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# Air Oxidation of Aromatic Acids

**Here is an important portion of process development work which led to construction of the Dow plant at Kalama, Wash., for conversion of toluene to phenol**

Benzene is the principal raw material used for the commercial production of synthetic phenol by four different, well established processes. A number of years ago, it appeared that toluene would be available in very large quantities and would be a cheaper source of the aromatic ring than benzene itself. Utilization of toluene for the production of phenol was suggested, and this research was undertaken to discover a practical way of accomplishing this transformation.

The catalytic oxidation of toluene to benzoic acid with air, in the liquid phase, is well known (*14*, *17*). Early workers discovered that pyrolysis of the copper(II) salt of benzoic acid produced some phenyl benzoate (*3*, *10*, *15*). In similar experiments (*1*, *2*, *8*, *9*, *11*) performed more recently, the presence of salicylic acid and phenol, in addition to the ester, was noted.

When copper(II) benzoate was heated at 200° to 250° C. in a variety of solvents, such as water, benzene, toluene, nitrobenzene, diphenyl ether, Decalin, or benzoic acid, a reaction occurred without the production of large amounts of tar. Benzoic acid was an especially desirable solvent because its high boiling point permitted the reaction to proceed at atmospheric pressure, it had excellent solvent properties, and it provided a reservoir of benzoic acid for regeneration of the copper(II) salt with air. When both air and steam were bubbled into liquid benzoic acid at a temperature of 200° to 240° C. in the presence of dissolved copper(II) benzoate, phenol and $CO_2$ were the principal products of reaction.

The conversion of toluene to phenol could then be visualized as a two-step, air oxidation process consisting of an initial conversion to benzoic acid, followed by the transformation of the latter to phenol and $CO_2$ (*7*). A heavy metal catalyst system was perfected which made it possible to oxidize liquid toluene to benzoic acid with high rates and yields exceeding 90%. In a similar manner, liquid benzoic acid was converted to phenol with air utilizing a copper catalyst and a metal promoter with yields approaching 90%, in the laboratory. The only process chemical required is air, and the phenol is not contaminated with side reaction products.

## Experimental

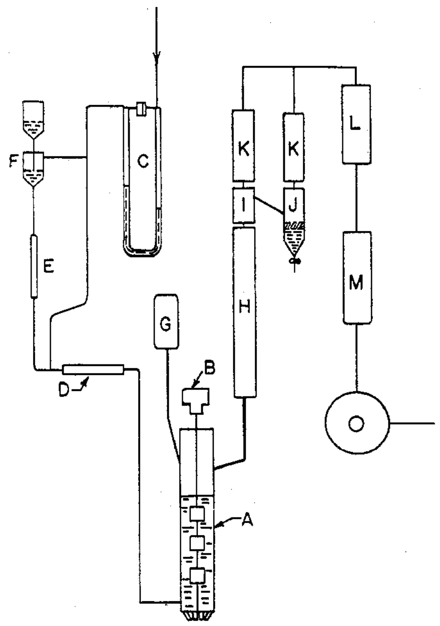
Early experiments were made with standard laboratory glassware. The assembly shown schematically below was gradually evolved over a period of time to accommodate the special requirements of this system. Most of the components were fabricated of borosilicate glass. The heated sections were wound with Nichrome resistance ribbon.

The reactor (*A*) was a borosilicate glass tube 2 by 17 inches with an operating volume of 250 ml. An air-steam mixture was introduced near the bottom of the reactor. Vigorous mechanical agitation ensured intimate contact between gas and liquid. The stirrer was powered with a small Gast air motor (*B*) at speeds of 2000 to 3000 r.p.m. The end of the stirring rod turned in a small graphite block carefully molded into the bottom of the reactor. Baffles were formed in the walls of the reactor to increase turbulence.

Air was metered to the system with an orifice flow meter (*C*). Liquid water was supplied to a heated metal tube (*D*) where it was evaporated and mixed with air. The flow rate of the water was measured with a rotameter (*E*) and regulated by the head of water in the supply vessel (*F*). The air-steam mixture leaving the evaporator was held at a temperature in excess of 250° C. Make-up benzoic acid was added through an opening in the top of the reactor from a heated vessel (*G*). The various components were connected with ball-joint fittings.

The vapors from the reactor were fed to the bottom of a 1-inch, 16-tray glass Oldershaw column (*H*). A vapor take-off head (*I*) was used. The reflux ratio was controlled by a General Electric time switch which actuated a solenoid valve. The column and accessories were obtained as stock items from Glass Engineering Corp. Thermowells were located at each tray of the column and at all other parts of the system which required external heat. Temperatures were measured with a Leeds and Northrup Speedomax recorder. Selector switches made it possible to record temperatures continuously for any 16 points in the system.

A two-phase liquid consisting primarily of phenol and water was collected in the product receiver (*J*). Water condensers (*K*) were used to supply reflux to the column and to condense the take-off vapors. The noncondensable gases passed through ice, dry ice, and $CaCl_2$ traps (*L*) to remove traces of water, phenol, and benzene. Carbon dioxide formed during the re-



**Laboratory assembly used to study production of phenol from toluene via benzoic acid accommodates special requirements of the system**

A. Reactor
B. Agitator motor
C. Air inlet flowmeter
D. Steam generator
E. Liquid water flowmeter
F. Water reservoir
G. Benzoic acid make-up reservoir
H. Column
I. Take-off head
J. Product receiver
K. Water condensers
L. Dry ice condensers
M. $CO_2$ trap
O. Wet test meter

action could then be absorbed and weighed directly with Ascarite (*M*). The total volume of effluent gas was measured with a wet test meter (*O*).

**Operating Procedure.** Run M-31 illustrates the method used. Two hundred and fifty grams of solid benzoic acid was mixed with 13.6 grams of MgO and enough basic $CuCO_3$ to provide 0.069 moles of copper(II) benzoate. The acid was melted in a beaker and slowly heated to 210° C. During this time, water and $CO_2$ vapors were evolved as magnesium and copper(II) benzoates were formed. The electrical heating circuits were turned on, the molten solution was poured into the reactor, and the mechanical stirrer was started. The air was turned on at a very low rate to prevent liquid from backing up in the system.

When the desired temperature was reached (230° C.), the air and water were turned on at a rate of 0.5 liter per minute and 1.0 gram per minute, respectively. At this point, the tendency for benzoic acid to sublime was aggravated to the extreme by large volumes of air and steam bubbling through the molten acid at a temperature near its boiling point. Acid would frequently solidify and plug the upper part of the system. When this happened, the air and steam inlet rate was immediately reduced to prevent a pressure increase in the reactor. When a few grams of phenol were present, a low melting mixture was formed which did not solidify in the condenser and this problem was eliminated.

After 30 to 60 minutes, enough phenol was produced for the column inventory. At this point, benzoic acid was confined to the bottom half of the column, and the take-off mechanism was actuated. Temperatures at the various plates (for a reactor temperature of 230° C.) were as follows: bottom, 225° C.; middle, 160° to 180° C.; top, 105° to 125° C. Equilibrium for the particular set of conditions imposed on the system was maintained by adjusting the take-off rate to maintain a temperature of 160° to 180° C. at the middle tray. The liquid level in the reactor was maintained by frequent additions of molten benzoic acid.

All parts of the system where elevated temperatures were required were either directly wound with Nichrome resistance ribbon or were inserted in glass sleeves heated in this manner. The reactor, evaporator, column, acid melter, and various connecting lines were wound as individual circuits to permit the necessary flexibility needed for temperature control.

**Oxidation of *p*-Toluic Acid.** The reactor was charged with 200 grams of *p*-toluic acid (melting point = 178.5° to 180° C.), 14 grams of copper(II) *p*-toluate, and 5 grams of MgO. The reactor temperature was maintained at 250° C., the air rate was 0.5 liter per minute, and the water rate was 1 gram per minute. The run time was 2 hours. A total of 20.6 grams of $CO_2$ was produced and 33.4 grams of cresol was distilled from the reactor. The cresol was pure *meta* isomer, as determined by infrared analysis.

**Oxidation of *m*-Toluic Acid.** The reactor was charged with 200 grams of *m*-toluic acid (melting point = 109° to 112° C.), 20 grams of copper(II) *m*-toluate, and 6.4 grams of MgO. The air rate was 1 liter per minute, the water rate was 1.5 grams per minute, and the run time was 1.5 hours. Twenty five grams of $CO_2$ and 40 grams of cresol were distilled overhead. The ratio of cresol isomers was determined by infrared analysis and was approximately as follows: *ortho* = 40%, *para* = 60%.

**Oxidation of *o*-Toluic Acid.** The reactor was charged with 250 grams of *o*-toluic acid (melting point = 103° to 105° C.), 0.33 mole of Cu, added as basic $CuCO_3$, and 0.47 mole of MgO. The temperature of reaction was 200° C., the air rate was 1 liter per minute, the water rate was 1.3 grams per minute, and the pressure was 485 mm. of mercury. Reduced pressure was needed to distill the cresol out of the reaction mixture at the relatively low temperature of reaction. A Gast high-volume vacuum pump was used. The run time was 8.5 hours. A total of 220 grams of make-up *o*-toluic acid was added during this period. The weight of cresol distilled overhead was 98 grams. It was found to be the pure *meta* isomer by infrared analysis.

**Analytical Procedure for Benzoic Acid Runs.** CARBON DIOXIDE. The $CO_2$ was absorbed with Ascarite and weighed directly. Moisture and traces of organic vapors were removed from the spent gas stream by means of ice, dry ice, and $CaCl_2$ traps.

PRODUCTS DISTILLED. The distilled material was composed primarily of water and phenol. A single, homogeneous liquid phase could be obtained by heating to temperatures above 75° C., where phenol and water are miscible in all proportions. A sample was withdrawn, accurately weighed, and titrated for phenol by the well known bromination method (*13*).

A small amount of benzoic acid was also present with the phenol. A weighed sample of the homogeneous phase was extracted with ether to remove the organic components. The ether phase was then extracted with saturated, aqueous $NaHCO_3$ solution to remove the benzoic acid selectively. The latter was recovered by acidification and extraction with ether. After evaporation of the ether, the acid was weighed directly. As a check, a sample of the acid was titrated with standard base.

REACTOR LIQUID. An accurately weighed sample (50 grams) of the reactor liquid (which usually was a hard solid at room temperature) was pulverized and mixed with 300 ml. of ether in a separatory funnel. The slurry was extracted with 50 to 75 ml. of 5% HCl. This treatment decomposed the metal benzoates present and transferred the metal catalysts to the aqueous phase for subsequent analysis by standard procedures.

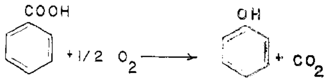
A certain amount of dark, insoluble material (labeled "tar") was present which usually collected at the interface between the ether and water phases. The tar was removed by filtration through a weighed, sintered glass funnel, and its weight was determined after drying overnight in a vacuum desiccator over $P_2O_5$.

The ether phase was diluted to 500 ml. A 100-ml. aliquot was extracted with two portions of aqueous bicarbonate to remove the benzoic acid. The combined bicarbonate extracts were agitated with fresh ether, separated, and the acid precipitated by acidification. The acid liberated was extracted with ether, dried, separated from the solvent by evaporation of the latter, and weighed directly.

In a similar manner, the combined ether phases from above were extracted with two portions of 5% NaOH to remove the phenol fraction which was also weighed directly. Evaporation of the remaining ether phase, after the removal of acid and phenols, gave the amount of neutral material which was also weighed directly. The results for run M-31 were as follows: benzoic acid = 73.4%, phenols = 5.5%, neutral = 9.3%, Cu = 1.3%, Mg = 1.3%, tar = 9.2%.

## Results and Discussion

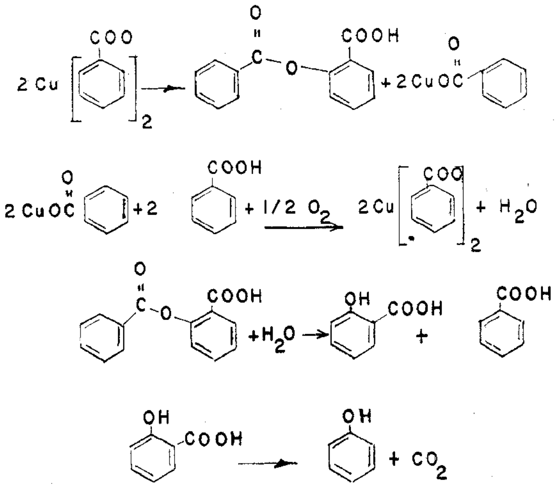
The oxidation of benzoic acid to phenol and $CO_2$, in the presence of copper(II) benzoate and steam, may be summarized by Equation 1. This



(1)

is the net result of a number of reactions which occur simultaneously in the system at equilibrium. These reactions are: thermal decomposition of copper(II) benzoate (Equation 2), regeneration of copper(II) benzoate (Equation 3), hydrolysis of benzoylsalicylic acid (Equation 4), and decarboxylation of salicylic acid (Equation 5).

**Thermal Decomposition.** When a solution of copper(II) benzoate and benzoic acid was heated in the absence of steam and oxygen at 230° C., the characteristic blue-green color initially present soon disappeared. On cooling,



a white solid was formed. This was pulverized and treated with ether to dissolve the benzoic acid. Insoluble white crystals remained on the filter which were identified as copper(I) benzoate by analysis. The latter accounted for all of the copper initially present. An equivalent amount of $CO_2$ was evolved during the heating cycle. It was removed from the system by a slow stream of nitrogen and absorbed with Ascarite. Phenyl benzoate and a trace of phenol were recovered from the ether solution used to isolate the copper(I) salt.

When copper(II) benzoate was heated in various other organic solvents, a color change and $CO_2$ liberation occurred in a manner similar to the benzoic acid system. With toluene, for example, copper(I) benzoate was deposited as large white crystals when the glass bomb was gradually cooled to room temperature, in virtually quantitative yield. Phenyl benzoate and benzoic acid were the principal organic products isolated in the absence of water.

**Regeneration.** As indicated above, copper(II) benzoate decomposed to copper(I) benzoate, benzoylsalicylic acid, and $CO_2$ when heated in molten benzoic acid in the absence of air and steam. When air was bubbled through this solution at 180° C. [where decomposition of copper(II) benzoate does not normally take place], a green color formed immediately and darkened in intensity, in direct proportion to the volume of air added. An amount of water equivalent to the copper oxidized was evolved when enough air was bubbled through the liquid. The colorless, copper(I) benzoate was oxidized with air and benzoic acid to the copper(II) form as shown in Equation 3.

By raising the temperature above 200° C., with the air turned off, the decomposition step could be repeated as described above. A substantial amount of the benzoic acid solvent could be converted to products by repeating the oxidation and regeneration steps in this manner.

**Hydrolysis and Decarboxylation.** These two steps are intimately related and must be considered together. Decomposition of the benzoylsalicylic acid intermediate to phenol and $CO_2$ may proceed by two different paths. First, hydrolysis precedes decarboxylation to give a salicylic acid intermediate as shown by Equations 4 and 5. The other sequence would involve decarboxylation, followed by hydrolysis with phenyl benzoate as the intermediate. Salicylic acid could be detected in the reaction mixture in low concentrations. This would be consistent with the first mechanism. Independent experiments have shown that salicylic acid decarboxylates very rapidly (half life measured in seconds at 230° C.) under the conditions of reaction being considered here at a rate faster than that at which benzoylsalicycli c acid decarboxylates in an identical medium.

The presence of this intermediate

## Results for Conversion of Benzoic Acid to Phenol

**Phenol yields above 80% were indicated**

| Run No. | Materials Added, Moles | | | Promoter | | Run Time, Hr. | Temp., ° C. | Av. Air Rate, Liter/Min. | Av. $H_2O$ Rate, Gram/Min. | Recovered, Moles | | | | | | | | PhOH Yield,[d] % | Material Balance[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | BzOH[a] | $O_2$[b] | Cu | Type | Moles | | | | | PhOH | $CO_2$ | Neutral material[c] | BzOH | Cu | Promoter | Tar, grams | $C_6H_6$ | | |
| M-15 | 2.67 | 0.63 | 0.069 | ... | ... | 6.5 | 238 | 1.0 | 1.15 | 1.03 | 1.36 | 0.034 | 1.18 | 0.061 | ... | 25 | ...[f] | 73 | 352/337 |
| M-16 | 2.92 | 1.05 | 0.057 | Co | 0.010 | 6.1 | 238 | 1.0 | 1.28 | 1.59 | 2.09 | 0.167 | 0.63 | 0.050 | ... | 44 | ...[f] | 83 | 393/398 |
| M-17 | 2.24 | 0.37 | 0.057 | ... | ... | 5.2 | 239 | 0.5 | 1.10 | 0.66 | 0.73 | 0.073 | 1.36 | 0.053 | ... | 7 | ...[f] | 90 | 290/286 |
| M-18 | 2.22 | 0.49 | 0.069 | ... | ... | 6.2 | 237 | 0.5 | 1.15 | 0.86 | 0.98 | 0.076 | 1.02 | 0.053 | ... | 14 | ...[f] | 84 | 291/282 |
| M-22 | 2.47 | 0.56 | 0.056 | Na | 0.256 | 5.8 | 239 | 0.33 | 1.12 | 0.95 | 1.15 | 0.021 | 1.22 | 0.048 | 0.25 | 14 | 0.077 | 79 | 330/323 |
| M-26[g] | 5.10 | 1.71 | 0.079 | K | 0.388 | 19.8 | 230 | 0.33 | 1.23 | 2.54 | 3.42 | 0.059 | 1.64 | 0.078 | 0.38 | 28 | 0.40 | 77 | 697/671 |
| M-27 | 2.32 | 0.47 | 0.057 | Mg | 0.198 | 5.8 | 235 | 0.33 | 1.17 | 0.87 | 0.94 | 0.026 | 1.28 | 0.054 | 0.19 | 3 | 0.038 | 89 | 311/301 |
| M-31[g] | 6.86 | 2.63 | 0.069 | Mg | 0.34 | 29 | 231 | 0.5 | 1.08 | 4.45 | 5.26 | 0.57 | 1.27 | 0.059 | 0.27 | 58 | 0.051 | 100 | 936/990 |
| M-32 | 2.65 | 0.64 | 0.057 | Ba | 0.19 | 6.5 | 231 | 0.5 | 1.08 | 1.09 | 1.27 | 0.031 | 1.28 | 0.059 | 0.18 | 6 | 0.025 | 84 | 373/356 |

[a] Total BzOH added to the system including the initial charge, make-up, and acid combined with the catalyst. [b] Calculated from $CO_2$ value assuming $O_2 = 2CO_2$. [c] Primarily PhCOOPh with some PhOPh. For ease of calculation, all of former assumed. [d] For yield calculation, all neutral material assumed recoverable as BzOH and PhOH. [e] Grams in/grams out. [f] Not measured. [g] Three 8-hour day runs with two shutdowns.

benzoylsalicylic acid was first indicated during the course of preliminary kinetic studies. The rate of $CO_2$ evolution went through a maximum value, in a manner typical of that for a series of reactions of the type proposed in Equation 3 followed by Equations 4 and 5. A run was made in which the reaction was quenched at the time when the maximum concentration of benzoylsalicylic acid was calculated. The presence of this material was confirmed with a high resolution infrared spectrophotometer.

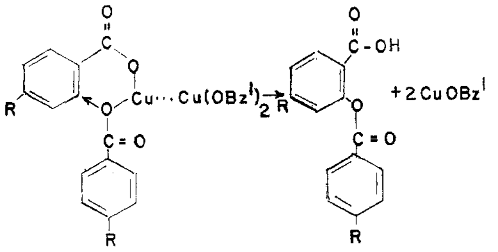
The over-all rate of $CO_2$ evolution from benzoylsalicylic acid, in molten benzoic acid, was substantially increased when steam was bubbled through the solution. This strongly suggested that the first path was making a substantial contribution when steam was added.

When the reaction was run in the absence of steam, a hydrolysis step was not possible. The amount of water produced by the reoxidation of copper(I) benzoate, Equation 3, was trivial. In this case, only decarboxylation of benzoylsalicylic acid could occur with the accumulation of the ester in the reaction medium (*16*). The presence of added steam appears to have an important effect on the system not only by producing phenol, rather than phenyl benzoate, as a product, but also in the actual mechanism of benzoylsalicylic acid decomposition. Perhaps a more quantitative interpretation will be possible when kinetic studies now in progress are completed.

The results of some runs are given in the table (p. 807). Most of these runs were of relatively short duration. The reactor liquid which remained at the end of the run represented a rather large proportion of the whole. This liquid was a relatively complex mixture, and any analytical errors could influence the final results. With runs M-26 and M-31, however, errors of this type became increasingly less significant. Phenol yields in excess of 80%, therefore, were quite realistic.

A number of other metal benzoate salts were used in conjunction with benzoic acid. A small amount of cobalt accelerated the rate of reaction approximately 65% (compare M-15 and M-16). However, tar formation was increased substantially. When sodium and potassium benzoates were added, the principal effect appeared to be an increase in the decarboxylation rate of benzoic acid. Substantial amounts of benzene were recovered. When magnesium benzoate was added, tar formation was repressed considerably. The initial blue-green color persisted for a relatively long period of time. The mode of action of the magnesium salt has not yet been determined.

A number of other metal benzoates were tested in this equipment in the absence of copper. These included iron, nickel, cobalt, mercury, and lead. Other metal benzoates tested in sealed glass bombs with benzoic acid were: potassium, cadmium, zinc, manganese, tin, aluminum, chromium, silver, indium, vanadium, zirconium, and uranium. Phenol was not produced in detectable amounts under conditions of reaction similar to those reported in the table (p. 807).



(6)

$Bz' = pRC_6H_4COO$

The molar yield of $CO_2$ was always slightly larger than that of phenol, even when phenol equivalents such as phenyl benzoate and benzene were included. This excess appears to correspond to phenol produced and further transformed to tar.

All three of the toluic acid isomers were oxidized in a manner similar to that used for benzoic acid. Slightly higher temperatures facilitated the distillation of the higher boiling cresols, except with *o*-toluic acid. Decomposition of the copper(II) salt of the latter took place rapidly at 200° C., and operation at reduced pressure permitted distillation of the cresol formed. Lower temperatures in the reactor reduced the rate of tar formation, which in general was noticeably higher than with benzoic acid.

Analysis of the cresol fraction revealed that the hydroxyl group did not become attached to the ring at the same carbon atom which held the departing carboxyl group: *m*-Cresol was the exclusive phenolic product produced from both *o*- and *p*-toluic acids. On the other hand, *m*-toluic acid gave a mixture of both *o*- and *p*-cresol. This orientation of products can best be explained by assuming that the hydroxyl group entered the ring at a position adjacent to the carboxyl group of the acid. This same orientation rule applies to a number of other aromatic carboxylic acids (*12*).

A cyclic intermediate, Equation 6, has been proposed to account for the steric course of the reaction. Copper(II) benzoate is shown as a dimer with the two copper atoms close to each other. This arrangement has been verified for copper(II) acetate (*4–6*), and there is evidence that the dimeric structure is preserved in solution (*5*).

If this condition applies to copper(II) benzoate in benzoic acid solution, the concerted reduction of a pair of copper(II) ions to the copper(I) form would provide the two electrons required for the oxidation of benzoic acid. Kinetic studies now in progress have indicated that this reaction is second order with respect to the concentrations of copper(II) benzoate. The location of the R-group in the *para* position illustrates how a *meta*- substituted phenol could be obtained by subsequent hydrolysis and decarboxylation, as shown in Equations 4 and 5. The products obtained from *ortho*- and *meta*-substituted starting benzoic acids are also consistent with this mechanism.

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