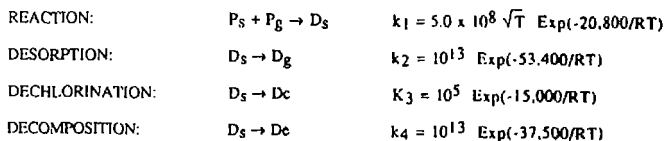# THEORETICAL ASPECTS OF PCDD/F-FORMATION IN INCINERATORS

R.K.N.V. Konduri, E.R. Altwicker, M.S. Milligan, R. Kolluri

The Isermann Department of Chemical Engineering
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

ABSTRACT: Catalytic formation of dioxins and furans is investigated theoretically based upon the incinerator observations and the laboratory data. The rates at which they form are different under laboratory and incinerator conditions. We have tried to resolve these discrepancies using a unified theory model.

INTRODUCTION: Formation of polychlorinated dioxins and furans (PCDD/F) during incineration of municipal waste is of public concern and this topic is under investigation at several leading research centers. Some pathways leading to their formation have been proposed, but quantitative data is still lacking. In a previous paper (Altwicker, et al., 1990), a global heterogeneous mechanism was proposed based upon the data available from incinerators, i.e.,

| | | |
|---|---|---|
| REACTION: | $P_s + P_g \rightarrow D_s$ | $k_1 = 5.0 \times 10^8 \sqrt{T} \ \text{Exp}(-20,800/RT)$ |
| DESORPTION: | $D_s \rightarrow D_g$ | $k_2 = 10^{13} \ \text{Exp}(-53,400/RT)$ |
| DECHLORINATION: | $D_s \rightarrow Dc$ | $K_3 = 10^5 \ \text{Exp}(-15,000/RT)$ |
| DECOMPOSITION: | $D_s \rightarrow De$ | $k_4 = 10^{13} \ \text{Exp}(-37,500/RT)$ |

The rate constants for desorption, dechlorination and decomposition were obtained empirically by matching with corresponding literature values (Dickson, et al., 1986 and Eiceman and Rghei, 1985). The activation energy for the first reaction was obtained by matching the observed temperature at which maximum PCDD formation occurs (about 300°C). This leaves the pre-exponential factor of the first reaction as a free parameter. Theoretical calculations indicated that the empirically fitted value is near the upper limit (5.0E(8)) (Zhdauov, 1988). The other important parameters are the particle diameter ($D_p$), particle loading ($N_p$), surface coverage ($\theta$) and average molecular weight of the precursor molecule which are assumed to be constant in this analysis. Sensitivity of this model to all parameters and empirically obtained pre-exponentials and activation energies is studied numerically and rationalized analytically. Due to space limitation, only the sensitivity of the model to the pre-exponential of the reaction step and the significance of the extent of the desorption are discussed.

SENSITIVITY OF THE MODEL TO $k_1$: Figure 1 shows the predicted surface and total dioxin concentration in the stack, $D_t = D_g + (Np)_{out} D_s$, gas as the pre-exponential of $k_1$ is $D_t$ as well as $D_s$ concentrations do not change with an increase in $k_1$ above $10^9$, close to the value used in our previous calculations. However, decreasing it influences the predicted values significantly.

SENSITIVITY OF THE MODEL TO THE EXTENT OF DESORPTION: Since the rate constant for the reaction step remains constant and the two solid phase and gas phase concentrations remain constant, the total amount of dioxin generated should be constant. However, the partitioning changes. We can fit this partitioning ratio to an incinerator partitioning factor we calculated (Konduri, 1989). The partitioning will have some effect on the total dioxin leaving the ESP because the gas leaving the ESP has a fixed particle loading. The asymptotics of $k_2$ leads to two limiting situations:

---

a    Little Desorption: The $k_2$ is very small, i.e., $k_1 >> k_2$. The $k_3$ and $k_4$ are small compared to $k_1$, based on the estimation of rate constants at 300°C. Under these conditions,

$$D_s/D_g = 2.8 \times 10^{-5} \quad \text{and} \quad D_t = 48.3 \text{ ng/m}^3$$

b    Significant Desorption: The $k_2$ is very large, i.e., $k_1 << k_2$. The analysis under these conditions yielded

$$D_{surface}/D_{gas} = 3.8 \times 10^{+6} \quad \text{and} \quad D_t = 750 \text{ ng/m}^3$$

In calculating $D_t$, a outlet particle loading of 0.058 gm/m$^3$ is used which is an average value observed in incinerators. The $D_s/D_g$ ratio seems to be very sensitive to the $k_2/k_1$ ratio. Moreover, large desorption also yields large total dioxin in the stack. When desorption is small, most of the dioxin settles in the ESP. On the contrary, when $k_2$ is small, due to high concentration of dioxin on the surface, the $D_t$ is very sensitive to the outlet particle loading in the gas stream leaving the ESP. The shift in desorption itself can explain an order of magnitude difference warranting a thorough study of this aspect.

However, the controversy between the laboratory and the incinerator data still prevails. There exists several orders of magnitude difference in the formation rates under incinerator conditions and the laboratory conditions. An unified theory is required to explain the differences between these data sets. We introduce a layer type solution to unify incinerator and laboratory kinetic observations

UNIFIED THEORY; LAYER TYPE BEHAVIOR: It is proposed that there exist two different time scales in the kinetics of PCDD/F formation; they are

Fast Time-Scale    Here, probably the time interval of the $O(10^{-3} - 10^{-1}$ sec$)$ dioxin formation takes place, beyond this formation reaction is quenched. This involves scaling the real time, t, with a parameter, $\epsilon$, which could be a function of the fraction of the number of vacant sites available for reaction. The fly ash formed in the combustion region is fresh and in the hotter regions remains so. As the fly ash particles enter the colder regions (the air pollution control equipment) they rapidly equilibrate with gas-phase precursor molecules (assuming fast adsorption rates) and reaction takes place very quickly. Thus a steep increase in dioxin concentration is observed in the boundary layer. If we also assume that the desorption of dioxin molecules is negligible, the number of available sites will be small after this initial time period hence making the parameter $\epsilon$ small. This situation can be expressed mathematically as

$$\frac{dY_{inner}}{d\tau} = f(k_1, P_s, P_g)$$

where $\tau = t/\epsilon$, $\epsilon = F$ (fraction of active sites available, surface structure)

Slow Time Scale    In the fast time scale, the rates of decomposition, dechlorination and desorption are very slow and have insignificant influence on the global rate of formation. As time increases, these processes will tend to dominant. Mathematically

$$\frac{dY_{outer}}{dt} = -(k_2 + k_3 + k_4) Y_{outer} \quad \Rightarrow \quad Y_{outer} = \text{Exp}[-C^*(k_2 + k_3 + k_4)^*t]$$

Theoretically, an analytical and smooth solution can be obtained by matching these two solutions $Y_{outer}$ and $Y_{inner}$ at the outer limit of the boundary layer (as $t/\epsilon \rightarrow \infty$ and $t \rightarrow 0$). The exact details of the model are under development. This solution can explain both the incinerator and the laboratory rates    The incinerator data falls into the former category and the laboratory falls in the latter category. Representative laboratory data and incinerator data are plotted in Figure 2 demonstrating the usefulness of this theory. This theory can potentially explain both catalytic and inhibitory effects

New laboratory data using selected gas phase precursors and calculations on the effect of particle size are in progress.

REFERENCES

1    Altwicker, E.R., Schonberg, J.S., R.K.N.V. Konduri, and M.S. Milligan. 1990, Haz. Waste & Haz Materials, Vol. 7, No. 1, pp. 73-88.

2.   Dickson, L.C., Hutzinger, O., Karasek, F.W. and Ozvolic, V., Int. J. Environ. Anal. Chem., Vol. 24, 55-74 (1986).

3.   Dickson, L.C., Ph.D. Thesis, Dept. of Chemistry, University of Waterloo (1987).

4.   Eiceman, G.A. and H.O. Rghei, Chapter 35 in Chlorinated Dibenzodioxins and Dibenzofurans in the Total Environment II, G. Choudhary, L.H. Keith, and C. Rappe, ed., Butterworth, Stoneham, MA, p. 515-523 (1985).

5.   Konduri, R.K.N.V., Unpublished results, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180 (1989).

6.   Zhdanov, V.P., Parlicek, J. and Knor, Z., Catal. Rev.-Sci. Eng., Vol. 30. No. 4, 501-517 (1988)

NOMENCLATURE

| | |
|---|---|
| $C$ | = constant of integration |
| $D_c$ | = dechlorinated surface dioxin molecule (ng/g) |
| $D_e$ | = decoposed surface dioxin molecule (ng/g) |
| $D_g$ | = gas phase dioxin molecule (ng/m$^3$) |
| $D_p$ | = particle diameter |
| $D_s$ | = surface dioxin molecule (ng/g) |
| $D_t$ | = total dioxin concentration (ng/m$^3$) |
| $K_1, K_2, K_3, K_4$ | = rate constants |
| $N_p$ | = number particles in the gas stream (g/m$^3$) |
| $P_g$ | = gas phase precursor molecule (molecules/cm$^3$) |
| $P_s$ | = surface precursor molecule (molecules/cm$^3$) |
| $t$ | = time |
| $T$ | = temperature |
| $Y_{inner}, Y_{outer}$ | = concentration solutions in their respective regions |

Greek Symbols

| | |
|---|---|
| $\theta$ | = surface coverage of precursor molecules |
| $\varepsilon$ | = small parameter, a function of sites available |
| $\tau$ | = time scale, $t/\varepsilon$ |

Figure 1: EFFECT OF THE PRE-EXPONENTIAL K1 ON THE PREDICTED DIOXIN CONCENTRATIONS



Figure 2: COMPARISON OF PROPOSED THEORY WITH EXPERIMENTAL DATA

▲ Incinerator

▣ Dickson (1987) (250°C)

◉ Present Work (250°C)

◉ Present Work (300°C)

▲ Present Work (350°C)