Bull Environ Contam Toxicol (2010) 85:568–572
DOI 10.1007/s00128-010-0127-5

Determination of Ozonization Reaction Rate Constants of Aromatic Pollutants and QSAR Study

Jian Lin Jiang · Xiang An Yue · Qiu Fen Chen · Zhen Gao

Received: 16 June 2010 / Accepted: 20 October 2010 / Published online: 5 November 2010

Abstract Rate constants of ozone with 39 aromatic compounds in aqueous solution were determined at 298 K. And optimized calculation was carried out at B3LYP/6-311G** level with DFT method. 10 molecular parameters obtained from calculations were selected as the descriptors to establish QSAR models for predicting the rate constants. These descriptors include structural, electronic and thermodynamic parameters. The optimum model was $-\log k' = 4.656 + 0.015CMA\text{-}1.684E_{\mathrm{LUMO}} - 3.057q\mathrm{H}^{+}$, of which square regression coefficient $R^2 = 0.791$, standard deviation SD = 0.126. Stability of the model was checked by leave-one-out cross-validation and variation inflation factor. The QSAR model showed that the main contribution to degradation was the *CMA* parameter.

Keywords Ozone · Degradation · Aromatic pollutants · QSAR

Aromatic compounds were widely used in chemical industry. When released in the environment as industrial gas exhausts or in wastewater streams, these compounds are serious threat to the ecosystems (Kušic′ et al. 2009). Most of them were toxic and persistent organic pollutants. The transformation of these pollutants in the environment occurs through physical, biological or chemical process. Physical treatment processes achieve removal by separation, producing concentrated sludge and leaving the problem of disposing of the transferred material (Catalkaya et al. 2003; Bali et al. 2003). According to prior investigations, some of the aromatic compounds have antibacterial activity. Ozonization is one of efficient water treatment technologies that is able to degrade organic and biological pollutions (Bertanza et al. 2001; Suarez et al. 2007).

The rate constants of reactions between aromatic pollutants and ozone are one of the important characteristics related to their degradation. Such data are valuable for the treatment of complex wastewaters containing several aromatic compounds by the degradation of ozone. Experimental determination of the rate constants of reaction plays an important role in the degradation of pollutants. Due to the complexity of analytical methods and the high cost of experiments, the application of the theoretical predictive method is fast and convenient for the preliminary assessment and estimation of degradation rates, and moreover cost-effective (Sabljic and Peijnenburg 2001). Quantitative structure–property relationship (QSPR) and quantitative structure–activity relationship (QSAR) modeling are two well theoretical predictive methods. Fatemi (2006) predicted ozone tropospheric degradation rate constant of organic compounds by using artificial neural networks. In addition, QSAR models were developed to predict degradation rate constants of tropospheric ozone and to study the degradation reactivity mechanism of 116 diverse compounds (Ren et al. 2007). The present study was conducted to determine the rate constants for the reaction of ozone with aromatic pollutants and the relationship between degradation rate constants and the structure of the aromatic

J. L. Jiang (✉) · X. A. Yue · Z. Gao
Key Laboratory for Petroleum Engineering of the Ministry of Education, China University of Petroleum, Beijing 102249, China
e-mail: jianlin92@163.com

J. L. Jiang · X. A. Yue · Z. Gao
Enhanced Oil Recovery Center, China University of Petroleum, Beijing 102249, China

Q. F. Chen
Petroleum Exploration & Production Research Institute, Sinopec, Beijing 100083, China

pollutants. Kinetic measurements results and QSAR/QSPR models were also utilized to assess the potential of ozonization as a means of eliminating aromatic pollutants.

Materials and Methods

In the present study, 39 chemicals of aromatic compound of analytical reagent quality were obtained from Sinopharm Chemical Reagent Co., Ltd. Ozone was generated by an ozone generator (Jinghua Jianqiao Environmental Protection Science and Technique Co., Ltd., DJ-Q2020A, China). The experiments were conducted in a three-necked flask of 250 mL. The original concentration of aromatic compounds was 5.00×10^{-4} mol/L and the volume of solution was 100 mL. HCl or NaOH was used to adjust pH to 7. During the experiment, ozone was continuously introduced into the reactor. The excess ozone in the outlet gas was absorbed by 10% $Na_2S_2O_3$ solution. All the experiments were conducted at 298 K. During the reaction process, the concentration of aromatic compounds was detected after different reaction time periods by UV spectrophotometry (Spectrumlab 752 s, LengGuang. Tech., China) at the maximum absorption wavelength (λ).

A total of 10 theoretical molecular descriptors were selected to describe aromatic compounds. These descriptors related to structural, electronic and thermodynamic parameters. They are molecular volume (V_m), polarizability (α), dipole moment (μ), energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), and most positive partial charge on a hydrogen atom (qH^+), are obtained directly from the Gaussian output files in this work. Atomic point charges were calculated based upon Mulliken population analysis. Thermodynamic parameters are as follows: standard enthalpies (H^θ), standard Gibbs energies (G^θ), standard entropy (S^θ). Connolly molecular area (*CMA*) was computed by CS Chem3D Ultra.

Calculations of molecular descriptors were carried out with Gaussian 98 program (Frisch et al. 1998). The geometries of all the aromatic compounds were optimized at the B3LYP/6-311G** level and frequency calculations were performed to confirm that the structures were at the minimal potential energy surface. The structural, electronic and thermodynamic parameters were calculated at 298.15 K and 1.013×10^5 Pa.

Partial least square (PLS) regression procedure was used to develop QSAR model. The quality of derived QSAR model was evaluated in terms of the LOO cross-validation correlation coefficient (q^2), the squared regression coefficient (R^2), the standard deviation (*SD*), *t* test as well as the Fisher test. Moreover, multi-collinearity between the descriptors of the model was checked by pairwise correlation coefficients.

Results and Discussion

The concentration and reaction time of 39 aromatic compounds were investigated during the ozonization process and experimental results for the four substituted phenol (3-Chlorophenol, 1,4-Dihydroxybenzene, 2-Naphthol and 2-Nitrophenol) are shown in Fig. 1. From Fig. 1, it can be seen the concentration of aromatic compounds linearly decreased with reaction time. Among the four compounds, the degradation rate of 1,4-Dihydroxybenzene is the fastest, while the degradation rate of 2-Naphthol is the slowest. Thus, it comes to the conclusion that ozone degradation reaction rate order is zero in the present study. Therefore, the reaction rate constants (k') are equal to the linear slop in Fig. 1.

Ozonization as an electrophilic reaction occurs in molecular solutions that have a high electron density. Aromatic compounds that have electron denoting groups have a high electron density on the carbon atoms of the benzene ring on the ortho and para position, they react actively with ozone. From Fig. 1 it is clearly seen that 1,4-Dihydroxybenezene reacts very fast with ozone, while 2-Nitrophenol and 2-Chlorophenol with electron withdrawing groups react much slower.

All the aromatic compounds and their calculated logarithm of reaction rate constants (Exp.) are listed in Table 1. And the molecular descriptors of aromatic compounds in the present study are also listed in Table 1.

Using the obtained molecular descriptors as variables, the correlation model of the apparent rate constants were developed by GQSAR2.0 program (Liu et al. 2003), in

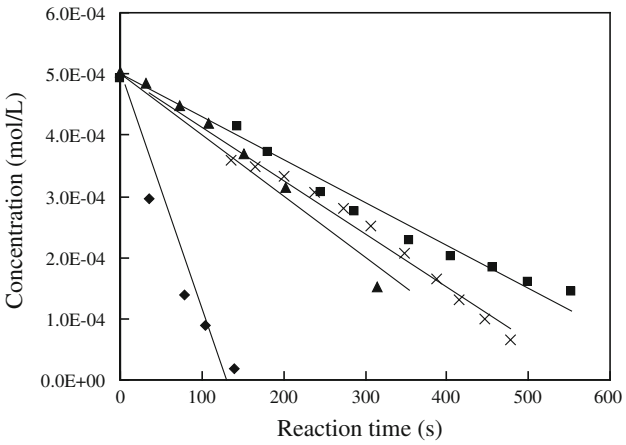

Fig. 1 Concentration of aromatic compounds as function of reaction time. (*filled diamond*) 1,4-Dihydroxybenzene (*filled square*) 2-Naphthol (*filled triangle*) 3-chlorophenol, (×)2-Nitrophenol

Table 1 Experimental, predicted $-\log k'$ and the molecular descriptors of aromatic compounds

No.	Molecule	*CMA* Å^2	E_{LUMO} eV	qH^+ e	μ Debye	$-\log k'$		
						Exp.	Pred.	Diff.
1	1-Aminonaphthalene	153.342	−0.038	0.205	1.628	6.304	6.458	0.154
2	1,4-Benzendiamine	121.169	−0.002	0.197	2.212	6.125	5.926	−0.199
3	2-Benzoylacetanilide	149.290	−0.027	0.229	3.393	6.366	6.304	−0.062
4	3-Chloroaniline	126.760	−0.018	0.209	3.254	6.028	6.003	−0.025
5	2-Chlorophenol	121.932	−0.025	0.271	0.928	5.893	5.753	−0.140
6	3-Chlorophenol	122.677	−0.026	0.251	1.166	5.901	5.827	−0.074
7	3-Chloro-4-fluoroaniline	131.171	−0.029	0.209	4.212	5.854	6.091	0.237
8	2,3-Dichloroaniline	139.892	−0.027	0.230	3.523	6.032	6.157	0.125
9	2,6-Dichloroaniline	140.334	−0.029	0.233	0.758	6.218	6.159	−0.059
10	3,4-Dichloroaniline	140.720	−0.030	0.212	4.561	6.210	6.231	0.021
11	2,3-Dichlorophenol	135.840	−0.035	0.278	4.086	6.026	5.961	−0.065
12	2,4-Dichlorophenol	137.110	−0.039	0.279	3.146	6.005	5.986	−0.019
13	2,5-Dichlorophenol	137.115	−0.038	0.255	1.295	6.019	6.055	0.036
14	2,6-Dichlorophenol	136.574	−0.037	0.398	2.046	5.608	5.608	0.000
15	3,5-Dichlorophenol	137.842	−0.039	0.254	2.425	6.044	6.071	0.027
16	1,2-Dihydroxybenzene	112.613	−0.009	0.244	0.538	5.741	5.663	−0.078
17	1,3-Dihydroxybenzene	113.006	−0.005	0.245	2.378	5.883	5.659	−0.224
18	1,4-Dihydroxybenzene	113.034	−0.015	0.244	2.655	5.627	5.679	0.052
19	2,6-Dinitrophenol	157.414	−0.130	0.276	4.012	6.519	6.459	−0.060
20	N,N-Dimethylaniline	151.988	−0.000	0.120	1.975	6.731	6.633	−0.098
21	2-Fluoroaniline	116.254	−0.008	0.216	1.715	5.932	5.804	−0.128
22	3-Fluoroaniline	116.427	−0.008	0.208	2.820	5.635	5.829	0.194
23	4-Fluoroaniline	116.435	−0.017	0.204	3.054	6.065	5.858	−0.207
24	2-Methoxyphenol	135.468	−0.000	0.244	0.617	5.932	6.001	0.069
25	3-Methoxyphenol	136.512	−0.001	0.247	0.875	5.971	6.009	0.038
26	2-Methylbenzamine	129.928	−0.001	0.205	1.749	6.061	6.034	−0.027
27	4-Methylbenzenamine	131.037	−0.003	0.202	1.463	5.978	6.066	0.088
28	3-Methylanline	129.924	−0.001	0.203	1.560	6.062	6.042	−0.020
29	2-Methylphenol	126.154	−0.006	0.246	1.136	5.633	5.861	0.228
30	3-Methylphenol	126.985	−0.010	0.245	1.639	5.817	5.884	0.067
31	4-Methylphenol	126.693	−0.011	0.245	1.408	5.722	5.881	0.159
32	1-Naphthol	149.497	−0.046	0.243	1.399	6.373	6.297	−0.076
33	2-Naphthol	150.417	−0.044	0.248	1.064	6.441	6.297	0.144
34	4-Nitroaniline	138.069	−0.079	0.220	7.181	5.987	6.206	0.219
35	2-Nitrophenol	132.347	−0.085	0.252	5.730	6.048	6.017	0.031
36	3-Nitrophenol	131.960	−0.095	0.252	5.790	5.983	6.019	0.036
37	4-Nitrophenol	132.578	−0.089	0.255	5.308	6.093	6.009	0.084
38	2-Nitroso-1-naphthol	164.155	−0.096	0.244	5.729	6.854	6.668	0.186
39	2,4,5-Trichlorophenol	151.073	−0.050	0.278	2.061	6.118	6.208	0.090

which the apparent rate constants are independent variables listing in Table 2. The squared regression coefficients (R^2), standardized deviation (SD), the squared regression coefficients of LOO cross-validation (q^2) and the Fisher test value F are also listed in Table 2.

According to the predictive performance, the best models are 3- and 4-variable models. The optimum model was determined by regression coefficients (R^2 and q^2). As is shown in Table 2, the values of R^2 increase with the number of variables. But when the number of variables increases from 3 to 4, the R^2 only increases by 0.009 and q^2 decreases by 0.003. Thus the tree-variable model (3) is selected as the optimum model with $R^2 = 0.791$, SD = 0.126 and $q^2 = 0.743$. All the predicted values of

Table 2 Regression model for calculating $-\log k'$ of aromatic compounds

No.	Model	R^2	*SD*	q^2	*F*
1	$-\log k' = 3.760 + 0.017CMA$	0.627	0.168	0.588	62.239
2	$-\log k' = 4.325 + 0.018CMA\text{-}2.623q\mathrm{H}^+$	0.768	0.133	0.727	59.487
3	$-\log k' = 4.656 + 0.015CMA\text{-}1.684E_{\mathrm{LUMO}}\text{-}3.057q\mathrm{H}^+$	0.791	0.126	0.743	44.041
4	$-\log k' = 4.881 + 0.015CMA\text{-}2.970E_{\mathrm{LUMO}}\text{-}3.397q\mathrm{H}^+ - 0.0260\mu$	0.800	0.123	0.740	34.065

$-\log k'$ (Pred.) by model (3) and the difference between experimental values and predicted values (Diff.) are presented in Table 1.

The optimum model contains three variables *CMA*, E_{LUMO} and $q\mathrm{H}^+$. These descriptors play an important role in the degradation of ozone. As is well known, the organic structure and functionality influence the mechanism of ozone consumption. For example, ozone attacks the weakest C–H bonds of aliphatic hydrocarbons and N–H bonds of amines proceeds with the formation of the radical HO_3 as the first unstable intermediate, inserts into double bonds of olefins and aromatic compounds with the formation of unstable ozonides, reacts with heteroatom compounds with the addition of an oxygen atom and the formation of oxo compounds and, being an active electron acceptor, it oxidizes molecules and organic anions by electron transfer (Denisova and Denisov 1998). In model (3), Connolly molecular area (*CMA*) is the molecular structural parameter that characterizes the cavity forming interactions. The energy of the lowest unoccupied molecular orbital represents reaction activity. The energies of frontier molecular orbitals, E_{HOMO} and E_{LUMO} were widely used in developing the QSAR model, for studying the various mechanisms of organic compounds, such as toxicity and degradability (Turabekova et al. 2008). The electrostatic descriptor $q\mathrm{H}^+$ reflects characteristic of the charge distribution of the molecule. This descriptor is related to the most positively charged atom in the molecule that is usually connected to the electron withdrawing. The negative sign of any descriptor in model (3) means that it is in direct proportion to the reactivity of compounds in ozone degradation. On the contrary, descriptors with positive sign in front of which will inversely affect the reactivity.

The predicted $-\log k'$ of all the aromatic compounds and the difference are together listed in Table 1. From Table 1, we can see the experimental values of the $-\log k'$ are close to the predicted values by model (3). The maximum deviation between the predicted values of the model (3) and the experimental values is 0.237 for the compound 3-Chloro-4-fluoroaniline. The correlation between predicted values and experimental values for apparent reaction rate constants can be observed from Fig. 2. It shows that the predicted values and experimental values exhibit good correlation, and the regression coefficient R^2 is 0.791 and standard deviation is 0.126.

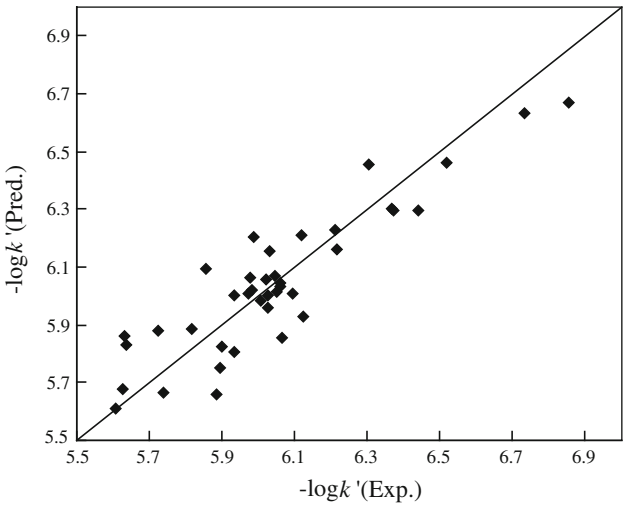

Fig. 2 Predicted values of $-\log k'$ by model (3) as function of experimental ones

To check the stability of optimum model, pairwise correlation coefficients, *t* test and the Fisher test are employed using SPSS 12.0 for windows program. Both the significance (probability) of the *t* value and the *F* value is 0.05. Pairwise correlation coefficients of optimum model are listed in Table 3. The correlation coefficients order between the experimental values of $-\log k'$ and independent variables are as follows: $CMA > E_{\mathrm{LUMO}} > q\mathrm{H}^+$. Among the dependent variables, the maximum correlation coefficient is 0.540 between E_{LUMO} and *CMA*, so the model (3) is acceptable.

The standard regression coefficients and *t* values of independent variables for model (3) are listed in Table 4, and all the absolute t values are larger than the standard

Table 3 Correlation coefficient (*r*) matrix for variables of model (3)

	$-\log k'$	*CMA*	E_{LUMO}	$q\mathrm{H}^+$
$-\log k'$	1.000	–	–	–
CMA	0.792	1.000	–	–
E_{LUMO}	0.413	0.540	1.000	–
$q\mathrm{H}^+$	0.330	0.162	0.380	1.000

Table 4 Checking statistical values for model (3)

Model	Regression coefficients	t	Sig.	VIF
Constant	4.656 ± 0.304	15.304	0	–
CMA	0.015 ± 0.002	7.775	0	1.416
E_{LUMO}	−1.682 ± 0.860	−1.958	0	1.611
$q\mathrm{H}^+$	−3.057 ± 0.585	−5.226	0	1.172

one. It indicates that three variables are able to accept. Moreover, Table 3 also showed that the Fisher test of optimum model is also passed ($F_{1-\alpha} = 1.704$). Furthermore, multicollinearity between the descriptors of model (3) was checked by calculating their variation inflation factors (VIF) to evaluate the correlation degree of each independent variable in the equation (Famini et al. 1992) in the present study. Here, VIF $= 1/(1-r^2)$, in which r is the correlation coefficient of multiple regressions between one variable and the others in the equation. If VIF = 1.0, no intercorrelation exists for each variable; if VIF ranges from 1.0 to 5.0, the related equation is acceptable; and if VIF is larger than 10.0, the regression equation is unstable and recheck is necessary. It can be seen from the Table 4, the max-VIF for model (3) is only 1.611, suggesting model (3) has obvious statistic significance.

In conclusion, the degradation of 39 aromatic compounds with ozone in aqueous solutions was experimentally determined. The results showed that the ozonization reaction order is zero. Based on the calculations of molecular parameter for aromatic compounds, the novel QSAR model for apparent reaction rate constants was developed by partial least square regression method. The optimum model contains three variables *CMA*, E_{LUMO} and $q\mathrm{H}^+$, of which the squared regression coefficient $R^2 = 0.791$, standard deviation SD = 0.126. The results of t test and F test suggested that the model exhibits optimum stability. Furthermore, the QSAR model provides some insights into what structural features are related to the ozonization rate constants of aromatic compounds.

Acknowledgments This research is supported by national significant science and technology projects of china (2008ZX05024-02-09).

References

Bali U, Catalkaya EC, Şengul F (2003) Photochemical degradation and mineralization of phenol: a comparative study. J Environ Sci Health A 38:2259–2275

Bertanza G, Collivignarelli C, Pedrazzani R (2001) The role of chemical oxidation in combined chemical–physical and biological processes: experiences of industrial wastewater treatment. Water Sci Technol 44:109–116

Catalkaya EC, Bali U, Sengul F (2003) Photochemical degradation and mineralization of 4-chlorophenol. Environ Sci Pollut Res Int 10:113–120

Denisova TG, Denisov ET (1998) Reactivity of ozone as a hydrogen-atom acceptor in reactions with antioxidants. Polym Degrad Stabil 60:345–350

Famini GR, Penski CA, Wilson LY (1992) Using theoretical descriptors in quantitative structure activity relationships: Some physicochemical properties. J Phys Org Chem 5:395–408

Fatemi MH (2006) Prediction of ozone tropospheric degradation rate constant of organic compounds by using artificial neural networks. Anal Chim Act 556:355–363

Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) GAUSSIAN 98, revision A.9. Gaussian, Inc., Pittsburgh

Kušic′ H, Rasulev B, Leszczynska D (2009) Prediction of rate constants for radical degradation of aromatic pollutants in water matrix: a QSAR study. Chemosphere 75:1128–1134

Liu SS, Yin CS, Wang LS (2003) VSMP: a novel variable selection and modeling method based on the prediction. J Chem Inf Comput Sci 43:964–969

Ren YY, Liu HX, Yao XJ, Liu MC (2007) Prediction of ozone tropospheric degradation rate constants by projection pursuit regression. Anal Chim Acta 589:150–158

Sabljic A, Peijnenburg W (2001) Recommendations on modeling lifetime and degradability of organic compounds in air, soil and water systems. Pure Appl Chem 73:1331–1348

Suarez S, Dodd MC, Omil F (2007) Kinetics of triclosan oxidation by aqueous ozone and consequent loss of antibacterial activity: Relevance to municipal wastewater ozonation. Water Res 41:2481–2490

Turabekova MA, Rasulev BF, Levkovich MG, Abdullaev ND, Leszczynski J (2008) Aconitum and Delphinium sp. alkaloids as antagonist modulators of voltage-gated Na^+ channels. AM1/DFT electronic structure investigations and QSAR studies. Comp Biol Chem 32:88–101