MECHANISM OF OXIDATION AND PYROLYSIS OF DIBENZOFURAN VALIDATED AT VERY LOW CONCENTRATION (~1 ppm)

Tritz A[1], Ziegler-Devin I[2], Bounaceur R[1], Simon Y[1], Marquaire PM[1] *

[1] Laboratoire Réactions et Génie des Procédés (UMR 7274) CNRS - Université de Lorraine, ENSIC, 1 rue Grandville, BP 20451, F-54001 Nancy, France
[2] LERMaB (EA 4370) Université de Lorraine, Faculté des Sciences et Technologies, BP 70239, F-54506 Vandoeuvre les Nancy, France

Introduction

The formation of "dioxins" ("PCDD/Fs"), in trace amounts, is inevitable in several high temperature industrial processes such as municipal waste incineration, recycling of scrap to produce steel in electric arc furnaces, sintering of iron ore, etc. To limit the emissions of dioxins (PCDD/Fs), there are three possibilities which in fact are complementary : to limit their formation by modifying the industrial process and the conditions of the reaction, to destroy the dioxins after their formation, or to trap the dioxins in the flue gas by an adsorption process. An efficient way of lowering the emissions of PCDD/Fs is an optimisation of the postcombustion process to keep the level of organics emitted as low as possible.

"Dioxins" or PCDD/Fs are a large family ; in previous studies[1,2] to investigate the thermal destruction of PCDD/Fs, we chose dibenzofuran (DBF) as a model molecule because dibenzofuran has the same structure and is less reactive than chlorinated PCDFs (the bond dissociation energy of C-Cl is lower than that of C-H). Moreover, the absence of chlorine atoms on dibenzofuran molecule avoids any problems of dioxin toxicity and oversimplifies the products analysis. Since dibenzofuran is less reactive than chlorinated furans and probably dioxins, reaction conditions leading to a total oxidation of dibenzofuran should also lead to a total destruction of "dioxins" (PCDD/Fs) [3]. Furthermore, the mechanism of dibenzofuran oxidation must be very similar to the mechanism of that of PCDFs.

A lot of studies concern the formation of dioxins and their mechanims [eg 4-7] but, as far as we know, there are very few about dibenzofuran or dibenzodioxin oxidation. We built a first detailed gas phase radical mechanism[8] of dibenzofuran oxidation accounting for all the reaction products found in our experimental study[1-2]. Some recent studies have investigated several oxidation elementary reaction steps by quantum chemistry [9] and in 2012, Summoogum et al[10] published the first experimental and theoretical study of oxidation of dibenzodioxin.

Because of experimental limitations, our first studies of oxidation of dibenzofuran[1,2] are obtained at relatively high concentrations (~1000 ppm). The reactivity strongly decreases when the reactant is very diluted, so it is important to obtain new experimental results at very low concentration of DBF.

Materials and methods

In the last study[11,12], we develop a new device which allows a kinetic study of the thermal decomposition of dibenzofuran at very high dilution (~2 ppm) at atmospheric pressure. The reaction is performed in a Continuous Jet Stirred Reactor (CJSR) made of quartz, with a residence time of 3 s ; temperature ranges from 500 to 950°C. The oxygen fraction is 0% for pyrolysis and 3% or 16% for oxidation studies, in very large excess in both cases. The main difficulty of this study is to realize and control a continuous gas flow of dibenzofuran because it is a solid compound in standard conditions. This study is limited to the analysis of DBF conversion and to aromatic products (> C_6) because the products are accumulated on a sorbent tube and quantified by GC equiped with a thermal desorber. The aim is to identify the first steps of the pyrolysis/oxidation reactions, so it is important to analyse the intermediary products of DBF decomposition. More than 30 species are observed, the main byproducts are derivatives of benzofuran, aromatics and VOCs.

In former studies[8,13,14], we proposed a first radical detailed mechanism of dibenzofuran decomposition in oxidation conditions. This mechanism was validated with experimental data obtained with higher range of dibenzofuran concentration (~1000 ppm) and it is also in agreement with the present knowledge on the oxidation of monoaromatic molecules.

In this paper, the new experimental data obtained at very high dilution (2 ppm) in pyrolysis and oxidation conditions are used to improve the detailed kinetic mechanism based on elementary steps. In oxidation, the major initiation is the bimolecular reaction with oxygen leading to DBF• radicals. In order to take into account the pyrolysis results, new initiation processes are added including the cleavage of C-O bond leading to a biradical, and the bimolecular initiation between two DBF molecules.
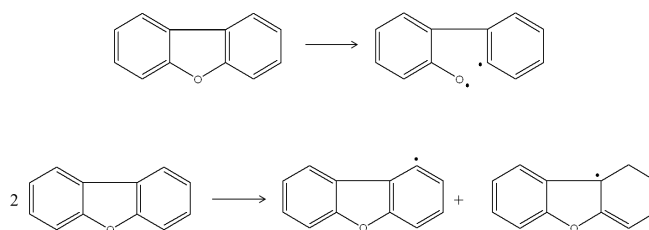
Several other reactions are added. The ipso-additions of hydrogen or methyl radicals on aromatic cycle of dibenzofuran and secondary products are new important pathways for the decomposition of dibenzofuran and the formation of benzene or toluene.
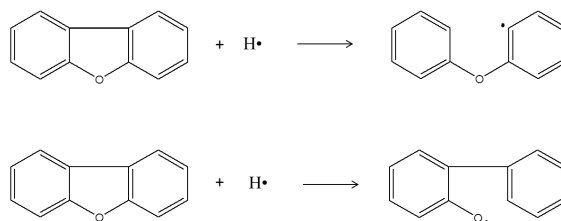
The other reactions added are mainly metathesis reaction (or H-transfer) and decomposition by ß-scission of news radicals and products. A systematic approach was used to build the reaction mechanism.

The final DBF pyrolysis and oxidation mechanism contains 252 species involved in 1369 elementary steps. The kinetics parameters come from database, literature or estimations[14]. The simulations were performed using Chemkin II software.

Results and discussion:
The proposed kinetic model is used to simulate the pyrolysis and the oxidation of DBF under our experimental conditions. The simulation of pyrolysis and oxidation show that the influence of temperature on the DBF conversion (Figure 1) is well estimated by the mechanism. An almost total conversion is observed around 800°C in oxidation conditions and 950°C in pyrolysis conditions.
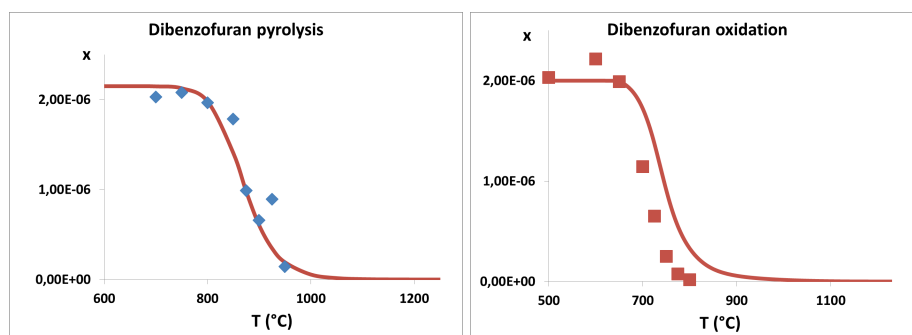
Fig. 1 : DBF conversion x°$_{DBF}$=2ppm, =3s, x°$_{O2}$=0 (pyrolysis) or 3% (oxidation). Experimental results (dots) and simulation (line)

The mechanism really accounts for the nature of the products observed as well as for their amounts, at least in the semi-quantitative way. Figure 2 presents the variation of some products quantity with the temperature in pyrolysis conditions. Both in pyrolysis and oxidation conditions, most of the compound quantities reach a maximum, which confirms that these species are intermediary products of DBF decomposition. For example, the influence of temperature on the mole fractions of toluene and benzofurane are quantitatively well reproduced by the model. Indeed, simulated and experimental curves are similar. For other products, as styrene and naphthalene, the variation of molar fraction versus temperature has the good shape and the same order of magnitude (over or under predicted by a factor 2 or 3). The shift between simulated and experimental mole fractions might be caused by a lack of reactions for the considered species or by the uncertainty on rate constants.
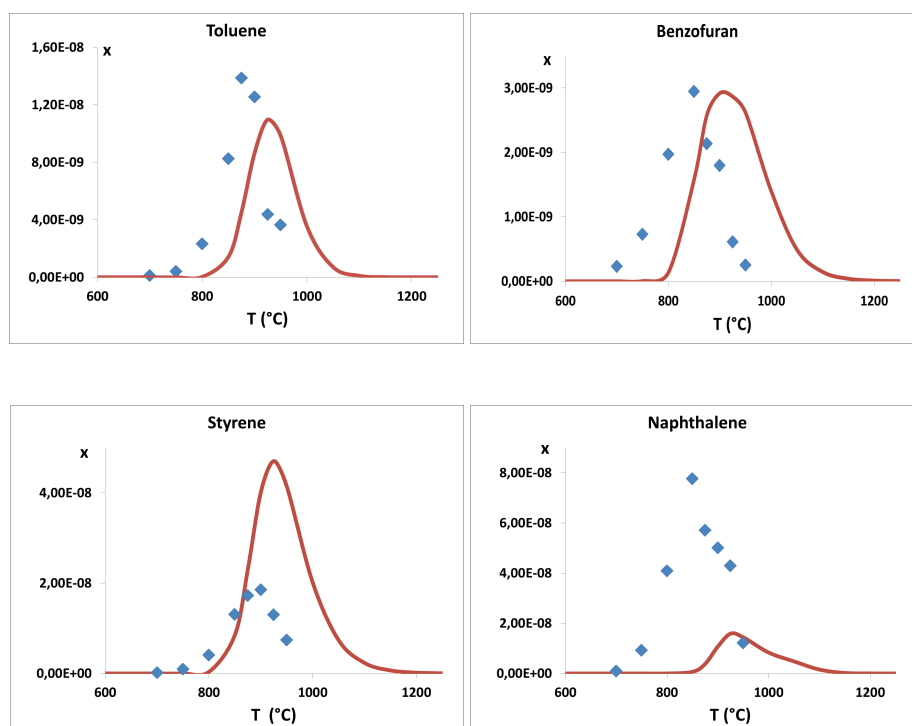

Fig. 2 : Evolution of compounds according to the temperature =3s, x°$_{DBF}$=2ppm, x°$_{O2}$ =0% Experimental results (dots) and simulation (line)

For the oxidation of dibenzofuran, the influence of temperature on reaction products is also well estimated by the present model. The global agreement between all the experimental data (pyrolysis and oxidation) and simulated compositions is satisfactory. We can conclude that this mechanism is validated and it can describe the major features of the pyrolysis and the oxidation of dibenzofuran at very low concentration. These results (experimental and mechanism) are very useful to understand the reaction of DBF decomposition. The mechanism of dibenzofuran is the main part of the mechanism of oxidation of PolyChlorinated DibenzoFurans (PCDFs) and it must be very similar to the oxidation mechanism of PolyChlorinated DibenzoDioxins (PCDDs).

This detailed mechanism is used to model the oxidation of dioxins in a postcombustion area of municipal waste incineration; some over-simplifications are used: PCDD/PCDF families are represented by the dibenzofuran and postcombustion aera is 0 D modeled (CFSTR reactor)[14]. This simplified approach brings a new contribution to understand these complex reactions and to allow the development of an efficient post-combustion (abatement of dioxins by total oxidation). The simulations of dibenzofuran oxidation show that the reactivity strongly decreases when the reactant is very diluted. The simulations show that the volatile organic compounds present in fume increase the thermal reactivity. The key parameter is the concentration of radicals which is controlled by the initiation rate and branching steps in oxidation mechanism. If the VOCs present in fume are not efficient enough, our results show that the addition of natural gas in flue gas, in low quantities (eg 1000 ppm), induces an important increasing of radical concentration and promotes the DBF oxidation very efficiently. Using a model or mechanism of dioxins decomposition, the optimization of post-combustion might reduce the level of emissions of PCDD/Fs. Some useful clues to design an efficient post-combustion chamber can be deduced.

References:
1. Marquaire PM, Wörner R, Rambaud P, Baronnet F. (1999); *Organohalogen Comp.* 40: 519-22
2. Wörner R, Rambaud P, Baronnet F, Marquaire PM. (2000); *Organohalogen Comp.* 45: 438
3. Arion A, Birat JP, Marquaire PM, Baronnet F. (2002); *Organohalogen Comp.* 56: 345
4. Sidhu S, Maqsud L, Dellinger B, Mascolo G. (1995); *Combust. Flame* 100: 11
5. Khachatryan L, Asatryan R, Dellinger B. (2003); *Chemosphere* 52: 695
6. Briois C, Visez N, Baillet C, Sawerysyn JP. (2006); *Chemosphere* 62: 1806
7. Altarawneh M, Dlugogorski BZ, (2014) *Organohalogen Comp.* 76,190-193
8. Marquaire PM, Bounaceur R, Baronnet F. (2003); *Organohalogen Comp.* 63: 377-80
9. Altarawneh M, Kennedy, E, Dlugogorski B, Mackie JC. (2008); *J. Phys . Chem A* 112: 6960–67.
10. Summoogum S, Altarawneh M, Mackie JC, Kennedy E, Dlugogorski B. (2012); *Combust. Flame* 159: 3056–65
11. Tritz A, Ziegler-Devin I, Perrin C, Marquaire PM. (2013) *Organohalogen Comp.* 75, 98-101
12. Tritz A, Ziegler-Devin I, Perrin C, Marquaire PM. (2014) *J. Environmental Chem. Eng.* 2: 143-53
13. Marquaire PM, Ziegler-Devin I, Bounaceur R, Baronnet F. (2008) *Organohalogen Comp.* 70: 1764
14. Ziegler-Devin I, Bounaceur R, Perrin C, Wörner R, Patisson P, Marquaire PM. (2013) *Chem. Eng. J.* 218: 154-63