# ROLE OF TEMPERATURE IN FORMATION AND EMISSION OF PCDD/F

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ABSTRACT

The de-novo synthesis of PCDD/F at about 300°C in the incineration facilities involves a Deacon type catalytic reaction.

The unimolecular rate theories can give an interesting insight into PCDD/F formation, while the phase changes play an important role in formation/emission. The PCDD/F emissions are a function of exit gas temperature. PCDD/F aerosol formation through nucleation can be a problem.

## DEACON PROCESS

Until a couple of years ago PCDD/F formation was thought to take place in the combustion zone and remedial actions revolved around the three T's of combustion. In the recent years a number of researchers demonstrated that the formation of PCDD/F takes place through de-novo synthesis at about 300°C through the catalytic action of copper à la Deacon process.
The Deacon process for the catalytic oxidation of HCl to $Cl_2$ proceeds under catalytic activity of $CuCl_2$/CuCl. In the vapor phase the three molecules $CuCl_2$, CuCl, and $Cl_2$ co-exist in equilibrium governed by the constant which is a rigorous function of the temperature. It is essential that all cuprious ions are present in the melt and the vapor, while the cupric ions are present in the liquid, solid and vapor phases.

Of special importance is that the formation of $Cl_2$ is enhanced by alkali halids as shown by Sachtler and Helle (1970). Vogg et al. (1989) found a significantly high correlation coefficient between PCDD/F and C, Cl, $Cu^+$ and $Cu^{++}$ in flue gas from one MSW incineration facility.

Since metalloenzyme catalysis plays an important role in the biological reactions, it would be interesting to know whether the copper plays some role in the fate of PCDD/F in the human body.

## PCDD/F FORMATION/DESTRUCTION EQUILIBRIA

The formation of PCDD/F from carbon, chlorine, oxygen and hydrogen under copper catalytic action can be considered in the terms of unimolecular gas-phase reaction theory visualized in Figure 1.

As shown by Weber and Marti (1986) unimolecular reaction rate theories can be applied to the chlorinated dioxins and related compounds. In these theories the educt molecules are involved in a process which may be regarded as of three stages: energization, transition to an activated complex and decay of this complex into the product.

In PCDD/F formation $Cu^{+}$, $Cu^{++}$ ions plays an essential part in the chlorination step and are possibly involved in the formation of an activated complex $A^{+}$. The energy $E^{*}$ of an activated complex is distributed among all its internal degrees of freedom. The energy wells in Figure 1 can illustrate the energy levels of $A^{*}$, $A^{+}$ and B for the PCDD/F formation. The large amount of the internal energy $E^{*}$ is distributed among the vibrational and rotational degrees of freedom. A small remaining part X is the energy in the reaction coordinates. This part X gives rise to the transition of the activated complex either in the direction towards the product or back to the educt molecules.

Weber and Marti (1986) reported that a linear mechanical model along the longest axis consisting of five rigid groups for 2, 3, 7, 8 TCDD has been solved. They report frequency factor of dechlorination of $10^{8.99}$ 1/s.

As in similar reactions the formation rate equation for PCDD/F = $P * z * e^{-E/RT}$ where P = probability factor, z = collision frequency, E = activation energy, R = gas constant, and T = temperature.

PHASE CHANGE AND NUCLEATION

The reaction of PCDD/F formation may involve both gas and condensed phase reaction. Laidler (1970) developed the equations describing the reaction rates in the vapor and condensed phase:

$$K = e^{(2)} \frac{kT}{h} \exp(S/R) * \exp^{(-E/RT)}$$

where T = temperature, k, h, R = Boltzmann, Planck, universal gas constants and S, E = entropy and energy of activation. The only difference between gas and condensed phase reaction rate constants is the e is squared in the gas phase expression. The thermodynamic of PCDD/F phase changes was studied by Rordorf (1986).

Vogg and Stieglitz (1986) studied the effect of thermal treatment of fly ash on the behaviour of PCDD/F in the temperature range between 120°and 600°C. While at 300°C practically all of PCDD/F were on the fly ash, at 400°C most of them were in the gas phase.

PCDD/F's present in a gas phase can upon temperature reduction either condense on the fly ash or undergo homogenous nucleation. The expression for the critical drop size $d^*$ for a homogenous nucleation at a given saturation ratio SR, and temperature was given by Reist (1984):

$$d^* = \frac{4YM}{pRT \ln (SR)}$$

where Y = surface tension, M = molecular weight, p = density.

Since the aerosols formed through the homogenous nucleation of PCDD/F would be in the submicron range they would be very difficult to collect in the particulate control equipment. The PCDD/F condensed on the fly ash are readily collected in the particulate control equipment and can be subsequently destroyed through the thermal treatment.

DEPENDENCY OF PCDD/F EMISSION ON TEMPERATURE

The Danish Ministry of Environment study, Miljøstyrelsen (1989) on PCDD/F emission from MSW incineration showed a clear correlation between the emission and exit gas temperature (Figure 2). The correlation indicates that the exit gas temperature can serve as a surrogate for PCDD/F emissions with the several advantages including simplicity and the real time measurement.

The dependency of the emissions on the flue gas temperature is supported by the above theoretical considerations since PCDD/F formation/emission is a complex function of copper catalytic activity, formation/destruction, and evaporation/condensation equilibria all governed by the temperature.

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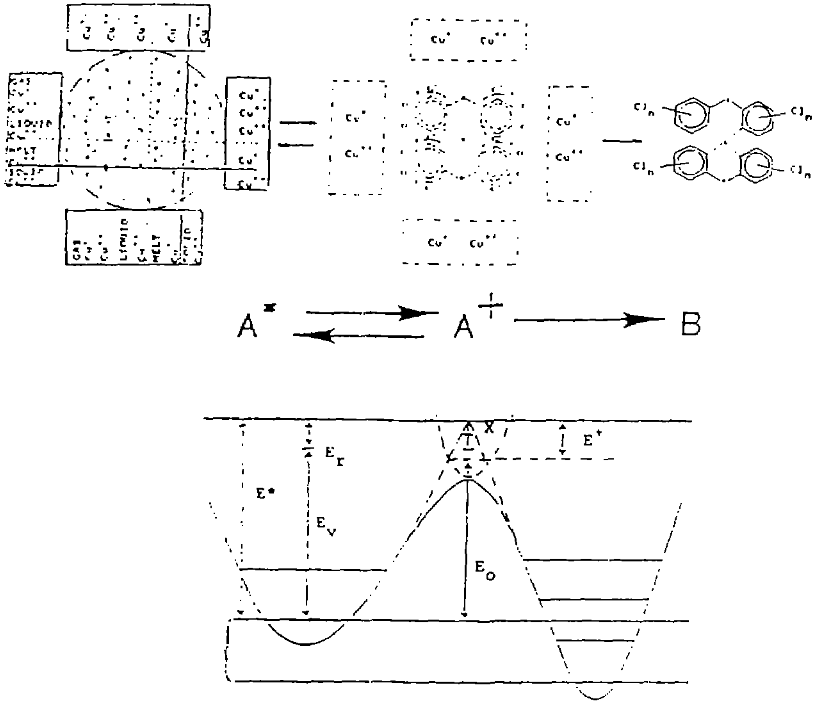


FIGURE 1 ENERGY DISTRIBUTION IN ACTIVATED COMPLEX

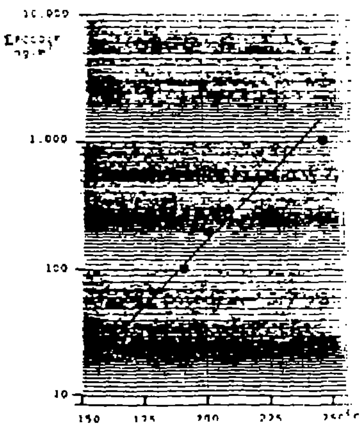


FIGURE 2

CORRELATION BETWEEN PCDD/F EMISSION AND EXIT GAS TEMPERATURE