

Theoretical and kinetic modelling study of phenol and phenoxy radical decomposition to CO and C₅H₆/C₅H₅ in pyrolysis conditions

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Introduction

Bio-oils from biomass fast-pyrolysis are an economically viable solution to reduce carbon footprint [1]. Lignin-derived bio-oils are a complex mixture of oxygenated species, including phenolic compounds such as phenol, anisole, guaiacol, catechol and vanillin (20-30% in weight) [2]. Hence, an accurate characterization of the pyrolysis and combustion kinetics of phenolic species, starting from phenol, is essential to assess the technical viability of these bio-oils. Furthermore, phenol plays a key role in the mechanism of oxidation of benzene, a building block of PAHs chemistry, precursors of soot and PM [3]. Finally, substituted phenolic species have recently gained attention for their antiknock properties and are being considered as possible octane boosters [4]. Nevertheless, the kinetics of phenol has not been systematically addressed yet, and the available experimental data are limited. Therefore, a theoretical approach for the prediction of accurate kinetics provides a major contribution to improve the current knowledge. This work investigates with *ab initio* methods the two main decomposition pathways of phenol: 1) the molecular pathway forming C₅H₆+CO, and 2) the radical pathway forming C₆H₅O+H. This latter pathway justifies the additional investigation of the decomposition of phenoxy radical (C₆H₅O) to CO and cyclopentadienyl (C₅H₅). For a consistent investigation of phenol kinetics, also the H-abstraction reactions from cyclopentadiene are included. The kinetic constants thus obtained are included in the CRECK kinetic model and validated with experimental data.

Methodology

The *ab initio* investigation of the potential energy surface was performed with EStokTP [5] (available at <https://github.com/PACChem/EStokTP>), an automatic tool to predict temperature and pressure dependent kinetics of reactions, that relies on external codes such as Gaussian and Molpro to perform electronic structure calculations and MESS to perform master equation simulations. The structures and frequencies were determined at the wB97XD/6-311+g(d,p) level, whereas the energies were computed at the CCSD(T)/aug-cc-pvtz level, with basis set corrections computed at MP2/aug-cc-pvtz and MP2/aug-cc-pvqz levels. The kinetic constants as a function of temperature (T=300-2500 K) and pressure were computed solving the master equation with the MESS solver [6]. MESS implements an efficient solution of the multi-well master equation using the Chemical Significant Eigenvalues approach and determining automatically phenomenological rate constants for all the considered reaction channels. The rate constants of the global reactions C₆H₅OH/C₆H₅O → CO+ C₆H₅/C₅H₅ were obtained from the phenomenological rate coefficients using a master equation-based lumping procedure: the time profiles of the species were computed according to the kinetic constants obtained in MESS; then, the overall decomposition constants were derived with a linear fitting on the exponential decay of the reactant. In this procedure, the product was considered as an irreversible sink. The backward kinetic constant was derived in a similar way. The constants thus obtained were fitted according to the usual modified Arrhenius expression. This lumping procedure allows to decrease the number of species necessary to describe phenol

decomposition with respect to what would be necessary using phenomenological rate coefficients. An estimate of the error introduced through this procedure is performed comparing results obtained using phenomenological and lumped rate constants.

The update rate parameters were included in the global POLIMI kinetic mechanism. The kinetic model was then compared with experimental data.

Results

1. Phenol decomposition

The decomposition of phenol and phenoxy radical to CO and a 5 carbon atoms ring proceeds via a similar mechanism. Figure 1 reports the PES determined for phenol. The reaction proceeds via a series of isomerisations to 2,4-Cyclohexadienone (W2) and 2,5-Cyclohexadienone (W3), followed by the ring closure (W4) and the final elimination of CO. Compared to the corresponding *ab initio* PES of Xu et al [7], the energy of the intermediate wells and TS differ by 2-3 kcal/mol, due to the different level of theory used.

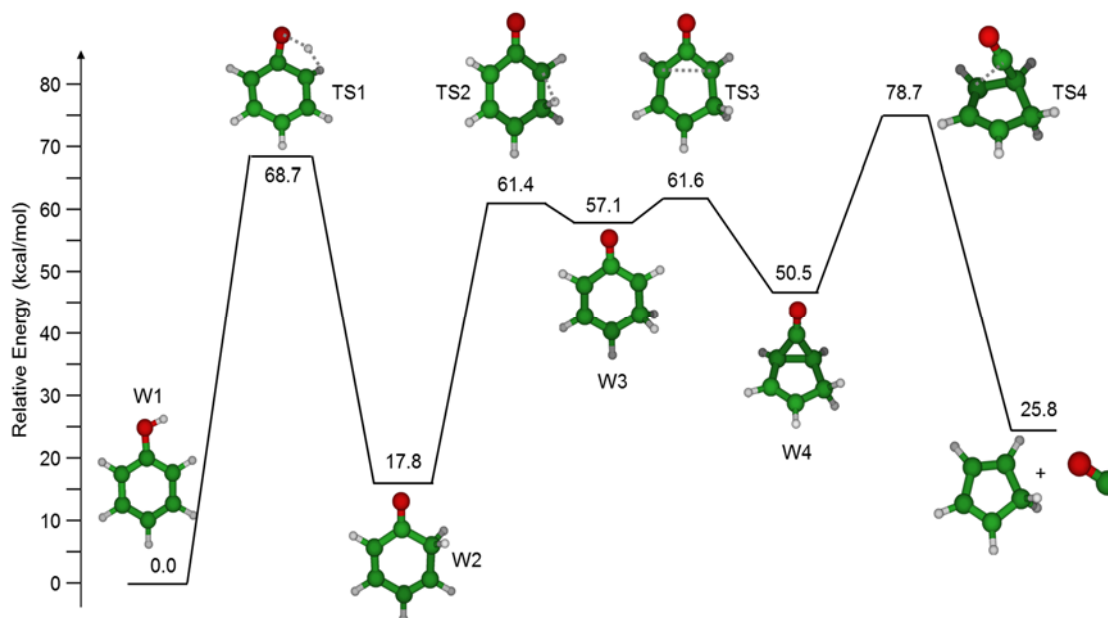


Figure 1: Potential Energy Surface of the reaction $C_6H_5OH = CO + C_5H_6$

The lumped kinetic constant for phenol decomposition determined post-processing MESS rates is compared in Figure 2 with that of Xu et al. [7], experimental data, and the previous constant adopted in CRECK model, that was obtained by reducing of a factor of 2 the one computed in [7] to improve the agreement in the simulation of extensive data sets where phenol decomposition plays an important role. The rate constant computed in this work is even smaller than the one adopted in the CRECK model, being up to a factor of 6 at 1400 K lower than that proposed by Xu et al. Figure 2 compares the present calculation with previous evaluations and with the experimental measurements of Horn et al [8].

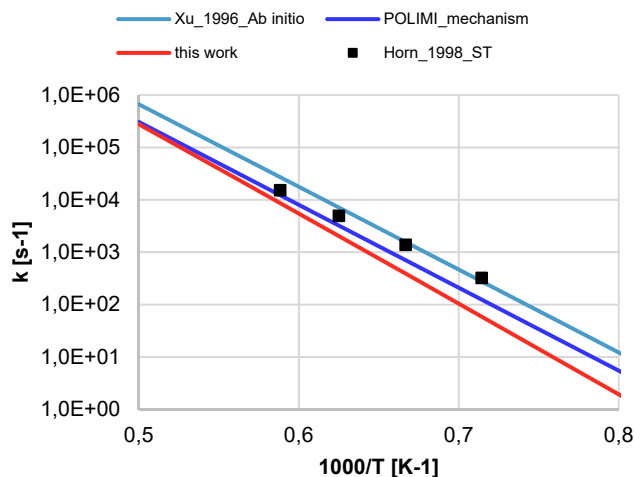


Figure 2: Kinetic constants for the reaction $C_6H_5OH = CO + C_5H_6$

The reasons for the difference with respect to the theoretical calculations of Xu et al. lies first of all in the higher level of the theoretical approach adopted in this work. Additional decomposition pathways are also being investigated, such as the direct ring opening, which may be followed by radical reaction pathways and therefore become relevant at high temperatures. Moreover, a second TS with a higher energy of 85.1 kcal/mol was found: this may also play a role in the decomposition at high temperature. Although experimental data would suggest that the computed kinetic constant is off by a factor of 5 [8], it must be considered that this constant was derived from the profiles of a shock tube experiment where a complex reaction network was analysed, and where the decomposition of phenol to phenoxy was neglected. Hence, these experimental data will be further investigated in light of the new findings to better assess the reference experimental constant. Concerning the comparison with the kinetic constant implemented in the CRECK mechanism, a value smaller than the current one would lead to an improvement of the agreement with experiments, as the model caused an excess of C_5H_6 with respect to the experimental results of phenol pyrolysis of Brezinski et al [9]. Nevertheless, a consistent comparison with the previous model can only be assessed after the determination of the full set of kinetic constants.

2. Phenoxy radical decomposition

The kinetic study of phenoxy radical is currently ongoing. The decomposition of phenol to phenoxy has a barrier of about 90 kcal/mol, hence this pathway is competitive with the C_5H_6 formation only at high temperature (above 1500 K, about 10% of phenol decomposes to phenoxy [7]). However, phenoxy radical rapidly decomposes to C_5H_5 . This reaction pathway proceeds with the immediate ring closure, similarly to the decomposition of phenol to C_5H_6 . However, in this case the loss of CO is preceded by the formation of a stable intermediate, C_5H_5CO , which is expected to be the rate determining step of this pathway [10].

3. H-abstraction reactions from cyclopentadiene

The abstraction of H from the CH_2 group of C_5H_6 by H, OH, OOH, O and CH_3 was investigated. The other carbon sites were not considered, as the activation energies of the H-abstractions from these sites are considerably higher. In the case of the abstractions by OH and O, also multireference CASPT2 methods were applied for the computation of geometries and energies. In light of the lack of experimental data, this theoretical treatment sets the benchmark

for the kinetics of this set of reactions. Furthermore, this theoretical approach establishes a protocol for the treatment of H-abstraction reactions by cyclic radicals providing also reverse rate constants (e.g. $C_5H_5 + CH_4 = CH_3 + C_5H_6$), useful to better assess reference kinetic parameters for H-abstractions by C_5H_5 within the CRECK model

Conclusions

Several reasons justify the need of a better understanding of phenol pyrolysis and combustion. This work presents an *ab initio* investigation of phenol decomposition to cyclopentadiene and phenoxy, and subsequent phenoxy radical decomposition to cyclopentadienyl. For completeness, also H-abstraction reactions from cyclopentadiene were studied. This systematic approach allowed a full revision and extension of the knowledge about the kinetics of phenol and phenoxy radical, and the understanding of its effects in pyrolysis and combustion modelling.

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