Fragment Model to Predict the Rate of Hydrolysis for Organic Compounds

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Hydrolysis is one of the key degradation processes in the environment. It is considered to be important under environmental conditions for a number of classes of organic compounds as carboxylic acid esters and amides, anhydrides, epoxides, isocyanates and isothiocyanates, carbamates, phosphate and thiophosphate esters, alkoxysilanes and halosilanes, and halogenated hydrocarbons. In contrast to its importance, the number of available experimental data is rather limited. Computer models are a promising alternative in order to overcome the respective data gaps.

Actually, the overall hydrolysis is a combination of the reaction with neutral water molecules and acid (H^+) and base (OH^-) catalysed degradation reactions. Depending on the chemical, these three processes will take place to a different degree. Since the acid and base catalysed degradation depends on the pH, the role of the individual processes and thus also the overall rate depend on the pH of the aquatic environment.

A feasible approach to model the rate of hydrolysis k_{hyd} is to express this rather complex system of reactions in terms of simple pseudo-first-order kinetics. The reaction with neutral water is directly addressed by a pseudo-first-order rate that is a constant for a given chemical and temperature and independent of the pH. Acid and base catalysed degradation rates are primarily derived as pH-independent second-order rate constant and then transformed into pseudo-first-order rates by application to a fixed pH and thus to given H^+ or OH^- concentrations. For the fixed pH the overall rate then can be calculated from the combination of the individual rates.

In the presented study, three independent fragment models are being developed for the individual pH-independent rate constants, and the overall rate constants is obtained by putting them together for a particular pH then. The model is implemented will be publically available after its finalisation in the OSIRIS edition of the software system ChemProp (UFZ Department of Ecological Chemistry 2014. ChemProp 6.2 http://www.ufz.de/index.php?en=6738).

The training set consists of about 1900 different compounds of all considerably hydrolysing compound classes. For ca. 500 substances of them, rates of the neutral reaction are available, and for the acid and base catalysed reaction there are data for 600 and 1120 chemicals, respectively. The models comprise ca. 60, 70, and 110 structural fragments for the estimation of the neutral, acidic, and basic rate. The overall performance with respect to the overall rate is ca. 0.9 with respect to the squared correlation coefficient of regression. The reliability of the model and the comparison to existing approaches will be discussed.