Mechanistic Investigations Concerning the Aqueous Ozonolysis of Bromacil

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Bromacil ozonolysis was examined to determine the mechanism of product formation in an effort to optimize a chemical−microbial remediation strategy for contaminated waters. Two debrominated products, 3-*sec*-butyl-5-acetyl-5-hydroxyhydantoin (**II**) (24%) and 3-*sec*-butylparabanic acid (**III**) (56%), and a dibromohydrin, 3-*sec*-butyl-5,5-dibromo-6-methyl-6-hydroxyuracil (**IV**) (20%), were formed. The latter compound, arising from HOBr addition to bromacil, reverted back to starting material, causing the treated solution to remain somewhat phytotoxic. Mass balance studies provided evidence for parallel reaction pathways as opposed to a series pathway where **II** gives rise to **III**. Addition of hydrogen peroxide slightly decreased the rate of bromacil degradation while the addition of *tert*-butyl alcohol (*t*-BuOH), a hydroxy radical scavenger, increased the degradation rate, strongly suggesting that the mechanism does not involve hydroxy radicals but direct ozone attack at the double bond. A much lower yield of **IV**, 6%, relative to the control was observed with H_2O_2, whereas a slightly higher yield, 23%, was found with *t*-BuOH.

Keywords: *Bromacil; remediation; bromohydrin; ozonolysis*

INTRODUCTION

Efforts have been underway to develop strategies to remediate pesticide-contaminated matrices, including ground and surface waters, irrigation and greenhouse effluents, and waste waters. Early observations showed that pesticide-containing solutions pretreated with ultraviolet light or ozone were more readily degraded by soil microflora and were significantly less phytotoxic (Saltzman *et al.*, 1982; Somich *et al.*, 1990); this led to development of binary (chemical−microbial) remediation processes (Somich *et al.*, 1990; Hapeman-Somich, 1991; Acher *et al.*, 1994; Hapeman *et al.*, 1995; Massey, 1995). Bromacil (5-bromo-3-*sec*-butyl-6-methyluracil, **I**), the pesticide of interest in this study, is a nonselective and relatively stable herbicide inhibiting photosynthesis and is used for general weed control on noncrop lands and citrus orchards (Worthing and Hance, 1991).

Photodecomposition of bromacil has been investigated in aqueous solutions (Kearney *et al.*, 1969) ($\lambda = 254$ nm) and in thin solid films ($\lambda = 254$ nm) (Jordan *et al.*, 1965) although the products were not identified. Experiments simulating natural conditions by exposure of aqueous solutions to direct solar irradiation (summer) for 4 months yielded only 2.2% of a single dealkylated photoproduct, indicating that bromacil is very stable toward sunlight (Moilanen and Crosby, 1974). Addition of methylene blue, a photosensitizer and generator of singlet oxygen, to an aerated aqueous solution (Acher and Saltzman, 1980) substantially increased the bromacil degradation rate. The two principal products were identified as 3-*sec*-butyl-5-acetyl-5-hydroxyhydantoin and a dimer linked at C5 (Acher and Dunkelblum, 1979). A comparison of the various oxidation methods, direct and indirect photolysis and ozonation, of bromacil was recently conducted (Acher *et al.*, 1994). Treated solutions were subsequently submitted to biomineralization using soil, activated sludge, and a previously isolated microorganism, *Klebsiella terragena* (strain DRS-I) (Hapeman *et al.*, 1995). All oxidized waste solutions showed enhanced biodegradation relative to the parent compound, and in general the phytotoxicity was removed. However, some phytotoxic effects were observed from the ozonated bromacil solutions. These data would suggest that ozonation be precluded in oxidation/biomineralization treatment strategies for bromacil; however, inherent problems also exist with photolytic oxidation. Waste systems that are opaque, for example, will not transmit light, which will impede degradation; furthermore, the photosensitizer, methylene blue, may be regulated in some areas, presenting an additional remediation issue.

The remaining phytotoxicity in the ozonated bromacil solutions was attributed *a priori* to the formation of the somewhat unstable dibromohydrin (Acher *et al.*, 1994). Formation of the dibromohydrin is novel in that bromohydrins formed during ozonation typically arise from bromide present in the initial system (Cavanaugh *et al.*, 1992; Glaze *et al.*, 1993). In this case, however, bromide is an ozonolysis byproduct that is subsequently involved in reactions with starting material. The focus of the current study is to elucidate the mechanism of bromacil oxidation when treated with ozone in an effort to minimize the formation of the phytotoxic oxidation product, i.e., the dibromohydrin. In addition, by determining whether degradation proceeds via direct ozonolysis or hydroxy radical (•OH), the conditions can be altered so as to optimize the oxidation rate.

EXPERIMENTAL PROCEDURES

Reagents. Bromacil was obtained gratis from Agan Ltd., Israel. Recrystallization from 2-propanol yielded chromatographically pure compound (needle crystals, mp 158−159 °C).

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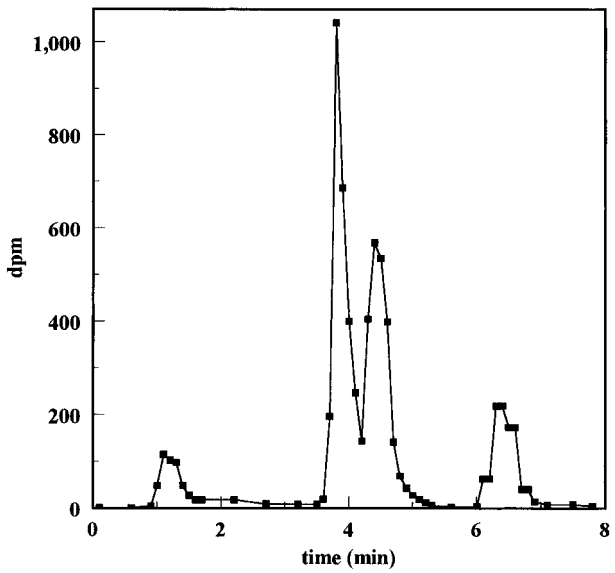

Figure 1. Total counts in HPLC eluent of [2-^{14}C]bromacil ozonolysis reaction mixture. Peaks at t_R = 1.1, 3.8, 4.4, and 6.4 min correspond to **II**, **III**, bromacil, and **IV**, and areas of 48, 275, 235, and 102 dpm·min, respectively.

Stock solutions of bromacil were prepared with ultrapure water (18 MΩ/cm, Modulab, type I HPLC, Continental Water System Corp., San Antonio, TX).

Ozonolysis of Bromacil. Ozonolysis experiments were carried out at room temperature in a previously described 550 mL reactor (Somich *et al.*, 1988). Ozone was generated using a PCI Model GL-1B ozone generator (PCI Ozone Corp., West Caldwell, NJ) with oxygen feed. Ozone (in oxygen) was fed into the reactor at a constant rate of 1 L/min; the stream was maintained by use of mass flow controllers. Ozone concentrations in the feed line (ca. 1.3% w/w ozone/oxygen) and the off gas line were determined using an ozone monitor (Model HC-12, PCI Ozone Corp.). Ozone concentrations in solution (0−11 μM) were measured using the indigo method (Bader and Hoigné, 1981). The amount of ozone consumed in the reaction was calculated by subtraction of the off gas and aqueous concentrations from the feed line concentration. Typical consumption ranged from 3 to 5 mol of ozone consumed per mole of bromacil degraded. Samples were removed at various intervals, purged with nitrogen, and immediately analyzed by HPLC as described below.

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 C-18 (ODS), 5 μm, end-capped, 4.6 mm × 25 cm steel-jacketed column (Beckman Instruments, Inc., Fullerton, CA).

Quantitation of Bromacil and Its Products. Standard curves for the purposes of quantitation were obtained by treating with ozone a 400 mL solution of 400 ppm of bromacil (1.53 mM) spiked with 30 μCi of [2-^{14}C]bromacil. Samples were removed periodically during the reaction and assayed directly by HPLC; effluent fractions were collected at 15 s intervals. Fractions were analyzed on a Beckman Model LS6000IC liquid scintillation counter (Columbia, MD) using ScintiVerse II cocktail (Fisher Chemical, Fisher Scientific, Fair Lawn, NJ). Chromatograms were reconstructed at each reaction time interval from the amount of radioactivity detected in each fraction. In addition to bromacil, only the three major products were observed in the ^{14}C chromatogram; several very minor products that were at the level of detection were not quantified (Figure 1). The area of each peak (in dpm·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 curves were used in subsequent runs to determine the concentration of **II**, **III**, and **IV**. The concentration of bromacil was obtained using a standard curve calculated from known concentrations of bromacil.

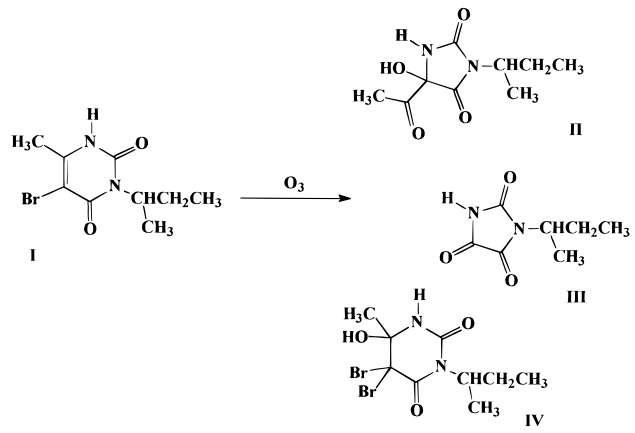

Figure 2. Products of bromacil ozonolysis.

Liquid Chromatography/Mass Spectrometry. LC/MS electron ionization (EI) spectra (70 eV) were obtained on a Hewlett-Packard Model 5988A mass spectrometer with 3.0 Pascal software equipped with a Hewlett-Packard Model 59980A particle beam LC/MS interface (desolvation chamber temperature = 50 °C; source temperature = 200 °C). LC separations were achieved employing a Zymark (Hopkinton, MA) Encore HPLC system equipped with the previously described Beckman C-18 analytical column using a 5 min linear gradient of 20−40% acetonitrile in acetic acid buffer (pH 4) at a rate of 0.4 mL/min.

Ozonolysis in the Presence of Hydrogen Peroxide. Solutions of 382 μM bromacil and 0, 0.069, 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, i.e., 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. Rates were determined relative to the control (no H_2O_2) run on the same day.

Ozonolysis in the Presence of *tert*-Butyl Alcohol. Solutions of 382 μM bromacil and 0, 13.3, or 52.9 mM *t*-BuOH 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. Rates were determined relative to the control (no *t*-BuOH) run on the same day.

RESULTS AND DISCUSSION

Ozonolysis of Bromacil. Three products, **II**−**IV**, and several very minor products were detected by HPLC when solutions of bromacil were treated with ozone (Figure 2). The structures of **II** (3-*sec*-butyl-5-acetyl-5-hydroxyhydantoin), **III** (3-*sec*-butylparabanic acid), and **IV** (3-*sec*-butyl-5,5-dibromo-6-methyl-6-hydroxyuracil) were determined previously (Acher *et al.*, 1994). The principal fragments from product mass spectra obtained by LC/MS (EI) of the reaction solution (Figure 3) were as follows. **II** mass (relative abundance): 185 (3), 172 (24), 171 (43), 142 (9), 116 (44), 115 (100), 70 (28). **III**: 155 (2), 141 (75), 115 (29), 84 (11), 70 (100), 56 (39). **IV**: 327, 329, and 331 (15); 301, 303, and 305 (28); 260 and 262 (9); 231 and 233 (13); 205 and 207 (100); 142 (55); 127 (18); 70 (41). The dibromohydrin, **IV**, was relatively unstable and after a day at room temperature would lose HOBr and re-form bromacil. Isolated yields of **II**, **III**, and **IV** obtained from flash column chromatography followed by semipreparative HPLC separation were ca. 5%, 20%, and 5% of **II**, **III**, and **IV**, respectively; the minor products were not isolated (Acher *et al.*, 1994). The actual product yields were determined using [2-^{14}C]-

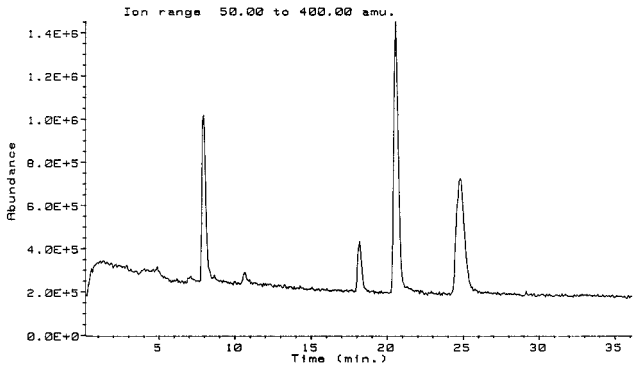

Figure 3. LC/MS total ion chromatogram of bromacil ozonolysis reaction mixture. Peaks at t_R = 7.9, 18.2, 20.6, and 24.8 min correspond to **II**, **III**, bromacil, and **IV**, respectively.

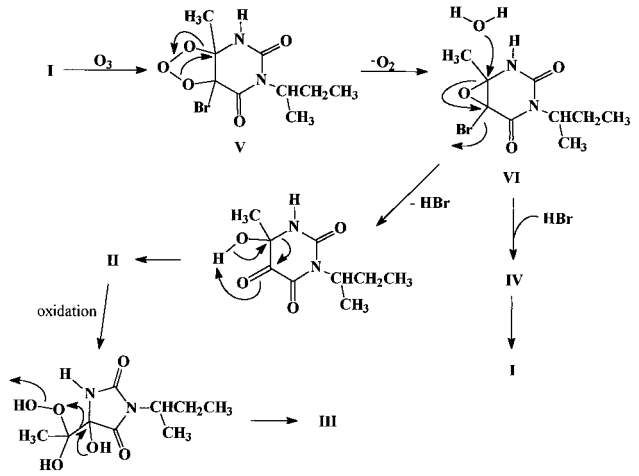

Figure 4. Proposed in-series mechanism for bromacil ozonolysis.

Table 1. Comparison of Oxidation Rates and Final Product Yields

		yield (%)		
reactn conditions	k' (min^{-1})	**II**	**III**	**IV**
O_3	0.29 ± 0.01	24	56	20
O_3 + 6.9 mM H_2O_2	0.23 ± 0.02	18	72	6
O_3 + 52.9 mM *t*-BuOH	0.97 ± 0.01	21	55	23

bromacil; treatment of aqueous bromacil with ozone afforded 24, 56, and 20% of **II**, **III**, and **IV**, respectively (Table 1; Figure 1).

Degradation Pathway: In-Series and Parallel Mechanisms. The simplest degradation pathway for bromacil ozonolysis, assuming direct attack by ozone rather than a hydroxy radical mechanism, might involve the formation of an ozonide, **V**, which upon collapse would give an unstable epoxide, **VI** (Figure 4). Loss of a proton and bromide followed by rearrangement would afford **II**. Further oxidation of **II** to a peroxide would subsequently yield **III**. Hydrolysis of the epoxide, **VI**, in the presence of hydrobromic acid would give rise to **IV**. This in-series mechanism contrasts with a parallel mechanism, where reaction of bromacil with ozone forms the ozonide, **V**, which can collapse to form **II** or **III** directly (Figure 5). The formation of **IV** in the parallel mechanism would arise from hypobromous acid, HOBr, attack on bromacil itself. These mechanisms are summarized in Figure 6.

The degradation profile of bromacil ozonolysis (Figure 7) clearly shows that the formation of **III** is independent of **II**. If **III** were a product of **II**, a delay would be expected in the formation of **III** and its appearance

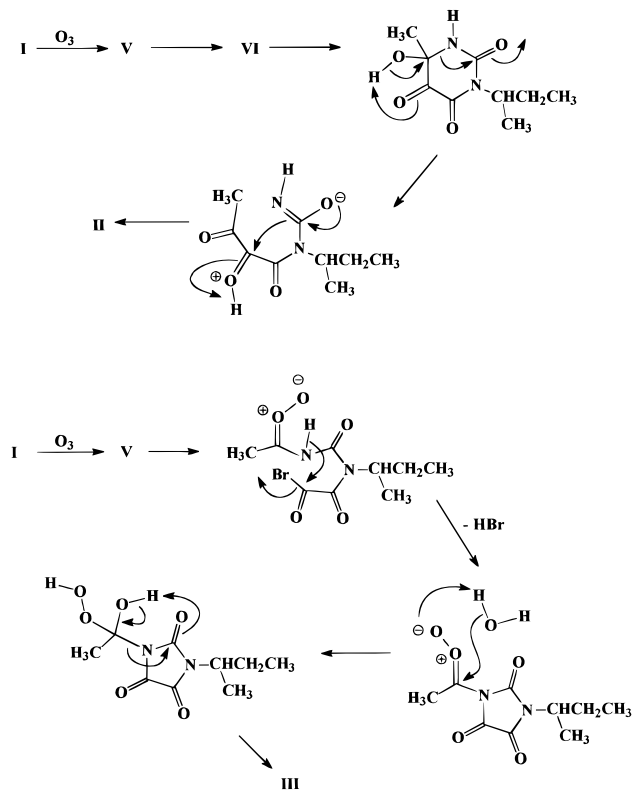

Figure 5. Proposed parallel mechanism for bromacil ozonolysis.

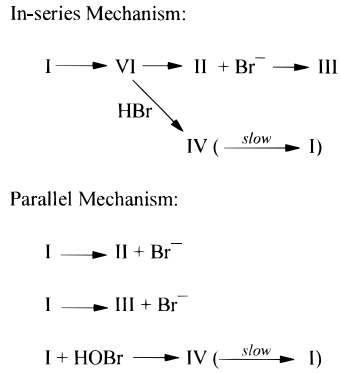

Figure 6. Summary of degradation pathways: in-series versus parallel mechanisms.

would correspond to a disappearance in **II**. Furthermore, the series mechanism cannot be operational to any extent because **II** does not decrease nor does **III** increase after all the bromacil is depleted. Therefore, the ozonolysis of bromacil proceeds via a parallel mechanism exclusively.

Reaction Kinetics. The kinetics of bromacil ozonolysis can be expressed as a function of the concentrations of bromacil, the oxidants, and HOBr (eq 1), where, k_2, k_3, and k_4 are the rate constants for the formation of **II**, **III**, and **IV**, respectively; [**I**] is the concentration of bromacil, [oxidant] is the concentration of ozone or $^{\bullet}$OH, and [HOBr] is the concentration of hypobromous acid. Ozone was continuously applied at a constant rate, and concentrations in the reactor increased rapidly to *ca.* <11 μM. Furthermore, the concentration of ozone is small relative to the concentration of bromacil as the initial concentrations of bromacil were approximately 2 orders of magnitude larger than those of ozone. The concentration of HOBr can also be assumed to be rather low because its in-situ production is slow (Haag and

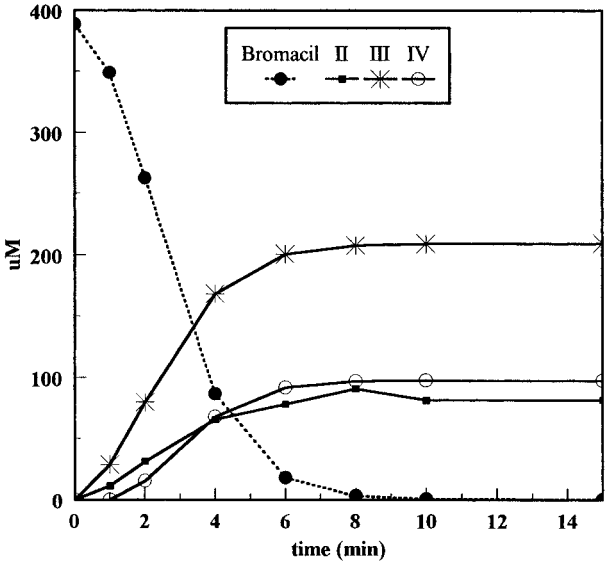

Figure 7. Bromacil ozonolysis product profile.

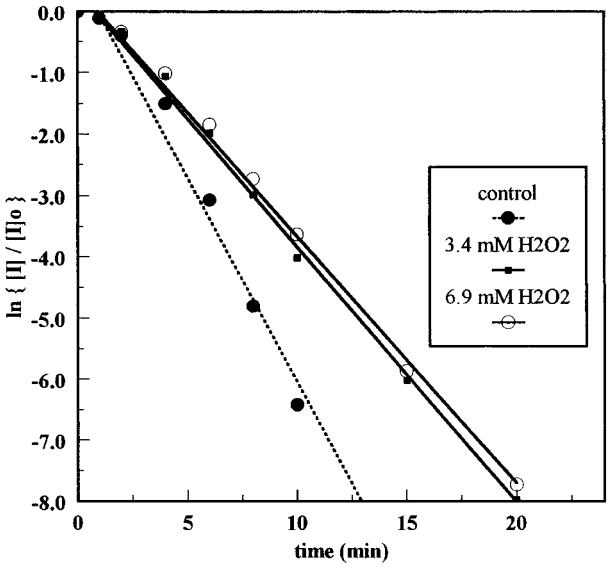

Figure 8. Bromacil ozonolysis in the presence of 0, 3.4, or 6.9 mM hydrogen peroxide: k'(no H_2O_2) = 0.29 min^{-1} (r^2 = 0.97), k'(3.4 mM H_2O_2) = 0.27 min^{-1} (r^2 = 0.97), k'(6.9 mM H_2O_2) = 0.23 min^{-1} (r^2 = 0.99).

Hoigné, 1983) and it is consumed fairly rapidly. The kinetic equation can then be reduced to the pseudo-first-order equation (eq 2) where k' is defined by eq 3.

$$d[\mathbf{I}]/dt = -k_2[\mathbf{I}][\text{oxidant}] - k_3[\mathbf{I}][\text{oxidant}] - k_4[\mathbf{I}][\text{HOBr}] \quad (1)$$

$$d[\mathbf{I}]/dt = -k'[\mathbf{I}] \quad (2)$$

$$k' = k_2[\text{oxidant}] + k_3[\text{oxidant}] + k_4[\text{HOBr}] \quad (3)$$

Direct Ozonolysis versus a •OH Mechanism. The oxidation of bromacil in the presence of ozone can proceed via direct attack of ozone on the carbon−carbon double bond or via a hydroxy radical mechanism, which is very typical of aqueous ozonation (Masten and Davies, 1994). The addition of hydrogen peroxide is expected to increase hydroxy radical processes in ozonation (Peyton and Glaze, 1987). In this study, however, addition of hydrogen peroxide did not effect a profound change in the rate of bromacil degradation, although the reaction was somewhat slower: k'(no H_2O_2) = 0.29 min^{-1} ± 0.01 min^{-1} versus k'(6.9 mM H_2O_2) = 0.23 min^{-1} ± 0.02 min^{-1} (Figure 8). A very slight decrease was observed in k' when 3.4 mM H_2O_2 was added, and no change was observed when 0.069 mM H_2O_2 was used (data not shown). This result was somewhat unexpected because, in previous studies, hydrogen peroxide increased the degradation rate of pesticides during ozonation (Somich *et al.*, 1988; Kearney *et al.*, 1988; Somich *et al.*, 1990). However, the product ratio showed an increase in the formation of **III** (72%) and a substantial decrease in the formation of **IV** to 6% (Table 1; Figure 9).

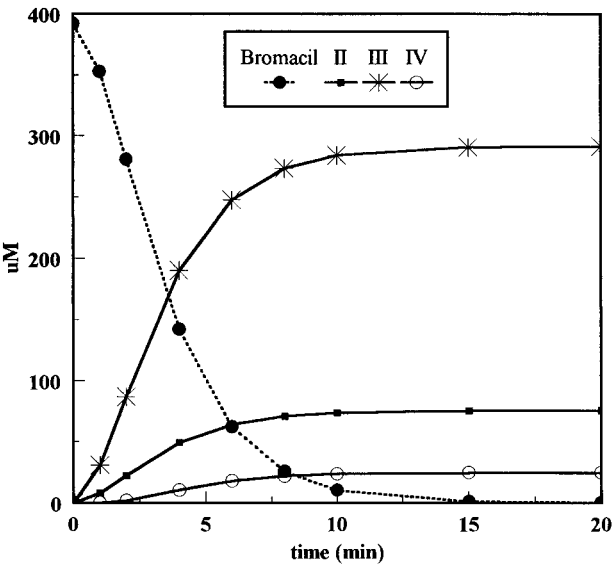

Figure 9. Product profile of bromacil ozonolysis in the presence of 6.9 mM hydrogen peroxide.

In contrast, the addition of *t*-BuOH, a known •OH scavenger, will cause a decrease in the rate of degradation if the mechanism involves hydroxy radical oxidation, because *t*-BuOH will compete with the substrate for •OH. Furthermore, hydroxy radicals can attack ozone and remove a portion of the ozone from the system (Peyton and Glaze, 1987). Alternatively, if the mechanism proceeds via direct ozone attack, addition of *t*-BuOH could effect an increase in the degradation rate by allowing more ozone to react directly with the substrate rather than •OH. In this study, treatment of bromacil with ozone in the presence of 52.9 mM *t*-BuOH increased the rate of degradation by nearly an order of magnitude: k'(no *t*-BuOH) = 0.29 min^{-1} ± 0.01 min^{-1} versus k'(52.9 mM *t*-BuOH) = 0.97 min^{-1} ± 0.01 min^{-1} (Figure 10). Interestingly, the yield of **IV** actually increased slightly to 23% (Table 1; Figure 11).

These experiments strongly suggest that the mechanism of bromacil ozonolysis proceeds via direct ozone attack on the double bond and not via a hydroxy radical mechanism. Furthermore, none of the major products of bromacil degradation involve oxidation or removal of the *sec*-butyl moiety on the imide nitrogen, as might be expected in a hydroxy radical system. If this process occurs, it is a very minor pathway at best. Apparently, the electron-withdrawing nature of the imide functionality is sufficient to deter attack by •OH on the *sec*-butyl.

Mechanism for Bromacil Degradation. Additional proof that the ozonolysis of bromacil does not involve hydroxy radicals was obtained by irradiating an aqueous solution of bromacil containing nitrate. (Nitrate has been shown to generate hydroxy radicals upon

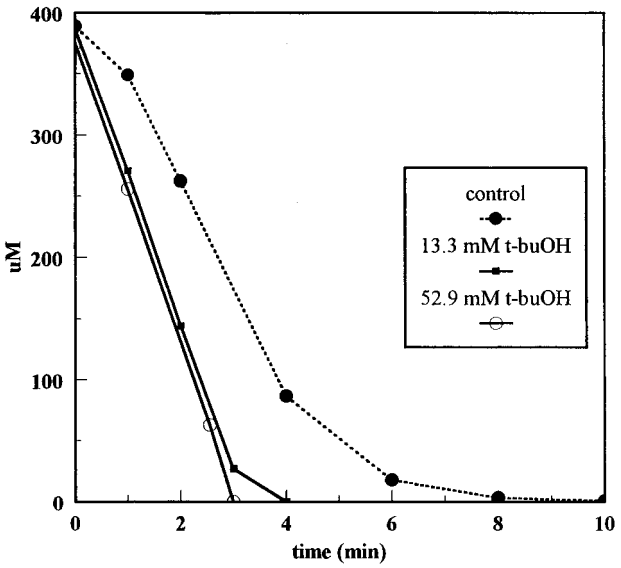

Figure 10. Bromacil ozonolysis in the presence of 0, 13.3 or 52.9 mM *t*-BuOH: k'(no *t*-BuOH) = 0.29 min^{-1} (r^2 = 0.97), k'-(13.3 mM *t*-BuOH) = 0.62 min^{-1} (r^2 = 0.90), k'(52.9 mM *t*-BuOH) = 0.97 min^{-1} (r^2 = 0.92).

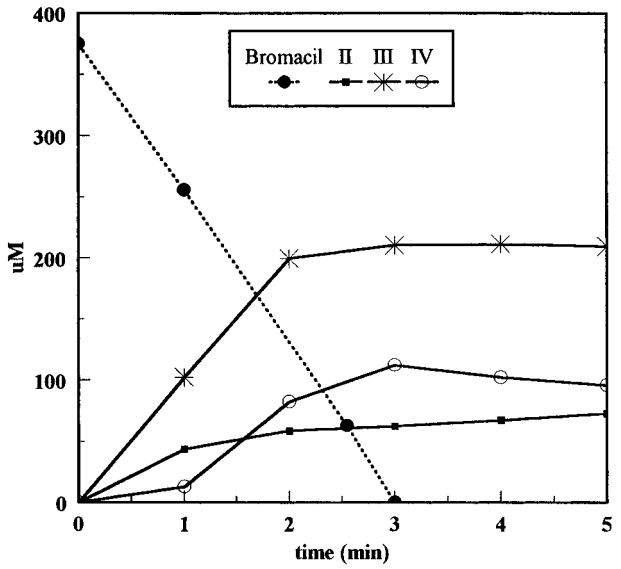

Figure 11. Product profile of bromacil ozonolysis in the presence of 52.9 mM *t*-BuOH.

irradiation (Zepp *et al.*, 1987).) The products generated during this process were examined by HPLC equipped with a photodiode array detector. None of the products observed had retention times or UV spectra similar to those of the products observed during ozonolysis (data not shown) (Anderson, 1996). A small amount of **II** was observed in an aqueous bromacil solution that contained no nitrate, which was not entirely unexpected (Acher and Dunkelblum, 1979; Acher *et al.*, 1994).

These data, then, are consistent with the following mechanism (Figure 5). Ozone attack on the bromacil carbon−carbon double bond gives rise to the ozonide, **V**, which can collapse to form the epoxide, **VI**. Opening of the epoxide and loss of Br^- followed by intramolecular rearrangement affords **II**. Alternatively, the ozonide can open directly, cleaving the C5−C6 bond. Bromide release, ring closure, and subsequent loss of the acyl-type moiety gives rise to **III**. Finally, Br^- can react directly with O_3 (k = 160 M^{-1} s^{-1}) (Haag and Hoigné, 1983) to give ^-OBr. The electrophilic addition of HOBr (HOBr ⇌ ^-OBr, pK_a = 8.8) to the C5−C6 double bond of bromacil yields **IV** (March, 1977; Haag and Hoigné, 1983; Cavanaugh *et al.*, 1992; Glaze *et al.*, 1993).

CONCLUSIONS

The mechanism for the ozonolysis of bromacil was shown to proceed via direct ozone attack as opposed to a hydroxy radical process. Furthermore, the reaction proceeds via parallel pathways as opposed to an in-series pathway. The dibromohydrin, which decomposes to the phytotoxic starting material, bromacil, is believed to be the reason for the residual phytotoxic effect of ozonated bromacil solutions (Acher *et al.*, 1994). The results presented here indicate that under conditions in which $^{\bullet}OH$ is scavenged, the rate of bromacil ozonolysis is significantly enhanced; however, the formation of the phytotoxic precursor, **IV**, remains constant or slightly increases. The addition of hydrogen peroxide, although a slower reaction, apparently diminishes the formation of **IV** substantially. The results of this work suggest that, in situations where photolytic remediation of bromacil is precluded and elimination of phytotoxicity is desirable, conditions which favor a hydroxy radical process (higher pH and H_2O_2 addition) would be preferred. This is generally the more common method of ozonation for most waste streams as decomposition of many organic species proceeds via a hydroxy radical process (Masten and Davies, 1994).

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