EVALUATION OF REACTIVITY OF PESTICIDES WITH OZONE IN WATER USING THE ENERGIES OF FRONTIER MOLECULAR ORBITALS

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Abstract—The rate constants of ozone with four groups of pesticides (4 phenolic-, 8 organonitrogen-, 8 phenoxyalkylacetic-, and 4 heterocyclic N-pesticides) were determined under controlled conditions at a pH of 7.5, ionic strength of ca 10^{-3} M, and 100 μM NaHCO₃. The rate constant for BPMC was first determined from a pseudo-first order reaction model, the rate constants for the other pesticides were then obtained by a competition kinetic method using BPMC as the first reference compound. The rate constants were found to vary widely according to the pesticides. The highest rate constant was 27,600 M^{-1} s^{-1} for PCP and the lowest was 61.8 M^{-1} s^{-1} for cyanazine. In order to quantify the effects of structure on the reactivity of pesticide with ozone, for each group of pesticides the rate constants were correlated with the energies of the highest occupied molecular orbital (E_HOMO). The logarithm of the rate constants was found to linearly increase with the increase of the E_HOMO values except for the phenoxyalkylacetic group. When all examined pesticides were included in the correlation analysis, the rate constants gave a statistically unsatisfactory correlation with a coefficient of 0.92, but showed a similar trend of increasing reactivity with increasing E_HOMO values of pesticides. The results of the correlation analysis suggested that the reactivity of pesticides with ozone follows the frontier orbital theory and can be estimated by E_HOMO. The rate constants for the phenoxyalkylacetic group could be estimated accurately by a two-parameter QSAR model based on absolute electronegativity and E_HOMO. © 2000 Elsevier Science Ltd. All rights reserved

Key words—drinking water treatment, frontier molecular orbital theory, highest occupied molecular orbital, ozone, pesticides, QSAR, rate constants

INTRODUCTION

The ozonation process has been used as an effective method for removing residual pollutants such as pesticides and other hazardous chemicals from raw water during drinking water treatment. Ozone selectively reacts with compounds containing heter atoms such as S, N, O, and Cl. Thus, pesticides, which usually have some heter atoms on the molecules, are often expected to be destroyed by ozonation. However, as has been found by many researchers, the reactivity of pesticides with ozone varies largely due to their diverse structural features (Reynolds et al., 1989; David and Haag, 1991).

The rate constant indicates the reactivity of a reaction, and it becomes of vital importance when deciding whether ozonation is an economically sound option for removing pesticides from raw water during drinking water treatment. The rate constants for ozonation of pesticides are usually acquired through a method of direct experimental determination. While this method provides exact results under the established experimental conditions, the results are not comparable with other rate constants obtained under different conditions. Further, direct determination of rate constants requires laborious and time-consuming techniques, which makes field. Therefore, an alternative procedure that can be used to estimate the rate constant of a pesticide from an existing database is desirable.

The recently developed quantitative structure–activity relationship (QSAR) procedure, estimates rate constants of organic compounds during oxidation processes based on chemical properties. Logical candidate predictors such as oxidation potentials, σ constants in the Hammett equation, and molecular orbital energies are employed to correlate with oxi-
dation rate constants of the compounds. Of the three predictors, the $\sigma$ constant in the Hammett equation is the one most commonly used for QSAR analysis of reactivity of compounds in the oxidation process. For example, the kinetics of the heterogeneous ozonation of o,p-activated aromatic organic compounds (Gould, 1987) and substituted phenols (Hoigne and Bader, 1983) have been successfully correlated with their $\sigma$ constants. While this method is useful for benzene derivatives, it is difficult to apply $\sigma$ constants to evaluate the reactivity of pesticides due to the diversity of their structure. Half-wave potentials have also been employed for QSAR analysis of oxidation rate constants of the reaction between substituted phenols with single oxygen (Tratnyek et al., 1991) and chlorine dioxide (Tratnyek and Hoigne, 1994); in this case, the difficulties inherent in the experimental measurement of the half-wave potentials of the organic compounds have limited the scope of application.

On the other hand, the energy of the highest occupied molecular orbital ($\epsilon_{\text{HOMO}}$) has recently been used to estimate the kinetic parameters of oxidation of organic compounds. $\epsilon_{\text{HOMO}}$ is a significant chemical property reflecting the potential of electron transfer between two reactants. Studies on $\epsilon_{\text{HOMO}}$-based correlation include oxidation of phenols and anilines by $\text{H}_2\text{O}_2$ catalyzed by horseradish peroxidase compound II (Sakurada et al., 1990) and oxidation of hydroxfluorocarbons and hydrofluoroethers by hydroxyl radicals (Cooper and Cunningham, 1992; Percival et al., 1995; Bartolotti and Edney, 1994). The fact that $\epsilon_{\text{HOMO}}$ can be readily calculated for almost all environmentally important compounds by using a standard technique of computational chemistry is a great advantage of $\epsilon_{\text{HOMO}}$ over other predictors.

In this study, in order to develop a simplified method for estimating the reactivity of pesticides with ozone, we focused on $\epsilon_{\text{HOMO}}$-based correlation analysis of the rate constants of reactions between pesticides and ozone. To reflect the effects of structural feature on the reactivity of pesticides, we selected four groups of pesticides (four phenolic-, eight organonitrogen-, eight phenoxalkylylactic-, and four heterocyclic N-pesticides) and determined their respective rate of degradation reactions under conditions close to those of natural waters.

THEORETICAL BACKGROUND

Pseudo-first order reaction model

On the assumption that the reaction between pesticides and ozone is of the first order with respect to ozone and pesticide concentrations, the decomposition rate can be formulated as:

\[ \frac{d[P]}{dt} = k_p[P][O_3] \]  

where $k_p$ is the rate constant for decomposition of a pesticide by $O_3$, and [P] and [O$_3$] are the concentrations of the pesticide and dissolved ozone, respectively. When experiments are conducted under conditions where the concentration of dissolved ozone is constant, the reaction rate becomes pseudo-first order. Upon integrating Eq. (1), Eq. (2) is obtained:

\[ \log\left(\frac{[P]_t}{[P]_0}\right) = -k_p[O_3]t = k_p t \]  

Thus, a plot of $\log([P]_t/[P]_0)$ vs $t$ yields a line from which $k_p$ can be determined.

Competition kinetic method

The competition kinetic method is another model to determine the rate constants for pesticide degradation by ozone. When ozonation is conducted in a mixture of two pesticides, Eqs. (3) and (4) can be obtained:

\[ \frac{d[P_1]}{dt} = k_1[P_1][O_3] \]  

\[ \frac{d[P_2]}{dt} = k_2[P_2][O_3] \]  

Dividing Eq. (3) by (4) then integrating the result gives Eq. (5):

\[ \log\left(\frac{[P_1]_t}{[P_1]_0}\right) = k_1/k_2 \log\left(\frac{[P_2]_t}{[P_2]_0}\right) \]  

Thus a plot of $\log([P_1]_t/[P_1]_0)$ vs $\log([P_2]_t/[P_2]_0)$ yields a line whose gradient gives $k_{P1}/k_{P2}$. If one of the rate constants is known, the other can be easily calculated.

In this experiment, the rate constant of BPMC degradation by $O_3$ was determined from the pseudo-first order reaction model. The other rate constants were then determined from the competition kinetic method using BPMC as the first reference compound due to the difficulty of keeping the quasi-constant concentration of ozone.

EXPERIMENTAL SECTION

Reagents and chemicals

The structures of the 24 pesticides selected are shown in Table 1. The pesticides were partly purchased from Riedel Haen (Seelze, Germany) and partly from Hayashi Co. (Tokyo, Japan). For high-performance liquid chromatography (HPLC), methanol and acetonitrile of HPLC grade and acetic acid of reagent grade were purchased from Wako Co. (Osaka, Japan) and used as supplied. The indigo reagent contained 1 mM sodium indigo trisulfonate in 0.02 M phosphoric acid and was purchased from Aldrich (USA). The other chemicals (NaI, H$_2$SO$_4$, NaH$_2$PO$_4$, Na$_2$S$_2$O$_3$) were of the highest grades commercially available. PIC-B8, of which the main compound is sodium octanesulfonate was from Waters (Japan), and the 5% solution of dimethylchlorosilane in toluene used for silanization of glassware was from SUPELCO.

Experimental procedures

The experiments were carried out in a batch-agitated glass reactor. The ozone-oxygen mixture was produced in an ozone generator with an oxygen cylinder as gas source.
A coarse-sintered glass dispersion tube was used for delivering the ozone–oxygen gas mixture. The reactor was placed in a water bath to keep the reaction temperature at 20°C. Effluent gas was introduced into a gas absorption bottle containing 2% KI solution to kill excess ozone. Synthetic raw water was prepared by dissolving 3.5 mg of a standard pesticide into 7 L Milli-Q pure water containing 0.001 M phosphoric acid. After pH was adjusted to 6 by adding sodium hydroxide, 100 μM NaHCO₃ was added to the solution dropwise to obtain a final pH of 7.5. These conditions were used to simulate average natural waters. Before feeding the ozone–oxygen mixture into the reactor, the gaseous ozone concentration was measured iodometrically (Kolthoff and Belcher, 1957). From the time the ozone–oxygen mixture began to be continuously fed into the reactor, samples were taken out at 1-min intervals for the whole 15-min reaction time to analyze the ozone and pesticide concentrations in the solution. The constant gaseous and dissolved ozone concentrations obtained in each reaction are shown in Table 2.

The concentrations of dissolved ozone were measured colorimetrically by the indigo method (Bader and Hoigne, 1981). Adsorption measurements were performed at 600 nm with a Model UV-160A UV-visible recording spectrophotometer (Shimadzu, Kyoto, Japan). The residual concentrations of pesticides were determined by HPLC (HP1090) directly after ozone in solution was decomposed to oxygen by adding Na₂S₂O₃ equivalent to the amount of residual ozone. Except for the analysis of diquat, liquid chromatography was carried out at a flow rate of 1 ml/min on a Develosil ODS-HG-5 column (4.6 mm I.D. × 150 mm, Nomura, Japan) under the conditions as shown in Table 2 with a column temperature of 40°C. The concentration of diquat was analyzed on a column of Supelco pKb-100 (4.6 mm I.D. × 150 mm, SUPELCO) by an ion-pairing HPLC method (ion-pairing agent: sodium octanesulfonate). Silanization of all glassware was carried out to prevent adsorption of the diquat cations onto glass surfaces. The injection volume was 250 μl.

**Calculations**

Molecular orbital calculations were carried out on a Power Macintosh 7500/100 computer using the CAChe Ver.3.9 package (CAChe Scientific, Oxford) which executes quantum mechanical calculations at a semi-empirical level based on the MOPAC 6.0 package (Stewart, 1990). The PM3 (Stewart, 1989) parametrizations of atomic wave-functions were implemented.

**RESULTS AND DISCUSSION**

**Determination of rate constants**

The experiment was performed at a pH of 7.5 and bicarbonate concentration of 100 μM. Before
determining the rate constant of the first reference substance of BPMC based on the pseudo-first order reaction model, the time needed to obtain a constant dissolved ozone concentration was investigated. We plotted the variation in concentration of dissolved ozone with time in a solution initially containing 2.4 mM BPMC under a condition of continuous ozone supply (Fig. 1). A constant dissolved ozone concentration of ca 7 mM was achieved in 5 min, when the BPMC concentration had decreased to 0.82 mM. Treating the 5th minute as the initial reaction time, a plot of log\[BPMC\]t/\[BPMC\]0 vs reaction time was obtained as shown (Fig. 2), which gives Eq. (6) of the pseudo-first order reaction model. The gradient of the plot gives \( k'p \) in Eq. (2). The absolute reaction rate constant for oxidation of BPMC can be derived to be 266.0 M\(^{-1}\) s\(^{-1}\) from \( k'p \) and the average dissolved ozone concentration of 7.7 mM (CV < 10%).

\[
\log[\text{BPMC}]_t/\text{[BPMC]}_0 = 0.12t + 0.03 \tag{6}
\]

The reaction rate constants of the other pesticides examined in this study were determined based on the competition kinetic method using BPMC as the first reference compound. The relationship between log\[BPMC\]t/\[BPMC\]0 and respective log\[P\]t/\[P\]0 of cyanazine, simazine, bromobutide, and NAC (Fig. 3) confirmed that the competition kinetic method fitted each of the ozonation reactions with a correlation coefficient higher than 0.99 suggesting that the competition kinetic method is a good model to determine rate constants to high accuracy. Using Eq. (5), each individual absolute reaction rate constant can be derived from the gradient of each respective plot shown in Fig. 3. Due to difficulties experienced in analyzing BPMC in the presence of other herbicides, subsequent experiments to determine reaction rate constant were conducted with different pairs of herbicides as shown in Table 3. The rate constants varied widely in accordance with the structures of the pesticides. Those from the group of phenolic pesticides seemed to be

**Table 2. HPLC conditions for determining residual concentration of pesticides in treated water and conditions of ozonation**

<table>
<thead>
<tr>
<th>No.</th>
<th>Pesticides (P)</th>
<th>CH\text{CN}/buffer(^a)</th>
<th>Wave length (nm)</th>
<th>RT (min)</th>
<th>Ozone concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>PCP(warfarin)</td>
<td>55/45(68/32)</td>
<td>215.4</td>
<td>11.8</td>
<td>2.11 ND</td>
</tr>
<tr>
<td></td>
<td>Warfarin(bentazone)</td>
<td>32/68(25/75)</td>
<td>210.4</td>
<td>30.2</td>
<td>1.1 0.01(43)</td>
</tr>
<tr>
<td></td>
<td>Dinoseb</td>
<td>50/50</td>
<td>270.4</td>
<td>6.5</td>
<td>1.6 ND</td>
</tr>
<tr>
<td></td>
<td>Dinoterb(bentazone)</td>
<td>60/40(25/75)</td>
<td>270.4</td>
<td>7.5</td>
<td>1.1 0.01(57)</td>
</tr>
<tr>
<td>B</td>
<td>Dicamba(NAC)</td>
<td>20/80(30/70)</td>
<td>210.4</td>
<td>3.8</td>
<td>2.3 0.08(34)</td>
</tr>
<tr>
<td></td>
<td>MCPA</td>
<td>40/60</td>
<td>230.4</td>
<td>5.7</td>
<td>1.0 0.05(20)</td>
</tr>
<tr>
<td></td>
<td>MCPP</td>
<td>35/65</td>
<td>236.4</td>
<td>13.0</td>
<td>2.4 0.10(25)</td>
</tr>
<tr>
<td></td>
<td>2,4-D</td>
<td>40/60</td>
<td>210.4</td>
<td>3.2</td>
<td>2.5 0.36(14)</td>
</tr>
<tr>
<td></td>
<td>2,4,5-T</td>
<td>27/73</td>
<td>210.4</td>
<td>13.9</td>
<td>2.6 0.14(21)</td>
</tr>
<tr>
<td></td>
<td>MCPB</td>
<td>45/55</td>
<td>230.4</td>
<td>20.4</td>
<td>2.0 0.12(22)</td>
</tr>
<tr>
<td></td>
<td>2,4,5-TP</td>
<td>73/27</td>
<td>210.4</td>
<td>8.7</td>
<td>2.4 0.14(19)</td>
</tr>
<tr>
<td></td>
<td>Dichlorprop</td>
<td>30/70</td>
<td>210.4</td>
<td>11.6</td>
<td>2.5 0.11(33)</td>
</tr>
<tr>
<td>C</td>
<td>Bentazone</td>
<td>30/70</td>
<td>220.4</td>
<td>6.3</td>
<td>1.7 0.10(41)</td>
</tr>
<tr>
<td></td>
<td>NAC</td>
<td>45/55</td>
<td>220.4</td>
<td>5.1</td>
<td>2.5 0.20(46)</td>
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<tr>
<td></td>
<td>Silduron</td>
<td>40/60</td>
<td>236.4</td>
<td>11.8</td>
<td>2.5 0.12(42)</td>
</tr>
<tr>
<td></td>
<td>Carbofuran</td>
<td>45/55</td>
<td>210.4</td>
<td>4.6</td>
<td>2.6 0.30(21)</td>
</tr>
<tr>
<td></td>
<td>Linuron</td>
<td>45/55</td>
<td>210.4</td>
<td>9.4</td>
<td>2.9 0.07(41)</td>
</tr>
<tr>
<td></td>
<td>BPMC</td>
<td>50/50</td>
<td>210.4</td>
<td>6.6</td>
<td>2.2 0.37(4.6)</td>
</tr>
<tr>
<td></td>
<td>Ipodione</td>
<td>50/50</td>
<td>215.4</td>
<td>18.7</td>
<td>2.4 0.32(19)</td>
</tr>
<tr>
<td></td>
<td>Bromobutide</td>
<td>55/45</td>
<td>210.4</td>
<td>8.7</td>
<td>2.4 0.34(23)</td>
</tr>
<tr>
<td>D</td>
<td>Simazine</td>
<td>30/70(45/55)</td>
<td>220.4</td>
<td>6.6</td>
<td>2.6 0.39(23)</td>
</tr>
<tr>
<td></td>
<td>Atrazine</td>
<td>30/70</td>
<td>220.4</td>
<td>5.2</td>
<td>2.0 0.34(28)</td>
</tr>
<tr>
<td></td>
<td>Diquat</td>
<td>20/80(25/75)(^b)</td>
<td>308.4</td>
<td>20.1</td>
<td>6.5 1.30(22)</td>
</tr>
<tr>
<td></td>
<td>Cyanazine</td>
<td>40/60(50/50)</td>
<td>220.4</td>
<td>3.7</td>
<td>2.6 0.36(24)</td>
</tr>
</tbody>
</table>

\(^a\)0.025MKH\text{PO}_{4}+H\text{PO}_{4}, \text{pH}=3.2.

\(^b\)\text{CH}_{3}\text{OH}/2 \text{mM PIC-B8}.

\(^c\)The variation (%) of aqueous concentration (mg/l) upon determining the rate constants of pesticides.
most easily decomposed by ozone, and PCP in this group showed the highest rate constant of 27,600 M\(^{-1}\) s\(^{-1}\) (Table 3). On the other hand, those from the group of heterocyclic N-pesticides were found to be the most difficult to decompose by ozone; the pesticide with the lowest rate constant was cyanazine (60.8 M\(^{-1}\) s\(^{-1}\)).

Comparison with literature values

Of the 24 pesticides examined in this study, rate constants of five pesticides have also been determined by Xiong and Graham (1992), (Table 3). The absolute rate constants we found were significantly higher than their literature counterparts. However, the times of the rate constants obtained in this study to the literature values remained almost unchanged for each pesticide (Fig. 4). Note that the literature values of the five pesticides were obtained using purine as the first reference compound. Moreover, the rate constant of purine was obtained at a bicarbonate concentration of 0.01 M in 0.2 M phosphate buffer, which were respectively 200 and 100 times higher than those used in our study. Since phosphate and bicarbonate ions are well known radical scavengers (Black and Hayon, 1970), it is possible that the differences of phosphate and bicarbonate concentrations resulted in the significant differences between the rate constants found in this study and those in the literature.

Correlation between rate constants with \(E_{HOMO}\)

When two reactants approach each other, a mutual perturbation of the molecular orbitals of both reactants occurs. According to the frontier orbital theory (Fukui et al., 1952; 1957), the reactivity of reactants is largely dependent on the energies of the frontier molecular orbitals, that is, the energies of HOMO and the lowest empty molecular orbital (LUMO). The smaller the difference in energy between the HOMO of the nucleophile (\(E_{HOMO}\)) and the lowest empty molecular orbital (LUMO) of the electrophile (\(E_{LUMO}\)), the larger the reactivity will be. Because ozone is a strong electrophile with \(E_{HOMO}\) of \(-13.0\) eV and \(E_{LUMO}\) of \(-2.216\) eV, it can be expected that a pesticide with a high \(E_{HOMO}\) will have a high rate constant of ozonation. There are numerous successful quantitative structure-activity applications in environmental fields, and most are established for substituted phenols based on the correlation between rate constants and oxidation potentials or \(\sigma\) constants. In this study, we chose the energy of the frontier molecular orbitals as the predictor to correlate with the ozonation rate constants for pesticides of diverse structures.

The \(E_{HOMO}\) values of the 24 objective pesticides calculated by the semi-empirical quantum mechanical method are given in Table 3 along with their kinetic parameters determined in this study. The logarithms of the rate constants of the four heterocyclic N-pesticides were plotted as a function of \(E_{HOMO}\) (Fig. 5). The rate constants correlate very
strongly with the $\epsilon_{\text{HOMO}}$ values and the following linear relationship was obtained:

$$
\log k_p = 0.79 \epsilon_{\text{HOMO}} + 9.2 \quad (n = 4, r^2 = 0.998, s = 0.04)
$$

(7)

The rate constants of atrazine and simazine have also been reported in the literature (Bolzacchini et al., 1994). The different rate constants of the two pesticides were explained as being due to steric effects. However, Fig. 5 indicated that the difference in reactivity of the two pesticides could be accounted for by the difference of their $\epsilon_{\text{HOMO}}$ values. From the correlation between the logarithm of the rate constants of the eight organonitrogen pesticides and the corresponding $\epsilon_{\text{HOMO}}$ values (Fig. 6), and that of the four phenolic pesticides (Fig. 7) we determined the relationships between $k_p$ and $\epsilon_{\text{HOMO}}$ values of these two pesticide classes (Eqs. (8) and (9), respectively).

$$
\log k_p = 0.37 \epsilon_{\text{HOMO}} + 5.9 \quad (n = 8, r^2 = 0.91, s = 0.06)
$$

(8)

$$
\log k_p = 0.97 \epsilon_{\text{HOMO}} + 11.3 \quad (n = 4, r^2 = 0.92, s = 0.23)
$$

(9)

Comparing Eqs. (7), (8), and (9), we found that the gradient of Eq. (9) was the largest, which suggests that the reactivity of the phenolic pesticides was most dependent on the $\epsilon_{\text{HOMO}}$ values, and vice versa for the organonitrogen pesticides. On the other hand, for the 8 phenoxyalkylacetic pesticides, the $\epsilon_{\text{HOMO}}$ values ranged from $-8.937$ to $-9.465$ eV, and the rate constants varied from 183 to 376 $\text{M}^{-1} \text{s}^{-1}$. No linear relationship between rate constants and $\epsilon_{\text{HOMO}}$ values was obtained. It is necessary to consider some other factors besides the relationship between rate constants and $\epsilon_{\text{HOMO}}$ values in order to get a complete understanding about such oxidation reactions.

Finally, the rate constants of all 24 pesticides were plotted against their respective $\epsilon_{\text{HOMO}}$ values (Fig. 8). It is clear that although some difference existed among the four groups, the trend that a higher $\epsilon_{\text{HOMO}}$ gives a higher $k_p$ applied to all of the
pesticides, and the rate constants can be estimated by the following equation.

$$\log k_p = 0.92 \epsilon_{\text{HOMO}} + 10.8 \quad (n = 24, \quad r^2 = 0.84, s = 0.27)$$

The dependence of rate constants of pesticides on $\epsilon_{\text{HOMO}}$ shows that the reaction between pesticide and ozone was controlled by the frontier orbital effect connected with partly covalent bonding in the transition state.

**Correlation between rate constants with absolute electronegativity**

The parameters of phenoxyalkylacitic pesticides in Table 3 show that the maximum variance for the LUMO energy reaches 0.892 eV, while the maximum variance of HOMO energy is 0.528 eV. Attempts to estimate rate constants by using the HOMO and LUMO energies yielded a correlation that was statistically satisfactory as shown in Fig. 9 and Eq. (11).

$$\log k_p = -0.116 \epsilon_{\text{HOMO}} + 0.351 \epsilon_{\text{LUMO}} + 1.510$$

$$\quad (n = 8, r^2 = 0.97, s = 0.0208)$$

To reasonably explain the significance of Eq. (11), the equation was rewritten as Eq. (12).

$$\log k_p = -0.467 \epsilon_{\text{HOMO}} - 0.702 \chi + 1.510$$

where $\chi$ is the absolute electronegativity. Parr and Pearson (1983) defined absolute electronegativity:

$$\chi = (I + A)/2 = -(\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$$

where $I$ and $A$ are the ionization potential and electron affinity, which can be approximated by $\epsilon_{\text{HOMO}}$ and $\epsilon_{\text{LUMO}}$ (Stewart, 1989), respectively. From Eq. (12), it is clear that, in the case of phenoxyalkylacitic pesticides, the lower the $\chi$ value, the higher the rate constants. The $\chi$ values of pesticide ranges from 4.44 to 4.99 which is smaller than that of ozone (7.608), so the difference in electronegativities between the two reactants actually drives the reactivity of phenoxyalkylacitic pesticide in ozonation.

**CONCLUSIONS**

We carried out a fundamental study to develop a
simplified method for estimating rate constants of pesticide degradation by ozone. The results of correlation analysis indicated that the reactivity of pesticides with ozone essentially follows the predictions of frontier orbital theory and can be estimated from the energy of the highest occupied molecular orbital ($\epsilon_{\text{HOMO}}$). This was especially true in the case where the correlation model was established based on the classification of pesticides according to their structural features. For phenoxyalkylacitic pesticides, a rate constant with higher accuracy was obtained by a two-parameter QSAR model that used absolute electronegativity and $\epsilon_{\text{HOMO}}$ as predictors.

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