Effect of Sorbic Alcohol on the Radiolysis of Aromatic Compounds in Aqueous Solution

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Sorbic alcohol ($CH_3CH{=}CHCH{=}CHCH_2OH$) and 2-phenylethanol ($C_6H_5CH_2CH_2OH$) or phenylacetic acid/phenylacetate ($C_6H_5CH_2COOH/C_6H_5CH_2COO^-$) have been studied as a model for the conjugated double bond (C−C═C−C═C−C−NH−) and phenyl (C_6H_5−C−C−O−) residues in 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyl-4,6-dienoic acid. The latter is known to play a key role in the toxicity of microcystins, which are well-known natural toxins found in water. Particular attention was focused on studying the products of the ionizing radiation-induced organic peroxyl radical intermediates in the separated systems compared to those obtained in the mixed solutions of sorbic alcohol and the aromatic compounds. The aromatic hydroxylation and peroxide yields reflect the respective reaction rate constants of the above solutes with •OH radicals at pH 7.0. In contrast, at pH 3.1 the effect of sorbic alcohol on decreasing the aromatic hydroxylation and increasing the peroxide yields is considerably higher than expected on the basis of •OH scavenging only. The results are discussed in terms of scrambled reactions between the peroxyl radicals in light of the lack of observed products arising from phenyl hydroxylation in the photocatalytic destruction of microcystin.

Introduction

Microcystins are well-known natural toxins found in water with the general structure cyclo(-D-Ala-L-*X*-erythro-*β*-D-methyl-aspartic acid-L-*Y*-ADDA-D-isoglutamic acid-*N*-methyl dehydro alanine), where *X* and *Y* represent amino acid segments and ADDA stands for 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyl-4,6-dienoic acid. Figure 1 shows the structural formula of microcystin-LR.

Recent evidence suggests that ADDA plays a key role in the toxicity of the microcystins. The stereochemistry of the conjugated diene group also influences the toxicity as well as the degree of methylation of the cyclic peptide.[1−7] It has been shown that TiO_2 photocatalysis effectively destroys microcystin-LR in aqueous solutions forming nontoxic byproducts.[8] Photocatalytic oxidation was enhanced in the presence of the electron acceptor H_2O_2, as is the case with many other pollutant destructions.[9] A detailed study of the photocatalytic oxidation of microcystin-LR shows the addition of •OH to the diene group of the ADDA at the earliest stage of the oxidation.[10,11] However, there are no oxidation intermediates, which can be attributed to the hydroxylation of the phenyl side group, although the reactivity of •OH toward phenyl rings ($k \approx 7 \times 10^9$ M^{-1} s^{-1}),[12,13] double bonds ($k \approx 3 \times 10^9$ M^{-1} s^{-1}),[14,15] and dienes ($k \approx 7 \times 10^9$ M^{-1} s^{-1})[14] is comparable.

The predominant objective of the present work is to study the distribution of the products of the reaction of •OH in mixed systems containing both diene and aromatic compounds in aqueous solutions. In other words, do the relative concentrations of final reaction products in the mixed system correspond to the relative reactivity of the competing solutes toward •OH? To answer this question, we studied sorbic alcohol ($CH_3CH{=}CHCH{=}CHCH_2OH$ (SA)) as a model of the conjugated double bond residue −C−C═C−C═C−C−NH− in ADDA and separately phenylacetic acid or 2-phenylethanol as models

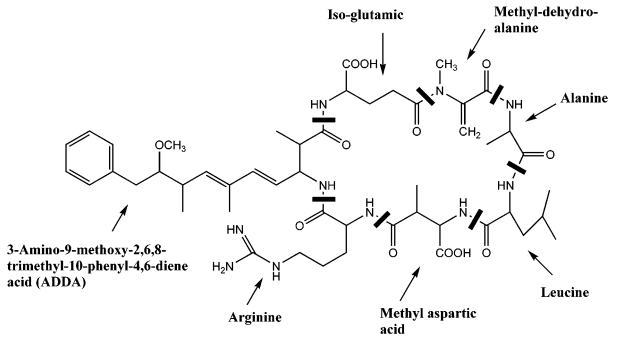

Figure 1. Formula of microcystin-LR.

of the phenyl C_6H_5−C−C−O− residue in ADDA. Particular attention was paid to the study of the products of the organic peroxy radical intermediates in the separated systems as well as in mixed solutions of SA and $C_6H_5CH_2CH_2OH$ or $C_6H_5CH_2COOH/C_6H_5COO^-$ in neutral and acidic solutions.

Experimental Section

Reagents. *trans,trans*-2,4-Hexadien-1-ol ($CH_3CH{=}CHCH{=}CHCH_2OH$, known as sorbic alcohol (SA)), phenylacetic acid, 2-phenylethanol, *o*-, *m*-, and *p*-$HOC_6H_4CH_2COOH$, and *o*-, *m*-, and *p*-$HOC_6H_4CH_2CH_2OH$ were purchased from Aldrich and used as received. H_2O_2 (Merck), catalase (Sigma), and potassium biphthalate (Baker Chemical) were also used as received. All experiments were carried out at room temperature.

***γ*-Irradiation.** *γ*-Radiolysis experiments were carried out with a ^{137}Cs source. The dose rate (9.3 Gy/min) was determined with the Fricke dosimeter. Irradiations were performed in sealed glass vessels containing 6.5 mL at pH 3.1 (1 mM HCl) or 7.0 (1 mM phosphate buffer). Solutions were equilibrated with N_2O or N_2O/O_2 (4:1 v/v) gas mixture at 1 atm of pressure for at least 10 min.

Product Analysis. Samples were analyzed by HPLC (Merck-Hitachi L-6200A) using a L-4500 diode-array detector. The

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products were eluted at a flow rate of 1 mL/min from an LiChroCART 75-4 Superspher 100 RP-18 column (Merck). The mobile phase in the $C_6H_4CH_2COOH$ system contained 10% CH_3CN in water (v/v) at pH 4.15 (50 mM phosphate buffer), and that in the $C_6H_4CH_2CH_2OH$ system contained 30% methanol in water (v/v). Calibrations were carried out with standard solutions of $C_6H_5CH_2CH_2OH$, *o*-$HOC_6H_4CH_2CH_2OH$, *m*-$HOC_6H_4CH_2CH_2OH$, *p*-$HOC_6H_4CH_2CH_2OH$, $C_6H_5CH_2COOH$, *o*-$HOC_6H_4CH_2COOH$, *m*-$HOC_6H_4CH_2COOH$, and *p*-$HOC_6H_4CH_2CH_2OH$. The retention times were 5.5 min (*p*-$C_6H_5CH_2CH_2OH$), 6.7 min (*m*-$HOC_6H_4CH_2CH_2OH$), 8.8 min (*o*-$HOC_6H_4CH_2CH_2OH$), 16.5 min ($C_6H_5CH_2CH_2OH$), 5.2 min (*p*-$HOC_6H_4CH_2COOH$), 6.7 min (*m*-$HOC_6H_4CH_2COOH$), 9.0 min (*o*-$HOC_6H_4CH_2COOH$), and 16.9 min ($C_6H_5CH_2COOH$). The radiolytic products of SA did not interfere with the detection of the aromatic compounds.

Hydroperoxides were analyzed by the molybdate-activated iodide assay.[16,17] The hydroperoxide concentration was determined by the addition of 1 mL of 0.15 M biphthalate buffer (pH 4), 1 mL of 0.3 M NaI, and 20 μL of 1 mM ammonium molybdate to 1 mL of irradiated solution. In view of the relatively slow oxidation of iodide by the organic hydroperoxides,[18] the buildup of I_3^- was followed at 350 nm until a plateau was reached. The concentration of the hydroperoxide was calculated as half of the I_3^- concentration using $\epsilon_{350} = 25\,000$ M^{-1} cm^{-1}. The organic hydroperoxide concentration was determined after the addition of 40 μL of 1.3×10^4 units/mL catalase to 1 mL of the irradiated sample.

Results and Discussion

Reaction 1 represents the radiation-induced formation of the primary radical and molecular species. The numbers in parentheses are the *G* values at low scavenger concentrations, which represent the concentrations of the species (in 10^{-7} M Gy^{-1}), and are somewhat higher in the presence of high solute concentrations. In the presence of N_2O, the solvated electrons are converted to $^{\bullet}OH$ radicals according to eq 2. The hydroxyl radicals usually react with organic solutes by H abstraction or by addition to double bonds or aromatic rings. Thus, SA is expected to undergo both H abstraction (reactions such as 3) as well as addition to the double bonds (reactions such as 4). Reaction 3 is expected to involve predominantly α-hydrogen atom abstraction, and the $^{\bullet}OH$ reaction with the aromatic compounds is expected to take place predominantly by addition to the benzene ring (a reaction such as 5 for $C_6H_5CH_2CH_2OH$). The respective reaction with $C_6H_5CH_2COOH$ is similar, although H abstraction also takes place in parallel (reaction 6). The organic radicals resulting from reactions 3−6 rapidly react with O_2 to produce the respective peroxyl radicals (reaction 7 for a general organic radical $R'R''HC^{\bullet}$). The fate of the peroxyl radical depends on the nature of the organic residue. Peroxyl radicals undergo a number of unimolecular processes. The ubiquitous ones are $HO_2^{\bullet}/O_2^{\bullet-}$ eliminations. In the case of aromatic peroxyl radicals, where both para and ortho isomers are produced, because of steric reasons, only the former eliminates $HO_2^{\bullet}$ and generates the respective stable hydroxylated product (a reaction such as 8 for $C_6H_5CH_2CH_2OH$).[19−21] The elimination of $HO_2^{\bullet}$ eventually forms H_2O_2 by the dismutation of $HO_2^{\bullet}/O_2^{\bullet-}$. Alkyl peroxyl radicals undergo the base-catalyzed elimination of $HO_2^{\bullet}$ when there is an −OH function in the α position with respect to the peroxyl radical (reaction 9 stands for R″= OH).[21,22] Peroxyl radicals, which do not decay in a unimolecular process, disappear bimolecularly, forming a tetroxide intermediate (reaction 10), which among other reactions (reactions 12 and 13) decomposes to give alkoxyl radicals (reaction 11).[21] Whenever the alkoxyl radical bears α-hydrogen atoms, a rapid 1,2-H shift occurs in water (reaction 12).[23,24] This rearrangement, which converts an alkoxyl radical to a α-hydroxy alkyl radical, also yields $O_2^{\bullet-}$. Thus, the reactions of $^{\bullet}OH$ with organic solutes in the presence of oxygen are complicated by the variety of intermediates and possible competing reactions.

$$H_2O\wedge\wedge\wedge \rightarrow e_{aq}^- (2.7)\ H^{\bullet} (0.6),\ ^{\bullet}OH (2.6),\ H_2O_2 (0.7),\ H_2 (0.45),\ H_3O^+ (3.7),\ OH^- (1.0) \quad (1)$$

$$e_{aq}^- + N_2O(H_2O) \rightarrow N_2 + {}^{\bullet}OH + OH^- \quad (2)$$

$$^{\bullet}OH + CH_3CH{=}CHCH{=}CHCH_2OH \rightarrow CH_3CH{=}CHCH{=}CHC^{\bullet}HOH + H_2O \quad (3)$$

$$^{\bullet}OH + CH_3CH{=}CHCH{=}CHCH_2OH \rightarrow CH_3CH(OH){-}C^{\bullet}HCH{=}CHCH_2OH \quad (4)$$

$$^{\bullet}OH + C_6H_5CH_2CH_2OH \rightarrow HOC_6H_5CH_2CH_2OH \quad (5)$$

$$^{\bullet}OH + C_6H_5CH_2CH_2OH \rightarrow C_6H_5CH_2C^{\bullet}HOH \text{ (or } C_6H_5C^{\bullet}HCH_2OH) + H_2O \quad (6)$$

$$R'R''HC^{\bullet} + O_2 \rightarrow R'R''HCO_2^{\bullet} \quad (7)$$

$$HOC_6H_5CH_2CH_2OH + O_2 \rightarrow p\text{-}HOC_6H_4CH_2CH_2OH + HO_2^{\bullet} \quad (8)$$

$$R'H(OH)CO_2^{\bullet} \rightarrow R'HC{=}O + HO_2^{\bullet} \quad (9)$$

$$R'R''HCO_2^{\bullet} + R'R''HCO_2^{\bullet} \rightarrow R'R''HCOOOOCHR'R'' \quad (10)$$

$$R'R''R'''COOOOCR'R''R''' \rightarrow 2R'R''R'''CO^{\bullet} + O_2 \quad (11)$$

$$R'R''HCO^{\bullet} \rightarrow R'R''(OH)C^{\bullet} \quad (12)$$

$$R'R''CHOOOOCHR'R'' \rightarrow 2R'R''C{=}O + H_2O_2 \quad (13)$$

$$R'R''CHOOOOCHR'R'' \rightarrow R'R''HCOOCHR'R'' + O_2 \quad (14)$$

Sorbic Alcohol System. The $^{\bullet}OH$ radical may add to one of the four double-bonded C atoms with the formation of a number of different intermediates of the type shown in reaction 4. H-abstraction is most likely to occur at the α-hydrogen. Because the reaction rate of $^{\bullet}OH$ with diene segments ($k \approx 7 \times 10^9$ M^{-1} s^{-1}) is about 3.5 times faster than α-hydrogen abstraction, it is expected that 75−80% of $^{\bullet}OH$ radicals add to the diene whereas most of the remaining abstract a H atom. The HPLC analysis shows the buildup of three distinct unidentified signals, which increase linearly with the time of irradiation up to at least 280 Gy (Figure 2). We determined at pH 3.1 that $G(H_2O_2) = 1.3$ and G(organic peroxides) = 1.5, whereas the respective values at pH 7.0 are 2.5 and 0.55. The total peroxide yield is thus 2.8 at pH 3.1 and 3.05 at pH 7.0, and the main effect of increasing the pH is an increase in the H_2O_2 yield at the expense of the organic peroxides. This may be expected in view of the general basic catalysis of reaction 9.[17,25] The primary radiation yield of H_2O_2 in water is $G_{H_2O_2} = 0.75$; therefore, the total

TABLE 1: Aromatic Hydroxylation and Peroxide Yields in $C_6H_5CH_2CH_2OH$ or $C_6H_5CH_2COOH/C_6H_5CH_2COO^-$ Solutions Equilibrated with a Mixture of 4:1 N_2O/O_2 (v/v) Unless Otherwise Indicated

scavenger	pH	*G*(ortho)	*G*(meta)	*G*(para)	$G(H_2O_2)$	*G*(organic peroxides)
$C_6H_5CH_2CH_2OH$[a]	3.1	<0.01	<0.01	<0.01	NA[b]	NA[b]
$C_6H_5CH_2CH_2OH$	3.1	0.31	0.34	0.43	1.12	0.55
$C_6H_5CH_2CO_2H$	3.1	0.79	0.64	0.55	1.30	0.20
$C_6H_5CH_2CH_2OH$[a]	7.0	0.11	0.11	0.19	NA[b]	NA[b]
$C_6H_5CH_2CH_2OH$	7.0	0.29	0.34	0.49	2.20	0.50
$C_6H_5CH_2CO_2^-$	7.0	0.71	0.43	0.35	1.75	0.15

[a] No oxygen present. [b] Not available.

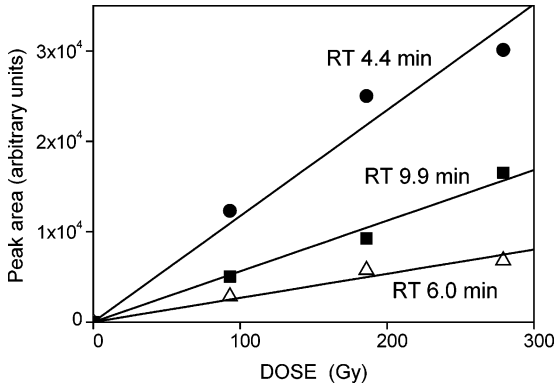

Figure 2. Linear buildup of HPLC signals induced by the irradiation of SA. Solutions were saturated with N_2O/O_2 (4:1) and contained 1 mM SA at pH 7.0 (1 mM phosphate buffer).

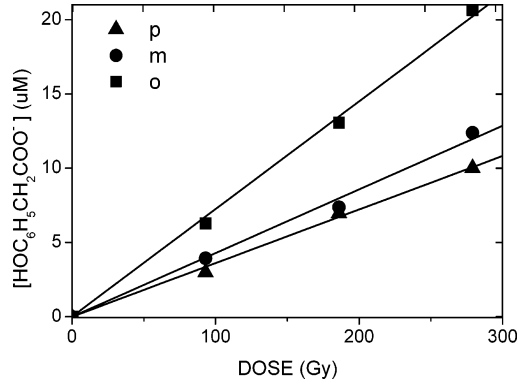

Figure 3. Radiation-induced hydroxylation of phenylacetate. Solutions were saturated with N_2O/O_2 (4:1) and contained 5 mM $C_6H_5CH_2COO^-$ at pH 7.0 (1 mM phosphate buffer).

peroxide yield is expected to be about $G = 3.7$ (i.e., each mol of alkyl peroxyl radical yields 0.5 mol of H_2O_2). The difference between the expected and measured yields is apparently due to peroxyl radical reactions leading to organic peroxides, which do not oxidize iodide.[18,26]

2-Phenylethanol and Phenylacetic Acid Systems. Hydroxylation of the benzene ring takes place at the ortho, meta, and para positions when the aromatic compound reacts with •OH in the presence of oxygen. The hydroxylation buildup is linear with the dose up to at least 280 Gy. Typical results are shown for $C_6H_5CH_2CO_2^-$ at pH 7.0 in Figure 3. In the presence of oxygen, the yields of the aromatic hydroxylation at pH 7.0 are similar to those obtained at pH 3 and are significantly higher than those measured in the absence of oxygen. The results are summarized in Table 1. Obviously, the aromatic hydroxylation accounts for considerably less than half of the products' yields, the total of which is expected to be equivalent to $G_{OH} + G_e \approx 6$. The yields of the organic peroxides are too low to make up the material balance. Consequently, more than half of the •OH radicals lead to the formation of products, which have not been

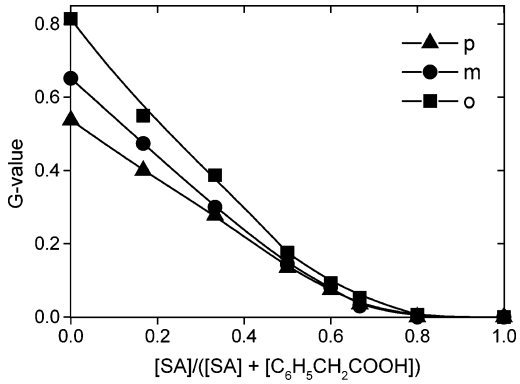

Figure 4. Effect of SA on the hydroxylation of phenylacetic acid at pH 3.1. Solutions were saturated with N_2O/O_2 (4:1) and contained 2.5 or 5 mM phenylacetic acid.

detected. In view of the considerably higher reactivity of the aromatic ring toward •OH, compared to the aliphatic segments, the majority of these products most probably result from aromatic hydroxylation intermediates.

As seen in Table 1, the hydrogen peroxide yield is higher than $G_{H_2O_2} = 0.75$ and is higher at pH 7.0 than at pH 3.1. This may be explained by the base-catalyzed elimination of $HO_2^•$ from peroxyl radicals.

Mixed Systems. Upon the irradiation of a mixed system containing SA and $C_6H_5CH_2CH_2OH$ or $C_6H_5CH_2CO_2H/C_6H_5CH_2CO_2^-$, the initial sites of •OH attack are determined by the relative reaction rates of the respective sites, although subsequent reactions may determine the relative concentrations of the final products. We found that the addition of SA to $C_6H_5CH_2CH_2OH$ or $C_6H_5CH_2CO_2H/C_6H_5CH_2CO_2^-$ both at pH 3.1 and 7.0 reduced the aromatic hydroxylation products in a concentration-dependent manner. Typical results for the effect of added SA on the aromatic hydroxylation of $C_6H_5CH_2CO_2H$ at pH 3.1 are shown in Figure 4, and the rest of the results are shown in Figures 1s−3s (Supporting Information).

The relative reaction rate of •OH with a scavenger, compared to its specific reaction rate with segments leading to measurable product(s), can be derived from the relation between G_{OH} and *G*(measured product). Thus, from the effect of SA on aromatic hydroxylation in the competing aromatic solutes, it is possible to derive the ratio k_{15}/k_{16} if reactions between intermediates do not offset the results of initial •OH attack.

$$^•OH + CH_3CH{=}CHCH{=}CHCH_2OH \rightarrow \text{radical products of SA} \quad (15)$$

$$^•OH + C_6H_5CH_2R \rightarrow \text{radical products of } C_6H_5CH_2R \quad (16)$$

However, if secondary reactions induce scrambling, then the final product distribution is not determined solely by the relative efficiencies of the •OH reactions, and the resulting apparent k_{15}/k_{16} will be erroneous. Consider •OH addition to a specific

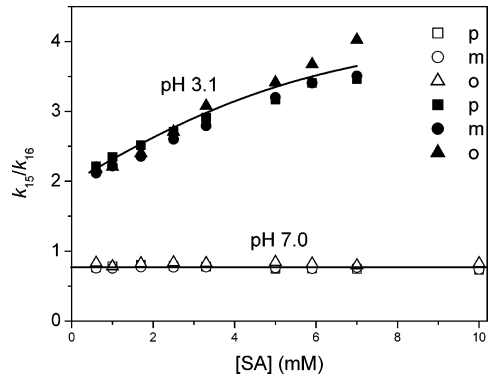

Figure 5. Effect of [SA] on the apparent ratio k_{15}/k_{16} at a constant [$C_6H_5CH_2CH_2OH$]. Solutions were saturated with N_2O/O_2 (4:1) and contained 5 mM $C_6H_5CH_2CH_2OH$ at pH 3.1 (solid symbols) or pH 7 (open symbols).

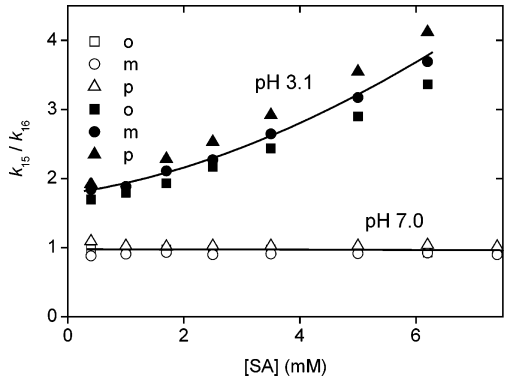

Figure 6. Effect of [SA] on the apparent ratio k_{15}/k_{16} at constant [$C_6H_5CH_2COOH$] and [$C_6H_5CH_2COO^-$]. Solutions were saturated with N_2O/O_2 (4:1) and contained a 5 mM aromatic scavenger at pH 3.1 (solid symbols) or pH 7 (open symbols).

site (reaction 17, where *x* stands for ortho, meta, or para positions), the reaction rate constant k_{17} can be expressed in terms of k_{16} and the respective *G* values, according to eq 18, where $G°(x\text{-}OH^{\bullet}C_6H_5CH_2R)$ is the yield of $x\text{-}OH^{\bullet}C_6H_5CH_2R$ in the SA-free system containing $C_6H_5CH_2R$ and N_2O/O_2.

$$^{\bullet}OH + C_6H_5CH_2R \rightarrow x\text{-}OH^{\bullet}C_6H_5CH_2R \qquad (17)$$

$$k_{17} = \frac{k_{16}G°(x\text{-}OH^{\bullet}C_6H_5CH_2R)}{G_{OH}} \qquad (18)$$

In the presence of both $C_6H_5CH_2R$ and SA, eq 19 is obtained:

$$G(x\text{-}OH^{\bullet}C_6H_5CH_2R) = \frac{G^0(x\text{-}OH^{\bullet}C_6H_5CH_2R)}{1 + k_{15}[SA]/k_{16}[C_6H_5CH_2R]} \qquad (19)$$

The values of k_{15}/k_{16}, which were calculated from measured aromatic hydroxylation using eq 19, are presented in Figures 5 and 6 as a function of [SA] at constant [$C_6H_5CH_2R$]. The results at pH 7.0 show that $k_{15}/k_{16} = 0.8$ and 1.0 for $C_6H_5CH_2CH_2OH$ and $C_6H_5CH_2CH_2COO^-$, respectively. The values of this ratio are in agreement with the known rate constant ratio of about 1 for the reaction of $^{\bullet}OH$ with phenyl groups[12,13] and conjugated double bonds.[14] At pH 3.1, the apparent k_{15}/k_{16} ratio increases with [SA], indicating scrambled reactions between the peroxyl radicals, which favor products derived from the diene compound. We do not know whether the decrease in aromatic hydroxylation beyond the expected effect of SA on the competition between

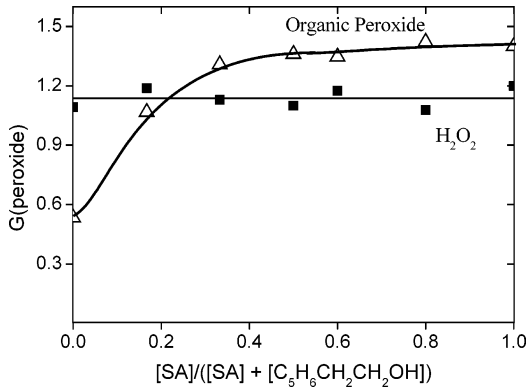

Figure 7. Effect of [SA] on the peroxide yields in a SA/$C_6H_5CH_2$-CH_2OH mixed system at pH 3.1. Solutions were saturated with N_2O/O_2 (4:1) and contained 2.5 or 5 mM $C_6H_5CH_2CH_2OH$.

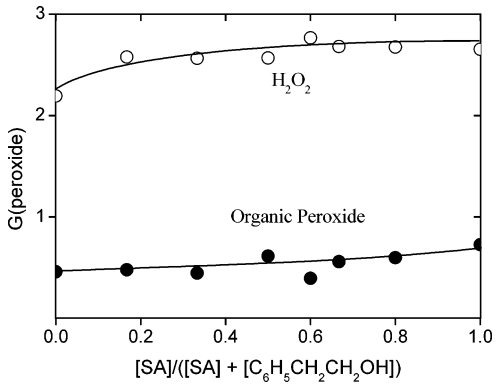

Figure 8. Effect of [SA] on the peroxide yields in a SA/$C_6H_5CH_2$-CH_2OH mixed system at pH 7.0. Solutions were saturated with N_2O/O_2 (4:1) and contained 2.5 or 5 mM $C_6H_5CH_2CH_2OH$.

reactions 15 and 16 is due to −OH transfer from the phenyl to the diene. More likely, the reason is the increase in the number of undetected aromatic products because of peroxyl intermediate scrambled reactions with SA peroxyl derivatives or superoxide radicals. The lifetime of peroxyl radicals at pH 7.0 is smaller than at pH 3.1 because of the base-catalyzed elimination of $HO_2^{\bullet}$. Hence the hydroxylation yields in neutral pH reflect the distribution of the hydroxyl radicals between the reactants of reactions 15 and 16.

H_2O_2 and Organic Peroxides in Binary Systems. The yields of H_2O_2 and organic peroxides in binary solutions containing SA and $C_6H_5CH_2CH_2OH$ at pH 3.1 or 7.0 are shown in Figures 7 and 8 as a function of the mole fraction of SA. Similar results were obtained for $C_6H_5CH_2COOH/C_6H_5CH_2COO^-$ and are shown in Figures 4s−5s (Supporting Information). At pH 3.1, the main contribution to $G(H_2O_2)$ is from the primary radiation yield. The yield of H_2O_2 in the separated systems at pH 3.1 is comparable; therefore, it is not surprising that it changes relatively little upon increases in [SA]/[$C_6H_5CH_2R$]. However, the organic peroxide yields in the SA system at pH 3.1 are much higher than the yield in the $C_6H_5CH_2R$ system, and as a result, the yield increases with [SA]/[$C_6H_5CH_2R$]. The average organic peroxide yield is observed at mole fractions of [SA]/([SA] + [$C_6H_5CH_2R$]) = 0.18 and 0.15 for $C_6H_5CH_2COOH$ and C_6H_5-CH_2CH_2OH, respectively, although under such conditions >80% of the hydroxyl radicals react with $C_6H_5CH_2R$. These results show that the formation of peroxides from SA is favored in the mixed system, apparently in relation to the nature of the scrambled reactions. The effect of [SA] on the peroxide yields at pH 3.1 is in line with its effect on the yields of the aromatic hydroxylation (e.g., Figure 4). The respective changes in

hydrogen and organic peroxide yields at pH 7.0 (e.g., Figure 8) are relatively small and do not enable a reliable analysis.

Conclusions

The aromatic hydroxylation and peroxide yields in the combined systems of SA and $C_6H_5CH_2CO_2H/C_6H_5CH_2CO_2^-$ or $C_6H_5CH_2CH_2OH$ reflect the respective reaction rate constants of these solutes with •OH radicals at pH 7.0. At pH 3.1, however, the effect of SA on decreasing aromatic hydroxylation and increasing peroxide yields is considerably higher than expected on the basis of •OH scavenging only. This must be associated with the nature of the scrambled reactions between the peroxyl radicals. Although SA strongly affects the yield of the aromatic hydroxylation beyond its reaction with •OH, relatively high concentrations are required to supress it completely. However, no aromatic hydroxylation was observed in the microcystin system, where •OH radicals have been generated by TiO_2 nanoparticle photolysis.[10,11] This apparent discrepancy can be rationalized by the much higher scrambling probability in microcystin, where both the aromatic and the diene moieties are linked together in the same molecule. The adsorption of microcystin to TiO_2 in a way in which surface •OH radicals are trapped by the diene, and therefore do not reach the phenyl, may also contribute to the observed lack of phenyl hydroxylation.

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Supporting Information Available: Effect of added SA on aromatic hydroxylation. Effect of [SA] on peroxide yields in $SA/C_6H_5CH_2COOH$ and $SA/C_6H_5CH_2COO^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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