QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS ON DIRECT PHOTOLYSIS OF SUBSTITUTED AROMATIC HALIDES

Lina Gao[1], Jingwen Chen[1,2], K.-W. Schramm[2], Xie Quan[1], A. Kettrup[2,3]

[1]School of Environmental Science and Technology, Dalian University of Technology, Zhongshan Road 158-129, Dalian 116012, P. R. China
[2]Institute of Ecological Chemistry, GSF-National Research Center for Environment and Health, D-85764, Neuherberg, Germany
[3]Lehrstuhl für Ökologische Chemie und Umweltanalytik, Technische Universität München, 85350 Freising-Weihenstephan, Germany

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and halogenated benzenes are widespread persistent environmental contaminants with high toxicity[1]. Direct photolysis may be an important transformation route for these compounds[2]. It was found that most environmental photochemical reactions follow pseudo-first-order kinetics[3]. Photolysis rate constants (k) and quantum yields (Y) are two key parameters characterizing photochemical reactions of organic pollutants[3]. Therefore they are indispensable for the fate assessment of organic pollutants. However, because of large expenditures in experimental determination, k and Y data are scarce for most halogenzted organic pollutants. Quantitative structure-property relationships (QSPR), which correlate and predict transport and transformation process data of organic pollutants from their structural descriptors, is a feasible way to study photolysis mechanism and generate predicted photolysis process data.

Methods and Materials

Quantum yields (Y) for selected halogenated benzenes were determined in water at 250-350 nm from RUL 3000 Å lamps[4]. Quantum yields for selected PCDD/Fs dissolved in water-acetonitrile at 313 nm or 300 nm from the Rayonet RPR 3000 Å lamp were determined by Choudhry and Webster[5], Dulin et al.[6], Kim and O'keefe[7]. The direct photolysis rate constants (k_s) of 10 PCDD/Fs in cuticular wax of *Prunus laurocerasus* exposed to sunlight were determined by Schuler et al[8]. It was based on these experimental values QSPR models were developed.

Molecular structural descriptors were calculated by using the PM3 Hamiltonian contained in the MOPAC (Ver. 6.0) program package. MOPAC was run with the following keywords: PM3, ESP, POLAR, DIPOLE, ENPART, PRECISE, BONDS, NOINTER. According to proposed mechanisms of photolysis for different groups of compounds, various quantum chemical descriptors were adopted in the model development.

Partial least squares (PLS) analysis[9] was used in developing models. Simca (Version 6.0) software was used to perform the PLS analysis. The criterion used to determine the model dimensionality, number of significant PLS analysis, is cross validation. With cross validation, when the fraction of the total variation of the dependent variables that can be predicted by a component (Q^2) for the whole data set is larger than a significance limit (0.097), the tested PLS component is considered significant. When the cumulative Q^2 for the extracted components (Q^2_{cum}) is larger than 0.5, the model is considered to have a good prediction ability.

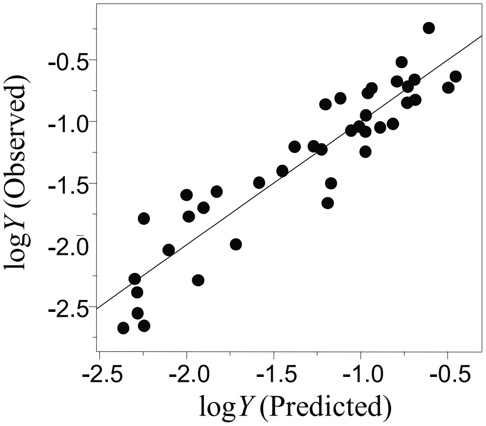

Figure 1. Plot of observed log*Y* versus that predicted for halogenated benzenes by QSPR model

Results and Discussion

Based on 19 molecular structural descriptors describing the overall character of the molecules and the nature of carbon-halogen bonds, a series of QSPR models were developed for *Y* of substituted aromatic halides[10]. Figure 1 shows a fitting result. In this model, five compounds were identified as outliers and thus removed during the model development. Among the five compounds, four were interpretable[10]. Based on factor analysis and PLS analyses, the compounds under study were grouped into three clusters, A (20 bromobenzenes and iodobenzenes), B (16 chlorobenzenes and 3-chloropyridine) and C (8 fluorobenzenes), as shown in Figure 2. By PLS analysis, one QSPR model was obtained for each group, for which the model fitting results is shown by Figure 3, 4 and 5. The QSPR models obtained after the grouping were more accurate and significant than the previous one. By further PLS analysis, cluster A was grouped into two subordinated clusters, cluster A1 (8 substituted iodobenzenes), and cluster A2 (12 substituted bromobenzenes)[10]. Based on the further classification, more accurate QSPR models were obtained. From these results it can be generally concluded that the Y values of the substituted aromatic halides are dependent on the overall characters of the molecules, the characters of the carbon-halogen bonds to be broken in the photolysis and the characters of the halogen atoms to be replaced in the photolysis. Substituted aromatic halides with large average molecular polarizability and molecular weight values tend to have low *Y* values. The results also clearly showed that grouping of the compounds under study based on mechanisms is of great importance to QSPR development.

Using PLS analysis and 27 quantum chemical descriptors, a QSPR model for the *Y* of PCDD was obtained, for which the fitting result was shown in Figure 6[11]. The QSPR result showed that increasing the number of chlorine atoms bonded with the parent dibenzo-*p*-dioxin, the largest positive atomic charge on a chlorine atom (q_{cl}) and dipole moment (μ) leads to decrease of log*Y* values. Increasing energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of the highest occupied molecular orbital (E_{HOMO}) and (E_{LUMO}- E_{HOMO}) values lead to increase of log*Y* values.

Using 13 fundamental quantum chemical descriptors and PLS analysis, a significant QSPR model was obtained for logk_S of 10 PCDD/Fs dissolved in cuticular wax of *Prunus laurocerasus*[12]. The model fitting results are shown in Figure 7. The results showed that logk_S values increase with the degree of chlorination of the homologues. PCDD/Fs with large values of q_{cl} , μ,and Q_o^- (the most negative atomic

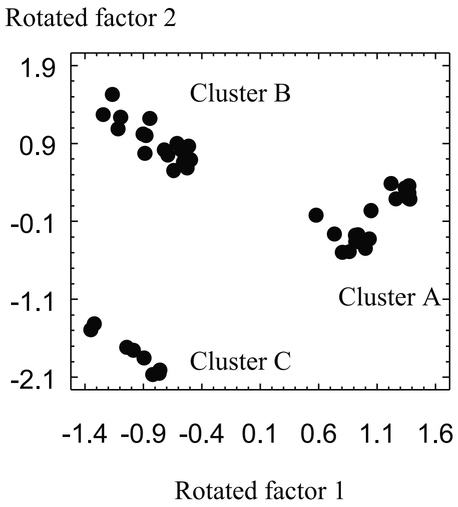

Figure 2. Plot of the first and second factor scores

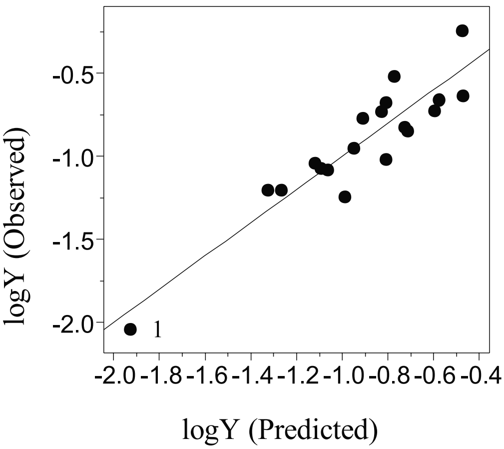

Figure 3. Plot of observed log*Y* versus that predicted by QSPR model for cluster A

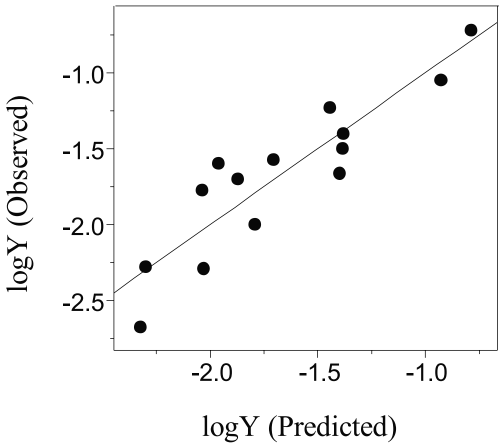

Figure 4. Plot of observed log*Y* versus that predicted by QSPR model for cluster B

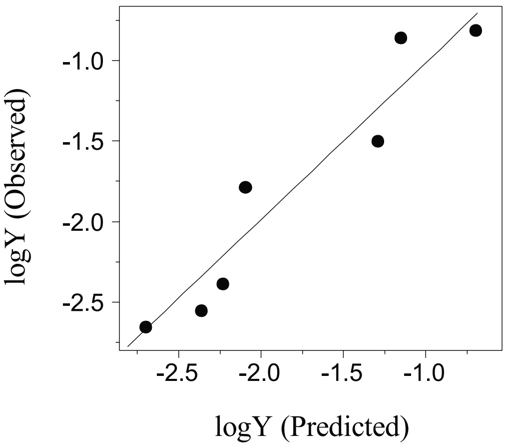

Figure 5. Plot of observed log*Y* versus that predicted by QSPR model for cluster C

charge on the oxygen atoms in a molecular) tend to photodegrade fast; PCDD/Fs with large values of E_{LUMO}, E_{HOMO}, and E_{LUMO}- E_{HOMO} tend to have low $\log k_{\mathrm{S}}$ values. The study also implied that the photodegradation mechanism of PCDD/Fs exposed to mercury lamps and sunlight may be different from each other.

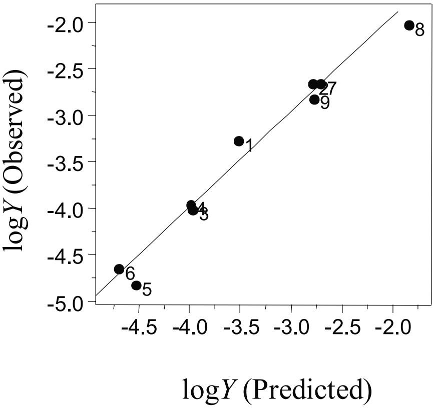

Figure 6. Plot of observed log$Y$ versus that predicted for PCDDs

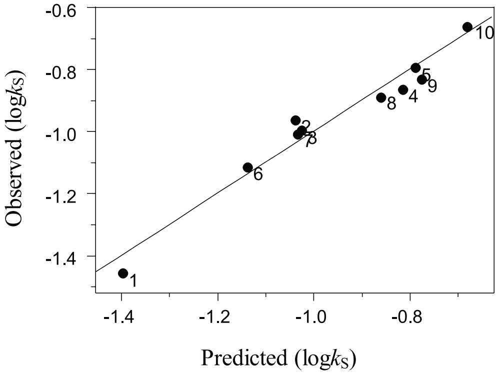

Fig. 6. Plot of observed and predicted logk_s values

Figure 7. Plot of observed and predicted logk_S values for PCDD/Fs

Ackowledgments

The study is supported by the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE (TRAPOYT), P. R. China. Jingwen Chen gratefully acknowledges the support from Alexander von Humboldt foundation.

References

1. Safe S. (1986) Ann Rev Pharmacol Toxicol. 26, 371.
2. Schwarzenbach R. P. and Gschwend P. M. (1993) Environmental Organic Chemistry. Wiley, New York, 437-484
3. Larson R. A. and Webster E. J. (1994) Reaction Mechanism in Environmental Organic Chemistry. Lewis Publishers, CRC Press, Ann Arbor, MI, 359-413
4. Chen J. W., Peijnenburg Willie J. G. M. and Wang L. S. (1998) Chemosphere, 36: 2833-2853.
5. Choudhy G. G. and Webster G. R. B. (1989) J Agric Food Chem. 37: 254-261.
6. Kim M. and O'Keefe P. W. (2000) Chemosphere, 41: 793-800.
7. Dulin D., Drossman H. and Mill T. (1986) Environ Sci Technol. 20: 72-77.
8. Schuler F., Schmid P. and Schlatter C. (1998) Chemosphere, 36: 21-34.
9. Wolds S., Wold H. and Dunn WJIII. (1984) Report UMINF-83, Department of Chemistry, University of Umeå, Sweden.
10. Chen J. W., Peijnenburg Willie J. G. M., Quan X., Chen S., Zhao Y. Z. and Yang F. L. (2000) Chemosphere, 40: 1319-1326.
11. Chen J. W., Quan X., Schramm K. W., Kettrup Antonius and Yang F. L. (2001) Chemosphere, 45:151-159.
12. Chen J. W., Quan X., Yang F. L. and Peijnenburg Willie J. G. M. (2001) Chemophere, 269: 163-170.