

Involvement of Free Radicals in the Aqueous-Phase Catalytic Oxidation of Phenol Over Copper Oxide

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Aqueous-phase oxidation of phenol over copper oxide was studied between 369–393°K and 1–17 atm oxygen pressure in batchwise mode. The reaction involves an induction period and a steady-state activity regime. The initial rate is first order in phenol and oxygen, but the rate is one-half order in oxygen in the steady-state activity regime. Heterogeneously catalyzed aqueous-phase phenol oxidation occurs by a free-radical mechanism which involves initiation on the catalyst surface, homogeneous propagation and either predominantly homogeneous or heterogeneous termination depending on catalyst concentration. That a free-radical mechanism is involved is indicated by the induction period, by the observed reaction kinetics, by free-radical inhibitor studies which show the same inhibitor efficiencies as observed in free-radical oxidation and by pH studies. The involvement of a heterogeneous-homogeneous reaction mechanism is indicated by dependence of the reaction rate on catalyst concentration.

NOMENCLATURE

<i>A</i>	Proportionality constant	<i>c</i>	Supported copper oxide catalyst in autoclave
<i>C</i>	Concentration, g moles/cm ³	DPA	Diphenylamine
<i>d_p</i>	Catalyst particle diameter, cm	<i>g</i>	Gas phase
<i>K_i</i>	Equilibrium constant for step <i>i</i>	<i>I</i>	Induction period
<i>k₁</i>	Rate constant for initial rate (autoclave) data, (cm ³) (g cat-atm-sec) ⁻¹	<i>l</i>	Liquid phase
<i>k₂</i>	Rate constant for steady-state activity (autoclave) data, (cm ³) (atm) ^{-1/2} (sec-g cat) ⁻¹	NMA	<i>N</i> -methylaniline
<i>k_i</i>	Rate constant for reaction step <i>i</i> (sec) ⁻¹ (other units dependent on step)	0	Initial value
<i>M</i>	Weight, g	ph	Phenol
<i>n</i>	Number of radicals terminated by each inhibitor molecule		
<i>P</i>	Pressure, atm		
<i>r</i>	Rate of reaction per unit weight catalyst, g moles (g cat-sec) ⁻¹		
<i>t</i>	Time, sec		
<i>V</i>	Volume, cm ³		
<i>Subscripts</i>			
AH	Inhibitor		
Al	Pure γ -alumina		

INTRODUCTION

The effective removal of organic chemicals from industrial wastewater is a problem of increasing importance. In situations involving high concentrations of toxic or refractory organics or limited land availability conventional treatment technology is often unsatisfactory or very costly, and physical-chemical treatment methods must be applied. Aqueous-phase catalytic oxidation is a possible technique which has recently attracted attention (1-5) including announcement of a commercial process (6, 7). There is little fundamental or design information available, and the mechanism

of aqueous-phase catalytic oxidation reactions has not been considered.

Uncatalyzed homogeneous free-radical oxidation usually involves two consecutive, interrelated periods; an induction period which corresponds to the time required for establishing a steady-state hydroperoxide concentration, and a steady-state rate of oxidation period which involves the decomposition of hydroperoxide into radicals and the involvement of these radicals in the oxidation reaction (8). The induction period, if observable, shows an autocatalytic nature which is more apparent at lower temperatures. Shibaeva, Metalitsa and Denisov (9, 10) observed short induction periods and autoacceleration in the uncatalyzed oxidation of phenol with molecular oxygen in aqueous solution and explained their results by a free-radical mechanism. They reported that hydrogen peroxide was formed and involved in the reaction and that phenol strongly inhibited hydrogen peroxide decomposition.

Transition metal salts in low concentrations have frequently been used in the liquid-phase oxidation of hydrocarbons. The characteristic behavior of these oxidations is similar to that of uncatalyzed, homogeneous free-radical oxidations, and they are assumed to involve a free-radical mechanism (11-13). The characteristics of heterogeneous and homogeneous liquid-phase oxidations catalyzed by transition metals are often similar (12) indicating the involvement of free radicals in heterogeneously catalyzed oxidation reactions. The involvement of a heterogeneous-homogeneous reaction mechanism in liquid-phase oxidation over solid catalysts in which free radicals are formed on the surface of the solid catalyst but undergo propagation and termination in solution was initially proposed by Meyer, Clement and Balaceanu (14). This mechanism has been used to explain the heterogeneously catalyzed liquid-phase oxidation of alcohols and alkylbenzenes (15), cyclohexene (16), tetralin (17), *p*-xylene (18), and cumene (19, 20). Induction periods are generally observed only at high catalyst:hydrocarbon ratios (16, 20) and in systems initially

free of hydrocarbon hydroperoxide (17, 19). They decrease with increasing temperature (21-23), decreasing catalyst concentration (15, 17), increasing initial hydroperoxide concentration (22) and increasing oxygen pressure (23).

Previous work on the aqueous-phase catalytic oxidation of phenol over copper oxide showed that the reaction involves an induction period and that the rate of reaction is other than first order in catalyst concentration (23). The present work establishes the mechanism of the heterogeneously catalyzed oxidation of phenol in aqueous solution over copper oxide and quantifies the effect of catalyst and phenol concentration, free-radical inhibitors, and pH on the initial rate and on the rate in the steady-state activity regime.

EXPERIMENTAL METHODS AND MATERIALS

Apparatus and Procedure

The apparatus has been described in detail elsewhere (23). It consisted of a heated, stirred, 1-liter autoclave with a glass liner operated batchwise. A sparger introduced oxygen immediately beneath the turbine stirrer, and a back-pressure regulator controlled the system total pressure.

Known amounts of distilled water (500 ml) and catalyst (0.2-6 g) were added to the autoclave, and the autoclave was heated to the desired temperature. At $t = 0$, a known amount of phenol (1.7-5.3 g), dissolved in distilled water, was injected into the autoclave through the gas sparger by oxygen; and the oxygen flow through the system was set at 1 ml/sec. Samples were taken periodically thereafter with sufficient flushing of the sample lines, and analysis was by gas chromatography using a thermoconductivity detector and a 6 ft by $\frac{1}{8}$ in. column of Poropak N. Reaction conditions included 369-393°K and 1-17 atm oxygen pressure.

Materials

The supported copper oxide catalyst was 10% CuO on γ -alumina (Harshaw Cu-0803 T $\frac{1}{8}$) and had a surface area of 140 m²/g and a porosity of 0.42 cc/g. X-Ray

analysis indicated copper present as cupric oxide and a small amount of copper aluminate, which was probably responsible for the green color of the catalyst. The catalyst was crushed, and the fraction passing through a 150-mesh screen was used. Unsupported cupric and cuprous oxide were BDH Analytical Reagent. The phenol was Baker "Analyzed Reagent," and the diphenylamine and *N*-methylaniline were Eastman Reagent (ACS) and practical grades, respectively.

RESULTS

Kinetic Studies

The rate of oxidation exhibits an induction period which is followed by a more-rapid rate, steady-state activity regime (23). In the steady-state activity regime \ln (conversion) vs time at constant oxygen pressure exhibits a linear relationship which holds through the highest conversions studied (>95%). The initial rate of oxidation is first order in both oxygen partial pressure and initial phenol concentration. First-order dependence on phenol with respect to time in the induction period is indicated by linearity of the \ln (conversion) vs time plots for this period. In the steady-state activity regime the rate shows one-half-order dependence on oxygen partial pressure and first-order dependence on phenol concentration. In accordance with these results, the rate of reaction per unit volume of catalyst was modeled according to:

$$-\frac{V_1}{M_c} \frac{dC_{ph}}{dt} = k_1 C_{ph} P_{O_2} \quad (1)$$

and

$$-\frac{V_1}{M_c} \frac{dC_{ph}}{dt} = k_2 C_{ph} P_{O_2}^{1/2} \quad (2)$$

for the induction period and the steady-state activity regime, respectively.

At constant initial phenol concentration the initial rate of phenol oxidation per gram of catalyst decreases markedly with increasing catalyst concentration at low catalyst concentrations and becomes inde-

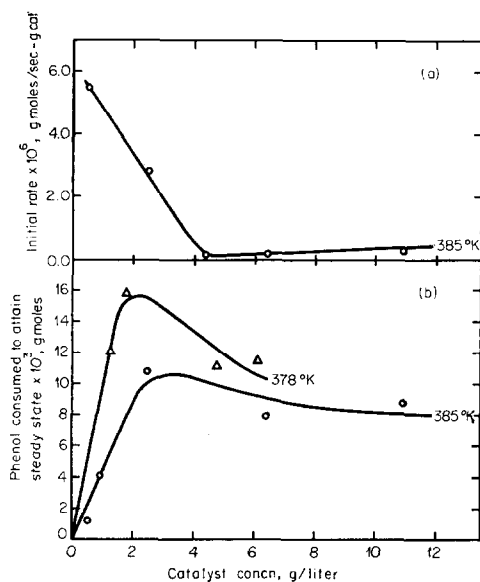


FIG. 1. Effect of catalyst concentration: (a) on initial rate of phenol oxidation, and (b) on phenol consumption during the induction period: 10.2 atm O_2 , 4.50 g phenol/liter.

pendent of catalyst concentration for higher concentrations. Figure 1a shows this behavior for 385°K; curves are drawn by eye. Similar behavior was observed at 378°K except that at the lowest catalyst concentrations a slight increase occurred before the rate began to decrease. A similar slight increase in rate per gram catalyst appeared to occur at the lowest catalyst concentrations in atmospheric pressure studies at 373°K. The rate dependence on catalyst concentration at low concentration and 385°K is complex in that it appears to change with increasing catalyst concentration.

The induction period, defined experimentally as the time required to achieve the steady-state activity regime, increases as the ratio of catalyst concentration to initial phenol concentration increases as shown in Fig. 2. The error in the initial rate and in the induction period is less than $\pm 15\%$. The solid curves are for a constant initial phenol concentration of 4.60 g/liter; the broken curve is for a constant catalyst concentration of 1.96 g/liter. The solid curve at 385°K indicates that the induction period is inversely proportional to the

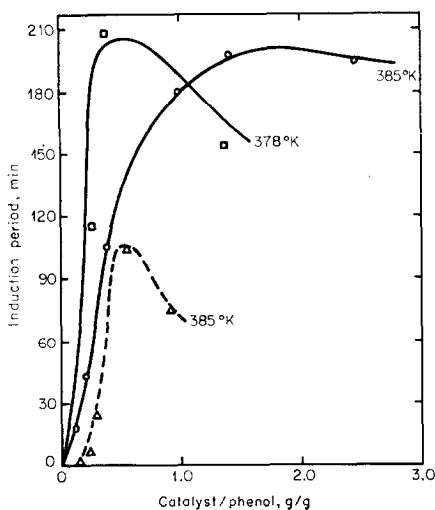


FIG. 2. Dependence of induction period on ratio of catalyst concentration to initial phenol concentration: 10.2 atm O_2 ; (—) 4.60 g phenol/liter and varying catalyst concentration, (---) 1.96 g catalyst/liter and varying phenol.

initial rate of oxidation per gram of catalyst (Fig. 1a). The broken line shows that as the catalyst concentration at fixed catalyst:phenol ratio decreases (higher initial rate of reaction per gram of catalyst) the induction period decreases. Figure 1b shows the extent of phenol consumption as a function of catalyst concentration for 378 and 385°K. Phenol consumption in the induction period also correlates inversely with the initial rate of reaction per gram of catalyst (Fig. 1a) and not with catalyst concentration.

Unsupported cuprous oxide exhibited a low rate and no observable induction period, and unsupported cupric oxide was essentially inactive at 385°K. Addition of pure, crushed and screened γ -alumina (~ 150 mesh) to a constant amount of supported copper oxide catalyst results in an apparent linear increase in the induction period (Fig. 3a) and a reduction in the initial rate of oxidation per gram of supported copper oxide (Fig. 3b). For 4.46 g of supported copper oxide/liter, the induction period increased by a factor of 2.8 when pure alumina equivalent to 2.7 times the constant amount of supported copper oxide catalyst was added. The amount of phenol

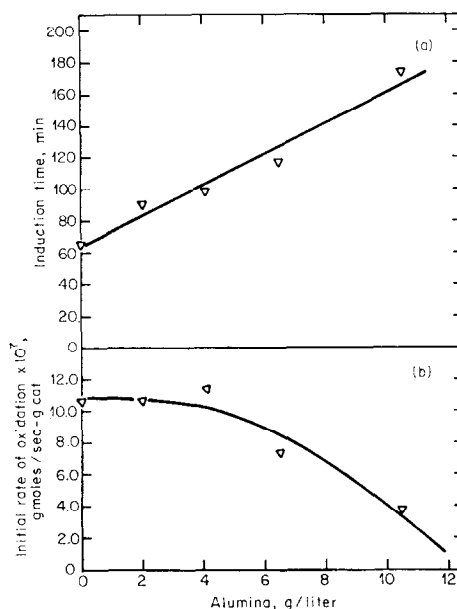


FIG. 3. Effect of pure γ -alumina on: (a) the phenol oxidation induction period and (b) the initial rate of oxidation: constant conditions: 390°K, 8.84 atm O_2 , and 4.46 g supported copper oxide catalyst/liter.

consumed in the induction period increases linearly with the amount of pure alumina added. This indicates that the alumina surface plays an inhibitory role in the reaction during the induction period. The rate per gram of supported copper oxide is independent of the amount of alumina added in the steady-state activity regime.

In the steady-state activity regime k_2 passes through a maximum as the catalyst concentration is increased with all other variables constant (Fig. 4). The error in k_2 is less than $\pm 10\%$. For a purely surface catalyzed reaction the rate of reaction per unit weight of catalyst should be independent of catalyst concentration until mass-transfer limitations become important, and then the observed rate per unit catalyst weight should decrease with increasing catalyst concentration. An increase is not to be expected and is indicative of a complexity in the reaction mechanism.

Inhibitor Studies

To explore the possible involvement of free radicals in the reaction and further clarify the reaction mechanism a series of

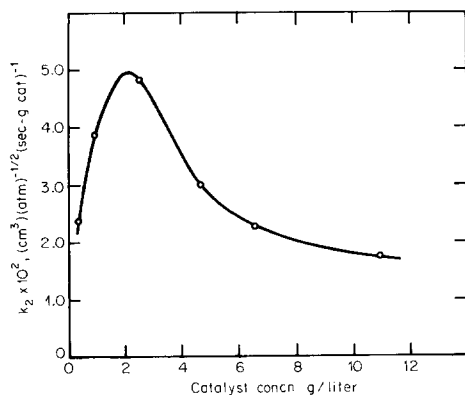


FIG. 4. Effect of catalyst concentration on steady-state rate of oxidation: 385°K, 10.2 atm O₂, 4.60 g phenol/liter.

runs was carried out in which the free-radical inhibitors diphenylamine and *N*-methylaniline were employed. The induction period increases linearly with initial inhibitor concentration (Fig. 5), and the initial rate of oxidation is strongly dependent on the inhibitor concentration (Fig. 6). Diphenylamine is much more effective than *N*-methylaniline. Phenol consumption in the induction period increases linearly with inhibitor concentration.

The initial inhibitor concentration also affects the steady-state rate constant although not as strongly. The highest inhibitor concentration for each inhibitor used reduced k_2 by only a factor of two; whereas these inhibitor levels reduced the initial rate by a factor of about 20. In the presence of inhibitors the steady-state rate was first order in oxygen partial pressure rather than one-half order as in the absence of inhibitors.

pH Studies

The effect of pH on phenol oxidation was determined in a series of runs at 376°K. The variation in pH was achieved by adding sulfuric acid. Figure 7 summarizes the results of these studies. The initial rate of oxidation is markedly affected by pH, having a maximum at a pH of about 4.0; whereas the steady-state activity is a much weaker function of pH. The induction period is inversely related to the initial

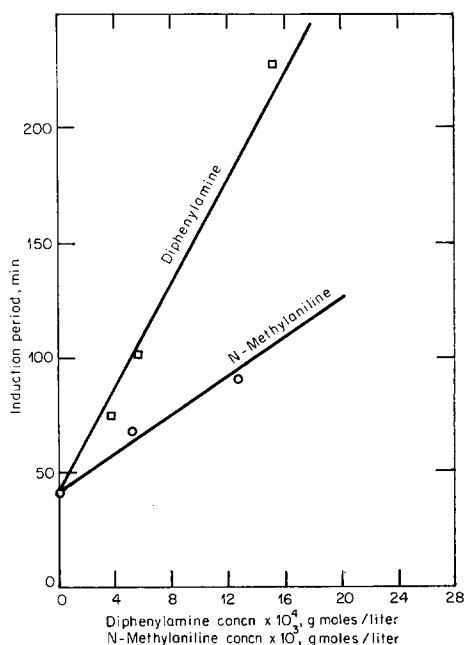


FIG. 5. Effect of initial inhibitor concentration on induction period: 385°K, 9.60 atm O₂, 4.60 g phenol/liter, 2.54 g catalyst/liter.

rate of oxidation as observed previously (Fig. 4). At the highest pH studied (pH = 11.5) the induction period was so long that transition to steady-state activity was not observed.

DISCUSSION OF RESULTS

Rates

Atmospheric pressure studies (23) and those reported here both show dependence of the initial rate of reaction per unit catalyst weight on catalyst concentration. That these variations are the result of phenomena other than gas-liquid mass-transfer limitations is indicated by the order of magnitude increase in the rate of reaction from the initial rate to that at the beginning of the steady-state activity regime, by the observed high negative order dependence on catalyst concentration even at very low catalyst concentrations, and by high observed activation energy (23). An order of magnitude increase in rate would not be possible if the initial rate already involved severe mass-transfer limitations.

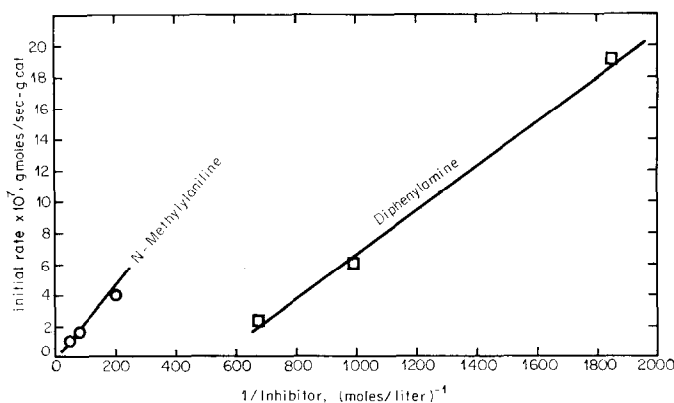


FIG. 6. Dependence of initial oxidation rate on inhibitor concentration: 385°K, 9.60 atm O₂, 4.60 g phenol/liter, 2.54-g catalyst/liter, initial rate without inhibitor was 3.05 × 10⁻⁶ g moles/(sec-g cat).

Similarly, the increasing rate per unit catalyst weight with increasing catalyst concentration at low concentrations, the first-order dependence on phenol concentration, the one-half order dependence on oxygen partial pressure (gas-liquid mass-transfer limitations should produce first-order dependence), the strong negative dependence on catalyst concentration near the max-

imum, and mass-transfer calculations indicate the absence of gas-liquid mass-transfer limitations in the steady-state activity regime. The behavior is due to kinetic phenomena. The observed rates do not involve intraparticle diffusional limitations and are dependent on catalyst, i.e., are not due to uncatalyzed homogeneous reaction (23).

Involvement of Free Radicals

Induction periods are frequently observed in homogeneous oxidations and usually imply a free-radical mechanism (8). Uncatalyzed aqueous-phase phenol oxidation shows these characteristics and appears to involve a free-radical mechanism (9, 10). The induction periods observed here are suggestive of this mechanism. The phenol oxidation induction period involves considerable consumption of phenol compared with little or no measurable conversion during the induction period in the homogeneous or heterogeneously catalyzed oxidation (using unsupported catalysts) of cyclohexene, isopropylbenzene or tetralin (8, 12, 14, 19-21). This considerable conversion during the induction period in phenol oxidation (Fig. 1b), the absence of an observable induction period with unsupported cuprous oxide and the marked increase in the induction period when pure γ-alumina is added with the supported copper oxide catalyst (Fig. 3a) indicate that the induction period is related to the alumina surface area.

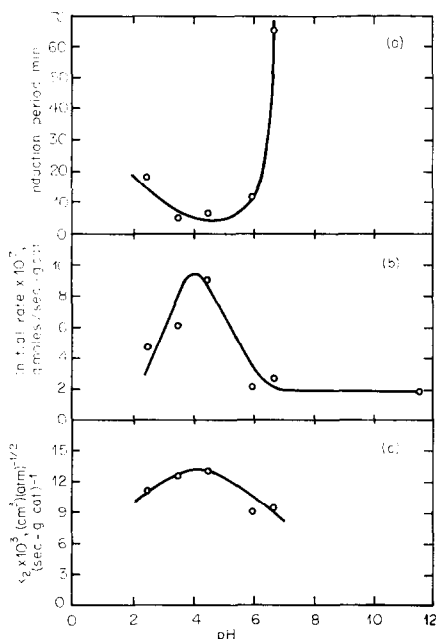


FIG. 7. Effect of pH on: (a) induction period; (b) initial rate of oxidation; (c) steady-state rate of oxidation: 376°K, 9.60 atm O₂, 4.60 g phenol/liter, 4.60 g catalyst/liter.

The marked dependence of the initial rate of reaction and of the length of the induction period on the initial inhibitor concentration (Figs. 5 and 6) essentially verifies the involvement of free radicals in the reaction. To achieve a 10-fold decrease in the initial rate from the uninhibited rate a molar concentration of *N*-methylaniline which is 4.6 times that of diphenylamine is required. The rate constant for reaction of diphenylamine and *N*-methylaniline with poly(peroxystyryl) peroxy radicals is reported to be 4.0×10^4 and 0.4×10^4 ($M\text{-sec}^{-1}$), respectively (25). Although the magnitude of inhibitor efficiency and kinetics depends on the oxidizing substrate, the relative efficiencies should not be reordered; and thus the efficiencies observed here are consistent with that expected in inhibition of homogeneous free-radical reactions (26). If the inhibitors were reducing the rate of phenol oxidation by some other mechanism such as adsorbing on active sites on the catalyst surface, they would most likely not show the same relative effectiveness shown in homogeneous, free-radical inhibition.

The inhibitors are not entirely consumed in the induction period as indicated by their reduction of the steady-state rate. This reduction is in the same relative order as the inhibitor efficiencies. Thus free radicals appear to be involved in the phenol oxidation.

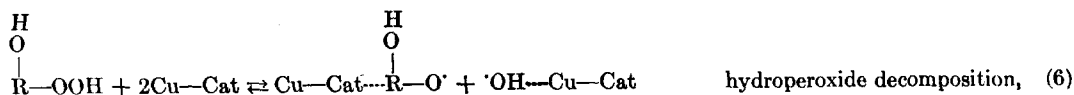
The rate dependence of pH provides further evidence of the involvement of free radicals. Typically free-radical reactions in aqueous media are pH dependent, and they typically show a maximum with pH. A rate maximum has been observed at a pH of

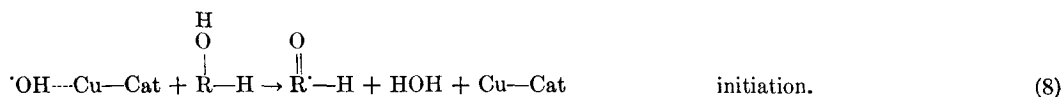
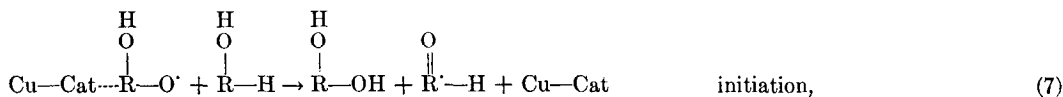
about 3.5 in the uncatalyzed aqueous-phase homogeneous oxidation of phenol with molecular oxygen (9) and in the H_2O_2 oxidation of organics in wastewater (27). This is consistent with our observed rate maximum at a pH of about 4.0 and supports a free-radical mechanism for catalyzed phenol oxidation.

If the reaction occurred only on the surface of the catalyst either via a radical or nonradical mechanism, the observed rate per unit weight of catalyst would normally be independent of the catalyst concentration. If reactions were to involve initiation of a chain on the catalyst surface and propagation of the reaction chain in homogeneous solution, the rate per unit catalyst weight could be a function of catalyst concentration. Termination could occur homogeneously or heterogeneously depending on the catalyst concentration as discussed below. Rate maxima with respect to catalyst concentration similar to ours have been reported in cumene oxidation over Co_3O_4 , CoO_3 and MnO_2 (15, 20), in cyclohexene oxidation over MnO_2 (16) and in tetralin oxidation over Mn_2O_3 (17); and the reaction mechanisms have been interpreted to involve a free-radical mechanism. The similar behavior observed in this work supports the proposed involvement of free radicals in a heterogeneous-homogeneous reaction mechanism.

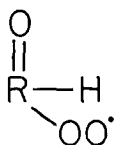
Reaction Mechanism and Intermediates

In view of the apparent involvement of free radicals the following reaction mechanism is suggested:





$\overset{\text{H}}{\text{R}}\text{-H}$ refers to phenol; $\overset{\text{O}}{\text{R}}\text{-H}$ refers to the phenoxy radical; and



to the peroxy radical where —OO^\cdot is located in the ortho- or para-position.

The phenoxy radical is readily formed by agents capable of one electron or hydrogen abstraction (28–30). The observation that the rate maximum occurs at low pH indicates that the phenolate ion is not important and that radical formation involves hydrogen abstraction. Hydrogen abstraction by catalyst to initiate free radicals in oxidation has been proposed (14, 16, 17, 20, 22). Phenolic hydroperoxides have been prepared and identified (30–32). Hydroperoxide decomposition [reaction (6)] occurs readily and is typically the

termination reactions (see below). Equation (3) follows our observation that supported copper oxide and manganese dioxide have markedly different initial activities in aqueous-phase phenol oxidation, and Eqs. (6)–(8) follow from our observation that their activities are identical in the steady-state activity regime (23).

This mechanism is supported by the appearance of low concentrations of catechol and hydroquinone and the apparent appearance of appreciable quantities of quinones (23). The presence of only small quantities of catechol and hydroquinone is reasonable since once formed they should be readily oxidized, respectively, to *p*- and *o*-benzoquinone (33, 34). Quinones have been identified in the sonocatalytic oxidation of phenol in aqueous solution (3, 35). Appreciable quantities of catechol, hydroquinone, and quinones are observed in homogeneous oxidation of phenol with various oxidizing agents (36–40).

The involvement of surface adsorbed oxygen represents another possible propagation pathway:



main source of radicals in hydrocarbon oxidations beyond the autocatalytic period. Reactions (3) and (6)–(8) are written as such to distinguish between the involvement of the metal oxide in the initiation step during the induction period, and the steady-state activity regime, and the involvement of the alumina surface area in determining the amount of phenol consumed in the induction period, the length of the induction period, and the probable involvement of the alumina surface area in

Reactions (9) and (10) provide one possible explanation of the high activity of cuprous oxide relative to cupric oxide. Reactions involving hydrogen peroxide formation, and its involvement in the oxidation are probably also present, but their importance was not determined in this work.

Kinetics

Induction period. The initial rate of oxidation is first order in phenol with respect

to both initial phenol concentration and time. This suggests that the surface sites are not saturated with phenol and that products of reaction initially neither compete effectively for active sites on the surface, nor accelerate or inhibit the reaction by other interactions. The initial rate is first order in oxygen partial pressure; whereas hydrocarbon oxidation over metal oxides is typically close to zero order in oxygen (41, 42).

The involvement of a heterogeneous-homogeneous mechanism in the induction period is indicated by the observed dependence of initial rate on catalyst concentration. Mechanistically the rapid decrease of initial rate per unit catalyst with increasing catalyst concentration (Fig. 3a) may be due to the increasing importance of chain termination on the catalyst surface. Thus catalyst at very low concentrations initiates chains which undergo many cycles in solution before termination; the length of these chains is reduced by the increased probability of termination as catalyst or alumina concentration is increased. Reactions (11) and (12) account for termination and inhibition:



where AH is an inhibitor. Equation (11) states our speculation that termination can occur on the alumina surface, and thus Al-cat refers to all alumina surface in the system, $M_c + M_{A1}$.

The rate equation derived from reactions (3), (4), (5), (9), (10), (11) and (12) using the steady-state approximation applied to radical species in the system is

$$\begin{aligned} -\frac{V_l dC_{\text{ph}}}{M_c dt} &= \frac{k_3[k_4 + k_{10}K_9(M_c/V_l)]}{k_{12}C_{\text{AH}} + k_{11}[(M_c + M_{A1})/V_l]} P_{\text{O}_2} C_{\text{ph}} \\ & \qquad (13) \end{aligned}$$

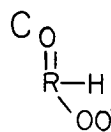
The terms retained in the denominator depend on the experimental conditions.

Termination on the catalyst is required to give negative dependence of rate per unit catalyst on catalyst concentration, and phenoxy radical termination is required to give first-order dependence on oxygen. The derived model predicts the rate trend observed with increasing catalyst concentration as well as fitting the phenol and oxygen dependence. The combination of propagation steps (4) and (10) gives a predicted order between minus one and zero, the exact value depending on the relative importance of the two propagation paths. This is consistent with the observation that the rate per unit weight of catalyst becomes independent of catalyst concentration at higher catalyst concentrations (Fig. 1a). Equation (13) also predicts quantitatively the effect of adding pure alumina with 4.6 g/liter of supported copper oxide catalyst to the autoclave (Fig. 3b). At this concentration of supported copper oxide (Fig. 1a) the initial rate should be somewhat insensitive to alumina concentration until it is approximately equivalent to that of the supported copper oxide catalyst, M_c/V_l (Fig. 3b).

For significant inhibition, i.e., $k_{12}C_{\text{AH}} \gg k_{11}(M_c + M_{A1})/V_l$, the initial rate should be inversely proportional to the inhibitor concentration multiplied by the inhibitor rate constant, Eq. (13). This is in accord with observation (Fig. 6). This relation gives $k_{12, \text{DPA}} = 4.6 k_{12, \text{NMA}}$.

Transition to the steady-state activity regime in free-radical oxidation is usually assumed to occur when a steady-state concentration of hydroperoxide is reached in the system. We speculate that the role of the catalyst alumina and pure alumina surfaces is to adsorb a reaction intermediate, that this intermediate is a hydro-

peroxide and that a certain concentration of hydroperoxide on the surface and possibly in solution is necessary to achieve the steady-state activity regime. Thus the interrelation observed between initial rate, induction period and phenol consumption in the induction period. Further, used catalyst, whose surface is already covered with this organic material, should and does exhibit as much as an order of magnitude shorter induction period although the initial rate is approximately the same (23). Vreugdenhil (19) has proposed a similar explanation for cumene oxidation over silica-supported silver.



steady-state approximation and assuming that the required steady-state hydroperoxide concentration is directly proportional to the catalyst concentration,

$$\begin{array}{c} \text{H} \\ \text{O} \\ | \\ [\text{R}-\text{OOH}]_s = A(M_c + M_{A1})/V_l, \end{array}$$

we obtain upon substituting into Eq. (14):

$$\tau_I = \frac{A(M_c + M_{A1})/V_l [k_{11}(M_c + M_{A1})/V_l + k_{12}C_{AH,0}]}{k_3(M_c/V_l)[k_4 + k_{10}K_9(M_c/V_l)]P_{O_2}C_{ph,0}} \quad (15)$$

The induction period can be expressed as the time required to reach the necessary, steady-state concentration of hydroperoxide for steady-state behavior, and for a linear extrapolation of the initial rate the induction period is

$$\tau_I = \frac{[\text{R}-\text{OOH}]_s}{k_5 \begin{array}{c} \text{C} \\ \parallel \\ \text{O} \\ | \\ \text{R}-\text{H} \\ | \\ \text{OO}^\cdot \end{array} C_{ph,0}} \quad (14)$$

where $\begin{array}{c} \text{H} \\ \text{O} \\ | \\ [\text{R}-\text{OOH}]_s \end{array}$ is the hydroperoxide concentration (or other reaction-produced system state) required for steady-state behavior. The linear extrapolation of the initial rate is satisfactory since the maximum phenol removal observed in the induction period was less than 20% of the initial amount charged. Solving Eqs. (3), (4), (5), (9), (10), (11) and (12) for using the

Again the terms retained depend on the experimental conditions.

Equation (15) predicts that the induction period should increase as (M_c/V_l) increases to a certain level and then become independent of (M_c/V_l) (Fig. 2); that the induction period should increase with increasing (M_{A1}/V_l) (Fig. 3); that it should increase with increasing effectiveness of the inhibitor (larger k_{12}) and increasing inhibitor concentration (Fig. 5); and that for constant catalyst concentration the induction period should be proportional to $(P_{O_2})^{-1}$ and show Arrhenius temperature dependence as observed (23).

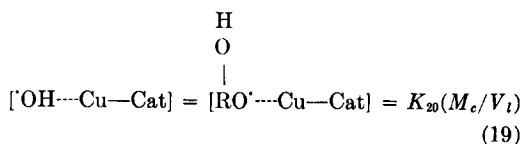
If the time dependence of phenol and inhibitor are taken into account with the inhibitor consumption being described by

$$-\frac{dC_{AH}}{dt} = \frac{k_{12}}{n} C_{AH} \begin{array}{c} \text{C} \\ \parallel \\ \text{O} \\ | \\ \text{R}-\text{H} \end{array} \quad (16)$$

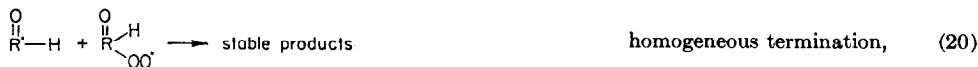
and if Eq. (13) is integrated with application of Eq. (16), the induction period is

$$\tau_I = \frac{k_{12}C_{AH,0} \exp[-\phi C_{ph,0}] + k_{11}((M_c + M_{A1})/V_l)}{k_3 k^* P_{O_2} (M_c/V_l)} \ln \frac{C_{ph,0}}{C_{ph,0} - C_{ph}^*} + \frac{k_{12}C_{AH,0} \exp[-\phi C_{ph,0}]}{k_3 k^* P_{O_2} (M_c/V_l)} \left\{ \phi \Delta + \frac{\phi^2 \Delta^2}{2 \cdot 2!} + \frac{\phi^3 \Delta^3}{3 \cdot 3!} + \dots \right\}, \quad (17)$$

where $\phi = k_{12}/(n k^* P_{O_2})$, $\Delta^m = C_{ph,0}^m - (C_{ph,0} - C_{ph}^*)^m$, $k^* = [k_4 + k_{10}K_9(M_c/V_l)]$ and C_{ph}^* is the phenol consumed in the induction period. Equation (17) requires a priori knowledge of phenol consumption in the induction period, and this shows com-



and assuming biradical terminations:



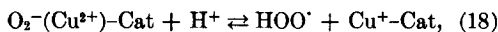
plexity (Fig. 2b) which we are not yet able to predict. It does predict correctly the in-

reactions (4), (5), (6), (7), (8), (9), (10), (19), (20) and (21) give

$$-\frac{V_l}{M_c} \frac{dC_{ph}}{dt} = \left[\frac{K_{19}k_6[k_7 + k_8][k_4 + k_{10}K_9(M_c/V_l)]}{M_c/V_l[k_{20} + k_{21}(M_c + M_{A1})/V_l]} \right]^{1/2} (P_{O_2})^{1/2} C_{ph}. \quad (22)$$

duction period behavior using Fig. 2b.

Solution pH could affect the rate through



through involvement in hydrogen peroxide decomposition and/or through altering the phenol environment so as to affect the ease and thus rate of hydrogen radical abstraction. The latter is consistent with known phenol chemistry. The optimum pH for maximum rate is about 4.0 for both the induction period and the steady-state regime.

Steady-state activity regime. The kinetics of the steady-state activity regime can be represented by a model involving phenol hydroperoxide decomposition on the catalyst as an initiation step with propagation in aqueous solution. In the induction period the rate of initiation is low; radical concentrations are probably low and biradical termination is probably not the major chain-termination mechanism. In the more-rapid steady-state activity regime homogeneous termination may become more important due to higher radical concentrations.

Assuming equilibrium between adsorbed hydroperoxide and radicals formed by hydroperoxide decomposition [Eq. (6)]

At low catalyst concentrations, where homogeneous termination would be expected to be important, the predicted rate per unit catalyst is between zero order and minus one-half order with respect to catalyst concentration depending on the relative magnitude of k_4 and $k_{10}K_9(M_c/V_l)$. Inclusion of "self-inhibition" by phenol or reaction products results in a predicted positive order of rate on catalyst concentration.

The observed rate is first order in phenol concentration and one-half order in oxygen partial pressure as predicted from the derived model. At low catalyst concentrations the rate shows approximately positive 0.2 order in catalyst concentration (Fig. 4) which could be explained by a combination of Eq. (21) and some involvement of self-inhibition which would increase the reaction order in catalyst concentration above zero. The exact cause of the increase at low catalyst concentration is not known. At higher catalyst concentrations heterogeneous termination on the surface of the catalyst could become more important or predominant. Equation (22) then predicts a higher negative order on catalyst concentration. The observed order in catalyst

concentration at higher concentrations is about -0.67 which could be explained by a combination of the two propagation and termination modes. If inhibitor is considered and Eq. (12) is used to represent termination, the predicted rate equation for the steady-state activity regime is first order in oxygen partial pressure; and this is in accord with our observations. Further Eq. (22) predicts a very weak dependence of rate on M_{A1} because of its location and the effect of taking the square root, and a very weak dependence of rate on M_{A1} was observed.

CONCLUSIONS

The heterogeneously catalyzed aqueous-phase oxidation of phenol occurs by a free-radical mechanism. Induction periods, which are observed with the supported catalyst, result primarily from the adsorption of a reaction intermediate, proposed to be a hydroperoxide, on the surface of the catalyst support and indicate a free-radical mechanism. Free-radical inhibitors reduce the rate of phenol oxidation by the same relative proportion that they reduce the rate in homogeneous free-radical oxidations. This essentially confirms the involvement of free radicals. Intermediates formed and pH effects further support the free-radical mechanism. The rate per unit weight of catalyst is dependent on the catalyst concentration suggesting that the reaction involves a heterogeneous-homogeneous mechanism.

The kinetics observed in the induction period and in the steady-state activity regime are both consistent with a model involving free radicals with initiation on the catalyst surface, propagation in homogeneous solution and either predominantly homogeneous or heterogeneous termination depending on the catalyst concentration. This is the first report known to the authors of a heterogeneous-homogeneous free-radical mechanism for catalytic oxidation in aqueous solution, and it adds to a growing list of gas- and liquid-phase catalytic oxidation reactions which appear to involve free radicals (14-22, 24, 43-47).

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