



ENVIRONMENTAL RESEARCH BRIEF

Transformations of Halogenated Hydrocarbons: Hydrolysis and Redox Processes

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Abstract

This report describes process models and rate constants that are necessary to predict the environmental fate of halogenated aliphatic hydrocarbons. Two important pathways for the transformation of this class of compounds in sediment and groundwater systems are abiotic reduction and abiotic hydrolysis. Models have been developed to explain the reactivity of the compounds in heterogeneous systems. Reduction rate constants are reported for 16 chloro-, bromo- and iodo-hydrocarbons, along with a structure reactivity relationship that correlates reactivity to general molecular descriptors. Redox reactivity of sediment or ground water samples is related to the organic content of sample solids. Neutral and alkaline hydrolysis rate constants, along with activation parameters have been measured for 18 chlorinated methanes, ethanes, propanes and ethenes. Hydrolysis half-lives for these compounds are calculated for typical environmental reaction conditions.

Introduction

In spite of the many biological degradation studies of halogenated hydrocarbons, a major environmental question of concern is why some halogenated hydrocarbons persist and why others are quite reactive and rapidly disappear. Furthermore, it is not clear what ecosystem properties dictate whether the compounds rapidly degrade or persist over months or years. It has become increasingly apparent that biological processes are inadequate to account for the environmental fate of these compounds. It is thus logical

that attention turn to abiotic processes in an attempt to answer these questions.

The occurrence of halogenated hydrocarbons as ubiquitous contaminants in the environment is well documented (Vogel et al., 1987). Specific compounds in this class of organics are widely used as industrial cleaning and degreasing solvents, high pressure lubricants, pesticides and freons as well as proposed freon substitutes. Assessing the fate of this class of compounds requires quantitative descriptions of redox and hydrolysis transformation processes. Such descriptive models have been developed for homogeneous abiotic processes such as hydrolysis. Similar algorithms are needed that describe redox transformation reactions in soil-water ecosystems.

This report presents our recent findings on environmental redox and hydrolysis fate processes. Abiotic reduction rate constants are given for 16 halogenated hydrocarbons along with structure reactivity relationships that can be used to assess reactivity of other compounds of the same class. Likewise, neutral and alkaline hydrolysis rate constants and activation parameters are given for 18 chlorinated methanes, ethanes, propanes and ethenes.

Discussion

Abiotic Redox Reactions

This discussion is divided into two parts beginning with a report of pseudo-first-order disappearance rate constants for halo-hydrocarbons and presentation of a structure reactivity relationship (SRR) of these rate constants with selected molecular descriptors. The second part presents a correlation of hexachloroethane reaction rate constants with system parameters that vary across a wide range of sediment characteristics to provide the capability to

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extrapolate decay rate constants from one aquatic system to another.

Correlation of Reactivity with Structure

Figure 1 lists the halogenated hydrocarbons along with the chemical structures that were used in developing the SRR's. Only compounds for which there are reported first-order disappearance rate constants obtained under defined reaction conditions are included. All the rate constants given in Table 1 were obtained under reducing conditions in sediment, saturated soil or aquifer samples.

$I_2C=CI_2$ Tetraiodoethene	$Cl_2=CCl_2$ Tetrachloroethene
IH_2C-CH_2I 1,2-Diiodoethane	C_6H_5-I Iodobenzene
$BrClHC-CHClBr$ 1,2-Dibromo-1,2-dichloroethane	$C_6H_6Cl_6$ Alpha-hexachlorocyclohexane
Cl_3C-CCl_3 Hexachloroethane	ClH_2C-CH_2Cl 1,2-Dichloroethane
$CH_3BrHC-CHBrCH_3$ 2,3-Dibromobutane	$Cl_2C=CH_2$ 1,1-Dichloroethene
BrH_2C-CH_2Br 1,2-Dibromoethane	$ClHC=CHCl$ Trans-1,2-dichloroethene
$C_6H_6Cl_6$ Gamma-hexachlorocyclohexane	$ClHC=CHCl$ Cis-1,2-dichloroethene
CCl_4 Carbontetrachloride	C_6F_{14} Perfluorohexane
$Cl_2HC-CHCl_2$ 1,1,2,2-Tetrachloroethane	$C_{10}F_{18}$ Perfluorodecaline
	DDT

Figure 1. Halogenated aliphatic and aromatic hydrocarbons selected for abiotic reduction studies in anaerobic sediments.

The compounds used in these correlations cover a broad section of structural features including halogenated methanes, ethanes, ethenes and aromatics. These compounds react by a variety of mechanisms in these reducing systems but they all apparently involve an initial "slow" electron transfer step in the reductive pathways. The different pathways are reflected in the different products as has recently been reported (Wolfe et al, 1989).

The disappearance rate constants were correlated with several molecular descriptors with the best correlation obtained with the carbon-halogen bond strength (BS), Taft's sigma constant (σ^*), and the carbon-halogen bond energy (BE) (Table 1). A plot of k_{obs} versus kcal is given in Figure 2 along with the regression analysis data. The reactivity covers about 4 orders of magnitude and gives a regression coefficient, R^2 of 0.989. This relationship provides a convenient way to estimate the relative reactivity of other halogenated hydrocarbons.

Correlation of Reactivity with Sediment Properties

Hexachloroethane was selected as a model compound to elucidate system properties that govern the reducing activity

of sediment and ground water samples. Data for the reduction of hexachloroethane include disappearance rate constants for a large number of sediment, soil and aquifer samples (Table 2). The data suggest a correlation between the rate constants and the organic carbon (OC) content of the samples.

The correlation is enhanced when one takes into account the fact that hexachloroethane can be significantly sorbed to the solid phase in some of the samples. In most cases, it was not possible to measure the distribution coefficient for hexachloroethane because it was reduced too fast to make the experimental measurements. It is, however, possible to estimate the fraction of hexachloroethane sorbed by use of the octanol-water partition coefficient and known relationships between octanol and organic carbon.

Linear regression analyses show that correcting the observed rate constants (k_{obs}) (Table 2) for the fraction sorbed (k_{corr}) significantly improves the correlation (Weber and Wolfe, 1987). The best correlation is with fraction organic carbon (OC) ($R^2 = 0.905$) and is shown in Figure 3 as a plot of k_{corr} versus k_{cal} along with the linear regression data.

Although there are other factors that contribute to the reduction of hexachloroethane, organic carbon (or a reducing agent that co-varies with organic carbon) is the most important descriptor, accounting for about 90 % of the variance of the data. It is likely that the correlation could be improved if sand were excluded from the sediment in the experiments since it has been shown by Jafvert and Wolfe, 1987, to have little reductive activity.

Hydrolysis

There are several reasons to measure the homogeneous, abiotic hydrolysis rate constants even for compounds that react very slowly under ordinary environmental conditions. First, because the residence time is long in aquifers, deep reservoirs and oceans, slow reactions can still be major factors in loss of pollutants that must travel a significant distance before they become potential problems for the environment or human populations. Second, the study of any biologically mediated process or heterogeneously catalyzed reaction must allow for the amount of reaction that occurs by a purely abiotic, homogeneous pathway.

The compounds for which neutral and alkaline hydrolysis rate constants were measured are given in Figure 4 in order of increasing reactivity. This suite of compounds includes 18 chlorinated methanes, ethanes, ethenes and propanes and spans 13 orders of magnitude in hydrolytic reactivity.

It is noteworthy that the relative rates of reactivity are dissimilar for the neutral and alkaline pathways. In the case of alkaline hydrolysis, 1,1,2,3,3-pentachloropropane was the most reactive while no reaction could be detected for carbon tetrachloride, 2,2-dichloropropane and 1,1,1-trichloroethane. For neutral hydrolysis, 2,2-dichloropropane was the most reactive and hexachloroethane was the least reactive.

The order of reactivities suggests that alkaline hydrolysis rate constants can be correlated with acidity of the proton being abstracted in the rate determining step. On the other hand, bond strength and steric factors appear to control the reactivity towards neutral hydrolysis. Presently attempts are

Table 1. Kinetic Data and Molecular Descriptors Used in the Structure Reactivity Correlations

Compound	BS ^a Kcal/mol e	σ^* ^b	BE ^c Kcal/mole	Avg.k min ⁻¹ ·pbs	t _{1/2} hr
Tetraiodoethene	55.5	3.52	53.8	9.22E-02	0.13
1,2-Diiodoethane	55.5	1.76	63.2	3.41E-02	0.34
1,2-Diclo-Dibrethane	68.0	4.14	63.2	4.99E-03	2.31
Hexachloroethane	81.0	6.30	63.2	2.33E-03	4.96
2,3-Dibromobutane	68.0	1.84	63.2	9.98E-04	11.6
1,2-Dibromoethane	68.0	2.04	63.2	5.45E-04	21.2
g-Hexachlorocyclohexane	81.0	3.15	63.2	1.51E-04	76.5
Carbontetrachloride	81.0	4.20	63.2	1.10E-04	105
Sym-Tetrachloroethane	81.0	4.20	63.2	7.30E-05	158
Tetrachloroethene	81.0	4.20	53.8	4.05E-05	285
Iodobenzene	64.0	1.12	20.0	2.55E-05	453
a-Hexachlorocyclohexane	81.0	2.10	63.2	2.37E-05	487
1,2-Dichloroethane	81.0	2.10	63.2	1.40E-05	825
1,1-Dichloroethene	81.0	2.10	53.8	4.37E-06	2643
1,2-T-Dichloroethene	81.0	2.10	53.8	3.47E-06	3328
1,2-C-Dichloroethene	81.0	2.10	53.8	3.40E-06	3397

^aCarbon-halogen bond energy.

^bTaft's sigma constant.

^cCarbon-carbon bond energy.

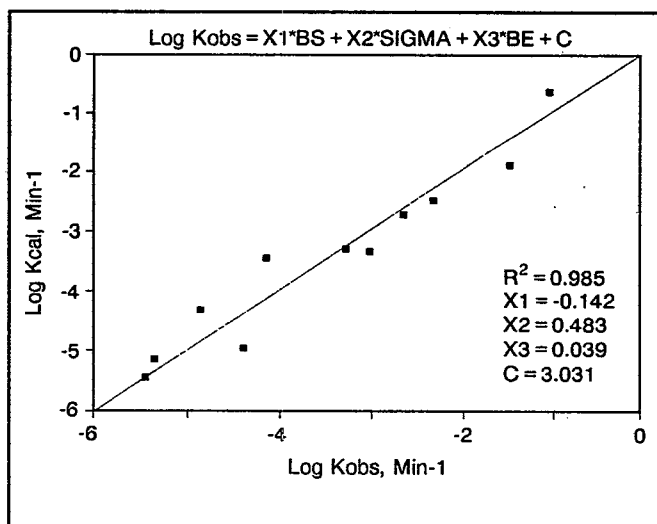


Figure 2. Structure reactivity relationship for abiotic reductive rate constants (K_{obs}) of halogenated hydrocarbons with carbon-halogen bond energies (BE), Taft sigma constants (σ^*) and carbon-carbon bond energies (BE).

under way to correlate the reactivity of the compounds with readily available molecular descriptors.

Kinetic data along with calculated half-lives at 25°C and pH 7 are given in Table 3. These calculations take into account

contributions from both neutral and alkaline processes at pH 7. Half-lives vary from 0.013 years for 1,1,2,3,3-pentachloropropane to 2.1×10^{10} years for 1,2-dichloroethene (Jeffers, et al, 1989). Thus, under hydrolytic reaction conditions typical of aquatic environments, reactivity varies over 12 orders of magnitude.

Table 2. Disappearance Rate Constants for Hexachloroethane in Selected Sediments and Aquifer Samples

Sediment Source	Fraction O.C.	Sediment Conc., g/g	Rate Constant k, min ⁻¹	t _{1/2} , hr
BarH	0.0221	0.08	5.00E-02	0.23
BarH	0.022	0.0895	3.51E-02	0.33
HickoryH	0.018	0.11	2.60E-02	0.44
Breukelveen	0.29	0.045	2.47E-02	0.47
BeaverD	0.056	0.2	2.00E-0 2	1.12
MemorP	0.043	0.055	1.90E-02	0.61
BarH	0.022	0.075	1.90E-02	0.61
Loosdr. Plassen	0.33	0.050	7.62E-03	1.52
Vechten	0.06	0.087	2.33E-03	4.96
EPA-B1	0.009	0.1	1.80E-03	6.42
Dommel	0.0053	0.469	1.22E-03	9.47
EPA-13	0.03	0.1	8.15E-04	14.2
EPA-11	0.015	0.1	7.88E-04	14.7
EPA-6	0.0072	0.1	4.47E-04	25.8
Lula, aq	0.000065	0.161	5.41E-05	213
Blythville, aq	0.00012	0.142	4.38E-05	264
Blythville,aq	0.00012	0.613	4.36E-05	265
Lula, aq	0.000065	0.689	3.01E-05	384

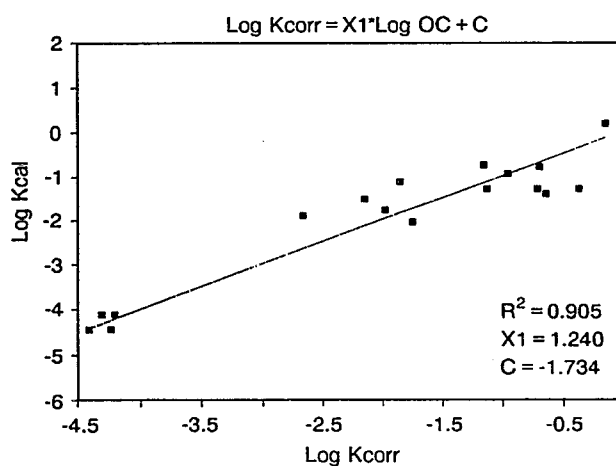


Figure 3. Correlation of abiotic reduction rate constants (k_{corr}) for hexachloroethane in anaerobic heterogeneous systems with fraction organic carbon (OC).

Table 3. Kinetic Data for the Neutral and Alkaline Hydrolysis of Chlorinated Methanes, Ethanes, Ethenes and Propanes in Distilled Water

Compound	k (neut,25) min-1	kb (pH7,25) min-1	kobs = k + kb min-1	t _{1/2} days
2,2 Dichloropropane	3.18E-04	0.00E + 00	3.18E-04	0.61
Pentachloroethane	4.93E-08	1.31E-04	1.31E-04	1.47
1,1,2,3,3-Pentachloropropane	4.71E-07	9.81E-05	9.85E-05	1.95
1,1,2,3-Tetrachloropropane	0.00E + 00	7.84E-05	7.84E-05	2.46
1,1,2,2-Tetrachloroethane	9.70E-09	3.02E-06	3.03E-06	63.5
1,1,1-Trichloroethane	1.24E-06	0.00E + 00	1.24E-06	155
1,3-Dichloropropane	5.87E-07	1.67E-12	5.87E-07	328
Carbon Tetrachloride	3.26E-08	0.00E + 00	3.26E-08	5905
1,1,1,2-Tetrachloroethane	2.60E-08	2.15E-09	2.82E-08	6826
1,1-Dichloroethane	2.15E-08	7.20E-14	2.15E-08	8953
1,2-Dichloroethane	1.83E-08	1.04E-11	1.83E-08	10519
1,1,2-Trichloroethane	5.19E-11	9.42E-09	9.47E-09	2.03E4
Chloroform	1.91E-10	5.22E-10	7.13E-10	2.71E5
Trichloroethene	0.00E + 00	1.07E-12	1.07E-12	1.80E8
1,1-Dichloroethene	0.00E + 00	1.09E-14	1.09E-14	1.7E10
Tetrachloroethene	0.00E + 00	1.37E-15	1.37E-15	1.4E11
Hexachloroethane	0.00E + 00	7.18E-16	7.18E-16	2.7E11
1,2-Dichloroethene	0.00E + 00	6.32E-17	6.32E-17	3.1E12

Conclusions

Redox reactivity is shown to vary 4 orders of magnitude for 16 halogenated hydrocarbons in sediment samples and hexachloroethane reactivity is shown to vary 4 orders of magnitude in going from aquifer samples to sediment samples. Hydrolytic reactivity of halogenated hydrocarbons is shown to vary 12 orders of magnitude at 25°C and pH 7. It is obvious that to accurately predict the fate of this class of compounds requires the appropriate rate constants and knowledge of eco-system parameters. For example, hexachloroethane does not react by hydrolysis pathways but is very reactive under reducing conditions. Also, comparison of the rate constants for the two reaction types provides an estimate of the contribution of each pathway and consequently the distribution of products.

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