Oxidation of Diazinon by Aqueous Chlorine: Kinetics, Mechanisms, and Product Studies

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The oxidation kinetics and mechanisms of diazinon, an organophosphorus pesticide, by aqueous chlorine were studied under different conditions. The oxidation is of first order with respect to both diazinon and chlorine. The oxidation rate is found to increase with decreasing pH. The second-order rate constants at pH 9.5, 10.0, 10.5, and 11.0 are determined to be 1.6, 0.64, 0.43, and 0.32 $M^{-1} s^{-1}$, respectively. Based on the rate constants at different temperatures, the activation energy is calculated to be 30 kJ/mol at pH 10.0 with a chlorine-to-diazinon ratio of 11:1, 33 kJ/mol at pH 11.0 with a 11:1 ratio, and 36 kJ/mol at pH 11.0 with a 5:1 ratio, respectively. Diazoxon is identified as the oxidation product by GC−MS. Ion chromatography analysis shows an increase of sulfate concentration as the reaction proceeds, indicating that sulfur is being oxidized to sulfate. This study indicates that oxidation by aqueous chlorine can significantly affect the fate of diazinon in the environment.

Keywords: *Diazinon; oxidation; chlorine; diazoxon*

INTRODUCTION

Esters and thioesters of phosphoric acid and thiophosphoric acid are widely used in agricultural practice as insecticides, herbicides, and, on a more limited scale, fungicides (Mortimer and Dawson, 1991). Concern about organophosphorus pesticides arises from the large amount applied and their persistence in the environment since pesticides are not specific for insect acetylcholinesterases but can also affect the nervous systems of humans. Previous studies have been focused on the hydrolysis of organophosphorus pesticides. Hydrolysis is pH- and temperature-dependent (Muehlmann and Schrader, 1957; Faust and Gomaa, 1972; Schwarzenbach et al., 1993) and can be catalyzed or inhibited by oxide surfaces (Torrents and Stone, 1994; Baldwin et al., 1995), dissolved metals and metal-containing surfaces (Mortland and Raman, 1967; Plastourgou and Hoffmann, 1984; Stone and Torrents, 1995; Stone et al., 1995) and metal oxides (Dannenberg and Pehkonen, 1998; Hong and Pehkonen, 1998).

Diazinon, a phosphorothioate commercially introduced in 1952, is used as a pesticide for different types of cultivation such as fruit trees, rice, sugarcane, corn, tobacco, and horticultural plants because of its inhibition of the acetylcholinesterases of most kinds of insects. Figure 1 shows the structure of diazinon. Diazinon is considered moderately toxic: 48-h LC 50 in killifish is 4.4 mg/L (Tsuda et al., 1997). However under certain conditions such as the contamination of hydrocarbon solvent with water (0.1−2%) plus exposure to elevated temperatures, diazinon can deteriorate to harmful substances including monothiotepp (O,S-TEPP) and sulfotepp (S,S-TEPP) which are known to be highly toxic and to have a strong inhibitory effect on cholinesterase enzyme systems (Gysin and Margot, 1958; Sovocool et
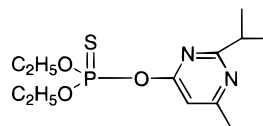

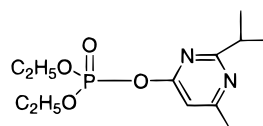**Figure 1.** Structure of diazinon.

Figure 2. Structure of diazoxon.

al., 1981; Soliman et al., 1982). Previous studies found the hydrolysis of diazinon to be relatively slow. Hydrolysis half-life at pH 7.0 and 25 °C is 178 days (Schwarzenbach et al., 1993). The hydrolysis rate also strongly depends on pH and temperature: half-lives at pH 3.1, 5.0, 7.4, 9.0, and 10.4 at 20 °C are 11.77, 740.7, 4435.8, 3263.0, and 144.9 h, respectively; at pH 3.1, the rate constant at 40 °C is larger than the one obtained at 10 °C by a factor of 7 (Faust and Gomaa, 1972). The presence of catalysts also affects the rate of hydrolysis. Dannenberg and Pehkonen (1998) applied ferrihydrite, goethite, and hematite and found both catalytic and inhibitory effects of these compounds under different conditions (i.e., different pH, temperatures, and dosages of catalysts). 2-Isopropyl-4-methyl-6-hydroxypyrimidine is the identified hydrolysis product under both acidic and basic conditions (Muhlmann and Schrader, 1957; Faust and Gomaa, 1972; Dannenberg, 1996).

For the oxidation of diazinon, previous studies were focused on ozonation. Ohashi et al. (1994) applied ozonation in the aqueous phase and found that diazoxon (Figure 2) was the oxidation product. They proposed that sulfur was oxidized to sulfate in solution after it was released from the diazinon molecule and that diazoxon was further hydrolyzed to diethyl phosphate

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and 2-isopropyl-4-methyl-6-hydroxylpyrimidine; these two compounds further degraded to acetic acid and formic acid. Ku et al. (1998) also studied the ozonation of diazinon in aqueous solution. They concluded that ozonation had been shown to be feasible for achieving nearly complete degradation of diazinon within 1 h. Their kinetic results showed that pH, temperature, and alkalinity had little influence on the ozonation of diazinon. According to the analyses by Tsuda et al. (1997), 48-h LC 50 in killifish for diazoxon is 0.22 mg/L, meaning that diazoxon is more toxic than diazinon. Faust and Gomaa (1972) also mentioned diazoxon as the oxidation product of diazinon. They pointed out that the anti-acetylcholinesterase activity of diazoxon proved to be higher than that of diazinon. According to a thorough literature search, none of the aforementioned studies investigated the reaction kinetics or mechanisms of diazinon oxidation by aqueous chlorine.

The current study is intended to evaluate the oxidation kinetics, mechanisms, and product(s) of diazinon by aqueous chlorine. Hypochlorite is used as the oxidant since it is the most commonly utilized reagent for disinfection (Montgomery, 1985) in both wastewater and drinking water treatment plants. The contact time usually ranges from 15 to 45 min (Tchobanoglous and Burton, 1991). Some treatment plants discharge the treated water without dechlorination. Since Amato et al. (1992) observed diazinon in municipal wastewater, it is very possible for diazinon to be oxidized by aqueous chlorine either in treatment plants or in ambient water systems immediately after treatment. The rates, mechanisms, and product(s) of diazinon oxidation by aqueous chlorine will assist in assessing the fate of diazinon in aquatic environments.

MATERIALS AND METHODS

Oxidation Experiments. Diazinon was obtained from Supelco (Bellefonte, PA) at 99% purity. Diazoxon was obtained from Chemservice (Westchester, PA) at 96% purity. Sodium hypochlorite solution (13%) was purchased from Aldrich (Milwaukee, WI). The hypochlorite solution was titrated periodically using DPD ferrous titrimetric method (Eaton et al., 1995) to measure the accurate concentration of chlorine because of the concern over the decomposition of chlorine with time.

Amber Pyrex bottles (to prevent the exposure to light which can decompose chlorine) of 250-mL size were used as reactors. Solutions were prepared from 18 MΩ cm water (deionized and distilled); 0.01 M phosphate (for pH 11.0) or borate buffer (for pH 9.5, 10.0, and 10.5) was used to cover the pH range. The initial concentration of diazinon was 6.58×10^{-5} M. Sodium hypochlorite was added 6–12 h after diazinon was mixed with buffer to make sure of the thorough dissolution of diazinon. The pH was monitored throughout the experiments and adjusted with concentrated sulfuric acid or sodium hydroxide. Samples were withdrawn periodically covering at least two half-lives (i.e., the final concentration of diazinon in the reaction mixture was one-fourth of the original concentration). Sodium sulfite was used to consume the extra chlorine in withdrawn samples, thus quenching further oxidation. Oxidation of diazinon was monitored by extracting a 10-mL aliquot of the stirred reaction mixture with 1.5 mL of benzene containing 4-chloro-3-methylphenol (Aldrich) as the internal standard for GC.

One experiment at pH 10.5 and 27 °C with sodium carbonate as the buffer (at a concentration of 0.01 M) was conducted to check if chlorine radicals were involved in the reactions since carbonate is an effective radical scavenger (Buxton et al., 1988). If radicals were involved in the reactions, the rate constant obtained in this experiment would be significantly lower than the rate constants observed in the experiments using borate as the buffer.

Chlorine Demand of Water and Reactors. Chlorine demand of deionized and distilled water and reactors can cause the real amount of chlorine reacting with diazinon to be lower than the calculated one since the water and reactors can consume a portion of the chlorine. The procedure for checking the chlorine demand of deionized and distilled water was as follows: Sodium hypochlorite at a concentration of 1.34×10^{-4} M was added in 0.01 M phosphate or borate buffer which was made with distilled and deionized water and stirred for 2–3 h. The solution was left under ultraviolet lamp for 6–8 h to decompose chlorine because chlorine is highly photoreactive at ultraviolet wavelengths of about 2600 Å and decomposes quickly (Scarpino et al., 1972). After the decomposition, the buffer was tested with the DPD ferrous titrimetric method (Eaton et al., 1995) to make sure there was no chlorine left in it. The buffer was chlorine-demand-free and used to conduct control experiments. To check the chlorine demand of the amber Pyrex reactors, a buffer with 6.71×10^{-4} M sodium hypochlorite was filled in a reactor bottle and kept stirring for 2–3 h. Then the reactor bottle was emptied and dried in the air. Later the control experiment was carried out in this chlorine-demand-free reactor.

GC and GC–MS Analyses. HP 5890 series II GC with an FID detector (Hewlett-Packard Co., Palo Alto, CA) was used for GC analysis. GC conditions were as follows: 30- × 0.53-mm i.d. fused silica capillary column with 1.5-μm film thickness (DB-5, J&W Scientific, Folsom, CA) and a carrier gas of nitrogen (10 psi) were used; initial temperature was 130 °C for 1 min; temperature increased at 17 °C/min up to 220 °C for 3 min; injector port temperature was 250 °C; detector temperature was 300 °C. GC standards for diazinon were prepared by making aqueous solutions of diazinon at 2.3×10^{-5}, 4.6×10^{-5}, 8.2×10^{-5}, and 1.4×10^{-4} M; 10 mL of solution was extracted with 1.5 mL of benzene containing the internal standard.

HP 5890 series II GC with HP 5970 MS detector (Hewlett-Packard) was used for GC–MS analysis. GC–MS conditions were as follows: 30-m × 0.25-mm i.d. fused silica capillary column with 0.25-μm film thickness (DB-5ms, J&W Scientific) and a carrier gas of helium (5.5 psi) were used; initial temperature was 80 °C; temperature increased at 3 °C/min up to 160 °C; injector port temperature was 225 °C; detector temperature was 250 °C. After the last sample was taken for the kinetics determination, the remaining reaction mixtures were extracted with benzene and served as GC–MS samples. Neat diazoxon was dissolved in benzene and subjected to GC–MS analysis as a standard.

Ion Chromatography Analysis for Sulfate Concentration. Sulfate concentrations in the reaction mixtures were analyzed with ion chromatography to check the valence state of sulfur after it was released from the diazinon molecule. The analysis was performed by Environmental Enterprises Inc. (Cincinnati, OH). The experiments were conducted at pH 10.5 with 7.79×10^{-4} M sodium hypochlorite. Since sulfite will be oxidized to sulfate by chlorine and therefore increases the concentration of sulfate, ferrous bromide was used instead of sodium sulfite to consume the extra chlorine in the samples.

Kinetic Concept. The rate law and its constants for the following reaction have been determined in this study:

$$a \text{ diazinon} + b \text{ chlorine} \rightarrow c \text{ product(s)} \quad (1)$$
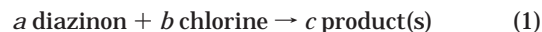
In the above equation, a is the reaction order with respect to diazinon and b is the reaction order with respect to aqueous chlorine. To get a and b, various dosages of sodium hypochlorite were used. For all kinetic measurements, initial molar concentration ratios of sodium hypochlorite to diazinon were varied from 3:1 to 20:1. Therefore, a and b could be obtained by eq 2:

$$\frac{-\text{d[diazinon]}}{\text{d}t} = k_{\text{r}}[\text{diazinon}]^a[\text{chlorine}]^b \quad (2)$$

For a first-order reaction in terms of diazinon,

$$\ln[\text{diazinon}] = k_{\text{obs}}t \tag{3}$$

where k_{obs} equals $k_r[\text{chlorine}]^b$, and k_r is the second-order rate constant.

Thermodynamic Approach. Oxidation reactions were carried out at four temperatures, room temperature (~ 26 °C), low temperatures of ~ 0 and 15 °C, and an elevated temperature of 34 °C, in order to study the effect of temperature on the oxidation rate and to obtain the activation parameters. Experiments at 0, 15, and 34 °C were conducted in large beakers filled with ice, a temperature-controlled cold room, and a thermostatically controlled water bath, respectively. These experiments were conducted under three conditions: at pH 11.0 with chlorine-to-diazinon ratio of 5:1, at pH 11.0 with a chlorine-to-diazinon ratio of 11:1, and at pH 10.0 with a chlorine-to-diazinon ratio of 11:1. According to eq 4:

$$\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^-, \quad K_A = 10^{-7.5} \tag{4}$$

the distribution of hypochlorous acid (HOCl) and hypochlorite ion (OCl$^-$) will change with pH, thus an understanding about the thermodynamic characteristics of the oxidation of diazinon with respect to hypochlorous acid and hypochlorite ion can be obtained. As a result, k_r can be expressed as

$$k_r = k_0[\text{HOCl}]/[\text{Cl}]_T + k_1[\text{OCl}^-]/[\text{Cl}]_T \tag{5}$$

The activation enthalpy, $\Delta H^{\ddagger}$, was determined by measuring the rate of reaction at four temperatures and plotting $\ln(k_r/T)$ versus $1/T$ based on eq 6; the activation entropy, $\Delta S^{\ddagger}$, was calculated according to eq 7. Arrhenius equation (eq 8) was used to calculate the activation energy by plotting $\ln k_r$ versus $1/T$ (Carey and Sundberg, 1984):

$$\ln(k_r/T) = -\Delta H^{\ddagger}/RT + \text{constant} \tag{6}$$

$$\Delta S^{\ddagger} = (\Delta H^{\ddagger}/T) + [R\ln(hk_r/\mathcal{K}kT)] \tag{7}$$

$$k_r = Ae^{-E_a/RT} \tag{8}$$

here k is Boltzmann constant, h is Planck's constant, and $\mathcal{K}$ is the transmission coefficient (~ 1).

Effect of pH on Kinetics. pH of 9.5, 10.0, 10.5, and 11.0 were selected to study the effect of pH on the oxidation rate. The reason for choosing 9.5 as the lowest pH was that oxidation at pH lower than 9.5 is so quick that the rate constants cannot be measured. However, based on pH and the percentage distribution of hypochlorous acid and hypochlorite ion, the oxidation rate constants of diazinon with these two species separately were calculated according to eq 4. Finally, the oxidation rate constant of diazinon by aqueous chlorine at any pH can be obtained by calculation according to eq 5.

RESULTS AND DISCUSSION

Reaction Order. For each experiment, plotting ln [diazinon] versus time resulted in a linear profile. This indicates that the oxidation is a first-order reaction with respect to diazinon. The determination of the rate constant of the experiment at pH 10.0 and room temperature is shown in Figure 3. Figure 4 is the plot of log k_{obs} versus log [chlorine]$_T$. Since the slope of the linear curve is close to 1, one can see that the oxidation with respect to chlorine is also a first-order reaction.

Oxidation Kinetics. Oxidation rate constants at four pH values at a chlorine dosage of 7.79×10^{-4} M (the molar concentration ratio of chlorine to diazinon is 11:1) are listed in Table 1. The calculated rate constants of k_0, k_1, and k_r at pH 7.0 and 8.0 are listed in Table 2. At pH 7.0 and 8.0, the second-order rate constant is 101
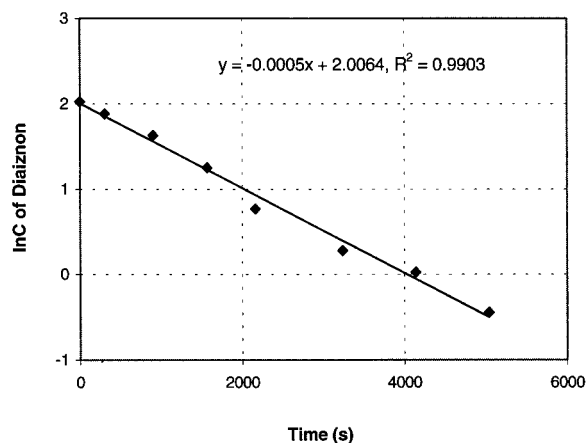

Figure 3. Oxidation of diazinon at pH 10.0 and 25.8 °C with 7.79×10^{-4} M sodium hypochlorite.
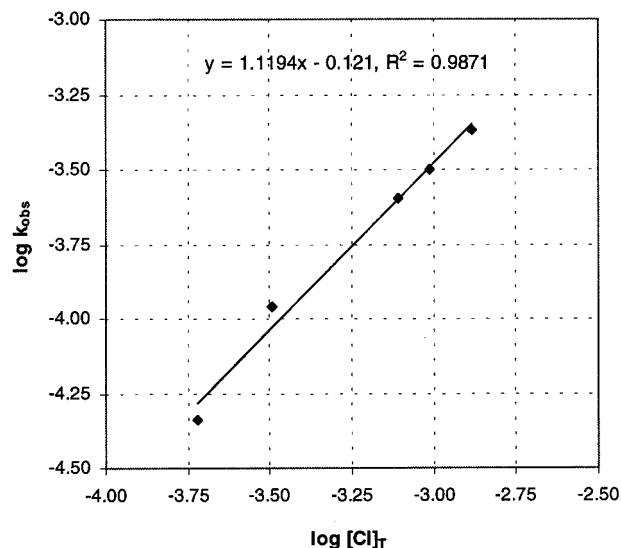

Figure 4. Reaction order with respect to chlorine.

Table 1. Oxidation Rate Constants at Different pH Values at Room Temperature at a Chlorine Dosage of 7.79×10^{-4} M

reaction conditions	$k_r \pm \text{SD}^a$ (M^{-1} s^{-1})	no. of expt
pH 9.5	1.6 ± 0.42	3
pH 10.0	0.64 ± 0.030	3
pH 10.5	0.43 ± 0.080	3
pH 11.0	0.32 ± 0.014	4

^{a} SD, standard deviation.

Table 2. Calculated Oxidation Rate Constants

constant	k (M^{-1} s^{-1})
$k_0{}^a$	130
$k_1{}^b$	0.27
k_r at pH 7.0	101
k_r at pH 8.0	32.0

^{a} k_0 is the intrinsic rate constant when diazinon is oxidized by hypochlorous acid. ^{b} k_1 is the intrinsic rate constant when diazinon is oxidized by hypochlorite ion.

and 32.0 M^{-1} s^{-1}, respectively. The typical chlorine residual after 15 min of contact time in the treatment plants is 0.5 mg/L which equals 7.0×10^{-6} M (Tchobanoglous and Burton, 1991). Using this value for a calculation, the oxidation half-life of diazinon is just 16.4 min at pH 7.0 and 51.6 min at pH 8.0. Compared to the hydrolytic half-life at pH 7.0, which is 178 days, oxidation by aqueous chlorine is much faster than hydrolysis.

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Table 3. Oxidation Rate Constants of Chlorine Demand Experiments

reaction conditions	description	k_r (M^{-1} s^{-1})
pH 9.5, 7.79×10^{-4} M NaClO, 27.0 °C	chlorine demand of the water	1.3
pH 10.0, 7.79×10^{-4} M NaClO, 27.0 °C	chlorine demand of the water	0.68
pH 11.0, 7.79×10^{-4} M NaClO, 27.2 °C	chlorine demand of the water	0.35
pH 10.5, 7.79×10^{-4} M NaClO, 27.1 °C	chlorine demand of the reactor	0.37

**Table 4. Oxidation Rate Constants under Different Temperature, pH, and Chlorine Dosages**

reaction conditions	$k_r \pm SD^a$ (M^{-1} s^{-1})	no. of expt
pH 10.0, 7.79×10^{-4} M NaClO, 0.8 °C	0.22 ± 0.028	3
pH 10.0, 7.79×10^{-4} M NaClO, 14.5 °C	0.35 ± 0.050	3
pH 10.0, 7.79×10^{-4} M NaClO, 33.9 °C	0.94 ± 0.039	3
pH 11.0, 3.22×10^{-4} M NaClO, 0.6 °C	0.088 ± 0.024	3
pH 11.0, 3.22×10^{-4} M NaClO, 13.7 °C	0.18 ± 0.028	3
pH 11.0, 3.22×10^{-4} M NaClO, 33.9 °C	0.48 ± 0.057	3
pH 11.0, 7.79×10^{-4} M NaClO, 0.6 °C	0.094 ± 0.027	3
pH 11.0, 7.79×10^{-4} M NaClO, 12.9 °C	0.14 ± 0.017	3
pH 11.0, 7.79×10^{-4} M NaClO, 34.3 °C	0.48 ± 0.029	3

^{a} SD, standard deviation.

The rate constant of the oxidation using sodium carbonate as the buffer is 0.33 M^{-1} s^{-1}. This value is quite close to the average rate constant under the same temperature and pH conditions with borate as the buffer, which is 0.43 M^{-1} s^{-1}. This indicates that there are probably no chlorine radicals involved in the oxidation of diazinon by aqueous chlorine.

Chlorine Demand of Water and Reactors. The observed rate constants using chlorine-demand-free buffer (see Table 3) at pH 9.5, 10.0, and 11.0 are 1.26, 0.68, and 0.35 M^{-1} s^{-1}, respectively. Not one of these values is significantly larger than the corresponding average rate constants listed in Table 1. This indicates that the deionized and distilled water has no significant chlorine demand. The observed rate constant obtained by using chlorine-demand-free reactor is 0.37 M^{-1} s^{-1}, which is even smaller than the average oxidation rate constant at pH 10.0, which is 0.43 M^{-1} s^{-1}. Therefore, the amber glass reactors can also be considered chlorine-demand-free.

Activation Parameters. Oxidation rate constants obtained under three reaction conditions are shown in Table 4. A plot of ln k_r versus $1/T$ under these conditions is shown in Figure 5. Figure 6 is the plot of ln k_r/T versus $1/T$ under the same conditions. R^2 of each curve is greater than 0.95 except the one at pH 11.0 with a chlorine-to-diazinon ratio of 11:1 in Figure 6. Activation energies, enthalpies, and entropies are listed in Table 5. Activation parameters for the hydrolysis of diazinon are shown in Table 6 for comparison. Activation energy is the energy difference between reactant molecules in the ground state and the transition state. It determines how rapidly the reaction occurs: a large activation energy corresponds to a large energy difference between ground states and transition states and results in a slow reaction because few reacting molecules collide with enough energy to climb the high activation energy barrier; a small activation energy results in a rapid reaction since almost all reacting molecules are energetic enough to climb to the transition state (McMurry, 1992). Activation energies obtained in this study (Table 5) are smaller than those of hydrolysis of diazinon (Table 6), which indicates that the energy requirements for the
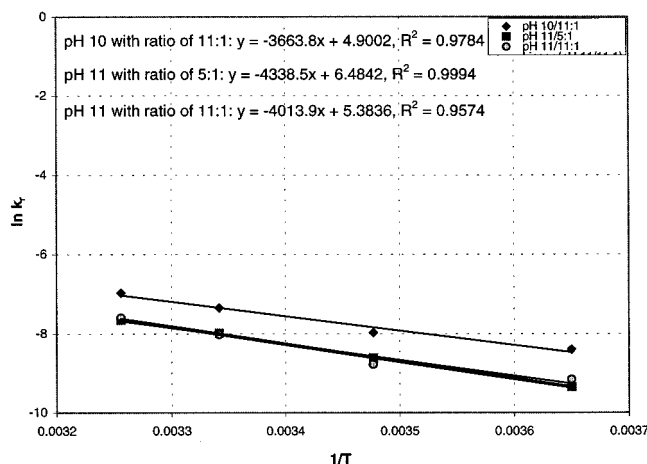
Figure 5. Determination of activation energies under three reaction conditions.
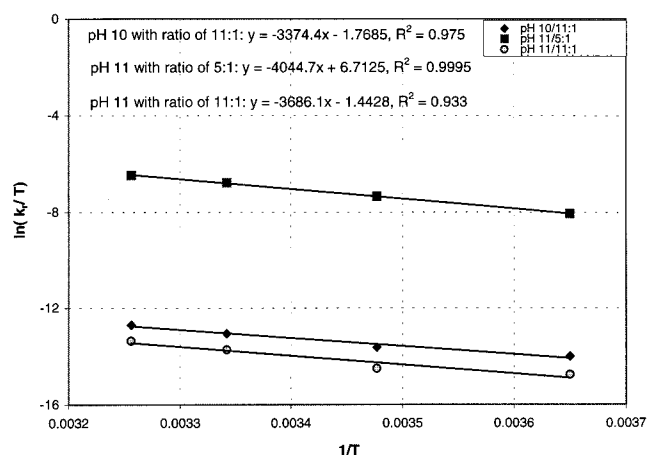
Figure 6. Determination of activation enthalpies under three reaction conditions.

Table 5. Thermodynamic Parameters for Oxidation of Diazinon

parameter	pH 10.0/ ratio 11:1	pH 11.0/ ratio 5:1	pH 11.0/ ratio 11:1
$\Delta H^{\ddagger}$ (kJ/mol)	28	33	31
E_a (kJ/mol)	30	36	33
$\Delta S^{\ddagger}$ (kJ/mol × K)	−0.21	−0.21	−0.19

Table 6. Thermodynamic Parameters for Hydrolysis of Diazinon^a

parameter	pH 5.7	pH 8.5
$\Delta H^{\ddagger}$ (kJ/mol)	77	120
E_a (kJ/mol)	80	130
$\Delta S^{\ddagger}$ (kJ/mol × K)	−0.11	0.030

^{a} Data from Dannenberg (1996).

formation of intermediates during the oxidation of diazinon are lower. This is in agreement with the much faster oxidation rates compared to hydrolysis rates. Based on the same principle, the activation energy at pH 10.0 is smaller than that at pH 11.0 indicating that the reaction of diazinon with hypochlorite ion is more energy-demanding. It should be noted that the activation entropies under the three conditions are very similar (Table 5). Since the entropy of activation is a measure of the degree of order (i.e., negative $\Delta S^{\ddagger}$) or disorder (i.e., positive $\Delta S^{\ddagger}$) produced in the formation of the activated complex, it is reasonable to conclude that the order produced in the formation of the activated
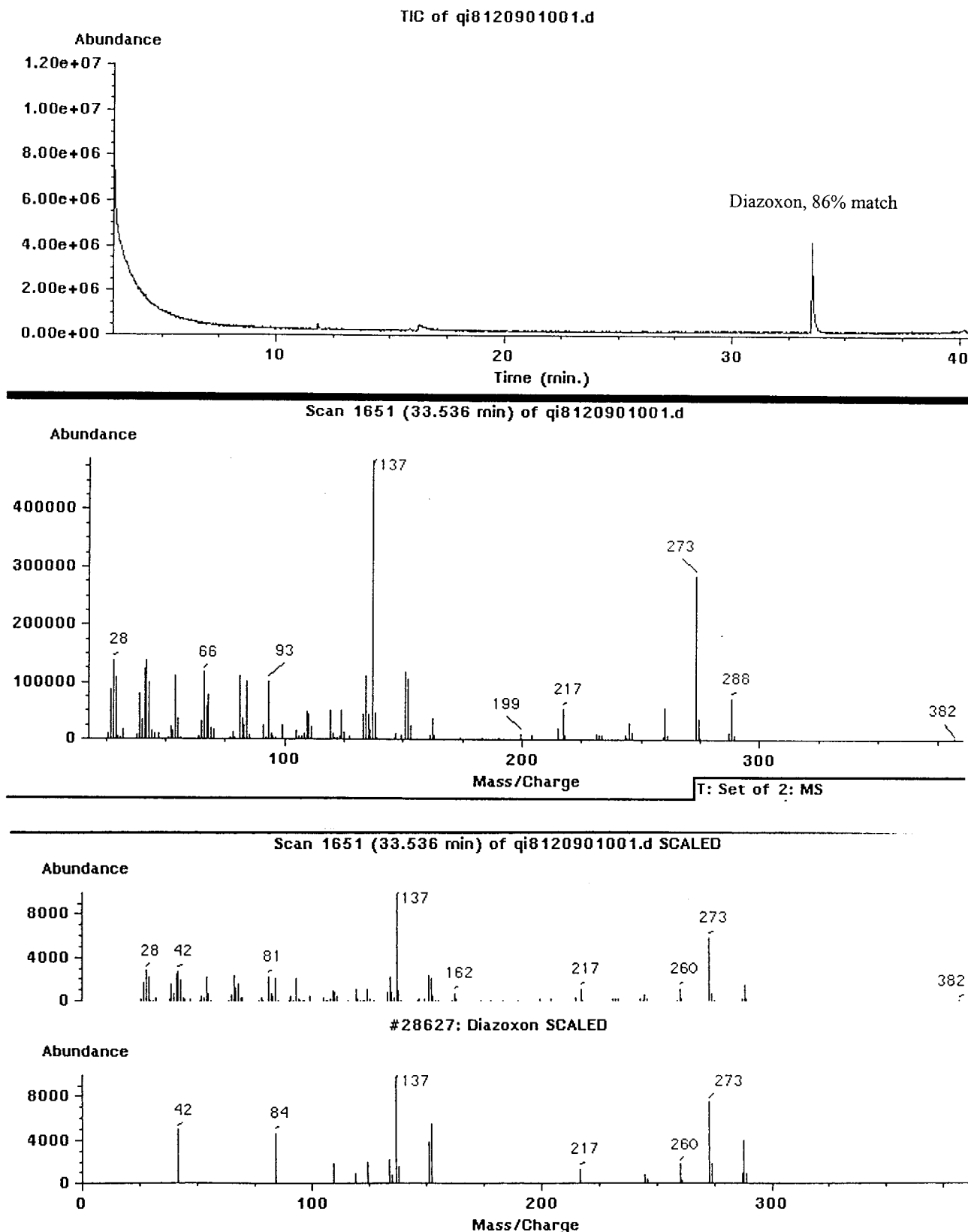
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Figure 7. GC—MS spectra of diazoxon standard and a reaction mixture.

complexes at both pH 10 and 11 is roughly at the same degree. Furthermore, because of the negativity of the entropies, we can conclude that these oxidation reactions involve a loss of translational, vibrational, or rotational degrees of freedom in going to the transition state since there is a decrease in the activation entropy of the system (Carey and Sundberg, 1984).

Effect of pH on Kinetics. The second-order rate constants at pH 9.5, 10.0, 10.5, and 11.0 are listed in Table 1. Unlike the ozonation of diazinon which is pH-independent (Ku et al., 1998), the oxidation of diazinon by aqueous chlorine is very sensitive to pH. The calculated intrinsic rate constants using hypochlorous acid (k_0) and hypochlorite ion (k_1) as the oxidant
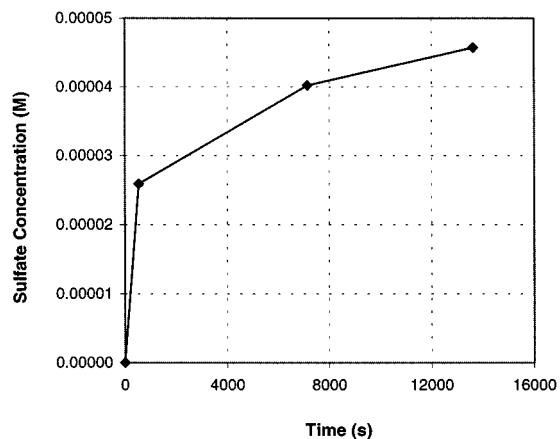
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Figure 8. Sulfate formation in the oxidation of diazinon at pH 10.5 and 27.4 °C with 7.79×10^{-4} M sodium hypochlorite.

separately are listed in Table 2. k_0 is larger than k_1 by a factor of 490, explaining why a small change in pH has a large influence on the observed rate constants. The reason oxidation of diazinon by hypochlorous acid is much faster can be explained by bond strength. Hydrogen atom and oxygen atom, oxygen atom and chlorine atom are connected by sharing electron pairs. For hypochlorous acid, the hydrogen atom donates one electron to the oxygen atom, thus the oxygen atom in hypochlorous acid is less electrophilic than the oxygen atom in hypochlorite ion. Therefore, the strength of the oxygen−chlorine bond in a hypochlorous acid molecule is weaker than that of the oxygen−chlorine bond in a hypochlorite ion. The oxygen−chlorine bond in hypochlorous acid is easier to break, therefore resulting in the fast oxidation rate when diazinon is oxidized by hypochlorous acid.

Product Identification. Diazoxon was the only identified product by GC−MS. The retention time of diazoxon was 32.242 min. Neat diazoxon yielded a very similar GC retention time (31.995 min). GC−MS spectra of a reaction mixture and diazoxon standard are shown in Figure 7. Since all experiments were conducted at high pH values, hydrolysis of diazoxon was also fast under those conditions and could not be neglected (the half-life of hydrolysis for diazoxon at pH 10.4 is 10.1 h; Faust and Gomaa, 1972); with this complication no mass balance was carried out for diazoxon. Figure 8 shows the increase in sulfate concentration in the reaction mixture as the oxidation progressed. The increase indicates that sulfur was oxidized to sulfate after it was released from the diazinon molecule. One may notice that the sulfate concentration of the last sample (45 μM) was somewhat lower than the corresponding sulfur concentration in diazinon molecules (79 μM). This can be explained by the fact that when ferrous bromide was added for sample dechlorination, iron(III) hydroxide was formed and precipitated. A fraction of the sulfate ions was adsorbed on the precipitate; therefore, the concentration of sulfate in the solution was decreased.

CONCLUSIONS

Oxidation rates of diazinon by aqueous chlorine obtained in this study are much larger than the corresponding hydrolysis rates. The second-order rate constants at pH 9.5, 10.0, 10.5, and 11.0 are 1.6, 0.64, 0.43, and 0.32 M^{-1} s^{-1}, respectively. The second-order reaction rate constants of diazinon with hypochlorous acid

and hypochlorite ion separately are 130 and 0.27 M^{-1} s^{-1}, respectively. At pH 7.0, the half-live of degradation of diazinon at a chlorine concentration of 0.5 mg/L (equaling 7.0×10^{-6} M) is just 16 min. Activation energies and enthalpies of the oxidation are smaller than those for hydrolysis of diazinon. Diazoxon is the only product identified by GC−MS. Sulfur is found to be oxidized to sulfate after it is released from the diazinon molecule. This study indicates that oxidation by aqueous chlorine can be another important pathway for the degradation of diazinon in aquatic systems.

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