

The High Yield Synthesis of Benzaldehydes from Benzylic Alcohols using Homogeneously Catalyzed Aerobic Oxidation in Acetic Acid

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Abstract: The kinetics and yields for the formation of benzaldehydes from benzylic alcohols via aerobic oxidation using homogeneous catalysts in acetic acid are reported. For compounds of the type $X-C_6H_4CH_2OH$ where $X=H$, 4- CH_3 , 4- OCH_3 , 4- Cl , 4- $COOH$ the observed yields were 84, 78, 57, 88 and 52 mol %, respectively. These yields are comparable to those reported for the stoichiometric Co(III)/Br oxidation of these same benzylic alcohols. These results are limited to benzylic alcohols. The high yields are possible for two reasons: 1) the rate of reaction exhibits two maxima in which the benzaldehyde is predominately being generated in the first phase and the carboxylic acid in the second and 2) the competing esterification of the benzylic alcohol with the acetic acid solvent is an order of magnitude slower. A variety of other catalysts were also evaluated which give lower yields

mainly because they are less active and the competing esterification reaction becomes more important. Water addition to the acetic acid increased the rate of acetylation of the alcohol, contrary to expectation. The oxidation of the benzaldehyde appears to be inhibited by the presence of the benzylic alcohol. Even though the rate of oxidation of the benzaldehyde, by itself, is equally reactive as the benzylic alcohol, the benzaldehyde does not significantly react until the benzylic alcohol concentration is very low. Two possible reasons, using a free-radical chain mechanism, are suggested to explain this behavior. A mechanism demonstrating why the stoichiometric and catalytic reactions give similar yields is given.

Keywords: autoxidation; benzylic alcohols; bromide; cobalt; manganese

Introduction

The conversion of alcohols to carbonyl compounds is one of the most basic organic chemical transformations.^[1] The use of molecular oxygen, present in the air at 20.9%, as the primary oxidant is especially economically useful and there are many previous reports using this approach.^[2] We report here the high yield synthesis of benzaldehydes from benzyl alcohols using homogeneous catalysts based on cobalt(II) and the highly active of metal/bromide catalysts^[3] such as the Co/Mn/Br mixture. The Co/Mn/Br-catalyzed aerobic oxidation of *p*-xylene to terephthalic acid, used in the production of polyesters, is a well-established, large-scale industrial process. The problems associated with metal/bromide catalysts, such as their corrosive characteristics, have been largely eliminated through 55 years of optimization of these processes in the polyester industry.

Autoxidation is defined as the reaction of organic substrates with molecular oxygen using a free radical chain mechanism. The oxidizability of a substrate is defined by the expression $k_p/(2k_t)^{1/2}$ where k_p and k_t are the propagation and termination rate constants, respectively. In the *non-catalyzed* autoxidation of methylaromatics the reactivities of the methyl group and intermediate benzylic alcohols and benzaldehydes, are 0.05, 0.85 and 290, respectively.^[4] Thus, since the reactivity of the benzaldehyde is far higher than the alcohol, high yields of benzaldehydes from benzylic alcohols are not expected. In *catalyzed* autoxidation, these reactivities can change. During modeling studies in the Co/Mn/Br-catalyzed oxidation of toluene the intermediate concentrations of the alcohols and aldehydes remain low, consistent with their oxidizability, *but* the alcohol is found to be 3 times more reactive than the aldehyde.^[5] Also with the Co/Mn/Br oxidation of hydroxymethylfurfural the alcohol group of this compound is preferentially oxidized to

the aldehyde so that high yields of the dialdehyde are observed.^[5] For these reasons, we subsequently investigated the metal/bromide-catalyzed autoxidation of benzylic alcohols ($X\text{-Ph-CH}_2\text{OH}$). Some of this work has been preliminarily published.^[5]

The kinetics of the Co/Br-catalyzed autoxidation of benzyl alcohol in acetic acid has been previously reported but no yields are stated.^[6] The stoichiometric oxidation of benzyl alcohol has been kinetically studied with Co(III) and Mn(III) with and without bromide.^[7] There is a report that benzyl alcohol inhibits the radical-chain oxidation of benzaldehyde.^[8]

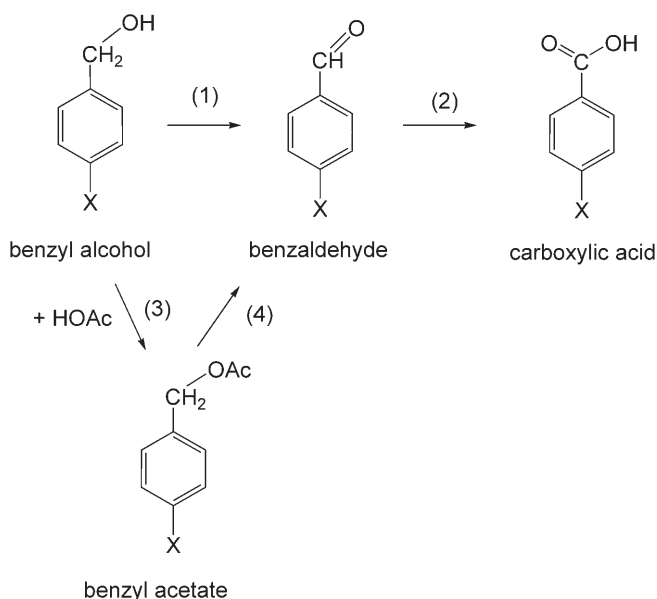


Figure 1. Reaction sequence observed during the aerobic oxidation of benzylic alcohols.

Results and Discussion

Reaction Sequence

The intermediates and products that form when benzylic alcohols were oxidized were established *via* GC/MS. Monitoring the reaction with GC and subsequent kinetic analysis are consistent with the sequence of reactions shown in Figure 1.

The author did briefly investigate the metal/bromide aerobic oxidation of 3-pentene-2-ol and 1-octanol. Both substances reacted but the yields to their corresponding aldehydes were low. Thus, so far, the results reported here are limited to benzylic alcohols.

Characterization of the Co/Mn/Zr/Br-Catalyzed Oxidation of Benzyl Alcohol

Since these reactions are performed at ambient atmospheric pressure, samples can be removed directly from the reactor and their compositions accurately determined at any given point in time during the reaction *via* subsequent GC and LC analysis. A typical result is given in Figure 2 for the Co/Mn/Zr/Br-catalyzed autoxidation of benzyl alcohol.

Up to 120 minutes, the principle reaction is reaction (1) – the reaction of benzyl alcohol to benzaldehyde. The competing reaction to give the benzyl acetate, reaction (3), is much slower as is reaction (2) to the benzoic acid. Subsequently the maximum benzaldehyde is 84%. After 120 minutes, the rate of reaction (2) suddenly increases and nearly quantitative yields of the benzoic acid are obtained. The benzyl acetate concentration also decreases after 120 min due to its oxidation and possibly hydrolysis.

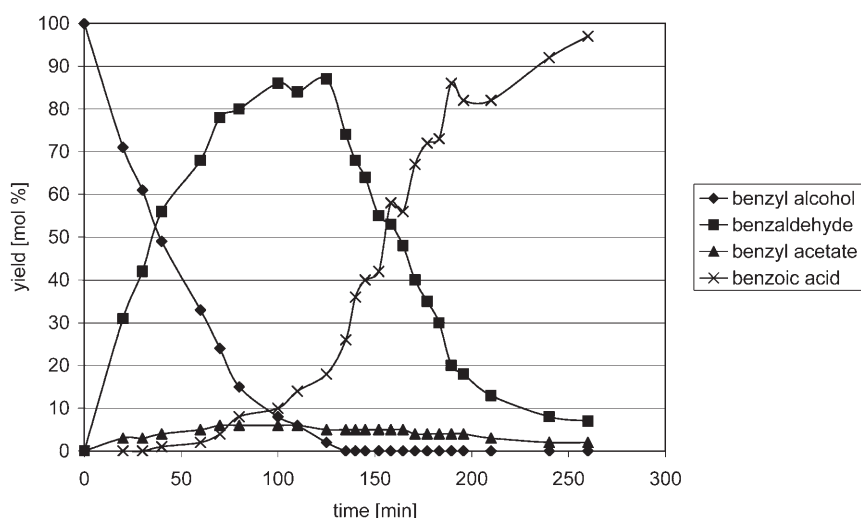


Figure 2. Distribution of products during the aerobic oxidation of benzyl alcohol; data from example 1 of Table 1.

Table 1. Initial conditions for the aerobic oxidation of benzylic alcohols and related reactions.

Example	Type of alcohol	Type of catalyst	[catalyst] M	[H ₂ O] (wt %)	T [°C]	[substrate] M
1	H	Co/Mn/Zr/NaBr	0.013/0.013/0.026/0.00050	0	75	0.790
2	H	Co/Mn/Zr/NaBr	0.013/0.013/0.026/0.00050	0	75	0.790
3	4-CH ₃	Co/Mn/Zr/NaBr	0.01/0.01/0.0049/0.06	0	80	0.150
4	4-OMe	Co/Mn/Zr/NaBr	0.013/0.013/0.026/0.00049	0	75	0.790
5	4-Cl	Co/Mn/Zr/NaBr	0.013/0.013/0.026/0.00047	0	75	0.791
6	4-COOH	Co/Mn/Zr/NaBr	0.01/0.01/0.0049/0.07	0	80	0.150
7	H	Co/Mn/Zr/NaBr	0.01/0.01/0.0049/0.02	0	80	0.944
8	H	Co/Mn/Zr/NaBr	0.013/0.013/0.026/0.00047	0	95	0.794
9	H	Co/Mn/Zr/NaBr	0.013/0.013/0.026/0.00049	3	75	0.790
10	H	Co/Mn/HBr	0.01/0.01/0.02	0	95	0.919
11	H	Co/Mn/HBr	0.01/0.01/0.02	5	95	0.926
12	4-Cl	Co/Mn/HBr	0.01/0.01/0.02	0	95	0.917
13	4-Cl	Co/Mn/HBr	0.01/0.01/0.02	5	95	0.921
14	H	Co/Zr	12.1/2.4	0	75	0.790
15	H	Co/Mn/NaBr	0.026/0.026/0.052	0	75	0.79

Table 2. Composition of the mixture at maximum benzaldehyde yield. See Table 1 for Initial conditions. Example 2 is the average value for five independent experiments.

Example	Type of alcohol	Time [h]	Conversion [%]	Benzaldehyde	Benzoic acid	Benzylic acetate	Selectivity to benzaldehyde
1	H	2.1	89.1	83.6	9.42	5.54	93.8
2	H	2.4	88.6 (2.4)	77.8 (4.0)	6.03 (3.2)	5.3 (0.9)	87.9 (5.5)
3	4-CH ₃	6.5	89.2	77.7	–	8.25	87.1
4	4-OMe	–	94.0	57.0	–	22.00	60.6
5	4-Cl	3.5	91.9	88.4	acid insoluble	4.77	96.2
6	4-COOH	3.1	75.0	52.0	–	–	69.3
7	H	2.5	93.7	71.5	17	6.7	76.3
8	H	1.6	88.8	59.7	6.52	6.52	67.2
9	H	15	100.0	78.0	8.90	22.0	78.0
10	H	1.8	86.1	66.0	5.74	10.8	76.6
11	H	3.9	93.8	54.8	6.23	24.2	58.4
12	4-Cl	1.8	92.5	75.6	3.35	12.1	81.7
13	4-Cl	8.3	93.3	62.7	2.31	27.6	67.2
14	H	–	80.0	60.0	0.00	31.0	75.0
15	H	–	90.0	72.0	4.80	13.0	80.0

Experimental details of this reaction are given in examples 1 of Tables 1–3. Table 1 gives the initial experimental conditions, Table 2 the composition of the mixture at the maximum observed benzaldehyde yield, and Table 3 the kinetic results assuming first-order disappearance of the reagents. When the benzaldehyde yield is at its maximum value of 84% the acetate yield is 5.5% (Table 2, example 1). This is consistent with the rate constants of $33.6 \times 10^5 \text{ s}^{-1}$ for the oxidation of benzyl alcohol and $1.35 \times 10^5 \text{ s}^{-1}$ for the esterification of the benzyl alcohol by the acetic acid solvent (Table 3, example 1). Reaction (1) is 24 times faster than reaction (3).

There are three unusual phenomena that occur in these reactions. 1) After the maximum benzaldehyde yield of 84% is reached, the benzaldehyde rapidly oxi-

dizes at a rate constant of $43.0 \times 10^5 \text{ s}^{-1}$. This is faster than the oxidation of benzylic alcohol ($33.6 \times 10^5 \text{ s}^{-1}$). This suggests that benzyl alcohol is inhibiting the reaction. 2) The rate of molecular oxygen uptake is biphasic with the second maximum occurring during the rapid oxidation of the benzaldehyde. 3) When the benzaldehyde begins to rapidly oxidize the color of the solution changes from light blue to green. Each of these phenomena are discussed further below.

Highest Yields to Benzaldehydes

The reported benzaldehyde yields contain a considerable amount of error since they are being obtained when its concentration is rapidly changing during reac-

Table 3. Kinetic analysis for the oxidation of benzylic alcohols and related reactions. See Table 1 for initial conditions. Standard deviation in parenthesis. Example 2 is the average value for five independent experiments.

Example	Type of alcohol	$k_1 (\times 10^5)^{[a]}$	$k_2 (\times 10^5)^{[b]}$	$k_3 (\times 10^5)$
1	H	33.6 (0.8)	43.0 (2.8)	1.35 (0.05)
2	H	29.4 (3.5)	32.7 (9.2)	1.37 (0.09)
3	4-CH ₃	10.7 (0.5)	—	2.19 (0.10)
4	4-OMe	—	—	—
5	4-Cl	20.0 (3.8)	13.2 (5.8)	0.99 (0.19)
6	4-COOH	22.7 (1.9)	—	5.1 (1.0)
7	H	28.1 (2.6)	63 (13)	1.37 (0.41)
8	H	44.4 (3.3)	101 (8.3)	5.73 (0.18)
9	H	4.78 (0.22)	—	1.39 (0.08)
10	H	38.0 (3.3)	70 (15)	5.91 (0.18)
11	H	18.1 (0.83)	—	5.61 (0.29)
12	4-Cl	39.9 (4.2)	—	5.17 (0.30)
13	4-Cl	8.47 (0.87)	—	3.15 (0.26)
14	H	—	—	—
15	H	—	—	—

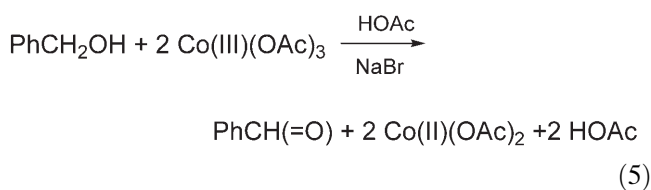
^[a] The rate constant k_1 and k_2 were obtained assuming first-order formation of the benzaldehyde and acetate from the benzylic alcohol.

^[b] Obtained from the rate of disappearance of the benzaldehyde.

tion. Since GC samples are taken at roughly 15 min intervals, the measured yield may not represent the highest yield that actually occurred in the reaction. Except for benzyl alcohol, no attempt was made to optimize the yields.

The reaction for benzyl alcohol discussed above appears to be general for benzylic alcohols. For compounds of the type $X-C_6H_4CH_2OH$ where $X=H$, 4-CH₃, 4-OCH₃, 4-Cl, 4-COOH the maximum observed yields were 84, 78, 57, 88 and 52 mol %, see examples 1–6 of Tables 1–3. These substituents were chosen because they represent a very large difference in reactivity of the corresponding substituted toluenes. The Hammett substituent values (σ) range from -0.78 to 0.42 for the methoxy to chloro groups, respectively,^[9] and give a difference in rates by a factor of 14.^[3]

Rather striking, is that the yields reported here (84, 78, 57, 88% for $X=H$, 4-CH₃, 4-OCH₃, 4-Cl) are quite similar to those reported for the *stoichiometric*, non-aerobic, Co(III)/Br oxidation of the same alcohols, reaction (5), which gave reported yields of 86, 81, 88, and 85%, respectively.^[10] The reason for this similarity is discussed below.



Influence of Experimental Variables

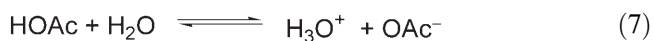
Temperature: For benzyl alcohol, increasing temperatures from 75 to 80 to 95 °C gave increasingly lower yields, see examples 1, 7, 8.

Water Concentration: It was initially thought that increasing the initial water concentration would increase the benzaldehyde yields because the water would suppress the rate of acetylation of the alcohol, reaction (6).



Experimentally just the opposite was observed. Invariably significantly higher concentrations of benzyl acetate were present at the maximum benzaldehyde yield which resulted in decreased yields. Compare examples 1 and 9 for benzyl alcohol with a Co/Mn/Zr/Br catalyst at 75 °C, examples 10, 11 for benzyl alcohol with a Co/Mn/Br catalyst at 95 °C, and examples 12, 13 for 4-chlorobenzyl alcohol with a Co/Mn/Br catalyst at 95 °C. There are at least two reasons for the increased acetate concentration:

- 1) Water is well-known to suppress the rate of oxidation and indeed this was found when comparing the rate constant for the oxidation of benzyl alcohol (k_1) in Table 3. The ratio of k_1 is $33.5/4.78=7$ in examples 1, 9, 2.1 in examples 10, 11 and 4.7 in examples 12, 13. Thus, a longer time occurs before the maximum yield is achieved at higher water concentration and the alcohol has a longer time to react with the acetic acid solvent.
- 2) Addition of water to acetic acid strongly affects the dissociation constant, pK_a .



Water is a stronger nucleophile than acetic acid and its addition to acetic acid increases both the acetate and hydronium ion concentrations. The pK_a of 100% acetic acid is 13.92, with 2.5% water it is 10.95, and with 5% water it is 9.64.^[12] This corresponds to an increase in the hydronium and acetate concentrations from 1.1×10^{-7} M to 3.3×10^{-6} M to 1.5×10^{-5} M, respectively. One does not see an increase in acetylation due to the increase in acetate concentration because the increase in acetate concentration is too small. This was demonstrated by measuring the rate of acetylation of benzyl alcohol with and without the presence of Co(II) acetate. The rate constants were, within experimental error, the same (3.03 and $2.71 \times 10^{-5} \text{ s}^{-1}$, respectively) at 75°C in 5% water/acetic acid. It is therefore suggested that it is the increase in acid concentration, by a factor of 138 on addition of 5 wt % water (2.78 M), that catalyzes the rate of acetylation accounting for the higher benzylic acetate formation. These arguments assume that the trends observed for acetic acid/water mixtures at room temperature, for which the pK_a s were measured, are the same as at 75°C and 95°C where the oxidation experiments were performed.

In light of the above, the complexity of these reactions can be appreciated by noting that the water concentration is constantly increasing during the oxidation:



Effect of Catalyst: A large number of different metal/bromide catalysts were evaluated to discern if improve-

ments in yield could be obtained. Also changes in their composition (molar ratios of the metals and bromide) and total catalyst concentration were evaluated. In general, but not invariably, as the activity of the catalyst increased, the yield increased. Thus for Co/Zr, Co/Mn/Br, and Co/Mn/Zr/Br catalysts at 75°C , their increased activity (in the order given see k_1 in Table 3) gave higher yields, compare examples 1, 14, 15. As the activity increased from 1.7 to 8.0 to 33 ($\times 10^5 \text{ s}^{-1}$), the yields increased from 60 to 72 to 84%. No yield improvements were observed with increases in catalyst concentration for X=H at 75°C with a Co/Mn/Zr/Br catalyst, for X=H at 95°C with a Co/Ce/Br catalyst, and X=Cl at 95°C for a Co/Mn/Br catalyst. Different types of catalysts were evaluated at 95°C . Observed maximum benzaldehyde yields were (yields in parenthesis) for X=H, Mn/Br (15), Co (65), Co/Br (61), Co/Ce/Br (67), Co/Mn/Br (66 at a Co/Mn/Br molar ratio of 1/1/2), Co/Mn/Br (61 at a Co/Mn/Br molar ratio of 1.8/0.2/2.0), Co/Mn/Br (63 at a Co/Mn/Br ratio of 1/1/1), and Co/Mn/Zr/Br (60). There is no obvious improvement in benzaldehyde yield with these different catalysts at 95°C .

Biphasic Uptake of Molecular Oxygen

The concentration of the oxygen in the vent gas emanating from the reactor is continuously measured hence the rate of reaction of dioxygen as a function of time can be calculated. The rate of oxygen uptake as a function of time for benzyl alcohol catalyzed by a Co/Mn/Zr/Br mixture at 75°C is given in Figure 3.

The rate of oxygen uptake slowly declines until 100 min. Then, unexpectedly, it again increases to a max-

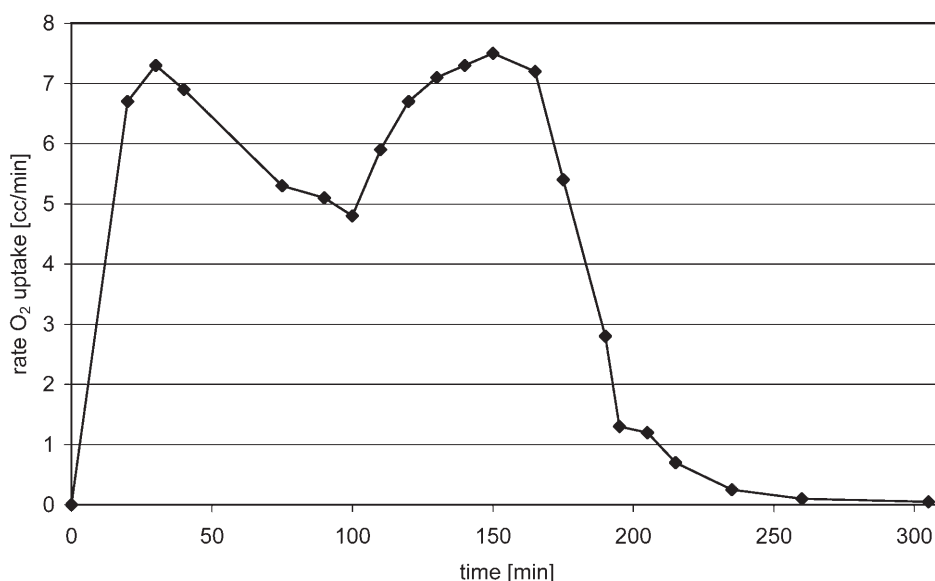
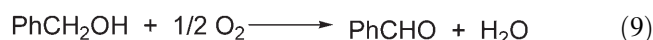


Figure 3. Rate of oxygen uptake with benzyl alcohol using a Co/Mn/Zr/Br catalyst. From example 1 in Table 1.

imum and subsequently declines in rate to nearly zero at around 250 min. This behavior has been observed 14 times in our laboratory with compounds of the type $X-C_6H_4CH_2OH$ where $X=H$, 4- CH_3 , 4- OCH_3 with Co/Mn/Zr/Br and Co/Zr catalysts at 75 °C. Biphasic behavior is not observed at 95 °C, however. The minimum in the rate of oxygen uptake at about 100 minutes occurs at the maximum concentration of benzaldehyde in solution, see Figure 2. So the subsequent increase in the rate of dioxygen uptake occurs due primarily to the oxidation of the benzaldehyde to the benzoic acid. The two maxima in oxygen uptake suggest that the reactivities of the benzylic alcohol and benzaldehyde are about the same since both substrates react with the same stoichiometric amount of dioxygen:



This is in agreement with the measured rates of oxidation of benzyl alcohol (k_1) and benzaldehyde (k_2), see example 2 of Table 3.

Such biphasic behavior has not been observed in our laboratory during the last nine years during which time numerous different alkylaromatic substrates have been similarly evaluated – except for the case of 3,4-dimethoxytoluene – which has been previously reported in detail.^[13] Other non-equilibrium behavior has been reported for the oscillating metal/bromide catalyzed aerobic oxidation of benzaldehyde^[14] in acetic acid.

Evidence for Inhibition by the Benzylic Alcohols

The high yield to the benzaldehyde from the benzylic alcohol is possible because: 1) the competing reaction to the acetate is slow and 2) the benzaldehyde does not significantly react until nearly all the benzyl alcohol is exhausted.

Example 2 on Table 3 gives average kinetic values over five experiments. From example 2 one finds that the competing reaction to the acetate (k_3) is 21 times slower than benzyl alcohol. [An independently measured value of the oxidation of benzyl acetate to benzaldehyde is also relatively slow, k_4 , is $2.95 (0.11) \times 10^{-5} s^{-1}$.]

The rate of oxidation of benzyl alcohol (k_1) and that of benzaldehyde (k_2) are, within experimental error, the same (example 2, Table 3). Assuming a set of elementary reactions where $A \rightarrow B \rightarrow C$ whose rates are the same would predict a maximum yield to the benzaldehyde of 34% rather than the experimentally observed 84%. Also the benzoic acid would immediately form and its predicted increase would be at a much faster rate than experimentally seen. Thus one has the conundrum that

even though in the same experiment one finds that the reactivities of the benzyl alcohol and benzaldehyde are the same, but also that the yields to benzaldehyde are very high. We suggest that, while the benzyl alcohol is present, it is inhibiting the oxidation of the benzaldehyde. It is only when the benzyl alcohol concentration falls to quite low values that this inhibition is sufficiently weak so that a rapid oxidation of the benzaldehyde occurs. This interpretation is also consistent with the biphasic molecular oxygen uptake since, in the absence of inhibition, simple monophasic behavior would be observed.

Carbon and hydrogen NMR was used to investigate if there were any interactions of benzyl alcohol with benzaldehyde. No changes were observed when a mixture of benzylic alcohol and benzaldehyde was measured as a function of temperature in deuteoacetic acid at 40, 60, 80, 95 °C. The NMR spectra of benzaldehyde and benzyl alcohol were examined in deuteochloroform and dimethyl sulfoxide. In DMSO the chemical shift of the H atom in the CHO group was 10.2 tau and the C atom was at 192 tau. However, there is a shift in these resonances in deuteoacetic acid to 9.7 and 195 tau, respectively. This may suggest a hydrogen bonding interaction of the acetic acid with the aldehyde moiety of the benzaldehyde, see Figure 4a. This could conceivably stabilize the benzaldehyde relative to the benzyl alcohol.

There are at least two other possibilities. It is known that acetic acid, water, and alcohols deactivate alkylperoxyl radicals with hydroxyl and carbonyl alpha-substituents, see Figure 4 b and c.^[15] It could be that the deactivation is much stronger for an alcohol hydrogen-bonding to the carbonyl substituent than to the hydroxyl substituent, hence, in essence, stabilizing the benzaldehyde when the benzyl alcohol is present. Another possibility is that, during the co-oxidation of the alcohol and aldehyde, the termination step of the radical-chain mecha-

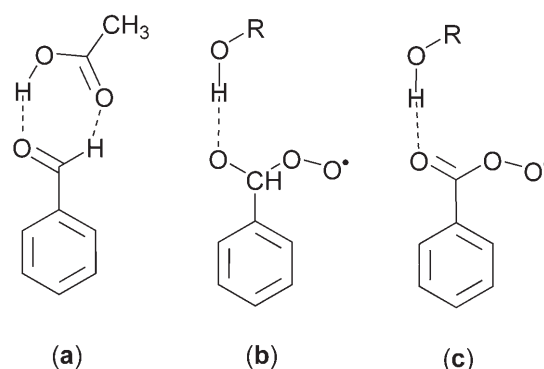


Figure 4. Possible hydrogen bonding Interactions during the aerobic oxidation of benzylic alcohols with benzaldehydes: (a) acetic acid with benzaldehyde; (b) alcohol with peroxy radical of alcohol; (c) alcohol with peroxy radical of aldehyde ($R=CH_2C_6H_5$).

nism associated with benzylic alcohol is significantly higher than that of benzaldehyde. This explanation is the same as that given previously for the strong reduction in reaction rate of cumene due to small amounts of tetralin.^[16]

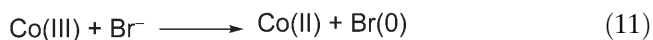
Overoxidation to Carbon Dioxide and Carbon Monoxide

The formation of carbon dioxide and carbon monoxide is one primary characteristic of aerobic oxidations. However, in these experiments their formation is not important. The observed carbon dioxide increase is only 0.01% above the normal content of carbon dioxide in air. No carbon monoxide was observed hence no measurable rate of decarbonylation expected from the acyl radical is occurring. Since no significant oxygen uptake occurs due to carbon oxide formation, the rates of oxygen uptake reflect only the oxidation of the benzylic alcohol, benzaldehyde, and benzyl acetate.

The Cause for the Color Change

The solution during the oxidation of the benzyl alcohols changes from light blue to intense green soon after the maximum in benzaldehyde concentration is observed. The green color is associated with the oxidation of benzaldehyde. A similar color change from pale blue to green is also seen during the oxidation of benzaldehyde alone, under identical conditions, when the conversion of the latter is approximately 50%.

It is known that autoxidation mixtures using cobalt catalysts without bromine are intense green in color due to a significant amount (10–50%) of the cobalt in solution existing as Co(III).^[17] The colors of autoxidations catalyzed by Co/Br are pale blue because the steady state concentration of Co(III) is not detectable. The pale blue color is that of Co(II) which has two weak crystal field bands at 450 nm with a molar absorptivity of around 15. A rapid reduction of Co(III) with bromide occurs in Co/Br-catalyzed autoxidations and is thought to be responsible for the steady state concentration of cobalt being predominately Co(II) (ligands omitted for simplicity):

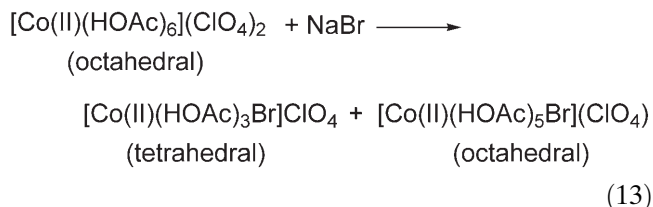


The bromide loss that occurs during these experiment was measured. This presumably occurs *via* bromine formation:



This was measured because if it occurred during oxidation of the benzylic alcohol so that 100% of it is lost, then the solution would experience a rapid formation of Co(III), accounting for the green color. The bromine loss was measured six times during complete benzylic alcohol oxidation at 75 °C and averaged 23.6% with a standard deviation of 7.6%. Therefore, this cannot account for the color change. The bromine loss measured during the oxidation of benzaldehyde, under the identical conditions, was 47%. It therefore appears that nearly all the bromine loss in our benzylic alcohol reactions occurs during the oxidation of benzaldehyde. Mechanistically, the greater loss of bromine during benzaldehyde *versus* benzyl alcohol oxidation suggests that the rate of bromine atom formation (Br[•]) is significantly faster during the oxidation of benzaldehyde than that of benzyl alcohol increasing the probability of reaction (12).

Samples were removed from the reactor before and after the color change during a Co/Mn/Zr/Br-catalyzed benzyl alcohol oxidation at 75 °C. The UV-VIS spectrum before the color change occurred consists of three absorptions at 530, 640, and 670 nm. This is consistent with the steady state oxidation states during reaction being Co(II), Mn(II), Zr(IV). The color is due to Co(II) since Mn(II) and Zr(IV) are transparent in the visible region. The crystal field analysis for cobalt(II) compounds assigns the first absorbance to an octahedral compound and the latter two to a tetrahedral species.^[18] A detailed analysis of the UV-VIS spectra of cobalt/bromide mixtures in acetic acid is available.^[19] Addition of bromide to cobalt(II) perchlorate at a 1:1 Co/Br mol ratio gives predominately monobromo octahedral and tetrahedral compounds:



Since the perchlorate and acetate are comparatively weak crystal field ligands, one can assume that the reported molar absorptivities also apply to the measurements reported here. The measured absorbance of the solution taken during the benzyl alcohol oxidation is consistent with 9% of the cobalt(II) existing as a Co(II)Br tetrahedral species with the remaining being octahedral Co(II). No Co(III) is present as evidenced by the lack of a broad intense band near 350 nm. When the solution turns to green, the observed absorbances can be assigned to 9% Co(II) tetrahedral species and 22% Co(III) and the remainder to Co(II) octahedral species.

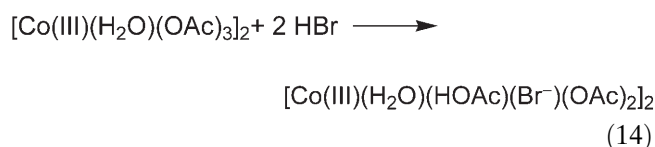
Currently we do not understand why Co(III) forms during a Co/Mn/Zr/Br-catalyzed oxidation of benzalde-

hyde and is not present when methylbenzenes are similarly oxidized. Co(III) formation does occur during the metal/bromide-catalyzed autoxidation of methylbenzenes when all of the ionic bromide forms benzylic bromides (PhCH_2Br), hence completely depleting the ionic bromide. Similarly, one could propose the formation of benzoyl bromide, PhCBr(=O) , during the oxidation of benzaldehyde. Benzoyl bromide has never been detected in the GC/MS studies, however. Benzylic bromides are quite stable during autoxidation but benzoyl bromide is expected to be hydrolytically unstable due to the presence of water. So currently one cannot explain why Co(III) formation occurs during benzaldehyde oxidations.

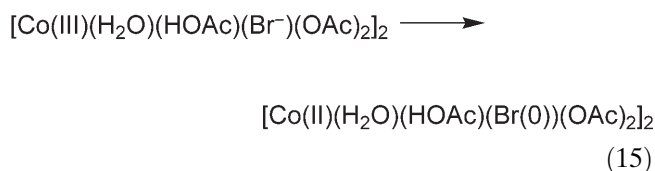
A Mechanism Demonstrating why Stoichiometric and Aerobic Oxidation of Benzylic Alcohols give Similar Yields

The metal salts used in metal/bromide oxidations in acetic acid have been shown to exhibit both redox and Lewis acid chemistry.^[20,21] We shall use the notation developed previously in which much of the chemistry occurs in the coordination sphere of the metals.^[20,21] Only ligands necessary for the mechanism are placed in the first coordination sphere of the metals.^[20,21]

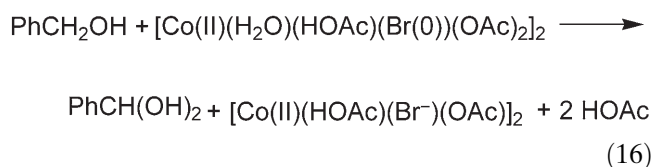
The stoichiometric oxidation is given in reactions (14)–(17). Since the bromide catalyzes the stoichiometric synthesis,^[10] bromide is first incorporated into the coordination sphere, reaction (14), and the reduced bromine species is subsequently used to oxidize the benzyl alcohol, reaction (16). A ligand replacement reaction occurs as the bromide enters the coordination sphere of the metal with the protons of the hydrobromic acid neutralizing two acetate ligands:



An internal redox reaction follows in which the metal oxidizes the bromide anion to the bromine atom, indicated by Br(0) [oxidation states are indicated within brackets ()]:



The product of reaction (15), a Co(II)-Br(O) species, is a dimer hence it is a two-electron oxidant which oxidizes the benzyl alcohol in one step to the *gem*-diol:



The water in the coordination sphere provides the oxygen atom for the *gem*-diol and the two protons neutralize the acetate in the coordination sphere to give two moles of acetic acid. The conversion of the *gem*-diol may be Lewis acid-catalyzed by Co(II) where formation of the cobalt(II)- H_2O bond is the thermodynamic driving force:

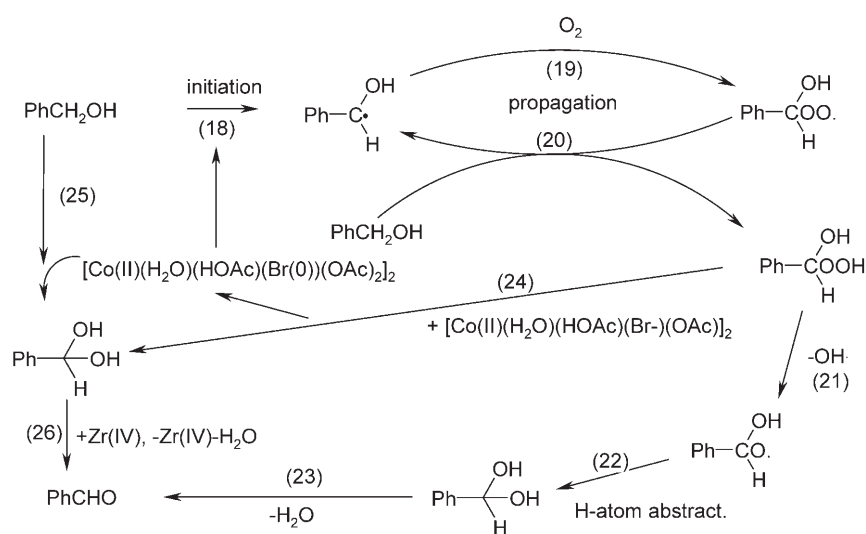
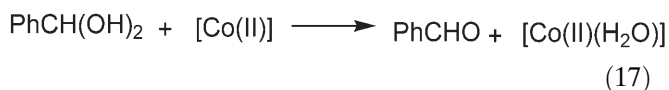
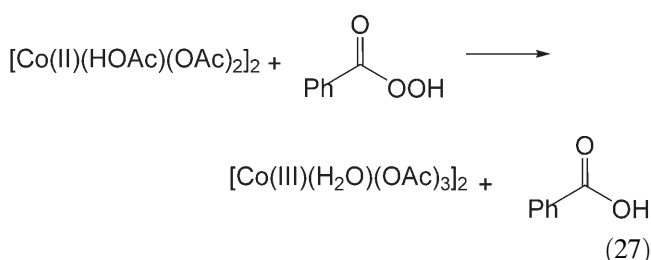


Figure 5. Proposed mechanism for the aerobic oxidation of benzyl alcohol to benzaldehyde.



The aerobic oxidation is given in Figure 5. The free radical chain mechanism is initiated in reaction (18) and propagated in reactions (19) and (20). This generates the peroxide of the benzylic alcohol. Generation of the benzaldehyde using *non-catalyzed* reactions proceeds by thermal dissociation of the peroxide [reaction (21)], hydrogen atom abstraction [reaction (22)] and dehydration of the *gem*-diol [reaction (23)]. The *metal-catalyzed* steps are the initiation step [reaction (18)] and reactions (24), (25), and (26). It will be assumed that the peroxide of the alcohol reacts with Co(II) in an identical fashion as it does with peroxy acids – a well-characterized, very rapid and selective reaction.^[11,22]



The *gem*-diol is directly produced from the benzyl alcohol peroxide, reaction (24). But importantly, the reaction produces as a by-product the same dimeric Co(II)-Br(O) oxidant species as in the stoichiometric reaction – and this obviously will react with another mole of benzyl alcohol to give the *gem*-diol [reaction (25)]. Thus two moles of the *gem*-diol are produced in the same catalytic cycle and 50% of the *gem*-diol produced is stoichiometric. [We do not suggest that the coordination compounds are identical in the stoichiometric and catalytic aerobic oxidations but only that the same Co(II)-Br(O) compound forms.] If we assume that reaction (24) is similar to that of peroxy acids, then this reaction will be much faster than the thermal dissociation of the peroxide [reaction (21)] and the non-catalyzed reactions become unimportant as has been previously demonstrated.^[11] Hence *the metal-catalyzed steps will dominate*. The Co(II)-Br(O) compound produced can also be used in the initiation step, reaction (18). But, since normally a large number of propagation steps occur for a single initiation reaction, the Co(II)-Br(O) species will be primarily used for the stoichiometric reaction. One can conclude that only slightly less than 50% of the oxidation of benzyl alcohol is stoichiometric and that the other 50% is a very rapid, selective reduction of the peroxide of benzyl alcohol. Therefore one has a mechanism that would predict similar benzaldehyde yields when a benzyl alcohol is oxidized stoichiometrically and well as catalytically. Also consistent with the domination of

metal-catalyzed steps is that the observed rate of carbon dioxide formation (discussed above) is very low since a high carbon dioxide formation rate accompanies non-catalyzed benzaldehyde oxidations.^[11] The Co/Mn/Zr/Br catalyst is more active than without Zr, i.e., the Co/Mn/Br catalyst.^[20] This may be partially because Zr(IV) is a much stronger Lewis acid than Co(II) hence the dehydration of the *gem*-diol [reaction (26)] is greatly enhanced. Evidence that Co(II)-Zr(IV) complexes exist in acetic acid has been summarized.^[20] Reactions (24) and (26) may therefore occur in a concerted manner in the coordination sphere of the metals.^[20]

Conclusions

High yields of benzaldehydes are not expected from benzylic alcohols in the non-catalyzed autoxidation since the aldehydes are much more reactive than the alcohols. Consistent with past work, however, the metal/bromide-catalyzed autoxidation opens up a number of new pathways which supercede those of a free radical chain mechanism. Indeed, the yields to benzaldehyde observed in this work are comparable to those observed in *stoichiometric* Co(III)/Br oxidation. Making an assumption that the peroxide of benzyl alcohol reacting with Co(II) is similar to peroxy acids, a mechanism is given explaining why stoichiometric and catalytic aerobic oxidations give similar benzaldehyde yields. The unusual biphasic behavior, observable in both the high yields to the benzaldehyde and benzoic acid as well as the rate of oxygen uptake, is difficult to rationalize without the development of a highly sophisticated, complex kinetic model.

Experimental Section

The glass autoclave, procedure, calculations, and GC and LC instruments has been previously described.^[6] The chemicals were used as received. Initial cobalt and manganese catalysts were their metal(II) acetate tetrahydrates and Zr(IV) as its acetate. The reactants, intermediates, by-products, and products formed in the reactions were confirmed by GC/MS. Yields were calculated from the GC data and occasionally checked by LC. Unless otherwise stated, all reactions were performed with a flow of air at 100 mL/min through the reactor with 100 g solvent at ambient atmospheric pressure. Periodically liquid samples were removed during reaction and analyzed *via* GC. At the same time, on-line gas analysis was performed for dioxygen, dinitrogen, carbon monoxide and carbon dioxide. Selected samples were analyzed for Co, Mn, Br *via* ICP (inductively coupled plasma). UV-VIS spectra were obtained on an HP instrument with diode array detector.

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