The Unusual Characteristics of the Aerobic Oxidation of 3,4-Dimethoxytoluene with Metal/Bromide Catalysts

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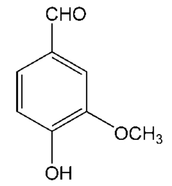
Abstract: DMtoluene (3,4-dimethoxytoluene; DM = 3,4-dimethoxy), a model compound for lignin oxidation, can be autoxidized in acetic acid using a Co/Mn/Br catalyst to its benzaldehyde in 51 mol % yield, and to its acid in 85–92 mol % yield. This synthesis is unusual because a number of unprecedented phenomena occur. 1) The rate of molecular oxygen reacting with the substrate is bi-phasic, i.e., two maximum in the rate of reaction are observed. 2) In the first phase, all of the 3,4-dimethoxytoluene is converted to intermediates, but very little to the carboxylic acid. 3) During the second maximum of activity, virtually all the intermediates are converted to the carboxylic acid with 95–100% mass accountability. 4) The rate of carbon monoxide and carbon dioxide formation is considerably higher during the second phase during which 5) 9–12% of methyl 3,4-dimethoxybenzoate (the methyl ester of the benzoic acid) is formed. Mechanisms are suggested for these unusual phenomena.

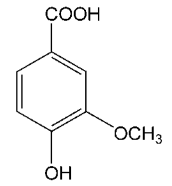
Keywords: autoxidation; catalytic hydrocarbon oxidation; C–H activation; cobalt; manganese; oxygen

Introduction

Lignin, a polymeric component of woody plants, is the second most abundant natural material. Commercial sources of lignin are spent liquors from the wood-pulp industry. Its exact structure is unknown and varies depending on the source of the lignin. It is known to be composed of substituted aromatic derivatives held together by aliphatic chains. It is *primarily* composed of *p*-hydroxybenzene, guaiacyl (4-alkyl-2-methoxyphenol), and syringyl (4-alkyl-2,5-dimethoxyphenol) units.[1,2] The syringyl group, for example, can be oxidized to vanillin and vanillic acid:



vanillin
4-hydroxy-3-methoxybenzaldehyde



vanillic acid
4-hydroxy-3-methoxybenzoic acid

A Co/Br-catalyzed autoxidation of lignin in acetic acid has produced vanillin and vanillic acid in yields of 1.9 and 3.0%, respectively.[3] The Co/Mn/Br/Zr-catalyzed autoxidation of lignin dissolved in acetic acid has resulted in *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, vanillin, vanillic acid, syringaldehyde, and syringic acid, i.e., the expected products from the oxidation of all three of the above mentioned groups.[4] Consequently we and others[5] have oxidized 3,4-dimethoxytoluene as a model compound. The closely related compound, 4-methoxytoluene, has been autoxidized with metal/bro-

Table 1. Comparison of the reactivity of 3,4-dimethxytoluene to selected toluenes (in acetic acid solvent from Hammett relationships[6])

	Type of Catalyst	[Co], M	Mol Ratio	Rho Value (std. dev.)	Relative Reactivity				
					$4\text{-}NO_2$	H	$4\text{-}CH_3$	$3,4\text{-di-}CH_3O$	$4\text{-}CH_3O$
1	Co/Br	0.02	2/2	−0.85 (0.08)	1.00	4.70	8.63	19.7	21.7
2	Co/Mn/Br	0.004	1/1/2	−1.28 (0.13)	1.00	10.3	25.6	88.2	102
4	Co/Mn/Zr/Br	0.01	1/1/0.19/2	1.33 (0.12)	1.00	11.2	29.0	105	122
5	Co/Ce/Br	0.04	4/0.4/1	1.38 (0.12)	1.00	12.3	33.0	125	147
6	Co/Mn/Cl/Br	0.019	1.9/.016/5.5/1.8	1.47 (0.21)	1.00	14.5	41.4	172	203
7	Co	–	–	−1.81	1.00	26.9	97.9	564	695
8	bromide	–	–	−1.82	1.00	27.4	100	584	720

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mide and other catalysts.[6,7] The author has reviewed the metal/bromide autoxidation of hydrocarbons up to the year 1995.[6] 251 different reagents have been oxidized in this manner in which 84% are alkylaromatic compounds. One can predict, and is substantiated herein, that the reactivity of 3,4-dimethoxytoluene is very high compared to that of toluene and other selected methylaromatic compounds, see Table 1.

Discussion

On the Synthesis of 3,4-Dimethoxybenzaldehyde and 3,4-Dimethoxybenzoic Acid *via* Autoxidation

The oxidation reaction occurs *via* a metal-catalyzed free radical chain mechanism.[6] 3,4-Dimethoxytoluene is a highly reactive substrate, see Table 1. It is 88 times more reactive than 4-nitrotoluene, 10 times more reactive than toluene and slightly less reactive than 4-methoxytoluene with a Co/Mn/Br catalyst. The rapid rate of reaction at 80 °C reflects this reactivity. The temperature is chosen so that the gases exiting the reaction have an oxygen content of at least 3–5%. This is done because the rate of reaction of radicals with dioxygen is diffusion controlled. If the oxygen content in the reactor is too low, radical coupling occurs which leads to by-products, often intensely colored, and a reduction in the rate of reaction since the steady state concentration of the free radicals is being decreased.

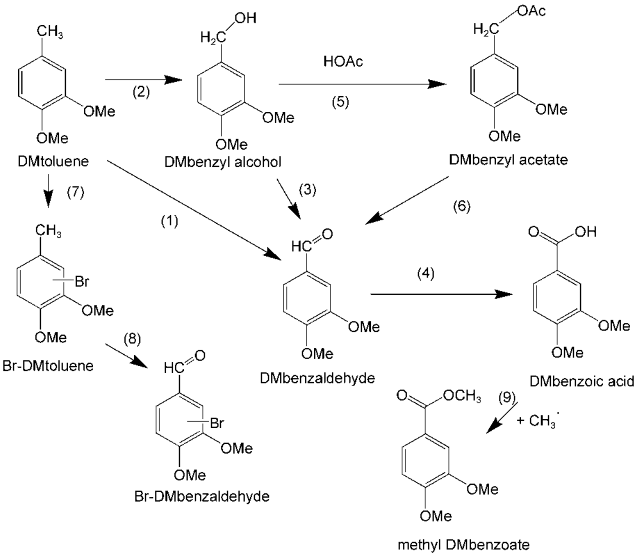

Figure 1. Suggested reaction sequence during the autoxidation of 3,4-dimethoxytoluene to 3,4-dimethoxybenzoic acid (DM = 3,4-dimethoxy).

The initial conditions used in the experiments are given on Table 2 and the yields in Table 3. The reaction sequence and intermediates formed are given on Figure 1. Intermediate concentrations as a function of conversion of 3,4-DMtoluene are given in table 4. 3,4-Dimethoxybenzaldehyde is obtained in 51% yield at a conversion of 97%. This yield is unusually high during autoxidation of methylaromatic compounds[6] since the usual maximum yields range from 15–35%. However, a 52% yield of the benzaldehyde has been reported for 4-methoxytoluene at a conversion of 67%.[7f] Trying to isolate this aldehyde from the other products would, of course, not be trivial.

Yields to the DMbenzoic acid are 75–80%. Since methyl DMbenzoate is the methyl ester of DMbenzoic acid (Figure 1) and the acid can be obtained by hydrolysis of the ester, it is possible to obtain 85–92% of 3,4-dimethoxybenzoic acid *via* subsequent hydrolysis. These yields are comparable to the oxidation of many other methylaromatic compounds such as toluene, *p*-xylene, etc.[6] using metal/bromide catalysts.

Doubling the catalyst concentration in examples 1 and 2 resulted in a 34% increase in the rate of reaction of 3,4-dimethoxytoluene, similar to that observed with other substrates such as *p*-xylene [10,8] and hydroxymethylfurfural.[8,9] The increased catalyst concentration also reduces, by more than 50%, the observed carbon dioxide formed, see Table 3. The increased bromide, however,

Table 2. Initial conditions for the autoxidation of 3,4-dimethoxytoluene.

	Catalyst Type	[DMtoluene], M	[catalyst], M	Time of rxn. [min]	Temp [°C]	Rate Constant [$s^{-1} \times 10^5$][d]
1	Co/Mn/Br	0.66	0.010/0.010/0.020	812	80	11.9(0.4)
2	Co/Mn/Br	0.66	0.020/0.020/0.040	499	80	16.0(0.8)
3[a]	Co/Mn/Br	0.61	0.020/0.020/0.040	524	60,80	9.04(0.82)
4[b]	Co/Mn/Br	0.66	0.020/0.020/0.040	351	80	13.2(1.5)
5[c]	Co	0.66	0.12	592	80, 95	–

[a] Initial reaction temperature was 60 °C. The temperature was increased to 80 °C at time 313 min.

[b] An additional, equimolar amount of HBr was added at 221 min. An additional equimolar amount of Co(II) acetate was added at 291 min.

[c] Increments of acetaldehyde were added to initiate the reaction at 21, 348, 499 min. The temperature was increased to 95 °C at 280 min.

[d] From first order regression analysis for the disappearance of 2,4-dimethoxytoluene.

Table 3. Final yields from the autoxidation of 3,4-dimethoxytoluene.

	Yield [mol %]							
	DMtoluene	DMaldehyde	Methyl DMbenzoate	DMbenzoic acid	DMbenzyl acetate	DMbenzyl alcohol	Total	CO_x/DMtoluene, mol/mol[a]
1	0	6.1	8.9	76	2.6	0	95	0.56
2	0	1.9	12	80	1.8	0	96	0.22
3	0	17.4	9.5	75	0.07	0	105	0.15
4	15	44	0.05	4.7	4.2	0	70	–
5	28	31	0	0	9.3	0.1	65	–

[a] CO_x is the sum of the carbon dioxide and carbon monoxide integrated over the entire reaction. The carbon dioxide content is 5–8 times higher than that of the carbon monoxide.

Table 4. Selected samples of the GC analysis of products during the aerobic oxidation of 3,4-dimethoxytoluene (from Example 2).

	1	2	3	4	5
Time, min	15	135	240	321	457
3,4-DMtoluene	67.6	32.9	3.2	0.0	0.0
bromo-3,4-DMtoluene	0.7	1.6	1.2	0.1	0.0
3,4-DMbenzaldehyde	2.9	27.5	51.2	19.9	2.1
methyl 3,4-DMbenzoate	0.0	0.0	0.9	3.9	7.6
3,4-DMbenzyl acetate	0.6	2.7	3.4	1.8	2.4
3,4-DMbenzyl alcohol	1.3	1.5	0.0	0.0	0.0
bromo-3,4-DMbenzaldehyde	0.0	0.2	1.1	1.3	0.4
3,4-DMbenzoic acid	0.0	2.2	19.5	62.6	83.3
Total	74.3	68.6	80.7	89.6	95.8
Organobromine (HBr basis) [%][a]	11	30	37	22	6.2

[a] Does not include bromo-3,4-DMbenzoic acid which was not measured.

also results in higher yields of the ring brominated compounds. The selectivity increase, i.e., reduction in carbon dioxide, has been previously rationalized.[9] The free radical chain mechanism is significantly modified in the presence of the catalyst so that the reaction pathways become predominately metal catalyzed. The cobalt selectively and rapidly reacts with the intermediate peroxy radicals, which by-passes the propagation step, and also reacts with the peroxy acid to directly produce the carboxylic product.

$$\text{DMperoxybenzoic acid} + [\text{Co(II)}]_2 \longrightarrow \text{DMbenzoic acid} + [\text{Co(III)}]_2 \quad (1)$$

In experiment #3 we lowered the temperature to 60 °C. Conducting an autoxidation with highly reactive substances often benefits from lower temperatures since the reaction rates are reduced allowing for more radicals to react with the dioxygen in solution. No improvement in yields or change in the amount of the methyl DMbenzoate occurred, however.

Ring-brominated compounds are formed from aromatic rings having high electron density.[6,10,11] The bromo-3,4-DMtoluene and bromo-3,4-DMbenzaldehyde occur with yields around 1% representing about 37% of the bromine added as catalyst to the system. Although almost certainly present, but not analyzed for, is bromo-DMbenzoic acid. The mass accountability of 95–100% at the end of the experiments indicates relatively low yields of Br-DMbenzoic acid.

Unusual Phenomena during the Oxidation of DMtoluene

There are five features that, in the author's experience, are unique to the metal/bromide autoxidation of 3,4-dimethoxytoluene.

1. Biphasic behavior: Normally, the rate of molecular oxygen uptake increases to a maximum, as the benzaldehyde concentration rises to its highest level and then decreases to zero as the intermediates (aldehyde, alcohol, acetate) are converted to the acid. Figure 2 illustrates that for DMtoluene the dioxygen rate decreases from 9 mL/min to 5 mL/min but then the rate of oxygenation again increases to 8 mL/min before a final, rapid decrease to zero. Bi-phasic behavior has been observed by us in the autoxidation of benzyl alcohol[9] and oscillating behavior has been observed for benzaldehyde[12] but never for an alkylaromatic compound. The two rate maxima will be referred to as the 1st and 2nd stages of the reaction.

This biphasic behavior is not being caused by the formation of non-active bromine species. This is because addition of hydrogen bromide near the end of the first stage of reaction, example 4, had no affect on the overall results. Also the high mass accountability at the end of the reaction indicates that inordinate amounts of bromo-DMbenzoic acid are not forming.

2. Rate of formation of the carboxylic acid: Normally in metal/bromide-catalyzed autoxidation the carboxylic acid starts to form almost immediately and rises rapidly as the conversion of the methylaromatic compound in-

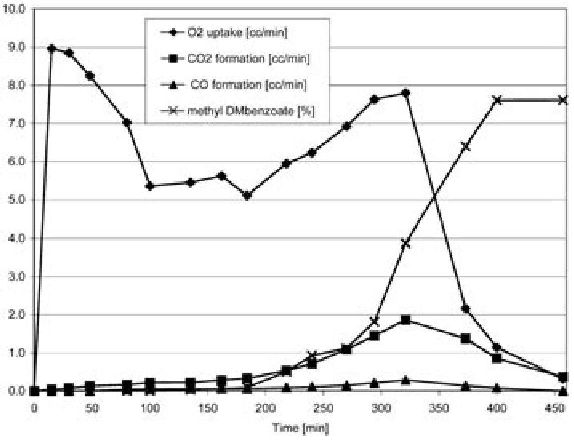

Figure 2. Rate of reaction of dioxygen and rate of formation of carbon monoxide, carbon dioxide, and methyl 3,4-DMbenzoate. From example 2 in Table 2.

creases to 100%.[13,14] Maximum benzoic acid concentration normally occurs as the conversion approaches 100%. The reason for this is that the benzaldehydes and benzylic alcohols are 5 and 15 times, respectively, more reactive than the methylaromatic compound.[8] In contrast, when the conversion of the DMtoluene is nearly 100%, the yield to DMbenzoic acid is only 8–18%. In fact, the first time this reaction was performed it was prematurely terminated because the GC indicated close to 100% conversion and the rate of oxygen uptake, which is continually monitored, was declining. It is during the 2nd stage that the rate of reaction again increases and that > 80% of DMbenzoic acid is formed, see Figure 2 and Table 3.

3. Formation of the methyl ester of the carboxylic acid in high yields (9–12%) has never been reported during autoxidation: The esters are seen in trace amounts during the commercial production of *p*-xylene to terephthalic acid.[6] All of the methyl DMbenzoate is produced in the 2nd stage of the reaction, see Figure 2.

4. The 2nd stage of high rate of oxygen uptake is accompanied by a very high rate of formation of carbon dioxide, see Figure 1: In example 2, during the first stage the values slowly increase from 0.08 to 0.23 mL/min but then rapidly rise to a maximum value of 1.8 mL/min during the 2nd stage. Carbon monoxide is seen as well but is less by about a factor of 5.

5. Use of a cobalt catalyst, without manganese and bromine, at significantly higher catalyst concentrations than used in metal/bromide catalysts, normally will oxidize a methylbenzene compound to its corresponding benzoic acid in high yields:[6] Although a significant amount of oxygen uptake initially occurred the final conversion was only 72%. Virtually no DMbenzoic acid was formed, see example 5 in Tables 1 and 2. The deep green coloration that normally occurs due to a high steady state concentration of cobalt(III) was not seen in this experiment. Addition of acetaldehyde or increasing the temperature usually further stimulates the rate of reaction but the reaction still resulted in low yields of intermediates with none of the desired benzoic acid being formed. Acetaldehyde is added because it is rapidly oxidized to peroxyacetic acid which, in turn, rapidly oxidizes the Co(II) dimer to Co(III). Co(III) is the active catalyst species because it is capable of oxidizing the alkylaromatic to the benzylic radical.

Some Possible Mechanisms for the Unusual Behavior

This is the first reported instance of biphasic behavior for the autoxidation of an alkylaromatic compound. The biphasic behavior seen here is similar to that reported for benzyl alcohol to benzoic acid using metal/bromide catalysts in acetic acid. In the first phase the benzyl alcohol almost completely reacts to form benzaldehyde in 80% yield. In the 2nd phase the predominately benzaldehyde solution then rapidly reacts to form benzoic acid in 88% yield.[8] 4-methoxybenzyl alcohol, an alcohol of similar reactivity to 3,4-dimethoxytoluene (see Table 1) also undergoes a biphasic reaction giving a maximum yield of 54% of 4-methoxybenzaldehyde.[15] It has been previously reported that the autoxidation of benzaldehyde is inhibited by increasing concentrations of benzyl alcohol.[16] So it is possible that the biphasic behavior is caused by the presence of alcohol moieties forming in solution. However for 3,4-dimethoxytoluene only relatively low amounts of the benzyl alcohol and acetates are observed – a total of about 5–7%. Perhaps unusually high amounts of the hydrate of 3,4-dimethoxybenzaldehyde, i.e., DMPhCH(OH)$_2$ form but this compound has not been detected in our GS/MS studies. We did detect the corresponding acetate of the hydrate i.e., DMPhCH(OH)(OAc) so this is a distinct possibility.

Two other unique phenomena that occur during the 2nd phase – the high rate of carbon dioxide formation and the formation of methyl DMbenzoate – are probably closely related. Isotopic labeling studies during the autoxidation of *p*-xylene, a commercial process which is quite similar to that described here, indicate that byproducts form from the methyl group of the acetic acid. Of particular importance is that the majority of the methanol and methyl acetate form from the oxidation of the acetic acid.[17] There is a close association of the *rate* of decomposition of the acetic acid to the rate of formation of methanol and methyl acetate.[18] The mechanisms of formation of these species are rationalized by the following set of reactions:

$$\underset{\text{acetic acid}}{CH_3COOH} + X \longrightarrow \underset{\text{acetoxy radical}}{CH_3COO\cdot} + HX \tag{2}$$

$$CH_3COO\cdot \longrightarrow CH_3\cdot + CO_2 \tag{3}$$

$$CH_3^\bullet + O_2 \longrightarrow CH_3OO^\bullet \longrightarrow \longrightarrow \underset{\text{methanol}}{CH_3OH} \tag{4}$$

$$CH_3OH + HOAc \longrightarrow \underset{\text{methyl acetate}}{CH_3OAc} + H_2O \tag{5}$$

X is either Co(III), a reduced bromide species (Br), or some organic radical species that abstracts a hydrogen atom from acetic acid. The acetoxy radical undergoes an exceedingly fast decomposition with a first-order rate constant of $1.6 \times 10^9\ s^{-1}$ at 60 °C.[19] It is important that no methanol and only traces of methyl acetate are detected by GC in the experiments described here. This suggests that methyl DMbenzoate is forming *via* a concerted mechanism within the coordination sphere of the metal. Methyl DMbenzoate forms during the 2nd phase which is initiated when the DMbenzaldehyde is at its highest concentration. Since DMbenzaldehyde forms the peroxybenzoic acid, we describe a possible mechanism starting with the peroxy acid.

The peroxy acid enters the coordination sphere of the substitutionally labile Co(II). The ligand displaced is the acetic acid since it is exceptionally weakly bound[20] (only ligands necessary for the mechanism are included in the coordination sphere):

$$Ph(C{=}O)OOH + [Co(II)(HOAc)_3]_2 \longrightarrow [Co(II)(HOAc)(\ Ph(C{=}O)OOH)]_2 + HOAc \tag{6}$$

The peroxy acid is known to very rapidly oxidize the Co(II) dimer to Co(III).[21]

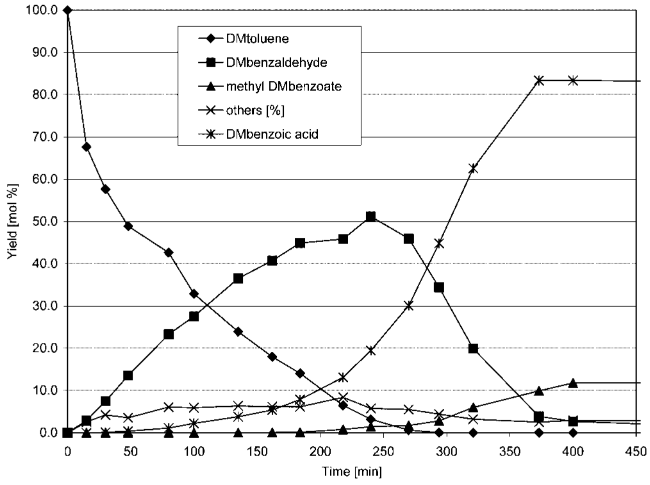

Figure 3. Product formation from the aerobic oxidation of 3,4-dimethyltoluene. 'others' are Br-DMtoluene, Br-DMbenzaldehyde, DMbenzyl alcohol, and DMbenzyl acetate (DM = 3,4-dimethoxy; from example 2 in Table 2).

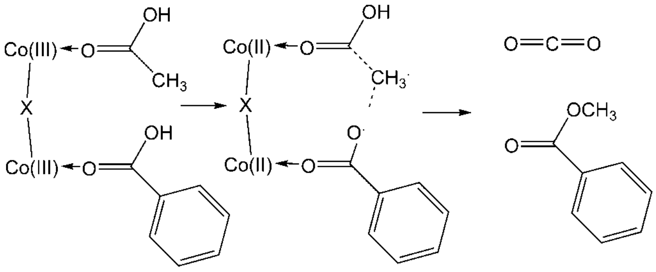

Figure 4. Suggested mechanism for the formation of methyl DMbenzoic acid from Co(III)

$$[Co(II)(HOAc)_2(\ Ph(C{=}O)OOH)]_2 \longrightarrow [Co(III)(H_2O)(\ Ph(C{=}O)OH)(OAc^-)_2]_2 \tag{7}$$

The cobalt(III) dimer can now simultaneously oxidize both the coordinated acetic acid and DMbenzoic acid to their respective radical moieties as shown in Figure 4. The acetoxy radical forms the methyl radical within the coordination sphere which attacks the aromatic acid radical generating the methyl-DMbenzoate and carbon dioxide. The mechanism given below is similar to the formation of benzylic bromide from Co(III)/bromide mixtures for which there is kinetic evidence.[20,22,23] One still needs to explain why this behavior is peculiar to DMtoluene oxidation and not to 4-methoxytoluene or toluene autoxidation. Perhaps the steric hindrance of the *meta*-methoxy group in the coordination sphere allows the methyl radical unusually good access to the DMbenzoic acid.

Other mechanisms are feasible such as the hydrolysis of the peroxybenzoic acid to DMbenzoic acid and hydrogen peroxide. Hydrogen peroxide can lead to hydroxyl radicals which can attack the acetic acid and lead to a mechanism similar to that described above.

Experimental Section

Cobalt and manganese salts were the metal(II) acetate tetrahydrates. Bromine source was 48% aqueous hydrobromic acid.

The reactor is a glass autoclave as previously described.[9] The source of dioxygen was air (20.9%) at ambient pressure. The flow rate of air through the reactor was 100 mL/min. Liquid samples were periodically removed and analyzed by GC and GC/MS. A continuous flow of the vent gases was passed through a GC and analyzed for dioxygen, dinitrogen, carbon monoxide and carbon dioxide.

The GC response factors for DMtoluene and DMbenzaldehyde were determined from known samples. Response factors for DMbenzyl alcohol, DMbenzyl acetate, methyl DMbenzoate were assumed to be the same as those of their corresponding toluene derivatives. The response factors for Br-DMtoluene and Br-DMbenzaldehyde were given a value of 1.5 similar to analogous compounds. The assumptions made in the response factors do not result in significant errors because these compounds form in only small amounts. alpha-Bromodimethoxytoluene, the benzylic bromide, was not detected. Its absence is expected for this highly reactive substrate.[22] The 3,4-dimethoxybenzoic acid yield was determined by HPLC calibration with a authentic sample of 3,4-DMbenzoic acid.

Solids of DMbenzoic acid precipitated from the reactor when cooled to room temperature. A 43% yield of DMbenzoic acid precipitated at room temperature in example 2 of Table 2. Higher yields presumably could have been obtained by partial evaporation of the filtrate. Washing the solids with water to remove the paramagnetic catalyst metals, and dissolution in deutero-DMSO, gave proton and carbon NMR spectra identical to those of an authentic sample of DMBenzoic acid. Samples for HPLC were prepared by taking weighed aliquots from the reactor and diluting them with acetic acid so that precipitation of DMbenzoic acid would not occur.

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