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Role of Amine Promoters in Cobalt/Bromide-Catalyzed Oxidations

An extensive amount of research has been conducted in the area of metal-catalyzed autoxidations in the past few decades. Within these studies, the emphasis has been on the organic chemistry, and detailed information on many of the metal catalysts used has been lacking in the literature (for a review on metal-catalyzed autoxidations see (*1*)). This often occurs even in well-studied industrial oxidation processes, such as the cobalt-catalyzed autoxidation of *p*-xylene to terephthalic acid. It has been reported by Hronec and coworkers that the addition of nitrogen donor ligands, such as pyridine (Py) or triethanolamine, to the cobalt/bromide-catalyzed autoxidations see (*1*)). This often occurs results in an unexplained, dramatic increase in oxidation rate (*2*). This manuscript reports the result of our investigation of the role of amine promoters in the cobalt-catalyzed autoxidation of *p*-xylene. We have found that amines stabilize Co(III) in a catalytically active and isolable form which not only is capable of oxidizing bromide to a bromine radical but also is resistant to reduction to Co(II) by peroxides; this stabilization leads to high steady-state Co(III) levels which increase the oxidation rates.

We have studied the oxidation of *p*-xylene in glacial acetic acid catalyzed by both $CoBr_2(Py)_2$ and anhydrous $CoBr_2$ in a medium-pressure, glass reactor (oxygen atmosphere) wherein oxidation rates were measured by oxygen uptake[1,2] (*3*); results of our studies are illustrated in Fig. 1. Initial rate from $CoBr_2(Py)_2$ is roughly three times faster than that obtained from $CoBr_2$[3,4]. Oxidation of *p*-xylene in glacial acetic acid catalyzed by $Co(OAc)_2 \cdot 4H_2O$ and two equivalents of pyridine under similar reaction conditions resulted in no observable oxygen uptake. The use of $Co(OAc)_2 \cdot 4H_2O$ alone improved the rate only slightly (less than 1% of the rate obtained by using $CoBr_2$).

From these studies, the following relative catalyst activities for *p*-xylene oxidation were obtained:

$$CoBr_2(Py)_2 > CoBr_2 \gg Co(OAc)_2 \cdot 4H_2O \gg Co(OAc)_2 \cdot 4H_2O/Py$$

These results show that the cobalt/bromide catalysts are much more active than the non-bromide-promoted catalysts and that the addition of an amine is activating in the bromide-promoted catalyst and deactivating in the non-bromide-promoted catalyst.

To discover more about the reactivities of these different catalysts, we have studied the reaction of pyridine- and non-pyridine-solvated Co(III) complexes with LiBr and H_2O_2. We previously have described the isolation and characterization of oxo-centered clusters $[Py_3Co_3O(OAc)_5OR]X$ (R = H, CH_3CO; X = $PyCoBr_3$, OAc, PF_6) (*4*). The oxo-centered complexes seem ideally suited to be used as model complexes for catalytic intermediates because they are isolable from actual oxidation reaction mix-

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[1] In addition to oxygen uptake, reactions have been followed on a Hewlett–Packard 5730A gas chromatograph by using a 10% GF1 on 100/120-mesh Chromosorb WHP column. Visible spectra were obtained on a Perkin–Elmer 552 spectrophotometer. $CoBr_2(Py)_2$ was prepared by using literature procedures (*3*).

[2] These oxidations have also been conducted satisfactorily in 95/5 acetic acid/water (v/v).

[3] These results have also been corroborated by using air as an oxidant and by monitoring the oxidation rate from reaction products by gas chromatography.

[4] Steady-state Co(III) concentrations are much higher in the $CoBr_2Py_2$-catalyzed reactions than in the $CoBr_2$-catalyzed reactions as determined by using visible spectroscopy; this has not been quantified owing to the uncertain nature of the species being observed.

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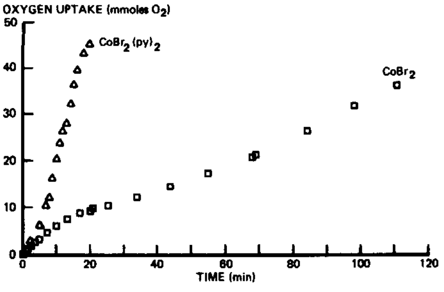

FIG. 1. Oxygen uptake in the autoxidation of *p*-xylene. Reaction conditions: 50 psig O_2, 100°C, 42 ml acetic acid, 67.1 mmol *p*-xylene, 1.1 mmol cobalt.

tures[5] and because they can oxidize bromide to a bromine radical; this oxidation has been demonstrated to result in an autocatalytic reaction in the presence of oxygen and an aromatic substrate (*4*).

Reactions of a 2.04 mM solution of $[Py_3Co_3O(OAc)_5OH][PF_6]$ (**1**) with a 30-fold molar excess of LiBr in 95/5 acetic acid/water results in the slow reduction of the Co(III) species to $[CoBr_4]^{2-}$ over an hour. In contrast, reaction of related non-pyridine-solvated clusters, such as $[(HOAc)_x(H_2O)_{3-x}Co_3O(OAc)_6][OAc]$ (**2**), with a similar excess of LiBr results in complete reduction of **2** to $[CoBr_4]^{2-}$ within a minute[6] (*5*). With H_2O_2 (200-fold molar excess), reduction of **1** and **2** to Co(II) occurs at rates comparable to the reduction observed with LiBr for each complex under similar conditions. In both cases, the reduction of Co(III) to Co(II) by H_2O_2 or LiBr proceeds at a rate roughly 100 times slower for **1** as compared to **2**. Deuterium labeling and ligand competition experiments analyzed by fast-atom-bombardment mass spectroscopy (FAB/MS) and variable-temperature proton NMR experiments show that neither $[Py_3Co_3O(OAc)_5OH][PF_6]$ nor $[Py_3Co_3O(OAc)_6][PF_6]$ exchange their acetate or pyridine ligands at room temperature.[7] In contrast, the non-pyridine-complexed Co(III) clusters, such as **2**, do exchange their ligands rapidly. These results show that the cobalt/pyridine oxo-centered clusters remain intact under ambient reaction conditions and that their reactivity does not arise from degradation via ligand loss to non-pyridine cobalt clusters or monomers. The stabilizing effect of pyridine is further indicated with the oxidation of Co(II) with H_2O_2. Mixing $Co(OAc)_2 \cdot 4H_2O$ in 95/5 acetic acid/water with any H_2O_2 results in rapid peroxide decomposition but no observable Co(III) formation.[8] In the presence of a slight, twofold excess of pyridine, however, the reaction of $Co(OAc)_2 \cdot 4H_2O$ with H_2O_2 gives within seconds a rapid color change from pink to brown, and a high concentration of Co(III) is observed by visible spectroscopy.[9]

There is evidence that Co(III) acetate complexes oxidize aromatic hydrocarbons via a reversible, electron transfer to form aromatic radical cations which subsequently lose a proton in the rate-determining step to form benzylic radicals (*6*). In this mechanism, the rate of electron transfer will be strongly dependent upon the reduction potential of the catalyst, which, in

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[5] These clusters have been isolated from the $CoBr_2(Py)_2$-, $CoBr_2$-, and $Co(OAc)_2 \cdot 4H_2O$/Py-catalyzed reactions.

[6] These non-pyridine-solvated clusters ("cobaltic acetate") are not as well characterized as the pyridine-solvated complexes. Similar complexes have been isolated and partially characterized by Ziolkowski and co-workers (*5*). FAB/MS spectra and derivatization by pyridine which leads to a mixture of $[Py_3Co_3O(OAc)_5OH]^+$ and $[Py_3Co_3O(OAc)_6]^+$ are consistent with the oxo-centered framework.

[7] These complexes will slowly exchange their ligands at elevated temperatures.

[8] The observations in these experiments do not depend on the concentration of either $Co(OAc)_2 \cdot 4H_2O$ or H_2O_2. See Ref. (*8*) for an example of a concentration-dependent reaction.

[9] The reaction of $Co(OAc)_2 \cdot H_2O$ and pyridine with H_2O_2 to produce Co(III) is very dependent on the cobalt concentration and on the manner in which the H_2O_2 is added. The H_2O_2 must be added slowly for the maximum effect; this may be related either to the rate of pyridine coordination to Co(III) or to the rate of cluster formation. Pyridine may also influence the type of cluster formed (complete Co(III) cluster, a mixed-valence complex, dimers, or trimers, for example).

turn, affects the catalytic activity. It is known that the addition of amine ligands to cobalt can decrease its reduction potential[10] (*7*). It is consistent with our results that the non-bromide-promoted cobalt/pyridine catalyst (which is inactive) possesses a reduction potential below that of *p*-xylene. Even without the presence of pyridine, decomposition by hydroperoxides in non-bromide-promoted cobalt catalysts leads to only low steady-state Co(III) levels. As a result, the oxidation is observed to proceed at low rates because of the inability of the catalyst to maintain an efficient radical chain.

When bromide is added to the oxidation reaction, the oxidation mechanism is changed so that the oxidation of bromide to a bromine radical is the key step. Bromine radical abstracts a hydrogen atom from an aromatic methyl group to produce a benzylic radical which maintains the radical chain (*4*, *8*). The lower oxidation potential of bromide does not require a high Co(III) concentration to promote an efficient radical chain. However, an increase in Co(III) concentration will lead to an increase in oxidation rate. Therefore, the Co(III) catalyst which is stable to reduction to Co(II) by hydroperoxides, but can still oxidize bromide to a bromine radical, will be a more efficient catalyst. The pyridine-solvated oxo-centered clusters meet both of these criteria. The high steady-state Co(III) level observed in the $CoBr_2(Py)_2$-catalyzed reactions is consistent with the increase in oxidation rate over the oxidation rate obtained in the $CoBr_2$-catalyzed reactions.[4]

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[10] The resting potential of $[Py_3Co_3O(OAc)_5OH]^+$ in acetic acid was found to be 780 mV while the resting potential of "cobaltic acetate" under similar conditions was found to be 920 mV. The "cobaltic acetate" was prepared by the addition of peracetic acid to an acetic acid solution of hydrous cobalt acetate (see footnote 6).

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