

PATTERN OF REGIOISOMERS OF POLYCHLORINATED NAPHTHALENES FORMED BY INCINERATION: CALCULATED THERMODYNAMIC VALUES AND CALCULATED REACTIVITIES OF REGIOISOMERS FOR SUBSEQUENT DECHLORINATION

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Introduction

Polychlorinated naphthalenes, PCN, are very likely to be formed in a thermodynamic controlled dechlorination reaction of octachloronaphthalene. From the presence of a specific isomer pattern can be concluded that a regioselective reaction mechanism takes place. Two different methods were used to describe and predict the isomer pattern of PCN on fly ashes of municipal waste incinerators, MWI's. Semi-empirical MO methods were used to calculate thermodynamic data.^{1,2,3,4} From the values of the heat of formation, ΔH_f° , the reaction enthalpies, $\Delta H_{\text{reaction}}^\circ$, were calculated. Second the reactivities of the positions in the naphthalene structure were calculated. Under the assumption regioselectivity is based on constant reactivity of the two major positions α and β , subsequent isomer pattern can be calculated^{5,6}.

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 package HyperChem 5.1 Professional, Hypercube, Inc., calculates ΔH_f° by optimizing the molecular geometry, until ΔH_f° reaches the minimum. The Standard Heat of Formation, ΔH_f° , of Cl_8N , Cl_7N , Cl_6N , Cl_5N and the intermediate σ -complexes of the reaction $\text{Cl}_x\text{N} + \text{H}^+ \rightarrow \sigma[\text{Cl}_x\text{N-H}]^+ \rightarrow \text{Cl}_{x-1}\text{N} + \text{Cl}^+$ as model for ipso-substitution were calculated by PM3. Subtraction of $\Delta H_f^\circ \sigma[\text{Cl}_x\text{N-H}]^+$ from $\Delta H_f^\circ \text{Cl}_x\text{N}$ gives the $\Delta H_{\text{activation}}^\circ$, subtraction of $\Delta H_f^\circ \text{Cl}_{x-1}\text{N}$ from $\Delta H_f^\circ \text{Cl}_x\text{N}$ gives $\Delta H_{\text{reaction}}^\circ$. With the equation $x_{i,\text{reaction}} = f_{\text{stat}} \{ \exp -\Delta H_{i,\text{reaction}}^\circ / RT / \{ \Sigma (\exp -\Delta H_{\text{reaction}}^\circ / RT) \} \}$ the relative abundance $x_{i,\text{reaction}}$ of Cl_xN were calculated. f_{stat} is a statistical factor including the educt-isomer ratios and for symmetrical educts the symmetry factor. The isomer distribution of reaction is calculated by the sum of x_i leading to the same product but via different reaction pathways within a homologue group.

The reactivity of the α - and β - position in the naphthalene structure is calculated from the isomer ratios of the both Cl_7N . The isomer ratio 1,2,3,4,5,6,7- Cl_7N : 1,2,3,4,5,6,8- Cl_7N of 90.5 : 9.5 gives a reactivity for the dechlorination / hydrogenation of the α -position of $a = 0.226$ and for the β -position of $b = 0.024$.

Subsequent dechlorination steps show the same reactivities in the positions α and β if the same interactions between neighboring chlorine atoms takes place. Under the assumption that steric

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stress is the main forcing power of the dechlorination, the number of neighboring chlorine will have an influence on the values of reactivities of a certain position. The values of a and b have to be corrected by a proportional factor in dependence of the number and position of neighboring chlorine atoms. The calculated formation rate of a certain isomer within a group of homologues is a function of the reactivity of all Cl_xN precursors and the number of reaction pathways leading to that isomer.

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

Results and Discussion

Table 1 shows the dechlorination / hydrogenation pathway, $\Delta H^\circ_{\text{activation}}$ and $\Delta H^\circ_{\text{reaction}}$, the position of the leaving chlorine and interactions between the neighboring chlorine atoms. Also presented are the values of reactivity for the different positions in the naphthalene structure. The lowest values of $\Delta H^\circ_{\text{activation}}$ appear always in the α -position of naphthalene moiety. The results of the semi-empirical geometry optimization show that the σ -complexes in α -position are less sterically hindered compared to β -position.

More important are the values of $\Delta H^\circ_{\text{reaction}}$, because they show a good relationship between enthalpy, steric interaction between leaving chlorine and neighboring chlorine atoms, reactivity and isomer distribution. The lower the endothermic energy the higher the reactivity and the yield of dechlorination of the considered position. The lowest endothermic $\Delta H^\circ_{\text{reaction}}$ values and highest values of reactivity show the chloronaphthalenes if a chlorine in α -position with neighboring chlorine in peri- and ortho-position is replaced by hydrogen (a = dechlorination in α -position with chlorine in peri- and ortho-position). That indicates that the peri-position of two chlorine is energetically unfavored in comparison to one chlorine and one hydrogen in peri position. The isomers formed via this reaction pathway appear in the highest amounts.

If the neighboring chlorine in peri position is missing (a' = dechlorination in α -position without a neighboring chlorine in peri-position) the values of $\Delta H^\circ_{\text{reaction}}$ and reactivities are comparable to those of the dechlorination in β -position if there are two chlorines as neighbors (b = dechlorination in β -position with chlorine in both ortho-positions).

The highest values of $\Delta H^\circ_{\text{reaction}}$ and lowest values of reactivity shows the dechlorination of chlorine in β -position without chlorine as neighbor (b'' = dechlorination in β -position without both neighboring chlorine in α -ortho- / β -ortho-position).

The isomer pattern calculated via $\Delta H^\circ_{\text{reaction}}$ and reactivities of regioisomers show very good conformity to the pattern found on fly ashes of MWI's, see figure 1 and 2. These results strongly indicate that one of the most important formation pathways of chloronaphthalenes on fly ashes of MWI's is a thermodynamically controlled dechlorination of the perchlorinated compound, whereby the steric interactions between the chlorine-substitutes strongly influence the reaction pathway.

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Table 1: $\Delta H^\circ_{\text{activation}}$, $\Delta H^\circ_{\text{reaction}}$ and position of the dechlorination / hydrogenation with interaction of neighboring chlorine atoms from $\text{Cl}_8\text{N} - \text{Cl}_6\text{N}$ and values of the reactivities

Dechlorination / Hydrogenation	$\Delta H^\circ_{\text{act}}$	$\Delta H^\circ_{\text{ret}}$	Position/ Interaction of Dechlor.	Dechlorination / Hydrogenation	$\Delta H^\circ_{\text{act}}$	$\Delta H^\circ_{\text{ret}}$	Position/ Interaction of Dechlor.
of 1,2,3,4,5,6,7,8-Cl ₈ N				of 1,2,3,5,6,8-Cl ₆ N			
→ 1,2,3,4,5,6,7-Cl ₇ N	181.95	0.93	a	→ 1,2,4,6,7-Cl ₅ N	187.23	1.75	a
→ 1,2,3,4,5,6,8-Cl ₇ N	190.27	4.27	b	→ 1,2,3,6,8-Cl ₅ N	182.49	4.43	a' _a
				→ 1,2,3,5,6-Cl ₅ N	186.10	2.57	a' _b
of 1,2,3,4,5,6,7-Cl ₇ N				→ 1,2,4,5,7-Cl ₅ N	188.70	4.38	b
→ 1,2,3,6,7,8-Cl ₆ N	183.95	4.37	a' _a	→ 1,2,4,5,6-Cl ₅ N	194.50	5.14	b' _a
→ 1,2,3,5,6,7-Cl ₆ N	183.32	1.74	a	→ 1,2,3,5,8-Cl ₅ N	192.46	5.25	b' _b
→ 1,2,3,4,6,7-Cl ₆ N	186.25	1.73	a	of 1,2,3,5,7,8-Cl ₆ N			
→ 1,2,3,5,7,8-Cl ₆ N	191.51	4.31	b	→ 1,2,4,6,7-Cl ₅ N	185.44	1.78	a
→ 1,2,3,5,6,8-Cl ₆ N	189.33	4.34	b	→ 1,2,3,7,8-Cl ₅ N	186.30	5.20	a''
→ 1,2,3,4,5,7-Cl ₆ N	189.67	4.36	b	→ 1,2,3,5,7-Cl ₅ N	181.92	1.82	a
→ 1,2,3,4,5,6-Cl ₆ N	193.56	5.11	b' _a	→ 1,2,4,6,8-Cl ₅ N	191.03	4.38	b
of 1,2,3,4,5,6,8-Cl ₇ N				→ 1,2,4,7,8-Cl ₅ N	192.85	5.14	b' _a
→ 1,2,3,5,7,8-Cl ₆ N	182.67	0.96	a	→ 1,2,3,5,8-Cl ₅ N	189.86	5.28	b' _b
→ 1,2,3,5,6,8-Cl ₆ N	181.07	0.99	a	of 1,2,4,5,6,8-Cl ₆ N (x2)			
→ 1,2,3,4,5,7-Cl ₆ N	180.56	1.02	a	→ 1,2,4,6,8-Cl ₅ N	181.23	1.05	a
→ 1,2,3,4,5,6-Cl ₆ N	184.52	1.77	a' _b	→ 1,2,4,5,6-Cl ₅ N	183.54	1.84	a' _b
→ 1,2,4,5,7,8-Cl ₆ N	189.76	4.29	b	→ 1,2,4,5,8-Cl ₅ N	190.55	5.23	b' _b
→ 1,2,4,5,6,8-Cl ₆ N	191.57	4.29	b	of 1,2,4,5,7,8-Cl ₆ N (x2)			
→ 1,2,3,4,5,8-Cl ₆ N	191.06	5.20	b' _b	→ 1,2,4,5,7-Cl ₅ N	179.65	1.08	a
				→ 1,2,4,7,8-Cl ₅ N	185.58	1.81	a' _b
of 1,2,3,4,6,7-Cl ₆ N (x2)				→ 1,2,4,5,8-Cl ₅ N	192.48	5.23	b' _b
→ 1,2,3,6,7-Cl ₅ N	184.58	4.58	a' _a	of 1,2,3,4,5,6-Cl ₆ N			
→ 1,2,4,6,7-Cl ₅ N	190.15	4.36	b	→ 1,2,3,7,8-Cl ₅ N	184.36	4.40	a' _a
→ 1,2,3,4,6-Cl ₅ N	192.70	5.20	b' _a	→ 1,2,3,5,6-Cl ₅ N	182.15	1.80	a
of 1,2,3,5,6,7-Cl ₆ N (x2)				→ 1,2,3,4,6-Cl ₅ N	184.75	1.82	a
→ 1,2,3,6,7-Cl ₅ N	187.63	4.57	a' _a	→ 1,2,4,7,8-Cl ₅ N	190.46	4.34	b
→ 1,2,3,5,7-Cl ₅ N	190.53	4.38	b	→ 1,2,4,5,6-Cl ₅ N	190.35	4.36	b
→ 1,2,3,5,6-Cl ₅ N	192.40	5.17	b' _a	→ 1,2,3,4,5-Cl ₅ N	189.56	5.40	b' _b
of 1,2,3,4,5,7-Cl ₆ N				of 1,2,3,4,5,8-Cl ₆ N (x2)			
→ 1,2,3,6,8-Cl ₅ N	182.97	4.40	a' _a	→ 1,2,3,5,8-Cl ₅ N	181.31	1.04	a
→ 1,2,3,5,7-Cl ₅ N	183.94	1.76	a	→ 1,2,3,4,5-Cl ₅ N	182.23	1.97	a' _b
→ 1,2,3,4,6-Cl ₅ N	189.54	2.57	a' _b	→ 1,2,4,5,8-Cl ₅ N	190.81	4.32	b
→ 1,2,4,6,8-Cl ₅ N	192.38	4.33	b	of 1,2,3,6,7,8-Cl ₆ N (x2)			
→ 1,2,4,5,7-Cl ₅ N	188.38	4.36	b	→ 1,2,3,6,7-Cl ₅ N	186.48	1.94	a
→ 1,2,3,4,5-Cl ₅ N	194.92	6.15	b''	→ 1,2,3,6,8-Cl ₅ N	188.27	4.40	b
				→ 1,2,3,7,8-Cl ₅ N	193.72	5.15	b' _a
reactivity:				reactivity:			
a	0.226			b' _a	0.022		
b	0.024			b' _b	0.022		
a' _a	0.024			a''	0.022		
a' _b	0.210			b''	0.018		

$\Delta H^\circ_{\text{activation}}$ ($\Delta H^\circ_{\text{act}}$) and $\Delta H^\circ_{\text{reaction}}$ ($\Delta H^\circ_{\text{ret}}$) in kcal/mol

Position and interaction of chlorine atoms in the dechlorination/hydrogenation:

a = dechlorination in α -position with chlorine in peri- and ortho-position

b = dechlorination in β -position with chlorine in both ortho-positions

a'_a / a'_b = dechlorination in α -position without a neighboring chlorine in peri- / ortho-position

b'_a / b'_b = dechlorination in β -position without a neighboring chlorine in α -ortho- / β -ortho-pos.

a'' = dechlorination in α -position without both neighboring chlorine in peri- and ortho-position

b'' = dechlorination in β -position without both neighboring chlorine in α -ortho- / β -ortho-pos.

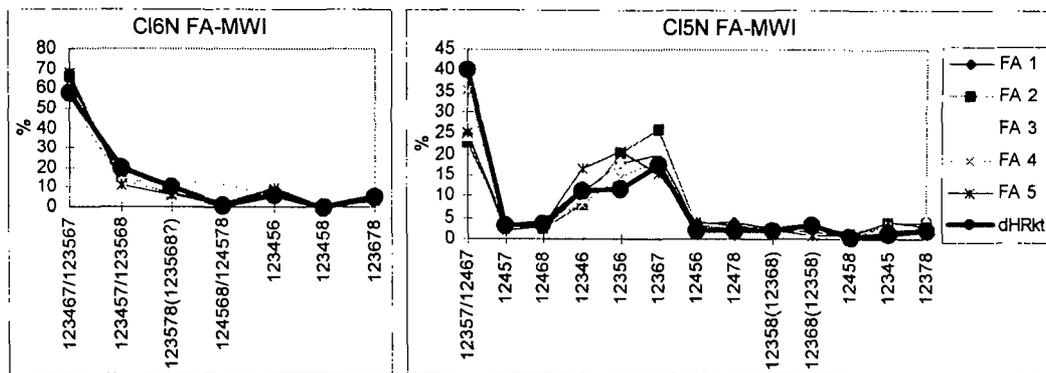


Figure 1: Cl₆N and Cl₅N isomer distribution calculated via $\Delta H^{\circ}_{\text{reaction}}$ in comparison to values on fly ashes of MWI's. The lines are only a help for visualizing the values, bolded are the calculated values.

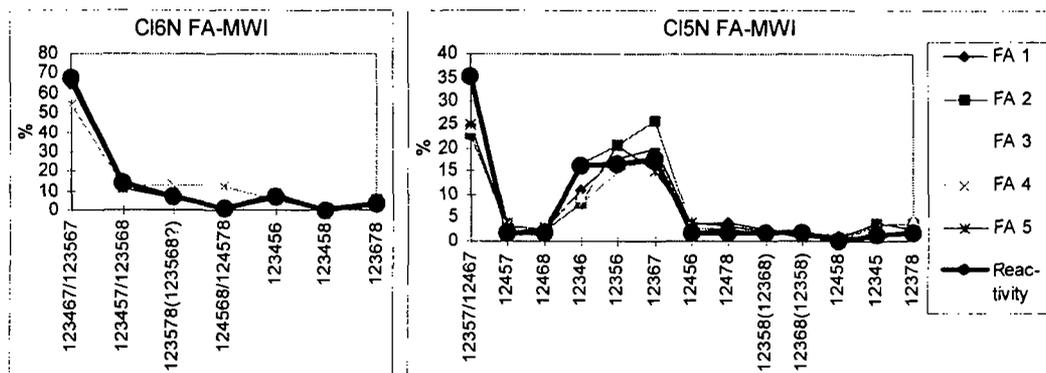


Figure 2: Cl₆N and Cl₅N isomer distribution calculated via reactivities of regioisomers in comparison to values on fly ashes of MWI's.

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