

Kinetics of Bromacil Ozonolysis

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Chemical oxidation processes have been used successfully in the degradation of organic pollutants, yet information is limited concerning the kinetic descriptions of the reaction mechanisms. In this study, the kinetics of bromacil (5-bromo-3-*sec*-butyl-6-methyluracil, a herbicide) ozonolysis was examined. From laboratory observations, a mechanism was proposed by which direct ozone attack occurred and the degradation pathway proceeded via two parallel reactions. The program MLAB was used to provide a numerical solution for the system of differential equations that described the mechanism. Rate parameters were determined using the slowest reaction system ($\text{H}_2\text{O}_2/\text{O}_3$). The kinetic model was then tested on a system with only bromacil and on a system containing a radical scavenger. This mathematical model is reasonably consistent with the experimental observations that the addition of hydrogen peroxide significantly reduces the formation of the byproduct responsible for the residual phytotoxicity of the waste stream.

Keywords: Bromacil; ozonolysis; ozonation; kinetics; wastewater treatment; modeling

INTRODUCTION

In recent years, elimination of pesticide waste has received considerable attention with the onset of stronger governmental regulations (Kruger and Seiber, 1984; Bourke et al., 1992). Furthermore, the agricultural community has become increasingly aware of the environmental impact of and problems associated with the improper disposal of pesticide waste. It is estimated that a single pesticide application spray rig generates 20 000 L of wash water per year (Nye, 1984). The long-term effects of depositing these excess pesticide solutions and equipment rinsates on the soil to degrade have become a issue to the pesticide applicator because the pesticides can be persistent in the environment and can contaminate surface water and groundwater (Aharonson, 1987; Parsons and Witt, 1988.)

Oxidation processes have been used for the treatment of industrial wastewater, contaminated groundwater, and landfill leachates. Many of these oxidation processes do not completely mineralize the parent compounds (that is, breakdown to CO_2 , H_2O , NH_3 , or NO_3^- and inorganic salts). Efforts have been underway to develop a binary remediation strategy whereby the waste stream is oxidized followed by microbial mineralization in a controlled bioreactor (Somich et al., 1990; Heinze et al., 1992, 1995; Lee et al., 1992; Hu and Yu, 1994; Hapeman et al., 1995; Massey, 1995; Stockinger et al., 1995). This binary process has been successfully demonstrated with pesticide waste using ozone as the oxidant and a waste-stream-tolerant microorganism (Hapeman et al., 1995). In this system, the primary purpose of the chemical oxidation stage was to decrease

the phytotoxicity of the herbicides and, thus, to increase the biodegradability of the pesticides.

Bromacil (**I**, Figure 1), a nonselective and somewhat persistent herbicide that inhibits photosynthesis, is used for general weed control on noncrop lands and citrus orchards (Worthing and Hance, 1991). Recent work has shown that bromacil-containing wastewater retained some of its phytotoxic effects after ozonolysis, thus diminishing the overall usefulness of the oxidation process (Acher et al., 1994). Bromacil ozonolysis was shown to give rise to three products: 3-*sec*-butyl-5-acetyl-5-hydroxyhydantion (**II**), 3-*sec*-butylparabanic acid (**III**), and 3-*sec*-butyl-5,5-dibromo-6-methyl-6-hydroxyuracil (**IV**) (Figure 1). The structures of these compounds were verified by NMR and mass spectral data (Acher et al., 1994; Hapeman et al., 1997). The mechanism for the formation of these three products was shown to consist of three parallel pathways (Hapeman et al., 1997). In a prior study it was observed that the formation of **IV** was the result of a rapid reaction between bromacil and Br_2 (Acher et al., 1994). Finally, ozonation processes, in general, proceed via a hydroxy radical ($\cdot\text{OH}$) process or by direct ozone attack on the substrate (Masten and Davies, 1994). In other experiments, the oxidation of bromacil was found to involve direct ozone attack as opposed to a $\cdot\text{OH}$ process (Hapeman et al., 1997).

During the ozonolysis of bromacil, bromide ions would be generated as a result of **II** and **III** production. Bromide could then be oxidized by ozone to hypobromate (OBr^-), which in turn protonates and could attack bromacil to form **IV** via an electrophilic addition across the C5–C6 double bond (March, 1977). However, over an extended period (>24 h), **IV** has been shown to decompose to re-form bromacil, and it is this process that is responsible for the residual phytotoxicity in the treated waste (Acher et al., 1994). These results clearly demonstrated that quantification of byproduct formation

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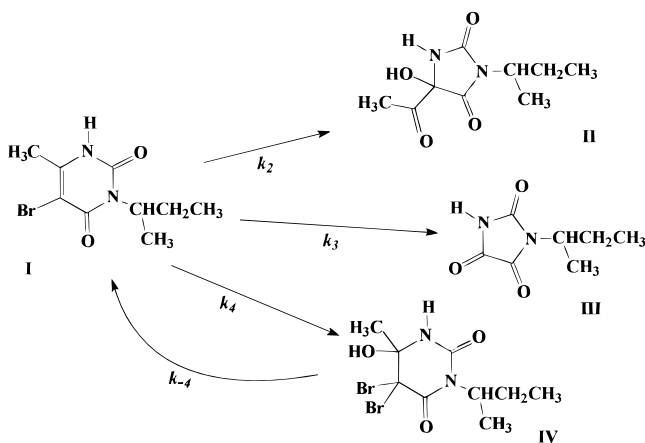


Figure 1. Ozonolysis of bromacil (Hapeman et al., 1997).

is equally as important as quantifying the disappearance of the parent compound.

To optimize the oxidation of bromacil and concomitantly minimize the formation of the undesirable phytotoxic products, an understanding of the reactions, mechanisms, and the kinetics involved is required. Substrate transformation can be described by a series of chemical reactions that are governed by rate laws. The kinetic parameters can then be incorporated into a system of differential equations, providing a mathematical description of the mechanism that is necessary for the full-scale implementation of the chemical process. The purpose of this paper is to describe the previously presented mechanism (Figure 1, Hapeman et al., 1997) mathematically and to determine the rate parameters from the resultant system of differential equations. These rate parameters determined under specific experimental conditions will subsequently be used to ascertain the ability of the model to predict the fate of bromacil in different matrixes.

THEORY

The mechanism for the bromacil ozonolysis, which has been shown to afford three products (**II**, **III**, and **IV**) via direct ozone attack along three parallel pathways, can be described by a series of differential equations (eqs 1–4). These equations, however, can be solved only if the change in the concentrations of HOBr and O_3 are known with respect to time.

$$d[\mathbf{I}]/dt = -k_2[\mathbf{I}][O_3] - k_3[\mathbf{I}][O_3] - k_4[\mathbf{I}][HOBr] + k_{-4}[\mathbf{IV}] \quad (1)$$

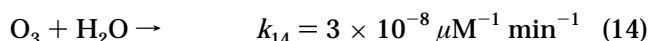
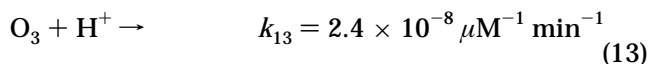
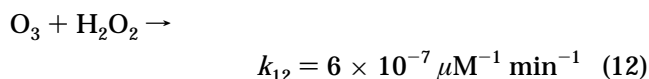
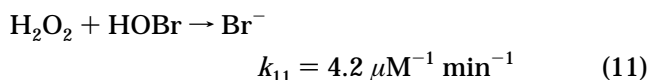
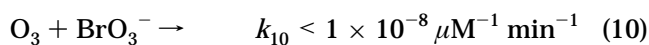
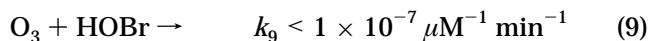
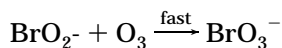
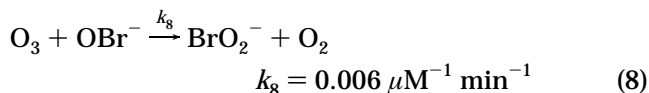
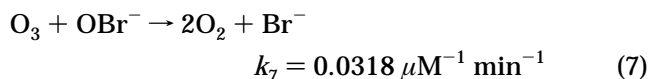
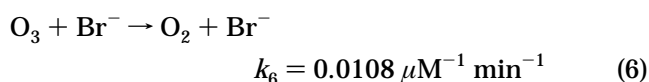
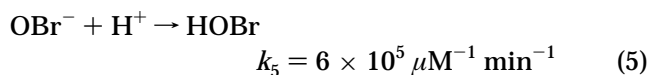
$$d[\mathbf{II}]/dt = k_2[\mathbf{I}][O_3] \quad (2)$$

$$d[\mathbf{III}]/dt = k_3[\mathbf{I}][O_3] \quad (3)$$

$$d[\mathbf{IV}]/dt = k_4[\mathbf{I}][HOBr] - k_{-4}[\mathbf{IV}] \quad (4)$$

HOBr is formed in situ via the following sequence of reactions. Aqueous bromide is generated as a result of bromacil degradation and concomitant formation of products **II** and **III**. Bromide then reacts with ozone to form hypobromate (OBr^-). Equation 5 is diffusion controlled, $k_5 = 6 \times 10^5 \mu M^{-1} \text{ min}^{-1}$ (Stumm and Morgan, 1981). Under the experimental conditions of this work (pH is 5.5), the equilibrium is shifted toward HOBr because the pK_a of HOBr is 8.8. The fate of bromine in a solution containing ozone is shown in eqs

5–11 and has been thoroughly described elsewhere (Staelin and Hoigné, 1982; Haag and Hoigné, 1983; Hoigné et al., 1985; Chelkowska et al., 1992; von Gunten and Hoigné, 1994). In the presence of hydrogen peroxide, the reduction of HOBr by H_2O_2 to form Br^- must also be considered (eq 11) (von Gunten et al., 1996). The reactions of HOBr, BrO_3^- , H_2O_2 , H^+ , and H_2O with ozone (eqs 9, 10, and 12–14) are very slow relative to the other reactions in this system and will have a negligible effect on the overall kinetics of the process. Thus, the concentrations of bromide and related species can then be described with regard to the bromacil system by the differential eqs 15–18. An additional equation, $d[H_2O_2]/dt$, was required to describe the second-order decay of the H_2O_2 concentration (pK_a of $H_2O_2 = 11.6$) (eq 19).



$$d[Br^-]/dt = k_2[\mathbf{I}][O_3] + k_3[\mathbf{I}][O_3] - k_6[O_3][Br^-] + k_7[O_3][OBr^-] + k_{11}[H_2O_2][HOBr] \quad (15)$$

$$d[OBr^-]/dt = -k_5[H^+][OBr^-] + k_6[O_3][Br^-] - k_7[O_3][OBr^-] - k_8[O_3][OBr^-] \quad (16)$$

$$d[\text{HOBr}^-]/dt = -k_4[\text{I}][\text{HOBr}] + k_5[\text{H}^+][\text{OBr}^-] - k_{11}[\text{H}_2\text{O}_2][\text{HOBr}] \quad (17)$$

$$d[\text{BrO}_3^-]/dt = k_8[\text{O}_3][\text{OBr}^-] \quad (18)$$

$$d[\text{H}_2\text{O}_2]/dt = -k_{11}[\text{H}_2\text{O}_2][\text{HOBr}] \quad (19)$$

The rate of change in the ozone concentration in the aqueous phase, $d[\text{O}_3]/dt$, is a function of the mass transfer coefficient, $k_L a$, from the gas phase (Biñ, 1995; Haas and Vamos, 1995), the rate of decomposition in water, $k_0 = 4200 \mu\text{M}^{-1} \text{min}^{-1}$ (Staelin and Hoigné, 1982; Hoigné et al., 1985), and the rate of decomposition, k_i , due to the presence of organic and inorganic substrates. This is described in eq 20, where P is the partial pressure of ozone in the gas phase, $H = 0.082 \text{ atm} \cdot \text{m}^3 \cdot (\text{g} \cdot \text{mol})^{-1}$ (Haas and Vamos, 1995) is the Henry's law constant for ozone, and S_i is the concentration of substrates available to react with ozone. The rate of change in the ozone concentration in the aqueous phase with respect to this system is described by eq 21.

$$d[\text{O}_3]/dt = k_L a(P/H) - [\text{O}_3] - k_0[\text{O}_3][\text{OH}^-] - \sum_i^n k_i S_i [\text{O}_3] \quad (20)$$

$$d[\text{O}_3]/dt = k_L a(P/H) - [\text{O}_3] - k_0[\text{O}_3][\text{OH}^-] - k_2[\text{O}_3][\text{I}] - k_3[\text{O}_3][\text{I}] - k_5[\text{OBr}^-][\text{H}^+] - k_6[\text{O}_3][\text{Br}^-] - k_7[\text{O}_3][\text{OBr}^-] - k_8[\text{O}_3][\text{OBr}^-]$$

MATERIALS AND METHODS

Reagents. Bromacil was obtained gratis from Agan Ltd., Israel. Recrystallization from 2-propanol yielded chromatographically pure compound (needle crystals, mp 158–159 °C). Stock solutions of bromacil were prepared with ultrapure water (18 M Ω , Modulab, Type I HPLC, Continental Water System Corp., San Antonio, TX). Ozone was generated using a PCI model GL-1B ozone generator (PCI Ozone Corp., West Caldwell, NJ) from pure oxygen. *tert*-Butyl alcohol was obtained from Fisher Chemical (Fair Lawn, NJ) and was used as a hydroxyl radical scavenger. Hydrogen peroxide, used to promote the generation of hydroxyl radicals, was obtained from Fisher as a 30–35% (by weight) technical grade product.

Ozonolysis of Bromacil. Solutions of 382 μM bromacil were subjected to ozonolysis at room temperature (20 ± 2 °C) in a 550 mL batch reactor with a fine sintered glass disk in the bottom for the introduction of ozone, a liquid sampling valve, and a gas outlet line (Figure 2). Ozone (in oxygen) was fed into the reactor at a constant rate of 1 L/min, and the stream was maintained by use of mass flow controllers. Ozone concentrations in the feed line ($\sim 1.3\%$ w/w ozone/oxygen or 500 $\mu\text{mol}/\text{min}$) and the off gas line were determined using an ozone monitor (model HC-12, PCI Ozone Corp.). Samples were removed at fixed time intervals via the sampling valve at the bottom of the reactor, and the aqueous ozone concentration ($\sim 11 \mu\text{M}$) was measured colorimetrically using the indigo method (Bader and Hoigné, 1981). Other samples were obtained, purged with nitrogen, and analyzed immediately by HPLC as described below. Although the solution was not buffered, the pH remained $\sim 5.5 \pm 0.2$.

Ozonolysis in the Presence of Hydrogen Peroxide. Solutions of 382 μM bromacil and three different concentrations of hydrogen peroxide (0, 0.07, 3.4, or 6.9 mM H_2O_2) were subjected to ozonolysis in a manner similar to that above on the same day under exactly the same conditions; that is, the generator was stabilized prior to the first run and was not shut

down between runs. Several sets of experiments were conducted, giving rise to similar results.

Ozonolysis in the Presence of *tert*-Butyl Alcohol. Solutions of 382 μM bromacil and three different concentrations of *tert*-butyl alcohol (0, 13, or 53 mM *tert*-butyl alcohol), a $\cdot\text{OH}$ scavenger, were subjected to ozonolysis on the same day under exactly the same conditions in a manner similar to that above. Several sets of experiments were conducted, giving rise to similar results.

HPLC Analyses. Samples were analyzed directly by HPLC employing two Gilson (Middleton, WI) model 303 HPLC pumps equipped with Gilson systems controller software and a Gilson model 116 UV detector (210 and 222 nm monitored). Separations were achieved using 40% acetonitrile/phosphoric acid buffer (pH 2) at a flow rate of 1.0 mL/min on an Ultrasphere C₁₈ (ODS), 5 μm , end-capped, 4.6 mm \times 25 cm, steel-jacketed column (Beckman Instruments, Inc., Fullerton, CA). A standard curve for bromacil was obtained from a prepared stock solution and diluted accordingly to known concentrations over the required range of experimental analysis.

Quantification of products **II–IV** was carried out by subjecting a 400 mL solution of 1.53 mM bromacil spiked with 30 μCi of [^{14}C]bromacil to ozonolysis. Samples were removed periodically and assayed directly by HPLC to analyze for bromacil and breakdown products. Effluent fractions were collected at 15 s intervals and analyzed on a Beckman model LS6000IC liquid scintillation counter (Columbia, MD) using ScintiVerse II cocktail (Fisher Chemical). Chromatograms were reconstructed at each reaction time interval from the amount of radioactivity detected in each fraction. In addition to bromacil, three major products were observed in the ^{14}C chromatogram (24% **II**, 56% **III**, and 20% **IV**); several very minor products (<1%) that were at the level of detection were not quantified (Hapeman et al., 1997). The area of each peak (in dpm $\cdot\text{min}$) corresponded to a known mass as determined from the total counts present in each run. The calculated mass was plotted versus the area of the peak obtained using the UV detector for each run. These standard curves were used in subsequent runs to determine the concentrations of products **II–IV**.

Kinetic Modeling. A kinetic model consisting of a series of differential equations was used to describe the experimentally observed concentrations of bromacil and oxidation products **II–IV**. MLAB (Civilized Software, Inc., Bethesda, MD), a program that employs the Marquardt–Levenberg curve-fitting method and minimizes the summation of the squares between the experimental data and a theoretical model, was used to determine a numerical solution to the system of nonlinear differential equations. The kinetic parameters, k_2 , k_3 , and k_4 , were determined from the best fit of the observed concentrations of **I–IV**. The model was then used to predict the concentrations of **I–IV** from the calculated values of k_2 , k_3 , and k_4 in a distilled water system and a radical scavenger system.

RESULTS

Ozonolysis of Bromacil. Ozonolysis of an aqueous solution containing only bromacil led to efficient substrate disappearance and rapid formation of the products **II** and **III**; a slight lag was observed in the formation of **IV** (Figure 3). This pattern is clearly indicative of a two parallel reaction process for the formation of **II** and **III** and the dependence of **IV** on the concomitant release and oxidation of bromide. In all experiments, **II–IV** accounted for >99% of the initial bromacil, indicating that the formation of other byproducts was not significant. Further oxidation of **II–IV** was minimal, and during the initial phase of the reaction, re-formation of bromacil via product **IV** degradation was a very minor process. Therefore, k_{-4} was assumed to be 0.

Determination of k_2 , k_3 , and k_4 . Three bromacil systems were examined: (1) bromacil, (2) bromacil with

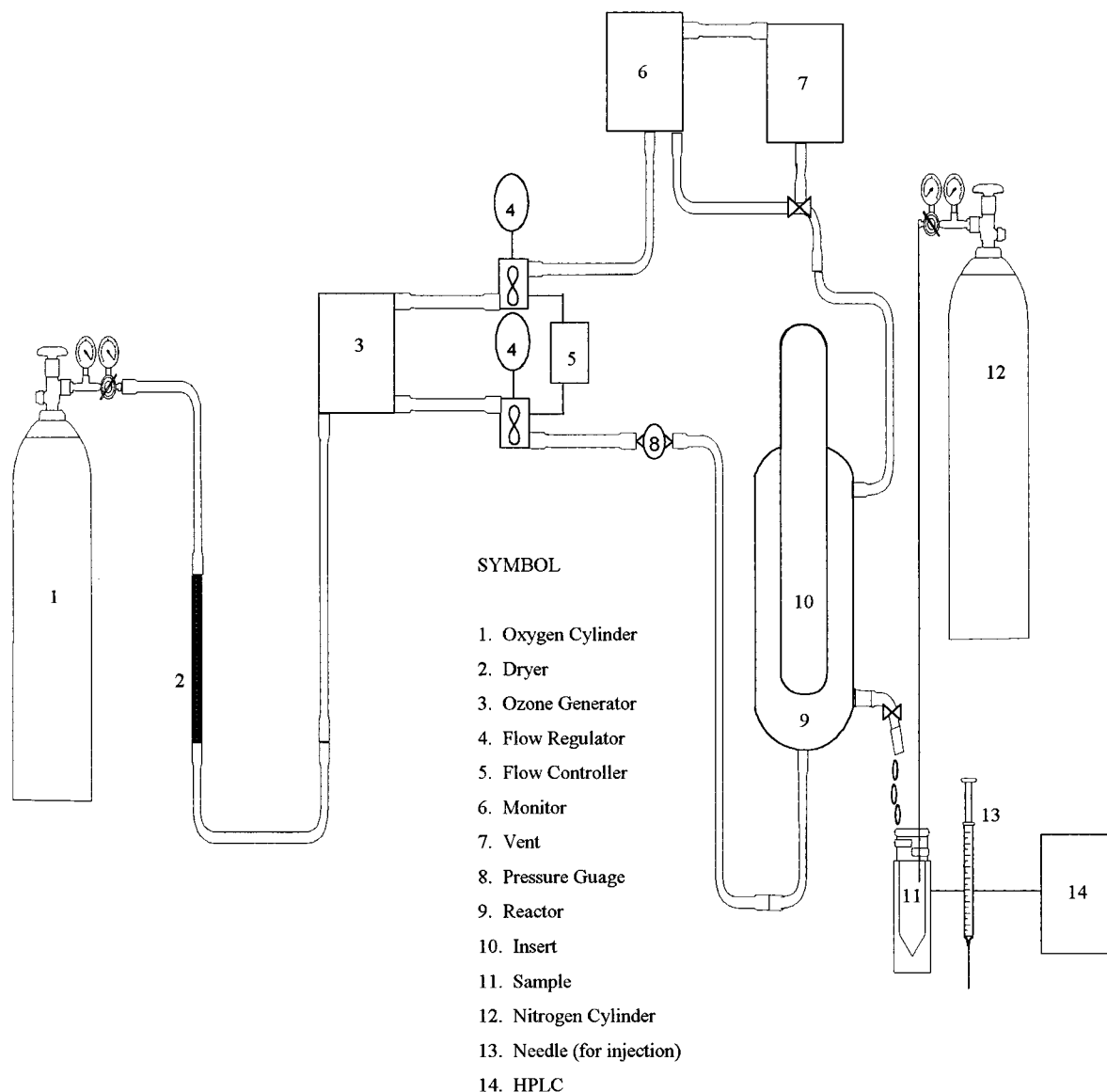


Figure 2. Experimental ozonolysis flow diagram.

hydrogen peroxide, and (3) bromacil with *tert*-butyl alcohol, a hydroxy radical scavenger. Previous studies showed that the degradation of bromacil was very fast in all three systems, with the slowest degradation rate of bromacil observed in the peroxide system (Anderson, 1996; Hapeman et al., 1997). The system with hydrogen peroxide was significantly slower than either the system with only ozone or the system with *tert*-butyl alcohol and was used to determine k_2 , k_3 , and k_4 .

An ASCII script was encoded with the necessary information for MLAB and included eqs 1–4, 15–19, and 21, the literature values for k_5 , k_6 , k_7 , k_8 , and k_{11} , and the experimental concentrations of I–IV, H_2O_2 , and O_3 . The calculated rate parameters from the O_3/H_2O_2 system over the period of 0–15 min (no bromacil remained after 15 min) were as follows: $k_2 = 0.0078 \pm 0.0007 \mu M^{-1} \text{ min}^{-1}$, $k_3 = 0.030 \pm 0.002 \mu M^{-1} \text{ min}^{-1}$, and $k_4 = 47 \pm 4 \mu M^{-1} \text{ min}^{-1}$ ($R^2 = 0.992$). Figure 4 shows a good fit of the experimental data and the predicted concentrations of bromacil and its degradation products.

To determine the effect of hydrogen peroxide concentration on the product formation, ozonolysis was conducted at three different H_2O_2 concentrations. The results are shown in Figure 5 and clearly illustrate that

while the overall rate of bromacil degradation decreased by <25% at the highest H_2O_2 concentrations, the amount of IV formed per mole of bromacil degraded decreased by as much as 83%. The different H_2O_2 concentrations were used as inputs for the initial conditions in model script, and the same trends as above were observed.

Testing the Kinetic Model on a Distilled Water System. The ozonolysis of bromacil was conducted in distilled water without hydrogen peroxide. The kinetic model was tested on this system. The ASCII script was modified to include the determined values for k_2 , k_3 , and k_4 from the previously described hydrogen peroxide/ozone system, and the initial concentration of hydrogen peroxide was set to 0. The model was used to predict the concentrations of I–IV as a function of time. The resultant theoretical curves are shown in Figure 6 and are reasonably consistent with the experimental data: $R^2 = 0.980$, where R^2 is a determination coefficient that provides an indication of the goodness of fit for all four concentration curves of I–IV with the actual data.

Testing the Kinetic Model on a System Containing a Radical Scavenger. A third reaction system that consisted of bromacil and *tert*-butyl alcohol, a $\cdot OH$

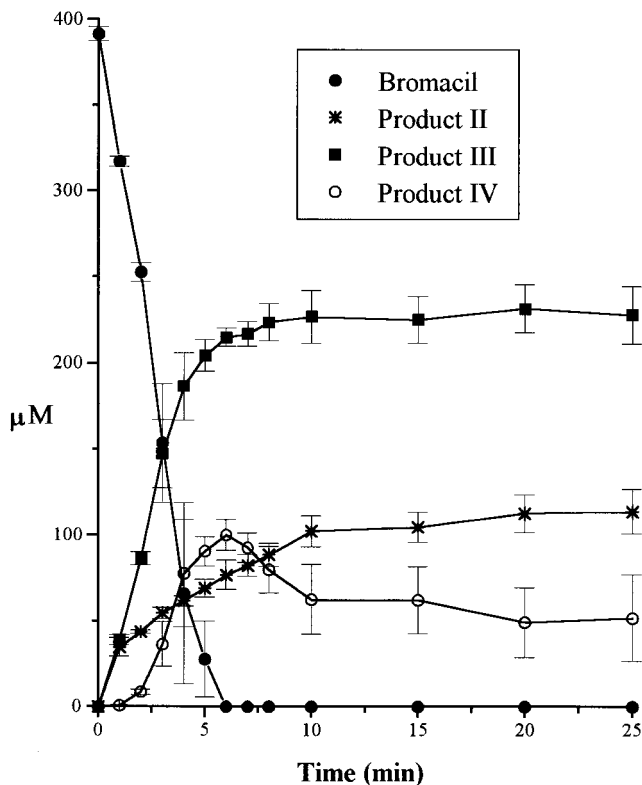


Figure 3. Ozonolysis of an aqueous solution of bromacil. Error bars represent the standard deviation for the five experiments performed on different days under the same reaction conditions.

scavenger, was examined. The same script was used to predict concentrations of bromacil and II–IV as a function of time. The resultant predicted curves are shown in Figure 7 and are reasonably consistent with the experimental data: $R^2 = 0.980$.

DISCUSSION AND CONCLUSIONS

The mechanism for the bromacil ozonolysis has been shown to proceed via a direct ozone reaction, as opposed to oxidation by hydroxy radicals, by which II and III are formed concomitantly and IV is formed after bromide is released from these reactions. Bromacil degradation was significantly enhanced under conditions in which the hydroxy radicals are scavenged and prevented from reacting with ozone. However, the amount of the phytotoxic precursor (IV) to bromacil degraded remained constant (Anderson, 1996). Alternatively, the addition of hydrogen peroxide decreased the rate of bromacil degradation and significantly altered the ratio of byproducts. The presence of hydrogen peroxide increases the concentration of hydroxy radicals that can react with ozone, thereby decreasing the ozone available to react with bromacil and more importantly bromide. At the same time, hydrogen peroxide reacts with the HOBr that is formed, decreasing the steady state concentration of HOBr at any given time. Thus, the formation of IV is decreased considerably (up to 83% under the conditions of this study). This further confirms the findings that the addition of hydrogen peroxide in ozonation treatment processes is particularly efficient at controlling the formation of brominated byproducts (Griffini and Iozzelli, 1996).

A kinetic model was used to determine the rate parameters and accurately predict the concentrations

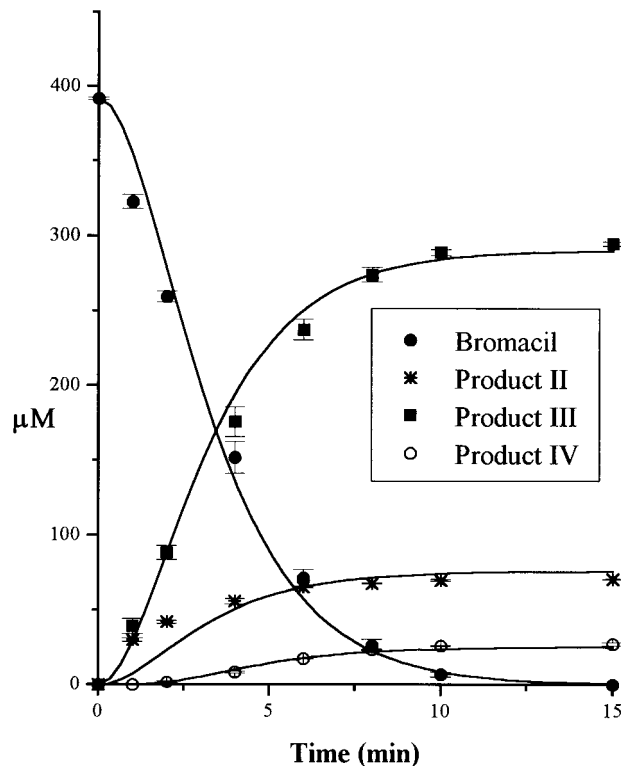


Figure 4. Modeling the ozonolysis of bromacil in the presence of 6.9 mM H_2O_2 . Symbols represent the experimental data, and the lines correspond to the model. Error bars represent the standard deviation for the three experiments performed on different days under the same reaction conditions. Note the differences in the concentrations of IV and III between this experiment and those shown in Figures 6 and 7.

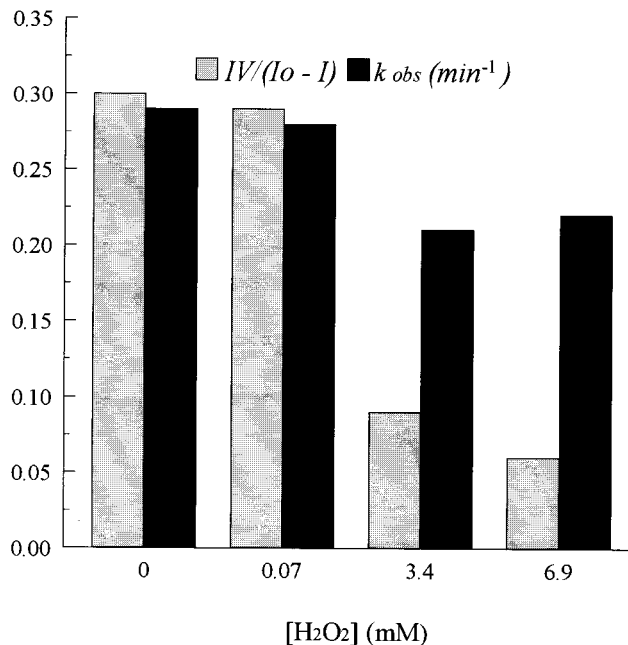


Figure 5. Effect of hydrogen peroxide concentration on the overall observed bromacil degradation rate $\left(\frac{[I]_0 - [I]}{[I]_0}\right)$ and on the formation of the phytotoxic precursor byproduct, IV (Anderson, 1996; Hapeman et al., 1997). $[I]_0$ is the initial concentration of bromacil, and $[I]$ is the concentration at $t = 6$ min.

of the products formed in different matrixes. The predicted data were reasonably consistent with that observed. The presence of other radical matrix components, such as organic matter, other radical scavengers, anions,

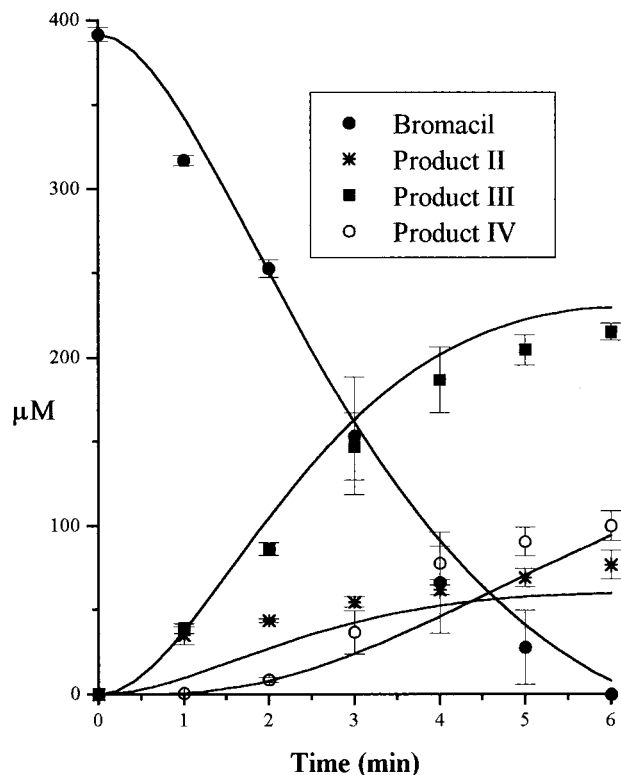


Figure 6. Modeling the ozonolysis of bromacil in distilled water. Symbols represent the experimental data, and the lines correspond to the model. Error bars represent the standard deviation for the five experiments performed on different days under the same reaction conditions.

and cations, may effect the distribution of byproducts and the degradation rate of substrate. While additional studies may be needed to address the influence of matrix components on the chemistry of ozone and HOBr, the above model is a necessary first step for optimization of the ozonolysis process, which requires the formation of the phytotoxic precursor to be minimized. Therefore, for the degradation of bromacil, conditions that favor hydroxy radical processes (high pH and H_2O_2 addition) are preferred. Furthermore, this study clearly demonstrates that a mechanistic understanding of the degradation process and its mathematical description can aid in visualization of the reaction conditions that will best meet treatment needs.

NOMENCLATURE

[Br⁻] = concentration of bromide (μM)
 [BrO₃⁻] = concentration of bromate (μM)
 H = Henry's law constant for ozone [$\text{atm}\cdot\text{m}^3\cdot(\text{g}\cdot\text{mol})^{-1}$]
 [HOBr] = concentration of hypobromous acid (μM)
 [H₂O₂] = concentration of hydrogen peroxide (μM)
 [I] = concentration of bromacil (I) (μM)
 [I]₀ = concentration of bromacil at $t = 0$ (μM)
 [II] = concentration of product II (μM)
 [III] = concentration of product III (μM)
 [IV] = concentration of product IV (μM)
 k_2 = rate parameter for the formation of II from I (eq 1) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_3 = rate parameter for the formation of III from I (eq 1) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_4 = rate parameter for the formation of IV from I (eq 1) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_{-4} = rate parameter for the formation of I from IV (eq 1) (min^{-1})
 k_5 = rate constant for the protonation of OBr⁻ (eq 5) ($\mu\text{M}^{-1}\text{min}^{-1}$)

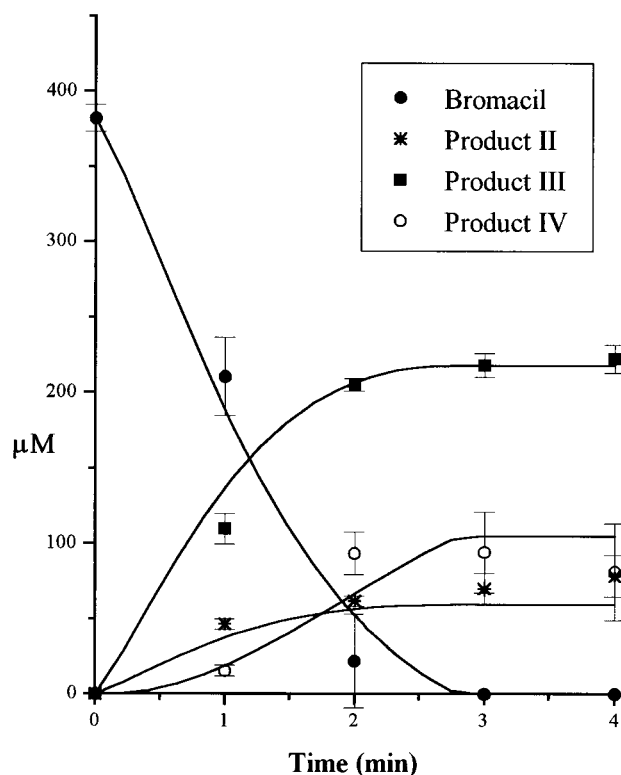


Figure 7. Modeling the ozonolysis of bromacil in the presence of 53 mM *tert*-butyl alcohol. Symbols represent the experimental data and the lines correspond to the model. Error bars represent the standard deviation for the three experiments performed on different days under the same reaction conditions.

k_6 = rate constant for the reaction of Br⁻ with O₃ (eq 6) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_7 = rate constant for the reaction of OBr⁻ with O₃ (eq 7) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_8 = rate constant for the reaction of OBr⁻ with O₃ (eq 8) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_9 = rate constant for the reaction of HOBr with O₃ (eq 9) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_{10} = rate constant for the reaction of BrO₃⁻ with O₃ (eq 10) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_{11} = rate constant for the reaction of HOBr with H₂O₂ (eq 11) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_{12} = rate constant for the reaction of O₃ with H₂O₂ (eq 12) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_{13} = rate constant for the reaction of H⁺ with O₃ (eq 13) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_{14} = rate constant for the reaction of H₂O with O₃ (eq 14) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 k_i = rate constant for the decomposition of ozone due to the presence of organic and inorganic substrates (eq 20) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 $k_{1,a}$ = mass transfer coefficient from the gas phase to liquid phase (eq 20) (min^{-1})
 k_o = rate constant of the decomposition ozone in water (eq 20) ($\mu\text{M}^{-1}\text{min}^{-1}$)
 [O₃] = concentration of ozone in solution (μM)
 [OBr⁻] = concentration of hypobromite ion (μM)
 P = partial pressure of ozone in the gas phase (atm)
 S_i = concentration of substrates available to react with ozone (eq 20) (μM)
 t = reaction time (min)

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