

KINETIC ISOTOPE EFFECT OF HYDROGEN IN HYDRODECHLORINATION OF POLYCHLORONAPHTHALENES

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Introduction

Polychloronaphthalenes(PCNs) were released into the environment as mixtures of congeners with different content of chlorine. It is known that only few congeners are persistent – PCNs 42, 52/60 and 66/67¹. All these PCNs have common structural feature – absence of a pair of chlorine atoms in *peri*-positions (1,8 or 4,5). In our effort to develop selective synthetic methods for PCNs we have found that reaction of PCNs with Cu in boiling acetic acid shows similar selectivity – only PCNs without *peri*-dichloro fragment are persistent in Cu/AcOH.

We tried to answer the question about the origin of the persistent PCN molecules in the environment – are they unchanged minor components of technical mixture or degradation products of higher chlorinated major components?

We believe the ratio of Protium/Deuterium can help to choose between the two possibilities. If persistent PCNs are unchanged components of technical mixture, the ratio H/D should be similar to that in technical product. If persistent PCNs are environmentally degraded, they should have higher H/D ratio, if there is kinetic isotope effect of Hydrogen in reaction of their hydrodechlorination in environmental media.

This report provides first results on KIE in model reaction of PCNs with Cu in AcOH/D₂O and CF₃COOH/D₂O.

Materials and Methods

Course of reactions, separation, purification and purities of products were controlled by GC/ECD. GC conditions were as follows : GC-Varian3700, inj. – Gerstel split/splitless at 250°C, column – DB-5(app. 50m), Det. – ECD(at 300°C), carrier gas – nitrogen, make-up – nitrogen. Pr.: 160 °C(2 min) - 20 °C/min - 280 °C(10 min) Purge 1.00-1.90 min. Structures of new compounds were confirmed by NMR (Bruker DPX-300).

1,2,4,6,8-PeCN and 1,2,4,5,6-PeCN were synthesized previously. 1,3,6,8-TeCN was prepared from naphthalene-2,7-disulfochloride via nitration and reaction of 1,8-dinitronaphthalene-3,6-disulfochloride with hexachlorocyclopentadiene.

1,8-Dinitronaphthalene-3,6-disulfochloride. 3.25g (0.01 mole) of naphthalene-2,7-disulfochloride were added to 10ml of Oleum with stirring, followed by 2.02g of KNO₃ (0.02 mole). The temperature was risen to 80°C in 1 hour and the mixture was stirred at this temperature for 10 hours. The mixture was allowed to cool and then was poured with precautions into 50g of ice. The yellow precipitate was filtered after 30 min, washed with 20 ml of water, dried on air, mixed with 20ml of benzene and 3 ml of SOCl₂ and kept at reflux for 5 hours. Solution was filtered and filtrate deposited crystals upon cooling.

Yield of 1,8-dinitronaphthalene-3,6-disulfochloride – 460 mg (11%). ¹H NMR(δ, ppm) 8.97d, 9.15d, J = 1.8Hz.

1,3,6,8-Tetrachloronaphthalene. 1,8-dinitronaphthalene-3,6-disulfochloride from the previous experiment was mixed with 2.5 ml of hexachlorocyclopentadiene and the mixture kept at reflux for 4 hours. The mixture was allowed to cool to room temperature, dissolved in hexane and separated on silicagel column with hexane as eluent. Fractions containing mainly the target compound (GC-ECD) were collected, evaporated to dryness and the residue recrystallized from ethanol. Yield of 1,3,6,8-Tetrachloronaphthalene – 66%. MP = 156°C. ¹H NMR(δ, ppm) 7.65d, 7.69d, J = 2.2Hz.

Determination of k_H/k_D. 5-10mg sample of a PCN, 20 mg of Cu powder and 1ml of a mixture of D₂O with CH₃COOH or CF₃COOH (1 : 1, mole/mole; [H]/[D] = 1/2) were refluxed for 4-6 hours, until precipitation (CuCl) ceased and/or peaks of a starting PCN disappeared on chromatogram. 2 ml of water were added and the suspension was extracted with 2ml of CCl₄. The extract was filtered and filtrate evaporated to a volume of 0.1-0.2 ml. 0.5 ml of CDCl₃ was added and solution analyzed by ¹H NMR. Integration of NMR signals produced the ratio of H/D in the position of the eliminated Cl. Multiplication by a factor of 2 ([D]/[H]) gave KIE (k_H/k_D).

Results and Discussion

1. Selectivity in chlorination of PCNs (production of Halowaxes). In naphthalene, α -positions(1,4,5,8) are more reactive than β -positions(2,3,6,7) to electrofylic reagents. For example, chlorination of naphthalene initially produces 85% of 1-chloronaphthalene and 15% of 2-chloronaphthalene (Fig. 1):

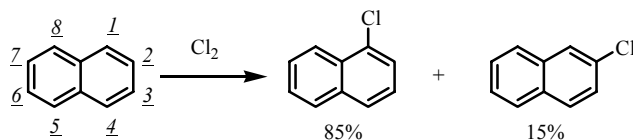


Figure 1. Selectivity of chlorination of naphthalene.

In course of further chlorination α -positions remain more active, than β . It is demonstrated on Fig. 2 by the fact that Halowax-1051, which is primarily OCN, contains as the main impurity ca 15% of 1,2,3,4,5,6,8-HpCN (β -H-HpCN) and very little of 1,2,3,4,5,6,7-HpCN (α -H-HpCN) :

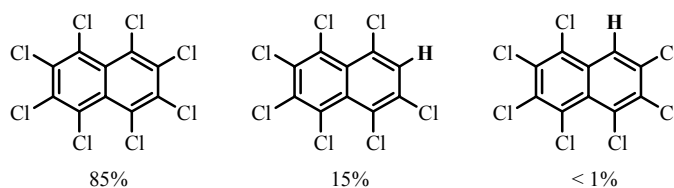


Figure 2. Composition of Halowax 1051.

2. Bioaccumulation/biomagnification of PCNs. In view of the fact that technical Halowaxes contain PCNs with non-chlorinated β -positions, rather than α -, it is intriguing why the persistent congeners have at least two α -positions unsubstituted (Fig. 3):

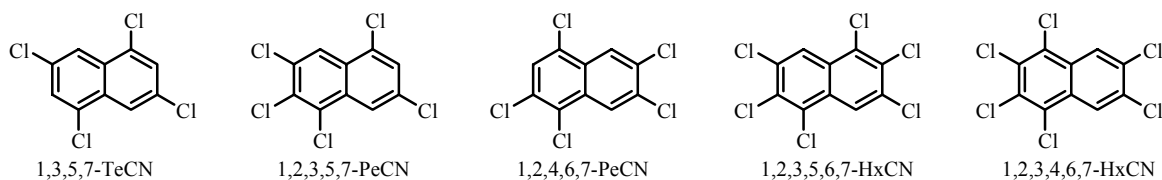
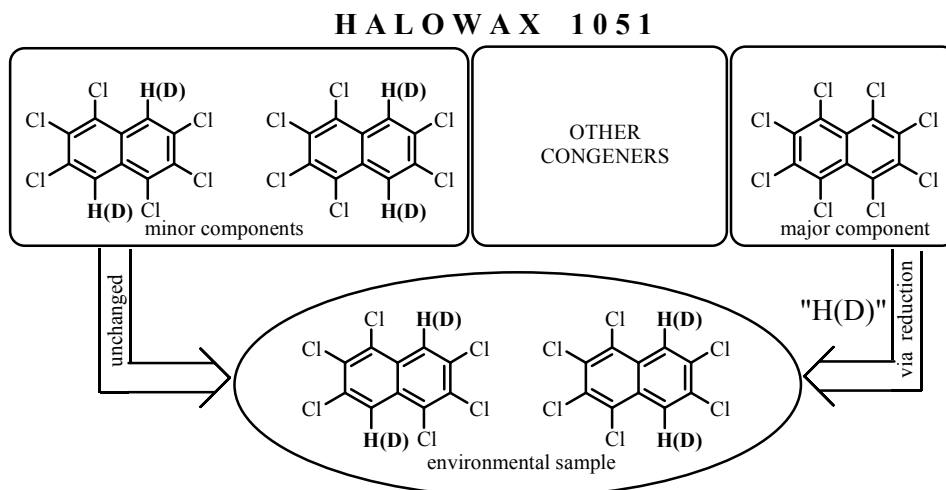


Figure 3. Persistent PCN congeners (BMF = 30-50)²

One of possible explanations is that these congeners are hydrodechlorination products of higher chlorinated major components of technical mixtures, rather than extremely persistent minor components.

Consider these two possibilities on the example of 1,2,3,5,6,7-HxCN/1,2,3,4,6,7-HxCN and think of the H/D ratio at the free positions of the naphthalene ring:



If two HxCNs found in the environment are unchanged molecules of the parent Halowax, the ratio H/D should be the same as in technical product. If these are formed from octachloronaphthalene via hydrodechlorination and there is KIE on formation of C-H bond – then the HxCN would be depleted in Deuterium. The ratio H/D would depend on the magnitude of KIE and proportion of degradation product/unchanged HxCN in a sample.

3. Selection of a model reaction. We had no technical possibility to perform degradation experiments with OCN in the environment. We decided to try to determine k_H/k_D in a model reaction of PCNs with Cu in $\text{CH}_3\text{COOH}/\text{D}_2\text{O}$ or $\text{CF}_3\text{COOH}/\text{D}_2\text{O}$. We have found earlier that PCNs react with Cu in AcOH only if they have two neighbor Cl atoms in *peri*-positions. PVNs without such pair of Cl are inert to Cu. Thus the selectivity of Cu (Fig.4) and “selectivity of the environment” are similar (Fig.3).

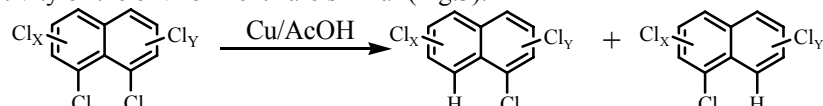


Figure 4. Reaction of PCNs with Cu in boiling AcOH.

Only α -Cl can be removed, and only if there is another Cl in *peri*-position. β -Cl are inactive.

4. Selection of model PCN congeners. For the determination of Protium/Deuterium ratio in a position of a “new” Hydrogen atom in the reaction product, the molecule has to conform to the following requirements: a) it must contain at least one “old” Hydrogen atom, b) these “new” and “old” Hydrogen atoms must be non-equivalent, c) signals of the “new” and the “old” Hydrogen atoms in ^1H NMR spectrum must be well-resolved from each other and from other signals in spectrum, d) reaction gives only one isomer. Of all 75 PCN congeners only two (1,3,6,8-TeCN and 1,2,3,6,7,8-HxCN) yield such products (1,3,6-TricCN and 1,2,3,6,7-PeCN, respectively). We chose to synthesize 1,3,6,8-TeCN because this is one of the four PCN congeners not described in the literature³.

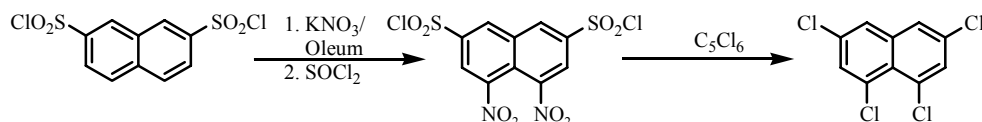


Figure 5. Synthesis of 1,3,6,8-TeCN.

Also we studied hydrodechlorination of 1,2,4,6,8-TeCN, 1,2,4,5,6-TeCN and 1,2,3,7,8-TeCN, despite these congeners yield two isomers. We did not expect that all necessary NMR signals would be resolved, but we hoped we can get “average” k_H/k_D values for two reactions (fig. 6), in an assumption that difference in KIE for similar processes are small.

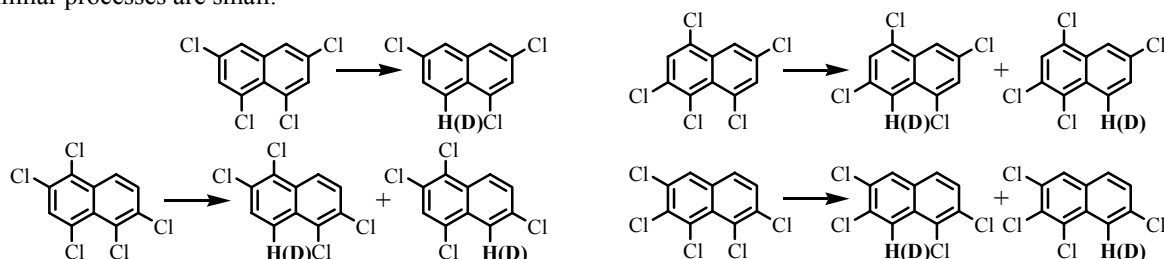


Figure 6. Hydrodechlorination of model PCNs.

5. KIE in the model reaction. We have studied reaction of the four PCNs with Cu in both $\text{CH}_3\text{COOH}/\text{D}_2\text{O}$ and $\text{CF}_3\text{COOH}/\text{D}_2\text{O}$ mixtures. Unfortunately, several experiments failed and we were unable to deduce a reasonable estimation for k_H/k_D . The KIE values calculated from the NMR data obtained so far are given in the Table 1.

Table 1. Kinetic isotope effect of hydrogen in hydrodechlorination of selected PCNs with Cu.

starting PCN	k_H/k_D in:	
	$\text{CH}_3\text{COOH}/\text{D}_2\text{O}$	$\text{CF}_3\text{COOH}/\text{D}_2\text{O}$
1,3,6,8-TeCN	8 ± 2	7 ± 1
1,2,4,5,6-PeCN		6 ± 1
1,2,4,6,8-PeCN		(28)

Generally speaking these values can not be called KIE, as there was no temperature control (mixtures were kept at reflux) and no attempt was made to prove that these KIE are true relative rates of formation of ^1H -isotopomer and ^2H -isotopomer. These are “pseudo $k_{\text{H}}/k_{\text{D}}$ ”, observed values in a single experiment.

6. Extremely high KIE value – 28 for hydrodechlorination of 1,2,4,6,8-PeCN. This value was calculated after careful integration of a spectrum with not fully resolved signals, high noise and background, incomplete conversion and in case of formation of two isomers (Fig. 7). Therefore it has to be considered as provisional.

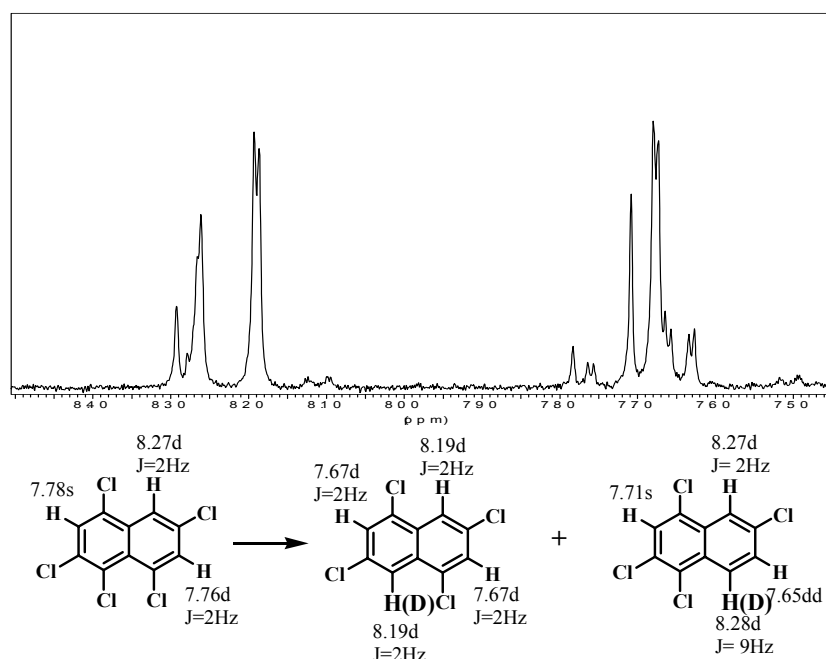


Figure 7. ^1H NMR spectrum of reaction products of 1,2,4,6,8-PeCN with Cu and assignment of the signals.

Nevertheless, the very small inclusion of Deuterium into the molecule of 1,3,5,7-TeCN is evident at a glance on the spectrum as fig. 7. Two highest signals (doublets) in the spectrum belong to α - (8.19ppm) and β - (7.67ppm) protons of the 1,3,5,7-TeCN. It means the amount of Deuterium in a “new” position is negligible. For instance, if the height of a signal at 8.19ppm was 95% of that of a signal at 7.67, this would correspond to $\text{KIE} = 18$.

The $k_{\text{H}}/k_{\text{D}}$ value of 28 and even smaller values (6-8) for other congeners are high enough to consider contribution of tunneling. Relative contribution of tunneling shall be higher at lower temperatures, therefore even higher KIE can be expected at temperatures characteristic for reactions in the environment

Thus we have confirmed that there is very high kinetic isotope effect in a model reaction of hydrodechlorination of PCNs. If KIE is similar in reactions of degradation of PCNs in the environment, the difference in D/H ratio would be high enough to distinguish between stable components of technical product and products of degradation in the environment.

Acknowledgements

The help of the staff of NMR laboratory of St.Petersburg State University is gratefully acknowledged.

References

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