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## Mechanism of PCDD/F Formation in Small Aliphatic Fuel Combustion and Discussion of the Trace Chemistries of Fire Hypothesis

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### Introduction

Two decades ago Bumb et al.<sup>1)</sup> suggested the trace chemistries of fire hypothesis which says that chlorinated dioxins may occur in the combustion of most types of organic material due to the existence of trace chemical reactions occurring in fire. In the late 1980's De Fre and Rymer<sup>2)</sup> have shown in a pilot-scale experiment that trace quantities of dioxins are produced in a CH<sub>4</sub> flame in the presence of HCl; Eklund et al.<sup>3)</sup> also detected dioxins when passing a CH<sub>4</sub>/HCl/O<sub>2</sub> mixture through a flow reactor in the temperature range 400-950°C. These experiments by De Fre and Rymer and Eklund et al. clearly demonstrated that there exist certain chemical reaction pathways by which dioxins can be formed from as simple molecules as CH<sub>4</sub>, HCl and O<sub>2</sub>. What these chemical reactions are and what their relation to the trace chemistries of fire hypothesis is will be discussed in this paper.

### Mechanism of T<sub>4</sub>CDD and T<sub>4</sub>CDF Formation in the CH<sub>4</sub>/HCl/O<sub>2</sub> System

A reaction mechanism for T<sub>4</sub>CDD and T<sub>4</sub>CDF formation in the CH<sub>4</sub>/HCl/O<sub>2</sub> system at temperature above 700°C is postulated and displayed in the table of the following pages. The reaction mechanism starts with only three kinds of molecule (CH<sub>4</sub>, HCl and O<sub>2</sub>), and consists of gas-phase elementary reactions known in flame chemistry, and leads to the tricyclic T<sub>4</sub>CDD/F structures at the end. The mechanism can be considered to have four parts: major elementary steps of CH<sub>4</sub> combustion (R1-R9), formation of chlorinated C<sub>1</sub> to C<sub>4</sub> species (R10-R65), formation of the first aromatic ring (R66-R73), and T<sub>4</sub>CDD/F formation (R74-R91).

Initiation for simplicity is shown to be brought about by the decomposition of CH<sub>4</sub> producing CH<sub>3</sub> and H which reacts with O<sub>2</sub> resulting in O and OH. More CH<sub>4</sub> are attacked by free radicals and atoms in R3 and R4. Most of the methyl radicals produced are oxidized to CO<sub>2</sub> following the pathway R5 to R9<sup>4)</sup>. Under combustion conditions HCl is not an irreversible sink for Cl atoms; generally Cl atoms can be produced through R10 and R11, and then take part in the free radical mechanisms<sup>7,8)</sup>. Chlorinated C<sub>1</sub> species including vinylchloride, dichloromethane, chloroform, carbon tetrachloride and their radicals are formed by R12 to R24. Combination of nonchlorinated and chlorinated methyl radicals in R25 to R30 leads to ethane and mono- to tetra-chloroethane, the degradation products of which are ethene and ethyne having different degrees of chlorination following R31 to R48. Recombination of C<sub>1</sub> and C<sub>2</sub> radical species in R49 to R56 gives C<sub>3</sub> radical species; recombination of C<sub>2</sub> radical species in R57 to R65 gives C<sub>4</sub> radical species.

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## Mechanism of T<sub>4</sub>CDD and T<sub>4</sub>CDF Formation in the CH<sub>4</sub>/HCl/O<sub>2</sub> System

Number	Elementary reaction	Reference
R1	$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	4,5
R2	$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	4,5
R3	$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	4,5
R4	$\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$	4,5
R5	$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	4,5
R6	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$	4,5
R7	$\text{CH}_2\text{O} + \text{O} \rightarrow \text{CHO} + \text{OH}$	4,5
R8	$\text{CHO} \rightarrow \text{CO} + \text{H}$	4,5
R10	$\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$	5,6,7,8
R11	$\text{HCl} + \text{O} \rightarrow \text{Cl} + \text{OH}$	5,7,8
R12	$\text{CH}_3 + \text{Cl} \rightarrow \text{CH}_3\text{Cl}$	5,6,9.
R13	$\text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{CH}_2\text{Cl} + \text{H}_2\text{O}$	5,6
R14	$\text{CH}_3\text{Cl} + \text{O} \rightarrow \text{CH}_2\text{Cl} + \text{OH}$	5,10
R15	$\text{CH}_3\text{Cl} + \text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{HCl}$	5,6
R16	$\text{CH}_2\text{Cl} + \text{Cl} \rightarrow \text{CH}_2\text{Cl}_2$	10,11,12
R17	$\text{CH}_2\text{Cl}_2 + \text{OH} \rightarrow \text{CHCl}_2 + \text{H}_2\text{O}$	6,10,12
R18	$\text{CH}_2\text{Cl}_2 + \text{O} \rightarrow \text{CHCl}_2 + \text{OH}$	10,12
R19	$\text{CH}_2\text{Cl}_2 + \text{Cl} \rightarrow \text{CHCl}_2 + \text{HCl}$	10,11
R20	$\text{CHCl}_2 + \text{Cl} \rightarrow \text{CHCl}_3$	13
R21	$\text{CHCl}_3 + \text{OH} \rightarrow \text{CCl}_3 + \text{H}_2\text{O}$	6,14
R22	$\text{CHCl}_3 + \text{O} \rightarrow \text{CCl}_3 + \text{OH}$	13,14
R23	$\text{CHCl}_3 + \text{Cl} \rightarrow \text{CCl}_3 + \text{HCl}$	6,11
R24	$\text{CCl}_3 + \text{Cl} \rightarrow \text{CCl}_4$	6,11
R25	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	4,5,14
R26	$\text{CH}_3 + \text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{Cl}$	5,9
R27	$\text{CH}_3 + \text{CHCl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2$	10,14
R28	$\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4\text{Cl}_2$	5,6,14
R29	$\text{CH}_2\text{Cl} + \text{CHCl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl}_3$	10,11,14
R30	$\text{CHCl}_2 + \text{CHCl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_4$	10,14
R31	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	4,5,6
R32	$\text{C}_2\text{H}_6 + \text{O} \rightarrow \text{C}_2\text{H}_5 + \text{OH}$	4,5
R33	$\text{C}_2\text{H}_6 + \text{Cl} \rightarrow \text{C}_2\text{H}_5 + \text{HCl}$	5,6,9
R34	$\text{C}_2\text{H}_3\text{Cl}_3 + \text{OH} \rightarrow \text{C}_2\text{H}_2\text{Cl}_3 + \text{H}_2\text{O}$	6
R35	$\text{C}_2\text{H}_3\text{Cl}_3 + \text{O} \rightarrow \text{C}_2\text{H}_2\text{Cl}_3 + \text{OH}$	a
R36	$\text{C}_2\text{H}_3\text{Cl}_3 + \text{Cl} \rightarrow \text{C}_2\text{H}_2\text{Cl}_3 + \text{HCl}$	11
R37	$\text{C}_2\text{H}_2\text{Cl}_4 + \text{OH} \rightarrow \text{C}_2\text{HCl}_4 + \text{H}_2\text{O}$	a
R38	$\text{C}_2\text{H}_2\text{Cl}_4 + \text{O} \rightarrow \text{C}_2\text{HCl}_4 + \text{OH}$	a
R39	$\text{C}_2\text{H}_2\text{Cl}_4 + \text{Cl} \rightarrow \text{C}_2\text{HCl}_4 + \text{HCl}$	11
R40	$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	4,5
R41	$\text{C}_2\text{H}_2\text{Cl}_3 \rightarrow \text{C}_2\text{H}_2\text{Cl}_2 + \text{Cl}$	11
R42	$\text{C}_2\text{HCl}_4 \rightarrow \text{C}_2\text{HCl}_3 + \text{Cl}$	11

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Number	Elementary reaction	Reference
R43	$C_2H_4 + Cl \rightarrow C_2H_3 + HCl$	5,6,9
R44	$C_2H_2Cl_2 + Cl \rightarrow C_2HCl_2 + HCl$	11,14
R45	$C_2HCl_3 + Cl \rightarrow C_2Cl_3 + HCl$	11,13,14
R46	$C_2H_3 \rightarrow C_2H_2 + H$	4,5
R47	$C_2HCl_2 \rightarrow C_2HCl + Cl$	14
R48	$C_2Cl_3 \rightarrow C_2Cl_2 + Cl$	13,14,21
R49	$CH_3 + C_2H_2 \rightarrow C_3H_4 + H$	22
R50	$CHCl_2 + C_2HCl \rightarrow C_3H_2Cl_2 + Cl$	a
R51	$CCl_3 + C_2HCl \rightarrow C_3HCl_3 + Cl$	a
R52	$CCl_3 + C_2Cl_2 \rightarrow C_3Cl_4 + Cl$	14 <sup>b</sup>
R53	$C_3H_4 \rightarrow C_3H_3 + H$	18,22
R54	$C_3H_2Cl_2 \rightarrow C_3H_2Cl + Cl$	a
R55	$C_3HCl_3 \rightarrow C_3HCl_2 + Cl$	a
R56	$C_3Cl_4 \rightarrow C_3Cl_3 + Cl$	20
R57	$C_2H_2 + C_2H_3 \rightarrow C_4H_4 + H$	7,9 <sup>b</sup> ,14,22
R58	$C_2HCl + C_2HCl_2 \rightarrow C_4H_2Cl_2 + Cl$	a
R59	$C_2HCl + C_2Cl_3 \rightarrow C_4HCl_3 + Cl$	a
R60	$C_4H_4 + Cl \rightarrow C_4H_3 + HCl$	7 <sup>c</sup> ,14,22 <sup>c</sup>
R61	$C_4H_2Cl_2 + Cl \rightarrow C_4HCl_2 + HCl$	a
R62	$C_4HCl_3 + Cl \rightarrow C_4Cl_3 + HCl$	a
R63	$C_2H_3 + C_2H_3 \rightarrow C_4H_5 + H$	17
R64	$C_2HCl_2 + C_2HCl_2 \rightarrow C_4H_2Cl_3 + Cl$	a
R65	$C_2HCl_2 + C_2Cl_3 \rightarrow C_4HCl_4 + Cl$	a
R66	$C_2H_2 + C_4H_3 \rightarrow \phi$	7,15 <sup>b</sup> ,17,22
R67	$C_2HCl + C_4HCl_2 \rightarrow \phi Cl_3$	a
R68	$C_2H_2 + C_4H_5 \rightarrow \phi + H$	7,9,15 <sup>b</sup> ,17
R69	$C_2HCl + C_4H_2Cl_3 \rightarrow \phi Cl_3 + Cl$	a
R70	$C_2HCl + C_4HCl_4 \rightarrow \phi Cl_4 + Cl$	a
R71	$C_3H_3 + C_3H_3 \rightarrow \phi$	18 <sup>d</sup> ,22
R72	$C_3H_2Cl + C_3HCl_2 \rightarrow \phi Cl_3$	a
R73	$C_3H_2Cl + C_3Cl_3 \rightarrow \phi Cl_4$	a
R74	$\phi Cl_3 + O_2 \rightarrow O\phi Cl_3 + O$	17 <sup>c</sup> ,18,26 <sup>e</sup> ,27
R75	$\phi Cl_3 + O_2 \rightarrow 1,2-O_2\phi Cl_2 + Cl$	27 <sup>e</sup> ,28 <sup>e</sup>
R76	$\phi Cl_3 + O \rightarrow O\phi Cl_2 + Cl$	26 <sup>c</sup>
R77	$\phi Cl_4 + O \rightarrow O\phi Cl_3 + Cl$	26 <sup>c</sup>
R78	$\phi Cl_3 + \phi Cl_4 \rightarrow \phi Cl_3\phi Cl_3 + Cl$	29,32 <sup>c</sup>
R79	$\phi Cl_3\phi Cl_3 + O \rightarrow 2-O\phi Cl_2\phi Cl_3 + Cl$	31 <sup>f</sup>
R80	$2-O\phi Cl_2\phi Cl_3 \rightarrow C_{12}H_4OCl_4$ (T <sub>4</sub> CDF) + Cl	30
R81	$O\phi Cl_2 + \phi Cl_4 \rightarrow \phi Cl_2O\phi Cl_3 + Cl$	30,33
R82	$\phi Cl_2O\phi Cl_3 \rightarrow C_{12}H_4OCl_4$ (T <sub>4</sub> CDF) + HCl	31
R83	$O\phi Cl_3 + \phi Cl_4 \rightarrow \phi Cl_3O\phi Cl_3 + Cl$	30,33
R84	$\phi Cl_3O\phi Cl_3 + O \rightarrow 2-O\phi Cl_2O\phi Cl_3 + Cl$	31 <sup>f</sup>

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Number	Elementary reaction	Reference
R85	$2\text{-O}\phi\text{Cl}_2\text{O}\phi\text{Cl}_3 \rightarrow \text{C}_{12}\text{H}_4\text{O}_2\text{Cl}_4 (\text{T}_4\text{CDD}) + \text{Cl}$	30
R86	$\text{O}\phi\text{Cl}_3 + \text{O}\phi\text{Cl}_3 \rightarrow 2\text{-O}\phi\text{Cl}_2\text{O}\phi\text{Cl}_3 + \text{Cl}$	33
R87	$2\text{-O}\phi\text{Cl}_2\text{O}\phi\text{Cl}_3 \rightarrow \text{C}_{12}\text{H}_4\text{O}_2\text{Cl}_4 (\text{T}_4\text{CDD}) + \text{Cl}$	30
R88	$\text{O}\phi\text{Cl}_3 + \text{C}_2\text{HCl} \rightarrow \text{C}_8\text{H}_3\text{OCl}_3 (\text{chlorobenzofuran}) + \text{Cl}$	37 <sup>9</sup>
R89	$\text{C}_8\text{H}_3\text{OCl}_3 + \text{C}_4\text{H}_2\text{Cl}_2 \rightarrow \text{C}_{12}\text{H}_4\text{OCl}_4 (\text{T}_4\text{CDF}) + \text{HCl}$	
R90	$1,2\text{-O}\phi\text{Cl}_2 + \text{C}_2\text{HCl} \rightarrow \text{C}_8\text{H}_3\text{O}_2\text{Cl}_3 (\text{chlorobenzodioxin})$	
R91	$\text{C}_8\text{H}_3\text{O}_2\text{Cl}_3 + \text{C}_4\text{H}_2\text{Cl}_2 \rightarrow \text{C}_{12}\text{H}_4\text{O}_2\text{Cl}_4 (\text{T}_4\text{CDD}) + \text{HCl}$	

a. In analogy to similar reactions for nonchlorinated hydrocarbons. All following points are referring to the original references: b. written as two elementary steps; c. Cl was H; d. written as three elementary steps; e. 1,4-quinone was suggested; f. O was OH; g. the sequence of O and C<sub>2</sub>H<sub>2</sub> addition is reversed.

The reactions for the formation of the first aromatic ring are given in R66 to R73. Aromatics formation from small hydrocarbon fuels is an actively studied subject in combustion research; there are about 18 different routes or key steps suggested by researchers as summarized by Westmoreland et al.<sup>16</sup> Currently the even number carbon route (R66, R68) and the odd number carbon route (R71) are generally believed to be the main routes of aromatics formation. In methane combustion the odd number carbon route is likely to be more important than the even number carbon route, since methane flames have an abundance of CH<sub>3</sub> radicals which combine with C<sub>2</sub>H<sub>2</sub> giving rise to C<sub>3</sub>H<sub>3</sub> and hence lead to more C<sub>6</sub>H<sub>6</sub> formation in R71<sup>22</sup>. R66, R68 and R71 have complex intermediates; diagrams showing the intermediates structures of R66 and R68 can be found in <sup>17,19,20,23,24</sup>, and those for R71 in <sup>17,20,25</sup>.

Chlorophenoxy radicals arise in R74, R76 and R77. Coupling of chlorobenzene, chlorophenyl or chlorophenoxy radicals and the subsequent displacement of Cl by O and ring closure lead to T<sub>4</sub>CDD/F structures shown in R78 to R87. Other routes of T<sub>4</sub>CDD/F formation in R88 to R91 are suggested by us. Since PAH growth in aliphatic fuel combustion generally involves the successive addition of C<sub>2</sub> and C<sub>4</sub> radical species to the first aromatic ring<sup>7,23,24,34-37</sup>, PCDD/Fs could be formed in a similar manner involving also O atoms. The product of R88, chlorobenzofuran, has been detected by Eklund et al.<sup>3</sup>

## Discussion about the Mechanism

Evidently for PCDD/F formation in aliphatic fuel combustion, the first aromatic ring must be produced at first, then PCDD/F may be formed from the aromatic compounds. In this respect the present mechanism is in agreement with all previous proposals. The feature of our mechanism is that it is more detailed and composed of elementary steps. Most of the molecule species in the mechanism such as chlorinated or nonchlorinated methane, ethane, ethene, ethyne, benzene, biphenyl and benzofuran have been reported by Eklund et al.<sup>3</sup> PCDD/Fs detected in CH<sub>4</sub>/HCl/O<sub>2</sub> systems are very likely to be formed by such a mechanism. The main purpose of this work is to illustrate how PCDD/F structures can arise from small hydrocarbons, so it is not a comprehensive mechanism, some relevant elementary reactions are not included here. Extension of the mechanism to other hydrocarbon fuels and PCDD/F isomers is feasible; heterogeneous elementary reactions should also be considered. It is known that gas-phase mechanism is not sufficient to

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explain the PCDD/F formation levels in incinerators because PCDD/F formation in incinerators is catalyzed by metallic species. Gas-phase mechanism may, however, play a role in PCDD/F formation for other combustion systems such as gasoline-fueled engines and gasoil burners.

## Discussion about the Trace Chemistries of Fire Hypothesis

Following the demonstration that PCDD/Fs are formed from CH<sub>4</sub> flames in the presence of HCl, De Fre and Rymen<sup>2)</sup> suggested that "methane is the simplest hydrocarbon and has no C-C bonds; if methane can give the novo PCDD/F generation, any hydrocarbon is able to; ... it can be assumed that the de novo synthesis from flue gas and HCl is a general phenomenon for all hydrocarbons". These suggestions seem to be reasonable from combustion chemistry considerations. In terms of the reaction mechanism presented in this paper, an essential argument is that PCDD/Fs can be formed starting from the recombination of methyl radicals in the presence of HCl and O<sub>2</sub>; in any practical combustion system methyl radicals and HCl are always present, therefore PCDD/F formation is expected to occur, albeit in extremely low yield, through certain chemical reactions such as those presented above. This is in agreement with the suggestion of the trace chemistries of fire hypothesis. The chemical mechanism of dioxin formation in this paper or similar papers by other researchers may be regarded as some of the trace chemistries of fire postulated by Bumb et al. At the time Bumb et al. made their proposal, the number of combustion sources known to emit trace quantities of dioxins was not very large. Nowadays dioxin emissions have been detected in almost all types of combustion systems owing to the improvement in sampling and analysis methods. Even for coal combustion which in the 1980's was reported to be below the PCDD/F detection limits, recent measurements have detected dioxin emissions<sup>39-42)</sup>. On the basis of these extensive PCDD/F measurement data it is considered that the trace chemistries of fire hypothesis is verified by the present PCDD/F measurement data base as a whole.

## Summary

A chemical mechanism for T<sub>4</sub>CDD/F formation in the CH<sub>4</sub>/HCl/O<sub>2</sub> system is presented. The mechanism consists of elementary reactions and illustrates how the tricyclic PCDD/F structures can arise in aliphatic fuel combustion. The product channels of PCDD/F formation seem to exist in the combustion of any hydrocarbon fuel such that PCDD/F are ubiquitous byproducts of combustion as suggested by the trace chemistries of fire hypothesis.

## Literature Cited

- (1) Bumb, R.R.; Crummett, W.B.; Cutie, S.S.; Gledhill, J.R.; Hummel, R.H.; Kagel, R.O.; Lamparski, L.L.; Luoma, E.V.; Miller, D.L.; Nestruck, T.J.; Shadoff, L.A.; Stehl R.H.; Woods, J.S. *Science*, **1980**, 210, 385-390.
- (2) De Fre, R.; Rymen, T. *Chemosphere*, **1989**, 19, 331-336.
- (3) Eklund, G.; Pedersen, J.R.; Stromberg, B. *Chemosphere*, **1988**, 17, 575-586.
- (4) Wamatz, J. in *Combustion Chemistry*, (Gardiner, W.C. ed.); Springer-Verlag; New York, **1984**, p.197.
- (5) Senkan, S.M. *Adv. Chem. Eng.* **1992**, 18, 95-196.

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- (6) Tsang, W. *Comb. Sci. Technol.* **1990**, 74, 99-116.
- (7) Frenklach, M. *Comb. Sci. Technol.* **1990**, 74, 283-296.
- (8) Yang, M.H.; Hamins, A.; Puri, I.K. *Comb. Flame*, **1994**, 98, 107-122.
- (9) Weissman, M.; Benson, S.W. *Int. J. Chem. Kin.* **1984**, 16, 307-333.
- (10) Ho, W.-P.; Barat, R.B.; Bozzelli, J.W. *Comb. Flame*, **1992**, 88, 265-295.
- (11) Taylor, P.H.; Dellinger, B.; Tirey, D.A. *Int. J. Chem. Kin.* **1991**, 23, 1051-1074.
- (12) Wang, H.; Hahn, T.O.; Sung, C.J.; Law, C.K. *Comb. Flame*, **1996**, 105, 291-307.
- (13) Chang, W.-D.; Senkan, S.M. *Environ. Sci. Technol.* **1989**, 23, 442-450.
- (14) Lee, W.-J.; Cicek, B.; Senkan, S.M. *Environ. Sci. Technol.* **1993**, 27, 949-960.
- (15) Smyth, K.C.; Miller, J.H. *Science*, **1987**, 236, 1540-1546.
- (16) Westmoreland, P.R.; Dean, A.M.; Howard, J.B.; Longwell, J.P. *J. Phys. Chem.* **1989**, 93, 8171-8180.
- (17) Miller, J.A.; Melius, C.F. *Comb. Flame*, **1992**, 91, 21-39.
- (18) Leung, K.M.; Lindstedt, R.P. *Comb. Flame*, **1995**, 102, 129-160.
- (19) Taylor, P.H.; Tirey, D.A.; Rubey, W.A.; Dellinger, B. *Comb. Sci. Technol.*, **1994**, 101, 75-102.
- (20) Taylor, P.H.; Tirey, D.A.; Dellinger, B. *Comb. Flame*, **1996**, 105, 486-498.
- (21) Taylor, P.H.; Tirey, D.A.; Dellinger, B. *Comb. Flame*, **1996**, 104, 260-271.
- (22) Senkan, S.; Castaldi, M. *Comb. Flame*, **1996**, 107, 141-150.
- (23) Frenklach, M.; Clary, D.W.; Gardiner, W.C.; Stein, S.E. *20th Symp. Comb.* **1985**; p. 887.
- (24) Bockhorn, H.; Fetting, F.; Wenz, H.W. *Ber. Bunsenges. Phys. Chem.* **1983**, 87, 1067-1073.
- (25) Stein, S.E.; Walker, J.A.; Suryan, M.M.; Fahr, A. *23rd Symp. Comb.* **1991**; p. 85.
- (26) Lovell, A.B.; Brezinsky, K.; Glassman, I. *22nd Symp. Comb.* **1989**; p. 1063.
- (27) Frank, P.; Herzler, J.; Just, Th.; Wahl, C. *25th Symp. Comb.* **1994**; p. 833.
- (28) Buth, R.; Hoyermann, K.; Seeba, J. *25th Symp. Comb.* **1994**; p. 841.
- (29) Ritter, E.R.; Bozzelli, J.W.; Dean, A.M. *J. Phys. Chem.* **1990**, 94, 2493-2504.
- (30) Bozzelli, J.W.; Wu, Y.-P.; Ritter, E.R. *Chemosphere*, **1991**, 23, 1221-1232.
- (31) Ritter, E.R.; Bozzelli, J.W. *Comb. Sci. Technol.*, **1994**, 101, 153-169.
- (32) Fahr, A.; Stein, S.E. *22nd Symp. Comb.* **1989**; p. 1023.
- (33) Grotheer, H.-H.; Louw, R. *Comb. Flame*, in press.
- (34) Frenklach, M.; Clary, D.W.; Gardiner, W.C.; Stein, S.E. *21st Symp. Comb.* **1986**; p. 1067.
- (35) Smedley, J.M.; Williams, A.; Bartle, K.D. *Comb. Flame*, **1992**, 91, 71-82.
- (36) Mulholland, J.A.; Sarofim, A.F.; Sosothikul, P.; Lafleur, A.L. *Comb. Flame*, **1993**, 92, 161-177.
- (37) Emdee, J.L.; Brezinsky, K.; Glassman, I. *23rd Symp. Comb.* **1991**; p. 77.
- (38) Beer, J.M. *22nd Symp. Comb.* **1989**; p. 1.
- (39) Harrad, S.J.; Fernandes, A.R.; Creaser, C.S.; Cox, E.A. *Chemosphere*, **1991**, 23, 255-261.
- (40) Cains, P.W.; Dyke, P. *Chemosphere*, **1994**, 28, 2101-2119.
- (41) Riggs, K.B.; Brown, T.D.; Schrock, M.E. *Organohalogen Compd.* **1995**, 24, 51-54.
- (42) Thuß, U.; Herzschuh, R. *Organohalogen Compd.* **1995**, 23, 471-476.