United States
Environmental Protection
Agency

Environmental Research
Laboratory
Athens GA 30613

Research and Development

EPA/600/S3-88/028 Sept. 1988

EPA

Project Summary

Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal: Volume 3. Data on 70 Chemicals

J. Jackson Ellington, Frank E. Stancil, Jr., William D. Payne, and Cheryl D. Trusty

To provide input data for a mathematical model to estimate potential ground-water contamination from chemicals in land disposal sites, hydrolysis rate constants were measured for 70 regulated chemicals under carefully controlled conditions. Hydrolysis rates were measured under sterile conditions at precisely controlled temperatures and at three hydrogen-ion concentrations (ph 3, 7, and 11). Conditions were adjusted to provide sufficiently precise rate constants to meet modeling requirements, as determined through model sensitivity tests. In addition to precise control of temperature and pH, precautions were taken to minimize impact of adventitious processes. Chemical concentrations as a function of incubation time in the constant temperature bath were measured by gas chromatography, liquid chromatography, or ion exchange chromatography. Identities and purities of the chemicals were determined by mass spectrometry supplemented, and in some cases, by infrared spectrometry.

Four chemicals (DL-*trans*-4-chlorostilbene oxide, benzyl chloride, 2, 4-dichlorophenoxyacetic acid methyl ester, and lindane) were used as standard reference compounds (SRCs) to ensure reproducibility of analytical operations and control of parameters that affect hydrolysis rates of chemicals in an aqueous environment. The methyl ester and lindane were used as SRCs in the pH ranges of 8 to 9.5 and 9.5 to 11, respectively. Benzyl chloride and the stilbene oxide were used in conjunction with neutral and acidic hydrolysis rate determinations, respectively. Determinations of the hydrolysis rates of the SRCs repeated at varying temperatures and pHs over a 2-year period yielded coefficients of variation of less than 12% in the measurements.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Hazardous and Solid Waste Amendments of 1984 to PL 98-616 (RCRA) stipulate that land disposal of "hazardous wastes" is prohibited unless the EPA Administrator determines that prohibition of some wastes is not required to protect human health and the environment because those particular wastes are not likely to reach unacceptable levels in groundwater as a result of land disposal. The amendments define hazardous waste

as any of 362 specific compounds (either part of or inclusive of Appendix VIII compounds). In compiling this list, major considerations were the toxicity and quantity of the waste material generated annually. In implementing the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA), EPA's Office of Solid Waste (OSW) will apply a decision rule based on a mathematical model of chemicals under consideration that considers horizontal underground movement of a chemical in a contaminated aquifer offsite to a withdrawal point based on advection, dispersion, sorption, and chemical hydrolysis. Application of the model requires as input the second- or first-order hydrolysis rate constants for those chemicals containing hydrolyzable functional groups.

It is necessary to acquire hydrolysis rate constants for each of the 362 chemicals except for solvents ("fast track" in the list), which will be treated as non-degrading, non-sorbing constituents and chemicals already banned by the State of California (listed as "California"). These two groups comprise 21 and 44 chemicals, respectively. The remainder of the 362 chemicals were separated for regulation into three factions by EPA's Office of Solid Waste: 81 in the "first third," 121 in the "second third," and 95 in the "third third." This report provides first- and second-order hydrolysis rate constants for all those organic compounds in the first and second "thirds" plus an additional 12 chemicals of interest (Table 1) for which satisfactory values were not developed in an earlier evaluation process. It also describes the laboratory experiments conducted to measure hydrolysis rate constants.

The Environmental Protection Agency has proposed that manufacturers and processors of the remaining 31 "third third" chemicals be required, under Section 4 of the Toxic Substances Control Act (TSCA), to perform testing for chemical fate including determination of hydrolysis rate constants.

Hydrolysis Measurements

A typical hydrolysis experiment consisted of preparing a spiking solution of the compound of interest, preparing buffer solutions, transferring spiked buffer to individual "rate point tubes" (15-ml sealed ampules), then monitoring disappearance over time by analyzing individual tubes and determining the amount of compound remaining.

Spiking solutions were prepared by dissolving the compound in acetonitrile, methanol, or water. The concentration was such that 0.1 ml diluted to 100 ml with buffer gave a test compound concentration that was $1x10^{-5}M$ or was 50% of the water solubility or less.

Initial screening hydrolysis runs were performed at three pH levels (3, 7, and 11). Buffer pH was measured at the temperature of the hydrolysis run. These initial hydrolysis runs were used to set pH and temperature conditions for subsequent rate constant measurements. The measurements of rate constants were normally performed in triplicate; however, some compounds required more replicates and some less.

Standard Reference Compounds (SRCs)

Chemical standards of known concentration have long been used for assuring reliability of quantitative chemical analyses, calibrating instruments, and measuring recoveries of analytes from various matrices. In a manner analogous to using chemicals of known concentration as standards for concentration measurement, chemicals whose hydrolysis rate constants have been measured with established precision by one experimenter or group can be used as SRCs by other experimenters in establishing and maintaining quality control in rate measurements.

Four compounds were used as SRCs for this study, one each for acid and neutral hydrolysis, and two for base hydrolysis. Reproduction of the hydrolysis rate constants of the SRCs at the established concentrations, pHs, and temperatures ensured that the experimental conditions were reproducible and helped evaluate the accuracy and precision of measurements for the other compounds.

Frequency Distribution of Hydrolysis Rate Constants

The frequency distribution of the measured/extrapolated half-lives for 127 of the 362 OSW compounds is represented in Figure 1. The actual hydrolysis rate constants for these compounds can be found in Tables 1 and 2 and reference 1 of the complete text. The 127 chemicals covered a wide range of chemical classes and chemical reactivity within each class. Thus, the distribution in Figure 1 (60% of half-lives < 3 years) might be considered as being representative of organic compounds in general.

Table 1. *Hydrolysis Rate Constant and Half-Lives at 25°C for Selected Compounds*

		Rate Constants			
CAS Number	*Compound*	*Acid* $M^{-1}hr^{-1}$	*Neutral* hr^{-1}	*Base* $M^{-1}hr^{-1}$	*Calculated Half-life at pH 7, 25°C*
108-90-7	Chlorobenzene[a]			<0.9	>900 yr
628-89-7	2-(2-Chloroethoxy) ethanol		$(3.2 \pm 0.1) \times 10^{-5}$		3 yr
107-07-3	2-Chloroethanol (41, 42)		4.5×10^{-6}	36.0	9.9 yr
594-20-7	2,2-Dichloropropane		$(4.7 \pm 0.2) \times 10^{-2}$		15 hr
95-50-1	1,2-Dichlorobenzene[a]			<0.9	>900 yr
541-73-1	1,3-Dichlorobenzene[a]			<0.9	>900 yr
106-46-7	1,4-Dichlorobenzene[a]			<0.9	>900 yr
24009-05-0	1-Hydroxychlordene[b]			$<1 \times 10^{-4}$	200,000 yr
608-93-5	Pentachlorobenzene[a]			<0.9	>900 yr
319-94-8	Pentachlorocyclohexene (gamma PCCH)		3.0×10^{-5}	74±3	2.1 yr
95-94-3	1,2,4,5-Tetrachlorobenzene[a]			<0.9	>900 yr
88-06-2	2,4,6-Trichlorophenol[c]		$(2.3 \pm 3.5) \times 10^{-7}$		>40 yr

[a] = Based on assumed base mediated 1% disappearance after 16d at 85°C and pH 9.70 (pH 11.26 at room temperature).
[b] = Based on assumed base mediated 5% disappearance after 48d at 85°C and pH 9.51 (pH 11.04 at room temperature).
[c] = Based on assumed 5% disappearance after 330 hr at 85°C.

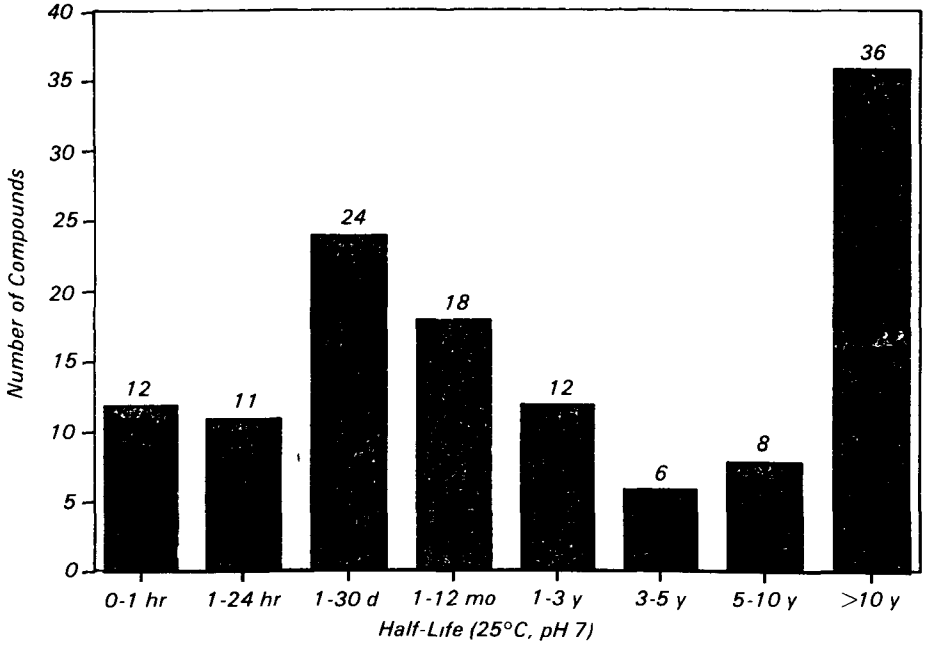


Figure 1. *Half-lives of OSW compounds.*

*The EPA authors **J. Jackson Ellington** (also the EPA Project Officer, see below), and **Frank E. Stancil, Jr.**, are with the Environmental Research Laboratory, Athens, GA 30613; William D. Payne is with Technology Applications, Inc., Athens GA 30613; and Cheryl Trusty is with the University of Georgia, Athens, GA 30613.*

The complete report, entitled "Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal: Volume 3. Data on 70 Chemicals," (Order No. PB 88-234 042/AS; Cost: $12.95, subject to change) will be available only from:

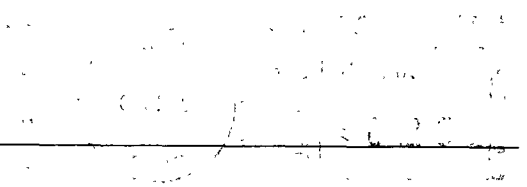
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Environmental Research Laboratory
U.S. Environmental Protection Agency
College Station Road
Athens, GA 30613

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268



Official Business
Penalty for Private Use $300

EPA/600/S3-88/028