

## Factors Affecting the Selectivity of the Oxidation of Methyl *p*-Toluate by Cobalt(III)

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The anaerobic oxidation of methyl *p*-toluate by cobalt(III) in acetic acid was investigated. Observed products were 4-carbomethoxybenzaldehyde (**2**), 4-carbomethoxybenzoic acid (**3**), 4-carbomethoxybenzyl acetate (**1**), 4,4'-dicarbomethoxybibenzyl (**6**), methyl 2,4-dimethylbenzoate (**8**), and methyl 3,4-dimethylbenzoate (**9**). Deuterium isotope labeling showed that **2** was not formed from **1**, but appeared to be formed directly from methyl *p*-toluate via 4-carbomethoxybenzyl alcohol (**5**). The ratio of (**2** + **3**) to **1** was 0.5 with  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}[\text{PF}_6]]$  and 1.0 with cobaltic acetate. Cobaltic acetate was generated in situ by the reaction of cobaltous acetate and peracetic acid. When the oxidation was carried out in the presence of chromium (0.05 equiv based on cobalt), the ratio increased dramatically and no **6** was observed. Other transition metals such as vanadium, molybdenum, and manganese had a similar effect, but were not as effective as chromium. Chromium was observed to form a mixed-metal cluster complex with cobalt. Treatment of an acetic acid solution of cobaltous acetate and methyl isonicotinate with  $\text{K}_2\text{CrO}_4$  produced a solid tentatively identified as  $[(\text{MIN})_3\text{Co}_2\text{CrO}(\text{OAc})_6][\text{CrO}_4\text{H}]$  (MIN = methyl isonicotinate). The selectivity for the oxidation of methyl *p*-toluate exhibited by the mixed-metal cluster complex was similar to that observed by the addition of chromium to oxidations using  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}[\text{PF}_6]]$ .

### Introduction

Many industrially produced aromatic carboxylic acids are generated from a cobalt-catalyzed autoxidation process.<sup>1</sup> Hence, research efforts to understand the role of Co(III) in these oxidation processes are important. For example, evidence suggests that some of the products in the catalytic oxidation process are the result of stoichiometric oxidations of organic intermediates by the metal catalyst.<sup>2</sup> In general, methylbenzenes are oxidized by cobaltic acetate to afford two main products, the benzaldehyde and the benzyl acetate, along with lesser amounts of dimeric products.<sup>3</sup> The reaction has been studied in both aqueous and anhydrous environments and in the presence of bromide ion.<sup>4</sup> The ratio of acetate to aldehyde appears to vary depending on the starting

hydrocarbon, temperature, concentration of reactants, and nature of the cobalt oxidant. The commonly accepted mechanism of the oxidation involves the formation of a cation radical via a reversible electron transfer from the hydrocarbon to the Co(III) followed by deprotonation<sup>5</sup> to give the benzylic radical. Subsequent oxidation of the benzylic radical by Co(III) leads to the oxygenated products.<sup>6</sup>

Therefore, in an attempt to provide insight into the chemistry involved in these processes, we report our work, which investigated: (i) the selectivity of the stoichiometric oxidation of methyl *p*-toluate by Co(III) in acetic acid solution under anaerobic conditions, and (ii) the effect of added transition metals on the ratio of the aldehyde to acetate product. Methyl toluate was chosen as our prototypical substrate, because its reactivity is similar to that of *p*-toluic acid, the least-reactive intermediate in the oxidation of xylene to terephthalic acid, and it helped to simplify the product analysis.

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**Table 1.** Stoichiometric Oxidation of Methyl Toluuate by 0.2 M Co(III) in Acetic Acid<sup>a</sup>

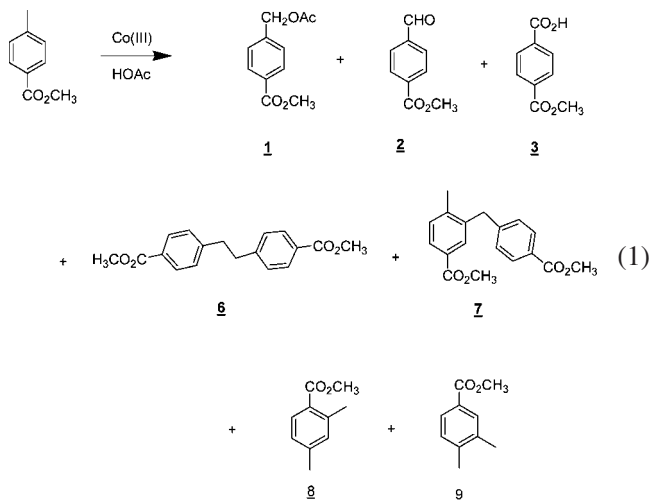
| entry  | T (°C) | water (%)      | 1  | 2  | 3  | 6 <sup>b</sup> |
|--|--------|----------------|----|----|----|----------------|
| Co(OAc) <sub>3</sub>   | 100    | 0 <sup>b</sup> | 54 | 17 | 29 | 0              |
| Co(OAc) <sub>3</sub>   | 100    | 3              | 52 | 17 | 30 | 0              |
| Co(OAc) <sub>3</sub>   | 100    | 10             | 50 | 19 | 31 | 0              |
| Co(OAc) <sub>3</sub>   | 160    | 3              | 52 | 34 | 13 | <1             |
| [py <sub>3</sub> Co <sub>3</sub> O(OAc) <sub>5</sub> OH][PF <sub>6</sub> ] | 160    | 0 <sup>c</sup> | 65 | 6  | 3  | 26             |
| [py <sub>3</sub> Co <sub>3</sub> O(OAc) <sub>5</sub> OH][PF <sub>6</sub> ] | 160    | 3              | 52 | 20 | 2  | 26             |
| [py <sub>3</sub> Co <sub>3</sub> O(OAc) <sub>5</sub> OH][PF <sub>6</sub> ] | 160    | 10             | 52 | 30 | 0  | 18             |

<sup>a</sup> Molar ratio (%) of methyl toluate derivatives. <sup>b</sup> Sum of products with MW 298. <sup>c</sup> 4:1 ratio of acetic acid/acetic anhydride. The reaction time was 2 h at 100 °C and 1 h at 160 °C.

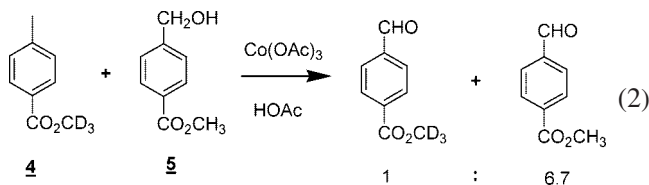
## Results

**Oxidation of Methyl Toluuate with Co(III).** The relative amounts of acetate and aldehyde products formed by the stoichiometric oxidation of methyl toluate by Co(III) in acetic acid solution depended upon the nature of the Co(III) species. The ratio of aldehyde to acetate was greater when cobaltic acetate was used than it was when [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>5</sub>OH][PF<sub>6</sub>] was used as the oxidant. Very little dimeric product resulting from the coupling of a benzyl radical was formed with cobaltic acetate, whereas it was a major product with [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>5</sub>OH][PF<sub>6</sub>]. The treatment of methyl toluate with cobaltic acetate (eq 1) in acetic acid at 100 °C gave a mixture of 4-carbomethoxybenzaldehyde (**2**), 4-carbomethoxybenzyl acetate (**1**), and 4-carbomethoxybenzoic acid (**3**) in yields of around 50% based on Co(III). The cobaltic acetate used in these experiments was prepared by the addition of excess peracetic acid to solutions of cobaltous acetate.<sup>7</sup> The ratio of the acetate to the sum of aldehyde and acid was around 1.1 when the reaction was carried out in 97% acetic acid. This ratio remained essentially unchanged when the reaction was carried out in 90% acetic acid, or in a 1:4 solution of acetic anhydride/acetic acid as a solvent (Table 1). When the reaction was carried out at 160 °C, the ratio of **1** to the sum of **2** and **3** was the same, but less **3** was formed and a trace of dimeric product, 4,4'-dicarbomethoxydiphenylethane (**6**), was detected. By contrast, a different product distribution was observed when [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>5</sub>OH][PF<sub>6</sub>]<sup>8</sup> was used as the source of Co(III). In addition to **1** (the major product), dimeric products consisting of mainly **6** along with small amounts of isomers (presumably a diphenylmethane derivative such as **7** and its isomer) were observed.<sup>9</sup> The formation of **7** is noteworthy because it has been shown that diphenylmethane derivatives can be converted to dicarboxyanthraquinones (an unwanted byproduct) under the conditions of the commercial terephthalic process.<sup>10</sup> The ratio of **1** to **2** decreased with increasing water concentration. Methyl 2,4-dimethylbenzoate (**8**) and methyl 3,4-dimethylbenzoate (**9**)

were formed as byproducts and typically comprised about 10–18% of the products derived from methyl toluate. The dimethyl benzoates, **8** and **9**, also have relevance to the commercial terephthalic process in that dimethylbenzoic acids are converted to trimellitic acid during the oxidation process, which leads to deactivation of the cobalt catalyst.<sup>1</sup> 4-Carbomethoxybenzyl alcohol (**5**) was also observed at 3–5% of the observed products.



**Deuterium Labeling.** Deuterium labeling experiments showed that the majority of **2** and **3** was not formed from **1** and that 4-carbomethoxybenzyl alcohol could be the precursor. A mixture of methyl-*d*<sub>3</sub> toluate (**4**) and 4-carbomethoxybenzyl acetate (**1**) (10:1 respectively) was reacted with cobaltic acetate as described above. The product mixture was analyzed by GC/MS, and the ratio of mass 167 to mass 164 was used to determine the relative amounts of 4-carbomethoxybenzaldehyde-*d*<sub>3</sub> and 4-carbomethoxybenzaldehyde **2**. The results showed that 92% of **2** contained the deuterium label. The ratio of nondeuterated to deuterated **1** present at the end of the reaction was 5:1 (determined by the ratio of *m/e* 208 to *m/e* 211). Thus, **1** and methyl toluate were oxidized at similar rates, and **2** was formed either directly from methyl toluate or through an intermediate other than **1**. In a similar experiment, a mixture of **4** and 4-carbomethoxybenzyl alcohol **5** (in a ratio of 19:1 respectively) was reacted with cobaltic acetate (eq 2).



The nondeuterated aldehyde was the overall major product (the ratio of **2/1/3** was 4.6/1/1.8, respectively) and GC/MS analysis showed the ratio of nondeuterated to deuterated **2** to be 6.7. A control experiment (carried out in the presence of Co(II)) showed that **5** was slow to esterify under reaction conditions and that only 24% was converted to **1**. Alcohol **5** was consumed much faster than methyl toluate, and could be the precursor to **2** and **3**.

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**Table 2.** Effect of Additives on the Mole Ratio of Methyl Toluate Oxidation Products Using  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  as an Oxidant at 160 °C

| additive                        | equivalents | 2  | 1  | 3  | ratio (2 + 3)/1 | 6  | yield <sup>c</sup> |
|---------------------------------|-------------|----|----|----|-----------------|----|--------------------|
| none                            |             | 16 | 42 | 5  | 0.5             | 35 | 43                 |
| K <sub>2</sub> CrO <sub>4</sub> | 0.2         | 68 | 3  | 29 | 32.8            | 0  | 57                 |
| K <sub>2</sub> CrO <sub>4</sub> | 0.05        | 77 | 8  | 14 | 10.9            | 1  | 53                 |
| Cr(OAc) <sub>3</sub>            | 0.2         | 77 | 13 | 11 | 7.0             | 0  | 33                 |
| V <sup>b</sup>                  | 0.2         | 74 | 20 | 4  | 3.8             | 1  | 55                 |
| V <sup>b</sup>                  | 0.05        | 55 | 31 | 5  | 1.9             | 10 | 54                 |
| Mn(OAc) <sub>2</sub>            | 1           | 42 | 37 | 21 | 1.7             | 0  | 8                  |
| Mo <sup>a</sup>                 | 2           | 48 | 33 | 6  | 1.7             | 10 | 13                 |
| Pd(OAc) <sub>2</sub>            | 0.1         | 20 | 44 | 4  | 0.5             | 31 | 41                 |
| Pd(OAc) <sub>2</sub>            | 0.2         | 22 | 63 | 5  | 0.4             | 8  | 46                 |
| Fe(OAc) <sub>2</sub>            | 0.2         | 16 | 46 | 4  | 0.4             | 34 | 39                 |
| Ni(OAc) <sub>2</sub>            | 0.2         | 16 | 44 | 5  | 0.5             | 34 | 42                 |
| RuO <sub>2</sub>                | 0.2         | 18 | 44 | 5  | 0.5             | 32 | 44                 |
| Na <sub>2</sub> WO <sub>4</sub> | 0.2         | 16 | 38 | 6  | 0.6             | 40 | 45                 |
| Ce(OAc) <sub>3</sub>            | 0.2         | 15 | 41 | 5  | 0.5             | 36 | 44                 |
| Cu(OAc) <sub>2</sub>            | 0.2         | 27 | 57 | 5  | 0.6             | 8  | 40                 |
| none                            |             | 15 | 41 | 3  | 0.4             | 41 | 51                 |

<sup>a</sup> Molybdic acid. <sup>b</sup> Vanadyl acetate. <sup>c</sup> The yield of the total products was based on Co(III). The concentration of Co(III) was 0.25 M.

**Additives.** The selectivity of the oxidation was dramatically altered by the presence of certain other transition metals. For example, the ratio of aldehyde/acetate products increased when the oxidation was carried out in the presence of chromium. Other transition metals such as vanadium, manganese, and molybdenum also increased the ratio, but were not as effective as chromium. The addition of palladium, iron, nickel, copper, or cerium acetates, or RuO<sub>2</sub> or sodium tungstate had little or no effect on the ratio of aldehyde to acetate (Table 2), although copper and palladium (0.2 equiv based on cobalt) decreased the amount of **6** that was formed. The presence of chromium affected the selectivity of the oxidation regardless of which form of Co(III) was used, but the effect of chromium was most pronounced when  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  was used as the oxidant. For example, the oxidation of methyl toluate (1.3 M) with  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  (0.08 M) in acetic acid (96%) at 160 °C in the presence of potassium chromate (0.05 M, 0.2 equiv based on cobalt) gave an (aldehyde + acid)/acetate ratio of 33:1. The ratio decreased to 11:1 when only 0.05 equiv of potassium chromate were used. The substitution of chromic acetate for potassium chromate gave a ratio of 7:1. When cobaltic acetate (generated by the oxidation of cobaltous acetate with peracetic acid) was substituted for  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$ , the ratio was 2.8 for both potassium chromate and chromic acetate. Little or no products resulting from benzyl radical coupling (such as **6**) or addition were observed when chromium was present. The use of potassium chromate alone resulted in a small amount of **2**

(less than 10% based on chromium) and the recovery of unreacted potassium chromate.

Products derived from the methyl radical (methyl dimethylbenzoate, picoline, and methane) were also produced during the reaction. Methyl dimethylbenzoates (**8** and **9**) were formed in the amount of 5% yield (based on Co(III)) when  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  was used alone (Table 3). Picoline was also detected in about 6% yield. The ratio of 2-picoline to other isomers was on the order of 6:1. The amount of **8** and **9** decreased to about 2% in the presence of chromium, and only a trace was detected when copper was added. This trend was also followed for picoline, where the yield was 2.5% in the presence of chromium and only 0.2% in the presence of copper. When cobaltic acetate was the source of Co(III), **8** and **9** were formed in a ~2% yield when the reaction was carried out at 160 °C, and only a trace was detected when the reaction was carried out at 100 °C. Methane and carbon dioxide were detected in the gas phase of the reaction in roughly equal amounts (11% based on the total amount of cobalt) when  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  was the oxidant. The yield of methane decreased to about 4% in the presence of chromium and to less than 0.5% in the presence of copper, but the yield of carbon dioxide remained essentially unchanged. Methane and carbon dioxide were observed in 3 and 4% yields respectively for cobaltic acetate at 160 °C; however, methane decreased to less than 0.5% when the reaction was carried out at 100 °C. Small amounts of carbon monoxide were also observed. Methyl acetate was produced in small amounts but was difficult to quantify due to the reaction of acetic acid and methyl toluate to give methyl acetate in amounts similar to that produced by the oxidation. The amount of methyl acetate qualitatively increased when the reaction was carried out in the presence of chromium or copper.

**Mixed-Metal Cluster Complex.** A mixed-metal cluster complex containing cobalt and chromium that exhibited similar selectivity to  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  with added chromium was isolated by the treatment of cobaltous acetate and pyridine with potassium chromate. The reaction of potassium chromate with cobaltous acetate and pyridine in acetic acid produced a brown solid containing cobalt and chromium. Electrospray mass spectroscopy in dimethyl formamide/methylene chloride solution indicated that the material was a mixture of  $[\text{Py}_3\text{Co}_2\text{CrO}(\text{OAc})_6][\text{CrO}_4\text{H}]$  and  $[\text{Py}_3\text{Co}_3\text{O}(\text{OAc})_6][\text{CrO}_4\text{H}]$ . Positive ions were observed at *m/e* 777 (major) and *m/e* 784, whereas only one negative ion was observed at *m/e* 117. Attempts to purify the mixture by recrystallization were unsuccessful. A pure compound was obtained by using methyl isonicotinate (MIN) in place of

**Table 3.** Observed Products from the Oxidation of Methyl Toluate at 160 °C<sup>a</sup>

| oxidant   | 8   | 9   | 2    | 1    | 3    | 6   | 5   | picoline | methane | CO <sub>2</sub> |
|---|-----|-----|------|------|------|-----|-----|----------|---------|-----------------|
| $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  | 4.0 | 1.5 | 12.1 | 16.0 | 2.8  | 7.8 | 0.8 | 5.3      | 11.0    | 10.7            |
| $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$ + 0.2 eq K <sub>2</sub> CrO <sub>4</sub> | 1.7 | 0.5 | 33.6 | 0.0  | 13.8 | 0.0 | 0.4 | 1.5      | 3.7     | 10.7            |
| $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$ + 0.2 eq Cu(OAc) <sub>2</sub>            | 0.1 | 0.0 | 12.6 | 16.2 | 2.0  | 2.9 | 1.2 | 0.1      | 0.3     | 9.3             |
| Co(OAc) <sub>3</sub>  | 1.5 | 0.7 | 11.6 | 17.2 | 13.9 | 0.0 | 2.4 |          | 3.3     | 4.3             |
| Co(OAc) <sub>3</sub> <sup>b</sup>   | 0.1 | 0.0 | 21.7 | 16.2 | 6.0  | 0.0 | 3.6 |          | 0.3     | 2.0             |

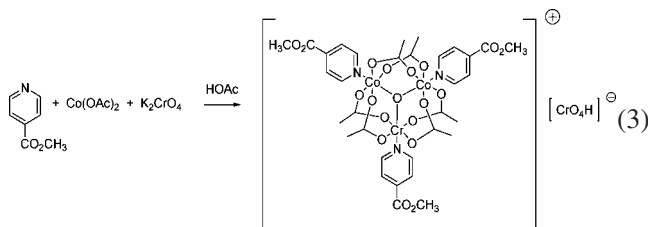
<sup>a</sup> The yield (%) was based on Co(III). The concentration of Co(III) was 0.2 M. The reaction time was 1 h. <sup>b</sup> The reaction temperature was 100 °C and the time was 2 h.

**Table 4.** Comparison of the Selectivity of the Mixed-Metal Cluster<sup>a</sup>

|   | 8  | 9 | 2  | 1  | 3  | 6  | 5  | yield <sup>b</sup> |
|---|----|---|----|----|----|----|----|--------------------|
| [(MIN) <sub>3</sub> Co <sub>2</sub> CrO(OAc) <sub>6</sub> ][CrO <sub>4</sub> H]                             | 7  | 3 | 63 | 0  | 26 | 0  | <1 | 51                 |
| [(MIN) <sub>3</sub> Co <sub>3</sub> O(OAc) <sub>6</sub> ][PF <sub>6</sub> ]                                 | 13 | 5 | 11 | 44 | 2  | 22 | 3  | 43                 |
| [py <sub>3</sub> Co <sub>3</sub> O(OAc) <sub>5</sub> OH][PF <sub>6</sub> ]                                  | 11 | 4 | 16 | 43 | 3  | 21 | 2  | 45                 |
| [py <sub>3</sub> Co <sub>3</sub> O(OAc) <sub>5</sub> OH][PF <sub>6</sub> ]+ K <sub>2</sub> CrO <sub>4</sub> | 7  | 3 | 76 | 0  | 14 | 0  | <1 | 48                 |
| [py <sub>3</sub> Co <sub>3</sub> O(OAc) <sub>5</sub> OH][PF <sub>6</sub> ]+ Cr(OAc) <sub>3</sub>            | 9  | 3 | 76 | 7  | 6  | 0  | <1 | 29                 |

<sup>a</sup> Mole ratio of the products. The concentration of Co(III) was 0.2 M. <sup>b</sup> The yield of the total products was based on Co(III). Methyl methylisonicotinate was not analyzed.

pyridine (eq 3). In this case, a compound formulated as [(MIN)<sub>3</sub>Co<sub>2</sub>CrO(OAc)<sub>6</sub>][CrO<sub>4</sub>H] was isolated in lower yield (31%) but was determined to be relatively pure by electro-spray mass spectroscopy. A signal was observed at *m/e* 951 (cation) and an anion signal was observed at 117. The exact mass was consistent with the formulations for the cation and anion. The infrared spectrum displayed absorptions at 1736 (m), 1610 (s), 1439 (s), 1418 (sh), 1327 (w), 1292 (s), 1127 (m), 1061 (w), 943 (m), 768 (m), 698 (s), 683 (m), 663 (m), 624 (w), 440 (m) and 422 (m) cm<sup>-1</sup>. The band at 943 cm<sup>-1</sup> was assigned to the chromate anion. Attempts to grow X-ray quality crystals were unsuccessful.



The oxidation of methyl toluate with [(MIN)<sub>3</sub>Co<sub>2</sub>CrO(OAc)<sub>6</sub>][CrO<sub>4</sub>H] gave a product distribution that was similar to that obtained by oxidation with [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>5</sub>OH][PF<sub>6</sub>] and added potassium chromate. Table 4 compares the selectivity of the isolated mixed-metal cluster to that of [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>5</sub>OH][PF<sub>6</sub>] alone and with added chromate and chromium acetate. The treatment of a slurry of [(MIN)<sub>3</sub>Co<sub>2</sub>CrO(OAc)<sub>6</sub>][CrO<sub>4</sub>H] in acetic acid with NH<sub>4</sub>PF<sub>6</sub> resulted in the metathesis of the chromate anion with hexafluorophosphate to give the compound tentatively identified as [(MIN)<sub>3</sub>Co<sub>2</sub>CrO(OAc)<sub>6</sub>][PF<sub>6</sub>]. The infrared spectrum showed the absence of the band at 943 cm<sup>-1</sup> and the appearance of two new bands at 841 and 558 cm<sup>-1</sup>, which were consistent with the replacement of the chromate anion with hexafluorophosphate. The infrared spectra of both chromium-containing compounds were very similar to that of [(MIN)<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>6</sub>][PF<sub>6</sub>] except for the presence of absorptions at 663 and 422 cm<sup>-1</sup>, which could be associated with the Co<sub>2</sub>CrO core.<sup>11</sup> The oxidation of methyl toluate with this compound gave results similar to those obtained using [(MIN)<sub>3</sub>Co<sub>2</sub>CrO(OAc)<sub>6</sub>][CrO<sub>4</sub>H], although the overall yield was lower.

## Discussion

The oxidation of an aromatic hydrocarbon by cobaltic acetate is thought to proceed through a radical cation

mechanism.<sup>3,12</sup> The radical cation is formed in a rapid equilibrium with the starting materials, and deprotonation leads to a benzylic radical. The subsequent oxidation of the benzylic radical by Co(III) was thought to generate a benzylic carbocation that was presumably trapped by the solvent to give the oxygenated products.<sup>13</sup> In view of our results, for example, the sensitivity of the product distribution to the oxidant, it seems unlikely that a free carbocation plays a major role in the formation of oxygenated products. The observed product distribution might be explained by the interaction of the metal complex with the benzylic radical<sup>14</sup> in a ligand transfer oxidation step involving a coordinated acetate or hydroxide.<sup>15</sup> For example, the addition of the benzyl radical to an oxygen atom of an acetate ligand would result in the reduction of Co(III) and the formation of the benzyl acetate. Conversely, the addition of the radical to a hydroxyl ligand (or the oxo-centered oxygen) would result in the reduction of Co(III) and the formation of the benzyl alcohol **5**, which would lead to **2**. Deuterium labeling showed that **5** was quickly oxidized to **2** under reaction conditions. The different product distribution exhibited by [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>5</sub>OH][PF<sub>6</sub>] is consistent with the lower reactivity of the pyridine-substituted cobalt clusters.<sup>16</sup> The observation of dimeric products in this case suggests a slower rate of oxidation of the benzylic radical and consequently a higher concentration of free benzylic radicals in solution. It is also noteworthy that the relative amount of **2** and **3** increased as the concentration of water was increased when [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>5</sub>OH][PF<sub>6</sub>] was used as the oxidant. Pyridine-substituted oxo-centered cobalt clusters are known to undergo substitution of bridging acetate ligands with bridging hydroxide ligands in aqueous acetic acid.<sup>17,18</sup>

Presumably, the presence of chromium or vanadium facilitates the formation of **5** or its equivalent. Similar selectivity was observed whether chromium was added in the form of Cr(III) or Cr(VI) or as a mixed-metal cluster

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(16) The rest potentials for [py<sub>3</sub>Co<sub>3</sub>O(OAc)<sub>6</sub>][OAc], [py<sub>3</sub>Co<sub>2</sub>CrO(OAc)<sub>6</sub>][CrO<sub>4</sub>H], and cobaltic acetate (generated in situ by the addition of peracetic acid to a solution of cobaltous acetate) were measured at room temperature in a 96% acetic acid solution against a 3 M Ag/AgCl electrode. The solutions were 0.1 M in cobalt and the observed potentials were 1074, 1149, and 1255 mV, respectively.

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complex. It is possible that a mixed-metal cluster complex formed in situ was responsible for the observed selectivity. It is not clear why the presence of chromium favored the production of **2** over **1**, but it is thought that the intermediate formation of a chromium alkoxide from a benzylic radical could play a role.<sup>19</sup>

The methyl dimethylbenzoates and picoline were presumably formed as a result of the addition of methyl radicals to methyl toluate and pyridine respectively. The methyl radicals were formed as a result of the thermal decomposition of the Co(III) complex to give initially the acetoxy radical that lost carbon dioxide to give the methyl radical.<sup>14</sup> The ratio of **8** to **9** was around 2.6 and was consistent with the nucleophilic nature of the methyl radical.<sup>20</sup> The observation of less product derived from methyl radical when the oxidation was carried out at lower temperature is also consistent with the thermal decomposition of Co(III) as a source of byproducts in cobalt-catalyzed oxidations.<sup>21</sup> Essentially no methyl dimethylbenzoates or picoline and very little methane were observed when the oxidation was carried out in the presence of Cu(II), which is known to be an efficient trap for methyl radicals.<sup>22</sup> The decrease in the yields of methyl dimethylbenzoate, methane, and picoline when the reaction was carried out in the presence of chromium suggests that chromium (in some form) is acting as a radical trap. The chromium radical trap might be more specific for benzyl radicals than for methyl radicals and thus affect the selectivity of the oxidation of methyl toluate by converting the intermediate benzyl radical to a chromium alkoxide and ultimately to **2**.

In summary, the oxidation of methyl toluate by Co(III) yields mainly the oxidation products **1**, **2**, and **3**, and in the case of  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$ , the radical coupling product **6** (and **7**) derived from the benzyl radical was formed in a major amount. Deuterium labeling experiments showed that most of **2** was not derived from **1**, but was probably formed from **5**. The selectivity of the oxidation was most affected by the pyridine ligand and the presence of catalytic amounts of chromium, copper, and certain other transition metals. The ratio of **1** to **2** (or **1** to **5**) increased dramatically when  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  was used as the oxidant in place of  $\text{Co}(\text{OAc})_3$ . However, this ratio decreased dramatically when the oxidation was carried out in the presence of chromium or vanadium regardless of the source of Co(III). A mixed-metal cluster complex that contained cobalt and chromium was isolated, and the complex showed selectivity similar to that observed upon the addition of chromium.

## Experimental Section

The ratios of deuterated products were determined by measuring the relative peak areas under the mass chromatogram for the ion in question. It was necessary to convert the sample to its trimethylsilyl ester to determine the ratio of deuterated to nondeu-

terated **3**. The analyses were carried out using a DB-5 capillary column and a Finnigan TSQ700 mass spectrometer. Methyl-*d*<sub>3</sub> toluate was prepared by the esterification of toluic acid with methanol-*d*<sub>4</sub>. The dimeric product (**6**) was identified by the comparison of its retention time and the mass spectrum to an authentic sample.<sup>23</sup> GC analyses were performed using a DB-5 capillary column (110 to 270 °C at 10 °C/min). A known amount of bibenzyl was added to the sample as an internal standard. A small amount of the sample was treated with excess bis(trimethylsilyl)trifluoroacetamide for the quantitation of **3** and **5**. Picoline and methyl acetate were analyzed using a DB-1701 column (40 to 250 °C at 15 °C/min). Yields of product based on Co(III) were calculated by multiplying the moles of a particular product by the moles of Co(III) required to produce that product and dividing by the theoretical amount of Co(III) charged to the reaction. Gas samples were analyzed by gas chromatography using an Agilent 3000A MicroGC gas analyzer equipped with parallel injection. ATR infrared spectra were collected on a Nicolet model 6700 spectrometer.

### Anaerobic Oxidation of Methyl Toluate–Cobaltic Acetate.

A solution of cobaltic acetate was prepared by the addition of 35% peracetic acid (282 mg; 1.3 mmol) to  $\text{Co}(\text{OAc})_2 \cdot 4(\text{H}_2\text{O})$  (330 mg; 1.3 mmol) dissolved in 5 mL of acetic acid. To this solution was added methyl toluate (1.00 g; 6.7 mmol). The resulting solution was transferred to a 25 mL glass bulb equipped with a 14/20 ground glass joint. The flask was connected to a vacuum line, and the solution was freeze–pump–thawed three times, and the flask was sealed with a torch while the mixture was frozen under a vacuum. The reaction mixture was heated for 2 h in a steam bath, during which time it developed a blue-brown color. The flask was broken open, and a portion of the reaction mixture was submitted for GC analysis. The amounts of products are listed in Table 1. For oxidations in 90% acetic acid, the same procedure was repeated except that 0.5 mL of acetic acid solvent was replaced with 0.5 mL of water. For oxidations in anhydrous acetic acid, the procedure was repeated except that 1 mL of acetic acid was replaced with 1 mL of acetic anhydride.

$[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$ . A resealable Carius tube equipped with a magnetic spin bar was charged with  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  (250 mg; 0.28 mmol), methyl toluate (0.50 g; 3.3 mmol), and 96% aqueous acetic acid (2.5 g). The mixture was purged with argon, sealed, and heated in an oil bath at 160 °C for 1 h, during which time the color changed from brown to blue. The mixture was removed from the bath, cooled, and vented. The product was weighed and analyzed by GC. This procedure was used for oxidations carried out in the presence of additives. The additive was charged along with the cobalt compound except when peracetic acid was used and the additive was added after the peracetic acid.

When gas samples were collected, a 50 mL Fischer–Porter bottle equipped with a spin bar, pressure gauge, and needle valve was charged with  $[\text{py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PF}_6]$  (893 mg; 1.0 mmol), methyl toluate (2.35 g; 16 mmol), and 96% aqueous acetic acid (11.77 g). The mixture was purged with nitrogen, and heated in an oil bath at 160 °C for 1 h. After cooling to room temperature, the pressure was recorded and the excess gas was collected in a gastight syringe and analyzed by GC. Methane and carbon monoxide were analyzed on a Molsieve column (10 m; 0.32 mm ID; 12 μm) isothermal at 100 °C with argon carrier gas. Carbon dioxide was analyzed using a Plot-U column (8 m; 0.32 mm ID; 30 μm) isothermal at 85 °C.

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**Co-oxidation of Methyl- $d_3$  Toluate (4) and 4-(Carbomethoxy)benzyl Acetate (1).** The same procedure described for the oxidation of methyl toluate was followed, except methyl- $d_3$  toluate (1.00 g; 6.4 mmol) and 4-(carbomethoxy)benzyl acetate (133 mg; 0.64 mmol) were added in place of methyl toluate. At the end of the reaction, the flask was broken open, and an aliquot of the reaction mixture was removed and filtered through silica and submitted to GC–MS analysis. The ratio of  $m/z$  167 to  $m/z$  164 was found to be 12.4:1. The ratio of  $m/z$  208 to  $m/z$  211 was found to be 5:1. Analysis of the product mixture by GC showed an increase of 0.16 mmol in the amount of **1** and a total of 0.16 mmol of **2** and **3**.

As a control experiment, the procedure above was repeated except that cobaltic acetate was replaced with cobaltous acetate. No mass at  $m/z$  211 was observed, demonstrating the methoxy groups do not exchange under the reaction conditions.

**Co-oxidation of Methyl- $d_3$  Toluate (4) and 4-(Carbomethoxy)benzyl Alcohol (5).** The procedure described for the oxidation of methyl toluate was followed except the methyl toluate was replaced with methyl- $d_3$  toluate (1.02 g; 6.6 mmol) and 4-(carbomethoxy)benzyl alcohol (**5**) (56 mg; 0.3 mmol). At the end of the reaction, the flask was broken open and an aliquot of the reaction mixture was removed and filtered through silica and submitted to GC–MS analysis. The ratio of  $m/z$  164 to  $m/z$  167 was found to be 6.7:1. The ratio of  $m/z$  211 to  $m/z$  208 was found to be 4.1:1. A control experiment similar to that described above showed no exchange of the methoxy groups.

**Preparation of Mixed-Metal Cluster.** To a 300 mL round-bottom flask was added  $\text{Co}(\text{OAc})_2 \cdot 4(\text{H}_2\text{O})$  (4.98 g; 20 mmol),

$\text{K}_2\text{CrO}_4$  (3.88 g; 20 mmol), and acetic acid (70 mL). The mixture was heated to 45 °C and allowed to cool. Methyl isonicotinate (4.52 g; 33 mmol) was added and the resulting mixture was stirred (magnetically) at ambient temperature for 2 h, during which time the color turned dark brown. The mixture was heated to a boil, removed from the heat, and allowed to stand overnight. The product was collected by filtration, washed with a small amount (15 mL) of acetic acid followed by three 50 mL portions of water, and air-dried. The yield was 3.90 g (33%) of brown needles. Anal. Calcd for  $\text{C}_{33}\text{H}_{40}\text{Co}_2\text{Cr}_2\text{N}_3\text{O}_{23}$ : C, 37.08; H, 3.75; N, 3.93; Co, 11.05; Cr, 9.74. Found: C, 36.71; H, 3.68; N, 3.72; Co, 11.2; Cr, 9.8.

To a 50 mL Erlenmeyer flask was added 2.0 g (2 mmol) of compound above, acetic acid (18 mL), and  $\text{NH}_4\text{PF}_6$  (1.28 g) dissolved in 2 mL of water. The resulting mixture was sealed with a stopper and stirred (magnetically) overnight. The mixture was filtered onto a glass frit. The color of the filtrate was yellow. The residue was washed with acetic acid and with water (3 15 mL), and air-dried to give 1.2 g of brown solid. Anal. Calcd for  $\text{C}_{33}\text{H}_{39}\text{Co}_2\text{CrF}_6\text{N}_3\text{O}_{19}\text{P}$ : C, 36.13; H, 3.56; N, 3.83; Co, 10.77; Cr, 4.74; P, 2.83; F, 10.40. Found: C, 35.40; H, 3.44; N, 3.68; Co, 11.43; Cr, 5.33; P, 2.56.

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