Pattern of Regioisomers of Polychlorinated Naphthalenes formed by Incineration: Calculated Thermodynamic Values for Subsequent Dechlorination

M. Schneider, D. Lenoir, K.-W. Schramm, A. Kettrup

GSF - National Research Center for Environment and Health, Institute of Ecological Chemistry, Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany

Introduction

Polychlorinated naphthalenes, PCN, are also formed like PCDD/F's and PCB's during incineration processes. PCN exhibit similar chemical and physical properties like polychlorinated biphenyls (PCB). Some of the isomers of PCN are known to be strongly bioaccumulating and showing dioxin-like toxic properties such as chloracne and liver damages.[1,2,3,4]

Thermodynamic data are a powerful tool to understand more about the formation mechanisms of these compounds during incineration processes. Since there are nearly no experimental thermodynamic values of PCN available, they have to be calculated by molecular modeling methods like semi-empirical MO methods.[5,6,7]

Methods and Materials

Quantum mechanical calculations of the thermodynamic stabilities of Cl_XN and intermediates of the dechlorination / hydrogenation from Cl_XN were carried out using semi-empirical Hamiltonian PM3. PM3, included in the program packet HyperChem 5.1 Professional, Hypercube, Inc., calculates ΔH°_f by optimizing the molecular geometry, until ΔH°_f reaches the minimum. With the ΔH°_f of Cl_XN, intermediate σ-complex and $Cl_{X-1}N$, the relative $\Delta H^\circ_{activation}$, $\Delta H^\circ_{reaction}$ and the relative abundance x_i of Cl_XN within a homologue group were calculated.

The isomer distributions within a homologue group obtained by calculations were compared with data, collected from 5 representative fly ashes of municipal waste incinerators (FA-MWI).

Results and Discussion

The Standard Heat of Formation, ΔH°_f , of Cl_8N, Cl_7N, Cl_6N, Cl_5N and the intermediate σ-complexes of the reaction $Cl_XN + H^+ \rightarrow \sigma\,[Cl_XN\text{-}H]^+ \rightarrow Cl_{X-1}N + Cl^+$ as model for ipso-substitution were calculated by PM3. Subtraction of $\Delta H^\circ_f\ \sigma\,[Cl_XN\text{-}H]^+$ and $\Delta H^\circ_f\ Cl_XN$ gives the $\Delta H^\circ_{activation}$, subtraction of $\Delta H^\circ_f\ Cl_{X-1}N$ and $\Delta H^\circ_f\ Cl_XN$ gives $\Delta H^\circ_{reaction}$. With the equation $x_{i,activation} = f_{stat}\{\exp -\Delta H_i{}^\circ_{activation} / RT\} \ / \ \{\Sigma\ (\exp -\Delta H^\circ_{activation} / RT)\}$ the relative abundance $x_{i,activation}$ and with equation $x_{i,reaction} = f_{stat}\{\exp -\Delta H_i{}^\circ_{reaction} / RT \ / \ \{\Sigma\ (\exp -\Delta H^\circ_{reaction} / RT)\}$ the relative abundance $x_{i,reaction}$ were calculated; f_{stat} is a statistical factor including the educt-isomer ratios and for symmetrical educts the symmetry factor. The isomer distribution of activation and reaction is calculated by the sum of x_i leading to the same product but via different reaction pathways.

Table 1: $\Delta H^{\circ}_{activation}$ and $\Delta H^{\circ}_{reaction}$ of the dechlorination / hydrogenation from Cl_8N – Cl_6N and calculated relative abundance

Dechlorination / Hydrogenation	Intermediate Species	ΔH°_{act}	ΔH°_{rct}	calc. rel. abund $x_{i,act}$	calc. rel. abund $x_{i,rct}$
of 1,2,3,4,5,6,7,8-Cl8N					
→ 1,2,3,4,5,6,7-Cl7N	σ [1,2,3,4,5,6,7,8-Cl8N-8H]+	181.95	0.93	0.996	0.905
→ 1,2,3,4,5,6,8-Cl7N	σ [1,2,3,4,5,6,8,7-Cl8N-7H]+	190.27	4.27	0.004	0.095
of 1,2,3,4,5,6,7-Cl7N					
→ 1,2,3,6,7,8-Cl6N	σ [1,2,3,6,7,8,4-Cl7N-4H]+	183.95	4.37	0.348	0.049
→ 1,2,3,5,6,7-Cl6N	σ [1,2,3,5,6,7,4-Cl7N-4H]+	183.32	1.74	0.532	0.287
→ 1,2,3,4,6,7-Cl6N	σ [1,2,3,4,6,7,5-Cl7N-5H]+	186.25	1.73	0.074	0.290
→ 1,2,3,5,7,8-Cl6N	σ [1,2,3,5,7,8,6-Cl7N-6H]+	191.51	4.31	0.002	0.051
→ 1,2,3,5,6,8-Cl6N	σ [1,2,3,5,6,8,7-Cl7N-7H]+	189.33	4.34	0.009	0.050
→ 1,2,3,4,5,7-Cl6N	σ [1,2,3,4,5,7,6-Cl7N-6H]+	189.67	4.36	0.007	0.049
→ 1,2,3,4,5,6-Cl6N	σ [1,2,3,4,5,6,7-Cl7N-7H]+	193.56	5.11	0.001	0.030
of 1,2,3,4,5,6,8-Cl7N					
→ 1,2,3,5,7,8-Cl6N	σ [1,2,3,5,7,8,4-Cl7N-4H]+	182.67	0.96	0.003	0.051
→ 1,2,3,5,6,8-Cl6N	σ [1,2,3,5,6,8,4-Cl7N-4H]+	181.07	0.99	0.009	0.050
→ 1,2,3,4,5,7-Cl6N	σ [1,2,3,4,5,7,8-Cl7N-8H]+	180.56	1.02	0.013	0.049
→ 1,2,3,4,5,6-Cl6N	σ [1,2,3,4,5,6,8-Cl7N-8H]+	184.52	1.77	0.001	0.030
→ 1,2,4,5,7,8-Cl6N	σ [1,2,4,5,7,8,3-Cl7N-3H]+	189.76	4.29	0.000	0.005
→ 1,2,4,5,6,8-Cl6N	σ [1,2,4,5,6,8,7-Cl7N-7H]+	191.57	4.29	0.000	0.005
→ 1,2,3,4,5,8-Cl6N	σ [1,2,3,4,5,8,7-Cl7N-7H]+	191.06	5.20	0.000	0.003
of 1,2,3,4,6,7-Cl6N (x2)					
→ 1,2,3,6,7-Cl5N	σ [1,2,3,6,7,4-Cl6N-4H]+	184.58	4.58	0.187	0.058
→ 1,2,4,6,7-Cl5N	σ [1,2,4,6,7,3-Cl6N-3H]+	190.15	4.36	0.004	0.067
→ 1,2,3,4,6-Cl5N	σ [1,2,3,4,6,7-Cl6N-7H]+	192.70	5.20	0.001	0.038
of 1,2,3,5,6,7-Cl6N (x2)					
→ 1,2,3,6,7-Cl5N	σ [1,2,3,6,7,5-Cl6N-5H]+	187.63	4.57	0.171	0.058
→ 1,2,3,5,7-Cl5N	σ [1,2,3,5,7,6-Cl6N-6H]+	190.53	4.38	0.024	0.066
→ 1,2,3,5,6-Cl5N	σ [1,2,3,5,6,7-Cl6N-7H]+	192.40	5.17	0.007	0.039
of 1,2,3,4,5,7-Cl6N					
→ 1,2,3,6,8-Cl5N	σ [1,2,3,6,8,4-Cl6N-4H]+	182.97	4.40	0.075	0.011
→ 1,2,3,5,7-Cl5N	σ [1,2,3,5,7,4-Cl6N-4H]+	183.94	1.76	0.039	0.066
→ 1,2,3,4,6-Cl5N	σ [1,2,3,4,6,8-Cl6N-8H]+	189.54	2.57	0.001	0.038
→ 1,2,4,6,8-Cl5N	σ [1,2,4,6,8,3-Cl6N-3H]+	192.38	4.33	0.000	0.012
→ 1,2,4,5,7-Cl5N	σ [1,2,4,5,7,3-Cl6N-3H]+	188.38	4.36	0.002	0.011
→ 1,2,3,4,5-Cl5N	σ [1,2,3,4,5,7-Cl6N-7H]+	194.92	6.15	0.000	0.003

Dechlorination / Hydrogenation	Intermediate Species	ΔH°_{act}	ΔH°_{rct}	calc. rel. abund $x_{i,act}$	calc. rel. abund $x_{i,rct}$
of 1,2,3,5,6,8-Cl6N					
→ 1,2,4,6,7-Cl5N	σ [1,2,4,6,7,5-Cl6N-5H]+	187.23	1.75	0.004	0.067
→ 1,2,3,6,8-Cl5N	σ [1,2,3,6,8,5-Cl6N-5H]+	182.49	4.43	0.094	0.011
→ 1,2,3,5,6-Cl5N	σ [1,2,3,5,6,8-Cl6N-8H]+	186.10	2.57	0.008	0.039
→ 1.2.4.5.7-Cl5N	σ [1,2,4,5,7,6-Cl6N-6H]+	188.70	4.38	0.001	0.011
→ 1,2,4,5,6-Cl5N	σ [1,2,4,5,6,7-Cl6N-7H]+	194.50	5.14	0.000	0.007
→ 1,2,3,5,8-Cl5N	σ [1,2,3,5,8,6-Cl6N-6H]+	192.46	5.25	0.000	0.006
of 1,2,3,5,7,8-Cl6N					
→ 1,2,4,6,7-Cl5N	σ [1,2,4,6,7,8-Cl6N-8H]+	185.44	1.78	0.004	0.067
→ 1,2,3,7,8-Cl5N	σ [1,2,3,7,8,5-Cl6N-5H]+	186.30	5.20	0.002	0.007
→ 1,2,3,5,7-Cl5N	σ [1,2,3,5,7,8-Cl6N-8H]+	181.92	1.82	0.040	0.066
→ 1,2,4,6,8-Cl5N	σ [1,2,4,6,8,7-Cl6N-7H]+	191.03	4.38	0.000	0.012
→ 1.2.4.7.8-Cl5N	σ [1,2,4,7,8,6-Cl6N-6H]+	192.85	5.14	0.000	0.007
→ 1,2,3,5,8-Cl5N	σ [1,2,3,5,8,7-Cl6N-7H]+	189.86	5.28	0.000	0.006
of 1,2,4,5,6,8-Cl6N (x2)					
→ 1,2,4,6,8-Cl5N	σ [1,2,4,6,8,5-Cl6N-5H]+	181.23	1.05	0.000	0.012
→ 1,2,4,5,6-Cl5N	σ [1,2,4,5,6,8-Cl6N-8H]+	183.54	1.84	0.000	0.007
→ 1,2,4,5,8-Cl5N	σ [1,2,4,5,8,6-Cl6N-6H]+	190.55	5.23	0.000	0.001
of 1,2,4,5,7,8-Cl6N (x2)					
→ 1,2,4,5,7-Cl5N	σ [1,2,4,5,7,8-Cl6N-8H]+	179.65	1.08	0.002	0.011
→ 1,2,4,7,8-Cl5N	σ [1,2,4,7,8,5-Cl6N-5H]+	185.58	1.81	0.000	0.007
→ 1.2.4.5.8-Cl5N	σ [1,2,4,5,8,7-Cl6N-7H]+	192.48	5.23	0.000	0.001
of 1,2,3,4,5,6-Cl6N					
→ 1,2,3,7,8-Cl5N	σ [1,2,3,7,8,4-Cl6N-4H]+	184.36	4.40	0.002	0.007
→ 1,2,3,5,6-Cl5N	σ [1,2,3,5,6,4-Cl6N-4H]+	182.15	1.80	0.009	0.039
→ 1.2.3.4.6-Cl5N	σ [1,2,3,4,6,5-Cl6N-5H]+	184.75	1.82	0.002	0.038
→ 1,2,4,7,8-Cl5N	σ [1,2,4,7,8,3-Cl6N-3H]+	190.46	4.34	0.000	0.007
→ 1,2,4,5,6-Cl5N	σ [1,2,4,5,6,3-Cl6N-3H]+	190.35	4.36	0.000	0.007
→ 1,2,3,4,5-Cl5N	σ [1,2,3,4,5,6-Cl6N-6H]+	189.56	5.40	0.000	0.003
of 1.2.3.4.5.8-Cl6N (x2)					
→ 1,2,3,5,8-Cl5N	σ [1,2,3,5,8,4-Cl6N-4H]+	181.31	1.04	0.000	0.006
→ 1,2,3,4,5-Cl5N	σ [1,2,3,4,5,8-Cl6N-8H]+	182.23	1.97	0.000	0.003
→ 1,2,4,5,8-Cl5N	σ [1,2,4,5,8,3-Cl6N-3H]+	190.81	4.32	0.000	0.001
of 1,2,3,6,7,8-Cl6N (x2)					
→ 1,2,3,6,7-Cl5N	σ [1,2,3,6,7,8-Cl6N-8H]+	186.48	1.94	0.244	0.058
→ 1,2,3,6,8-Cl5N	σ [1,2,3,6,8,7-Cl6N-7H]+	188.27	4.40	0.073	0.011
→ 1,2,3,7,8-Cl5N	σ [1,2,3,7,8,6-Cl6N-6H]+	193.72	5.15	0.002	0.007

$\Delta H^{\circ}_{activation}$ (ΔH°_{act}) and $\Delta H^{\circ}_{reaction}$ (ΔH°_{rct}) in kcal/mol

Table 1 shows the dechlorination / hydrogenation pathway, the intermediate, $\Delta H^\circ_{activation}$ and $\Delta H^\circ_{reaction}$ and the calculated values for relative abundance $x_{i,activation}$ and $x_{i,reaction}$. The lowest values of $\Delta H^\circ_{activation}$ appear always in the α-position of naphthalene moiety, these are the intermediates Cl_xN-1H, -4H, -5H, -8H. The results of the semi–empirical geometry optimization show that the σ-complexes in α-position are less sterically hindered compared to β-position. But more important are the values of $\Delta H^\circ_{reaction}$, because they show a good relationship between enthalpy and isomer distribution. The lower the endothermic energy the higher the yield of dechlorination of the considered position. The lowest endothermic $\Delta H^\circ_{reaction}$ values show the chloronaphthalenes if one of the two chlorine in α-position is replaced. That indicates that the peri-position of two chlorine is energetically unfavored in comparison with one chlorine and one hydrogen. The lowest endothermic values of $\Delta H^\circ_{reaction}$ show the Cl_xN with four chlorine in α-position (0.9 – 1.1 kcal/mol, α_{peri}-dechlorination), next is three chlorine in α-position and having chlorine as a neighbor in β-position or four chlorine in α-position without chlorine as a neighbor (1.7 – 1.9 kcal/mol, α_{peri}-dechlorination). Interesting is the behavior of dechlorination of chloronaphthalenes if there is one chlorine with one hydrogen in peri position (α'-dechlorination) or if there is one chlorine in β-position having two chlorines as neighbors (β_{vic}-dechlorination), both nearly show the same values of $\Delta H^\circ_{reaction}$ (4.3 – 4.5 kcal/mol) what means both positions have nearly the same probability for dechlorination.

The highest values of $\Delta H^\circ_{reaction}$ shows the dechlorination of chlorine in β-position with one or no chlorine as neighbor (5.1 - 6.2 kcal/mol, β-dechlorination).

Table 2 shows the isomer distribution calculated via $\Delta H^\circ_{activation}$ and $\Delta H^\circ_{reaction}$ in comparison to a mean value of fly ash of MWI's.

The main dechlorination pathway of Cl_8N is the loss of chlorine in the α-position (α_{peri}-dechlorination) (0.93 kcal/mol vs. 4.27 kcal/mol in β-position) leading to 1,2,3,4,5,6,7-Cl_7N in 90.5 % yield. This 1,2,3,4,5,6,7-Cl_7N is preferably dechlorinated in the other peri-position of two chlorine (α_{peri}-dechlorination), leading to the 1,2,3,4,6,7-Cl_7N and 1,2,3,5,6,7-Cl_7N. Both have nearly the same heat of formation (ΔH°_f) and therefore similar $\Delta H^\circ_{reaction}$ and lead to the assumption both are formed in equal ratios, because both isomers coelute on a DB5 column and can only quantified as sum. The subsequent dechlorination of the both main Cl_7N-isomers, 1,2,3,4,6,7- and 1,2,3,5,6,7-Cl_7N, leads among others, to the both main Cl_6N-isomers 1,2,3,6,7- and 1,2,3,5,6-Cl_6N. At this point in the dechlorination pathway α'-dechlorination and β_{vic}-dechlorination get more likely (because of the lack of α_{peri}-positions) and the isomer distribution becomes broader.

There is a poor relationship between calculated isomer distribution by $\Delta H^\circ_{activation}$ that indicates that the formation of Cl_xN on fly ash is not a kinetically controlled dechlorination reaction. But there is a good relationship between calculated isomer distribution by $\Delta H^\circ_{reaction}$ and the isomer distribution. These results strongly indicate that one of the most important formation pathways of chloronaphthalenes on fly ash of MWI's are via a thermodynamically controlled dechlorination of the perchlorinated compound. This result should be contrasted to the pattern of chlorinated dibenzodioxins[7]. The pattern obtained here can be explained by the reactivity of the PCDD compounds, as it was shown for the calculated HOMO – LUMO values. Our investigations on formation of chlorinated aromatics have shown, that first the perchlorinated compounds are formed, which get further dechlorinated[8].

Table 2: Isomer distribution calculated via $\Delta H°_{activation}$ and $\Delta H°_{reaction}$ vs. mean values of FA MWI

	calc. Isom.distr. % Activation	calc. Isom.distr. % Reaction	mean % FA MWI		calc. Isom.distr. % Activation	calc. Isom.distr. % Reaction	mean % FA MWI
Cl7N				Cl5N			
1,2,3,4,5,6,7-Cl7N	99.63	90.50	90.55	1,2,3,4,5-Cl5N	0.02	1.02	3.79
1,2,3,4,5,6,8-Cl7N	0.37	9.50	9.45	1,2,3,4,6-Cl5N	0.33	11.46	11.29
Cl6N				1,2,3,5,6-Cl5N	2.44	11.60	19.30
1,2,3,4,5,6-Cl6N	0.14	5.93	9.02	1,2,3,5,7-Cl5N	10.27	19.71	12.08
1,2,3,4,5,7-Cl6N	2.02	9.83	6.57	1,2,3,5,8-Cl5N	0.05	1.92	2.11
1,2,3,4,5,8-Cl6N	0.00	0.29	0.00	1,2,3,6,7-Cl5N	60.27	17.43	20.52
1,2,3,4,6,7-Cl6N	7.43	29.03	32.39	1,2,3,6,8-Cl5N	24.24	3.33	1.62
1,2,3,5,6,7-Cl6N	53.25	28.72	32.39	1,2,3,7,8-Cl5N	0.60	2.01	3.81
1,2,3,5,6,8-Cl6N	1.83	10.00	6.57	1,2,4,5,6-Cl5N	0.01	2.06	3.59
1,2,3,5,7,8-Cl6N	0.52	10.20	7.00	1,2,4,5,7-Cl5N	0.52	3.43	2.89
1,2,3,6,7,8-Cl6N	34.80	4.91	4.60	1,2,4,5,8-Cl5N	0.00	0.21	0.64
1,2,4,5,6,8-Cl6N	0.00	0.54	0.73	1,2,4,6,7-Cl5N	1.19	20.22	12.08
1,2,4,5,7,8-Cl6N	0.00	0.54	0.73	1,2,4,6,8-Cl5N	0.04	3.50	3.05
				1,2,4,7,8-Cl5N	0.01	2.10	3.23

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