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THE EFFECT OF LIQUOR COMPOSITION ON THE RATE OF REACTION OF
LIGNIN MODEL COMPOUND ACETOGUAIACONE IN OXYGEN AND ALKALI

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ABSTRACT

Acetoguaiacone (AV; 4-hydroxy-3-methoxyacetophenone) was reacted with oxygen (1.02 mPa) at 80°C in different alkaline solutions. All reactions exhibited a pseudo first order dependence on the initial AV concentration and showed a faster reaction rate in systems buffered with carbon dioxide than in other buffered alkaline systems. At pH values greater than eight, the reactions of AV in oxygen/noncarbonate buffered solutions had very similar reaction rates. The rate of degradation of AV was much less when reacted with oxygen at a pH lower than the pKa of AV. The composition of the buffer and the pH had a significant effect on the yield of oxidation products. The existence of carbonate radicals ($\text{HC}\ddot{\text{O}}_3$) and radical anions (CO_3^-) is postulated to account for the faster reaction rate of AV with oxygen in carbonate buffers. These radicals are known to be generated in aqueous carbonate solutions when hydroxyl radicals are present. The addition of DMSO (a known hydroxyl radical scavenger) to AV-oxygen-sodium hydroxide, AV-oxygen-borate buffer, and AV-oxygen-sodium bicarbonate buffer led to slower reaction rates, with the latter exhibiting the greatest rate reduction. These results suggest both hydroxyl radicals and carbonate radicals can play important roles during the oxygen-alkali reactions of AV.

INTRODUCTION

Aoyagi, Hosaya, and Nakano¹ have shown that apocynol (α -methylvanillyl alcohol) and AV are consumed more rapidly by oxygen in

aqueous sodium carbonate than in aqueous NaOH solution. Oxygen delignification of wood proceeds more slowly in carbonate solutions than in caustic². The reasons for this rapid degradation of AV (often considered a lignin model) in carbonate solutions by oxygen is the objective of this research.

RESULTS AND DISCUSSION

Initial experiments using duplicate reactions of AV (33.6 mM) were carried out in 1.25N NaOH (pH 12.8), 1.25N Na₂CO₃ (pH 10.8), and 1.25N NaHCO₃ (pH 8.9) at 80°C and 1.02 MPa O₂. Samples were collected over a period of 24 hours and were analyzed by GLC techniques for the disappearance of AV. The curves in Figure 1 record the disappearance of AV in these different alkaline systems.

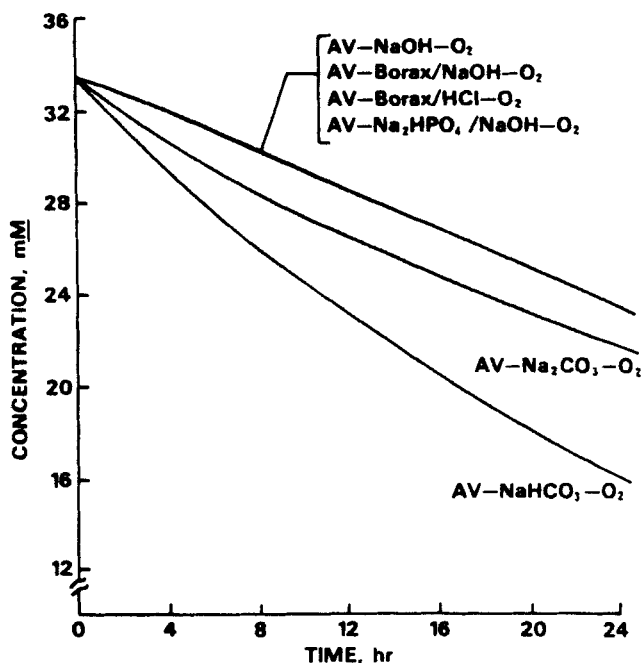


Figure 1. Disappearance of AV (33.6 mM) at 80°C and 1.2 mPa O₂ in various alkaline solutions.

Since statistical analysis showed the 3 plots to be unique and statistically distinguishable from one another at the 95% confidence level on the basis of the students t test,³ data points for the various plots were omitted. In agreement with Aoyagi *et al.*,¹ AV was degraded more rapidly in Na₂CO₃ solution than in NaOH solution by oxygen. The rate of degradation of AV was greatest in NaHCO₃ solution.

The differential method of kinetic analysis was employed to determine if the increased rate of disappearance of AV with decreasing pH was due to acceleration without alteration of existing reaction mechanisms or if it was the result of a change in reaction kinetics.^{4,5} Two additional pairs of reactions were therefore carried out at initial AV concentrations of 11.2 mM and 100.8 mM in each of the three alkaline systems. The logarithmic plots of the initial rates of reaction vs. the initial concentrations of AV (11.2 mM, 33.6 mM, and 100.8 mM) gave straight lines with slopes of 1.05 (AV-NaOH-O₂), 1.16 (AV-Na₂CO₃-O₂), and 1.07 (AV-NaHCO₃ - O₂). All these systems exhibit an apparent first order kinetic dependence on AV concentration at the beginning of the reaction. The rate constants evaluated from the intercepts of the logarithmic plots were as follows: AV-NaHCO₃-O₂ (0.030 ± 0.003 hr⁻¹) > AV-Na₂CO₃-O₂ (0.019 ± 0.002 hr⁻¹) > AV-NaOH-O₂ (0.016 ± 0.002 hr⁻¹). Changing the ionic strength of the reaction of AV with oxygen in NaOH from 1.25 to 0.8 to 0.4 but maintaining the pH approximately constant had no detectable effect upon the initial rate of reaction with oxygen although different product distributions were attained. It is likely that the rate of reaction of AV with oxygen does change with hydroxyl anion concentration at 80°C, since it does so at 120°C⁶. Under these conditions the change in rate is within experimental error. Thus, AV appears to react by the same initial mechanism in all these alkaline media, and the mechanism is accelerated as the pH is diminished from 12.8 to 8.9 by means of carbonate buffers.

Acetoguaiacone was next reacted with oxygen in two borax buffer solutions: borax/NaOH (initial pH, 10.8) and borax/HCl

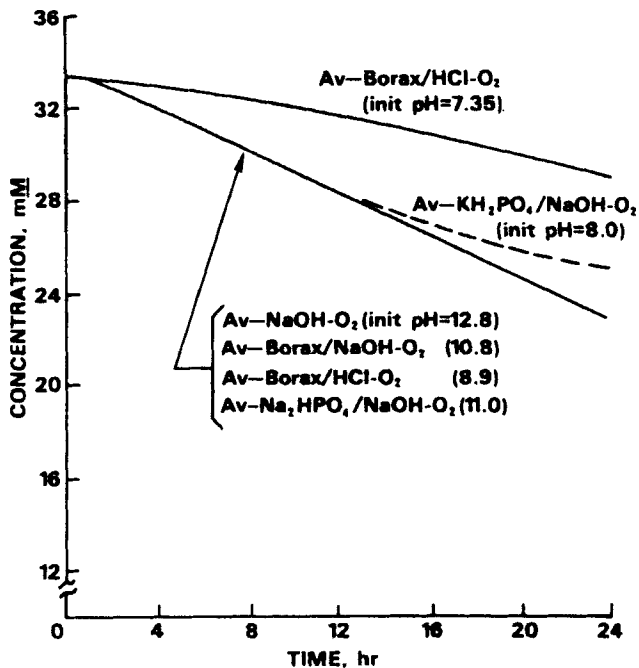


Figure 2. Disappearance of AV (33.6 mM) at 80°C and 1.2 mPa O₂ in various alkaline solutions.

(initial pH 8.9). A phosphate buffer system, NaHPO₄/NaOH (initial pH 11.0) was also used. Statistical analysis showed these three plots to be indistinguishable from each other and indistinguishable from the AV-NaOH-O₂ plot discussed earlier (Figure 2). Differences in the rates of reaction of AV probably exist but are within experimental error. Thus, under these conditions, no difference in the rate of reaction of AV with oxygen is observed if the reaction pH is greater than the pK_a of AV.

Another series of experiments was undertaken to investigate the effect of reacting AV with oxygen in alkaline solutions in which the pH was slightly greater than the pK_a of AV (7.5). The first experiment, employing phosphate buffer (initial pH 8.0), initially followed anticipated behavior (Figure 3), but the reaction rate slowed significantly as the pH of the solution decreased

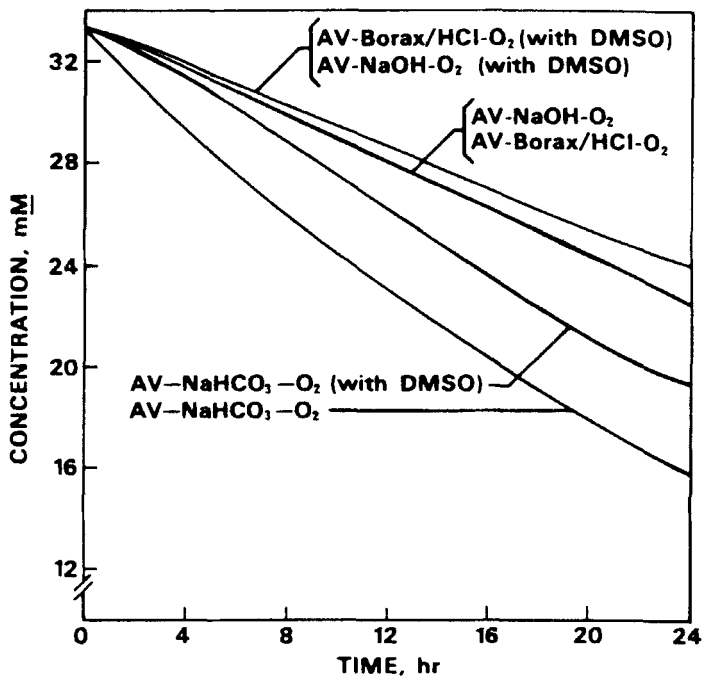


Figure 3. Disappearance of AV (33.6 mM) at 80°C and 1.2 mPa O₂ in various alkaline solutions with and without the addition of 66.7 mM DMSO.

to a final value of 7.1 (less than the pKa of AV). This behavior would be expected if the phenolate ion concentration became the rate controlling species involved in this oxidation.^{8,9} The second reaction, carried out at pH 7.35 (below the pKa of AV),¹⁰ showed the anticipated slower rate of degradation due to the lesser quantity of phenolate ion. Thus, in noncarbonate buffers, the major change in the rate of reaction depends upon whether the pH of the reaction solution is above or below the pKa of AV. This result probably applies to all phenols in general. Research to be published elsewhere indicates a slight dependence of the rate of degradation of AV on hydroxyl anion concentration at high temperatures.⁶

TABLE 1

Methanol, Acetic Acid, and Insoluble Precipitate Production from AV (33.4 mM) After 24-Hour Oxidation in Different Alkaline Media at 80°C, 1.02 MPa O₂

Reaction	Initial pH	Final pH	MeOH, mole % ^a	CH ₃ COOH, mole % ^a	Insoluble Precipitate ^b
AV-NaOH-O ₂ ^c	12.8	12.6	65	90	0
AV-Na ₂ CO ₃ -O ₂	10.8	10.2	56	50	0
AV-NaHCO ₃ -O ₂	8.9	8.7	53	50	+
AV-borax/ NaOH-O ₂	10.8	10.4	59	55	0
AV-borax/ HCl-O ₂	8.9	8.5	51	50	+
AV-Na ₂ HPO ₄ / NaOH-O ₂	11.0	10.0	53	50	0
AV-KH ₂ PO ₄ / NaOH-O ₂	8.0	7.1	48	50	+
AV-NaOH/ KCl-O ₂	12.0	N.A.	68	80	0

^a% of theoretical available for consumed AV.

^b0 = no observable precipitate, + = precipitate observed.

^cDecreasing the ionic strength at pH 12.7 from I = 1.25 to 0.8 and 0.4 had no effect on the rate of degradation of AV, little effect on acetic acid production, but increased methanol production to 74 mole%.

Although increases in pH beyond the pK_a of AV do not obviously affect the reaction rate or the rate controlling steps, they do play an important role in subsequent reactions (Table 1). Demethoxylation (production of methanol) accounts for a greater proportion of degraded AV at higher pH than at lower pH. This is consistent with the findings of other researchers.^{1,11,12} A plausible route for the production of methanol involves the conversion of the appropriate cyclohexadienone hydroperoxide into the corresponding orthoquinone intermediate and methanol by attack of a hydroxyl anion at a methoxyl group.^{11,13,14}

The production of acetic acid is probably the result of a Dakin-like degradation of the appropriate cyclohexadienone hydroperoxide by a mechanism proposed by Kratzl *et al.*^{15,16} The high

acetic acid production in the AV-NaOH-O₂ reaction is due to the increased formation of the hydroperoxide anion (pK_a ~ 11.5¹⁷) by the strong base. Tests have shown that the yields of methanol and acetic acid were increased with decreasing ionic strength at constant pH.

A black precipitate was formed when the media of the reactions conducted at pH 8.9 were acidified to pH 1.5 with strong mineral acid. No precipitate appeared when the media of the reactions conducted at higher pH were acidified. Ultraviolet, infrared, and GLC-MS analysis indicated that this material was probably a polymerization product derived from AV. The tendency of quinones to undergo condensation reactions during autoxidation is known, and this happens to lignin when Na₂CO₃ is used as cooking liquor.^{1,17} Since the precipitate was observed only after reactions at pH 8.9, it is possible that it was not formed at high pH. If formed at higher pH values, it may have degraded to small products. This speculation is consistent with the generally lower critical oxidation potentials of ligninlike dimers compared to the monomers.^{15,16}

Many of the carboxylic acid products from the reaction solutions were identified as their trimethylsilyl (TMS) derivatives by GLC-MS. The identification was made by interpretation and comparison of spectra with those in the literature (library) and (in most cases) by comparison with the GLC retention times and mass spectra of authentic samples. A typical gas chromatogram is shown in Figure 4. The principal products detected after 24 hours of reaction are seen in Table 2. Maleic acid was missing in the AV-NaOH-O₂ systems, whereas 2-hydroxyisobutyric acid was found only in the latter. More products (oxalic and malonic acids) were detected after reaction in the AV-NaHCO₃-O₂ system. Despite the errors involved (standard deviations in the range of 10 to 30%), the high yields of oxalic and malonic acids in the reaction of AV-NaHCO₃-O₂, and oxalic and succinic acids in the reaction of AV-borax/NaOH-O₂ are thought to be significant. Calculations show that the total acids (including acetic acid) based on the carbon balance account for ca. 20-40% of consumed AV. (Most of the dif-

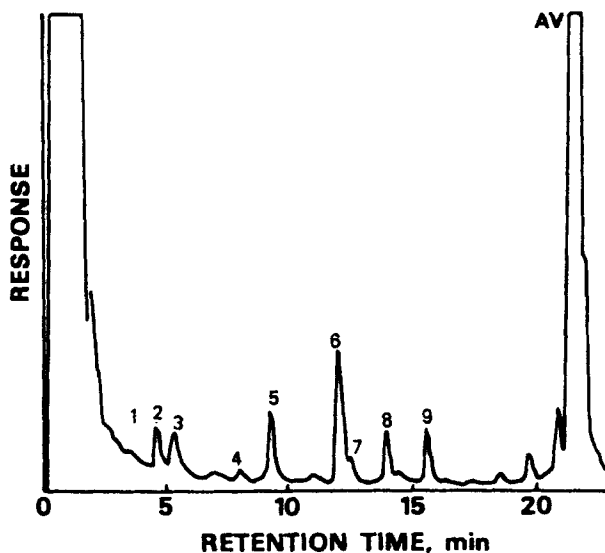


Figure 4. Gas chromatogram of the acidic products of AV in oxygen (MPa) and sodium carbonate (1.25N) at 80°C (initial pH = 10.8) 1 - hydroxyisobutyric acid,* 2 - lactic acid,* 3 - glycolic acid,** 4 - oxalic acid,** 5 - malonic acid,** 6 - succinic acid,** 7 - maleic acid,** 8 - hydroxymalonic acid,* 9 - malic acid**.

*Identified by GLC-MS, and comparison with library.

**Identified as above, and by comparisons with an authentic sample.

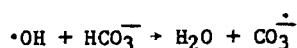
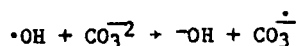
TABLE 2

Carbon Balance of Acidic Products After 24-hour Reaction of 33.4 mM AV in Different Oxygen-alkali Systems

Product	AV-NaOH-O ₂	AV-Na ₂ CO ₃ -O ₂	AV-NaHCO ₃ -O ₂	AV-borax/ NaOH-O ₂
	%	%	%	%
Hydroxyiso- butyric acid	0.6	--	--	--
Lactic acid	0.6	1.0	1.5	1.2
Glycolic acid	1.5	1.0	1.5	1.2
Oxalic acid	0.3	0.6	27.8	6.3
Malonic acid	1.0	2.1	9.0	1.2
Succinic acid	2.1	2.7	2.4	3.9
Maleic acid	--	0.3	2.1	3.9
Hydroxymalonic acid	1.5	1.0	1.5	2.1
Malic acid	0.6	1.0	2.4	1.0
Acetic acid	26.9	18.0	26.9	18.0

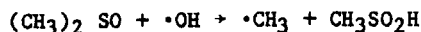
ference is probably due to the formation of carbon dioxide and carbon monoxide).

A survey of the literature indicated that the difference in behavior between carbonate and bicarbonate buffers compared to the phosphate and borate buffers might be attributed to unique reactions of aqueous carbonate solutions. Researchers¹⁸⁻²⁰ have demonstrated by absorption spectroscopy that carbonate radical anions can be generated in aqueous solution from the interaction of bicarbonate and carbonate ions with hydroxyl radicals. Similar interactions between powerful organic radicals (possibly even singlet oxygen) and carbonate ions can also be imagined.



On the basis of the information available in the literature, we propose that the unexpectedly fast reactions in the carbonate buffers in these experiments is due to the generation of carbonate radicals and carbonate radical anions by hydroxyl radicals (frequently claimed to be formed during autoxidative reactions).¹⁴ Because of resonance stabilization, these carbonate species would be expected to be more stable than the hydroxyl radical and less likely to be decomposed by secondary reactions. Chen, Hoffman, and Parsons²¹ have demonstrated that although carbonate radicals are less reactive than the hydroxyl radical, they are more specific toward phenolic anions than the latter.

Other workers using e.s.r./rapid mixing techniques have demonstrated that a rapid reaction occurs between hydroxyl radicals and DMSO²² to give methylsulfinic acid and methyl radical. This reaction was used to test for the presence of hydroxyl radical during autoxidation of AV.



The reaction of AV (33.6 mM) with oxygen (1.02 MPa) in NaHCO₃ (pH 8.9), borax (pH 8.9), and NaOH (pH 12.8) was slowed when 66.7 mM DMSO was added as a scavenging agent. The slopes of the AV disappearance curve (Figure 3) show a decrease when compared to the controls reacted in the absence of DMSO. Statistical analysis indicated the differences exhibited between the borax-DMSO and the caustic-DMSO solutions and their controls are marginal, whereas the difference between the bicarbonate-DMSO system and the uninhibited bicarbonate reaction is statistically unambiguous.

These results are summarized in Table 3, which compares the initial rates of reaction of AV in different alkaline media under otherwise constant reaction conditions. The effect of the addition of DMSO is to inhibit the autoxidation of AV in NaHCO₃ solution and is postulated to result from the quenching of hydroxyl radical, which would otherwise generate carbonate radicals. It is likely that the lesser effect of DMSO on AV in borax buffer (pH 8.9) and caustic (pH 12.8) is also real.

TABLE 3

The Initial Rate of AV Degradation (33.4 mM) in Different Alkaline Media at 80°C and 1.2 MPa O₂

Reaction	Ionic Strength	pH Initial + Final	Initial Rate of AV Degradation, mM/hour
AV-NaOH-O ₂	1.25	12.8 + 12.6	0.4 ± 0.06
AV-NaOH-O ₂ -DMSO	1.25	12.8 + n.a.	0.3 ± 0.05
AV-Na ₂ CO ₃ -O ₂	1.875	10.8 + 10.6	0.8 ± 0.10
	1.25	10.8 + 10.6	0.8 ± 0.10
AV-NaHCO ₃ -O ₂	1.25	8.9 + 8.7	1.1 ± 0.15
AV-NaHCO ₃ -O ₂ -DMSO	1.25	8.9 + n.a.	0.6 ± 0.09
AV-NaOH/KCl-O ₂	0.8	12.7 + 12.6	0.4 ± 0.06
	0.4	12.6 + 12.5	0.4 ± 0.06
AV-borax/NaOH-O ₂	0.185	10.8 + 8.8	0.4 ± 0.06
AV-borax/HCl-O ₂	0.185	8.9 + 8.0	0.4 ± 0.06
AV-borax/HCl-O ₂ -DMSO	0.185	8.9 + n.a.	0.3 ± 0.05
AV-Na ₂ HPO ₄ /NaOH-O ₂	0.185	11.0 + 7.9	0.4 ± 0.06
AV-KH ₂ PO ₄ /HCl-O ₂	0.185	8.0 + 7.1	0.4 ± 0.06
AV-borax/HCl-O ₂	--	7.35 + n.a.	0.1 ± 0.04

The more rapid degradation of AV in the noninhibited bicarbonate system (compared to all other reactions) can be rationalized on the basis of the flow diagram for autoxidation of lignin and lignin models described by Gratzl.¹⁶ The source of the stable carbonate radical with considerable specificity for phenolate ions is not lost by the catalytic process and is available for repeated oxidation and reduction cycles as shown in Figure 5.

The similarity of the rates of reaction of AV in the AV-NaOH-O₂-DMSO system (pH 12.8) to the AV-borax/HCl-O₂-DMSO system (pH 8.9) suggests that pH is not a significant parameter in the absence of carbonate. Thus, the effect (if any) of ozonide radicals (O₃⁻)^{19,23} and O⁻ radicals on AV at high pH compared to the hydroxyl radicals at lower pH (pK_a of OH, 11.9)²⁴ is not detectable in our experiments. The slower rate of reaction of AV in

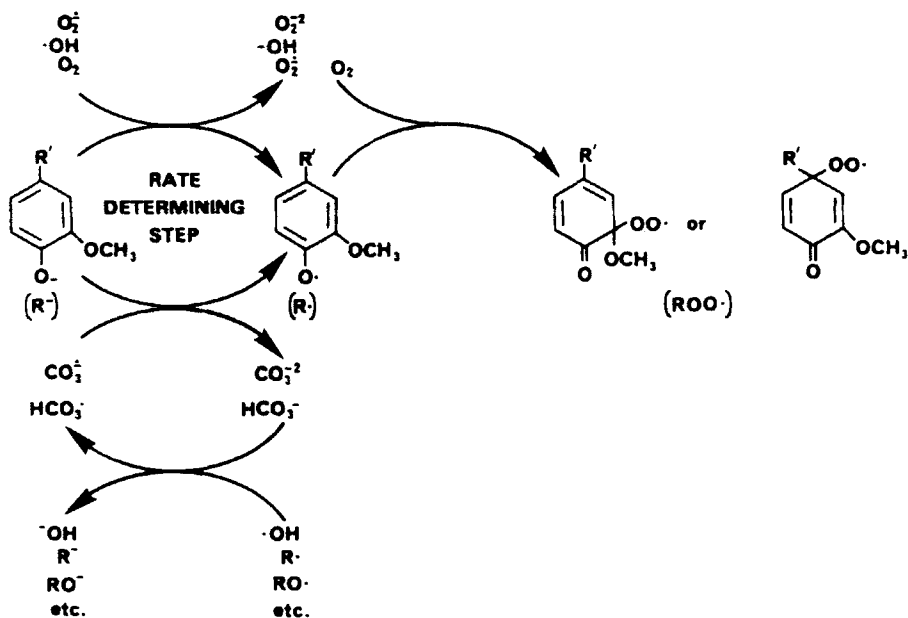


Figure 5. Species involved in the electron transfer rate determining step during oxygen-alkali oxidation of phenolic compounds.

the AV-Na₂CO₃-O₂ system compared to the AV-NaHCO₃-O₂ system is probably not due to any difference in the reactivity of carbonate and bicarbonate ions for hydroxyl radical. The pK_a of the bicarbonate radical (HCO₃[•]) is 9.6.^{21,25} Carbonate radical anions will predominate in carbonate buffers and bicarbonate radicals will predominate in bicarbonate buffers. Since the bicarbonate radicals lack a negative charge, they can react more readily with phenolate anions than the carbonate radical anion and hence give a faster reaction rate.

CONCLUSIONS

The reaction of AV with oxygen at 80°C in different alkaline media exhibits apparent first order dependence on AV concentration. The rate of reaction of AV (at constant concentration) in noncarbonate buffered solutions is not affected (within experimental error at 80°C) by the pH, ionic strength, and nature of the buffer as long as the pH is greater than the pK_a of AV. The nature of some of the reaction products and their relative amounts is affected by the pH, buffer, and possibly ionic strength of the reacting solution. This behavior demonstrates the importance of the phenolate anion in controlling the initiation stage of these reactions and the significance of pH and liquor composition on subsequent reactions.

The reaction of AV proceeds at a faster rate in carbonate buffers than in sodium hydroxide solution, in agreement with data in the literature. The reaction is fastest in sodium bicarbonate solution, although the concentration of dissolved oxygen is less than in pure caustic solutions.²⁶ This behavior may be attributed to the generation of carbonate radical anions (CO₃^{•-}) and bicarbonate radicals (HCO₃[•]) by interaction of dissolved carbonate with hydroxyl radicals. This hypothesis is consistent with the observation that the addition of small quantities of DMSO (a known hydroxyl radical quencher) inhibited the degradation of AV in bicarbonate solution to a greater extent than it did in borax buffers and sodium hydroxide solutions.

EXPERIMENTAL

A Teflon-lined reactor (ca. 1 liter capacity) equipped with an air-driven magnetic stirrer was employed for these reactions. It was immersed in an oil bath maintained at $80 \pm 0.5^\circ\text{C}$. Samples were removed at various times through Teflon lines by a procedure described previously.²⁷

Acetoguaiacone (Aldrich Chemical Company, Inc. Milwaukee, Wisconsin) was recrystallized twice from ether. Analysis by GLC and NMR showed no detectible impurities. Ultrapure chemicals including sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium tetraborate, and potassium dihydrogen phosphate were purchased from Alfa Division, Ventron Corp., Danvers, Massachusetts.

Reaction solutions containing alkaline liquors (triply distilled water, 200 mL) and AV were prepared and added to the reactor in a nitrogen atmosphere. The reactor was removed from that atmosphere, and the cover was bolted into place. The sample and oxygen lines were attached (with valves closed), and it was heated in an oil bath until the contents reached 80°C . The reactor was then pressurized with oxygen (1.02 MPa), the sample line was purged, and a zero-time sample was taken (25 mL). From this volume 10 mL was taken for peroxide analysis, and 4 to 8 mL were employed for other analyses.

Unreacted AV was analyzed in triplicate by quantitative GLC of the trimethylsilyl (TMS) derivatives using acetosyringone (3,5-dimethoxy-4-hydroxyacetophenone) as an internal standard. A Varian 1200 GLC was employed using a stainless steel column (150 x 0.28 cm) packed with 5% OV-17 on 80/90 mesh Anakrom ABS.

Peroxide²⁸ and methanol²⁹ analyses followed procedures described in the literature. Acetic acid was measured in triplicate by GLC techniques using a Varian 1200 employing a stainless steel column (150 x 0.285 cm) equipped for off-column injection and packed with 10% AT-1000 on 80/100 Chromosorb W-AW. An internal standard (butyric acid) was added gravimetrically to an accurately weighed sample of reaction solution (ca. 1.0 mL).

Other carboxylic acids were determined after 24 hours reaction by deionization (5 mL) through an Amberlite IR-120 (H⁺) column (5 mL) and eluted with water (3 x 5 mL). The combined eluates were made alkaline with ammonia, concentrated to syrups, and vacuum evaporated (2x) with 1,2-dichloroethane to remove the last traces of water. Chloroform (0.4 mL) was added, and the solution was reacted with BSTFA and 1% TMCS (0.4 mL, Pierce Chemical Co.). After shaking 12 hours, the silylated sample was analyzed by GLC using a Hewlett-Packard 5840A with a glass column (150 x 0.28 cm) equipped for off-column injection and packed with 3% OV-17 on 80/100 mesh Gas Chrom. Q.

Mass spectral analysis was achieved by interfacing the Hewlett-Packard 5940 GLC to a Hewlett-Packard 5985 GC/MS system. The spectra of the identified acids were compared with literature values and with authentic compounds where possible.

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