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HYPOTHETICAL ROLE OF BENZINE AS AN INTERMEDIATE IN PCDF/Ds FORMATION DURING COMBUSTION PROCESSES

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Introduction

Thermal reactions are recognized as a main source of PCDF/Ds in the environment, as PCDF/Ds might be found in the emissions of various combustion processes, independently from the fuel¹. Among different combustion sources, municipal solid waste incinerators and hazardous waste incinerators are believed to contribute the most significant share of the 'dioxin' level in the environment. Experimental research has confirmed the presence of PCDF/Ds in the combustion fumes from either low- or high-temperature waste incineration²⁻⁴. The results of the PCDF/D research are well documented for a number of process conditions, although the formation mechanism is still the subject of research and discussion. Altwicker⁵ proposed to consider the following schemes: (1) formation from carbonaceous matrices within the fly ash ('*de novo*'), (2) formation from chemically similar compounds, (3) other C, H, O, Cl combinations (which may be also classified as '*de novo*'), and (4) rapid formation/combustion intermediates. '*De novo*' processes have to involve very active substrates. We propose to consider the possibility of benzene, acting as active intermediate in PCDF/D formation. Hypothetical reactions involving benzene and aromatic hydrocarbon peroxides, which are usually the first steps of hydrocarbon oxidation are discussed in the paper.

Kinetic Background

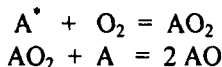
High temperature reactions in the gaseous phase show the homolytic character, so breaking of the chemical bond does not cause the separation of the electron pair. For the first order reactions, where kinetic constants achieve values of about 10^{-4} sec^{-1} , reaction half time is about 2 hours. According to calculations by Emanuel and Knorre⁶, for 15 kJ/mole, the energy of C-C bond in the ethylgroup of the ethylbenzene, $T_{1/2} = 2$ hours can be reached at 820 K. In the case of hydrogen abstraction from propylene (C-H bond scission), for $Q = 18,6$ kJ/mole, the same half-time is achieved at 1014 K. Van't Hoff principle, allows us to estimate that the increase of temperature of 120 degrees might increase the reaction rate to milliseconds.

Homolytic reactions are typical for high temperature conditions in gaseous phase, and usually free radicals act as intermediates. Recombination of complicated radicals is immediate and does not require any activation energy. In the case of atoms or very simple radicals, the presence of third contact molecule, which are able to collect the energy excess, can guarantee formation of stable product. But it seems probable, that PCDF/D synthesis occurs with the participation of complicated radicals and steric parameters play the most significant role. So, benzene and benzene peroxides might be the most suitable substrates.

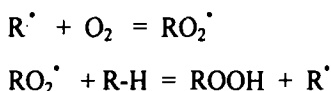
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Hydrocarbons Peroxides.

The theory of peroxides as first step intermediates during hydrocarbon oxidation, was formulated for the first time by Bach and Engler at the end of 19th century. According to this theory, peroxide molecule reacts with another molecule of the original hydrocarbon, to the hydrocarbon oxide.



Energy of the O-O chemical bond in the dioxygen molecule exceeds 3 - 4 times energy of O-O bond in peroxides. As a result, peroxides react much more easily with hydrocarbons than dioxygen. Formation of peroxides as a first step of organic substance oxidation was proved by many researches. In the present versions of peroxide theory, rather excitation of hydrocarbon molecule than oxygen molecule is postulated, according to the scheme presented by reactions:

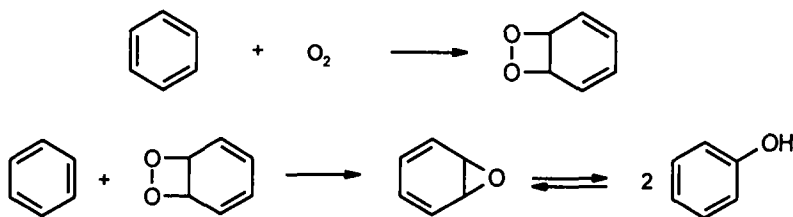


where R^{\cdot} - radical of organic substance undergoing oxidation.

The rate of the reactions the above reactions is described by the chain reaction propagation constant and the activation energy. Activation energy depends on the energy of the disrupted bond, so breaking of the C-H bond requires high energy. Methane and benzene are resistant to oxidation, although at higher temperatures (675 K or 775 K, respectively) and especially in the catalyst's presence, they may undergo oxidation at a noticeable rate (via peroxide intermediates). Activation of dioxygen molecules cannot be also excluded at higher temperatures, and might be confirmed by the formation of nitrogen oxide from oxygen and nitrogen in the combustion processes.

Benzene Peroxides

Benzene, although resistant to the oxidation, at the temperature range of 850 - 1100 K, and pressure of 0.02-0.5 MPa, can be oxidized to phenol without any catalysts. The technological phenol production, based on this mechanism, achieves the 50% efficiency. Reaction from benzene to phenol might be described by the following scheme:



Among the side products, the existence of very active ortodinone cannot be excluded:



The above peroxides might lead to the dibenzodioxins or dibenzofuranes in the one step reaction (with steric coefficient close to one).

ORGANOHALOGEN COMPOUNDS

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Benzene and Its Radicals

The existence of benzene was firstly mentioned by Wittig in 1942. He claims the existence of such intermediate like benzin in the reactions of halogenated benzenes. In the following decades, experimental evidence of benzene existence was found. Formation of both, ortho- and meta-cresols during chlorobenzene hydrolysis confirmed, according to Roberts, the temporary existence of benzene⁷. Stikes found the spectrochemical proof for benzin creation and proposed the mechanism of diphenylene formation with benzene as an intermediate⁷.

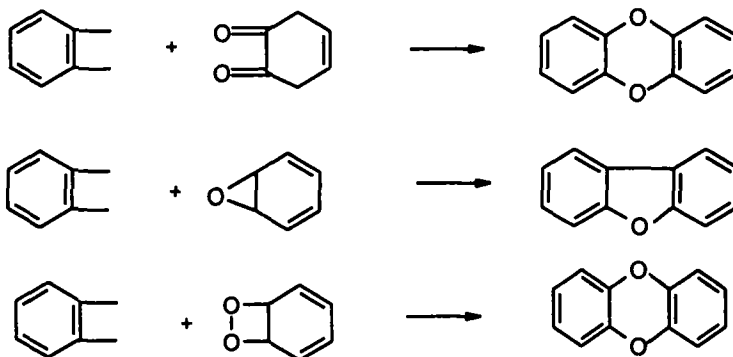


The stress caused by the trivalent bond makes the benzene molecule very unstable. Roberts claimed that stability of benzene can be compared with the stability of cyclopentene. Because of its nonstability, benzene can easily form the diradical, which can recombined with other radicals or form the dibenzofuranes or dibenzodioxines with oxides and peroxides of benzene.



Dioxins and Furans Synthesis

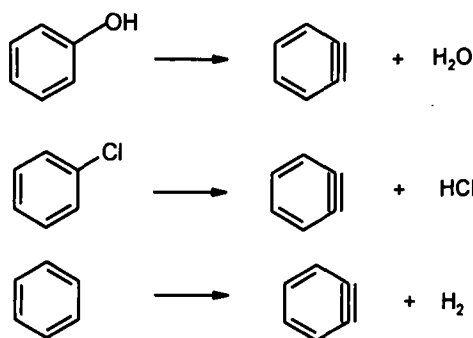
We propose the mechanism of dibenzodioxins and furans in one step reaction involving benzene diradicals, according to the scheme presented in the following reactions:



Some researchers^{5,8,9} have proposed the PCDF/D formation from chlorophenols and chlorobenzenes over fly ash (low temperature reactions), but there is lack of the data on transformation of chlorobenzenes and chlorophenols into benzene chloroderivatives, so in our model, PCDF/Ds result rather of dibenzodioxins and dibenzofurans chlorination.

Benzene, required as substrate, can be formed within the high-temperature processes. Which one of the following reactions takes place under the real conditions in the combustion gases, depends on the temperature and composition of the gaseous phase.

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As chloroorganic compounds undergo destruction during high temperature combustion, the mechanism based on benzene as the intermediate should describe better the phenomena of PCDF/D formation, than the condensation of chlorophenols. Reactions with splitting off the HCl or H₂ could occur during reagent preheating, while preheated reagents condense. But they could not occur during cooling, when reagents undergo destruction.

Conclusions

The described hypothetical mechanism is one of the attempts to explain, why PCDF/D formation is so common, easy and rapid under various combustion conditions. Benzene, essential in the proposed scheme, can be commonly found in all combustion gases, as a result of pyrolysis or synthesis from high temperature generated acetylene. Incineration temperatures are high enough to perform homolytic reactions, in which organic radicals, including benzene (benzene diradical) are generated. Benzene peroxides are also formed with high rate in all incineration processes. There is only a one step reaction from benzene and peroxides as substrates to dibenzo-p-dioxins or dibenzo-p-furans as products. Reaction does not require activation energy; steric factor is high, so rate is also very high. PCDF/Ds can be formed from chloroderivatives of benzene and peroxybenzene or via chlorination of already generated dibenzo-p-furans and dioxins. Chloride, needed for the process, might originate from either inorganic chloride compounds or combustion of chloride organic substances.

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