

MECHANISM OF OXIDATION OF FURANS AND DIOXINS

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Introduction

Incineration and similar thermal processes lead to the formation of "dioxins" (polychlorinated dibenzo-p-dioxins and dibenzofurans, or "PCDD/Fs") in trace amounts. Their toxicity and their low biodegradability need to keep their formation as low as possible by using all the available techniques. 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, the conditions of the reaction,....,
- to destroy the dioxins after their formation,
- to trap the dioxins in the flue gas by an adsorption process.

The mechanisms of dioxins formation are very complex and not yet fully understood (eg.¹⁻⁵). Therefore it seems that an efficient way of lowering the emissions not only of PCDD/Fs but also of other organic molecules, which are harmful for the environment and possible precursors of PCDD/Fs, is an optimisation of the (post-) combustion process to keep as low as possible the level of organics emitted. Polychlorinated dibenzodioxins and furans are a large family : 210 congeners of which 17 are toxic. To investigate the experimental conditions leading to a minimum emission of PCDD/Fs (in situ destruction), we have chosen as a model reaction the oxidation of dibenzofuran (DBF) because the dibenzofuran has the same structure and is more stable than PCDD/Fs (the BDE of C-H is 425 kJ/mol and that of C-Cl is 337), and moreover it is not toxic.

Experimental Results

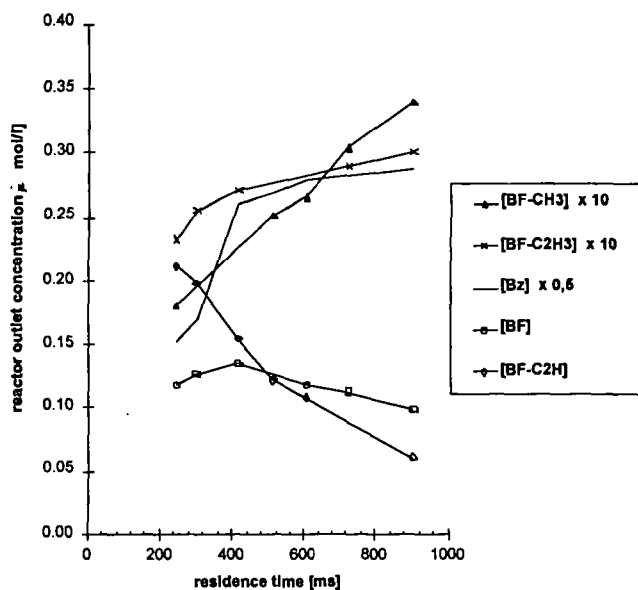
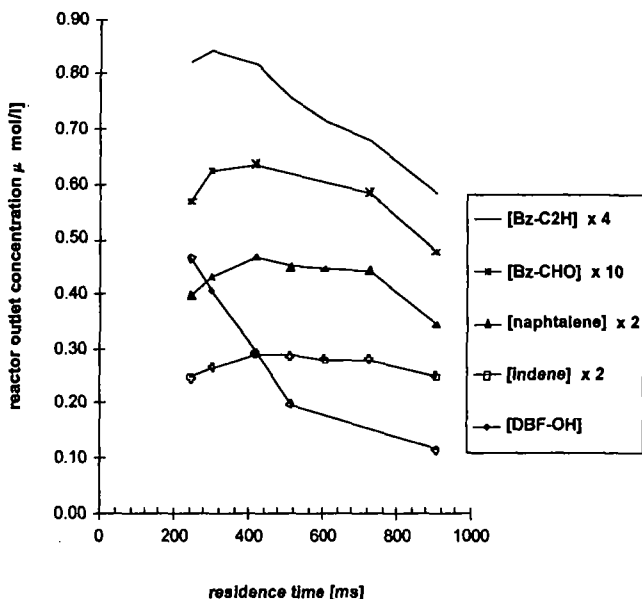
The experiments were performed in a quartz Continuous Jet Stirred Reactor. The DBF oxidation has been studied at around 900°C, at atmospheric pressure, and high dilution : 1200 ppm of DBF; the equivalence ratio was 0.7 to 7 for oxygen, and the residence time ranged from 0.3 to 1 second. Many products were observed in fuel-rich conditions, and we were able to identify and quantify 25 carbonaceous products : CO, CO₂ were the major products ; hydrocarbons and aromatic products (CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₄, benzene and substituted derivatives, benzofuran and substituted derivatives, indene, naphthalene and dibenzofuranol) ranged from 10 to 0.1 % of DBF initial concentration⁶.

We performed a parametric study of the reaction by following the influence of reaction parameters on the conversion of dibenzofuran and product distribution. The influence of oxygen ratio is very strong ; at 900°C and 330 ms, for x°DBF of 1250ppm, the reaction was studied with x°O₂ ranging from 0.2 to 2.1%. The experimental results show that , under an excess of oxygen (2.1%), it is possible to obtain a total consumption of DBF but also a complete destruction of all the intermediate products in these experimental conditions. This suggests that post-combustion techniques may be effective to destroy the furan molecules and the associated aromatic degradation products. This point is important because the PCDD/Fs can be formed again in the cooling

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section of the equipment (heat exchangers, filters...) by the "de Novo" reaction; for this reason, it is necessary to destroy all the intermediate products.

The influence of the residence time (between 250 and 900 ms) is presented in figures 1 and 2.



Some products have a concentration which decreases with the residence time, or has a maximum, or increases; we can deduce the order of the successive reaction products from the curves concentration vs time. It appears that dibenzofuranol (DBF-OH) and acetylbenzofuran (BF-C2H)

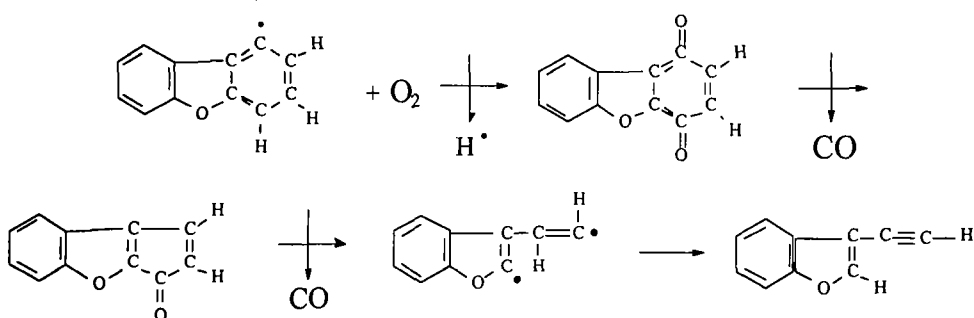
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can be considered as (pseudo-) primary products. These results are used to build a first reaction scheme.

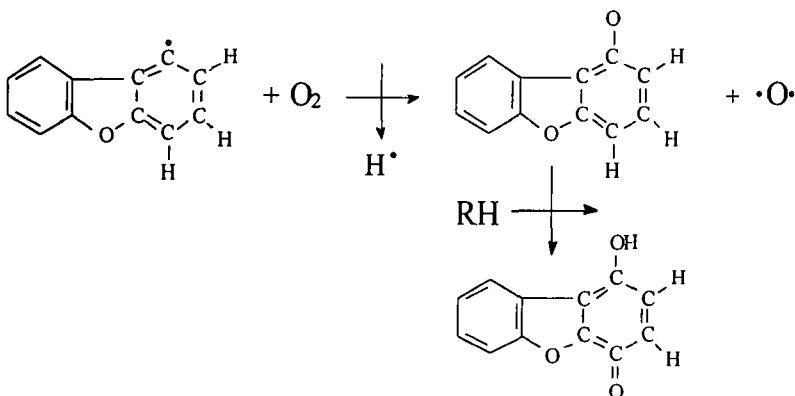
Interpretation and Reaction Scheme

Taking into account the available literature on the oxidation reactions of aromatic compounds⁷⁻⁹ 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 aromatic molecules¹⁰.

There are two parallel reaction channels in this reaction scheme; only the first steps are detailed here. The low temperature channel leads to the formation of a quinone which can give, by loss of CO, an acetybenzofuran found as a pseudo-primary product (*from DBF radical site 1*):



At higher temperature an alkoxy channel leads to the formation of dibenzofuranol found as a pseudo-primary product (*from DBF radical site 1, 2, 3 or 4*):



It is worth noting that this mechanism has not been confirmed by a simulation because of the lack of kinetic data; it has not been possible either to use the current techniques for the estimation of thermodynamic and kinetic parameters since a number of group values are not available¹¹.

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Conclusion

To investigate the experimental conditions leading to a minimum emission of PCDD/Fs by total oxidation, we have studied the oxidation of dibenzofuran, because it has the same structure and is more stable than PCDD/Fs. Our results on dibenzofuran oxidation suggest that an optimisation of the conditions of the combustion (temperature, residence time, oxygen concentration, mixing) not only lowers the amounts of PCDD/Fs but also that of other organic products. The present study has led to a better understanding of the oxidation of dibenzofuran and to a detailed reaction scheme which can be the basis of further studies.

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