**Abiotic hydrolysis – Fully predictable?**

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Next to photolysis, redox reactions and microbial degradation, hydrolysis is a very important transformation reaction which chemicals encounter in the environment. The main reasons is that water as a reactant is ubiquitous in all compartments. Furthermore hydrolysis often serves as an initial reaction enabling consecutive reactions to take place.

In the 1960s and 1970s much research has been done to elucidate reaction mechanisms of the most prominent hydrolysable functional groups, e. g. carboxylic acid esters and amides, halogenated hydrocarbons, organic phosphates or carbamates. Based upon those experimental data LFER equations (*linear free energy realationship*) and QSAR models (*quantitative structure-activity relationship*) for predicting rate constants of hydrolyses have been developed. Although they have not experienced much enhancement since the 1980s these models are still used today (e.g. EPISuite’s HYDROWIN).

Under the aspect of REACH legislation in Europe such prediction models gain more importance again to decrease experimental effort, to fill data gaps and to save resources. Astonishingly, it turns out that, despite of all the past efforts, hydrolysis models show significant gaps. Two of the major weaknesses of existing models are the inadequate coverage (i) of the pH range and (ii) of the classes of chemicals.

The hydrolysis rate constants of nine carboxylic acid esters have been experimentally determined at three different pH-values (3, 7 and 11). Generally basic hydrolysis (reaction with OH-) is assumed to dominate the hydrolysis of carboxylic acid esters even at lower pHs. Models like HYDROWIN therefore calculate the half life time only based on that reaction type. But our results showed that all of the investigated esters also exhibit neutral hydrolysis (reaction with H2O) and four of them even acid-catalyzed hydrolysis (H+-promoted reaction with H2O). As a consequence the discrepancy between experimental and modeled results increased to four orders of magnitude at pH 3. The experimental data was used to validate an improved model for calculation of hydrolysis rate constants for carboxylic acid esters, which also includes neutral and acid-catalyzed hydrolysis now.

Some important classes of chemicals are not at all covered in existing models, for example thiocarbamates. The thiocarbamate group is a functional group of pesticides and pharmaceuticals. Hydrolysis experiments at different pHs (pH 3 to 10) were carried out for fifteen compounds with different substituents to investigate the influences on the hydrolysis rate constants. The results show that hydrolysis is mainly dominated by basic hydrolysis. However, the mechanism is not fully clear yet since our data suggests an overlapping of hydrolysis and an acid-base equilibrium. With these data, an existing model will be extended to enable the prediction of hydrolytic half lifes of thiocarbamates.

The examples clearly depict that hydrolysis, although deeply investigated in the past, still keeps open questions, which need to be addressed and solved if prediction models shall reach the quality to seriously substitute laboratory experiments.