



ENVIRONMENTAL RESEARCH BRIEF

Fate Constants for Some Chlorofluorocarbon Substitutes

Heinz P. Kollig and J. Jackson Ellington*

Abstract

The availability of fate constants for 16 aqueous cleaners and terpenes is addressed. These compounds are likely substitutes for chlorinated solvents and chlorofluorocarbons. Comparison of fate data available from EPA's Office of Toxic Substances, the database CHEMFATE, and additional fate data computed for this report shows how few experimental values are currently published. Almost all can be estimated, however, using computational techniques.

Introduction

This report addresses the availability of fate constants for 16 aqueous cleaners and terpenes. These compounds have been proposed as likely substitutes for chlorinated solvents and chlorofluorocarbons. Major users of these cleaners and terpenes are the electronics, computer, and metal finishing industries. The Environmental Research Laboratory-Athens (ERL-Athens) is currently planning research on chlorofluorocarbons and has obtained a draft report by EPA's Office of

Toxic Substances (OTS) entitled *Fate and Exposure Assessment of Aqueous and Terpene Cleaning Substitutes for Chlorofluorocarbons and Chlorinated Solvents*, authored by Sidney Abel, III, Exposure Assessment Branch, Exposure Evaluation Division, April 26, 1990, revised draft. It will be referred to herein as the OTS report. Although the OTS report contains a substantial number of fate constants, ERL-Athens, because of its expertise in measuring and evaluating published data of environmental fate constants, investigated the possibility of adding more fate constants to those in the OTS report.

The OTS report was based on 21 aqueous cleaners and 8 terpene compounds that the Office of Air and Radiation had identified as the most likely substitutes for chlorinated solvents and chlorofluorocarbons. The OTS report deliberates quite well on the fate and exposure of these compounds with respect to the environment, fully covering these areas. However, the limited number of fate constants prompted the preparation of the present document to a) enlarge the set of fate constants in the OTS report and b) provide more detailed information on some of the isomers involved.

We reviewed the database CHEMFATE (1), which stores experimental data extracted from primary or secondary publications and some computed values. We also computed values using the database QSAR (2), which, in addition to containing measured values from the literature, will compute chemical

*Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA 30613-7799.



properties, behavior, and toxicity using quantitative structure-activity relationships. The structure-activity models are totally automated and have been judged reliable by the Environmental Research Laboratory-Duluth's Structure-Activity Research Program. Alkalis, silicates, phosphates, and borates as well as an assessment of their environmental fate and exposure are not addressed.

Discussion

The OTS report lists two terpinene isomers, the alpha and the beta with CAS numbers of 99-86-5 and 99-85-4, respectively. Actually, 99-85-4 is the CAS number for gamma-terpinene, and beta-terpinene has the CAS number 99-84-3. The beta isomer (99-84-3) is prepared synthetically and will, therefore, not be addressed here, whereas the alpha (99-86-5) and the gamma (99-85-4) isomers occur naturally. Property values are quite similar for the three isomers.

Limonene (7705-14-8) and dipentene (138-86-3) are optically inactive isomers. Limonene is a mixture of (R)-(+)-limonene (5989-27-5) and (S)-(-)-limonene (5989-54-8). Names preferred by the Chemical Abstracts Service Registry:

7705-14-8 Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (\pm) -

138-86-3 Cyclohexene, 1-methyl-4-(1-methylethenyl)-

5989-27-5 Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (R)-

5989-54-8 Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (S)-

Table 1 shows the values for six properties cited in the OTS report for the 16 chemicals selected for this evaluation. Nine water soluble compounds are followed by seven terpenes.

Table 2 shows the values found in the database CHEMFATE (1) for the same constants and chemicals listed in Table 1. CHEMFATE calls dipentene (138-86-3) limonene.

Table 3 shows values calculated by the database QSAR (2) using computational techniques for the same properties and chemicals listed in Table 1.

When comparing data in the three tables, it becomes obvious that Table 3 contains the most data. It is not surprising that CHEMFATE contains the least data because it stores data for only a small number of chemicals. Some of the values in Table 1 are identical to those in Table 2, especially K_{ow} and Henry's law constant values. They may have been estimated with the same computational programs, yet both the OTS report and CHEMFATE give different sources for the computations. The programs could, however, still be the same.

The use of more and more environmental fate data in the prediction of processes relevant to the fate of chemicals in the environment is predicated by the need for a cleaner environment. The number of entries shown in Table 1 indicates that a substantial amount of data is available for this particular set of chemicals. However, in general, when compared to the number of chemicals for which data are required, relatively few of the needed constants have been published, and furthermore, many of the published constants are of questionable reliability or applicability because many early experiments were conducted using criteria that are very different from the stringent

criteria needed for predictions today. The inherent complexity and prohibitively large cost of the measurement process calls for reliable computational techniques or computer expert systems that use computational algorithms based on fundamental chemical structure theory that allows estimation of values for any parameter that depends upon the chemical's molecular structure. Present computational techniques are based on property-reactivity correlations for which relationships often hold only within limited classes of chemicals.

Most of the data in Table 3 were calculated by QSAR with techniques based on property-reactivity correlations. The error in these methods varies greatly—from 1 to 2% to an order of magnitude. The error can exceed an order of magnitude if the chemical falls outside the class for which the correlation was established. QSAR gives the average percent error for some parameters. The highest average error of 47% is given for some vapor pressure values. Single digit errors were observed for other parameters. However, one must remember that this is an average error obtained from a set of chemicals that the correlation was established for and will be different for any particular chemical in the set or even unknown for a chemical not included in the set. The true error can only be found when a measured value is available.

The organic-carbon-normalized partition coefficient (K_{oc}) and Henry's law constant are not included in QSAR for computation. Values for these parameters were calculated by hand using the values from the different parameters indicated in the footnotes of Table 3. Computational techniques in general have a problem computing values for salts and organometallics. Wherever there is a blank in Table 3, QSAR did not estimate a value. Predictions of Henry's law constants for triethanolamine, the EDTA tetrasodium salt, EDTA, and sodium gluconate resulted in very small values, due to the use of either a very small vapor pressure or a very high water solubility value. Although these values are subject to large errors, it is certainly safe to say that these chemicals will not readily volatilize from water. A computed high water solubility value indicates that the compound is infinitely soluble or miscible with water in all proportions. The error involved in calculating Henry's law constant may increase with increasing water solubility. Mackay and Shiu (7) point out that the calculation of Henry's law constant using the vapor pressure and the water solubility is valid only for solutes that have a water solubility of less than a few percent. This certainly means that Henry's law constants for ethanalamine, diethanolamine, triethanolamine, the EDTA tetrasodium salt, sodium gluconate, and EDTA can incorporate a large error with diethylene glycol *n*-butyl ether being a borderline candidate having a water solubility of 7.33%. All other compounds listed have water solubilities of much less than 1%. Henry's law constant values were calculated by dividing the water solubility value into the vapor pressure value (7-8).

Many of the data in Tables 1 and 3 agree fairly well, and it appears that some of the data ($\log K_{ow}$) were estimated using the same computational program. The OTS report gives as the origin "values are estimated," and, at one point, the report states that AUTOCHEM was used to compute values. AUTOCHEM is a computational program incorporated in the Graphical Exposure Modeling System (GEMS) located on the VAX Cluster in the National Computer Center in Research Triangle Park, North Carolina, under management of OTS. Generally, the OTS report does not provide specific references. The differences between the data in Tables 1 and 3 may be due

Table 1. Values Cited in OTS Report

	K_{ow} log	pK_a	K_{oc}	Vapor Pressure mm Hg	Water Solubility mg/L	Henry's Law Constant atm-m ³ /mole
Diethylene glycol n-butyl ether 112-34-5	1.0		83	0.02	miscible	
Ethanolamine 141-43-5	-1.31			0.40	miscible	4E-8
Diethanolamine 111-42-2	-1.43			<0.01	soluble	3.87E-11
Triethanolamine 102-71-6	-1.50			<0.01	miscible	3.38E-19
Sodium xylene sulfonate 1300-72-7	3.15				3.15E3	
EDTA tetrasodium salt 64-02-8					1.30E6	
Sodium gluconate 527-07-1					4.30E5	
Dodecanedioic acid 693-23-2	3.07		724.4	1.157E-4	2.201E4	1.594E-8
EDTA 60-00-4					soluble	
Dipentene 138-86-3	4.232		1.05E4	1.21	8.97	2.42E-2
alpha-Pinene 80-56-8	3.972		5.78E3	7.98	21.50	6.56E-2
beta-Pinene 127-91-3	3.972		5.78E3	7.98	21.50	6.56E-2
Anethole 104-46-1	3.314		1.27E3	0.287	136.54	4.10E-2
alpha-Terpinene 99-86-5	4.412		1.05E4	1.21	5.63	3.85E-2
gamma-Terpinene 99-85-4	4.232		1.05E4	1.21	8.97	2.42E-2
Terpinolene 586-62-9	4.232		1.05E4	1.21	8.97	2.42E-2

to the fact that the computational programs in AUTOCHEM and QSAR were written by different people, and perhaps even different classes of chemicals were used to generate the correlations. However, this does not explain the difference of about two orders of magnitude between the values for the Henry's law constant for anethole. Based on the greater water solubility and smaller vapor pressure, compared to the other terpenes, one would expect the Henry's law constant to be smaller than those for the other terpenes. This observation supports the value listed in Table 3. No reason can be given for the large difference in the water solubility values for dodecanedioic acid or the Henry's law constants for diethanolamine and triethanolamine. The true error associated with an estimated value can only be obtained by comparing it with a reliably measured value that was determined under environmentally realistic conditions.

Partitioning between water and natural soils, sediments, and aquifer materials is an important process affecting transformation rates, toxicity, and the ultimate disposition of organic chemicals in the environment. Research focusing on the partitioning of neutral organic compounds has shown that adsorption of these compounds is usually controlled by hydrophobic interactions. Generally, octanol-water partition coefficients (K_{ow}) have been used extensively for estimating the partitioning of organic compounds to sedimentary materials. This is a straightforward process for neutral organic compounds. Estimating the parti-

tioning of ionizable organic compounds, however, must take into account dissociation.

Ethanolamine, diethanolamine, triethanolamine, sodium xylene sulfonate, dodecanedioic acid, and EDTA are ionizable compounds for which K_{ow} 's are listed in Tables 1, 2, and 3. It is not clear whether these values are for the neutral or the ionized forms. If a reported K_{ow} value is for the neutral form and the compound exists predominantly as an ion, the calculated sorption coefficient can be orders of magnitude different from the real value. Considering the dissociation constant, pK_a , in calculating the sorption coefficient will avoid this inaccuracy. For example, diethanolamine has an estimated (QSAR) pK_a value of 8.39. The compound will exist in its neutral form at pH 10.39 and will be predominantly ionized at pH 6.39. The water solubility will change within this pH range and affect the K_{ow} value and sorption coefficient. Jafvert et al. (5) discuss this problem in more detail. It should be pointed out that the log K_{ow} value of 3.15 for sodium xylene sulfonate in the OTS report appears suspiciously high. The value might actually be -3.15 but is meaningless unless the pH is also given.

The fate of the terpenes in the atmosphere will be largely controlled by their reaction with hydroxyl radicals. Using the appropriate rate constants and an average tropospheric hydroxyl radical concentration of 5×10^5 molecules cm^{-3} reported by Atkinson (6), we calculated the half-lives shown in Table 4

for three of the terpenes. The calculated half-lives are a factor of 1.4 to 14 greater than the corresponding values in the OTS report. Sources of the degradation data were not given in the OTS report. Hydrolysis of these compounds in water is expected to be negligible.

References

1. CHEMFATE is a database storing environmental data managed by the Syracuse Research Corporation (Merrill Lane, Syracuse, New York 13210) for OTS. P. H. Howard, G. W. Sage, and A. Lamacchia. 1982. The Development of an Environmental Fate Data Base. *J. Chem. Inf. Comput. Sci.* 22: 38-44.
2. Quantitative Structure-Activity Relationships (QSAR) is an interactive chemical database and hazard assessment system designed to provide basic information for the evaluation of the fate and effects of chemicals in the environment. QSAR was developed jointly by the U.S. EPA Environmental Research Laboratory, Duluth, Minnesota, the Montana State University Center for Data Systems and Analysis, and the Pomona College Medicinal Chemistry Project.
3. SPARC Performs Automated Reasoning in Chemistry (SPARC) is a prototype computer expert system being developed by scientists at ERL-Athens and the University of Georgia. S. W. Karickhoff, L. A. Carreira, C. Melton, V. K. McDaniel, A. N. Vellino, and D. E. Nute. 1989. Computer Prediction of Chemical Reactivity--The Ultimate SAR. U.S. Environmental Protection Agency, Athens, GA. EPA/600/M-89/017.
4. W. J. Lyman, W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. Environmental Behavior of Organic Compounds. McGraw-Hill, New York, NY.
5. C. T. Jafvert, J. C. Westall, E. Grieder, and R. P. Schwarzenbach. 1990. Distribution of hydrophobic ionogenic organic compounds between octanol and water: organic acids. *Environ. Sci. and Technol.* 24(12): 1795-1803.
6. R. Atkinson. 1986. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. *Chem. Rev.* 86: 69-201.
7. D. Mackay and W. Y. Shiu. 1981. A critical review of Henry's law constants for chemicals of environmental interest. *J. Phys. Chem. Ref. Data* 10(4): 1175-1199.
8. D. Mackay, W. Y. Shiu, and R. P. Sutherland. 1979. Determination of air-water Henry's law constant for hydrophobic pollutants. *Environ. Sci. Technol.* 13(3): 333-337.

Table 2. Values Cited in Database CHEMFATE

	Kow log	pK _a	K _{oc}	Vapor Pressure mm Hg	Water Solubility mg/L	Henry's Law Constant atm-m ³ /mole
<i>Diethylene glycol n-butyl ether</i>						
112-34-5						
<i>Ethanolamine</i>	-1.31	9.4994		0.26	<i>miscible</i>	4E-8
141-43-5						
<i>Diethanolamine</i>	-1.43	8.96	4	2.8E-4	<i>miscible</i>	3.87E-11
111-42-2						
<i>Triethanolamine</i>	-1.59	7.92		3.59E-6	<i>miscible</i>	3.38E-19
102-71-6						
<i>Sodium xylene sulfonate</i>						
1300-72-7						
<i>EDTA tetrasodium salt</i>				24	1.03E6	
64-02-8						
<i>Sodium gluconate</i>						
527-07-1						
<i>Dodecanedioic acid</i>						
693-23-2						
<i>EDTA</i>		0.26				
60-00-4						
<i>Dipentene</i>						
138-86-3						
<i>alpha-Pinene</i>				5		
80-56-8						
<i>beta-Pinene</i>						
127-91-3						
<i>Anethole</i>						
104-46-1						
<i>alpha-Terpinene</i>						
99-86-5						
<i>gamma-Terpinene</i>						
99-85-4						
<i>Terpinolene</i>						
586-62-9						

Table 3. Estimated Values in Database QSAR and Other Calculated Values as Indicated

	Kow log	pK _a	K _{oc} ^e	Vapor Pressure mm Hg	Water Solubility mg/L	Henry's Law Constant ^f atm-m ³ /mole
Diethylene glycol n-butyl ether 112-34-5	0.905	17.0 ^a	9.3	0.170	7.33E4	4.9E-7
Ethanolamine 141-43-5	-1.30	9.67	0.6	16.9	9.85E6	1.4E-7 ^h
Diethanolamine 111-42-2	-1.46	8.39	0.4	0.577	2.49E7	3.2E-9 ^h
Triethanolamine 102-71-6	-1.75	6.37	0.2	1.51E-3	8.03E7	3.7E-12 ^h
Sodium xylene sulfonate 1300-72-7		^b	52 ^d	9.01E-4		7.8E-8 ^g
EDTA tetrasodium salt 64-02-8		2.39	2 ^d	9.59E-14		5E-20 ^h
Sodium gluconate 527-07-1		13.1	3 ^d	4.13E-10		3E-16 ^h
Dodecanedioic acid 693-23-2	3.07	4.44	590	1.16E-4	37.9	9.3E-7
EDTA 60-00-4	-5.01	1.39	1E-3	1.82E-8	2.58E12	3E-21 ^h
Dipentene 138-86-3	4.23	^c	1.76E3	1.03	5.24	3.5E-2
alpha-Pinene 80-56-8	4.12	^c	1.14E3	2.31	11.4	3.6E-2
beta-Pinene 127-91-3	4.12	^c	1.48E3	1.50	7.15	3.8E-2
Anethole 104-46-1	3.31	^c	332	0.131	1.08E2	2.4E-4
alpha-Terpinene 99-86-5	4.41	^c	2.33E3	1.25	3.14	7.1E-2
gamma-Terpinene 99-85-4	4.23	^c	1.76E3	0.811	5.24	2.8E-2
Terpinolene 586-62-9	4.23	^c	1.76E3	0.702	5.24	2.4E-2

^aComputed value from SPARC (3).

^bComputational techniques will not estimate a value. The salt is ionized at environmental pHs.

^cComputational techniques will not estimate a value. The compound will not ionize at environmental pHs. The pK_a is estimated to be very high.

^dValue was estimated using equation 4-5 in Lyman et al. (4) and the water solubility from the OTS report.

^eValues were estimated using equation 4-5 in Lyman et al. (4) and the water solubilities from QSAR (2).

^fValues were estimated using the vapor pressure and the water solubility values from QSAR (2).

^gValue was estimated using the vapor pressure from QSAR (2) and the water solubility from the OTS report.

^hThe high water solubility of more than a few percent may incorporate a large error in the estimation of the Henry's law constant.

Table 4. Atmospheric Degradation

	<i>Atmosphere Half-Life OTS Report Time (min.)</i>	<i>Atmosphere Half-Life Calculated from Atkinson Data Time (min.)</i>
<i>Dipentene 138-86-3</i>	28	384
<i>alpha-Pinene 80-56-8</i>	31	
<i>beta-Pinene 127-91-3</i>	216	297
<i>Anethole 104-46-1</i>	55	
<i>alpha-Terpinene 99-86-5</i>	16	64
<i>gamma-Terpinene 99-85-4</i>		
<i>Terpinolene 586-62-9</i>	8	