Kinetic isotope effects in environmental chemistry: natural distribution of Deuterium in different positions of pinene and theoretical analysis of isotopic distribution in polychlorobornanes

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Introduction

It is well-known that isotope ratios of common elements ($^{1}H/^{2}H$, $^{12}C/^{13}C$, $^{35}Cl/^{37}Cl$) are different in different organic compounds, and also different in the same substances from different sources. Recently it has attracted attention of environmental chemists. In particular, $^{12}C/^{13}C$ ratios in different formulations of Toxaphene and in different Halowaxes were found significant enough to distinguish between the sources [1,2].

Moreover, isotope ratios in specific positions of a molecule are usually also different. Official EC method for determination of geographic origin of wine is based on ^{2}H NMR determination of D-content in CH_2 and CH_3 groups of ethanol [3].

The reason for different isotope ratios is primary kinetic isotope effect (KIE) – different isotopes react with slightly (in some cases – significantly) different reaction rates. For instance, KIE for hydrogen $k(^{1}H)/k(^{2}H)$ can reach the theoretical maximum of 8, $k(^{12}C)/k(^{13}C)$ – 1.09, $k(^{35}Cl/^{37}Cl)$ – 1.015.

The goal of our research is to determine how this effect can influence isotope distribution in molecules of persistent chloroorganic pollutants. We have started with Toxaphene, because we expected significant isotope effects during its synthesis and degradation and also because big differences in D content in different positions of terpenes is a well-known fact [4].

In the present report we will discuss our experimental results on D-content in different positions of *a*-pinene and give an example of theoretical analysis of distribution of D in Toxaphene congeners derived from this particular specimen.

Materials and Methods

α-Pinene was of Russian origin, $a_{[D]} = -42^{o}$(neat). ^{2}H NMR spectra were recorded independently on Bruker AM-300 and on Bruker AMX-500 spectrometers from neat samples in 5mm and 10mm NMR tubes respectively. Integration of both spectra gave similar results.

For free-radical chlorination a typical value of $k(^{1}H)/k(^{2}H) = 2$ was arbitrarily taken.

Results and Discussion

D-NMR spectra recorded over the weekend allowed determination of relative D content in different positions of *a*-pinene with 10% accuracy (Fig. 1)

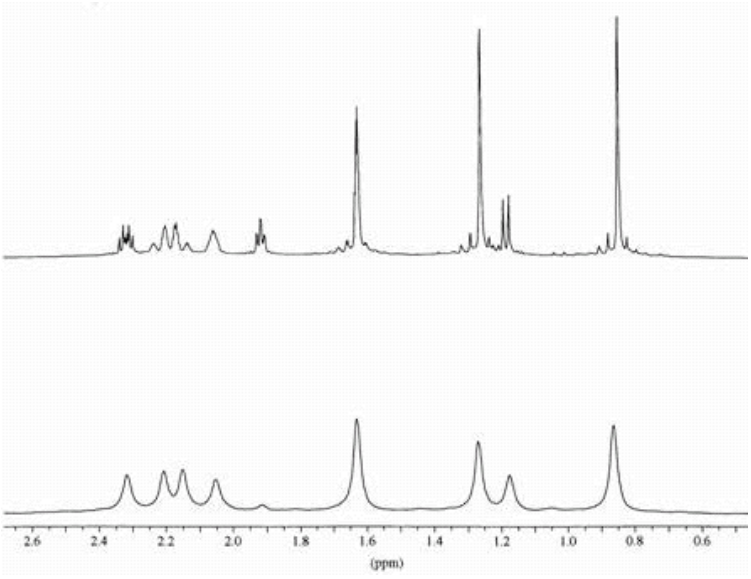

Figure 1. ^{1}H (upper) and ^{2}H (lower) NMR spectra of *a*-pinene (notice a very low response of D at 1.9ppm).

NMR assignment was made with help of two-dimensional NMR techniques. Relative content of Deuterium in each position is given below (relative to H-5) (Fig. 2).

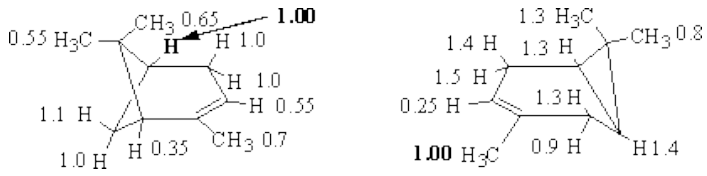

Figure 2. Relative D-content in different positions of *a*-pinene(left) and *d*-carene(right) [4].

D-content in a saturated ring part of a molecule (two CH_2-groups) is close to 1. D-content in methyl groups is lower, from 0.55 to 0.7. Also D-content at double bond is lower – 0.55. The most D-depleted position is at another bridgehead, with 3 times lower D-content.

In case of *a*-pinene the difference between the highest and the lowest D-content (0.35 and 1.1) is not as big as in case of *d*-carene (0.25 and 1.5), but still significant. This reflects Deuterium enrichment and depletion due to KIE on different steps of biosynthesis of these terpenes.

Let's consider now how the distribution of Deuterium would vary on the way from *a*-pinene to polychlorobornanes.

a-Pinene → bornylchloride → polychlorobornanes.

It was known from literature and it was confirmed by us recently that hydrochlorination of *a*-pinene yields bornylchloride with preservation of enantiomeric purity (Fig. 3).

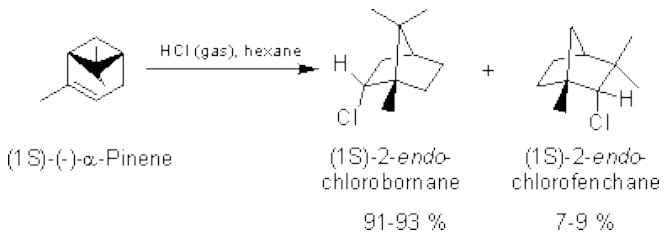

Figure 3. Enantioselective hydrochlorination of *a*-pinene.

This is a good evidence that no 2,6-H-shift and probably no other rearrangement occurs besides the main process – the expansion of a 4-membered ring into a 5-membered ring (Fig.4).

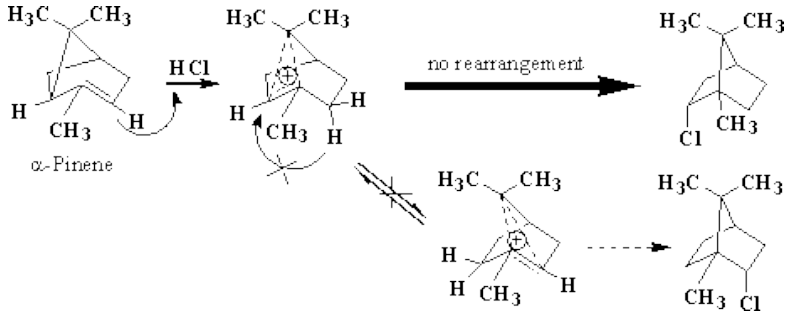

Figure 4. Mechanism of preservation of enantioselectivity in hydrochlorination of *a*-pinene.

Deuterium distribution in bornylchloride derived from the studied specimen of *a*-pinene should then be as shown in Fig. 5.

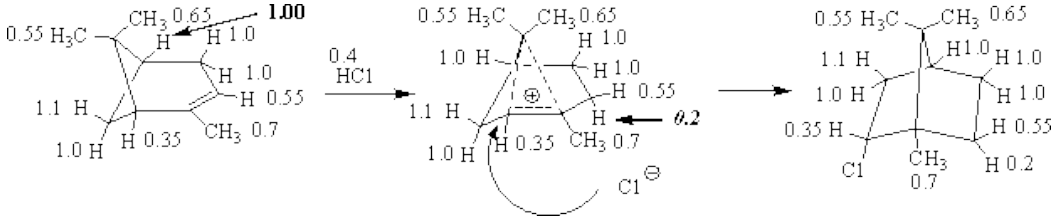

Figure 5. Transformation of *a*-pinene to bornylchloride with preservation of D-content at specific positions. Notice D-content of added HCl(italics).

HCl used for hydrochlorination is formed in reactor as by-product of chlorination of bornylchloride. We have arbitrarily taken an average content of D in *a*-pinene (0.8) and hypothesized that $k(^1H)/k(^2H) = 2$ for addition of HCl to double bond as well as for abstraction of H from R-H by Cl-radical. D-content of HCl should then be 0.8/2 = 0.4, and D-content at 6-endo position of bornylchloride should be 0.4/2 = 0.2 !

Now we shall consider the particular case of chlorination/dechlorination:

Bornylchloride → Parlar no. 26 → Parlar no. 50 → Parlar no. 26

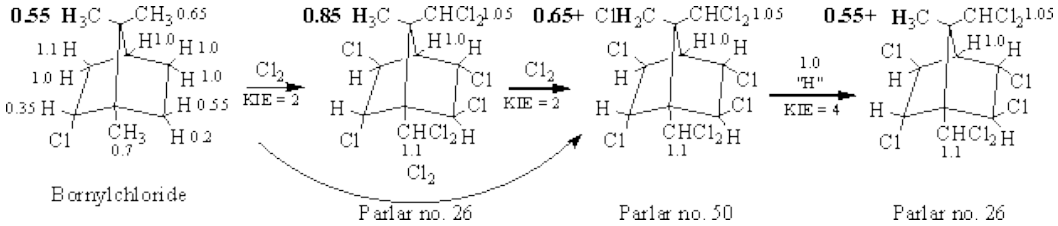

Figure 6. Changes in D-content with chlorination of bornylchloride to Parlar no. 26 and to Parlar no. 50 and with dechlorination of Parlar no. 50 to Parlar no. 26.

We have used the known method for calculation of enrichment in heavier isotope with conversion [5]. First we shall consider D-content in CH_3, CH_2Cl and $CHCl_2$ groups (C-8). In Bornylchloride D-content is 0.55. Upon conversion of

this CH_3 group enrichment in deuterium would occur. We have estimated conversion of this Me group in Toxaphene as 80%, based on our data on the composition of Toxaphene [6]. With KIE = 2 this should result in ca. 50% enrichment, therefore D-content in Me group of Parlar 26 would be 0.85. D-content in CH_2Cl of Parlar 50 will be ca. 20% higher than in the corresponding CH_3 of bornylchloride due to KIE at the stage of formation, and somewhat higher still due to enrichment as a result of further chlorination. In contrast, $CHCl_2$ groups would be additionally enriched in D by a factor of 24/15 due to combined KIE after two chlorination steps.

D-content in Parlar 26 formed from Parlar 50 by hydrodechlorination ($k(^1H)/k(^2H) = 4$ was used) will be somewhat lower, 0.55. Therefore it will be possible to determine the origin of Parlar 26 (technical product or metabolite) by D-content in its CH_3 group. D-content at bridgehead H will be the same for all Toxaphene congeners.

We believe further research into isotope composition of Toxaphene congeners and other pollutants and studies on KIEs in reactions of their formation and degradation are promising and may give a tool for looking at “environmental history” of a molecule.

References

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