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# DETAILED MECHANISM OF DIBENZOFURAN OXIDATION

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## Introduction

A number of high temperature industrial processes such as municipal waste incineration, recycling of scrap to produce steel in electric arc furnaces, sintering of iron ore, etc , lead to the formation of "dioxins" (PolyChlorinated Dibenzo-p-Dioxins and PolyChlorinated DibenzoFurans, or "PCDD/Fs") in trace amounts. Their toxicity needs to keep their formation as low as possible by using all the available techniques (process modification, post-treatment,...). To limit the emissions of dioxins (PCDD/Fs), there are three possibilities which in fact are complementary :

- to limit their formation by choosing "clean" raw materials, by modifying the industrial process, the conditions of the reaction,
- to destroy the dioxins after their formation,
- 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.

## Total gas phase oxidation for dioxins abatement

"Dioxins" or PCDD/Fs are a large family; among the 210 congeners, 17 chlorinated in 2, 3, 7, 8 are toxic. To investigate the experimental conditions leading to a minimum or zero emission of PCDD/Fs (in situ destruction), we have chosen dibenzofuran (DBF) as a model molecule because dibenzofuran has the same structure and is more stable than PCDD/Fs (the bond dissociation energy of C-Cl is lower than that of C-H). Moreover, the absence of chlorine atoms on the dibenzofuran molecule avoids any problem of dioxin toxicity, whereas a non-toxic chlorinated molecule can be transformed after various reactions into toxic species if they become chlorinated in 2,3,7,8. Since dibenzofuran is more stable than chlorinated dioxins or furans, reaction conditions leading to a total oxidation of dibenzofuran should also lead to a total destruction of "dioxins" <sup>1</sup>. Furthermore, the mechanism of dibenzofuran oxidation must be very similar to the mechanism of that of PCDD/Fs.

In previous investigations<sup>1,2</sup>, we studied DBF oxidation between 800 and 950 C, at atmospheric pressure, and high dilution in helium: 0.12% of DBF; the equivalence ratio was 0.7 to 7 for oxygen, and the residence time ranged from 0.3 to 1 second. The experiments were performed in a quartz Continuous Jet Stirred Reactor. Many products were observed in fuel-rich conditions, and we were able to identify and quantify 25 carbonaceous products: CO, CO<sub>2</sub> were the major products; other reaction products are CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>4</sub>, benzene and substituted derivatives, benzofuran and substituted derivatives, indene, naphthalene and dibenzofuranol. Hydrocarbons and aromatic products ranged from 10 to 0.1 % of DBF initial concentration.

Our experimental results on the oxidation of dibenzofuran in the gas-phase at temperatures higher than 900 C show that the initial concentration of oxygen and the flow conditions (turbulence, back-mixing) seem to be the most important parameters. A total combustion is obtained for an equivalence ratio of 0.8 and we can expect to avoid a catalytic or "de-Novo" formation of dioxins at lower temperature since the concentration of hydrocarbon intermediates is kept at an extremely low level. These results on dibenzofuran oxidation suggest that an optimisation of the conditions of the post-combustion does not only lowers the amounts of PCDD/Fs but also those of other organic products and very low concentration levels are obtained. Some useful clues to design an efficient post-combustion chamber are deduced<sup>3,4</sup>.

In a former study<sup>2</sup>, we proposed a radical reaction scheme which led to a better understanding of the oxidation of dibenzofuran, in qualitative agreement with the reaction products found in our experimental investigation. The purpose of the present study is to build a detailed radical mechanism incorporating available or estimated kinetic data.

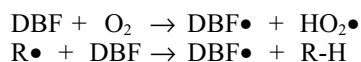
### Mechanism of Dibenzofuran Oxidation

Taking into account the available literature on the oxidation reaction of aromatic compounds and our experimental results, we have built a radical mechanism accounting for all the reaction products found in our experimental study and also in agreement with the present knowledge on the oxidation of monoaromatic molecules<sup>eg. 5-8</sup>; there are, as far as we know, no published data for dibenzofuran or dibenzodioxin oxidation; some data are available only for the formation of dioxins<sup>eg. 9-12</sup>.

A systematic approach was used to build the reaction mechanism and for many reactions without available data, the kinetic parameters were estimated from analogous reactions and modified by taking thermochemistry into account<sup>13</sup> when it was possible. For the dibenzofuran oxidation part (from DBF to toluene and benzene) we obtained a detailed mechanism which comprises 96 elementary reaction steps including 28 molecules and 20 radicals.

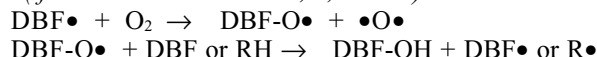
The mechanism of DBF oxidation is described in five parts:

1- The formation of DBF• radical (four isomers: *radical site 1, 2, 3 or 4*), is obtained from the bimolecular initiation process or through a metathesis reaction with any radical R. involved in the reaction

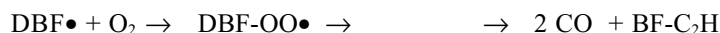


From DBF• radical, the oxidation mechanism of dibenzofuran consists of two parallel and competing channels (parts 2 and 3):

2- The formation of PAHs is controlled by the radical DBF-O• obtained through a branching step of DBF• with O<sub>2</sub>. This explains the formation of 4 isomers of dibenzofuranol (DBF-OH), followed by phenylacetylene (Bz-C<sub>2</sub>H), and three products: naphthalene, indene and benzaldehyde (Bz-CHO). The first steps of this alkoxy channel lead to the formation of dibenzofuranol found as a primary product (*from DBF radical site 1, 2, 3 or 4*):



3- The formation of benzofuran is controlled by O<sub>2</sub> addition to DBF• radical, giving a peroxide, then a quinone leading to the destruction of an aromatic cycle by CO elimination. This explains the formation of benzofuran and its derivatives BF-C<sub>2</sub>H, BF-CH<sub>3</sub>, BF-C<sub>2</sub>H<sub>3</sub>. The first steps of this channel lead to acetylbenzofuran, found as a pseudo-primary product (*from DBF radical site 1 or 4*):



4- The formation of monoaromatic products, benzene, toluene, styrene and phenol, is obtained from a phenyl radical formed in the parallel steps 2 and 3.

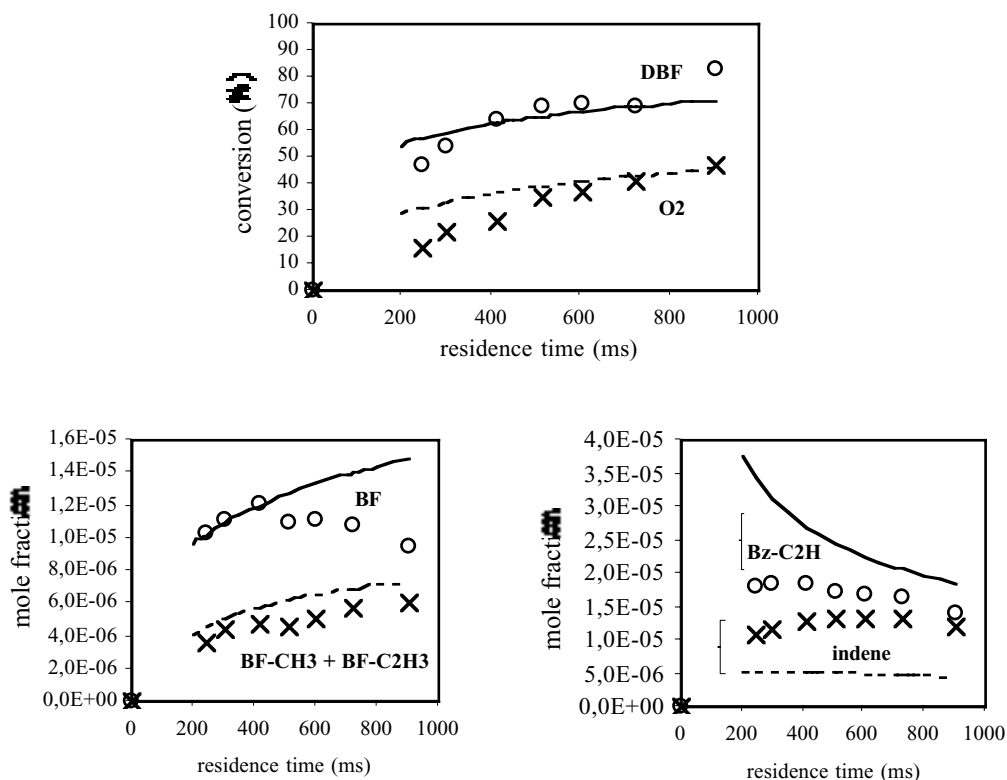
5- The oxidation of phenyl and benzyl radicals also leads to the aliphatic reaction products (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>4</sub>,...) and to the final products CO and CO<sub>2</sub>; this part is well-known and we use a published mechanism<sup>8</sup>.

A first test of the mechanism incorporating the best values of rate constants (available or estimated) is performed by studying the influence of residence time at 900 C, 0.12 % molar of DBF in helium at atmospheric pressure and 1.5 % of O<sub>2</sub> (equivalence ratio of 1.2). The figures (below) show the comparison between experimental (points) and simulated values (curves, obtained by using software Chemkin II). We obtain a good agreement for the conversions of reactants, a rather good agreement for most aromatic products and at least a good order of magnitude for the others. We can conclude that this mechanism can describe the major features of the oxidation of dibenzofuran.

## Conclusions

Taking into account our experimental results and the literature data, we have proposed a detailed mechanism which accounts for chemical species which were identified in our experimental investigation of DBF oxidation. We have been able to explain the formation (or the absence of formation) of various isomers observed in our experiments. This rather satisfactory agreement between our experimental results and the assumptions made by other research teams working on the oxidation of aromatic compounds at high temperature<sup>14</sup> confirms the proposed mechanism. By comparison with benzene oxidation<sup>5-7</sup>, we also propose two parallel oxidation channels of oxidation of dibenzofuran leading to different series of products, the importance of which depends on the temperature: the peroxide channel would be preponderant at temperature below 800 C, whereas for higher temperatures, the channel leading to PAHs would be more important.

Despite the uncertainties on many estimated kinetic parameters, the proposed mechanism accounts for oxidation of dibenzofuran at high temperature (900 C). The mechanism of dibenzofuran is the main part of the mechanism of oxidation of PolyChlorinated DibenzoFurans and it must be very similar to the oxidation mechanism of PolyChlorinated DibenzoDioxins. A detailed mechanism will be useful for modeling the abatement of dioxins by total oxidation in a postcombustion chamber, or to study the influence of the co-reactants which are in the smoke. This approach can bring a substantial contribution to the development of an efficient post-combustion chamber.



figures: conversions and some aromatic products vs residence time  
(experimental results / simulation)

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