Diphenic Acid and 2-Phenylbenzoic Acid from Decarboxylation of Copper Phthalate

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Copper(I) phthalate when heated in quinoline above ca. 120° is decarboxylated giving mainly diphenic and 2-phenylbenzoic acids. Depending on the conditions varying amounts of benzoic acid, salicylic acid, phenyl benzoate, and biphenyl are also formed, though generally in smaller amounts.

Decarboxylation of copper(I) 2-nitrobenzoates in quinoline may give 2,2′-dinitrobiphenyls.1–4 In the presence of iodoarenes decarboxylative coupling to unsymmetric 2-nitrobiphenyls is the major reaction.1,2,4–6 An ortho nitro group accelerates copper-catalysed decarboxylation and also reactions of halogenobenzenes with organocopper compounds. This apparent paradox has analogies also for the carboxyl group. The facile decarboxylation of phthalic acid has been utilised for industrial production of benzoic acid.7 2-Iodobenzoic acid reacts very rapidly with copper acetylides and 2-bromo-phenzoic acids react readily with several nucleophiles in the copper-catalysed Hurtley reaction.5,9

We have studied the decarboxylation of copper(I) phthalate in quinoline at temperatures between 120 and 160°. The reactions were interrupted when one mol of carbon dioxide had been evolved per mol of phthalate.

The acids were converted to methyl esters and yields were determined after chromatographic separation or in some cases by gas chromatography.


Acta Chem. Scand. 27 (1973) No. 3
As shown in the scheme and in Table 1 formation of diphenic acid is a major reaction, which may be followed by further decarboxylation to 2-phenylbenzoic acid and eventually to biphenyl. The formation of biphenyl derivatives seems to be favoured by high concentration, at which formation of benzoic acid is less marked (at 120° and 0.8 M gross concentration the reaction mixture is heterogeneous). In most reactions metallic copper precipitated, indicating the stoichiometry of the reaction.

Table 1. Products (yields in per cent) from decarboxylation of copper(I) phthalate in quinoline. The reactions were interrupted after evolution of one mol of carbon dioxide per mol of phthalate. Products isolated, the acids as methyl esters (exceptions starred with yields determined by gas chromatography). Concentrations refer to initial approximate gross concentrations.

<table>
<thead>
<tr>
<th></th>
<th>120°</th>
<th>120°</th>
<th>130°</th>
<th>130°</th>
<th>160°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4 M</td>
<td>0.8 M</td>
<td>0.4 M</td>
<td>0.8 M</td>
<td>0.4 M</td>
</tr>
<tr>
<td></td>
<td>360 min</td>
<td>280 min</td>
<td>200 min</td>
<td>360 min</td>
<td>160 min</td>
</tr>
<tr>
<td>Diphenic acid</td>
<td>18</td>
<td>27</td>
<td>36</td>
<td>57</td>
<td>0</td>
</tr>
<tr>
<td>2-Phenylbenzoic acid</td>
<td>10</td>
<td>28</td>
<td>50</td>
<td>15</td>
<td>60*</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>27</td>
<td>21</td>
<td>5</td>
<td>8</td>
<td>14*</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>16</td>
<td>5</td>
<td>4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Biphenyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Phenyl benzoate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Unreacted phthalic acid</td>
<td>10</td>
<td>10</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>81</td>
<td>91</td>
<td>95</td>
<td>86</td>
<td>88</td>
</tr>
</tbody>
</table>

Decarboxylation of copper(I) diphenate was investigated separately (Table 2). The diphenate decarboxylates considerably slower than phthalate, but more rapidly than 2-phenylbenzoate. Thus, it seems possible to direct the reaction towards diphenic acid or to 2-phenylbenzoic acid.

The formation of salicylic acid from copper phthalate is surprising since the reactions were performed under nitrogen. When oxygen was bubbled through the reaction mixture (at 140–160°) the carbon dioxide evolution was slower than usual and less biphenyl derivatives were formed. After evolu-

Table 2. Decarboxylation of copper(I) diphenate, initial gross concentration ca. 0.4 M in quinoline. Reactions were interrupted after evolution of one mol of carbon dioxide per mol of diphenate. Product yields in per cent determined by gas chromatography of the methyl esters, the biphenyl determined on the neutral fraction.

<table>
<thead>
<tr>
<th></th>
<th>140°, 370 min</th>
<th>160°, 290 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Phenylbenzoic acid</td>
<td>40</td>
<td>80</td>
</tr>
<tr>
<td>Diphenic acid, unreacted</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>—</td>
<td>ca. 10</td>
</tr>
</tbody>
</table>

*Acta Chem. Scand. 27 (1973) No. 3*
tion of 0.25 mol of carbon dioxide per mol phthalate a 13 % yield of salicylic acid (based on copper phthalate) could be isolated.

Preliminary experiments on the decarboxylation of copper(I) 3- and 4-nitrophthalates have shown the formation of dinitrotriphenyl derivatives as well as formation of nitrosalicylic acids.

DISCUSSION

There are several indications that copper-promoted decarboxylation of aromatic acids proceeds via the copper(I) salts to give arylocopper compounds, which usually undergo further reactions \(^1\) \(\text{to}^4, \text{to}^6\) but under certain conditions may accumulate in the reaction mixture.\(^5, \text{to}^6\) For phthalic acid analogies are provided by the formation of stable organomercury compounds \((1)\) from mercury(II) phthalates,\(^1, \text{to}^2\) and by the formation of arylcobalt derivatives \((\text{e.g.} 2)\) from phthalic anhydride and octacarbonyldicobalt or tetracarbonyl-
obscobalt hydride.\(^3, \text{to}^4\)

\[
\begin{align*}
\text{Hg} & \quad \text{Co(CO)}_6 \quad \text{Cu} \\
\text{COOH} & \quad \text{COOCu}
\end{align*}
\]

It is tempting to assume an analogous organocopper intermediate \((\text{e.g.} 3)\) to account for the results of the present investigation. Such an intermediate could be expected to give copper(I) diphenate and metallic copper. Alternatively it could react with protons to give benzoic acid or be oxidised to salicylic acid. A similar intermediate is possible also in the reaction between 2-bromobenzoic acid and metallic copper which gives diphenic acid in aqueous alkaline solution.\(^9\)

The formation of benzoic acid and 2-phenylbenzoic acid in the aprotic medium indicates abstraction of protons from the solvent or other compounds present, and is analogous to but less marked than the formation of nitrobenzenes from copper(I) nitrobenzoates.\(^1\) \(\text{to}^5\)

The formation of salicylic acid during decarboxylation of copper(I) phthalate reminds of the copper-catalysed, “oxidative decarboxylation” of benzoic acid to phenol via salicylic acid derivatives,\(^1, \text{to}^4\) a reaction which forms the basis of the Dow phenol process.\(^1\) The mechanism is not well known. However, a rapid exchange of the \textit{ortho} hydrogens in copper(II) benzoate in heavy water has been observed.\(^1\) The latter reaction might be interpreted in terms of “cupration”, a reaction, which has been also suspected in the thiophene series.\(^1\) \(\text{to}^3\) \(\text{to}^9\) From these considerations it seems possible that the decarboxylation of copper(I) phthalates and the Dow process may have a common intermediate, possibly of the general type indicated in formula 3. If this were true several new transformations of both phthalic and benzoic acids would be possible.

\textit{Acta Chem. Scand.} 27 (1973) No. 3
The copper-promoted reactions of copper(I) phthalate should also be compared with thermal reactions of silver phthalates, which may give for example biphenylene, presumably via benzyne.21

The present results raise several new problems. The kinetics of phthalic acid decarboxylation is probably not quite analogous to that for 2-nitrobenzoic acid. The factors governing the formation of salicylic acids are not yet defined and should be investigated further. The interactions between the phthalic acids and the quinoline seem to be important and are now being investigated.

EXPERIMENTAL

_Copper(I)_ salts. Phthalic acid (0.2 mol) and copper(I) oxide (0.2 mol) were boiled in xylene (ca. 300 ml) for 20 h with continuous removal of water (3.4 ml) from the azoetropes. The yellow-grey _copper(I)_ phthalate was filtered off, washed with hot xylene and dried in vacuum; yield 80 %. For analysis the product was treated with nitric acid and titrated with EDTA at pH 7 to 8 against murexide. (Found: Cu 43.3. Calc. for C₂₃H₁₄O₄Cu: Cu 43.6.) Similarly diphenic acid and copper(I) oxide in boiling xylene gave _copper(I)_ d-phenate. (Found: Cu 34.2. Calc. for C₁₃H₁₂O₄Cu: Cu 34.6.)

_Decarboxylations._ The appropriate copper salt (generally 0.01 mol) was suspended in quinoline (25 ml, in some experiments 12.5 ml) in a three-necked flask equipped with a nitrogen inlet tube (ca. 8 ml nitrogen/sec), a powerful magnetic stirrer and a reflux condenser. The outlet gases were passed through a U-tube with activated charcoal and some magnesium perchlorate _via_ a three-way valve to U-tubes for carbon dioxide absorption (Ascarite and magnesium perchlorate). The reaction flask was immersed in a thermostated oil bath, a vigorous stirring maintained (important) and the carbon dioxide evolved was determined from the weight increase for the Ascarite tubes. When 0.01 mol of carbon dioxide had evolved the reaction mixtures were allowed to cool and diluted with ca. 200 ml ether. An excess 2 M hydrochloric acid was added to dissolve the quinoline and the mixture filtered. The solid phase was apparently mainly metallic copper. The ether phase of the filtrate was separated, washed with hydrochloric acid and with water and then extracted with sodium hydrogen carbonate solution. Acidic and neutral fractions were recovered in the usual way. The basic fraction, which was mainly quinoline, was not investigated. Alternatively, the reaction mixture was treated directly with aqueous alkali and acids recovered from solids and alkaline extract.

The acid fractions were screened by thin-layer chromatography on silica gel using ethanol:water:aqueous ammonia (25 %) (35:13:2 volumes) containing thymol blue (3 mg/100 ml).22 This system separated benzoic, salicylic, and diphenic acids, but 2-phenylbenzoic acid was not well separated from diphenic acid.

The acids were methylated with diazomethane in ether/methanol. The mixtures of methyl esters were investigated by gas chromatography (5 % SE 30 on Chromosorb W) or thin-layer chromatography (20 % toluene in light petroleum or 20 % toluene and 20 % di-isopropyl ether in light petroleum). Generally, the ester mixtures were separated on silica gel columns using similar solvent systems.

The isolated esters were identified by m.p., infrared spectra and sometimes mass spectra, or after hydrolysis as the acids. 2-Phenylbenzoic acid was also characterised by its conversion with sulphuric acid into fluorenone.

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REFERENCES


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Decarboxylation of Copper Phthalate


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