

Determination of the Apparent Reaction Rate Constants for Ozone Degradation of Substituted Phenols and QSPR/QSAR Analysis

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Received 3 Sep. 2009;

Revised 27 Nov. 2009;

Accepted 4 Apr. 2009

ABSTRACT: Although extensive experimental work has been carried out during the last several years, experimental reaction rate constants are available only for hundreds of compounds. Therefore, it is useful to develop a theoretical prediction method, which can be used to obtain estimates of the necessary kinetic parameters. One of the most successful approaches to predict chemical properties starting only from molecular structural information is quantitative structure–activity/property relationships modeling (QSAR/QSPR). The purpose of this paper is to study the relationships between concentrations of 26 substituted phenols and reaction times during the ozonation process and determine the reaction orders and apparent reaction rate constants ($-\lg k'$). Then, optimized geometries of the substituted phenols were carried out at the B3LYP/6-311G** level using the Gaussian 03 software package. The structural and thermodynamic parameters obtained were taken as theoretical descriptors to establish a novel QSPR/QSAR model for $-\lg k'$ of the substituted phenols, with a regression coefficient $R = 0.909$ and standard deviation $SD = 0.141$. Finally, the stability of the model for $-\lg k'$ predictions was checked by the t -test, showing satisfactory results. Results obtained reveal the reliability of QSPR/QSAR model for the prediction of ozone degradations rate constant of organic compounds.

Key word: Ozonation, Degradation rate, Density functional theory (DFT), Multiple linear regressions, Structural and thermodynamic parameters, E_{LUMO}

INTRODUCTION

With the development of the chemical industry, substituted phenols have been increasingly used for the synthesis of drugs and other chemicals. Substituted phenolic compounds, most of which are persistent and/or toxic organic pollutants, can be categorized as carcinogens, or malformation and mutation causing substances. Among these compounds, chlorophenol has been considered as one of 129 controlled priority pollutants by the U.S. Environmental Protection Agency (Keith, *et al.*, 1979). In recent years, increasing attention has been paid to phenols in wastewater (Kuscu, *et al.*, 2005; Fang, *et al.*, 2006; Subramanyam, *et al.*, 2007; Dalal, *et al.*, 2007; Xie, *et al.*, 2008). Because the molecular structure of substituted phenols has a benzene ring with high chemical stability, it is difficult to completely degrade them by conventional biochemical or physical chemistry means.

Ozonation is one of the most efficient technologies for treating wastewaters. Due to intensive oxida-

tion, ozone can degrade most organic compounds into CO_2 and H_2O . A number of novel advanced ozonation processes have been developed to improve oxidation efficiency. Shen *et al.* (2008) studied the kinetics and mechanisms of degradation of p-chloronitrobenzene in water by ozonation and concluded that the phenols can undergo ring-opening reactions to produce low molecular carboxylic acids and finally CO_2 . The main intermediate products were phenol, p-chlorophenol, p-nitrophenol, 2-chloro-5-nitrophenol, 5-chloro-2-nitrophenol, 5-nitro-catechol, para-benzoquinone, 5-nitro-1,2,3-trihydroxy phenol, trihydroxy semiquinone and glycolic acid. Sánchez-Polo *et al.* (2007) compared the efficiency of UV photodegradation in combination with various advanced oxidation processes (O_3 , UV/ H_2O_2 , O_3 /activated carbon) for the degradation of naphthalenesulfonic acids in aqueous solution and investigated the kinetics and the mechanisms involved in these processes. Chu *et al.* (2007) investigated the ozonation of synthetic wastewater containing an azo dye, CI Reactive Black 5, using a microbubble genera-

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tor and a conventional bubble contactor. Harrison et al. (2007) explored the degradation mechanisms of citronellal reactions with ozone and OH radicals. Gramatica et al. (1999) studied the tropospheric degradation of organic compounds by OH, NO₃ radicals and ozone and developed statistical models for predicting the oxidation rate constants of OH and NO₃ for many heterogeneous compounds by the quantitative structure-activity relationship (QSAR) and quantitative structure-property relationship (QSPR) method. In addition, QSPR/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 aim of the present study was to analyze the ozonation efficiency and the relationship between degradation rate and the structure of substituted phenols. The apparent reaction rate constants ($-\lg k'$) for the ozone degradation of 26 common substituted phenols were measured for the first time in this study. In addition, optimized geometries of substituted phenols were carried out at the B3LYP/6-311G** level using the Gaussian 03 program. Finally, correlation of the model between the apparent reaction rate constants and calculated parameters was established by the QSPR/QSAR method.

MATERIALS & METHODS

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 250 mL three-necked flask. The initial concentration of substituted phenol was 5.00×10^{-4} mol/L and the volume of solution was 100 mL. During experiments, ozone was continuously introduced into the reactor and maintained at a constant concentration (0.00118 mol/L). Excess ozone in the outlet gas was absorbed by 10% sodium thiosulfate solution. All experiments were conducted at 298.15 K. During the reaction process, the concentrations of substituted phenols were detected after different reaction time periods by UV spectrophotometer at their maximum absorption wavelengths (Spectrumlab 752s, LengGuang Tech., China). The reaction order and apparent reaction rate constants were obtained from the chemical reaction rate equation. At the same time, blank experiments with 4-nitrophenol and 2,3-dichlorophenol was carried by replacing ozone with the continuous introduction of air into the reactor at the same rate. After an equal time to the ozone degradation, we found that the concentrations of these two compounds were virtually unchanged. The results indicate that disappearance of substituted phenols was due to the reaction with ozone alone.

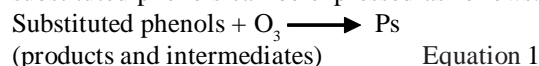
All calculations for the 26 substituted phenols were carried out with the Gaussian 03 program. The

geometries of all the substituted phenols were optimized at the B3LYP/6-311G** level and frequency calculations were performed to ensure they were at the potential energy surface minima. The structural and thermodynamic parameters were calculated. Structural parameters in this study included molecular volume (V_i), molecular average polarizability (α), dipole moment (μ), energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), the most negative atomic partial charge in molecule (q) and the most positive partial charge on a hydrogen atom ($q\text{H}^+$). Thermodynamic parameters calculated were as follows: standard enthalpies (H^θ), standard Gibbs energies (G^θ), standard entropy (S^θ), standard heat capacities at constant volume (C_v^θ), and thermal correction to energy (E_{th}^θ).

To determine the optimum number of components for the correlation model, the leave-one-out (LOO) cross-validation procedure was used to validate the derived QSPR/QSAR model by the SPSS for Windows (version 12.0) software program. The quality of the derived QSPR/QSAR model was evaluated in terms of the LOO cross-validation correlation coefficient (q), the squared regression coefficient (R), the standard deviation (SD) and the t -test.

RESULTS & DISCUSSION

The reaction equation for ozone degradation of substituted phenols can be expressed as follows.



Based on Equation 1, the ozone degradation rate equation can be presented as follows.

$$-dC_t/dt = k C_t^m C_{\text{O}_3}^n \quad \text{Equation 2}$$

where C_t (mol/L) and C_{O_3} (mol/L) are the concentrations of substituted phenols and ozone in aqueous solution, respectively, at reaction time t ; k is the reaction rate constant, and m and n are the reaction orders of substituted phenols and ozone, respectively. Because the concentration of ozone was always saturated in the ozonation process, it can be regarded as a constant, assuming that C_{O_3} has no influence on the ozone diffusion rate under stirring in aqueous solution. Thus Equation 2 can be simplified as Equation 3.

$$-dC_t/dt = k' C_t^m \quad \text{Equation 3}$$

where $k2$ is an apparent reaction rate constant and m is then the total reaction order.

When total reaction order (m) is zero, the reaction equation can be shown as Equation 4.

$$C_t = C_0 - k' t \quad \text{Equation 4}$$

where C_0 is the initial concentration of substituted

phenol in the reaction system. If the total reaction order (m) is unity, the reaction equation can be shown as Equation 5.

$$\lg(C_t/[C]) = \lg(C_0/[C]) - k' t \quad \text{Equation 5}$$

where $[C]$ is the unit concentration.

The concentrations versus reaction time of ozone degradation for 26 substituted phenols were investigated during the ozonation processes and the experimental results for the four substituted phenols (1,4-dihydroxybenzene, 2-naphthol, 3-chlorophenol and 2-nitrophenol) are shown in Fig. 1. It can be seen that the concentration of substituted phenols decreased linearly with reaction time. Among these four compounds, the ozone degradation of 1,4-dihydroxybenzene was the fastest, while 2-naphthol was the slowest. Thus, it can be concluded that the aqueous ozone degradation reaction rate equation is in agreement with Equation 4. Therefore, the reaction order is zero and the apparent reaction rate constant ($-k'$) is equal to the linear slope in Fig. 1.

All substituted phenols and their calculated structural parameters at the B3LYP/6-311G** level are listed in Table 1 and their calculated thermodynamic parameters and apparent reaction rate constants ($-\lg k'$) are listed in Table 2. Using the resulting structural and thermodynamic parameters as variables, correlation equations for the apparent rate constants were developed by multiple linear regressions with SPSS 12.0, in which the apparent rate constants were the independent variables listed in Table 3. The regression coefficients (R), standard deviations (SD), the regression coefficients of LOO cross-validation (q) and the Root Mean Square of Prediction (RMSEP) are also listed in Table 3.

The optimum equation was determined by comparing the regression coefficients (R and q). As shown in Table 3, the values of R increased with the number of variables. Thus the four-variable Equation.9 was selected as the optimum equation with $R = 0.909$, $SD = 0.141$ and $q = 0.856$. The optimum equation contains four variables E_{LUMO} , α , q and S . Inspection of Equation 9 may lead to the following interpretations: (1) $-\lg k'$ decreases with E_{LUMO} . This is because reaction activity increases with the E_{LUMO} value so it is easier for substituted phenols with larger E_{LUMO} values to degrade than those with smaller E_{LUMO} values. (2) The smaller the q (the value is negative) value is, the smaller $-\lg k'$ will be. This is because if the charge is more negative, the electron acting with ozone is more easily lost and therefore $-\lg k'$ decreases. (3) Furthermore, S° expresses the degree of disorder: the larger the degree of

disorder, the larger the degradation ability. (4) In addition, if α increases, $-\lg k'$ increases, i.e. the apparent rate constant decreases. The volume of the molecule increases with increasing α , the molecule is thus more stable and $-\lg k'$ increases. The predicted $-\lg k'$ of all the substituted phenols and the differences between them and experimental values are listed together in Table 2. From Table 2, we can see the experimental values of $-\lg k'$ were close to the values predicted by Equation 9. The maximum deviation between the values predicted by Equation 9 and the experimental values is -0.290 for the compound 2,6-dinitrophenol and the second large difference is -0.262 for 3-methoxyphenol. The standard regression coefficients and t -values of the independent variables in Equation 9 are listed in Table 4. The order of the standard regression coefficients is as follows: $\alpha > S^\circ > E_{LUMO} > q$. Thus, it can be concluded that α effects $-\lg k'$ most strongly. Moreover, it can be seen that all t -values are larger than the standard t -value, indicating that all four variables are significant. Therefore, it can be concluded that the optimum equation (Equation 9) obtained in this study is robust.

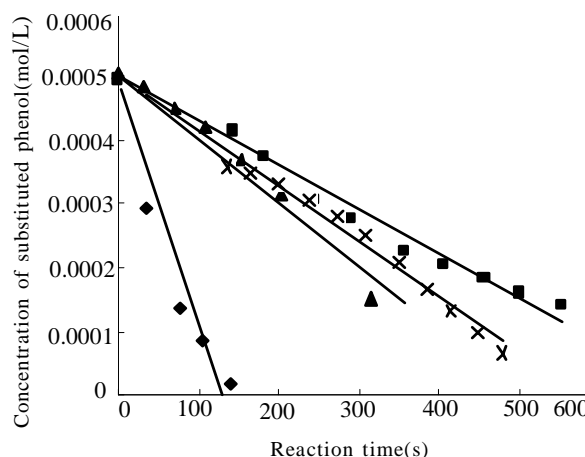


Fig. 1. Plots of concentration of substituted phenols vs. reaction time

(◆) 1,4-Dihydroxybenzene, (■) 2-Naphthol, (▲) 3-chlorophenol, (×) 2-Nitrophenol

Furthermore, in order to check the reliability of the predictive model developed in this study, the 26 substituted phenols in Table 1 were divided into two groups: the first three compounds of every four in order were included in the first group (training sets) and the remaining compounds were all included in the second group (external test sets). Using the same regression method as mentioned above, validation models that fitted the $-\lg k'$ values with the parameters of the 20 compounds in first group were created as shown in Equation 10.

$$\text{Equation 10}$$

$$-\lg k' = 9.124 + 6.195 q + 0.016 \alpha - 0.007 S^\circ - 3.090 E_{LUMO}$$

$$n = 20, R = 0.918, SD = 0.149, q = 0.833, RMSEP = 0.130$$

Table 1. Structural descriptors of substituted phenols by B3LYP/6-311G

No.	Molecule	V_m^m Å ³	E_{HOMO} eV	E_{LUMO} eV	qH^+ e	q^- e	μ Debye	α 10^{-30} esu
1	2,4,6-Trinitrophenol	203.101	-0.2204	-0.1085	0.2540	-0.3206	3.6877	127.281
2	2,6-Dinitrophenol	176.395	-0.2836	-0.1296	0.2762	-0.3236	4.0117	97.496
3	2-Nitroso-1-naphthol	209.666	-0.2063	-0.0964	0.2439	-0.2884	5.7286	127.918
4	3,4-Dimethylphenol	171.615	-0.2166	-0.0046	0.2446	-0.3676	1.1054	89.904
5	1,4-Dihydroxybenzene	138.393	-0.2083	-0.0149	0.2441	-0.3695	2.6551	68.587
6	4-Methylphenol	152.856	-0.2199	-0.0106	0.2448	-0.3657	1.4076	77.361
7	4-Methoxyphenol	163.083	-0.2056	-0.0122	0.2441	-0.3701	2.5445	82.020
8	4-Nitrophenol	156.045	-0.2625	-0.0889	0.2555	-0.3411	5.3084	82.145
9	1,3-Dihydroxybenzene	137.988	-0.2200	-0.0052	0.2451	-0.3607	2.3776	68.373
10	3-Methylphenol	154.748	-0.2250	-0.0105	0.2450	-0.3636	1.6385	76.992
11	3-Nitrophenol	154.144	-0.2575	-0.0953	0.2522	-0.3494	5.7901	79.891
12	1,2-Dihydroxybenzene	136.445	-0.2303	-0.0086	0.2438	-0.3840	0.5377	67.856
13	2-Methylphenol	150.496	-0.2234	-0.0058	0.2457	-0.3686	1.1355	76.853
14	2-Naphthol	186.203	-0.2147	-0.0436	0.2477	-0.3607	1.0642	111.764
15	1-Naphthol	192.065	-0.2108	-0.0456	0.2430	-0.3536	1.3987	110.373
16	2-Nitrophenol	152.743	-0.2588	-0.0855	0.2520	-0.3106	5.7302	80.015
17	2-Methoxyphenol	163.070	-0.2094	0.0001	0.2437	-0.3507	0.6173	81.900
18	3-Methoxyphenol	158.683	-0.2169	-0.0013	0.2472	-0.3630	0.8754	81.673
19	2-Chlorophenol	145.459	-0.2395	-0.0254	0.2707	-0.3392	0.9279	75.148
20	2,4-Dichlorophenol	176.517	-0.2412	-0.0392	0.2787	-0.3394	3.1456	87.828
21	2,3-Dichlorophenol	172.864	-0.2466	-0.0350	0.2780	-0.3378	4.0858	86.732
22	2,5-Dichlorophenol	173.440	-0.2449	-0.0380	0.2554	-0.3359	1.2947	88.129
23	3,5-Dichlorophenol	167.624	-0.2529	-0.0385	0.2541	-0.3492	2.4247	87.972
24	2,4,5-Trichlorophenol	190.325	-0.2498	-0.0496	0.2783	-0.3313	2.0605	99.814
25	3-Chlorophenol	146.784	-0.2405	-0.0260	0.2505	-0.3551	1.1662	75.571
26	5-Methyl-2-isopropylphenol	213.776	-0.2198	-0.0064	0.2456	-0.3738	1.4971	114.914

Table 2. Experimental and predicted $-\lg k'$ of substituted phenols and their thermodynamic descriptors by B3LYP/6-311G

No.	$-\lg k'$		TE Hartree	ZPE 10 ³ J/mol	H ⁰ Hartree	G ⁰ Hartree	F th 10 ³ J/mol	C _v ⁰ J/mol K ⁻¹	S ⁰ J/mol K ⁻¹
	Exp.	Cal.							
1	6.064	6.191	-590.561	391.737	-590.402	-590.447	416.576	160.724	398.241
2	6.519	6.229	-716.657	288.143	-716.536	-716.584	314.800	158.402	422.329
3	6.854	6.863	-590.543	387.426	-590.384	-590.431	414.028	166.983	413.530
4	5.552	5.767	-386.206	418.182	-386.037	-386.079	441.236	141.783	375.732
5	5.627	5.707	-382.792	284.051	-382.676	-382.714	302.022	112.554	338.088
6	5.722	5.882	-346.879	344.837	-346.740	-346.778	362.075	109.127	334.335
7	5.514	5.701	-422.102	358.189	-421.957	-421.999	379.665	130.963	368.418
8	6.093	6.102	-512.110	281.037	-511.994	-512.036	301.934	126.909	371.384
9	5.883	5.722	-382.795	284.716	-382.678	-382.716	302.378	111.771	336.092
10	5.817	5.680	-346.880	345.192	-346.740	-346.781	364.698	117.215	362.740
11	5.983	6.032	-512.107	280.484	-511.991	-512.034	301.533	127.583	373.330
12	5.741	5.673	-382.790	283.901	-382.675	-382.712	300.097	102.646	327.632
13	5.633	5.759	-346.880	346.044	-346.740	-346.780	364.966	116.708	345.833
14	6.441	6.376	-461.229	396.441	-461.069	-461.110	417.521	140.796	366.385
15	6.373	6.344	-461.226	395.621	-461.066	-461.109	417.446	141.955	373.535
16	6.048	6.192	-512.098	280.732	-511.983	-512.025	301.738	126.968	372.799
17	5.932	5.768	-422.099	358.864	-421.954	-421.995	380.133	130.399	366.046
18	5.971	5.709	-422.106	358.750	-421.960	-422.002	379.966	130.549	365.836
19	5.893	5.989	-767.175	249.725	-767.073	-767.111	267.027	106.600	340.151
20	6.005	6.023	-1226.790	223.851	-1226.696	-1226.738	244.651	123.750	372.292
21	6.026	6.009	-1226.787	224.023	-1226.692	-1226.734	244.693	123.261	370.359
22	6.019	6.040	-1226.791	223.826	-1226.697	-1226.739	244.634	123.784	372.242
23	6.044	5.973	-1226.794	223.439	-1226.700	-1226.742	244.241	124.328	372.585
24	6.118	6.111	-1686.410	199.040	-1686.324	-1686.369	222.840	138.792	399.304
25	5.901	5.902	-767.174	248.812	-767.071	-767.110	266.404	107.993	342.632
26	5.643	5.672	-464.854	566.298	-464.626	-464.676	596.948	185.075	444.299

Table 3. Regression equations for $-\lg k'$ of substituted phenols

Eq.	Equation	R	SD	q	RMSEP
6	$-\lg k' = 9.551 + 10.248 q'$	0.732	0.210	0.656	2.230
7	$-\lg k' = 8.034 + 7.700 q' + 0.007 \alpha$	0.799	0.194	0.678	2.227
8	$-\lg k' = 9.751 + 9.154 q' + 0.015 \alpha - 0.005 S^{\theta}$	0.870	0.163	0.826	0.172
9	$-\lg k' = 8.769 + 5.017 q' + 0.0171 \alpha - 0.007 S - 3.581 E_{LUMO}$	0.909	0.141	0.856	0.159

The RMSEP value of Equation 10 for the external test set (the second group) is 0.130. Moreover, the SD value of Equation 10 (0.149) is smaller and the values of R and q are similar to those obtained from Equation 9. t -values of the independent variables for Equation 10 are listed in Table 4, indicating that all the values are larger than the standard t -value. These results confirm that the model obtained is reliable and has good predictive ability.

Table 4. Checking statistical values for Equation 9 and 10

Variables	SR	$T (t_{\alpha/2}=1.706)$ (Equation 9)	$T (t_{\alpha/2}=1.725)$ (Equation 10)
E_{LUMO}	-0.4784	-2.904	-2.080
q'	0.3584	2.414	2.398
α	0.8717	5.700	4.909
S	-0.8127	-4.716	-4.038

CONCLUSION

Ozonation is one of the most efficient technologies for treating wastewaters. However, the experimental determination of such reaction rate constants is difficult, costly and time-consuming, and there are many uncertainties in chamber conditions. Therefore, reliable theoretical models to estimate rate constants of the degradability of chemicals are strongly required. Among them, quantitative structure–activity/property relationships (QSAR/QSPR) study is a useful and effective alternative approach to predict rate constants of this process. In this study, the ozone degradations of 26 substituted phenols in aqueous solutions were investigated at 298.15 K. The results show that the ozonation reaction order is zero and the apparent reaction rate constants of all substituted phenols were obtained from the chemical reaction rate equation. Based on the optimized geometries of substituted phenols, using the Gaussian 03 program, a novel QSPR/QSAR model for apparent reaction rate constants ($-\lg k_2$) was developed by a multiple linear regression method. The optimum model (Equation 9) obtained in this work contains four variables E_{LUMO} , q' , α and S , for which the regression coefficient $R = 0.909$ and the standard deviation $SD = 0.141$. Furthermore, the optimum equation shows that $-\lg k_2$ increases with increasing q' and α and decreases with increasing E_{LUMO} and S . The results of the t -test indicate that the model exhibits optimum stability.

ACKNOWLEDGEMENTS

Financial support by the provincial Natural Science Foundation of Zhejiang (Y507280) is gratefully acknowledged.

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