

COMPARISON OF THE ROLES OF CHLORINE ATOMS AND HYDROXYL RADICALS IN FORMATION OF PCDDs FROM OXIDATIVE PYROLYSIS OF 2, 4, 6-TRICHLOROPHENOLLavrent Khachatryan^a, Alexander Burcat,^b and Barry Dellinger^a.^aDepartment of Chemistry, Louisiana State University, Baton Rouge, LA, 70803^bFaculty of Aerospace Engineering, Technion-Israel Institute of Technology, Haifa, 32000, Israel**Abstract**

The comparative roles of the important chain carriers, OH and Cl were determined through reaction kinetic modeling of the oxidative pyrolysis of 2, 4, 6-trichlorophenol (TCP) in the presence of 300 ppm of hexane and 4% O₂. Two sub-models from the literature were combined to track the behavior of Cl and OH in this reaction system. Surprisingly, no significant differences in the model results were observed for models that did not generate Cl (rxns. 1-71) and models that included Cl generation (rxn. 72-106). OH was the dominant chain carrier within the short, 71 reaction scheme as well as the expanded, 106 reaction scheme below 1050 K. Above 1050 K, Cl was an important chain carrier in the expanded scheme, and its temperature dependence tracked the behavior of OH at these temperatures.

Introduction

Our recent reports¹⁻³ on the homogeneous mechanisms of the gas-phase PCDD/F formation summarized the current status of PCDD/F reaction kinetic formation models⁴. Following the realization that phenoxy radicals were very un-reactive with oxygen, a modified model was proposed to explain formation rates of dioxins by purely gas-phase reactions of phenoxy radicals¹. The importance of the role of labile chain carriers, H, Cl, O, OH, HO₂, and alkyl radicals (R) were identified. In our model, OH proved to be the dominant chain carrier¹. However, other publications directed attention toward Cl, not only as a chlorination agent, but also as an active chain carrier in the formation of PCDD and chlorinated aromatic pollutants^{5,6}.

In these models, the main channel for the decomposition of chlorinated phenoxy radicals was expulsion of CO (the dominant oxygen containing product) and formation of chlorinated cyclopentadienyl radical (CPD), C₅H₂Cl₃^{1,2}. For the sake of simplicity, the further decomposition of chlorinated CPD radicals was not considered which naturally led to a low steady state concentration of Cl vs. OH¹. To more fully assess the role of Cl in overall chain processes over wide temperature ranges, it is important to release these atoms from C₅H₂Cl₃ using reasonable decomposition pathways and associated reaction kinetics.

In this work, we compare the roles of OH and Cl in the formation of PCDD during the oxidative pyrolysis of 2, 4, 6-trichlorophenol (TCP) in the presence of 300 ppm of hexane and 4% O₂ and compare the results to previously published experimental studies⁷. We utilized two sub-models already published, the core model (reactions 1-71, not shown) presented by us¹ and a sub-model published by Babushok and Tsang⁸ which presents a detailed mechanism of PAH formation from chlorinated propargyl radicals (cf. **Table 1**, reactions 75-105), and reactions recently developed by us to link these two sub-models (cf. **Table 1**, reactions 72-74 and 106).

Methods and Materials

For the detailed balancing of the reaction in the combined schemes, it was necessary to perform calculations of the thermodynamic parameters of additional chlorinated species. The thermochemistry of 15 chlorinated species (stable molecules, radicals and intermediates) for reactions 72-74 and 106 and the added sub-model (rxns. 75-105) were calculated. The fundamental vibrations of the species and their moments of inertia were calculated using the DFT/B3LYP/6-31G* *ab-initio* method. Reverse rate parameters were determined from the thermochemistry of the reactions in combination with detailed balancing. The calculated thermochemical parameters (<http://garfield.chem.elte.hu/Burcat/burcat.html>) were input to the CHEMKIN kinetic modeling code which calculated reaction energies and reverse rate parameters using the forward rate parameters that were provided as a separate input to CHEMKIN.

Table 1
Cl Generating Reaction Schemes Presented in CHEMKIN Format ^a

<i>New decomposition reactions of chlorinated CPD radicals</i>			
72. $2C_5H_2CL_3 = C_{10}H_4CL_4 + 2CL$	2.00E+13	0.0	4000.0
73. $C_5H_2CL_3 = C_5CL_3H_2$	7.50E+11	1.0	77000.0
74. $C_5CL_3H_2 = C_3HCL_2 + C_2HCL$	3.70E+11	0.0	30000.0
<i>Sub-model from ^{b 8}</i>			
75. $C_3HCL_2 + CL_2 = C_3HCL_3 + CL$	5.00E+12	0.0	7249.0
76. $C_3HCL_2 + OH = C_2HCL + CO + HCL$	1.00E+13	0.0	0.0
77. $C_3HCL_2 + H = C_3H_2CL + CL$	1.00E+14	0.0	0.0
78. $C_3HCL_2 + CL = C_3HCL_3$	3.00E+13	0.0	0.0
duplicate			
79. $C_3HCL_3 = C_3HCL_2 + CL$	2.00E+15	0.0	71530.0
duplicate			
80. $C_3HCL_2 + O = CO + C_2HCL + CL$	3.00E+13	0.0	0.0
81. $C_3HCL_3 + OH = C_3CL_3 + H_2O$	1.00E+07	1.9	-160.0
82. $C_3HCL_3 + H = C_3CL_3 + H_2$	7.00E+05	1.9	4450.0
83. $C_3HCL_3 + H = C_3HCL_2 + HCL$	1.20E+14	0.0	5215.0
84. $C_3HCL_3 + CL = C_3CL_3 + HCL$	1.30E+13	0.0	170.0
85. $C_3HCL_3 + O = C_3CL_3 + OH$	4.80E+04	2.7	2103.0
86. $C_3HCL_3 + OH = C_3HCL_2OH + CL$	1.50E+12	0.0	1801.0
87. $C_3HCL_3 + H = C_3H_2CL_2 + CL$	5.00E+13	0.0	6005.0
88. $C_3CL_3 + CL_2 = C_3CL_4 + CL$	4.00E+12	0.0	7799.0
89. $C_3CL_3 + H = C_3HCL_3$	1.00E+14	0.0	0.0
90. $C_3CL_3 + O = C_2CL_2 + CO + CL$	5.00E+13	0.0	0.0
91. $C_3CL_3 + CL = C_3CL_4$	5.00E+13	0.0	0.0
duplicate			
92. $C_3CL_4 = C_3CL_3 + CL$	4.00E+15	0.0	50000.0
duplicate			
93. $C_3CL_4 + OH = C_2CL_2 + CO + CL + HCL$	5.60E+12	0.0	2392.0
94. $C_3CL_4 + H = C_3HCL_3 + CL$	1.20E+15	0.0	14809.0
95. $C_3CL_4 + O = C_2CL_2 + CO + 2CL$	2.00E+13	0.0	1321.0
96. $C_3H_3 + C_3H_3 = C_6H_6$	1.00E+13	0.0	0.0
97. $C_3H_3 + C_3H_2CL = C_6H_5CL$	1.00E+13	0.0	0.0
98. $C_3H_3 + C_3HCL_2 = C_6H_4CL_2$	1.00E+13	0.0	0.0
99. $C_3H_3 + C_3CL_3 = C_6H_3CL_3$	1.00E+13	0.0	0.0
100. $C_3H_2CL + C_3H_2CL = C_6H_4CL_2$	1.00E+13	0.0	0.0
101. $C_3H_2CL + C_3HCL_2 = C_6H_3CL_3$	1.00E+13	0.0	0.0
102. $C_3H_2CL + C_3CL_3 = C_6H_2CL_4$	1.00E+13	0.0	0.0
103. $C_3HCL_2 + C_3HCL_2 = C_6H_2CL_4$	1.00E+13	0.0	0.0
104. $C_3HCL_2 + C_3CL_3 = C_6HCL_5$	1.00E+13	0.0	0.0
105. $C_3CL_3 + C_3CL_3 = C_6CL_6$	1.00E+13	0.0	0.0
<i>New reaction of Cl with hexane</i>			
106. $Cl + C_6H_{14} = C_6H_{13} + HCl$	2.0 E+14	0.0	0.0

^a Reaction rate units are in cm^3 , mole, sec, activation energies in calories. $C_{10}H_4CL_4$ denotes chlorinated naphthalene. $C_5H_2CL_3$ and $C_5CL_3H_2$ are cyclic and linear pentadienyl radicals, respectively.

^b For the following rxns. ⁸:

$C_3HCL_3 + O = C_3HCL_2O + CL$, $k = 1.00E+13 \exp(-1321 \text{ cal/mol/RT})$;

$C_3CL_3 + OH = C_3CL_2 + HOCL$, $k = 1.00E+13 \text{ cm}^3/\text{mol}\cdot\text{sec}$ the polynomials for CHEMKIN are not yet finalized and, therefore not included in the sub-model.

The results from modeling calculations and experiments are compared in **Figure 1**, (curves 2, 2', 3, 3' and 4, 4') and (curves 1, 1'), respectively and **Table 2**.

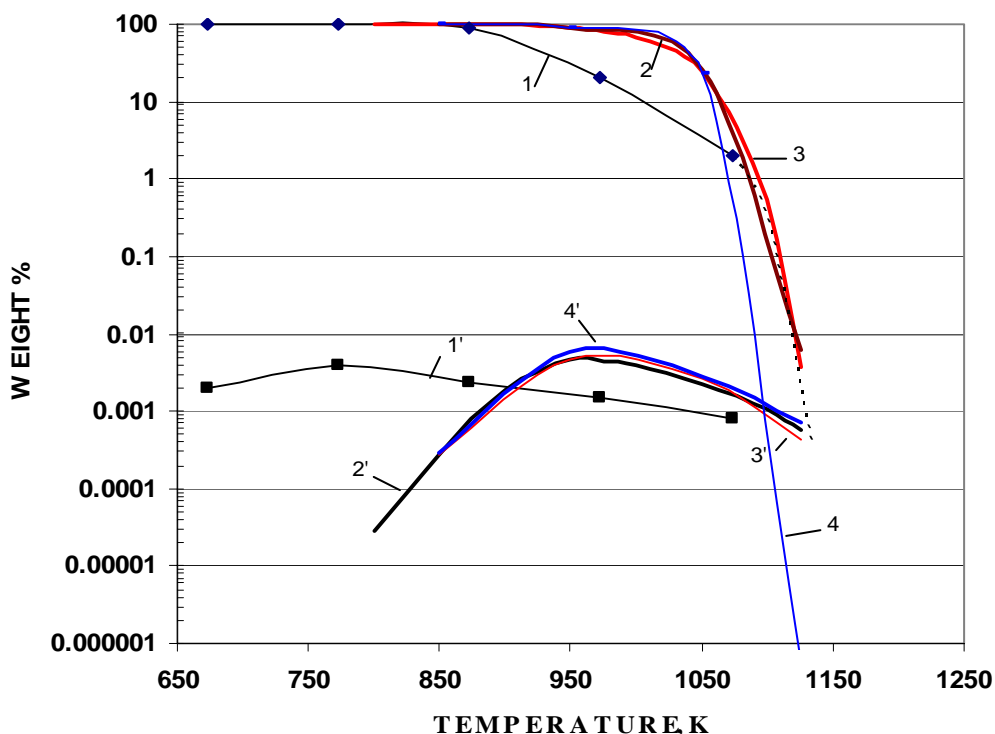


Figure 1. Comparison of gas phase modeling and experimental results for the oxidation of 15 ppm 2, 4, 6 - trichlorophenol in 4% O₂ in N₂, and 300 ppm hexane in a 1.0 cm i.d. fused silica flow reactor for a reaction time of 2.0 s⁷. Curves 1 and 1': Experimental results for 2, 4, 6 - TCP decomposition (curve 1) and 1, 3, 6, 8 TCDD formation (curve 1')⁷. Curves 2 and 2': Model results (71 reactions) for 2, 4, 6 - TCP decomposition and 1, 3, 6, 8 TCDD formation². Curves 3 and 3': the same model² for 2, 4, 6 - TCP decomposition and 1, 3, 6, 8 TCDD formation with updated polynomials. Curves 4 and 4': Model results for 2, 4, 6 - TCP decomposition and 1, 3, 6, 8 TCDD formation via homogeneous, gas-phase reactions for the expanded scheme with 106 reactions.

Table 2.

Comparison of OH/Cl Molar Ratios from Modeling of TCP Pyrolysis for Expanded (106 reactions) and Core (71 reactions, results in parenthesis) Reaction Schemes.

T, K	OH	Cl	OH/Cl
850*	5.18E-11	8.43E-15	6.1E+3
(71 rxns')	(5.12E-11)	(4.5E-15)	(1.14E+4)
950	2.79E-09	1.25E-12	2.2E+3
(71 rxns')	(2.46E-09)	(8.05E-14)	(3.0E+4)
1050	1.15E-08	5.59E-11	2.0E+2
(71 rxns')	(1.13E-08)	(1.84E-12)	(0.6E+4)
1125	4.56E-08	2.35E-08	1.94
(71 rxns')	(5.2E-08)	(1.34E-10)	(390)

Surprisingly, there was very little difference between the models (cf. **Figure 1** and **Table 2**). OH was the dominant chain carrier for both models below 1050 K. Cl does participate as a chain carrier above 1050 K, tracking the impact of OH; however, it is still a secondary chain carrier to OH.

Acknowledgements

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