

HIGH TEMPERATURE OXIDATION OF DIOXINS

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Introduction

High temperature incineration and similar thermal processes lead to the formation of «dioxins» (polychlorinated dibenzo-p-dioxins and dibenzofurans, PCDD/F) in trace amounts. Their toxicity and their low biodegradability need to keep their formation as low as possible by using all the available techniques (process modification, post-treatment,...).

The mechanisms of dioxin formation are not yet fully understood. It has been shown^{1,2} that there are three parallel pathways of formation: in the gas-phase around 600°C, catalytic formation in the 300-500°C temperature range due to the presence of dust particles and the «de Novo» reaction proposed by Stieglitz et al³ which is a reaction of gasification of soot particles at ca. 300°C. This means that the cooling section of the flue gas may play an important role in the formation of PCDD/F.

Therefore it seems that an efficient way of lowering the emissions not only of PCDD/F but also of other organic molecules, which are harmful for the environment and possible precursors of PCDD/F, is an optimisation of the (post-) combustion process to keep as low as possible the level of organics emitted.

To investigate the experimental conditions leading to a minimum emission of PCDD/F (in situ destruction), we have chosen a model reaction. The oxidation of dibenzofuran (DBF) was chosen because it has the same structure and is more stable than PCDD/F (the BDE of C-H is 425 kJ/mol and that of C-Cl is 337). Moreover it is not toxic.

Experimental Method

The experiments were performed in a quartz Continuous Jet Stirred Reactor already used in previous investigations⁴ operated at around 900°C, 300 ms, atmospheric pressure, and high dilution: 1200 ppm of DBF; the equivalence ratio was 0.7 to 7 for oxygen. Since the vapour pressure of DBF is very low we have built a special evaporating device heated at ca. 300°C. A flow of helium carries the required amount to a tubular reactor inlet where oxygen and a make-up of helium are added to the flow coming from the evaporator.

Reaction products are analysed by gas chromatography after a quench by a flow of helium. Heavy products are trapped at low temperature prior to their analysis.

Experimental Results

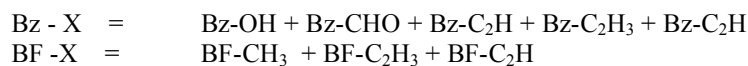
Emission Control and Abatement Technologies P084

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 : 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 concentration (cf. table 1).

table 1: products of DBF oxidation at: 900°C , 300 ms , $X_{\text{DBF}} = 1200\text{ppm}$, $X_{\text{O}_2} = 1,5\%$

in % of DBF °

CO	CH ₄	Bz	BF	IN	DBF
264	3,1	2,5	0,9	0.96	60
CO ₂	C ₂ H ₂	Bz - X	BF -X	N	DBF-OH
50	9,4	3,1	1,8	1,6	3,3



We performed a parametric study of the reaction by following the influence of reaction parameters on the conversion of dibenzofuran (xDBF). We investigated the effect of :

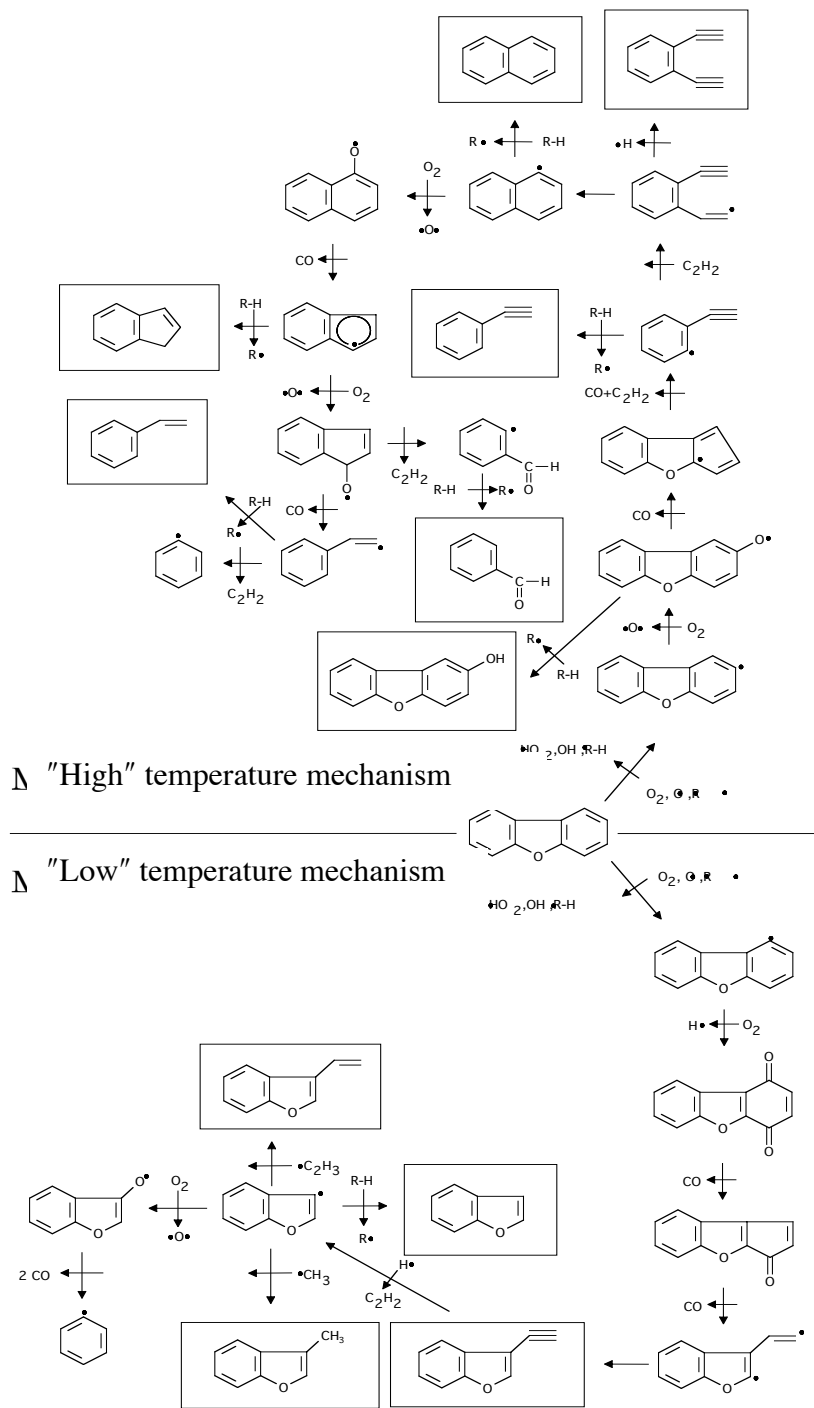
- partial pressure of dibenzofuran $x^{\circ}\text{DBF}$ (600 to 1300 ppm),
- initial concentration of oxygen ($x^{\circ}\text{O}_2$ ranging from 0,2 to 2.10 % corresponding to a richness varying from 7 to 0.7),
- temperature between 800 and 950°C,
- residence time τ between 245 and 903 ms.

Our experimental results have been used to build a reaction mechanism which will be summarised later on. It seems important to show, by studying the influence of oxygen concentration, that it is possible to destroy completely the reactant (dibenzofuran) ; all the reaction products are also completely oxidised in the following experimental conditions :

$$\tau = 900^{\circ}\text{C}, x^{\circ}\text{DBF} = 1251 \text{ ppm}, \tau = 324 \text{ ms}$$

Interpretation and Reaction Scheme

Taking into account the available literature on the oxidation reaction of aromatic compounds⁵⁻⁷ (rather limited compared to that describing the oxidation of alkanes) 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 molecules⁸.



Two parallel reaction channels can account for the reaction scheme ; the low temperature channel leads to the formation of a quinone which can give , by loss of CO an unsaturated (acetylenic) structure found as a primary product.

At higher temperature an alkany channel leads to the formation of dibenzofuranol found as a primary product.

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 were not available⁹.

Conclusion

The present study has led to a better understanding of the oxidation of dibenzofuran and to a reaction scheme which can be the basis of further studies.

Concerning the formation of PCDD/F and other undesirable organic products, our results on dibenzofurane oxidation suggest that an optimisation of the conditions of the combustion (temperature, residence time, oxygen concentration, turbulence) not only lowers the amounts of PCDD/F but also that of other products.

Acknowledgements

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