and combustion of phenolic species

Formula	Nomenclature	Structure	Name in kinetic model
C ₆ H ₆	Benzene		C ₆ H ₆
C ₆ H ₅	Phenyl radical		C ₆ H ₅
C ₆ H ₄ O ₁	1,2-Epoxybenzene/Phenoxy diradical		C ₆ H ₄ O
C ₆ H ₆ O ₁	Phenol		C ₆ H ₅ OH
C ₆ H ₅ O ₁	Phenoxy radical		C ₆ H ₅ O
C ₆ H ₅ O ₁	Hydroxyphenyl radicals		RPHENPH
C ₇ H ₆ O ₁	Benzaldehyde		C ₆ H ₅ CHO
C ₆ H ₆ O ₂	Catechol		CATECHOL
C ₆ H ₅ O ₂	Catechol phenoxy radical		RCATEC
C ₆ H ₅ O ₂	Catechol phenyl radicals		RCATEPH

C7H8O1	Cresols		CRESOL
C7H7O1	Cresol phenoxy radicals		RCRESOLO
C7H7O1	Hydroxy benzyl radicals		RCRESOLC
C7H8O2	Guaiacol		GUAIACOL
C7H7O2	Guaiacol phenyl radicals		RGUAIPH
C7H6O2	Salicylaldehyde		SALICALD
C7H5O2	Salicylaldehyde phenyl radicals		RSALICPH
C7H8O1	Anisole		C6H5OCH3
C7H7O1	Anisol phenyl radicals		RANISPH
C7H6O3	3,4-dihydroxybenzaldehyde		C7H6O3
C7H5O3	3,4-dihydroxybenzaldehyde phenoxy radicals		RC7H5O3
C8H6O3	4-hydroxy-isophthalaldehyde		C8H6O3
C8H8O3	Vanillin		VANILLIN

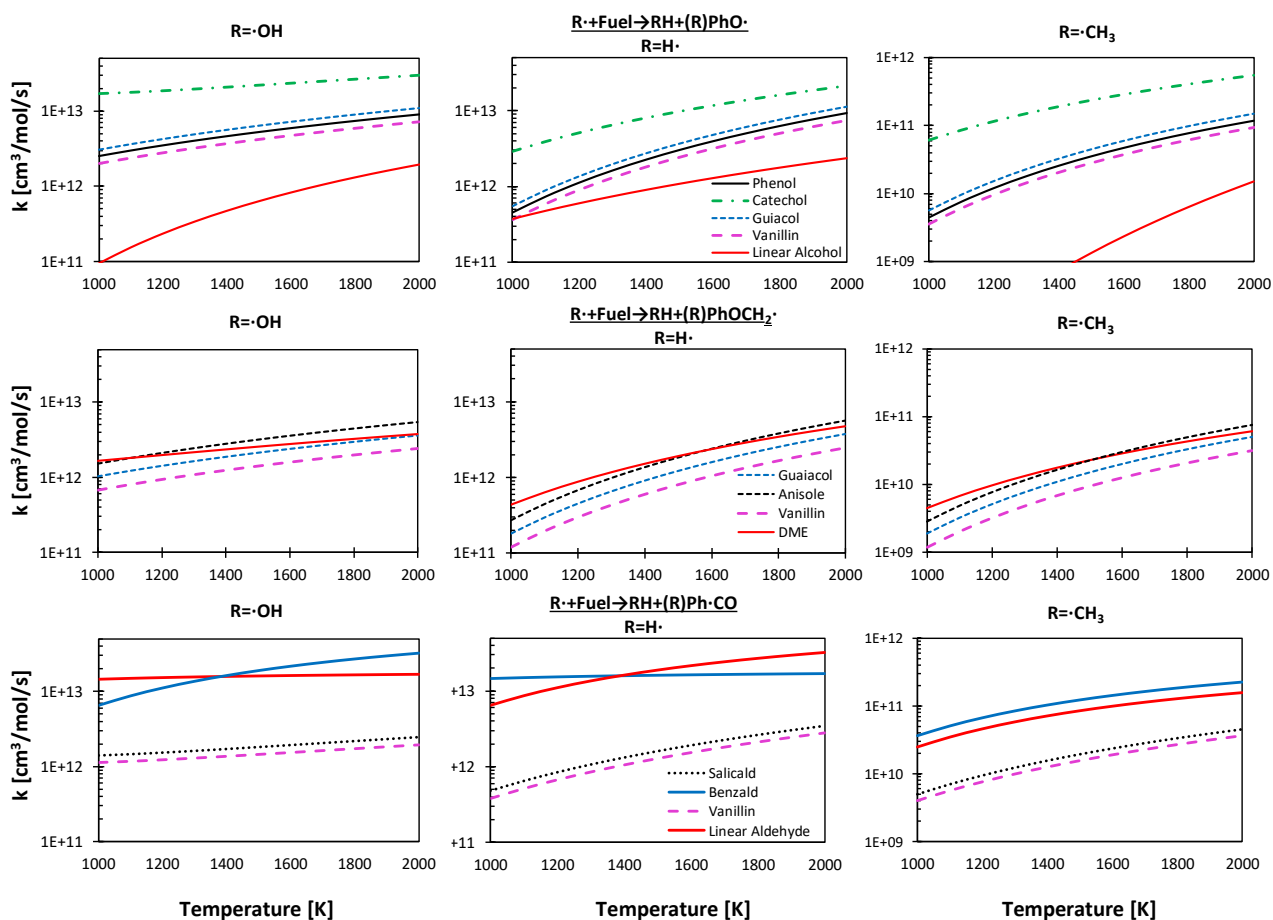


Figure S1: Comparisons between the rate constants of relevant H-abstraction reactions from similar functional groups in phenolic species addressed in this study and rate constants adopted for linear molecules carrying the same functional group. Rate constants are on a per H-atom basis.

Figure S1 reports a comparison between dominant H-abstraction reactions in phenolic species pyrolysis and oxidation. All the reported values are on a per H-atom basis. For completeness, also the rate constants adopted in previous studies for oxygenated compounds carrying the same substitution are reported. Namely, rate constant for H-abstractions from the $-OH$ group in linear alcohols are from Pelucchi et al. [1], rate constants concerning the $-OCH_3$ are from Frassoldati et al. [2] and values for aldehydes oxidation from Pelucchi et al. [3]. Different lines of Figure S1 show the effect of different radicals ($R=H$, OH , CH_3) abstracting a H-atom from a specific oxygenated functional group ($R(Ph)-OH$, $R(Ph)-OCH_2$, $R(Ph)-(C=O)H$). Columns show the effect of different abstraction sites on the rate constants for the same abstracting radical. The differences in bond dissociation energies (BDEs) discussed in the manuscript (Figure 2) are reflected in the relative magnitude of the different H-abstraction channels. In the case of $R(Ph)-OH$, the BDEs of the O-H bond in guaiacol, phenol and vanillin are very similar, thus resulting in quite similar rate constants (within a factor of ~ 1.5 in the temperature range of interest). The strong reduction in the BDE of O-H resulting from the ortho-

substitution of an additional O-H group in catechol justifies the increase of the rate constant of a factor of ~3-5. In linear alcohols molecules the O-H bond has a dissociation energy of about 103 kcal/mol [4], therefore the remarkable difference observed in Figure S1.

Concerning R(Ph)-OCH₃, the slight increase (~1.5 kcal/mol) of the BDE of the C-H bond in the methoxy group when moving from anisole, to guaiacol and vanillin is reflected in the relative values of H-abstraction rate constants. The rate constants for anisole are ~1.4 times higher compared to guaiacol and ~2.0 compared to vanillin. Very similar bond energies have been calculated for the same C-H bond in dimethyl-ether (DME) [5]. This justifies the very similar values between DME and the substituted aromatics with a methoxy functional group.

The C-H bonds in R(Ph)-(C=O)H functional groups increase of ~2.5 kcal/mol and ~5 kcal/mol between benzaldehyde and salicylaldehyde or vanillin, respectively. H-abstraction reactions from benzaldehyde are an order of magnitude, or more, faster compared to vanillin and salicylaldehyde. The same applies to the case of a linear aldehydes (e.g. n-butanal, [3]). Rate constants for the benzaldehyde subset already implemented in the CRECK model served as a basis to derive H-abstractions involving the carbonyl function in salicylaldehyde and vanillin, however minor adjustments were necessary to improve the agreement with the limited number of experimental targets in guaiacol and vanillin pyrolysis (Figure 11 and Figure 15).

References

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- [2] Frassoldati, Alessio, et al. "Kinetic modeling study of ethanol and dimethyl ether addition to premixed low-pressure propene–oxygen–argon flames." *Combustion and Flame* 158.7 (2011): 1264-1276.
- [3] Pelucchi, Matteo, et al. "An experimental and kinetic modelling study of n-C4C6 aldehydes oxidation in a jet-stirred reactor." *Proceedings of the Combustion Institute* (2018). <https://doi.org/10.1016/j.proci.2018.07.087>
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- [5] Burke, Ultan, et al. "An ignition delay and kinetic modeling study of methane, dimethyl ether, and their mixtures at high pressures." *Combustion and flame* 162.2 (2015): 315-330.