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Partition Behavior of Hexachlorocyclohexane Isomers

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Hexachlorocyclohexane (HCH, $C_6Cl_6H_6$) is a persistent chemical that can be found around the globe in various environmental compartments. Much research has been conducted on its environmental fate, but there remains a controversy regarding the basic physicochemical properties of its isomers. We have therefore measured additional partition data for α-, β-, and γ-HCH using chromatographic measurements to resolve this existing controversy. The results reveal a distinctly different partition behavior of β-HCH compared to α- and γ-HCH. The ability of various models to predict this partition behavior from molecular structure was investigated. SPARC and EPI-suite failed to predict any isomeric differences. COSMOtherm, a quantum chemical software, correctly predicted the qualitative differences between the isomers, but in some cases, the predicted absolute values differed by more than 1 order of magnitude. In addition, the COSMOtherm software was used to predict partition data for the three isomers of the flame retardant hexabromocyclododecane (HBCD) revealing results similar to HCH.

Introduction

Hexachlorocyclohexane (HCH) exists in various isomers that differ in their 3-dimensional structure, i.e., the position of the chlorines relative to the ring.[1] Technical HCH, which has been used and is still being used in developing countries as an insecticide with γ-HCH being the active ingredient, contains (60 to 70) % α-HCH, (5 to 12) % β-HCH, (10 to 12) % γ-HCH, (6 to 10) % δ-HCH, and (3 to 4) % ϵ-HCH. For assessing the global distribution of HCH, it is essential to know the equilibrium partition coefficient of the isomers between air, water, and sorbing phases such as soil organic matter. Typically, the air/water, K_{aw}, and octanol/water, K_{ow}, partition coefficients of a compound are used as characteristic descriptors of its environmental partitioning behavior. Unfortunately, some of the published data for specific HCH isomers are highly contradictory. For example, the reported experimental log air/water partition coefficients for γ-HCH at 25 °C range from −3.06 to −4.82.[2] This is likely due to the fact that they come from different research groups and are derived from various methods. As a consequence, not only the absolute partition coefficients of the isomers but also their behavior relative to each other remain unclear.

Others have already tried to clarify this unsatisfying situation, but a controversy remains. On the basis of a critical evaluation of available literature data, Xiao et al.[1] have recommended a selection of partition data that suggest similar octanol/water partitioning for α-, β-, and γ-HCH but a substantially divergent air/water partitioning for β-HCH compared to the other isomers (see Table 1). In contrast, Abraham et al.[2] have derived interaction descriptors (based on a different selection of various experimental partition data from the literature) for the HCHs which actually suggest that the different isomers have a very similar partition behavior in any partition system including air/water (see Tables 1 and 3).

Table 1. Preferred Values for Air/Water, K_{aw}, and Octanol/Water, K_{ow}, Partitioning of the HCH Isomers as Suggested by Xiao et al.[1] and Abraham et al.[2]

	$\log(K_{aw}/L_w\ L^{-1}{}_a)$ at 25 °C		$\log(K_{ow}/L_w\ L^{-1}{}_o)$ at 25 °C	
	Xiao et al.	Abraham et al.	Xiao et al.	Abraham et al.
α-HCH	−3.58	−3.79	3.81	3.70
β-HCH	−4.82	−4.06	3.84	3.61
γ-HCH	−3.96	−4.10	3.70	3.62

Both research groups selected their data such that they were self-consistent for each isomer; i.e., the partition coefficients for various solvent–water–air systems could be transformed by use of a thermodynamic cycle. The diverging results with respect to the air/water partitioning indicate that self-consistency alone is not a sufficient criterion for the selection of reliable data. Such a situation can occur if the available data pool contains a rather high portion of unreliable data, rather than just a few outliers, or if a subjective preselection of data occurs. From the data in Table 1, it appears that the agreement on the K_{ow} data is sufficiently good, but it remains unclear which, if any, of the K_{aw} data should be trusted and how similar or varying these isomers would sorb in other environmental systems. Closing this gap is necessary not only for reliable predictions of the global fate of these isomers but also if we want to evaluate monitoring data of HCH to gain a better understanding of the underlying processes governing their environmental distribution.[3] The vast amount of reported environmental concentrations of HCHs, and information we can learn from them, can only be effectively utilized if reliable partition data are available.[3]

The goal of this work was to clarify these open questions by measuring as little additional partition data as necessary. To this end, we have measured the HCH isomers in two environmental systems: humic acid/air and quartz surface/air partitioning. This would have been sufficient to isolate and directly demonstrate the relevance of HCH structure on their environmental partitioning. However, we also intended to check and if

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Table 2. Measured Sorption Constants of the HCH Isomers from Air to Quartz and Humic Acid (HA)

	$K_{i,\text{quartz,air}}/\text{m}^3\cdot\text{m}^{-2}$ at 90 % rh				$K_{i,\text{humic acid,air}}/\text{L}\cdot\text{kg}_{\text{HA}}^{-1}$, 0 % rh
	35 °C	45 °C	55 °C	extrapolated to 15 °C	60 °C
α-HCH	$1.36\cdot10^{-2}$	$4.23\cdot10^{-3}$	$1.68\cdot10^{-3}$	$1.43\cdot10^{-1}$	$1.55\cdot10^{6}$
β-HCH	$1.11\cdot10^{-1}$	$2.50\cdot10^{-2}$	$7.67\cdot10^{-3}$	2.23	$3.02\cdot10^{6}$
γ-HCH	$1.37\cdot10^{-2}$	$5.89\cdot10^{-3}$	$2.57\cdot10^{-3}$	$9.22\cdot10^{-2}$	$9.12\cdot10^{5}$

Table 3. Redetermined LSER Descriptors for Three HCH Isomers Based on the Sorption Data Presented Here

		L_{i16}		A_i		B_i		S_i	
	V_x	lit.[2]	this work	lit.[2]	this work	lit.[2]	this work	lit.[2]	this work
α-HCH	1.58	7.32	7.34 ± 0.1	0	0	0.71	0.47 ± 0.07	0.73	1.20 ± 0.18
β-HCH	1.58	7.49	7.63 ± 0.1	0	0.12 ± 0.08	0.90	0.58 ± 0.07	0.88	1.18 ± 0.18
γ-HCH	1.58	7.47	7.57 ± 0.1	0	0	0.68	0.50 ± 0.07	0.91	1.28 ± 0.19

necessary revise the interaction descriptors that Abraham et al.[2] had derived. We have argued before that these descriptor scales by Abraham and co-workers[4,5] are in principle a much more powerful tool for describing and understanding the partition behavior of any nonionic, organic compound in any partition system than correlations with log K_{ow} or vapor pressure, though the latter are still common practice in environmental chemistry.[6] With the correct interaction descriptors at hand, it would become possible to derive consistent K_{aw} partition coefficients as well as partition coefficients of the HCH isomers in a large number of other partition systems. To derive revised descriptors, we needed partition measurements in addition to the humic acid/air and quartz surface/air partitioning. We obtained these additional data from gas chromatographic retention measurements on three different stationary GC phases. These stationary phases were calibrated with a diverse set of compounds whose descriptor values were already known from the literature. The good reproducibility of retention measurement implies that this method generally yields highly precise results. Thus, accurate results for the interaction descriptors could be expected.

Theory

A polyparameter linear free energy relationship (pp-LFER) of the following form is able to describe all types of partitioning of any nonionic organic chemical provided that the respective system and compound descriptors are known[7]

$$\log K_{i12} = l_{12}L_i + s_{12}S_i + a_{12}A_i + b_{12}B_i + v_{12}V_i + c_{12} \quad (1)$$

K_{i12} is the equilibrium partition coefficient of compound i between phases 1 and 2. Note that eq 1 can just as well be used to describe the net retention volumes, log V_{net}, of organic chemicals in various chromatographic systems. The capital letters in eq 1represent compound specific interaction descriptors for the various types of interactions a compound i can undergo. L_i is the logarithm of the hexadecane/air partition coefficient at 25 °C in units of $\text{m}^3_{\text{air}}/\text{m}^3_{\text{hexadecane}}$ and V_i is the McGowan characteristic volume in units of $(\text{cm}^3\cdot100\ \text{mol}^{-1})$. These descriptors are needed to describe nonspecific interactions (van der Waals interactions and cavity formation) between the analyte and the sorbent. The remaining three descriptors stand for various specific intermolecular interactions: A_i characterizes the H-donor (or electron-acceptor) property of the compound; B_i stands for the H-acceptor (or electron-donor) property; and S_i is called the dipolarity/polarizability descriptor. The small letters represent the complementary system descriptors for any phases 1 and 2. Here, we deduce the compound descriptors L_i, S_i, A_i, B_i, V_i of the HCH isomers as follows: the partition constants, K_{i12}, or net retention volumes, V_{net}, for various partition systems (e.g., GC phases, humic acid/air, and quartz/air) were measured for about 50 to 80 calibration compounds for which reliable compound descriptors were known from the literature. These data enabled us to set up equations of the form of eq 1 for each of these partition systems. We then measured the partitioning of the HCH isomers in each of these systems and determined their descriptors by fitting the measured partition constants to the previously calibrated equations (see also ref 8 for similar work). Note that eq 1 deviates a little from the traditional LSER equations that have been deviced by Abraham et al.[9] The traditional equations could have been used here just as well as eq 1. Our preference for eq 1 is due to the fact that eq 1 allows the use of the thermodynamic cycle which is not possible with the traditional LSER equations.[7]

Experimental Section

GC Stationary Phases. The net retention volumes on the various GC columns were determined from the retention time of the respective peaks as marked by their first moment and the volumetric flow rate of the carrier gas as measured with a mass flow meter (F-111C-HAD-11-V; Bronkhorst, Switzerland). Methane or air was used as the nonretainable tracer. Retention on an Apolane-87 column (Alltech, 5 m, 0.45 mm id, 0.4 μm coating thickness) was measured at 110 °C. Retention on the apolar Apolane-87 is completely controlled by nonspecific interactions and can therefore be used to derive the hexadecane/air partition coefficients of the HCH isomers (see Supporting Information). Retention on Rtx-200 (Restek 15 m, 0.25 mm id, 1 μm coating thickness, crossbond trifluoropropyl methyl polysiloxane (TFPMPS)) at 130 °C and a preparative column filled with polyurethane foam (LM 2033 from Foampartner, Switzerland) at 95 °C gave information about the A_i and S_i values of our target compounds. All experimental data for the Apolane-87 and TFMPS column are listed in Table S1 and S2 in the Supporting Information together with the respective pp-LFER equation. Partition coefficients of the HCH isomers on PU foam are reported in Table S3 in the Supporting Information. The calibration measurements as well as experimental details for the PU-foam are described in ref 10.

Humic Acid. Sorption from air to Leonardite humic acid (provided from the International Humic Substances Society) coated on silanized glass beads (Alltech, 100/120 mesh) was measured at 60 °C and 0 % relative humidity with an Inverse Gas Chromatography method using an ECD or FID for detection. Details of the method are described in ref 11. The high temperature was needed to reduce the observed sorption to a level that could be quantified in our experimental setup. While this temperature is clearly above ambient conditions, this has no effect on our goal to elucidate the relative sorption behavior of the HCH isomers or to derive compound descriptors. The measured values for the HCH isomers are shown in Table 2, and values for the 94 other organic compounds that served

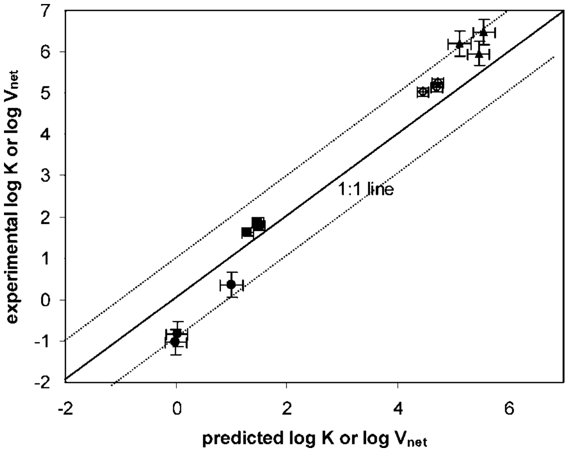

Figure 1. Measured logarithmic net retention volumes, log V_{net}, on: ◇, polyurethane foam (mL, 95 °C); □, TFMPS (mL,130 °C); ▲, log K values for humic acid ($L\cdot kg_{HA}^{-1}$, 60 °C, 0 % rh); and •, quartz ($m^3\cdot m^{-2}$, 15 °C, 90 % rh) compared to values that were calculated with the relevant calibrated pp-LFER equations using the compound descriptors from ref 2. Error bars indicate the experimental standard deviation (x-axis) and the standard deviation of the relevant pp-LFER equation (y-axis). The dashed lines indicate a deviation of 1 order of magnitude from the 1:1 line.

to calibrate the pp-LFER equation for humic acid are given in Table S4 in Supporting Information.

Quartz Surface. Sorption of the HCH isomers was measured at 90 % relative humidity and (35, 45, and 55) °C and then extrapolated via the van't Hoff equation to 15 °C. These data are reported in Table 2. All experimental details as well as the calibration of the pp-LFER equation for sorption to the quartz surface at 15 °C are published in ref 12.

Results and Discussion

The data in Table 2 already clearly demonstrate a substantial difference in the environmental partition behavior of the HCH isomers. This is most pronounced in the adsorption on the quartz surface. These isolated data do not allow any general conclusions though, and they do not solve the controversy on the air/water partition data. Such a more comprehensive picture of the partition properties of the HCH isomers can only emerge from a reliable set of LSER descriptors for all three isomers. Hence, in a next step we checked the published LSER descriptors. The McGowan volume of the HCH isomers as the first of the five required LSER descriptors can be calculated by a simple increment method and is therefore not in question. Retention measurements on an Apolane-87 column allowed us to derive the log hexadecane/air partition coefficients, L_i, shown in Table 3. Our results are in good agreement with the values from Abraham et al.[2] In those cases where a small discrepancy occurred, we relied on our own values for the further calculations of the other descriptors.

Figure 1 shows our measured sorption data on polyurethane foam, TFMPS, humic acid, and quartz compared to values that were calculated with the relevant calibrated pp-LFER equations (all listed in Supporting Information) using the compound descriptors A_i, B_i, and S_i from Abraham et al.[2] and the L_i measured here. The results show a significant deviation indicating that the published A_i, B_i, and S_i descriptors need to be revised.

We have therefore redetermined values for A_i, S_i, and B_i by fitting all of our own experimental sorption data (i.e., quartz/air and humic acid/air sorption coefficients as well as the retention data on three different stationary phases) plus K_{ow} data from the literature to the respective system equations using the compound descriptors as fitting parameters. For the K_{ow} values, we have chosen those from Xiao et al.[1] which differ only slightly from the preferred values selected by Abraham et al.[2] (see Table 1). The descriptor values resulting from this procedure are reported in Table 3 along with the descriptor values published earlier by Abraham for comparison. Figure 2 shows that the new descriptors can describe all our experimental data within the respective error margin.

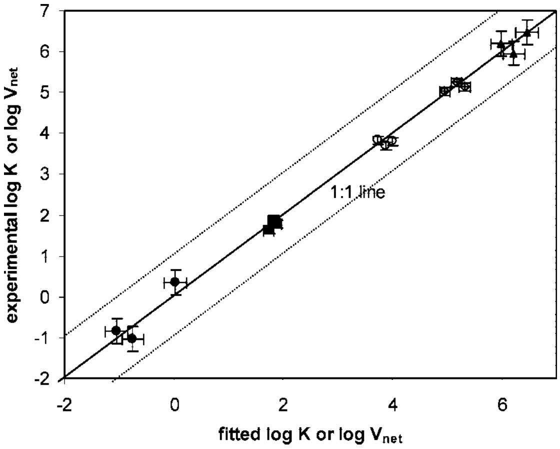

Figure 2. Measured logarithmic net retention volumes, log V_{net}, on: ◇, polyurethane foam (mL, 95 °C); □, TFMPS (mL,130 °C); ▲, log K values for humic acid ($L\cdot kg_{HA}^{-1}$, 60 °C, 0 % rh); and •, quartz ($m^3\cdot m^{-2}$, 15 °C, 90 % rh) compared to values that were calculated with the relevant calibrated pp-LFER equations using the fitted compound descriptors (Table 3). Error bars indicate the experimental standard deviation (x-axis) and the standard deviation of the respective pp-LFER equation (y-axis).

Table 4. Log K_{aw} and Log K_{oa} Partition Constants at 25 °C Calculated with Revised Compound Descriptors Using pp-LFER Equations from Reference 7 and Experimental Values from the Literature[1,24] for Comparison

	calcd log K_{aw}	exptl log K_{aw}	calcd log K_{oa}	exptl log K_{oa}
α-HCH	−3.68	−3.58	7.67	7.61
β-HCH	−4.68	−4.82	8.37	8.88
γ-HCH	−4.10	−3.96	7.97	7.85

The new descriptor values reveal that β-HCH does indeed differ substantially from the other two isomers in that it is a stronger H-acceptor (B_i descriptor) and even has a significant H-donor property, whereas the other isomers have no H-donor properties and are weaker H-acceptors. Abraham et al.[2] did not identify any of the isomers as H-donor, and their B_i and S_i values also differ significantly from those found here.

What can now be said about the environmental partitioning of HCHs? Our experimental sorption data for quartz give direct evidence that there are environmental partition processes where the HCH isomers differ substantially from each other (by more than 1 order of magnitude on quartz, see Table 2). To clarify the questionable air/water partition coefficients and to get another key parameter for assessing environmental partitioning, we calculated air/water and the octanol/air partition constant, K_{oa}, using our revised descriptors in combination with existing pp-LFER equations (Table 4). Experimental values for log K_{oa} from the literature are also listed in Table 4 for comparison.

This yields differences between the various HCH isomers similar to what had been postulated by Xiao et al.[1] In general, such differences do not necessarily result in a substantially different environmental behavior. However, here it appears that the specific values for K_{aw} and K_{oa} of the HCHs fall into a sensitive range where one would indeed expect significant differences in environmental partitioning.[13]

Table 5. Comparison of Partition Constants for HCH Isomers from this Work and Predicted with COSMOtherm

	log K_{ow}		log K_{aw}		log $K_{humic\ acid,air}$ (60 °C)	
	pred. with COSMOtherm	lit.[1]	pred. with COSMOtherm	this work	pred. with COSMOtherm	this work
α-HCH	3.69	3.81	−5.17	−3.68	7.28	6.19
β-HCH	3.41	3.84	−6.39	−4.68	8.23	6.48
γ-HCH	3.55	3.70	−5.39	−4.10	7.41	5.96

Predicting the Isomeric Differences from Molecular Structure

Structural isomers having such varied partitioning behavior was, in our opinion, an outcome that no expert in the field would have anticipated based on knowledge of the 3D structure. It was thus also of interest for us to check how various models that predict partitioning from molecular structure deal with this effect. Neither US-EPA's EPI Suite (http://www.epa.gov/opptintr/exposure/docs/episuite.htm) nor SPARC (http://ibmlc2.chem.uga.edu/sparc/) are designed to account for the exact three-dimensional structure of a molecule which is an essential prerequisite for distinguishing the HCH isomers. The SMILES notation used for entering the molecular information into these models is identical for all HCH isomers and so are the calculated partition constants. In contrast, the quantum-chemical software COSMOtherm (version C2.1, COSMOlogic GmbH, Leverkusen, Germany)[14–16] is in principle able to distinguish the three-dimensional structures of the HCH isomers and is designed to predict any type of partitioning including air/water, octanol/water, and humic acid/air partition data.[17]

A comparison between predicted and experimental values (Table 5) shows two interesting features: (i) predicted and experimental values agree quite well for octanol/water partitioning, but they differ by more than 1 order of magnitude for air/water and humic acid/air partitioning; (ii) despite the in some cases bad prediction of the absolute partition constants, the relative differences of the isomers are represented correctly in the predictions, i.e., similar partitioning for the α- and γ-HCH isomers and significantly higher K_{ow}, K_{aw}, and $K_{HA,air}$ partition constants for the β-HCH isomer. A closer look at the COSMOtherm calculations (see color-coded pictures of the calculated molecular surface charges in the Supporting Information) reveals the β isomer as being the strongest electron acceptor among all the isomers, which agrees with the *A* values (H-bond donor = e-acceptor) derived above. However, in contrast to the *B* values in Table 3, almost no e-donor (= H-bond acceptor) properties in any of the isomers is predicted by the quantum-chemical predictions.

Partitioning of HBCD Isomers

1,2,5,6,9,10-Hexabromocyclododecane is a high-production-volume flame retardant. The technical product comes as a mixture of three diastereoisomers: α-, β-, and γ-HBCD (see ref 18 for three-dimensional structures). The isomer pattern found in sediment samples resembles that of the technical product; i.e., the γ-isomer dominates. However, in biological samples, the α-isomer is predominantly detected.[19–21] This may be due to different metabolization behavior of the isomers rather than a different partition behavior.[19] So far, little is known about the partition behavior of the isomers, but a behavior analogous to the HCH isomers has been hypothesized.[22] We therefore also used the COSMOtherm software to calculate octanol/water and air/water partitioning of the HBCD isomers (see Table 6).

Table 6. COSMOtherm Calculations for Octanol/Water and Air/Water Partitioning of HBCD at 25 °C

	log K_{ow}	log K_{aw}
α-HBCD	5.59	−8.84
β-HBCD	5.44	−9.20
γ-HBCD	5.53	−8.64

The calculated isomeric differences do indeed show parallels to the HCH isomers. The K_{ow} values differ only slightly which is quite consistent with results from Hayward et al. [23]based on an HPLC-retention method. Differences in the air/water partitioning constants are more pronounced. Whether these differences are large enough to induce a substantially different environmental fate is not clear yet. Note that, similar to the HCHs, the absolute values of the calculated air/water partition constants may be considerably off the real values.

Conclusions

In this work, we could confirm a significantly different behavior of β-HCH compared to α- and γ-HCH in the partitioning from air to other environmental phases such as water, quartz surface, and humic acid. These differences are expected to result in a different global partitioning of these compounds. The presented interaction descriptors will allow us to accurately estimate the partitioning behavior of all three isomers in all systems for which pp-LFER equations exist. This allows for a comprehensive understanding of the HCH partitioning far beyond the experimental data presented here.

Among various models based on molecular structure only the quantum-chemical software COSMOtherm was found to be able to predict isomeric differences for the various HCH isomers. It must be noted though that the predicted absolute values were considerably off in several instances. Nevertheless, this software might also be helpful to gain a better understanding of other pollutants that exist in different isomeric structures as shown here for the flame-retardant hexabromocyclododecane.

Acknowledgment

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Supporting Information Available:

Measured partition data and retention volumes for HCH isomers and calibration compounds in various partition systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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