

Detailed Kinetics of the Pyrolysis and Oxidation of Anisole

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Pyrolysis, gasification and combustion of biomass are promising alternative energy sources. The kinetic understanding of these processes is crucial in the design and optimization of large-scale units. This paper proposes a detailed kinetic model for the pyrolysis and oxidation of anisole, a model compound for the lignin fraction of biomass. Model predictions are compared to a wide range set of experimental data. The chemistry of the highly resonant phenoxy radical is relevant in the formation of important intermediates, as cresols, phenol and cyclopentadiene. This kinetic study further confirms the importance and the role of resonantly stabilized radicals such as benzyl and phenoxy radicals.

1. Introduction and Motivation of the Work

With the decline of fossil fuels, the increase in oil prices and the environmental concern, bio-fuels are expected to gain significant relevance in the upcoming future (Demirbas, 2007). Biomass can represent an alternative source of energy, due to its availability, no net CO₂ emissions and lower NO_x and SO_x emissions than fossil fuel feedstocks. Biomass is composed of a mixture of cellulose, hemicellulose and lignin, together with extractives, ashes and moisture. The transformations occurring in biomass processing need a better understanding, in order to define optimal operating conditions of large scale processes (Bridgwater et al., 1999). Chemical kinetics, coupled with transport phenomena, are useful to characterize the primary and secondary decomposition of the biomass. This paper is focused on the kinetic model of the secondary pyrolysis and oxidation of anisole. The hierarchical modularity of detailed kinetic schemes allows to couple this sub-model with a more general kinetic scheme of pyrolysis and oxidation of hydrocarbon fuels. The choice of anisole, the first aromatic component with a methoxy group, derives from the consideration of lignin structure (Klein and Virk, 2008). Lignin is an aromatic-based polymer, in which aromatic units possess a set of propanoid and methoxy-phenol substituents. Details on the overall kinetic model used in the present work have been already discussed (Calonaci et al., 2010). Finally, this kinetic study highlights the relevant role of the chemistry of anisole, phenol and cresol, and also is a first step towards the kinetic description of more substituted aromatic compounds.

2. Kinetic Mechanism of Pyrolysis and Oxidation of Anisole

Many kinetic studies of pyrolysis and oxidation of anisole discuss the different reaction paths as well as the open issues relating this reaction system. Table 1 summarizes a few relevant reactions of anisole pyrolysis and oxidation.

Table 1: Relevant reactions in pyrolysis and combustion of anisole.

Reactions	A [s ⁻¹]	Eact [cal/mol]
1 C ₆ H ₅ OCH ₃ → C ₆ H ₅ O+CH ₃	3.00E+15	63000
2 CH ₃ +C ₆ H ₅ O → CH ₃ C ₆ H ₄ OH	4.00E+09	0
3 H+C ₆ H ₅ OCH ₃ → C ₆ H ₆ +CH ₃ O	1.00E+09	8000
4 H+C ₆ H ₅ OCH ₃ → C ₆ H ₅ OH+CH ₃	1.00E+10	6000
5 H+C ₆ H ₅ OCH ₃ → H+CH ₃ C ₆ H ₄ OH	1.00E+09	5000
6 OH+C ₆ H ₅ OCH ₃ → C ₆ H ₅ OH+CH ₃ O	1.00E+09	0
7 H+C ₆ H ₅ OCH ₃ → H ₂ +C ₆ H ₅ OCH ₂	7.10E+10	10500
8 CH ₃ +C ₆ H ₅ OCH ₃ → CH ₄ +C ₆ H ₅ OCH ₂	1.20E+09	11500
9 OH+C ₆ H ₅ OCH ₃ → H ₂ O+C ₆ H ₅ OCH ₂	1.20E+10	3500
10 HO ₂ +C ₆ H ₅ OCH ₃ → H ₂ O ₂ +C ₆ H ₅ OCH ₂	1.60E+09	19000
11 O ₂ +C ₆ H ₅ OCH ₃ → HO ₂ +C ₆ H ₅ OCH ₂	5.00E+10	49000
12 H+C ₆ H ₅ O → C ₆ H ₅ OH	6.00E+11	0
13 C ₆ H ₅ O → cyclic-C ₃ H ₅ +CO	5.00E+11	43920
14 H+C ₆ H ₅ O → cyclic-C ₃ H ₆ +CO	1.50E+11	0

As already mentioned, this reaction subset has been directly coupled with a more general and validated kinetic scheme of pyrolysis and oxidation of hydrocarbons (Ranzi et al., 2001), very recently extended also to alcohol fuels (Grana et al., 2010). The overall kinetic scheme, including anisole reactions and the relevant reactions of phenol and cresol, is available on the web (<http://creckmodeling.chem.polimi.it/>). Anisole decomposition is initiated through the thermal homolysis of the relatively weak C-O bond in the methoxy group, according to the reaction (R1): C₆H₅OCH₃ → C₆H₅O + CH₃. Suryan et al. (1989) already observed that the fission of the C-O bond accounts for the extensive conversion of anisole and the formation of the resonantly stabilized phenoxy radical C₆H₅O, with a resonance energy of ~17.5 kcal/mol (Pecullan et al., 1997). Because of the stability of phenoxy radical its concentration is dominant and plays a significant role in anisole pyrolysis and oxidation. This radical can follow three prevailing reaction pathways with the formation of cresol, phenol and cyclopentadienyl radical. The radical recombination reaction with CH₃ to form *o*- and *p*-cresols (through a cyclohexadienyl intermediate), the H-recombination to form phenol and the decomposition to cyclopentadienyl radical and CO are the three main reaction paths of phenoxy radical. The CH₃ radical can either go through H-abstraction reactions to form methane, or recombine with cyclopentadienyl radicals to form methylcyclopentadiene, or eventually recombine with another CH₃ radical to form ethane. The phenoxy radical can also react to form benzofuran, dibenzofuran and dioxins through different recombination and condensation reactions. Cyclopentadienyl, phenoxy and unsaturated radicals and molecules further contribute to the formation of polycyclic aromatic species (PAHs), soot and char deposits on the reactor walls.

The comprehensive reaction mechanism of anisole, with the relevant intermediate of the phenoxy radical, is well described by the flux analysis schematically reported in Fig. 1.

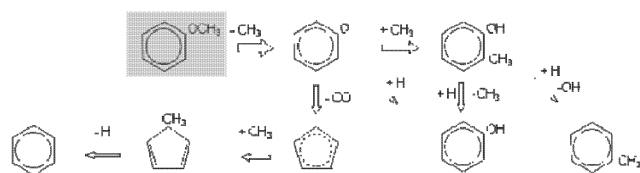


Fig. 1: Pyrolysis of anisole, $T=1000\text{K}$, $\tau=20\text{ms}$, conversion=60%. Reaction flux analysis. Arrow thickness stands for the relative importance of different reaction paths.

This analysis refers to the results of the pyrolysis experiments conducted in the Princeton atmospheric pressure flow reactor (Pecullan et al., 1997). The cited work discusses and supports the above reaction mechanism on the basis of different experimental measurements at about 1000 K, in pyrolysis and different oxidation conditions (equivalence ratios: $\Phi=1.7$, $\Phi=1$ and $\Phi=0.6$). The authors also propose a first anisole sub-mechanism, also highlighting the role of cyclopentadiene, methylcyclopentadiene and cyclopentadienyl radicals to form benzene and PAHs.

Fig. 2 shows a comparisons between experimental measurements reported in Pecullan et al. (1997) and predictions obtained with the presented model both in pyrolysis and oxidation conditions. Following usual practice employed for comparison with flow reactor data, predicted profiles are shifted of roughly 10-15 ms in order to match the fuel conversion. Both experiments and model predictions confirm that anisole decomposition is not extensively influenced by the presence of oxygen. Methylcyclopentadiene predictions well agree with experimental measurements, while the successive benzene formation seems underestimated. CO yields are in good agreement with the experimental measurements, thus suggesting a reasonable accuracy in the kinetics of the phenoxy radical decomposition (Fig. 2). Two major deviations need to be highlighted. The first one refers to the yields of cresol and phenol. Phenol is notably underestimated and cresol consumption is underestimated, even if a high rate value is assumed for the reaction: $\text{H} + \text{CH}_3\text{C}_6\text{H}_4\text{OH} \rightarrow \text{CH}_3 + \text{C}_6\text{H}_5\text{OH}$. Reaction paths that lead to a rapid and primary formation of phenol might be envisaged, as indicated by the tight slope of the phenol experimental curve. The evident excess of cresol at high residence times suggests that cresol reactivity need to be increased. To our knowledge, there is a lack of experimental information regarding cresol pyrolysis and oxidation. A similar limited agreement with the experimental data was also observed by Pecullan et al. (1997): low phenol yields, together with the overestimation of cresol. They also searched, with poor success, for alternative reaction pathways to form phenol, such as a unimolecular elimination of the methylene singlet from anisole or the recombination of phenoxy radicals with subsequent consumption of the dimer. A second point relates to the underestimation of methane. Primary CH_3 is mainly formed by the initial anisole decomposition [R1]. Ethane formation is solely due to methyl radicals recombination and the slight ethane overestimation seems to indicate a corresponding over-estimation of methyl radical. On the contrary, the underestimation of methane, obtained by H abstraction reactions of methyl radical, suggests an insufficient CH_3 formation. Similar deviations were also observed and discussed (Pecullan et al., 1997).

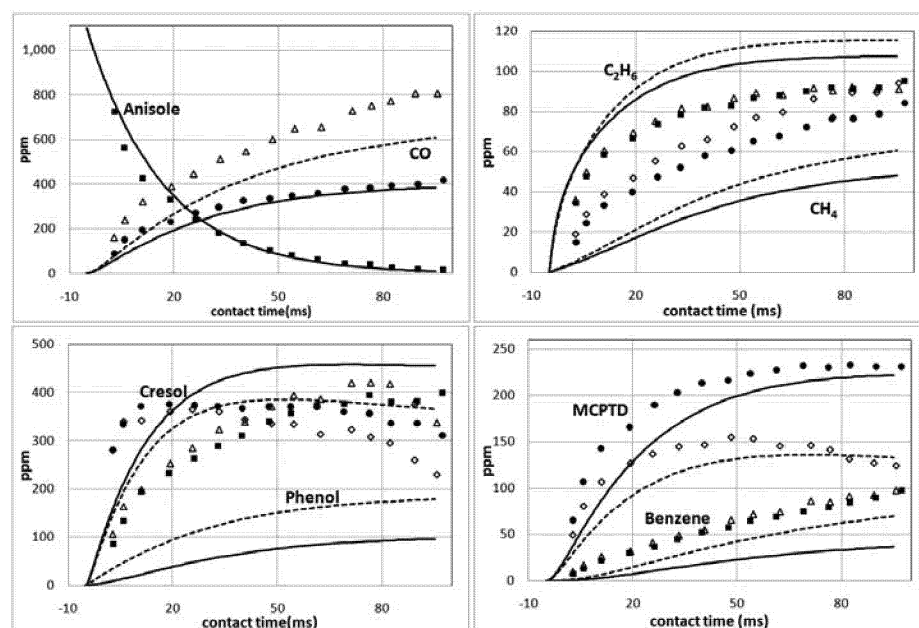


Fig. 2: Comparison between experimental measurements (Pecullan et al., 1997) and model predictions. Pyrolysis: solid lines and symbols; oxidation, $\Phi=0.62$: dashed lines and empty symbols.

The H abstraction reactions on anisole to form the reactive anisyl radical ($C_6H_5OCH_2$) are of negligible importance in the operating conditions of the Princeton flow reactor. Rearrangement and dehydrogenation reactions of anisyl radical form benzaldehyde: $C_6H_5OCH_2 \rightarrow H + C_6H_5CHO$. Mulcahy et al. (1967) investigated CH_3 reactions with anisole, confirming the high reactivity of the anisyl radical. Benzaldehyde and methane are found to be the major products, suggesting that the reaction goes through the above mentioned steps. CH_3 addition on anisyl, or on the aromatic ring are of very limited importance. Arends et al. (1993), studied the gas-phase thermal decomposition of anisole diluted in a 10-fold excess of hydrogen at atmospheric pressure in a tubular flow reactor over the temperature range 793-1020 K. Due to the large excess of H_2 , and the high H radical concentration, the role of H abstraction reactions on anisole and successive reaction of anisyl radical becomes more evident. The formation of phenol, both from phenoxy radical recombination with H radicals and from H-abstraction of phenoxy radical on H_2 , are also enhanced. Another relevant reaction path is the addition of H atoms on anisole: $H + C_6H_5OCH_3 \rightarrow CH_3 + C_6H_5OH$. Fig. 3 shows the reaction flux analysis in these conditions. Cresol and cyclopentadiene reaction paths become of limited importance, while H abstraction with anisyl radical and benzaldehyde formation account for ~ 20 -30% of anisole decomposition. Table 2 shows the comparison between predicted and measured selectivities of major products, both for the low and the high temperature regions reported (Arends et al., 1993).

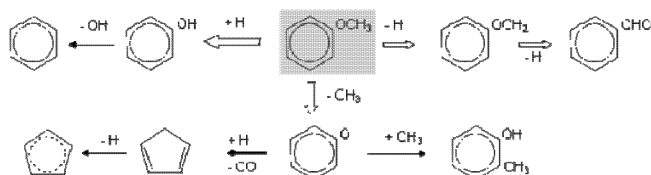


Fig. 3: Hydrogenolysis of anisole, $T=813\text{K}$, $\tau=3.5\text{s}$, conversion=30%. Reaction flux analysis. Arrow thickness stands for the relative importance of different reaction paths.

Table 2: Hydrogenolysis of anisole. Comparison between model predictions and experimental selectivities of major species (Arends et al., 1993).

	813K		873K		1007K	
	exp	mod	exp	mod	exp	mod
CO	22.21	17.25	34.4	22.78	27.7	19.47
CH ₄	70.44	70.1	87	84.05	76.3	79.6
Phenol	63.72	63.97	60.4	67.27	56.26	64.18
Cresol	16.32	3.74	1.1	0.62	8.8	5.74
Benzaldehyde	11.93	10.27	4.1	2.63	5.36	5.78
Benzene	16.32	16.67	17.3	17.73	9.8	4.4
Cyclopentadiene	0.35	2.91	5	7.46	9.9	13.36
Me-cyclopentadiene	nc	0.21	nc	0.11	3.18	1.64
Naphtalene	nc	0.16	0.3	1.38	0.09	0.18
Dibenzofuran	0.48	0.55	0.8	0.31	0.65	1.09

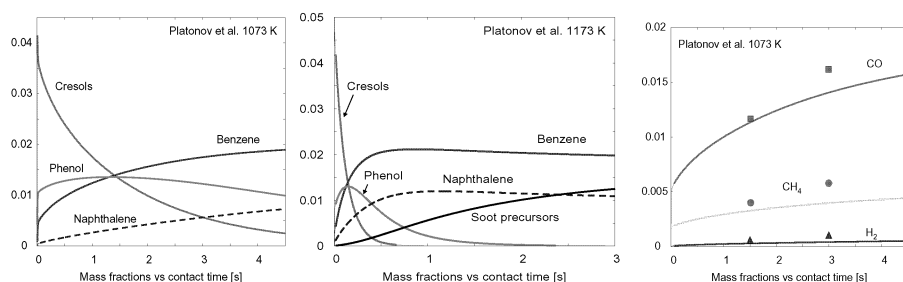


Fig. 4: Pyrolysis of anisole. Predicted yields of intermediates vs time at 1073K - 1173K. Comparison of experimental data and model prediction for the major gaseous products.

Platonov et al. (2001) studied the pyrolysis of anisole at high severity ($T=1023\text{-}1173\text{K}$) and contact times up to 4.5 s. A large detail of PAH and tar components as well as the distribution of oxygen in different functional groups is also reported. These severe pyrolysis conditions allow to better analyse the role of successive reactions of resonantly stabilized radicals such as phenoxy and benzyl like radicals. Fig. 4A and B show the predicted yields of relevant intermediates at 1073 and 1173 K. Anisole decomposes in few ms at these temperatures. Successive reactions of cresols and phenol become of interest in describing the evolution of the system. At 1073 K, cresol is the first intermediate and it decomposes with large phenol and benzene formation. At higher temperatures, also phenol is largely decomposed with the successive formation of naphthalene, PAH and soot. Fig. 4C compares experimental and predictions of major

gas components. Pyrographite and gas products increase by increasing the temperature or the contact time. Conversely, there is a clear decrease in tar components.

3. Conclusions

A detailed kinetic model of anisole pyrolysis and oxidation is discussed in this paper on the basis of several comparisons with experimental data. Relevant information on the reaction mechanism, with highlights on the major reaction paths and intermediates, can be taken from this kinetic modelling work. This kinetic study points out that the phenoxy radical, together with phenol and cresols are relevant intermediates in anisole pyrolysis. The reactivity of these compounds is therefore interesting, not only in the light of further development and extensions of this reaction mechanism, but also with consideration to environmental and toxicity issues associated to some of the major products and intermediates (e.g. phenols, benzofuran, dioxins).

4. Acknowledgements

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