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Oxidation of Benzoic Acid to Phenol in the Vapor Phase

I. Mechanistic Aspects

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The vapor-phase oxidation of benzoic acid to phenol over copper catalyst supported on alumina has similar features to those described for the homogeneous system. The mechanism of reaction involves cupric benzoate as the principal intermediate and the rate of its formation on the catalyst surface is the rate-determining step. Molecular oxygen reoxidizes the reduced copper species of catalyst. No oxidation of phenol occurs on the catalyst in an inert atmosphere. The oxidation of benzoic acid in the presence of optimal concentration of oxygen and water follows a first-order rate equation with the rate constant $k = 0.124 \pm 0.014$ hr^{-1} at 285°C and the apparent activation energy 63.0 ± 4.5 kJ mol^{-1}.

INTRODUCTION

In the conventional Dow process (*1*) for the manufacture of phenol, benzoic acid is oxidized in the liquid phase at 200–250°C. The most active catalyst for this reaction is copper with various promoters in the form of soluble salts. Air and steam are sparged into the melt to produce phenol which is simultaneously stripped from the system. In an effort to reduce the formation of tar products and catalyst regeneration problems in this process a vapor-phase oxidation of benzoic acid has been pursued (*2*). In the first patents (*3, 4*) dealing with this problem, the selectivity of phenol production was very low. Recently, further patents of Lummus (*5*), Mitsubishi (*6, 7*), Sumitomo (*8–10*), and Stamicarbon (*11*) have been issued on the vapor-phase oxidation of benzoic acid to phenol. The most efficient catalyst for this reaction is copper promoted with various metals supported on carriers, e.g., alumina, kieselguhr, diatomaceous earth. On these catalysts the selectivity to phenol approaches 70–90 mol% at approximately 50 mol% per pass conversion of benzoic acid and it is reached at a very high space velocity. In this process the tars and nonvolatile residues which are generated in the liquid-phase process are not produced. However, information about the effect of operating conditions, catalyst aging, kinetics, and mechanism of the vapor-phase oxidation of benzoic acid to phenol are not available. The major goals of this paper are to obtain data about selectivity, catalyst aging, and mechanism of this oxidation process.

EXPERIMENTAL

Materials. Benzene, benzoic acid (BzOH), diphenyloxide (DPO), diphenyl (DP), and phenol (PhOH) were of analytical grade purity. Methylbenzoate and methyl-*p*-toluate were commercial products (>99% purity). Cupric benzoate was prepared from sodium benzoate and $CuSO_4$, according to Ref. (*12*).

Catalysts. The $Cu–Al_2O_3$ catalyst (10 wt% CuO) was prepared by impregnation of known particle size alumina (surface area 116 m^2 g^{-1} specific pore volume 0.264 cm^3 g^{-1}, mean diameter of pores 4.5 nm) with 0.77 *M* aqueous solution of $Cu(NO_3)_2$ for 24 hr. After evaporation of water the catalyst was dried at 100°C and calcined at 750°C for 2 hr in air. Some part of this cata-

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lyst was impregnated (24 hr) with 1.34 *M* aqueous solution of KOH and after evaporation, dried, and finally calcined at 500°C for 11 hr (designated as Cu–K–Al_2O_3 containing 10 wt% K_2O, surface area 58 m^2 g^{-1}). The Cu(II) benzoate (10 wt%) supported on alumina (BzCu–Al_2O_3) was prepared by impregnation for 24 hr of alumina (1.0–1.6 mm; 116 m^2 g^{-1}) with copper benzoate in pyridine solution. After evaporation of pyridine under vacuum, the catalyst was dried at 150°C for 1 and 2 hr at 200°C. Catalyst Cu–Py–Al_2O_3 was prepared by washing Cu–Al_2O_3 catalyst with excess of pyridine and further treated in the same way as BzCu–Al_2O_3 catalyst. The catalyst CuPc–Al_2O_3 (CuPc 10 wt%) was prepared by impregnation (24 hr) of the above described alumina with a pyridine solution of copper phthalocyanine and further treated as for BzCu–Al_2O_3 catalyst.

Apparatus and procedure. Oxidation reactions were carried out at atmospheric pressure by a conventional flow method. The fixed bed reactor was made of Pyrex tubing 2.3 cm in i.d. and 55 cm in length and was placed in a vertical furnace. A thermocouple was used for the measurement of the temperature of the catalyst bed at various locations, usually in the middle of the catalyst bed. Water, benzene solution of benzoic acid (1–5 wt%), and air or oxygen were injected directly into the reactor and vaporized in a preheating chamber. Prior to the reaction, 45–47 g of the catalyst was heated to desired temperature in an air flow. Each run under steady-state conditions lasted 4–7 hr and the composition of the outlet stream was analyzed every 30 min.

The organic products, unreacted benzoic acid, benzene, and water were collected in a cooled trap and the benzene-aqueous mixture was analyzed at 30-min intervals. The gaseous products were analyzed for oxygen and carbon dioxide by gas chromatography with thermal conductivity detectors using two 80-cm columns packed with 5A molecular sieve (40–60 mesh) and Porapack Q (60–80 mesh) operating at 70°C with hydrogen as carrier gas. The main oxidation products, phenol, diphenyloxide, diphenyl, and unreacted benzoic acid were analyzed in benzene phase using a Packard 430 gas chromatograph with flame ionization detectors. Glass columns (0.3 × 120 cm) packed with 10% Apiezon L + 2% H_3PO_4 on Chromosorb W (80–120 mesh) were programmed from 150 to 240°C at 10°C min^{-1}. The composition of the products was confirmed by Varian MATT 111 mass spectroscopy. The content of products in the aqueous phase was determined on the basis of experimentally estimated distribution coefficients of these compounds and in some samples by gas chromatography. The formation of quinone compounds was determined by iodometric titration after evaporation of benzene from the samples.

The conversion of benzoic acid, the yields of reaction products, and the selectivity of phenol formation were defined as follows:

$$\text{conversion } (\%) = \frac{\text{moles of BzOH reacted}}{\text{moles of BzOH fed}} \times 100$$

$$\text{yield } (\%) = \frac{\text{moles of PhOH produced}}{\text{moles of BzOH fed}} \times 100$$

$$\text{selectivity } (\%) = \frac{\text{moles of PhOH produced}}{\text{moles of BzOH reacted}} \times 100.$$

The time factor is defined as the ratio W/F_X, where W is the weight of catalyst and F_X is the weight feed rate of component X.

Infrared spectra. After several hours of runs and rapid cooling in an inert atmosphere the catalysts were analyzed by IR spectroscopy (Specord IR 71, Zeiss Jena, GDR) using the KBr technique. Some catalysts were also extracted with pyridine and after evaporation of pyridine, the solid product was analyzed by IR, X-ray, and atomic absorption spectroscopy.

X-Ray analysis. The X-ray diffraction data of fresh and used catalysts or their solid pyridine extracts were obtained using a conventional spectrometer with Cu$K\alpha$ radiation at 36 kV and 16 mA.

RESULTS

Kinetics

Preliminary measurements were designed to find the effect of operating conditions on the selectivity and lifetime of catalysts for the vapor phase oxidation of benzoic acid to phenol. The measurement of the temperature profile in the catalyst bed at 1–5% concentration of BzOH in the feed showed practically isothermal conditions even at high conversion. Since the selectivity of reaction shows a quite marked dependence on particle size (Fig. 1) all kinetic runs were carried out with particles not exceeding 1.8 mm in diameter. Furthermore, experimental measurements were performed at mass velocities which were sufficient to eliminate interparticle transport phenomena (determined at the maximum concentration of benzoic acid in the feed and constant time factor). Under these conditions results obtained with Cu–K–Al_2O_3 catalyst (Fig. 2) are only negligibly influenced by external diffusion.

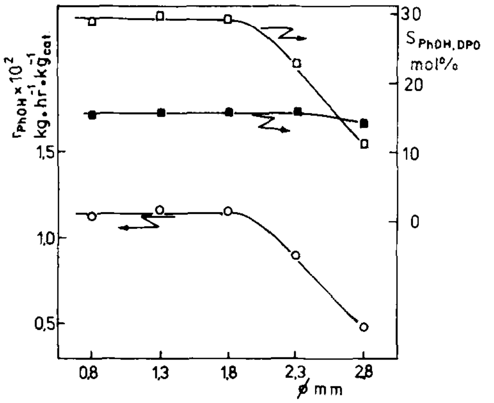


FIG. 1. Dependence of the rate of phenol formation (○) and selectivity to PhOH (□) and diphenyl + diphenyloxide (■) on the average particle size of catalyst. Conditions: reaction temperature 285°C, catalyst Cu–K–Al_2O_3, feed rate of benzene 1.1 kg hr^{-1} kg$_{cat}^{-1}$, H_2O = 0.5 kg hr^{-1} kg$_{cat}^{-1}$, O_2 = 33.4 liters hr^{-1} kg$_{cat}^{-1}$.

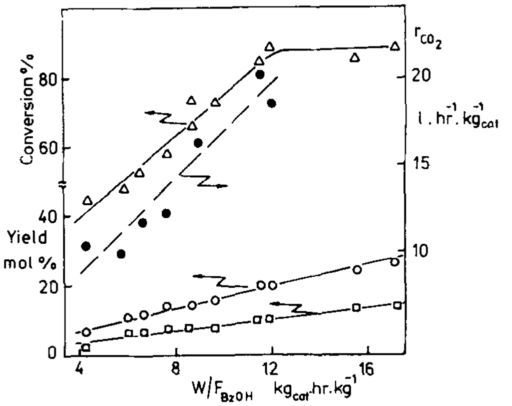


FIG. 2. Benzoic acid conversion (△), phenol (○), and diphenyl + diphenyloxide (□) yield and the rate of CO_2 formation (⊗) as a function of feed rate of benzoic acid. Conditions as in Fig. 1.

Effect of reaction temperature. The temperature dependence of the reaction over Cu–K–Al_2O_3 catalyst determined at the steady state of BzOH conversion provided sufficiently accurate data to allow an Arrhenius plot to be made for the rate of benzoic acid consumption (Fig. 3). The apparent activation energy corresponding to Fig. 3 is 63.0 ± 4.5 kJ mol^{-1}.

Effect of water concentration. The activity and selectivity of the catalyst is strongly influenced by the presence of water vapor in the reactant stream. In the absence of water, the conversion of BzOH within a few minutes of reaction at 285°C is almost total but the yield of PhOH decreases dur-

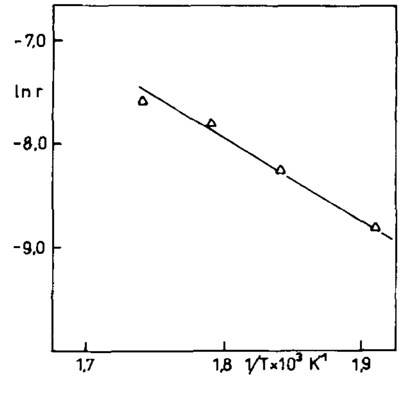


FIG. 3. Effect of temperature on the rate of oxidation.

ing the first 2 hr from 10.0 to 2.0%. Under these conditions the course of reaction is not stable and after 2 hr of reaction the BzOH conversion rapidly decreases, e.g., in 10 hr to 45%. The presence of water increases the selectivity of phenol formation and the lifetime of the catalyst (more than 10 hr). In the concentration region corresponding to molar ratios H_2O : BzOH from 40 : 1 to 80 : 1, the reaction rate and selectivity is independent of H_2O concentration (Fig. 4). A higher amount of water in the feed retards the oxidation process.

Effect of oxygen concentration. The dependence of benzoic acid oxidation on the concentration of molecular oxygen has three stages (Fig. 5). The reaction of BzOH on Cu–K–Al_2O_3 catalyst at 285°C in the absence of molecular oxygen is characterized by its almost total conversion in the first 1 to 2 hr period, followed by rapid catalyst deactivation. Thus, after 6.5 hr of reaction, the conversion of BzOH decreases to 53% and the yield of phenol formation from 6.5 mol% in the first hour to 2.0 mol%. In the concentration region corresponding to molar ratios of O_2 : BzOH from 2 : 1 to 4 : 1, the reaction rate is independent of oxygen concentration and the activity and selectivity of the catalyst are stationary during more than 15 hr of operation. At a higher excess of oxygen, the rate of carbon dioxide formation increases, the production of PhOH is very low and decarboxylation of BzOH to benzene and CO_2 proceeds preferentially.

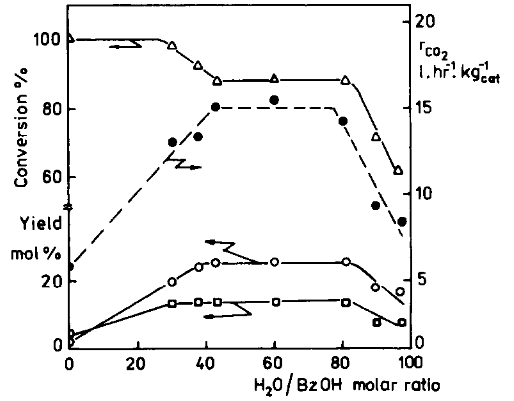


FIG. 4. Effect of molar ratio of H_2O/BzOH in the feed to the reactor on the conversion of BzOH and formation of reaction products. Conditions and curves as in Fig. 2. The data were obtained under stationary conditions, except for the run in the absence of water (in the second hour).

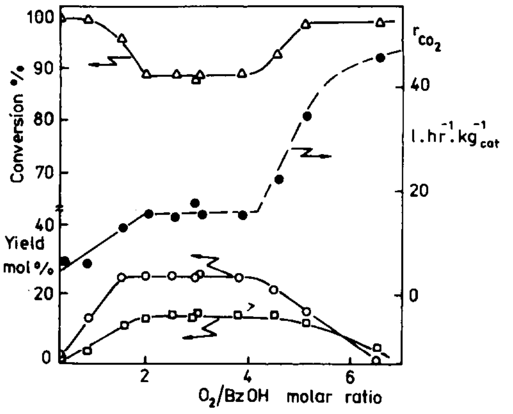


FIG. 5. Dependence as in Fig. 4, but vs molar ratio of O_2/BzOH. The data in the absence of oxygen are for the second hour of reaction.

Lifetime and regeneration of catalyst. Dependent on experimental conditions the steady-state activity of Cu–K–Al_2O_3 catalyst after several hours (20–75) of operation slowly decreases. X-Ray analysis of particles taken from the catalyst bed at different locations along its length shows that catalyst aging is caused by the reduction of active CuO to Cu_2O or, in the top layer of the catalyst bed, even to metallic copper. It was found that the catalyst can be regenerated at a temperature of about 300°C in the presence of molecular oxygen (during 1–2 hr) which reoxidizes copper species to CuO. However, after each regeneration cycle, a certain period (ca. 2–5 hr) is needed for reaching the steady-state activity of catalyst (Fig. 6). In the first stage of every period almost all BzOH is converted (it is absent in the output) and the formation of reaction products continually rises.

DISCUSSION

Reaction Mechanism

The activity–selectivity properties of the cupric oxide catalyst in the vapor–phase

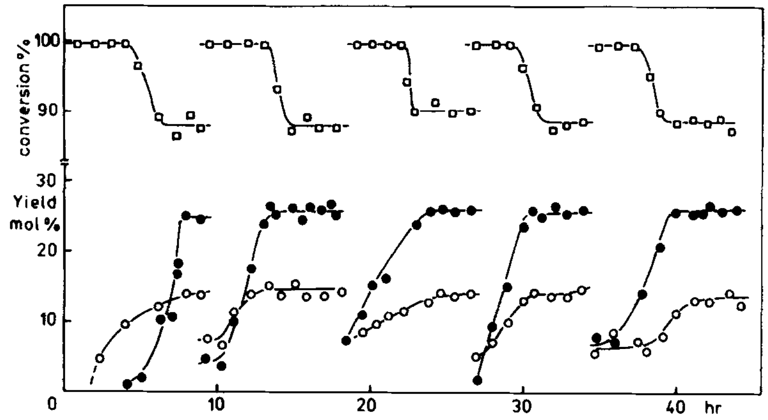


FIG. 6. Activity of Cu–K–Al_2O_3 catalyst after several regeneration cycles. Experimental conditions as in Fig. 1, regeneration 1.5 hr at 285°C by molecular oxygen (21.3 liters hr^{-1} kg_{cat}^{-1}), (□) benzoic acid, (●) phenol, (○) DP + DPO.

oxidation of BzOH to PhOH are in many cases similar to those for the liquid-phase oxidation of BzOH in the presence of homogeneous copper compounds (*2, 13, 14*). The basic underlying feature of both these reactions is the participation of the organometallic intermediate, cupric benzoate. Formation of this compound on the catalyst surface during steady-state runs under the considered experimental parameters was followed by ir spectroscopy of the rapidly cooled catalyst and also its pyridine extract (Fig. 7). The bands in the region 1300–1650 cm^{-1} relate to the benzoate anion (*15*); the band at 1400 cm^{-1} is assigned to the carboxyl symmetric vibration, the strongest band at 1550 cm^{-1} to the carboxyl antisymmetric vibration of ionized benzoic acid, and the band at 1620 cm^{-1} to benzene ring vibrations. The presence of benzoate anion was also confirmed in a pyridine extract of Cu–K–Al_2O_3 catalyst. Analysis using atomic absorption spectroscopy shows that in the extract, copper ions predominate and potassium and aluminum are present only in minor amount. Therefore, cupric benzoate is formed on the catalyst surface, and this was also proved by X-ray analysis (Fig. 8).

The catalytic activity of cupric benzoate as an actual intermediate formed in vapor-phase oxidation of BzOH was tested after its deposition on alumina (BzCu–Al_2O_3 catalyst). These experiments allow us to compare also the influence of the catalyst carrier on the selectivity of the oxidation. It

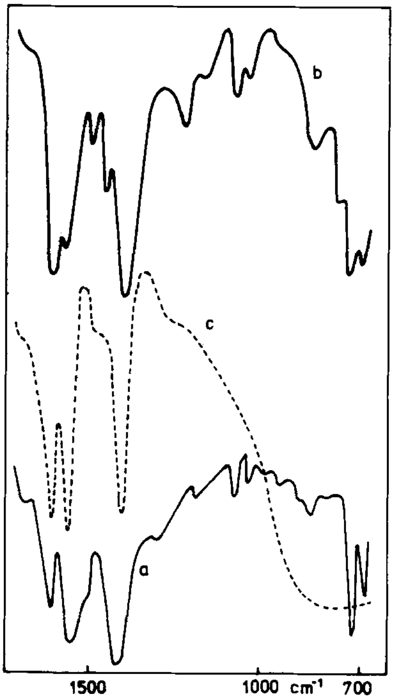


FIG. 7. Infrared spectra of BzCu (a), solid product from extraction of Cu–K–Al_2O_3 catalyst by pyridine (b), and rapidly cooled Cu–K–Al_2O_3.

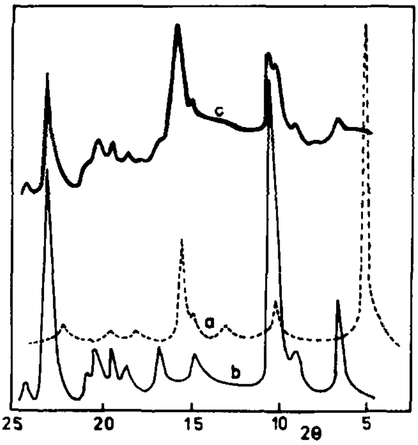


FIG. 8. X-Ray spectra of BzCu (a), adduct of BzCu and pyridine (b), and product from extraction of Cu–K–Al_2O_3 catalyst by pyridine (c).

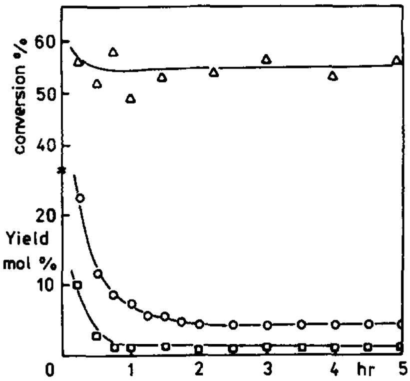


FIG. 9. Time dependence of BzCu–Al_2O_3 catalyst activity. Conditions as in Fig. 1.

was found that over this catalyst phenol is produced immediately after injection of BzOH to the reactor (Fig. 9). Since the yield of PhOH in the first few minutes of reaction is rapidly decreasing and later levels off to a stationary value, this suggests that the rate of cupric benzoate formation on the catalyst surface is lower than the rate of its decomposition. In contrast to Cu–K–Al_2O_3 catalyst, the lower stationary value of PhOH formation over BzCu–Al_2O_3 catalyst is caused by a lower concentration of copper on the carrier (the amount of BzCu corresponds only to 3.1 wt% of CuO) and by different acidic properties of the catalyst carrier as a consequence of its washing in the pyridine medium (Table 1). The

TABLE 1

Activity of Various Catalysts in the Vapor-Phase Oxidation of Benzene Derivatives

Catalyst	Composition (molar ratio) BzOH : H_2O : O_2 : X	Conversion % BzOH or[a,b,c]	Yield (mol%) PhOH	Yield (mol%) DP + DPO	r_{CO_2}[d]
Cu–K–Al_2O_3	1 : 60.2 : 2.0 : 0	88.0	26.1	14.0	15.6
	0 : 60.2 : 2.0 : 0.5[a]	46.7[a]	—	0	15.9
	0 : 60.2 : 0 : 0.5[a]	1.0[a]	—	0	0.2
	0 : 67.1 : 3.4 : 1.0[b,e]	94.1[b]	20.1	0.5	24.2
	0 : 73.8 : 3.7 : 1.0[c,e]	100 [c]	Traces[f]	0	36.9
Cu–Al_2O_3	1 : 60.2 : 2.0 : 0	55.0[e]	11.0	1.5	9.8
Cu–Py–Al_2O_3	1 : 60.0 : 2.0 : 0	53.3[e]	6.2	1.0	4.8
CuPc–Al_2O_3	1 : 60.0 : 2.0 : 0	10.1[e]	0	0	0.4
BzCu–Al_2O_3	1 : 60.0 : 2.0 : 0	54.2	4.5	1.1	0.6

Note. Conditions: 285°C, feed BzOH = 0.057 kg hr^{-1} kg_{cat}^{-1}; H_2O = 0.5 kg hr^{-1} kg_{cat}^{-1}; benzene = 1.1 kg hr^{-1} kg_{cat}^{-1}; O_2 = 21.3 liters hr^{-1} kg_{cat}^{-1}.

[a] PhOH feed 0.0183 kr hr^{-1} kg_{cat}^{-1}.

[b] Methylbenzoate feed 0.057 kg hr^{-1} kg_{cat}^{-1}; O_2 = 33.4 liters hr^{-1} kg_{cat}^{-1}.

[c] Methyl-*p*-toluate, conditions as in b.

[d] Rate of CO_2 formation (in liters hr^{-1} kg_{cat}^{-1}

[e] Reaction at 300°C;

[f] Phenol + cresols.

last mentioned influence is evident from differences between the activity of Cu–Al_2O_3 and Cu–Py–Al_2O_3 catalysts. The fact that formation of phenol proceeds through cupric benzoate as intermediate is supported by further experiments with PcCu–Al_2O_3 catalyst. Thus, copper phthalocyanines, which at the temperature of oxidation (ca. 300°C) are thermally highly stable (*16*) are not converted to cupric benzoate and, therefore, over this catalyst no phenol is produced (Table 1). The very low conversion of BzOH (ca. 10%) at the reaction temperature is probably caused by a decarboxylation reaction catalyzed by the carrier.

Experiments with BzCu–Al_2O_3 catalyst suggest (Fig. 9) that the rate of thermal decomposition of cupric benzoate is higher than the rate of its formation. This was supported by another set of experiments over Cu–K–Al_2O_3 catalyst with a stopped flow feed of benzoic acid and water. Thus, under steady-state conditions the input of BzOH (but not oxygen) to the reactor was every 20 min stopped for 20 min. After each cycle the activity of catalyst gradually dropped and after 4–6 cycles the yield of PhOH was only 7–12%. However, the catalyst again reached its former activity only after 3–5 hr of continuous injection of BzOH. As is seen from Fig. 6 in every run after each interruption of reaction there exists a certain "induction period" needed to reach stationary conditions. It was found (Fig. 10) that this period is a function of the feed rate of BzOH to the reactor. Assuming that the amount of BzOH "adsorbed" on the catalytically almost inactive PcCu–Al_2O_3 catalyst is approximately the same also on the Cu–K–Al_2O_3 catalyst carrier, then the extra consumed BzOH at 285°C corresponds in all runs to about 50–60% conversion of copper oxide to cupric benzoate.

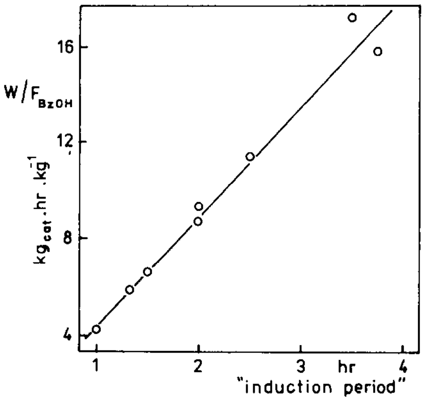


FIG. 10. Effect of feed rate of BzOH on the "induction period." Conditions as in Fig. 1.

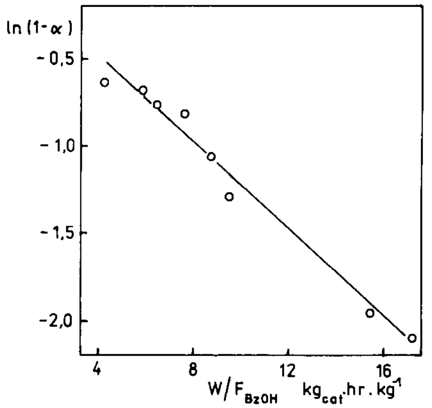
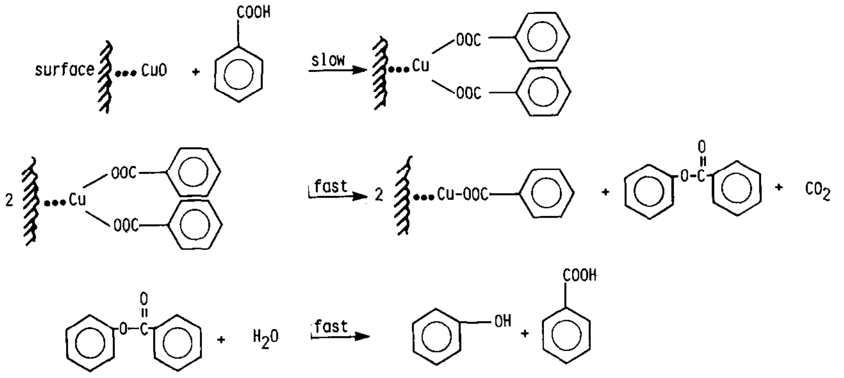


FIG. 11. Test of first-order reaction mechanism.

The results of kinetic experiments also indicate that formation of cupric benzoate is the rate-determining step in BzOH oxidation. Thus, at a sufficiently high concentration of oxygen and water in the reactant feed (Figs. 4 and 5), the overall rate of benzoic acid oxidation follows a first-order dependence on the BzOH concentration in the feed (Fig. 11) with a rate constant $k = 0.124 \pm 0.014$ hr^{-1} at 285°C.

It appears that an important step in the manufacture of phenol by the liquid-phase oxidation of benzoic acid is also oxidation of cuprous to cupric salt (*17, 18*). Thus, thermal decomposition of cupric benzoate at 220–240°C proceeds with an activation energy of about 249 kJ mol^{-1} (*19*) and in diphenyl ether solvent, but in the absence of acid, about 178 kJ mol^{-1} (*14*). Because the activation energy of the liquid-phase oxidation of benzoic acid in the presence of copper compound is substantially lower, 41 kJ mol^{-1} (*14*) or 65 kJ mol^{-1} (*18*), this indicates that the thermal decomposition of cupric benzoate is not responsible for the oxidation of benzoic acid.

Based on the above discussion, the reaction mechanism of phenol formation by oxidation of benzoic acid in the vapor phase and the liquid phase is very similar (*13*, *14*). It implies that cupric benzoate is the key species formed on the catalyst surface and that this thermally decomposes to produce phenol precursors (reactions 1–3)

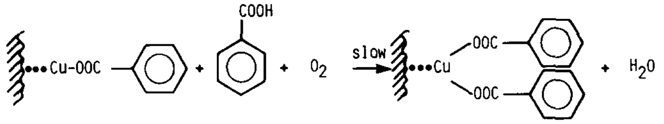


(1)

(2)

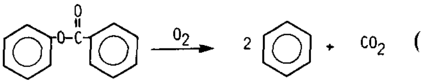
(3)

In the absence of molecular oxygen cuprous benzoate does not regenerate, the yield of PhOH formation decreases and the catalyst loses its activity (Fig. 5). Reduced copper salt is regenerated with oxygen but our assumption is that this step is the rate-determining one:



(4)

Phenol is formed prior to hydrolysis of phenyl benzoate or benzoyl salicylic acid (*13*). However, in the absence of water in the inlet feed, decomposition of this intermediate product predominates:

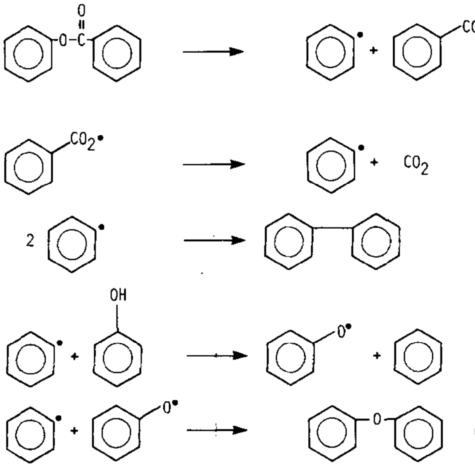


(5)

The small amount of phenol produced under these conditions is probably caused by water formed in the catalyst regeneration step (reaction 4).

The rate of hydrolysis or decomposition of phenyl benzoate at temperatures of about 300°C must be very high, because this intermediate was not identified among the reaction products. In the case of the oxidation of methyl-*p*-toluate, decomposition through reaction 5 is probably more rapid than hydrolysis of this product (reaction 3). This suggestion was experimentally confirmed in the liquid-phase hydrolysis of phenyl benzoate and tolyl toluate (*20*, *21*). Despite the presence of an optimal amount of water and oxygen in the feed, methyl-*p*-toluate is preferentially oxidized to toluene and carbon dioxide, and phenol or cresols are produced only in trace yields (Table 1). Such a course of reaction is not caused by an ester type of reactant because under the considered conditions methyl benzoate is oxidized to phenol with a yield only a little lower than that from benzoic acid.

The main difference between the homogeneously and heterogeneously catalyzed oxidation of benzoic acid is the formation of by-products. Owing to the lower temperature of oxidation in the liquid phase (200–250°C) phenyl benzoate is the principal by-product, especially if the reaction is carried out in the absence of water (*1*, *17*). In the vapor-phase process at a temperature of about 300°C this product is unstable and probably rapidly decomposes to benzene and CO_2. Moreover, new by-products, namely diphenyl and diphenyloxide, are formed. However, the above-mentioned experiments suggest that formation of these compounds is not caused by a different mechanism of vapor-phase oxidation of BzOH but by differences in reaction temperature. Diphenyl(DP) and diphenyloxide (DPO) are not produced by phenol oxidation (Fig. 9) but probably via nonselective decomposition of cupric species or decomposition of phenyl benzoate (reactions 6–10).



(6)

(7)

(8)

(9)

(10)

The latter reactions proceed also in the presence of water. The propagation reaction of phenyl radicals with the phenol molecule predominates over bimolecular termination (reaction 8) because the rate of DPO production is approximately four times higher than for DP. In most runs quinones are present in the reaction products only in a negligible amount and if they are formed during the homogeneous phenol oxidation they are probably rapidly oxidized to carbon dioxide at the temperature of 300°C.

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