Conversion of Benzaldehyde into Benzyl benzoate from
the Reaction with Lithium Metal in Hexane

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Abstract: The reaction of benzaldehyde with lithium metal was studied in two solvents and several temperatures as a model for more complex processes. Conditions were achieved to favor the adsorption of reactant on the metal surface, as well as to slow down diffusion of the reactive species to solution: reaction within adsorbed species produces benzyl benzoate in high yield.

Catalysis by metal surfaces is a very well known phenomenon widely used in research and in industrial processes. The Fischer-Tropsch reaction is known to be catalyzed by group VIII metals and the mechanism/s, by which the reaction occurs is an area of active research, strong metal-surface interactions have been reported and alkali metals have been recently shown to be promoters in that reaction.

We have explored the synthetic usefulness of the carbonylation of organolithiums and studied the mechanism of reactions of phenyllithium with CO as a simple model for the likely reactions that could occur on the catalyst surface in the Fischer-Tropsch process. The methane activation to produce formaldehyde has been also shown to have mechanistic connections with that system.

We recently investigated the kinetics of the reactions that occur between benzaldehyde and lithium metal in THF, and results show that the complex reaction scheme shares a common intermediate with that of PhLi+CO. In the present work we describe the usefulness of a surface reaction of benzaldehyde with the lithium metal to produce benzoyl benzoate in good yield. The results illustrate how adsorption phenomena linked to solvent effects could be constructively used to lead the reaction toward the production of the ester. The benzaldehyde-ester disproportionation was previously reported to be catalyzed by boric acid (17% benzaldehyde conversion after 6 hs. at 250°C), and by some organo transition-metal complexes.

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TABLE 1. Reaction of benzaldehyde, 1, with lithium metal in THF.

<table>
<thead>
<tr>
<th>[1], M</th>
<th>[Li], mg</th>
<th>T, °C</th>
<th>% main products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.23a</td>
<td>812</td>
<td>37</td>
<td>15</td>
</tr>
<tr>
<td>0.22b</td>
<td>333</td>
<td>48</td>
<td>13</td>
</tr>
<tr>
<td>0.16a</td>
<td>708</td>
<td>52.5</td>
<td>3</td>
</tr>
<tr>
<td>0.23b</td>
<td>319</td>
<td>58</td>
<td>14</td>
</tr>
</tbody>
</table>

THF=30 mL, bTHF=20 mL.

In the reaction of 1 with lithium metal in THF solution, the main product is, as expected, the reduction product: benzyl alcohol, 2. Very small amounts of coupling products such as benzil, 3, and benzoin, 4, were also isolated (see Table 1), which among other evidence, indicate that electron transfer from the lithium to the benzaldehyde adsorbed on the metal surface occurs giving the benzoyl radical, 5. (see Scheme 1 below). Table 1 shows that for the reactions at low temperatures a substantial amount of unreacted 1 is recovered adsorbed on the metal surface; the kinetics of the reaction exhibit a sigmoid behavior typical of heterogeneous reactions where adsorption effects are present. At temperatures ≥ 48°C the reactions show reproducible kinetics and determination of all the partial rates involved in the complex reaction scheme was possible.

Likely reactive species on the metal surface/solution layer

Taking into account those results it was thought that conditions could be achieved to take advantage of the adsorption phenomena to lead the reaction toward the formation of other products as well as to confirm the involvement of surface effects. Reactions of related organolithium compounds were previously found to be highly sensitive to the features of the medium; since hexane is a non-basic, noncoordinating solvent, the electron transfer first step producing the radical anion-lithium cation pair, should slow down compared to THF, as had been observed for other related SET. Further reactions would also slow down, allowing the reactant and reactive intermediates to remain longer on the metal surface. Factors such as: low temperatures and poorly solvating media were examined to produce benzyl benzoate, 6. Two examples are gathered in Table 2 which show that the reaction of 1 with lithium in hexane at 20°C produces exclusively 6 in good yields if the reaction is allowed to finish. When the reaction was carried out at higher temperatures (not shown) shorter reaction times were observed, but the yields of 6 decrease significantly and 2-4 were also obtained, showing the influence of diffusion at those temperatures.
TABLE 2. Reaction of benzaldehyde, 1, with lithium metal in hexane at 20°C. a

<table>
<thead>
<tr>
<th>Reaction</th>
<th>time, days</th>
<th>Yields, mmol</th>
<th>Percentages of 1</th>
<th>%</th>
<th>% 1 recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[1]</td>
<td>[2]</td>
<td>[6]</td>
<td>conversion</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>5.25</td>
<td>0.03</td>
<td>0.855</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.90</td>
<td>0.03</td>
<td>3.44</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.075</td>
<td>0.03</td>
<td>4.47</td>
<td>99</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>3.60</td>
<td>-</td>
<td>0.015</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.15</td>
<td>-</td>
<td>0.16</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.99</td>
<td>0.01</td>
<td>0.83</td>
<td>46</td>
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<tr>
<td></td>
<td>8</td>
<td>0.03</td>
<td>0.03</td>
<td>1.6</td>
<td>89</td>
</tr>
</tbody>
</table>

a \( \text{Li} = 290 \text{mg}, \text{hexane} = 15 \text{mL}. \) b A: [1] = 0.60 M. Rate constant calculated after a lag period, \( t = 0.5 \text{ day} \), is \( (16.1 \pm 0.8) \text{ s}^{-1} \). B: [1] = 0.24 M. Rate constant calculated after a lag period, \( t = 2 \text{ days} \), is \( (9.7 \pm 0.8) \times 10^{-6} \text{ s}^{-1} \).

SCHEME

\[
\begin{align*}
\text{PhCHO} + \text{Li} & \rightarrow_k k_1 \text{PhCHO/Li} \\
\text{PhCHO/Li} & \rightarrow_k k_2 [(\text{PhCHO})^- \text{Li}^+] \\
\text{PhCHO/Li} + (\text{PhCHO})^- & \rightarrow_k k_3 [\text{PhCO}^- + \text{PhCH}_2\text{O}^-] \\
[\text{PhCH}_2\text{O}^- + \text{PhCO}^-] & \rightarrow_k k_4 (\text{PhCOOCH}_2\text{Ph})^- \\
(\text{PhCOOCH}_2\text{Ph})^- + \text{PhHCO} & \rightarrow_k k_5 \text{PhCOOCH}_2\text{Ph} + \text{PhHCO}^- \\
\end{align*}
\]

The observed results can be rationalized in terms of the reaction Scheme shown above. The first (and slow) step is adsorption of benzaldehyde on the lithium surface, (symbolized in the Scheme by PhCOH/Li, and overall rate \( k_I \)), which is responsible for the "lag" in the reaction time observed. Electron transfer, \( k_2 \), from the lithium to the adsorbed 1 produces the (radical anion, \( 7^- \)-lithium cation) pair. Then, 7 transfers a hydride (\( k_3 \)) to unreacted adsorbed 1 giving the benzoyl radical, 5, and the benzyl alcohol anion, 8, as determined in THF. Due to the properties of hexane, 5 and 8 are expected to remain longer in the solvent cage, allowing reaction within the cage (\( k_4 \)) before diffusion occurs. As a result, the benzyl benzoate radical anion, 9, is formed, which transfers an electron to unreacted 1, producing 6 and a fresh benzaldehyde radical anion. This reaction scheme explains not only the production of 6, but also the absence of detectable amounts of 3 and 4. Reaction within the
cage on the double layer at the surface metal, prevents the concentration of 5 required for the formation of benzil and other reactions to occur.

The kinetics of this reaction were followed as previously described for the reaction in THF. The simulated curves agreed satisfactorily with the experimental data. The formation of 5 was confirmed by trapping with CCl₄, the EPR spectra of the reaction mixtures under conditions of Table 1 were coincident with that of benzil radical anion independently prepared.

Masnovi and Maticic studied the inverse reaction, i.e. decomposition of the benzyl benzoate radical anion in hexane. Although the authors did not find appreciable amounts of benzoyl radical, examination of the reaction of benzoic anhydride showed that fragmentation occurs to afford benzoyl radical. Ashby recently proposed formation of the benzaldehyde radical anion, 7, as an intermediate in the Cannizzaro reaction.

The present results show the mechanistic link between this reaction and that of PhLi+CO, afford additional clues for the Fischer-Tropsch model, and provide an alternative route for the conversion of benzaldehyde into 6 in high yields, using a cheaper catalyst and milder reaction conditions than those reported before.

**Experimental**

Benzaldehyde and solvents were purified and made anhydrous as previously described. A Brucker EPR 200D(X band) TE102 cavity was used for recording the EPR spectra. Lithium wire (Merck, >99%, diam. 3 mm) was weighed under ligroin, washed with anhydrous hexane and cut into small pieces into the reaction flask containing a small portion of solvent, under a positive stream of dry argon, to avoid contact of lithium with the atmosphere. The flask was capped with a non-air stopper, and alternatively evacuated and flushed with nitrogen several times; reagents and solvents were transferred by syringes using techniques described for the manipulation of air-sensitive compounds. The reaction was followed by taking 0.2 mL aliquots of the reaction mixture at time intervals, quenching with 1 mL of acetic anhydride, and analyzed by GC, using benzophenone as internal standard. Runs were made at least in triplicate, the reproducibility was quite satisfactory. For preparative purposes, the reaction was allowed to finish, the reaction mixture filtered and distillation of the hexane under reduced pressure afforded pure benzylbenzoate.

**REFERENCES**


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