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Project Summary

Hydrolysis Rate Constants for Enhancing Property-Reactivity Relationships

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Rate constants for hydrolysis in water of 10 classes of organic compounds are examined with the objective of establishing new or expanding existing property-reactivity correlations. These relationships then can be used to predict the environmental hydrolysis of chemicals that have similar molecular structure. The compound classes covered by this report include aliphatic and aromatic carboxylate esters, alkyl and aromatic halides, amides, carbamates, epoxides, nitriles, phosphate esters, alkylating agents, halogenated ethers, and oxidized sulfur compounds. Three predictive techniques (the first based on empirical correlations with derived constants, the second using infrared spectra, and the third relying on fundamental calculations requiring only chemical structure) were used to predict and compare hydrolysis rate constants for simple alkyl esters. The predicted rate constants were generally within a factor of two of each other and the laboratory-determined values.

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 Ordering information at back).

Introduction

Each year more than 1000 new chemicals are introduced into commerce and thus into the environment worldwide. Regulators and scientists need reliable data on the persistence, mobility, toxicity and possible risk to humans or environmental ecosystems associated with these new chemicals as well as the more than 65,000 compounds currently in use. The possible persistence of these chemicals and accompanying risk of exposure to humans and other species of concern has resulted in a demand on regulators to provide effective techniques for quantifying chemical mobility and fate.

As part of the effort to evaluate chemical constituents of wastes under consideration for land disposal, EPA's Office of Solid Waste (OSW) uses a relatively simple model to estimate potential groundwater contamination at specified withdrawal points in proximity to a landfill. This model calculates horizontal chemical movement in the aquifer based on advection, dispersion, sorption and transformation. Hydrolysis is the only transformation process specifically considered at this time.

To apply this model to chemicals of interest to OSW, hydrolysis rate constants for 98 chemicals were previously obtained either from literature sources or laboratory determinations using protocols developed at EPA's Environmental Research Laboratory-Athens. The objective of this report was to examine the rate data and organize them by compound class, with the goal of either enhancing existing property-reactivity correlations (PRCs) or developing new PRCs if sufficient data have been generated for a particular class of chemicals. These correlations then can be applied to new chemicals in wastes being considered by OSW for regulation.

Property Reactivity Correlations and Prediction Programs

The use of PRCs for predicting rate and equilibrium constants for organic reactions is well established. Pharmaceutical and pesticide manufacturers routinely use historical data on existing compounds in designing new products to either increase or decrease potency and/or persistence while decreasing or eliminating unwanted side effects. Any chemical released to the environment is subjected to a wide variety of conditions that can transform it to a different product. PRCs offer a means for estimating kinetic constants for important transformation processes such as hydrolysis, photolysis, and redox reactions.

Two approaches for establishing PRCs that are less dependent on measured kinetic data are being developed at ERL-Athens. One approach involves developing a method for predicting environmental fate constants of chemicals based on their infrared spectra. Even though many reactivity parameters may be amenable to this approach, to date, only alkaline hydrolysis of organic esters has been considered in depth. Another approach involves developing a prototype computer program SPARC (SPARC Performs Automated Reasoning in Chemistry) that uses computational alogrithms based on fundamental chemical structure theory. This allows estimation of values for a broad variety of reactivity parameters both kinetic and equilibrium--ultraviolet light absorption, dissociation constants, and various reaction rate constants, or any parameters that depend on molecular structure. The agreement of the alkaline hydrolysis rate constants for carboxylate esters calculated by all of the above methods as well as determined in the laboratory is discussed.

Hydrolysis Rate Constant Data

For many chemicals, hydrolysis can be the dominant pathway for degradation in the environment. Functional groups that are potentially susceptible to hydrolysis are:

1. Aliphatic and aromatic carboxylate esters
2. Alkyl and aromatic halides
3. Amides
4. Carbamates
5. Epoxides
6. Nitriles
7. Phosphate esters
8. Alkylating agents
9. Halogenated ethers
10. Oxidized sulfur compounds
11. Miscellaneous Compounds

The report summarizes hydrolysis rate constant data and half-lives for chemicals in the above classes at pH 7 in aqueous solution at 25°C.

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The complete report, entitled "Hydrolysis Rate Constants for Enhancing Property-Reactivity Relationships." (Order No. PB 89-220 479/AS; Cost: $15.95, subject to change) will be available only from:

National Technical Information Service
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