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An expanded reaction kinetic model of the CuO surface-mediated formation of PCDD/F from pyrolysis of 2-chlorophenol

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Abstract

An expanded reaction kinetic model, including 17 surface reactions, is proposed to explain the yields of PCDD/F obtained in an experimental study of the reaction of 2-chlorophenol over a CuO/silica surface. The mechanism is loosely based on the gas-phase mechanism for PCDD/F formation widely discussed in the literature. The principal differences are the impact of chemisorption of 2-chlorophenols to metal oxides on radical formation and the steric hindrance of oxygen-centered radicals on the surface inhibiting radical–radical reaction pathways that lead to formation of dibenzo-*p*-dioxin (DD). Gas-phase molecule–surface-bound adsorbate reactions are the preferred route of DD formation, while radical–radical surface reactions are the main channel for dichloro-dibenzofuran (DCDF) formation. These results suggest that the Langmuir–Hinshelwood (LH) mechanism, involving radical–radical surface reactions, and the Eley–Rideal mechanism, involving a gas-phase molecule and surface-bound adsorbate, are responsible for PCDF and PCDD formation on surfaces, respectively. The calculated yields of DCDF and DD are in reasonable agreement with experimental results.

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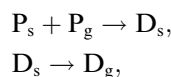
Keywords: Modeling; Dioxins; Catalysis; Radicals; Kinetics

1. Introduction

One of the major challenges in developing predictive models of particle-mediated pollutant formation in combustion systems is the construction of reliable surface, reaction-kinetic mechanisms. While the homogeneous, gas-phase chemistry of various light fuels such as hydrogen and methane is relatively well-known (Miller and Bowman, 1989; Frenklach et al., 1995), large uncertainties exist in the reaction paths of surface-mediated reaction mechanisms for even these very simple species. No detailed reaction-kinetic models of the surface mechanisms of formation of complex organics such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) have been developed. In addition to the complexity of the mechanism, a

major difficulty is the lack of reaction kinetic parameters (pre-exponential factors and activation energies) of surface reactions.

In 1985, the first attempt to model the surface-catalyzed formation of PCDD/F was performed (Shaub and Tsang, 1985). A two-step heterogeneous mechanism was proposed to explain the levels of PCDDs observed in flue-gases of combustion systems:



where P is precursor, D is dioxin, the subscript “s” denotes a surface, and the subscript “g” denotes the gas-phase. This mechanism resembles the so-called Eley–Rideal (ER) mechanism rather than the Langmuir–Hinshelwood (LH) mechanism in which both reactants are associated with the surface (Altwicker et al., 1990; Milligan and Altwicker, 1996b; Huang and Buekens, 2000).

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A significant adjustment to the kinetic parameters of this mechanism and an extended, four-step global scheme was subsequently proposed (Altwicker et al., 1990). These new steps were:

$D_s \rightarrow \text{Pro}$ (products of dechlorination),

$D_s \rightarrow \text{DPro}$ (decomposition products).

More recently a modified catalytic model to explain PCDD formation on fly-ash surfaces was suggested (Huang and Buekens, 2000). This four-step global model was based on the assumption that coupling of two chlorophenol molecules adsorbed on a fly-ash surface forms PCDD through a LH-type mechanism:

$P + s \rightarrow P_s$,

$P_s \rightarrow P + s$,

$P_s \rightarrow \text{decomposition product}$,

$P_s + P_s \rightarrow \text{PCDD}$.

An expression for PCDD formation was derived using relevant kinetic parameters. A single step, global mechanism based on the precursor mechanism has also been proposed to explain PCDD/F emissions from solid waste incinerators (Stanmore, 2002, 2004).

In this manuscript, we report the development of a numerical, multiple-step, reaction kinetic surface-model based on experimental data for the surface-mediated (5% CuO/SiO₂) conversion of 2-monochlorophenol (2-MCP) to dichlorodibenzo-*p*-furan (DCDF) and dibenzo-*p*-dioxin (DD) under pyrolytic conditions (Lomnicki and Dellinger, 2003a). The performance of the reaction kinetic model is assessed by comparing the numerical predictions with experimental measurements using the SURFACE CHEMKIN (version 3.7.1) code (Kee et al., 2002). SURFACE CHEMKIN and other similar surface codes have been used successfully to develop surface reaction kinetic models of various chemicals, e.g., the catalytic combustion of methane (Hickman and Schmidt, 1993; Deutschmann et al., 1994, 1996; Raja et al., 2000) or hydrogen (Aghalayam et al., 2000) on metal surfaces (mostly Pt and Pd).

Our results support the validity of previously published mechanism and provides new insight concerning the formation of PCDD/Fs in combustion processes by successfully reproducing the high yields of formation of PCDD/F at low temperatures that cannot be explained using a purely gas-phase model (Khachatryan et al., 2003a,b).

2. Model development

Four tenets were used in the development of our reaction kinetic model:

1. The order of magnitude of kinetic parameters (especially pre-exponential factors) were based on typical values from surface transition-state theory (Krylov et al., 1972; Boudart and Djega-Mariadassou, 1984; Zhdanov, 1988).

2. Modifications to the pre-exponential factors and the activation energies were based on comparison to analogous reactions and fit to experimental results of other researchers (Shaub and Tsang, 1985; Altwicker et al., 1990; Huang and Buekens, 2000).
3. Gas-phase reaction kinetic parameters could be adapted to surface conditions. Activation energies for the gas-phase reactions were considered upper limits for the analogous surface reaction. Decreasing the activation energy of the corresponding surface reaction is a common approach (Walas, 1989; Stanmore, 2002).
4. Kinetic parameters estimated based on the assumptions 1–3 were fit to the experimental rates of formation of PCDD and PCDF in our experiments.

Using this framework, a 17 step surface expanded model was developed by optimizing the kinetic parameters in the reaction mechanism. The detailed mechanism and reaction parameters are depicted in Table 1. Each reaction expression is in the SURFACE CHEMKIN format (PLUG Application) (Kee et al., 2002). The SURFACE CHEMKIN has broad capabilities to solve complex chemical and physical problem.

For clarity, chemical models of the surface reactions between adsorbed molecules and bound radicals or between two bound radicals are presented for each reaction in Section 3.1. According to the SURFACE CHEMKIN formalism, two types of species are defined in this study: gas-phase (no special designation accompanied to the chemical symbol, for instance H₂O, C₁₂H₈O₂, etc.) and surface (denoted by “(S)”).

The dominant reactive surface site is a hydroxyl group attached to copper ions, CuOH(S, II) (Alderman et al., 2003) which is denoted as OH(S). Bivalent copper on the outermost layer of the solid (SiO₂) is covered by surface-bound hydroxyl groups (see Section 3.1). A terminal oxygen ion on an adjacent copper surface site, CuO[−](S, II), is depicted as O(S) in the kinetic scheme (Table 1, Reactions 8, 12 and 13). During adsorption on OH(S), 2-MCP is converted to a surface species designated as C₆H₄OCl(S) located on the same copper atom. The OH(S) has been replaced by C₆H₄OCl(S) in the outer surface layer.

For catalytic reactions, rates that are usually given in terms of “weight of catalyst” should be converted to an “effective area of catalyst” (CHEMKIN requirement) based on the surface area of the catalyst. The rates are expressed as per unit area, based on the site density for the SITE phase, as given in the surface chemistry input file. For one SITE phase solution (the number of sites, $n = 1$) the number of moles of species k on the surface, is given by

$$N_k = Z_k(n)\Gamma_n A,$$

where $Z_k(n)$ is the site fraction (fraction of sites occupied by species k in phase n) of species k on surface site n (in our case $n = 1$ and surface site is CuOH(S, II) or OH groups bound to copper); Γ_n is the density of sites occupied by species k (in mol/cm²); and A is the catalyst surface

Table 1

Core model for the surface catalyzed formation of PCDD/F

Surface reactions ^a	$k = AT^n \exp(-E/RT)^b$			Units
	A	n	E	
1. $C_6H_4OHCl + OH(S) \Rightarrow C_6H_4OCl(S) + H_2O$	1.00E + 12	0.0	21 000.0	cm ³ /mol s
2. $C_6H_4OCl(S) + H_2O \Rightarrow C_6H_4OHCl + OH(S)$	1.00E + 13	0.0	25 000.0	cm ³ /mol s
3. $C_6H_4OCl(S) \Rightarrow C_6H_4OCl(S, en)$	1.00E + 12	0.0	0.0	s ⁻¹ (electron-transfer)
4. $C_6H_4OCl(S, en) \Rightarrow C_6H_4OCl(S, ke)$	5.00E + 12	0.0	0.0	s ⁻¹
5. $C_6H_4OCl(S, ke) \Rightarrow C_6H_4OCl(S, en)$	7.00E + 13	0.0	0.0	s ⁻¹
<i>Furan formation, LH mechanism</i>				
6. $2C_6H_4OCl(S, ke) \Rightarrow C_{12}H_8O_2Cl_2(S)$	1.00E + 21	0.0	22 000.0	cm ² /mol s
7. $C_{12}H_8O_2Cl_2(S) \Rightarrow C_{12}H_8OCl_2 + H_2O$	4.00E + 12	0.0	33 500.0	s ⁻¹
<i>Precursor for dioxin formation</i>				
8. $C_6H_4OCl(S, ke) + O(S) \Rightarrow C_6H_4O_2Cl(S, oe)$	1.00E + 21	0.0	0.0	cm ² /mol s
9. $C_6H_4O_2Cl(S, oe) \Rightarrow C_6H_3ClOOH(S)$	1.00E + 13	0.0	18 000.0	s ⁻¹
<i>Dioxin formation, ER mechanism</i>				
10. $C_6H_3ClOOH(S) + C_6H_4OHCl \Rightarrow C_{12}H_8O_3Cl(S) + HCl$	6.0E + 17	0.0	19 000.0	cm ³ /mol s
11. $C_{12}H_8O_3Cl(S) \Rightarrow C_{12}H_7O_3(S) + HCl$	1.00E + 13	0.0	20 000.0	s ⁻¹
12. $C_{12}H_7O_3(S) \Rightarrow O(S) + 8C + 0.5CO + 0.5CO_2 + 1.5C_2H_4 + 0.5H_2O$	3.00E + 12	0.0	37 000.0	s ⁻¹
13. $C_{12}H_7O_3(S) \Rightarrow C_{12}H_7O_2 + O(S)$	5.00E + 13	0.0	35 500.0	s ⁻¹
14. $C_{12}H_7O_2 + C_6H_4OHCl \Rightarrow C_{12}H_8O_2 + C_6H_4OCl$	3.00E + 13	0.0	8600	cm ³ /mol s
<i>Dioxin formation, LH mechanism</i>				
15. $2C_6H_4OCl(S, en) \Rightarrow C_{12}H_8O_2Cl(S) + Cl$	3.00E + 20	0.0	25 000.0	cm ² /mol s
16. $C_{12}H_8O_2Cl(S) \Rightarrow C_{12}H_8O_2 + Cl$	1.00E + 13	0.0	18 000.0	s ⁻¹
17. $C_6H_4OCl(S) \Rightarrow C_2H_2 + CO + 3C + HCl + 0.5H_2$	1.00E + 12	0.0	30 000.0	s ⁻¹

^a (S) – surface species; (S, ke), (S, en) – keto- and enol-mesomers of surface-bound 2-chlorophenoxyl radical, respectively and (S, oe) – keto-mesomer bound to a surface oxygen.

^b A units: mole-cm-s-K and E units: cal/mol. Each rate constant is discussed in the text.

area. The surface site fractions of species $Z_k(n)$ are guessed and do not affect the final solution if initial guesses for each species are consistent (Kee et al., 2002). To avoid “inconsistent initial guesses” as defined within the CHEMKIN kinetic package, we first performed an AURORA well-stirred reactor simulation under similar conditions to obtain starting guesses for the surface site fractions. For the catalyst of 5% CuO/SiO₂ (1 g) with surface area of $A = 500 \text{ m}^2/\text{g}$, the density of sites, Γ_m , equals $\sim 1.65 \times 10^{-10} \text{ mol/cm}^2$ (the density of the terminal hydroxyl groups bound to copper). All these data are included in SURFACE CHEMKIN surface input file.

The input conditions for the PLUG input file were the same as for our previously reported experimental reaction conditions: [2-chlorophenol] = 88 ppmv in a helium atmosphere and a flow rate of 1.0–1.5 cm³/min (to maintain a constant contact time with the catalyst bed of $\sim 0.2 \text{ s}$ over a temperature range of 473–723 K) (Lomnicki and Dellinger, 2003a).

The outputs of the model were the final concentrations of all species included in the reaction mechanism (Table 1). In SURFACE CHEMKIN, a reaction rate has units of mol/(cm² s). The rate constants of ER-type reactions have units of cm³/mol s, and LH-type reactions have units of cm²/mol s. For a reaction involving only one surface-species, CHEMKIN assigns units of s⁻¹ (Kee et al., 2002).

This scheme is developed along several assumptions to satisfy SURFACE CHEMKIN demands: (1) a perfect cat-

alyst surface; (2) no mass diffusion limitations, not only by cross-section, but also through pores; (Lomnicki and Dellinger, 2003a,b), (3) plug flow over the catalyst bed, and (4) a maximum of monolayer surface coverage.

One of the most important limitations of the CHEMKIN package is low surface coverage of the catalyst. Although estimation of the surface coverage of potential precursors involved considerable uncertainty, we believe that for our experimental conditions, 5% CuO is spread over a large area of SiO₂ (500 m²/g) and low surface coverage of 0.001–0.0001 is achieved. This is a typical surface coverage range for incinerator fly-ash (Altwick et al., 1990).

The CHEMKIN package requires input of thermodynamic data to calculate reverse reaction rates from input forward reaction rates (Kee et al., 2002). However, we assumed irreversible reactions, and thermodynamically calculated reverse rates were not used in our model. To execute the program for our scheme of irreversible reactions, a dummy thermodynamic data set was used for all of the surface species so that CHEMKIN would process the input file.

3. Results and discussion

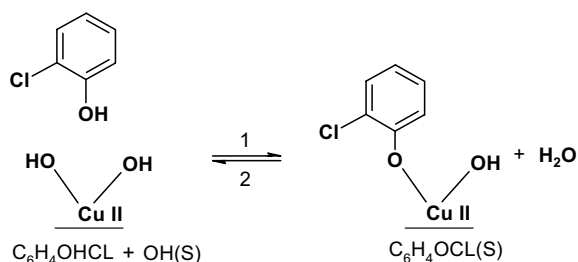
We first describe the nature of the reactions included in our model and the processes by which the reaction kinetic

factors were assigned. We then compare the results of the model with experiment.

3.1. Surface reactions

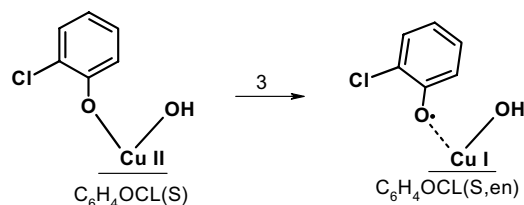
The mechanism consists of four sets of reactions that describe key processes: (1) adsorption–desorption of reactant 2-MCP (Reactions 1 and 2); (2) surface reactions of adsorbed species (Reactions 3–5, 8, and 9); (3) formation of “dioxin” products, viz. 4,6-dichlorodibenzofuran, DCDF, (Reactions 6–7) and non-chlorinated dioxin, DD, (Reactions 10, 11, and 13–16), and (4) formation and desorption of major “non-dioxin” products, viz. CO, CO₂, HCl, H₂, H₂O etc., (Reactions 12 and 17).

The adsorption Reactions 1 and 2 in Table 1 are treated as a simple reversible chemisorption–desorption processes (Milligan and Altwicker, 1996a,b). The 2-chlorophenol reactant is converted to a chemisorbed 2-chlorophenolate via Reaction 1.



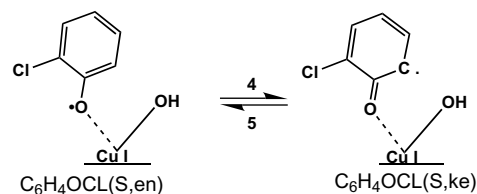
For a single-center adsorption of molecular species, (Milligan and Altwicker, 1996b) the range of variation of pre-exponential factors is $A = 6.0 \times 10^8$ – 6.0×10^{12} cm³/mol s (Krylov et al., 1972). The activation energy for this process has been previously assigned as $E_a = 21\,000$ cal/mol (Huang and Buekens, 2000). The reverse reaction, Reaction 2, can be considered an example of a unimolecular desorption reaction in presence of a water with $A \sim 1.0 \times 10^{13}$ cm³/mol s (Krylov et al., 1972). The desorption activation energy of chlorophenol from fly-ash surfaces has been previously estimated to be $E_a = 35\,000$ cal/mol (Huang and Buekens, 2000). We assign A and E values for Reactions 1 and 2 as $A_1 = 1.0 \times 10^{12}$ cm³/mol s, $E_1 = 21\,000$ cal/mol, $A_2 = 1.0 \times 10^{13}$ cm³/mol s, and $E_2 = 25\,000$ cal/mol.

The initial surface reaction of the adsorbed 2-chlorophenol is Reaction 3, which is an electron transfer reaction (redox reaction) in the adsorbed layer. Note that most transition-metal oxides are redox-active (Henrich and Cox, 1994). As an intramolecular process in the adsorbed layer an pre-exponential factor of $k_3 = A = 1.0 \times 10^{12}$ s^{−1} is assigned, which is within the range of 10^{10} – 10^{13} s^{−1} typically assigned for such reactions (Krylov et al., 1972).



Using FTIR absorption spectrometry and XANES, we have performed experimental studies that conclusively demonstrate that chemisorbed 2-chlorophenolate is rapidly 100% converted to the 2-chlorophenoxy radical with concomitant 100% reduction of Cu(II) (Alderman et al., 2003). The reaction is sufficiently fast to be considered barrierless with an assigned $E_a = 0$ cal/mol. This reaction does not represent the near complete rupture of the Cu–O bond and desorption of a chlorophenoxy radical, which would of course have significant activation energy. We have in fact demonstrated using EPR spectroscopy that the phenoxy radical is formed and stays associated with the surface of the CuO (Dellinger et al., 2007). This suggests that the radical is still somehow bonded to the surface even though the parent phenolate has reduced Cu(II) to Cu(I). Although this is an unusual reaction, our experimental evidence for it is strong, and the assignment of the kinetic rate parameters are reasonable and justified.

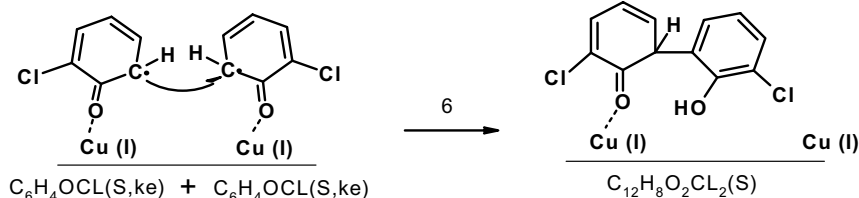
Reactions 4 and 5 are considered as reversible, surface, keto–enol equilibrium mesomerization (“isomerization” between resonance structures) reactions:



In valence bond formalism, resonance structures do not truly exist and are only meant as a way of envisioning structures and stabilization of these structures through resonance. Thus, Reactions 4 and 5 are not true chemical reactions. Nonetheless, a gas-phase, oxygen-centered phenoxy radical may be more accurately depicted on the surface as a carbon centered radical. Furthermore, our experimental data, as well as that of other researchers, clearly suggest that the phenoxy radical sometimes reacts in a manner more consistent with a carbon-centered radical, and at other times, more consistent with an oxygen-centered radical. One could also envision Reactions 4/5 as reversible tautomerization reactions involving the CuOH hydrogen atom that forms the molecular keto/enol-tautomer of 2-chlorophenol and a Cu–O·. The kinetic parameters for Reactions 4 and 5 were assigned as barrier-

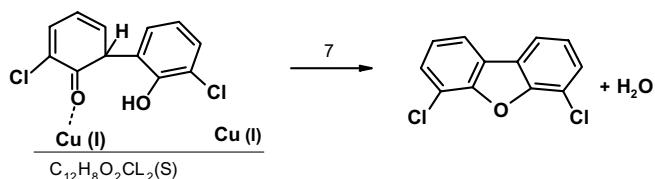
less with A_4 and A_5 of $5.0 \times 10^{12} \text{ s}^{-1}$ and $7.0 \times 10^{13} \text{ s}^{-1}$, respectively.

Reactions 6 and 7 are the radical–radical pathways for PCDF formation on the surface in analogy to the gas-phase reactions (Born et al., 1989; Sidhu and Dellinger, 1997; Weber and Hagenmaier, 1999; Wiater and Louw, 2001; Khachatryan et al., 2004). Indeed the experimental data for 2-MCP adsorption over CuO/silica clearly indicate that there is a large population of stable, carbon-centered radicals on the surface of copper oxide (Lomnicki and Dellinger, 2003b). The recombination of two surface bound, carbon-centered radicals, Reaction 6, is an LH-type of reaction (bimolecular reaction in the adsorbed layer). The two reaction partners likely originally adsorbed at non-vicinal surface sites. The species then undergo surface migration to vicinal sites where they can react.



The coupling of these radicals resembles the Ullmann type of reaction of halogenated (fluoro-, iodo-substituted) phenyl radicals observed on Cu(111) crystal surfaces (Meyers and Gellman, 1995). The coupling of the adsorbed phenyl groups is the rate limiting step in this pathway, for which the activation energy ranges from 20 000 to 27 000 cal/mol (Meyers and Gellman, 1995). Since the pre-exponential factor for similar reactions is in the range of 6.0×10^{22} – $6.0 \times 10^{15} \text{ cm}^2/\text{mol s}$, (Krylov et al., 1972) we assigned a reaction rate constant $k_6 = 1.0 \times 10^{21} \exp(-22\,000/RT \text{ cal/mol}) \text{ cm}^2/\text{mol s}$ for the surface–radical coupling process.

The surface-bound $\text{C}_{12}\text{H}_8\text{O}_2\text{CL}_2(\text{S})$ can be further converted to 4,6-DCDF by a concerted elimination of water, Reaction 7 (Lomnicki and Dellinger, 2003a,b). A two-step process where hydrogen abstraction is followed by hydrogen displacement is also possible but it not included in our mechanism.



The keto–enol adduct can be converted to PCDF but with a high activation energy of $\sim 60\,000 \text{ cal/mol}$ which

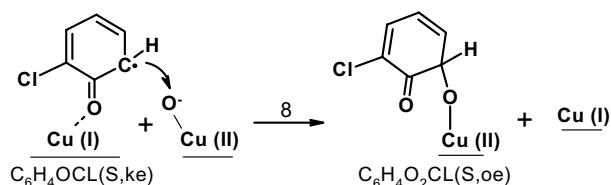
minimizes the possibilities of gas-phase formation of PCDF through intramolecular rearrangements. The difficulties of such types of conversion, i.e. conversion of bis-enol adducts into dibenzofurans in the gas-phase, has been previously discussed (Wiater et al., 2000). It is reasonable that the surface-assisted conversion, especially for the keto–enol form, Reaction 7, has a much lower activation energy. As a unimolecular reaction on an adsorbed layer, a pre-exponential factor of $4.0 \times 10^{12} \text{ s}^{-1}$ was chosen from the range of 10^{10} to 10^{13} s^{-1} (Krylov et al., 1972). An activation energy of $E_a = 33\,500 \text{ cal/mol}$ was assigned for this key reaction to fit with experimental data (*vide supra*).

We have not included an ER mechanism for PCDF formation in our model. The oxygen-centered $\text{C}_6\text{H}_4\text{OCl}(\text{S, ke})$ radical can be attacked by a gas-phase 2-chlorophenol through displacement of the gas-phase hydroxyl group by

the surface-bound $\text{C}_6\text{H}_4\text{OCl}(\text{S, ke})$ radical. *Ab-initio* calculations for the analogous gas-phase displacement of hydroxyl of phenol by an oxygen-centered phenoxyl radical mesomer indicate that the process is endothermic by $\sim 60\,000 \text{ cal/mol}$ with potentially higher activation energy. Even if the surface can decrease the barrier of such a reaction, this alternative channel does not appear to be important because it will only form 1-chlorodibenzofuran which was experimentally observed in trace quantities.

Carbon-centered surface radicals may undergo further surface transformations through interaction with the terminal oxygen ion of adjacent copper oxide sites, as depicted in Reaction 8. We consider various types of electrophilic activated oxygen species (O_2^- , O_2^{2-} , O^- , O^{2-}) incorporated as structural (“lattice”) oxygen as models of the adjacent oxide (Centi et al., 2001). These oxygen species are in a dynamic equilibrium with the bulk species and are stabilized by co-ordination with surface metal ions. At high temperatures (above 200–250 °C), these species may not be readily distinguishable from one another due to their facile interconversion. The electrophilic O_2^- , O^- , etc. species are reactive and, for instance, can attack alkenes inducing C–C bond rupture and formation of oxidized products including CO and CO_2 (Centi et al., 2001). The O_2^- (superoxide) is the most commonly reported species, and its formation is detected for a broad range of oxides and reaction conditions (Che and Tench, 1982). We depict these adsorbed oxygen species as Cu(II) (O^-) in the figures and O(S) (as adsorbed oxygen species) in the reaction model.

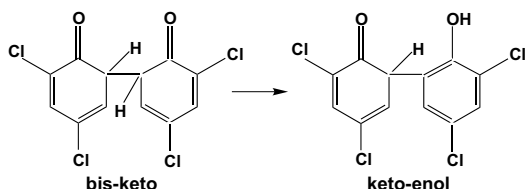
Similar reactions have been previously proposed to explain the formation of 2-chlorocatechol and 2-chloroquinone (Lomnicki and Dellinger, 2003b). Reaction 8, reaction of the carbon-centered radical with a surface O^- (Centi et al., 2001), is treated as a fast, barrierless surface reaction with a pre-exponential factor of $1.0 \times 10^{21} \text{ cm}^2/\text{mol s}$ that was selected from the range of 6.0×10^{15} – $6.0 \times 10^{22} \text{ cm}^2/\text{mol s}$ quoted in the literature (Krylov et al., 1972).



The $\text{C}_6\text{H}_4\text{O}_2\text{CL(S, oe)}$ product can further react following two pathways: (1) to form chlorinated quinone and catechol (Lomnicki and Dellinger, 2003a) (not addressed in this model) or tautomerize to surface species $\text{C}_6\text{H}_3\text{CLOOH(S)}$ (Reaction 9) as a precursor for DD formation (Reactions 10–14).



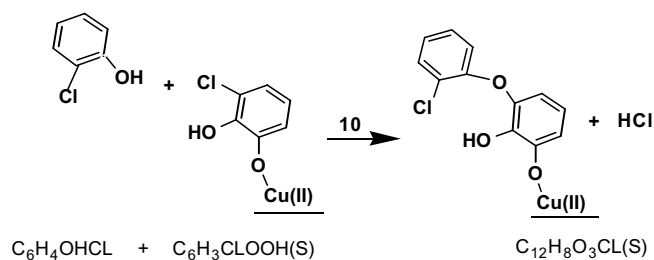
Ab initio calculations for the analogous gas-phase reaction, yield an activation energy of 38000 cal/mol for the intramolecular tautomerization (hydrogen transfer) reaction that converts the bis-keto tautomer to the keto–enol tautomer (Khachatryan et al., 2004).



We assigned a considerably lower value of 18000 cal/mol to the surface-assisted, Reaction 9 to fit the experimental yield of DD.

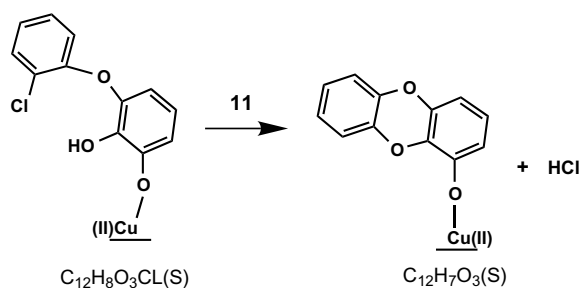
Competitive ER and LH mechanisms for DD formation (Altwicker et al., 1990; Milligan and Altwicker, 1996b; Huang and Buekens, 2000) were both considered in our model. It is much easier to draw surface-mediated pathways of formation of PCDDs via LH pathways. However, our previously published experimental studies of the oxidation and pyrolysis of 2-MCP over a CuO/silica surface

clearly indicated that PCDDs were formed by ER pathways, while PCDFs were formed by a LH pathway. ER pathways are discussed in the literature as alternative pathways to the much more common LH pathways for some reactions (Janssen et al., 1987; Jin and Chu, 2006) occurring by collision of gas-phase molecules with the adsorbed species with “disturbed” electronic configurations (Boudart and Djega-Mariadassou, 1984). As a starting point, we considered the rate parameters for the formation of the surface-bound “pre-dioxin” via an ER pathway (Reaction 10) that has been previously estimated as $k_{10} = 275(T/973)^{1/2} \exp(-11500 \text{ cal/mol}/RT)$ (Shaub and Tsang, 1985). This reaction involves a concerted elimination of HCl resulting in the formation of an ether linkage.



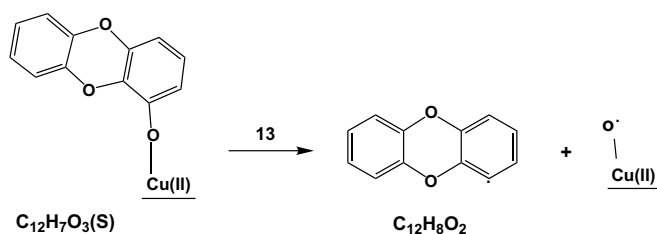
However, to fit experimental data, values of $5.0 \times 10^8(T)^{1/2} \text{ cm}^3/\text{s}$ (which is six orders of magnitudes greater than the previous estimate) and 20800 cal/mol were assigned in subsequent models for the pre-exponential factor and activation energy, respectively (Altwicker et al., 1990). The latter pre-exponential factor is close to the upper limit for the pre-exponential factor estimated from surface theory of $6.0 \times 10^{17} \text{ cm}^3/\text{mol s}$ (Zhdanov, 1988). Based on these considerations, a rate constant of $k_{10} = 6.0 \times 10^{17} \exp(-19000 \text{ cal/mol}) \text{ cm}^3/\text{mol s}$ was assigned in our model for Reaction 10. These rate parameters are actually consistent with displacement of a chlorine atom on the surface-bound phenolate by a gas-phase phenoxyl radical. In practice, it would be difficult to distinguish whether the reaction involves gas-phase phenoxyl radicals or gas-phase phenols, and it is not particularly useful to speculate on which the actual reacting species is since both reactions would yield the same product. Furthermore, since the experimental data clearly indicates an ER mechanism is active for PCDD formation, there are few other choices available as reactants involved in PCDD formation.

Reaction 11 resembles the process of dioxin formation from chlorophenyl-hydroxyphenoxy ether in ST model and 45000 cal/mol was proposed for the activation energy of the gas-phase reaction (Shaub and Tsang, 1983). The activation energy of surface dioxin formation was fit to the experimental data as 20000 cal/mol which is consistent with a lowering of the gas-phase activation energy by association with the surface.



The pre-dioxin species adsorbed on the surface through the oxygen, $\text{C}_{12}\text{H}_7\text{O}_3\text{(S)}$ can be released from the surface by thermal degradation. Such reactions are known and described in literature (Ihm and White, 2000). In the case of adsorbed phenol, release can be through breaking carbon-carbon bonds to form CO and CO_2 , or rupture of the carbon-oxygen bond to form phenyl (subsequently benzene) (Ihm and White, 2000). The first case corresponds to the decomposition of chemisorbed pre-dioxins in our model, Reaction 12 (Table 1). The assigned pre-exponential factor for the decomposition of adsorbed pre-dioxins, $3.0 \times 10^{12} \text{ s}^{-1}$, and activation energy, 37 000 cal/mol, were fitted to the experimental data based on an initially assigned activation energy value of 40 000 cal/mol reported for decomposition of PCDDs on fly-ash (Altwicker et al., 1990).

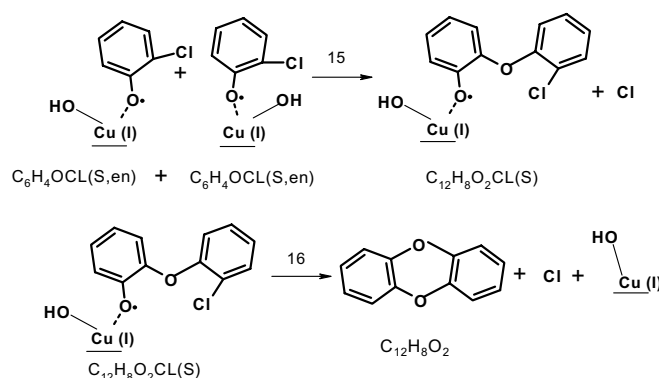
The second possibility produces DD in our model via Reaction 13 and Reaction 14 (not shown) in which the gas-phase $\text{C}_{12}\text{H}_7\text{O}_2$ radical formed in Reaction 13 abstracts a hydrogen atom from a gas-phase 2-MCP molecule to form the molecular DD. In Reaction 13, we depict a carbon-oxygen bond rupture to form the DD radical. Hydrolysis of the Cu-O-DD bond seems more probable and probably does occur, result in the formation of a hydroxylated DD. However, our experimental studies clearly demonstrate that DD is chemisorbed to the surface at lower temperatures and is desorbed as DD at higher temperatures (Lomnicki and Dellinger, 2003a). Thus based on our experimental data, the C-O bond rupture depicted in Reaction 13 appears to occur, and this type of reaction has been reported for phenol with the subsequent formation of benzene (Ihm and White, 2000). The reaction path preference depends on various factors such as geometry of adsorption, strength of the metal-oxygen bond, surface coverage, etc. (flat adsorption promotes C-C cleavage, while perpendicular adsorption promoted C-O cleavage). Both reactions usually occur with different yields. In our model, homolytic C-O bond rupture will produce DD by Reactions 13 and 14 (see illustration and Table 1).



The resulting Cu(II)O^\bullet species is quickly converted to Cu(II)O^- (Centi et al., 2001) which we assigned in the model as O(S), Table 1. The rate parameters for Reaction 13 are based on fits with experimental data with $E_{13} = 35\,500 \text{ cal/mol}$ and $A_{13} = 5.0\text{E} + 13 \text{ s}^{-1}$.

After desorption the radical species $\text{C}_{12}\text{H}_7\text{O}_2$ is converted to dioxin, Reaction 14 (Table 1) by H abstraction reaction in the adsorbed layer. The rate parameters were assumed to be close of reaction of phenyl radicals with aromatics, which range from 10^9 to $10^{10} \text{ cm}^3/\text{mol s}$ near room temperature (Fahr and Stein, 1988). Taking activation energy 8600 cal/mol from the reaction of phenyl with methane (NIST Chemical Kinetics Database, 1998), the assigned reaction rate parameters of Reaction 14 are $3.0\text{E} + 13 \exp(-8600 \text{ cal/mol}/RT) \text{ cm}^3/\text{mol s}$, where the pre-exponential factor was obtained from fits to the experimental data.

The LH mechanism for formation of DD is described by Reactions 15 and 16.



These reactions are analogous to the gas-phase reactions: radical-radical recombination with formation of an ether adduct and further Smiles-type rearrangement of the adduct to form DD, respectively (Wiater and Louw, 2001; Louw and Ahonkhai, 2002; Khachatryan et al., 2003a,b). Reaction 15 again resembles the Ullman-type of reaction of halogenated (fluoro-, iodo-substituted) phenyl radicals on the surface (Meyers and Gellman, 1995). Although, one might reason that the activation energy of this reaction on a surface should be significantly reduced from the analogous reaction in the gas-phase, we assigned high activation energy of 25 000 cal/mol in comparison with the Reaction 6 for the following reasons:

1. Our experimental studies demonstrated that the formation of DD proceeded by an ER pathway rather than an LH pathway as depicted in Reaction 16 (Lomnicki and Dellinger, 2003a).
2. The experimental results have shown a distinct preference for reactions involving carbon-centered, keto radicals $-\text{C}_6\text{H}_4\text{OCl(S, ke)}$ (Lomnicki and Dellinger, 2003b). This suggests that they are more favorable structure on the surface.

3. For enol-radicals, $C_6H_4OCl(S, en)$, the site of the unpaired electron is below the ring and near the surface which represents a steric restraint toward radical–radical recombination reactions (Reaction 15) in comparison to keto-radicals, $C_6H_4OCl(S, ke)$, in which the unpaired electron is located on a more readily accessible ortho-carbon (Reaction 6).

For these reasons, the rate constant for Reaction 15 is assigned a value of $3.0 \times 10^{20} \exp(-25000 \text{ cal/mol}) \text{ cm}^2/\text{mol s}$ for surface-bound 2-chlorophenoxy radicals. Actually, two reactions are possible involving two different forms of the radical: (1) coupling of two oxygen centered phenoxy radicals yielding DD (Table 1 and discussed above), and (2) the coupling of oxygen- and carbon-centered radicals leading to 1-MCDD (not discussed here), both of which were observed experimentally.

The conversion of the adsorbed ether adduct to DD, Reaction 16, occurs according the Smiles rearrangement mechanism with a fitted activation energy of 18000 cal/mol for the surface-mediated reaction versus a previously proposed gas-phase activation energy of $\sim 36500 \text{ cal/mol}$ (Khachatryan et al., 2003b).

Reaction 17 is a decomposition of adsorbed $C_6H_4OCl(S)$. Activation energy 40000 cal/mol has been suggested previously for the decomposition of adsorbed chlorophenoxy species in the kinetic modeling of PCDD formation from chlorophenol catalyzed by incinerator fly-ash (Huang and Buekens, 2000). Best fits for our modeling scheme resulted in an activation energy for Reaction 16 of 30000 cal/mol.

For simplicity we do not consider further conversion reactions beyond the decomposition of DCDF and DD or their precursors.

3.2. Experimental vs. modeling results

The results of the SURFACE CHEMKIN modeling calculations and experiment (Lomnicki and Dellinger, 2003a) are compared in Fig. 1. The results are fit as a function of reaction temperature which is a much more stringent test of the model than the usual comparison as a function of reaction time. An excellent fit was obtained for DCDF over a wide temperature range of 500–673 K. DD yields agreed well with experimental results from 500 to 613 K but deviated by up to a factor of 2 at higher temperatures. The agreement of the model at lower temperatures but not at higher temperatures suggests that there may be an additional mechanism of formation at higher temperature not included in the model. For example, *de novo* formation from carbon formed in the pyrolysis of 2-MCP at higher temperatures may make a significant contribution.

A “brute force” sensitivity analysis of the model was performed in which the rate coefficients were simply multiplied by a factor of two and the percent change in DD/DCDF yields at different temperatures was calculated (Khachatryan et al., 2003b). The most sensitive reactions

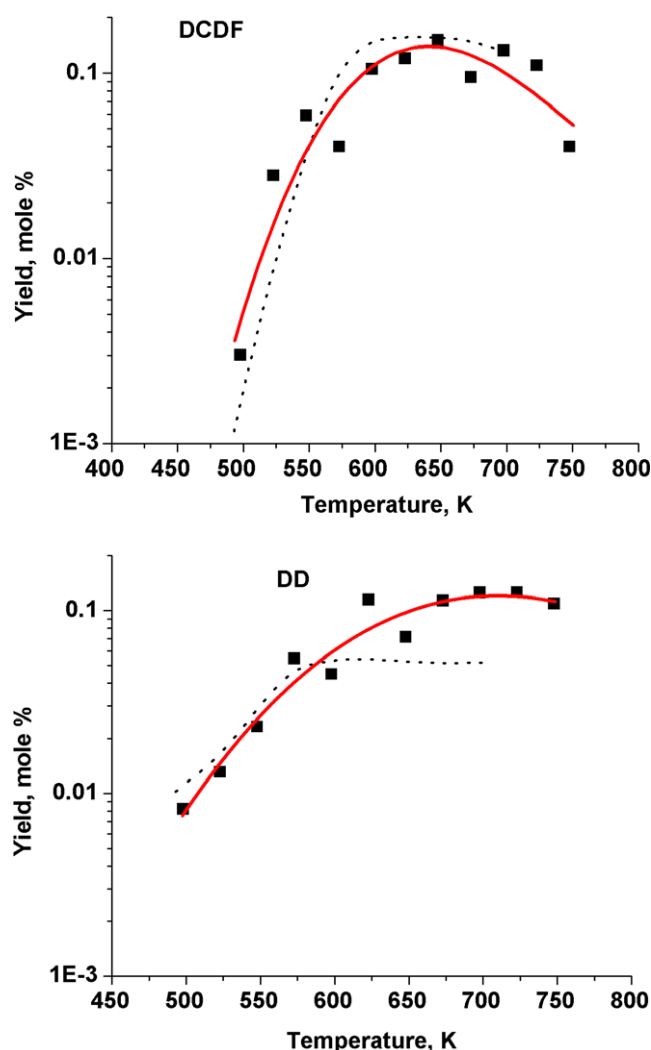


Fig. 1. Experimental (solid lines) and calculated (dashed lines) mole percent yields of DCDF and DD from pyrolysis of 88 ppmv of 2-MCP over 5% CuO/SiO₂ (1 mg).

towards DD and DCDF formation (in order of sensitivity) were #13, 5, 10 and 7, 6, 4, respectively. This analysis revealed the relative impact of ER and LH mechanisms on DD and DCDF formation. While for DCDF formation there is a single LH mechanism (Reactions 6 and 7) in the scheme, the formation of DD may involve separate ER (Reactions 10–14) and LH (Reactions 15 and 16) mechanisms.

Below $\sim 653 \text{ K}$, the ER mechanism is dominant for DD formation, i.e. removal of Reactions 10–14 (ER mechanism for DD formation) results in a decrease of DD yield by a factor of 2.8 at almost unchanged yields of DCDF at 573 K, while removing Reactions 15 and 16 (the LH mechanism) from the scheme decreases the DD yield by factor of 1.8 at the same temperature. However, above 653 K when all the gas-phase MCP is completely consumed, the LH mechanism is dominant as is confirmed by removal of Reactions 15 and 16 with an observed decrease in the predicted concentration of DD by a factor of 2 versus a decrease of only a factor of 1.3 with removal of Reactions

10–14. An analogous affect was observed for the experimental dependence of DD yields on initial 2-MCP concentration. DD concentration decreases by a factor of ~ 2.2 at 503 K by decreasing the initial 2-MCP concentration by a factor of 2. A directly proportional dependence on the initial concentration is indicative of an ER mechanism rather than LH mechanism for DD formation.

4. Conclusions

1. We have made a first attempt at development of an expanded reaction kinetic model including 17 surface reactions to explain the yields of DCDF and DD from chlorinated phenols using 2-MCP and 5% CuO/SiO₂ as a model fly-ash surface. The calculated yields of DCDF and DD correlated well with experimental observations up to 613 K for both DCDF and DD and up to 673 K for DCDF.

2. This surface, reaction kinetic scheme is based on previously developed gas-phase pathways for PCDD/F formation discussed widely in the literature. The most significant differences are the lowering of some activation energies by the surface and the steric hindrance of oxygen centered radicals such that radical–radical reactions for DD formation are not favorable for the surface (LH mechanism), while analogous radical–radical reactions are dominant in the gas phase. An ER pathway involving reaction of a surface-bound adsorbate with a gas-phase molecule is the preferred route of DD formation. An LH pathway involving radical (surface-bound)–radical (surface-bound) reactions is the main channel for DCDF formation which is similar to the gas-phase route for DCDF formation.

3. Significant uncertainties of numerous rate parameters (pre-exponential factors and activation energies) and the use of empirical fitting for surface reactions suggests that additional attention be paid to calculating and estimating rate parameters for key chlorinated hydrocarbon reactions.

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