Preconversion Catalytic Deoxygenation of Phenolic Functional Groups

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Introduction to Catalytic Deoxygenation of Phenols by CO.

Recent research in our laboratories has established the viability of the catalytic deoxygenation of phenols by carbon monoxide. The deoxygenation of phenols is a problem of both fundamental and practical importance. The deoxygenation of phenols to arenes is a simple, yet a difficult chemical transformation to achieve. The phenolic C-O bond energy of 103 kcal/mol is as strong as a benzene C-H bond and over 10 kcal/mol stronger than the C-O bonds of methanol or ethanol.

\[ D(C-O) = 103 \text{ kcal/mol} \]
\[ D(O-H) = 85 \text{ kcal/mol} \]
\[ D(C-H) \leq 103 \text{ kcal/mol} \]

Catalytic hydrodeoxygenation (HDO) of phenols over sulfided Mo/γ-Al₂O₃, Ni-Mo/γ-Al₂O₃, Co-Mo/γ-Al₂O₃ or other supported metal oxide catalysts can be achieved, at exceedingly high hydrogen pressures (> 100 atm) and temperatures (> 200 °C).²⁻¹⁰ Arene ring hydrogenation generally competes effectively with hydrodeoxygenation,²⁻¹⁰ and was found to occur an order of magnitude faster than HDO.⁹ As a consequence, most of the hydrogen is consumed in hydrogenation of the aromatic rings. HDO catalysts are easily poisoned.⁵ Moreover, the HDO side product, water, is found to dramatically impair HDO activity by occupying anion vacancies on the catalyst surfaces.⁹

The inefficiency of catalysts for phenol deoxygenation in the presence of hydrogen can be attributed to the absence of a low energy mechanistic pathway for the hydrogenolysis of the strong phenol C-O bond. We are currently studying new transition metal catalysts for the efficient and selective deoxygenation of phenols using the CO/CO₂ couple to remove phenolic oxygen atoms. The deoxygenation of phenols by CO, eq 1, is thermodynamically favored by over 20 kcal/mol; however, remarkably no commercial catalysts are yet available for this important reaction.

\[
\text{C}_6\text{H}_5\text{OH} \text{ (l)} + \text{CO} \text{ (g)} \rightleftharpoons \text{C}_6\text{H}_4\text{H} \text{ (l)} + \text{CO}_2 \text{ (g)}
\]
\[ \Delta G_{298} = -20.7 \text{ kcal/mol} \]
The key to our studies involves the exploitation of the recently discovered insertion of CO into the M-O bonds of metal phenoxides, eq 2, and subsequent decarboxylation to afford CO$_2$ and a metal phenyl complex, eq 3, which can produce benzene by protonation or hydrogenation, eq 4 and 5.

\[
\begin{align*}
\text{M-O-} & \text{C-O-} \quad + \quad \text{CO} \quad \rightleftharpoons \quad \text{M-C-O-} \quad \text{(2)} \\
\text{O} & \quad \text{M-C-O-} \quad \rightleftharpoons \quad \text{M-} & \text{C-O-} & \text{M-phenyl} \quad + \quad \text{CO}_2 \quad \text{(3)} \\
\text{M-} & \text{C-phenyl} \quad + \quad \text{H}^+ \quad \rightleftharpoons \quad \text{M}^+ & \text{C-phenyl} \quad \text{(4)} \\
\text{M-phenyl} & \quad + \quad \text{H}_2 \quad \rightleftharpoons \quad \text{M-H} & \text{C-phenyl} \quad \text{(5)}
\end{align*}
\]

In contrast to hydrodeoxygenation of phenols, for which no obvious low energy pathways exist for C-O bond rupture, the thermodynamic driving force for CO$_2$ elimination, in eq 3, is high. Moreover, cooperative metal arene-π interactions or metal stabilized benzyne intermediates are likely to be important in facilitating the deoxygenation by CO$_2$ loss.

Our initial phases of research focus on identifying catalyst requirements essential for low temperature deoxygenation of phenols. These studies make use of soluble transition metal catalysts and phenols. These well defined systems are chosen because they are amenable to facile characterization by routine spectroscopic methods (IR, NMR, UV-Vis) at modest temperatures and pressures. The advantage of transition metal catalysts is that their study provides a richly detailed knowledge of fundamental chemical mechanisms for catalysis. Our ongoing studies focus on mono(aryloxide) potential catalysts of the class: Ir(triphos)(O-Ph), [Pt(triphos)(O-Ph)]$^+$ and Rh(triphos)(O-Ph).

\[
\text{P} \quad \text{P} \quad \text{M} \quad \text{O} \quad \text{P} \quad \text{P}
\]

M=Ir, Pt, and Rh
This provides a series of compounds which are expected to have the following order of reactivity toward CO insertion: \( \text{Rh(triphos)}(\text{O-Ph}) > \text{Ir(triphos)}(\text{O-Ph}) > [\text{Pt(triphos)}(\text{O-Ph})]^+ \).

**Recent Advances in Catalytic Deoxygenation of Phenols by CO.**

Given that HDO chemistry is currently not carried out separately of HDS and HDN, the use of carbon monoxide to affect the corresponding hydrodesulfuration and hydrodenitrogenation is being explored. With this in mind, we have broadened our platinum mediated chemistry to include model compounds for the hydrodenitrification and hydrodesulfurization of heteroatom containing arenes using carbon monoxide.

*Synthesis of \([\text{Pt(triphos)}(\text{NHPh})]\)[PF$_6$]:* To a benzonitrile solution of Pt(triphos)(Cl)][PF$_6$] (0.1543g, 0.1693 mmol) was added LiNH€'-h, freshly made from aniline (0.0631g, 0.6780 mmol) and butyllithium (.6781 mil). The solution quickly turned dark orange and the solution was stirred for 30 min. To the solution 7 volumes of anhydrous diethyl ether was added and then the solution was quickly filtered and cooled to -20 overnight. The yellow solid produced was collected and washed with anhydrous diethyl ether and the solid dryed overnight in vacuo.

$^{31}$P(1H) NMR (BzCN, 80.98 MHz, $\delta$, ppm): $A_2B_2X$, $(P_A) = 45.0$, $^1J(P_A-Pt) = 2648$ Hz; $(P_B) = 82.0$, $^1J(P_B-Pt) = 2564$ Hz, $^2J(P_A-P_B) < 1.5$ Hz.

![31P(1H) NMR spectrum of [Pt(triphos)(NHPh)][PF$_6$]](image.png)
Synthesis of \([Pt(triphos)(SPh)]PF_6\): To an acetonitrile solution of excess NaPF_6 and \([Pt(triphos)(Cl)]Cl\) (0.2573 g, 0.3214 mil) was added NaS-Ph (0.0437 g, 0.3384 mil) and the solution turned orange. The solution was filtered, and evaporated in vacuo. The solid was extracted into methylene chloride, precipitated with hexanes, filtered and the solid dried in vacuo. ¹H NMR (CD₂Cl₂, 200 MHz, δ ppm); 2.15 (m, 4H, P-CH₂), 2.3 - 2.7 (m, 4H, P-CH₂), 6.49 (t, 2H, m - CH), 6.62 (m, 1H, p - CH), 6.80 (d, 2H, o - CH), 7.2 - 8.0 (m, 25H, triphos phenyl). ³¹P(¹H) NMR (BzCN, 80.98 MHz, δ ppm): A₂BX, (P_A) = 43.6, ¹J(P_A-Pt) = 2601 Hz; (P_B) = 88.3, ¹J(P_B-Pt) = 2321 Hz, ²J(P_A-P_B) = 5.7 Hz. Anal. Calcd. for C₄₁H₃₉SF₆P₄Pt: C, 48.84; H, 3.89. Found: C, 48.57; H, 3.97.

Our current focus is on the reaction of these complexes with carbon monoxide and the isolation of any intermediates. Analysis of the product gases for carbon dioxide and solution for organic products will also take place.
References


