Geophysical Research Abstracts,
Vol. 10, EGU2008-A-07973, 2008
SRef-ID: 1607-7962/gra/EGU2008-A-07973
EGU General Assembly 2008

pH-dependency of Carbon and Nitrogen Kinetic Isotope Fractionation Associated with Hydrolysis of the Phenylurea Herbicide Isoproturon

H. Penning, M. Elsner

Institute of Groundwater Ecology, Helmholtz Zentrum München – German Research Center for Environmental Health, Neuherberg, Germany (holger.penning@helmholtz-muenchen.de / Fax: +49 (0)89 31873361 / Phone: +49 (0)89 31872916)

Compound specific isotope analysis (CSIA) is uniquely suited to provide valuable information on the fate of organic compounds in the environment. The method has been applied in biogeochemistry and environmental science to trace their (bio)chemical degradation reactions through the isotope enrichment that is caused by kinetic isotope effects (1). Such approaches do not rely on analysis of metabolites, as transformation reactions can be identified by the strength and pattern of isotope enrichment in the parent compound itself (2).

Here we apply CSIA to the herbicide isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea), which is extensively used and has been detected in surface and groundwater above the regulatory limit. Hydrolysis is one of three known initial degradation reactions, finally forming 4-isopropylaniline, dimethylamine, and CO_2. However, these metabolites are not readily detected in the environment and, in particular, 4-isopropylaniline is hypothesized to form covalent bonds to organic matter. The hydrolysis pathway as a natural degradation route may therefore have been overlooked so far. Consequently, we aimed at quantifying isotope effects of the hydrolysis of isoproturon, in order to lay the basis for later assessment of the importance of abiotic hydrolysis in the environment.

The hydrolysis of isoproturon was investigated at 60˚C and at pH 3, 4, 6, 7, 8, 10, and 12. Isotope analysis was accomplished by an innovative analytical method, where iso-

proturon was quantitatively fragmented into 4-isopropylphenylisocyanate (ISO) and dimethylamine (DMA), so that isotopic enrichment factors could be determined in both fragments separately (3). Isotopic fractionation of both nitrogen and carbon was lowest at pH 7 or 8 with $\varepsilon_{ISO-carbon}$ = -3.0 per mil, $\varepsilon_{ISO-nitrogen}$ = -8.4 per mil, $\varepsilon_{DMA-carbon}$ = -1.2 per mil, and $\varepsilon_{DMA-nitrogen}$ = -7.7 per mil. Fractionation increased under alkaline and acidic conditions showing most negative values at pH 12 with $\varepsilon_{ISO-carbon}$ = -4.5 per mil, $\varepsilon_{ISO-nitrogen}$ = -10.7 per mil, $\varepsilon_{DMA-carbon}$ = -2.5 per mil, and $\varepsilon_{DMA-nitrogen}$ = -19.3 per mil. In the case of carbon, enrichment factors were consistently larger in the isocyanate fragment than in the DMA fragment, despite the fact that a larger number of carbon atoms (n=10) "diluted" position-specific fractionation. This reflects the fact that a kinetic isotope effect (KIE) is primarily expected at the urea carbonyl carbon, which becomes the central atom of the isocyanate group after fragmentation. Correcting for the number of non-reacting carbon centers, KIE_C values of 1.03 (pH 7) to 1.05 (pH 12) can be estimated at this position. In contrast, fractionation in the DMA fragment (n=2) reflects "undiluted" secondary isotope effects (KIE_C = 1.001 to 1.002) at the two methyl centers of the dimethylamine group. In the case of nitrogen, there is only one N center in each fragment so that enrichment factors are directly representative of the respective position-specific KIEs.

Overall primary nitrogen isotope effects (KIE_N = 1.008 to 1.020) indicate that pronounced changes of bonding occurred at both nitrogen atoms of the urea group - either in a concerted reaction involving both centers, or in competing reactions where either dimethylamine or 4-isopropylaniline was initially liberated. Both scenarios are possible, since the hydrolysis might either happen by a general acid-/base-catalyzed hydrolysis involving a tetrahedral intermediate; or through a stepwise mechanism, in which a zwitterionic intermediate is formed prior to elimination of dimethylamine. Kinetic and isotope data support the stepwise mechanism, which also explains the pH-dependency of observed KIEs. With this detailed isotopic understanding of the reaction it is now possible to confirm hydrolysis of isoproturon in incubation studies and later apply CSIA in the field to assess the importance of this degradation pathway of the herbicide isoproturon.

(1) Schmidt, T. C.; Zwank, L.; Elsner, M.; Berg, M.; Meckenstock, R. U.; Haderlein, S. B. *Analytical and Bioanalytical Chemistry* **2004**, 378, 283-300.

(2) Elsner, M.; Zwank, L.; Hunkeler, D.; Schwarzenbach, R. P. *Environmental Science & Technology* **2005**, 39, 6896-6916.

(3) Penning, H.; Elsner, M. *Anal. Chem.* **2007**, 79, 8399-8405.