Compilation, Evaluation, and Selection of Physical-Chemical Property Data for α-, β-, and γ-Hexachlorocyclohexane

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A complete set of temperature-dependent physical-chemical property data (aqueous solubility (S_W), octanol−water partition coefficient (K_{OW}), vapor pressure (P), Henry's law constant (H), octanol−air partition coefficient (K_{OA}), and octanol solubility (S_O)) for α-, β-, and γ-hexachlorocyclohexane (HCH) is derived by evaluating, averaging, and regressing all experimentally obtained values reported in the literature. Properties for each isomer are adjusted slightly to ensure thermodynamic consistency. That adjustment is sized according to, and is smaller than, the uncertainty apparent from the range of reported experimental values. The data analysis confirms that an unusually high K_{OA} and an unusually low H reported for β-HCH are in agreement with the measured S_W and P values when these are converted to the liquid state. Linear solvation energy relationships fail to predict the observed differences in the partitioning behaviors of the three isomers.

Introduction

The environmental fate of an organic chemical is strongly influenced by its distribution between various phases or compartments. Simple empirical relationships with an organic chemical's aqueous solubility (S_W), vapor pressure (P), octanol−water partition coefficient (K_{OW}), Henry's law constant (H), octanol−air partition coefficient (K_{OA}), and solubility in octanol (S_O) are traditionally used to characterize phase distribution in the environment. Models of organic pollutant fate thus usually require these physical-chemical properties as input parameters. Knowledge of the temperature dependence of the physical-chemical properties is necessary to quantify phase distribution at temperatures other than (20 or 25) °C. Over the relatively small environmentally relevant temperature range, this can be conveniently expressed through the respective internal energies of phase transfer (ΔU).

It is a considerable experimental challenge to reliably measure very low concentrations of organic chemicals in the gas and aqueous phases. As a result, for many sparingly soluble or semivolatile organic chemicals, the reported values for a property from independent measurements can show large discrepancies. Pontolillo and Eganhouse[1] illustrated that it is impossible to derive the true S_W and K_{OW} values for *p,p*′-dichlorodiphenyltrichloromethylmethane (*p,p*′-DDT) and *p,p*′-dichlorodiphenyldichloroethylene (*p,p*′-DDE) on the basis of the available studies because reporting errors, multilevel referencing, a common lack of precision information, and other problems lead to a multitude of property data with an initimidating degree of inconsistency.

Recently, Beyer and co-workers[2] presented an adjustment technique to derive internally consistent sets of property data for one chemical, and they applied it to several organic substances. This algorithm is based on the thermodynamic relationships between the various physical-chemical properties. Li et al.[3] further complemented that approach by developing a rigorous and transparent procedure for compiling and evaluating measured data from the literature, selecting literature-derived values through averaging or linear regression, and making estimates of the uncertainty of these values. These uncertainty estimates determine the extent of relative adjustment applied in the adjustment algorithm. The procedure was applied to 16 PCB congeners, and the resulting set of data shows consistency not only among the various partitioning properties for one congener but also for one property across various congeners.[3]

Technical hexachlorocyclohexane (HCH), which 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, has been widely used as a pesticide on the global scale since the 1940s. As prominent organochlorinated contaminants, HCH isomers have been detected around the world.[4] Whereas, for the longest period of time, attention has been directed to quantifying and understanding the environmental behavior of the active insecticidal ingredient, γ-HCH, and the major constituent of the technical product, α-HCH, recent investigations indicate suprisingly divergent environmental behavior for the β-HCH isomer (Figure 1). This includes a higher potential for bioaccumulation[5] and different transport pathways in the North Pacific.[6] Interpretation of such discrepancies requires a thorough grasp of the differences in the partitioning properties of the various isomers.

A large number of studies have reported physical-chemical properties for the α- and γ-isomers. More recently, the partitioning properties for the β-HCH isomer have been measured, and some of them appear to suggest considerable deviations from those for α- and γ-HCH. Such deviations may be due to the unusually high crystal energy of the β-isomer, which has a higher degree of symmetry than the other isomers (Figure 1). The objective of this work is to use the procedures described by Beyer et al.[2] and Li et al.[3] to derive a property data set for α-, β-, and γ-HCH that makes use of all available measured data and is internally consistent. Partitioning property measurements for other HCH isomers are too rare to allow this procedure to be applied.

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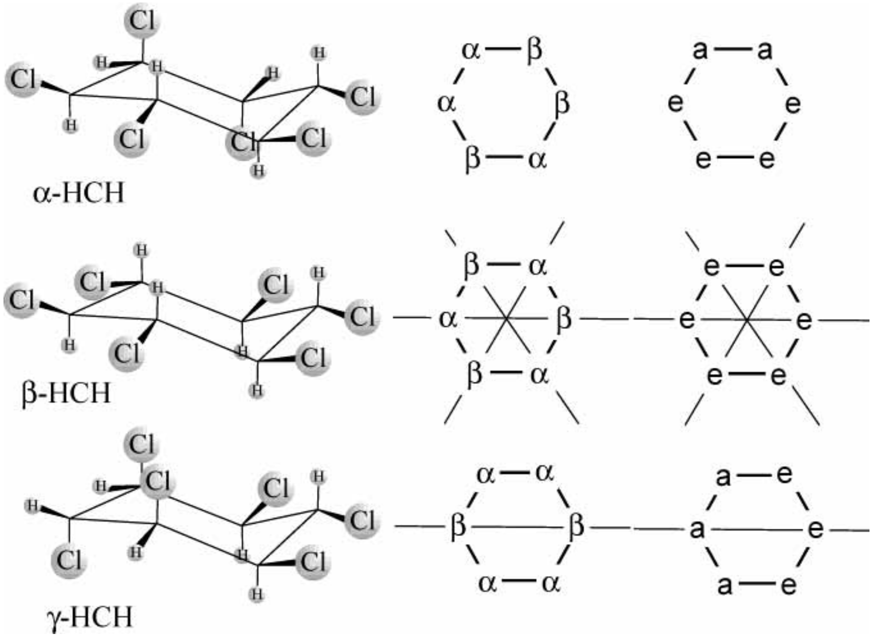

Figure 1. Structures of the α-, β-, and γ-isomers of hexachlorocyclohexane. γ-HCH has one plane of symmetry, and β-HCH has three planes of symmetry, whereas α-HCH is a chiral molecule. The diagrams on the right indicate the chlorine substitutions in the axial (a) and equatorial (e) orientations.

Methods

The principles and steps involved in the evaluation, selection, and adjustment procedure have been described previously[2,3] and will not be repeated here in detail. Briefly, the steps are as follows. Chemical Abstracts Service Source Index (CASSI) and other databases[7] are used to obtain and identify all the published literature on measured physical-chemical properties for the selected HCH isomers. Despite our efforts for comprehensiveness, it is likely that additional data sources exist that escaped our attention. To avoid multilevel referencing, only original data sources are considered; that is, no quoted values are included.[1] Values that refer to the same set of experiments, differ substantially from a cluster of other reported values, or are highly inconsistent with the other property values for the same chemical are eliminated from the data set. Values measured indirectly, such as those derived from chromatographic retention times, are only included if there is an insufficient number of directly measured values. Estimated values are excluded.

The measured data are converted into appropriate and identical units and compiled in spreadsheets. If no exact experimental temperature is provided, a temperature of 23 °C is assumed to apply. If the data are reported as a linear equation, discrete values are calculated for four or five temperatures, which are either the experimental temperatures indicated in the reference or temperatures in the environmentally relevant range. The HCH isomers are solids at environmental temperatures. The reported solid-phase vapor pressure and solubility values (P_S, S_{WS}, S_{OS}) are converted into the properties of the supercooled liquid (P_L, S_{WL}, S_{OL}) using compound specific entropy of fusion values ($\Delta_{fus}S$) and melting point temperatures (T_M) in eq 1:

$$S_{WS}/S_{WL} = S_{OS}/S_{OL} = P_S/P_L = \exp(-\Delta_{fus}S((T_M/T) - 1)/R) \quad (1)$$

R is the ideal gas constant, and T is the experimental temperature in kelvin. If a compound-specific $\Delta_{fus}S$ is not available, a generic default value of 56 J·K^{-1}·mol^{-1} is used.

If measured values for a property exist at several temperatures, a linear regression equation between the logarithm of all noneliminated data and reciprocal absolute temperature is derived. The value for 25 °C obtained from the regression line and the product of the slope of the regression line and R are chosen as literature-derived values (LDVs) for the property and the corresponding internal energy of phase transfer, respectively. If measurements had only been performed within the fairly small temperature range (20 to 25) °C, the values are adjusted to 25 °C by using an estimated energy of phase transfer. In such cases the LDV is the logarithmic mean of the noneliminated values. The arithmetic mean would give undue weight to higher values. Temperature-dependent S_{OL}[8] and K_{OA}[9] for the HCHs had only been measured by a single study, respectively. The LDVs for ΔU_O and ΔU_{OA} were taken directly from the relevant studies.

For each LDV, an uncertainty estimate (u_X) between 1 and 5 was assigned on the basis of the size of the database, the deviations between different measurements, and the general reliability of data reported by a particular research groups. For example, a large u_X, indicating high uncertainty, was assigned to properties for which few or no directly measured data exist (e.g. K_{OA} for all the isomers) or for which several reported values are highly divergent (e.g. S_{WL} of β-HCH), whereas properties that had been measured directly several times with accepted techniques yielding comparable values would deserve a low u_X (e.g. K_{OW} for γ-HCH). It is not feasible to use strictly numerical criteria in the assignment of uncertainty, rendering the assessment somewhat subjective. The uncertainty parameters are used to achieve consistency among the properties for one chemical. Therefore, the relative size of u_X for the properties of one HCH isomer is more important than the relative size for one property of different isomers.

The LDVs were adjusted using the algorithm by Beyer et al.[2] This technique adjusts a set of physical-chemical property values in such a way that they conform to thermodynamic constraints (Figure 2) yet deviate as little as possible from the original values. For example, on the basis of a thermodymanic triangle, log K_{OA} should equal

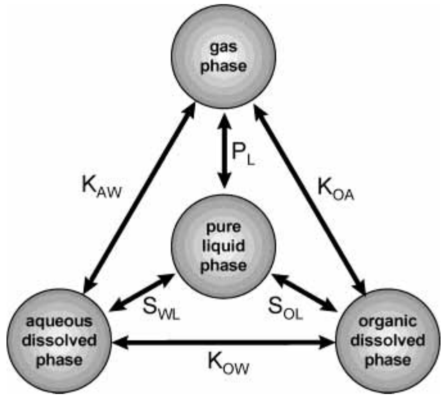

Figure 2. Illustration of the relationship between the six investigated partitioning properties. Any three properties forming one of the four triangles in this figure need to be consistent with each other.

log S_{OL} − log P_L/RT. The LDVs of the three properties generally do not satisfy this condition, and thus, they need to be adjusted so that they do. If LDVs exist for all six partitioning properties, four such thermodynamic triangles exist. The extent of the adjustment to each property is scaled according to the uncertainty factor (u_X) assigned to it. The adjusted values are referred to as final adjusted values (FAVs). Missing property values (such as the S_{OL} for β-HCH) are calculated at the same time. Because the HCHs are not very hydrophobic (log $K_{OW} < 4$), we ignore the effect of the mutual solubility of octanol and water on the partitioning of the HCH isomers between octanol and water, and we assume that K_{OW} equals S_{OL}/S_{WL}. For a detailed account of the thermodynamic basis of the adjustment procedure and the equations on which it is based, see ref 2. A computer program with the algorithm is available from www.usf.uos.de/projects/elpos/download/adjust.en.html.

Results

The physical-chemical properties for α-, β-, and γ-HCH are compiled in Tables 1−3. At the top of each section of the table are the data that are included in the derivation of the LDVs, including the experimental temperature, the method used, and the reference. For comparison and completeness, the data that are not included in the derivation of the LDVs are listed toward the bottom of each section of the table, together with the reason for exclusion. The LDVs and the FAVs at 25 °C for each property are also included in Tables 1−3. A summary of the LDVs at 25 °C is presented in Table 4 along with the uncertainty estimates (u_X) assigned to each property. Such LDVs could be derived for all properties, except for the solubility of β-HCH in octanol, for which no measured data are available. The corresponding FAVs and percentage adjustment are listed in Table 5. The internal energies of phase transfer (ΔU), their origins, and their uncertainty estimates are presented in Table 6. Lack of measured data prevented the derivation of LDVs for ΔU_W of α- and β-HCH and for ΔU_O of β-HCH. The FAVs for ΔU and the required percentage of adjustment are presented in Table 7. Plots of the logarithm of a property, which include the measured data, LDVs, and FAVs, versus reciprocal absolute temperature are shown in Figures 3−8.

Discussion

Property Values at 25 °C. The literature-derived values for the three HCH isomers are reasonably consistent. The maximum required adjustment to the LDVs at 25 °C is 34%. In general, however, much smaller adjustments on the order of 10% were sufficient to obtain consistency. This is an indication of both the accuracy of the measurements and the success of the procedure used in deriving the LDVs. The variability in the entries for a property in Tables 1−3 gives an approximate indication of the uncertainty of the measured values. The required adjustments are normally well within this uncertainty and further confirm that the procedures applied in the selection of the LDVs eliminated at least some of the experimental error.

Melting point temperatures well above 50 °C imply that the HCH congeners are solids at environmentally relevant temperatures. The conversion of the experimentally accessible properties of the solid to those of the subcooled liquid depends on the knowledge of the entropy or enthalpy of fusion. Uncertain entropies of fusion ($\Delta_{fus}S$) or the use of a default value can lead to significant errors in the calculated liquid property, especially for substances with a high melting point temperature. However, no experimentally determined $\Delta_{fus}S$ for β-HCH, the isomer with by far the highest melting point, could be obtained, making it necessary to use a default value. It is encouraging to see nevertheless good consistency between the five LDVs for this isomer, which points to accurate measurements and suggests that the real entropy of fusion is likely close to the default value.

A comparison of the FAVs for the three isomers reveals that the β-HCH partitions more strongly from the gas phase into water and octanol than the other two isomers. It had previously been noted that the Henry's law constant of the β-isomer is 1 order of magnitude lower[10] and its K_{OA} value 1 order of magnitude higher than those of α- and γ-HCH.[9] The fact that the LDVs for water solubility, vapor pressure, and K_{OW} for β-HCH are consistent with both the low K_{AW} and the high K_{OA} lends further credibility to these values. According to the FAVs, this divergent behavior of the β-HCH is not due to an unusually low volatility (the vapor pressure of the β-isomer is only marginally lower than that of γ-HCH) but is caused by a higher solubility in water and octanol.

Comparison with Linear Solvation Energy Relationship (LSER) Predictions. Recently, Abraham et al.[11] derived solvation descriptors for the HCH isomers from data on chromatographic retention times and partitioning properties. In contrast to the FAVs, the solute descriptors for β-HCH did not deviate substantially from those of the α- and γ- isomers. The solute excess molar refractivity (E), the McGowan characteristic volume (V), and the summation hydrogen bond acidity (A) are identical, whereas the solute dipolarity/polarizability (S), the summation hydrogen bond basicity (B), and the gas−hexadecane partition coefficient (L) are very similar for the three isomers.[11] Accordingly, partitioning properties predicted for β-HCH using LSERs are comparable to those of α- and γ-HCH; that is, the predicted K_{AW} and K_{OA} values for the three isomers are within 0.3 log units of each other. This in turn implies large deviations between the FAVs and the LSER predicted partition coefficients for β-HCH of almost 1 order of magnitude (Figure 9). Abraham et al.[11] had noted that the descriptors for β-HCH are not "very different from those of the other isomers, although some physicochemical properties of β-HCH are considerably different, for example, mp [i.e., melting point], water solubility, and vapor pressure. However, these properties are functions of the crystal energy that cancels out when transfers between solvents are considered." Our data analysis suggests that the latter statement is not correct. Although the subcooled

Table 1. Reported and Selected Physical-Chemical Properties for α-HCH[a]

registry no.	319-84-6	melting point/°C	158
name	(1α,2α,3β,4α,5β,6β)−1,2,3,4,5,6-hexachlorocyclohexane	$\Delta_{fus}S$/J·K^{-1}·mol^{-1}	71.92 (ref 14)
molar mass/g·mol^{-1}	290.85		

Aqueous Solubility

t/°C	S_{WS}/mol·m^{-3}	S_{WL}/mol·m^{-3}	log(S_{WL}/mol·m^{-3})	method	ref	note	
28	0.00698	0.291	−0.54	slow stirring-GC	15		
25	0.00688	0.325	−0.49	generator column-GC	16		
25	0.00560	0.264	−0.58	shake flask-GC	17		
20	0.0344	2.01	0.30		18	not used, outlier	
LDV at 25 °C		0.293		log mean			
FAV at 25 °C		0.333				log(S_{WL}/mol·m^{-3}) = −398.5/(T/K) + 0.859	Figure 3

Octanol−Water Partition Coefficient

t/°C	log K_{OW}	method	ref	note		
25	3.81	shake flask-GC (RI)	15			
28	3.82	shake flask-GC	19			
25	3.78	slow stirring-GC/HPLC	20			
5	3.92	slow stirring-SPME-GC	21			
25	3.79					
45	3.75					
LDV at 25 °C	3.81	linear regression		log K_{OW} = 374.5/(T/K) + 2.55	$r^2 = 0.8385$	Figure 4
FAV at 25 °C	3.94			log K_{OW} = 266.2/(T/K) + 3.04		Figure 4

Vapor Pressure

t/°C	P_S/Pa	P_L/Pa	log(P_L/Pa)	method	ref	note		
0	0.000200	0.73	−1.54	effusion manometer	22			
10	0.000867	1.21	−1.11					
20	0.00333	3.31	−0.72					
30	0.0119	4.38	−0.35					
40	0.0387	6.75	−0.01					
50	0.116	9.77	0.31					
60	0.327	19.8	0.61					
70	0.867	0.84	0.89					
0		1.47	−1.75	GC-retention time	23	calc from a linear equation		
10		2.00	−1.29					
20		2.95	−0.86					
30		4.12	−0.45					
40		5.69	−0.08					
20	0.002	8.03	−0.95	relative loss rate	24			
LDV at 25 °C			−0.61	linear regression		log(P_L/Pa) = −3434/(T/K) + 10.91	$r^2 = 0.991$	Figure 5
FAV at 25 °C			−0.61			log(P_L/Pa) = −3497/(T/K) + 11.12		Figure 5

Henry's Law Constant

t/°C	H/Pa·m^{-3}·mol^{-1}	log(H/Pa·m^{-3}·mol^{-1})	method	ref	note		
0.5	0.104	−0.98		25			
10	0.225	−0.65					
23	0.677	−0.17					
35	1.34	0.13					
45	3.27	0.51					
25	1.239	0.09		26			
10	0.17	−0.77		27			
20	0.43	−0.37					
30	0.92	−0.04					
35	1.52	0.18					
40	2.21	0.34					
5	0.094	−1.03	dynamic headspace method	10			
10	0.15	−0.82					
20	0.38	−0.42					
30	0.79	−0.10					
35	1.32	0.12					
5	0.098	−1.01	bubble stripping method	10			
10	0.13	−0.89					
20	0.42	−0.38					
30	0.92	−0.04					
35	1.24	0.09					
23	2.36	0.37		28	outlier		
LDV at 25 °C		−0.19	linear regression		log(H/Pa·m^3·mol^{-1}) = −3171/(T/K) + 10.45	$r^2 = 0.962$	Figure 6
FAV at 25 °C		−0.13			log(H/Pa·m^3·mol^{-1}) = −3099/(T/K) + 10.26		Figure 6

Table 1 (Continued)

Octanol−Air Partition Coefficient

t/°C	log K_{OA}	method	ref	note	
5	8.39	generator column-GC	9	reported as a linear regression equation	
10	8.18				
15	7.98				
20	7.79				
25	7.61				
LDV at 25 °C	7.61	directly taken		log K_{OA} = 3231/(T/K) − 3.23	Figure 7
FAV at 25 °C	7.464			log K_{OA} = 3235/(T/K) − 3.39	Figure 7

Octanol Solubility

t/°C	S_{OS}/mol·m^{-3}	S_{OL}/mol·m^{-3}	log(S_{OL}/mol·m^{-3})	method	ref	note		
4	21.9	2663	3.43	shake flask	8			
12	32.4	2701	3.43					
20	51.3	2996	3.48					
LDV at 25 °C		3050		linear regression		log(S_{OL}/mol·m^{-3}) = −257.8/(T/K) + 4.35	$r^2 = 0.826$	Figure 8
FAV at 25 °C		2872				log(S_{OL}/mol·m^{-3}) = −132.2/(T/K) + 3.90		Figure 8

[a] The subscripts O and W refer to octanol and water, whereas the subscripts S and L refer to the solid and liquid states. H designates the Henry's law constant between air and water. LDV stands for literature-derived value and FAV for final adjusted value.

Table 2. Reported and Selected Physical-Chemical Properties for β-HCH[a]

registry no.	319-85-7	melting point/°C	315
name	(1α,2β,3α,4β,5α,6β)−1,2,3,4,5,6-hexachlorocyclohexane	$\Delta_{fus}S$/J·K^{-1}·mol^{-1}	56.0 (default value)
molar mass/g·mol^{-1}	290.85		

Aqueous Solubility

t/°C	S_{WS}/mol·m^{-3}	S_{WL}/mol·m^{-3}	log(S_{WL}/mol·m^{-3})	method	ref	note	
28	0.000688	0.42	−0.38	slow stirring-GC	15	not at 25 °C, used anyhow, because T dependence judged minor compared to variability in measurements	
25	0.000825	0.58	−0.24	generator column-GC	16		
25	0.00241	1.68	0.23	shake flask-GC	17		
20	0.00550	4.81	0.68		29, 30	not at 25 °C, used anyhow, because T dependence judged minor compared to variability in measurements	
20	0.0172	15.0	1.18		18	not at 25 °C, and outlier	
LDV at 25 °C		1.18		log mean			
FAV at 25 °C		1.44				log(S_{WL}/mol·m^{-3}) = 110.1/(T/K) − 0.211	Figure 3

Octanol−Water Partition Coefficient

t/°C	log K_{OW}	method	ref	note	
25	3.80	shake flask-GC	15		
28	3.80	shake flask-GC	19		
25	3.84	slow stirring-GC/HPLC	20		
5	3.99	slow stirring-SPME-GC	21		
25	3.88				
45	3.87				
LDV at 25 °C	3.84	log mean at 25 °C			
FAV at 25 °C	3.92			log K_{OW} = 847.5/(T/K) + 1.07	Figure 4

Vapor Pressure

t/°C	P_S/Pa	P_L/Pa	log(P_L/Pa)	method	ref	note
0	0.00000173	0.00408	−2.39	effusion manometer	22	
10	0.00000840	0.0118	−1.93			
20	0.0000373	0.0327	−1.49			
30	0.000153	0.0859	−1.07			
40	0.000560	0.207	−0.68			
50	0.00191	0.476	−0.32			
60	0.00600	1.04	0.02			
70	0.0176	2.15	0.33			
80	0.0493	4.35	0.64			
90	0.129	8.37	0.92			

Table 2 (Continued)

Vapor Pressure (Continued)

t/°C	P_S/Pa	P_L/Pa	log(P_L/Pa)	method	ref	note		
80	0.0493	4.35	0.64					
90	0.129	8.37	0.92					
100	0.320	15.5	1.19					
110	0.765	28.0	1.45					
20	0.0000290	0.0254	−1.60		24			
5		0.0117	−1.93	GC retention time	Bidleman, unpublished	calc from a linear regression		
15		0.0317	−1.50					
25		0.0803	−1.10					
35		0.192	−0.72					
45		0.433	−0.36					
LDV at 25 °C			−1.21	linear regression		$\log(P_L/\text{Pa}) = -3563/(T/\text{K}) + 10.74$	$r^2 = 0.994$	Figure 5
FAV at 25 °C			−1.28			$\log(P_L/\text{Pa}) = -3563/(T/\text{K}) + 10.67$		Figure 5

Henry's Law Constant

t/°C	H/Pa·m^{-3}·mol^{-1}	log(H/Pa·m^{-3}·mol^{-1})	method	ref	note		
25	0.045	−1.35	equilibrium concentration ratio	26			
5	0.0054	−2.27	bubble stripping method	10			
10	0.0092	−2.04					
20	0.022	−1.66					
30	0.053	−1.28					
35	0.088	−1.06					
LDV at 25 °C		−1.43	linear regression		$\log(H/\text{Pa·m}^{-3}\text{·mol}^{-1}) = -3454/(T/\text{K}) + 10.16$	$r^2 = 0.992$	Figure 6
FAV at 25 °C		−1.43			$\log(H/\text{Pa·m}^{-3}\text{·mol}^{-1}) = -3673/(T/\text{K}) + 10.89$		Figure 6

Octanol−Air Partition Coefficient

t/°C	log K_{OA}	method	ref	note	
5	10.06	generator column-GC	9	reported as a linear regression equation	
15	9.44				
25	8.87				
35	8.33				
45	7.83				
LDV at 25 °C	8.87	directly taken		$\log K_{OA} = 4937/(T/\text{K}) - 7.69$	Figure 7
FAV at 25 °C	8.74			$\log K_{OA} = 4391/(T/\text{K}) - 5.98$	Figure 7

Octanol Solubility

	S_{OL}/mol·m^{-3}	log(S_{OL}/mol·m^{-3})	method	ref	note	
FAV at 25 °C	11 816	4.07			$\log(S_{OL}/\text{mol·m}^{-3}) = 957.6/(T/\text{K}) + 0.861$	Figure 8

[a] The subscripts O and W refer to octanol and water, whereas the subscripts S and L refer to the solid and liquid states. H designates the Henry's law constant between air and water. LDV stands for literature-derived value and FAV for final adjusted value.

Table 3. Reported and Selected Physical-Chemical Properties for γ-HCH (Lindane)[a]

registry no.	58-89-9	$\Delta_{fus}S$/J·K^{-1}·mol^{-1}	67.11 (DTA, ref 32) 62.79 (phase equilibrium, ref 33) 58 (Rordorf, unpublished work) 40.88 (DSC method, outlier, ref 14) 61.23 (avg of refs 23, 31, 32, and 33 and Rordorf, unpublished work)
name	(1α,2α,3β,4α,5α,6β)-1,2,3,4,5,6-hexachlorocyclohexane		
molar mass/g·mol^{-1}	290.85		
melting point/°C	114		
$\Delta_{fus}S$/J·K^{-1}·mol^{-1}	61.10 (DSC, ref 23) 57.16 (DSC, ref 31)		

Aqueous Solubility

t/°C	S_{WS}/mol·m^{-3}	S_{WL}/mol·m^{-3}	log(S_{WL}/mol·m^{-3})	method	ref	note
25	0.030	0.269	−0.57	shake flask-colormetric	34	
25	0.025	0.225	−0.65	slow stirring-polarography	35	
35	0.041	0.272	−0.57			
45	0.048	0.237	−0.63			
25	0.026	0.232	−0.63	shake flask-GC	36	
28	0.025	0.208	−0.68	slow stirring-GC (RI)	15	
25	0.027	0.241	−0.62	generator column-GC	16	
15	0.0074	0.0925	−1.03	slow stirring (sonicator stirring)-GC	37	
25	0.023	0.210	−0.68			
35	0.039	0.258	−0.59			
45	0.052	0.257	−0.59			

Table 3 (Continued)

Aqueous Solubility (Continued)

t/°C	S_{WS}/mol·m^{-3}	S_{WL}/mol·m^{-3}	log(S_{WL}/mol·m^{-3})	method	ref	note
24	0.027	0.251	−0.60	shake flask-GC	38	
25	0.025	0.222	−0.65	generator column-SPME-GC	39	
LDV at 25 °C		0.233		log mean of values at 25 °C		log(S_{WL}/mol·m^{-3}) = −749.8/(T/K) + 1.83 $r^2 = 0.337$ Figure 3
FAV at 25 °C		0.247				log(S_{WL}/mol·m^{-3}) = −788.4/(T/K) + 2.04 Figure 3

Octanol−Water Partition Coefficient

t/°C	log K_{OW}	method	ref	note
25	3.72	shake flask-GC (RI)	15	
28	3.72	shake flask-GC	19	
25	3.69	slow stirring-GC/HPLC	20	
25	3.69	slow stirring-SPME-GC	39	
5	3.85	slow stirring-SPME-GC	21	
25	3.72			
45	3.73			
23	3.30	shake flask-GC	40	room temp, assumed to be 23 °C; not used, outlier
25	3.51	shake flask-GC	41	not used, outlier
20	3.57	shake flask-HPLC	42	not used, outlier
LDV at 25 °C	3.70	log mean		log K_{OW} = 282.2/(T/K) + 2.78 $r^2 = 0.455$ Figure 4
FAV at 25 °C	3.83			log K_{OW} = 533.2/(T/K) + 2.04 Figure 4

Vapor Pressure

t/°C	P_S/Pa	P_L/Pa	log(P_L/Pa)	method	ref	note
0	0.0000387	0.00083	−3.08	effusion manometer	22	
10	0.000240	0.0036	−2.45			
20	0.00125	0.013	−1.88			
30	0.00600	0.046	−1.34			
40	0.0257	0.146	−0.84			
50	0.103	0.440	−0.36			
60	0.371	1.22	0.09			
70	1.23	3.16	0.50			
80	3.85	7.80	0.89			
90	11.5	18.6	1.27			
20	0.00435	0.046	−1.34	gas saturation-GC	43	
30	0.0171	0.13	−0.88			
40	0.0608	0.35	−0.46			
30	0.0167	0.13	−0.89			
30	0.0173	0.13	−0.88			
20	0.0233	0.25	−0.61	evaporation rate	44	
40	0.340	1.93	0.29			
60	3.46	11.4	1.06			
20	0.00260	0.0275	−1.56	relative loss rate	24	
30	0.0419	0.321	−0.49	gas saturation-GC	45	
20	0.00940	0.0993	−1.00			
10	0.00221	0.0329	−1.48			
0	0.000449	0.00967	−2.01			
−10	0.0000844	0.00270	−2.57			
−20	0.00000735	0.000361	−3.44			
−30	0.00000170	0.000133	−3.88			
19.63	0.00374	0.0400	−1.40	Knudsen-diffusion	46	
24.95	0.00737	0.0663	−1.18			
28.42	0.0116	0.0934	−1.03			
33.58	0.0225	0.155	−0.81			
37.82	0.0381	0.231	−0.64			
37.86	0.0396	0.239	−0.62			
43.32	0.0718	0.371	−0.43			
48.06	0.123	0.556	−0.26			
53.07	0.217	0.856	−0.07			
37.35	0.0562	0.345	−0.46	Knudsen-effusion	47	
39.35	0.0776	0.449	−0.35			
44.35	0.102	0.513	−0.29			
44.85	0.117	0.581	−0.24			
48.35	0.162	0.727	−0.14			
49.35	0.200	0.870	−0.06			
53.35	0.295	1.16	0.06			
54.85	0.331	1.25	0.10			
55.35	0.363	1.35	0.13			
56.35	0.398	1.44	0.16			
62.85	0.832	2.54	0.41			
63.35	0.813	2.45	0.39			
65.35	0.977	2.81	0.45			
66.35	1.05	2.93	0.47			

Table 3 (Continued)

Vapor Pressure (Continued)

t/°C	P_S/Pa	P_L/Pa	log(P_L/Pa)	method	ref	note		
69.85	1.58	4.08	0.61					
71.35	1.91	4.73	0.67					
71.85	1.78	4.36	0.64					
73.35	2.24	5.29	0.72					
74.35	2.40	5.54	0.74					
74.85	3.09	7.05	0.85					
80.35	4.07	8.19	0.91					
80.85	4.27	8.48	0.93					
83.85	7.08	13.1	1.12					
87.35	7.08	12.2	1.09					
88.85	9.33	15.5	1.19					
93.85	12.3	18.4	1.26					
99.35	23.4	31.2	1.49					
25	0.00670	0.0601	−1.22		Rordorf, unpublished			
50	0.150	0.643	−0.19					
75	2.00	4.55	0.66					
100	20.0	26.3	1.42					
125	150	122	2.09					
0		0.00476	−2.32	GC-retention time	23	calc from a linear regression		
10		0.0142	−1.85					
20		0.0395	−1.40					
30		0.103	−0.99					
40		0.250	−0.60					
LDV at 25 °C			−1.11	linear regression		log(P_L/Pa) = −3890/(T/K) + 11.94	$r^2 = 0.959$	Figure 5
FAV at 25 °C			−1.12			log(P_L/Pa) = −3905/(T/K) + 11.98		Figure 5

Henry's Law Constant

t/°C	H/Pa·m^{-3}·mol^{-1}	log(H/Pa·m^{-3}·mol^{-1})	method	ref	note		
23	0.202	−0.70	wetted-wall column	48			
0.5	0.0721	−1.14	gas purging	25			
10	0.126	−0.90					
23	0.339	−0.47					
35	0.624	−0.21					
45	1.17	0.068					
25	0.521	−0.28	wetted-wall column	26			
10	0.0730	−1.14		27			
20	0.180	−0.75					
30	0.390	−0.41					
35	0.580	−0.24					
40	0.800	−0.097					
5	0.0390	−1.41	dynamic headspace method	10			
10	0.0620	−1.21					
20	0.140	−0.85					
30	0.330	−0.48					
35	0.600	−0.22					
5	0.0440	−1.36	bubble stripping method	10			
10	0.0540	−1.27					
20	0.150	−0.82					
30	0.340	−0.47					
35	0.550	−0.26					
LDV at 25 °C		−0.57	linear regression		log(H/Pa·m^{-3}·mol^{-1}) = −2940/(T/K) + 9.29	$r^2 = 0.917$	Figure 6
FAV at 25 °C		−0.51			log(H/Pa·m^{-3}·mol^{-1}) = −3117/(T/K) + 9.94		Figure 6

Octanol-Air Partition Coefficient

t/°C	log K_{OA}	method	ref	note	
5	8.67	generator column-GC	9	reported as a linear regression equation	
10	8.45				
15	8.24				
20	8.04				
25	7.84				
LDV at 25 °C	7.84	directly taken		log K_{OA} = 3415/(T/K) − 3.61	Figure 7
FAV at 25 °C	7.74			log K_{OA} = 3521/(T/K) − 4.07	Figure 7

Table 3 (Continued)

Octanol Solubility								
t/°C	S_{OS}/mol·m^{-3}	S_{OL}/mol·m^{-3}	log(S_{OL}/mol·m^{-3})	method	ref	note		
4	100	1852	3.27	shake flask	8			
12	141	1961	3.29					
20	182	1923	3.28					
LDV at 25 °C	1969			linear regression		$\log(S_{OL}/\text{mol·m}^{-3}) = -84.1/(T/\text{K}) + 3.58$	$r^2 = 0.435$	Figure 8
FAV at 25 °C	1679					$\log(S_{OL}/\text{mol·m}^{-3}) = -255.0/(T/\text{K}) + 4.08$		Figure 8

[a] The subscripts O and W refer to octanol and water, whereas the subscripts S and L refer to the solid and liquid states. *H* designates the Henry's law constant between air and water. LDV stands for literature-derived value and FAV for final adjusted value.

Table 4. Literature-Derived Values (LDVs) and Assigned Uncertainty Estimates (*u*) for the Physical-Chemical Properties of α-, *β*-, and *γ*-HCH at 25 °C[a]

	S_{WL}/mol·m^{-3}		K_{OW}		P/Pa		H/Pa·m^3·mol^{-1}		K_{OA}		S_{OL}/mol·m^{-3}	
compd	LDV	u_W	LDV	u_{OW}	LDV	u_A	LDV	u_{AW}	LDV	u_{OA}	LDV	u_O
α-HCH	0.293	3	6.47×10^3	2	0.248	2	0.652	2	4.05×10^7	5	3050	5
β-HCH	1.18	4	6.91 ×	3	0.0613	3	0.0374	3	7.39×10^8	5		
γ-HCH	0.233	1	5.05×10^3	1	0.0772	1	0.272	2	6.98×10^7	4	1969	5

[a] Water solubility (S_{WL}), octanol solubility (S_{OL}), and vapor pressure (P_L) refer to the liquid state. *H* designates the Henry's law constant between air and water.

Table 5. Internally Consistent Physical-Chemical Properties of α-, *β*-, and *γ*-HCH at 25 °C after Adjustment (FAV: Final Adjusted Value)[a]

	S_{WL}/mol·m^{-3}		K_{OW}		P_L/Pa		H/Pa·m^3·mol^{-1}		K_{OA}		S_{OL}/mol·m^{-3}	
compd	FAV	adj	FAV	adj	FAV	adj	FAV	adj	FAV	adj	FAV	adj
α-HCH	0.333	14%	8.63×10^3	33%	0.245	−1%	0.735	13%	2.91×10^7	−28%	2870	−6%
β-HCH	1.44	22%	8.22×10^3	19%	0.0529	−14%	0.037	−2%	5.54×10^8	−25%	11800[b]	
γ-HCH	0.247	6%	6.79×10^3	34%	0.0757	−2%	0.306	12%	5.50×10^7	−21%	1680	−15%

[a] The required percentage of adjustment to achieve consistency is also given. Water solubility (S_{WL}), octanol solubility (S_{OL}), and vapor pressure (P_L) refer to the liquid state. *H* designates the Henry's law constant between air and water. [b] No literature-derived value exists, and the final adjusted value is calculated from the other properties.

Table 6. Literature-Derived Values (Δ*U*) and Assigned Uncertainty Estimates (*u*) for the Internal Energies of Phase Transfer of α-, *β*-, and *γ*-HCH in kJ·mol^{-1}

compd	ΔU_W	u_W	ΔU_{OW}	u_{OW}	ΔU_A	u_A	ΔU_{AW}	u_{AW}	ΔU_{OA}	u_{OA}	ΔU_O	u_O
α-HCH			-7.2^{b}	3^{b}	63.3^{e}	2^{e}	58.2^{h}	2^{h}	-61.9^{k}	5^{k}	4.9^{l}	4^{l}
β-HCH			-5.8^{c}	5^{c}	65.7^{f}	3^{f}	63.7^{i}	2^{i}	-94.5^{k}	5^{k}		
γ-HCH	14.4^{a}	4^{a}	-10.4^{d}	4^{d}	72.0^{g}	1^{g}	53.8^{j}	2^{j}	-58.0^{k}	5^{k}	1.6^{l}	5^{l}

[a] Regression of log S_{WL} versus 1/(*T*/K) using data from refs 15, 16, 34, 35, 36, 37, 38, and 39. [b] Regression of log K_{OW} versus 1/(*T*/K) using data from refs 15, 19, 20, and 21. [c] Regression of log K_{OW} versus 1/(*T*/K) using data from refs 15, 19, 20, and 21. [d] Regression of log K_{OW} versus 1/(*T*/K) using data from ref 21. [e] Regression of log P_L versus 1/*T* using data from refs 22, 23, and 24. [f] Regression of log P_L versus 1/*T* using data from refs 22 and 24 and Bidleman et al., unpublished work. [g] Regression of log P_L versus 1/(*T*/K) using data from refs 22, 23, 24, 43, 44, 45, 46, and 47 and Rordorf, unpublished work. [h] Regression of log K_{AW} versus 1/(*T*/K) using data from refs 10, 25, 26, and 27. [i] Regression of log K_{AW} versus 1/(*T*/K) using data from refs 10 and 26. [j] Regression of log K_{AW} versus 1/(*T*/K) using data from refs 10, 25, 26, 27, and 48. [k] Derived from data given in ref 9. [l] Regression of log S_{OL} versus 1/(*T*/K) using data from ref 8.

liquid vapor pressure of *β*-HCH is indeed comparable to those of the other isomers, the subcooled liquid water solubility, K_{AW}, and K_{OA} are not.

The solvation descriptors for *β*-HCH were largely derived from gas−liquid chromatographic retention times.[11] The retention behaviors of the three HCH isomers on gas chromatographic columns are indeed very similar; that is, they elute generally close to each other. The failure of the LSERs to identify the divergent partitioning behavior of the *β*-isomer may thus indicate that partitioning into liquid chromatographic stationary phases is not always a good surrogate for partitioning into bulk phases such as octanol. This also highlights the limitations of property estimation methods based on gas chromatographic retention times,[12] in particular their limitations in discriminating among the partitioning properties of chemicals with similar structures but large differences in melting points.

Energies of Phase Transfer. The measured temperature dependences of the properties for α- and *γ*-HCH are in excellent agreement. The required adjustment to the Δ*U* values is usually less than 30%. Only the measured temperature dependence of the octanol solubilities (ΔU_O) had to be adjusted by a higher percentage, which can be explained by the relatively small size and large uncertainty of the ΔU_O values. Also for *β*-HCH, the need for adjusting the LDVs for the Δ*U* values is usually minor—the maximum adjustment, needed for ΔU_{OW}, is only about 10 kJ·mol^{-1}.

Table 7. Internal Energies of Phase Transfer of α-, β-, and γ-HCH after Adjustment (FAV: Final Adjusted Value)[a]

	ΔU_W/kJ·mol^{-1}		ΔU_{OW}/kJ·mol^{-1}		ΔU_A/kJ·mol^{-1}		ΔU_{AW}/kJ·mol^{-1}		ΔU_{OA}/kJ·mol^{-1}		ΔU_O/kJ·mol^{-1}	
compd	FAV	adj	FAV	adj	FAV	adj	FAV	adj	FAV	adj	FAV	adj
α-HCH	7.6		−5.1	−29%	64.5	1.9%	56.8	−2.4%	−61.9	0.1%	2.5	−49%
β-HCH	−2.1		−16.2	181%	65.7	0%	67.8	6.6%	−84.1	−11%	−18.3	
γ-HCH	15.1	5.1%	−10.2	−2%	72.3	0.4%	57.2	6.3%	−67.4	16%	4.9	203%

[a] The required percentage of adjustment to achieve consistency is also given. If no percentage of adjustment is given, no literature-derived value existed and the value was calculated from the other properties.

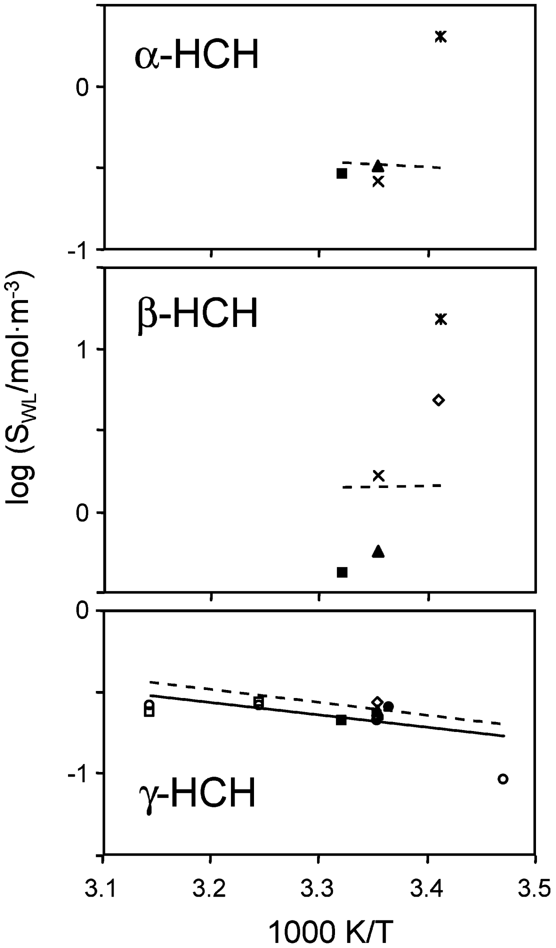

Figure 3. Relationships between the logarithm of the liquid solubility in water in moles per cubic meter (log S_{WL}) of α-, β-, and γ-HCH and the reciprocal absolute temperature in kelvin (T) based on data from Kurihara et al. (■),[15] Weil et al. (▲),[16] Kanazawa et al. (×),[17] Slade (∗),[18] Isnard and Lambert (◇),[29,30] Lipke and Kearns (shaded triangle),[34] Richardson and Miller (—),[35] Masterton and Lee (△),[36] Biggar and Riggs (○),[37] Chiou et al. (●),[38] and Paschke et al. (□).[39] The solid line (—) indicates the linear regression through the literature-derived values; the dashed line (- - -) represents the final adjusted values.

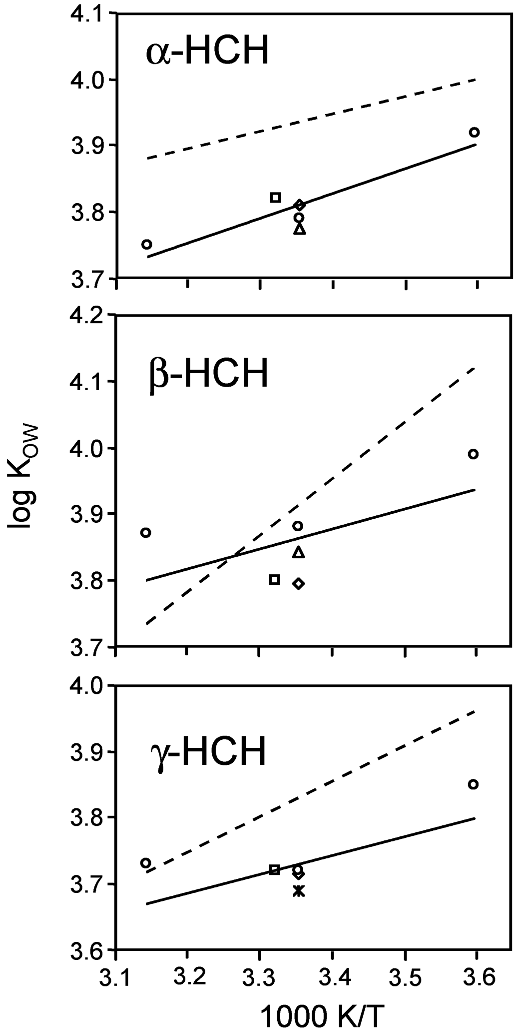

Figure 4. Relationships between the logarithm of the octanol−air partition coefficient (log K_{OW}) of α-, β-, and γ-HCH and the reciprocal absolute temperature in kelvin (T), based on data from Kurihara et al. (◇),[15] Kurihara and Fujita (□),[19] De Bruijin et al. (△),[20] Paschke and Schüürmann (∗),[21] and Paschke et al. (○).[39] The solid line (—) indicates the linear regression through the literature-derived values; the dashed line (- - -) represents the final adjusted values.

The FAVs suggest that the air−water and air−octanol partitioning equilibria of β-HCH are more strongly influenced by temperature than those of the other two investigated isomers. The FAVs further suggest that the ΔU_O for β-HCH has a different sign from that of the other isomers, that is, displays an opposite temperature dependence. Because there are no measured data for the ΔU_O and ΔU_W of β-HCH, ΔU_A is not being adjusted. A negative ΔU_O value for β-HCH is needed to account for a significantly higher ΔU_{OA} value reported for this isomer by Shoeib and Harner.[9] It is obviously possible that ΔU_A for β-HCH is higher or ΔU_{OA} should be lower. However, even though the ΔU_{OA} values of all three isomers are assigned a high uncertainty (u_{OA}), the maximum adjustment to any of these values is only 16.3%.

Conclusions

By using information for all partitioning properties simultaneously instead of one at a time, it is easier to constrain the range in which the true value for a property will lie. An internally consistent set of physical-chemical property data for three HCH isomers is derived on the basis of all experimentally obtained values reported for these isomers in the literature. The final adjusted data set should

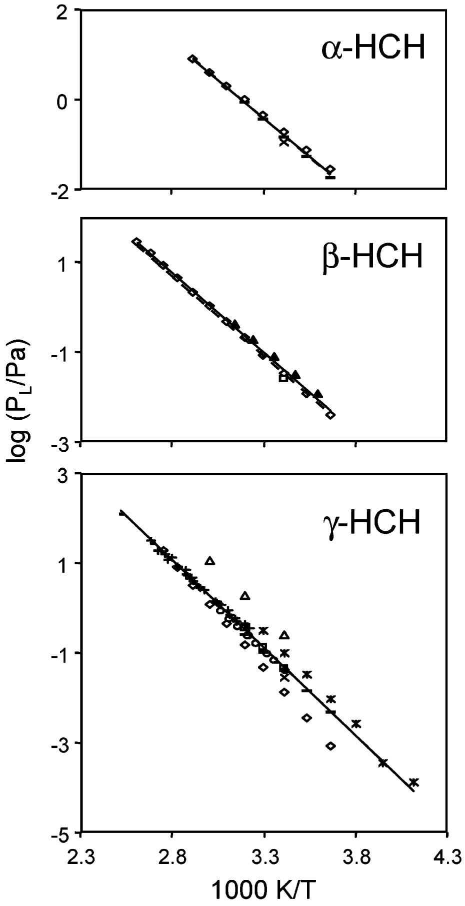

Figure 5. Relationships between the logarithm of the liquid vapor pressure in pascal (log P_L) of α-, β-, and γ-HCH and the reciprocal absolute temperature in kelvin (T), based on data from Balson (◇),[22] Hinckley et al. (−),[23] Dobbs and Cull (×),[24] Bidleman et al. (▲), Spencer and Cliath (□),[43] Gückel et al. (△),[44] Wania et al. (∗),[45] Boehncke et al. (○),[46] Giustini et al. (+),[47] and Rordorf, unpublished data (−). The solid line (—) indicates the linear regression through the literature-derived values; the dashed line (- - -) represents the final adjusted values.

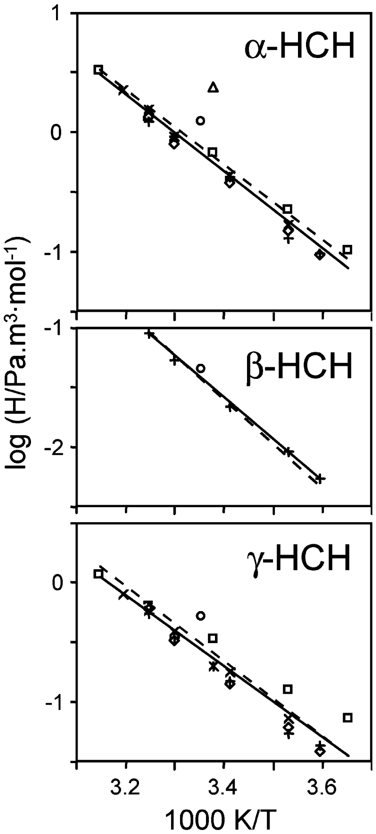

Figure 6. Relationships between the logarithm of the Henry's law constant in pascal cubic meters per mole (log H) of α-, β-, and γ-HCH and the reciprocal absolute temperature in kelvin (T), based on data from Sahsuvar et al. (dynamic headspace method) (◇),[10] Sahsuvar et al. (bubble stripping method) (+),[10] Kucklick et al. (□),[25] Altschuh et al. (○),[26] Jantunen and Bidleman (×),[27] Atlas et al. (△),[28] and Fendinger and Glotfelty (*).[48] The solid line (—) indicates the linear regression through the literature-derived values; the dashed line (- - -) represents the final adjusted values.

be useful when seeking to interpret the differential fate of HCH isomers in the environment.[13] They will also be indispensable in chemical fate modeling, especially when the intention is to evaluate the fate of individual isomers or understand changes in isomeric composition (e.g. α/γ-ratios). Internally consistent values of the six partitioning properties at a particular temperature can be obtained by inserting the FAVs in Tables 5 and 7 in the following equation:

$$\log K(T) = \log K(25\ °\mathrm{C}) - (\Delta U_{XY} + R(298.15\ \mathrm{K}))/(\ln(10)\ R)(1/T - 1/298.15\ \mathrm{K}) \quad (2)$$

where the K stands for the physical-chemical property and ΔU_{XY} for the corresponding internal energy of phase transfer. T is temperature in kelvin. The subscripts X and Y describe different phases.

The final adjusted values indicate a partitioning behavior for the β-isomer which differs substantially from those of the other two investigated HCHs. In particular, it partitions much more strongly from the gas phase to the aqueous and octanol phases. This difference cannot be explained by the higher crystal energy of the β-HCH, and it is also not in accord with the retention behavior on gas chromatographic columns. Caution should thus be applied when estimating partitioning behavior of closely related substances from gas chromatographic retention times or when using LSER equations with solvation descriptors which are solely derived from chromatographic data.

The divergent partitioning behavior of β-HCH may result in substantially different environmental pathways. Scavenging of organic vapor by rain becomes increasingly important at Henry's law constants below 0.1 Pa·m^3·mol^{-1}, and it is likely that β-HCH is scavenged much more efficiently than α- and γ-HCH. This will limit its atmospheric long-range transport potential relative to those of α- and γ-HCH, and it could account for the different distribution patterns of HCHs in the Northern Pacific and the Arctic Ocean.[6] A higher K_{OA} value implies stronger retention of β-HCH in soils and plant foliage. In contrast to α- and γ-HCH, the β-isomer may even sorb to atmospheric particles at very low ambient temperatures, such as occur in polar regions. The FAVs suggest that the log K_{OW} for β-HCH is comparable to those of the α- and γ-isomers. This implies that more efficient bioaccumulation observed for the β-HCH[5] is more likely due to higher resistance to metabolic conversion than to higher lipophilicity.

A data evaluation exercise as presented here can indicate what additional types of measurement would be most effective in further constraining the partitioning characteristics of an organic chemical. The study suggests that the reported data for α- and γ-HCH are generally very consistent and their partitioning characteristics are thus

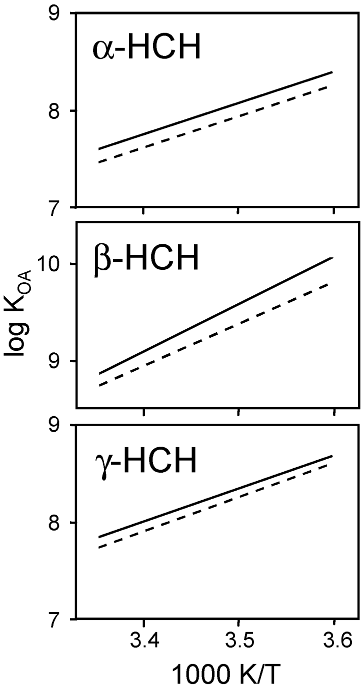

Figure 7. Relationships between the logarithm of the octanol−air partition coefficient (log K_{OA}) of α-, β-, and γ-HCH and the reciprocal absolute temperature in kelvin (T). The final adjusted values (dashed line, - - -) are somewhat lower than the measured data reported by Shoeib and Harner (solid line, —).[9]

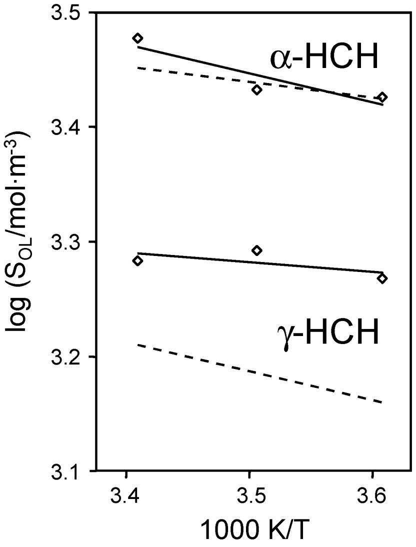

Figure 8. Relationships between the logarithm of the liquid solubility in octanol (log(S_{OL}/mol·m^{-3})) of α- and γ-HCH and the reciprocal absolute temperature in kelvin (T), based on data from Niimi (◇).[8] The solid line (—) indicates the linear regression for the values from Niimi;[8] the dashed line (- - -) represents the final adjusted values.

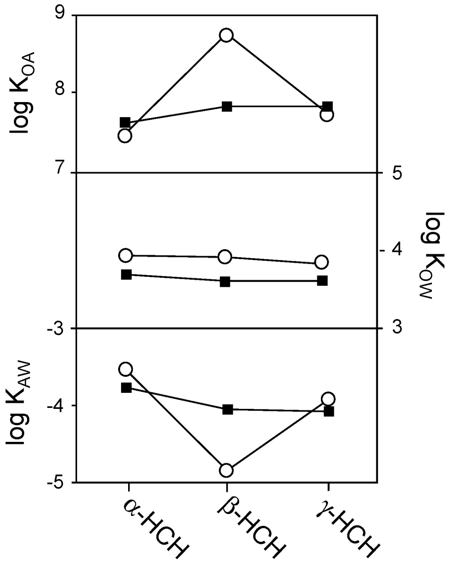

Figure 9. Comparison of the final adjusted values (○) for the log K_{OA}, log K_{OW}, and log K_{AW} of α-, β-, and γ-HCH with the values (■) predicted using the linear solvation energy relationships and solvation descriptors from Abraham et al.[11] Discrepancies are large for the log K_{OA} and log K_{AW} of β-HCH.

already better established than those of most other highly chlorinated organic substances. Although only few measurements of the properties of the β-isomer have been conducted, the reported data are encouragingly consistent. Most useful would be measured values of the entropy of fusion, as well as measurements of the water solubility as a function of temperature for that isomer. It would also be desirable to have independent validation of β-HCH's unusually high K_{OA} and low K_{AW}. Although the data availability for the remaining HCH isomers is poor, it may not be justified to expend great effort on the determination of their properties, considering that they are generally not detected in the environment.

Literature Cited

(1) Pontolillo, J.; Eganhouse, R. P. *The search for reliable aqueous solubility* (S_W) *and octanol−water partition coefficient* (K_{OW}) *data for hydrophobic organic compounds: DDT and DDE as a case study*; U.S. Geological Survey Water-Resources Investigations Report 01-4201; 2001; 51 pages.

(2) Beyer, A.; Wania, F.; Gouin, T.; Mackay, D.; Matthies, M. Selecting Internally Consistent Physicochemical Properties of Organic Compounds. *Environ. Toxicol. Chem.* **2002**, *21*, 941−953.

(3) Li, N.; Wania, F.; Lei, Y. D.; Daly, G. L. A Comprehensive and Critical Compilation, Evaluation and Selection of Physical Chemical Property Data for Selected Polychlorinated Biphenyls. *J. Phys. Chem. Ref. Data* **2003**, *32*, 1535−1590.

(4) Lakaschus, S.; Weber, K.; Wania, F.; Bruhn, R.; Schrems, O. The Air-Sea Equilibrium and Time Trend of Hexachlorocyclohexanes in the Atlantic Ocean Between the Arctic and Antarctica. *Environ. Sci. Technol.* **2002**, *36*, 138−145.

(5) Willett, K. L.; Ulrich, E. M.; Hites, R. A. Differential Toxicity and Environmental Fates of Hexachlorocyclohexane Isomers. *Environ. Sci. Technol.* **1998**, *32*, 2197−2207.

(6) Li, Y.-F.; MacDonald, R. W.; Jantunen, L. M. M.; Harner, T.; Bidleman, T. F.; Strachan, W. M. J. The Transport of β-Hexachlorocyclohexane to the Western Arctic Ocean: a Contrast to α-HCH. *Sci. Total Environ.* **2002**, *291*, 229−246.

(7) Mackay, D.; Shiu, W.-Y.; Ma, K.-C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate* (CD-ROM); Chapman & Hall/CRCnetBase: Boca Raton, FL, 2000.

(8) Niimi, A. J. Solubility of Organic Chemicals in Octanol, Triolein and Cod Liver Oil and Relationships Between Solubility and Partition Coefficients. *Wat. Res.* **1991**, *25*, 1515−1521.

(9) Shoeib, M.; Harner, T. Using Measured Octanol-Air Partitioning Coefficients to Explain Environmental Partitioning of Organochlorine Pesticides. *Environ. Toxicol. Chem.* **2002**, *21*, 984−990.

(10) Sahsuvar, L.; Helm, P. A.; Jantunen, L. M. M.; Bidleman, T. F. Henry's Law Constants for α-, β-, and γ-Hexachlorocyclohexanes (HCHs) as a Function of Temperature and Revised Estimates of Gas Exchange in Arctic Regions. *Atmos. Environ.* **2002**, *37*, 983−992.

(11) Abraham, M. H.; Enomoto, K.; Clarke, E. D.; Sexton, G. Hydrogen Bond Basicity of the Chlorogroup; Hexachlorocyclohexanes as Strong Hydrogen Bond Bases. *J. Org. Chem.* **2002**, *67*, 4782−4786.

(12) Wania, F.; Lei, Y. D.; Harner, T. Estimating Octanol-Air Partition Coefficients of Nonpolar Semivolatile Organic Compounds from Gas Chromatographic Retention Times. *Anal. Chem.* **2002**, *74*, 3476−3483.

(13) Walker, K.; Vallero, D. A.; Lewis, R. G. Factors Influencing the Distribution of Lindane and Other Hexachlorocyclohexanes in the Environment. *Environ. Sci. Technol.* **1999**, *33*, 4373−4378.

(14) Plato, C.; Glasglow, A. R., Jr. Differential Scanning Calorimetry as a General Method for Determining the Purity and Heat of Fusion of High Purity Organic Chemicals. Application to 95 Compounds. *Anal. Chem.* **1969**, *41*, 330−336.

(15) Kurihara, N.; Uchida, M.; Fujita, T.; Nakajima, M. Studies on BHC Isomers and Related Compounds. V. Some Physicochemical Properties of BHC Isomers. *Pestic. Biochem. Physiol.* **1973**, *2*, 383−390.

(16) Weil, V. G.; Duré, G.; Quentin, K. E. Wasserlöslichkeit von insektiziden chlorierten Kohlenwasserstoffen und polychlorierten Biphenylen im Hinblick auf eine Gewässerbelastung mit diesen Stoffen. *Wasser- Abwasserforsch.* **1974**, *7* (6), 169−175.

(17) Kanazawa, J.; Yushima, T.; Kiritani, K. Contamination of Ecosystem by Pesticides II. *Kagaku* (Science) **1971**, *41*, 384 (in Japanese).

(18) Slade, R. E. The γ-Isomer of Hexachlorocyclohexane (Gammexane). An Insecticide with Outstanding Properties. *Chem. Ind.* **1945**, *40*, 314−319.

(19) Kurihara, N.; Fujita, T. Composition of Partition Coefficients of Polychlorinated Hydrocarbons. *Bull. Inst. Chem. Res., Kyoto Univ.* **1983**, *61*, 89−95.

(20) De Bruijn, J.; Busser, F.; Seinen, W.; Hermens, J. Determination of Octanol/Water Partition Coefficients for Hydrophobic Organic Chemicals with the “Slow-Stirring” Method. *Environ. Toxicol. Chem.* **1989**, *8*, 499−512.

(21) Paschke, A.; Schüürmann, G. Octanol/Water-Partitioning of Four HCH Isomer at 5, 25, and 45 °C. *Fresenius Environ. Bull.* **1998**, *7*, 25−263.

(22) Balson, E. W. Studies in Vapour Pressure Measurement. III. An Infusion Manometer Sensitive to 5 × 10−4 mmHg. Vapour Pressures of DDT and Other Slightly Volatile Substances. *Trans. Faraday Soc.* **1947**, *43*, 54−60.

(23) Hinckley, D. A.; Bidleman, T. F.; Foreman, W. T. Determination of Vapor Pressures for Nonpolar and Semipolar Organic Compounds from Gas Chromatographic Retention Data. *J. Chem. Eng. Data* **1990**, *35*, 232−237.

(24) Dobbs, A. J.; Cull, M. R. Volatilization of Chemicals-Relative Loss Rates and the Estimation of Vapor Pressures. *Environ. Pollut., Ser. B* **1982**, *3*, 289−298.

(25) Kucklick, J. R.; Hinckley, D. A.; Bidleman, T. F. Determination of Henry's Law Constants for Hexachlorocyclohexane in Distilled Water and Artificial Seawater as a Function of Temperature. *Mar. Chem.* **1991**, *34*, 197−209.

(26) Altschuh, A.; Bruggemann, R.; Santl, H.; Eichinger, G.; Piringer, O. G. Henry's Law Constants for a Diverse Set of Organic Chemicals: Experimental Determination and Comparison of Estimation Methods. *Chemosphere* **1999**, *39*, 1971−1887.

(27) Jantunen, L. M. M.; Bidleman, T. F. Temperature-dependent Henry's Law Constant for Technical Toxaphene. *Chemosphere: Global Change Sci.* **2000**, *2*, 225−231.

(28) Atlas, E.; Foster, R.; Giam, C. S. Air-Sea Exchange of High Molecular Weight Organic Pollutants: Laboratory Studies. *Environ. Sci. Technol.* **1982**, *16*, 283−286.

(29) Isnard, P.; Lambert, S. Estimating bioconcentration factors from octanol−water partition coefficient and aqueous solubility. *Chemosphere* **1988**, *1*, 21−34.

(30) Isnard, P.; Lambert, S. Aqueous solubility and *n*-octanol/water partition coefficient correlations. *Chemosphere* **1989**, *18*, 1837−1853.

(31) Donnelly, J. R.; Drewes, L. A.; Johnson, R. L.; Munslow, W. D.; Knapp, K. K. Purity and Heat for Environmental Standards as Determined by Differential Scanning Calorimetry. *Thermochim. Acta* **1990**, *167*, 155−187.

(32) Sabbah, R.; An, X. W. Enthalpies de Fusion et de Sublimation de l'Isomere γ d'Hexachlorocyclohexane. *Thermochim. Acta* **1991**, *178*, 339−341.

(33) Kuber, M. V.; Kulkarni, S. B.; Biswas, A. B. Phase equilibriums of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane in binary systems. *Z. Phys. Chem. (München)* **1958**, *17*, 155−162.

(34) Lipke, H.; Kearns, C. W. DDT-Dehydrochlorinase III. Solubilization of Insecticides by Lipoprotein. *J. Econ. Entomol.* **1960**, *53*, 31−35.

(35) Richardson, L. T.; Miller, D. M. Fungitoxicity of Chlorinated Hydrocarbon Insecticides in Relation to Water Solubility and Vapor Pressure. *Can. J. Bot.* **1960**, *38*, 163−175.

(36) Masterton, W. L.; Lee, T. P. Effects of Dissolved Salts on Water Solubility of Lindane. *Environ. Sci. Technol.* **1972**, *6*, 919−921.

(37) Biggar, J. W.; Riggs, I. R. Apparent Solubility of Organochlorine Insecticides in Water at Various Temperatures. *Hilgardia* **1974**, *42*, 383−391.

(38) Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E. Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ. Sci. Technol.* **1986**, *20*, 502−508.

(39) Paschke, A.; Popp, P.; Schüürmann, G. Water Solubility and Octanol/Water-Partitioning of Hydrophobic Chlorinated Organic Substances Determined by Using SPME/GC. *Fresenius' J. Anal. Chem.* **1998**, *360*, 52−57.

(40) Platford, R. F. The environmental significance of surface films. II. Enhanced partitioning of lindane in thin films of octanol on the surface of water. *Chemosphere* **1981**, *10*, 719−722.

(41) Noegrohati, S.; Hammers, W. E. Regression Models for Octanol-Water Partition Coefficients, and for Bioconcentration in Fish. *Toxicol. Environ. Chem.* **1992**, *34*, 155−173.

(42) Kishi, H.; Hashimoto, Y. Evaluation of the Procedure for the Measurement of Water Solubility and *n*-Octanol/Water Partition Coefficient of Chemicals: Results of a Ring Test in Japan. *Chemosphere* **1989**, *18*, 1749−1759.

(43) Spencer, W. F.; Cliath, M. M. Vapor Density and Apparent Vapor Pressure of Lindane (BHC). *J. Agric. Food Chem.* **1970**, *18*, 529−530.

(44) Gückel, W.; Kästel, R.; Lewerenz, J.; Synnatschke, G. A Method for Determining the Volatility of Active Ingredients Used in Plant Protection. Part III. The Temperature Relationship Between Vapor Pressure and Evaporation Rate. *Pestic. Sci.* **1982**, *13*, 161−168.

(45) Wania, F.; Shiu, W. Y.; Mackay, D. Measurements of the Vapor Pressure of Several Low-Volatility Organochlorine Chemicals at Low Temperatures with a Gas Saturation Method. *J. Chem. Eng. Data* **1994**, *39*, 572−577.

(46) Boehncke, A.; Martin, K.; Müller, M. G.; Cammenga, H. K. The Vapor Pressure of Lindane (1,2,3,4,5,6-Hexachlorocyclohexane)—A Comparison of Knudsen Effusion Measurements with Data from Other Techniques. *J. Chem. Eng. Data* **1996**, *41*, 543−545.

(47) Giustini, A.; Brunetti, B.; Piacente, V. A Sublimation Study of Lindane. *J. Chem. Eng. Data* **1998**, *43*, 447−450.

(48) Fendinger, N. J.; Glotfelty, D. E. A Laboratory Method for the Experimental Determination of Air/Water Henry's Law Constants for Several Pesticides. *Environ. Sci. Technol.* **1988**, *22*, 1289−1293.

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