JOURNAL OF CATALYSIS 22, 287-296 (1971)

Heterogeneous Catalysis in the Oxidation of p-Xylene in the Liquid Phase

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Received June 23, 1970; revised January 12, 1971

The liquid phase oxidation of *p*-xylene with molecular oxygen has been studied in the temperature range 100 to 130°C. Cobalt$_{\mathrm{II,III}}$ oxide, MnO_2 and ruthenium on alumina were used as catalysts.

Only one methyl group was attacked during the oxidation. As major products of the reaction, *p*-methyl benzyl alcohol, *p*-tolualdehyde, and *p*-toluic acid were identified and quantitatively determined using gas liquid chromatography. Only traces of *p*-methylbenzyl hydroperoxide and 4-4′-dimethylbibenzyl were found.

Product distribution studies at four different temperatures from 115 to 130°C, gave evidence of parallel routes for the formation of the alcohol and the aldehyde.

The oxygen absorption rate showed an auto-accelerating nature and was a function of the aldehyde concentration. The apparent orders with respect to catalyst amount and *p*-xylene concentration were 0.5 and 1.0, respectively. The oxygen absorption rate was independent of the oxygen partial pressure in the range 100 to 800 mm Hg.

INTRODUCTION

Very little has been published to date about the mechanism of *p*-xylene oxidation in the liquid phase in the presence of soluble catalysts such as naphthenates or stearates of transition metals. The information available on the effect of heterogeneous catalysts on the liquid phase oxidation of *p*-xylene is also meagre.

Most of the reported work (*1–3*), relates to the establishment of the optimum conditions for high conversion of *p*-xylene to *p*-toluic or terephthalic acids. In most cases, temperatures between 120 and 180°C and pressures from one to several atmospheres were used.

Previous work carried out by A. Mukherjee (*4*) indicated a similarity between homogeneous and heterogeneous catalysis in the oxidation of tetralin. The present study concerns the conditions under which the oxidation of *p*-xylene can be initiated through the use of transition metal oxides.

EXPERIMENTAL

The reaction was studied in an apparatus similar to that used by Cooper and Melville (*5*), in their investigations of the oxidation of *n*-decanal.

In the present study, the reactor tube was made with a precision smooth tapered joint into which fitted a Teflon-coated inner joint. This provided for a vacuum-tight seal without the use of any lubricants. Prior to each experiment, the reactor tube was heated to redness to burn off any organic impurities and then cooled in a desiccator. This was found necessary for run reproducibility. The proper amount of catalyst was added and then 1 ml of *p*-xylene was introduced and the tube attached to the reaction system. The remaining procedure is the same as that described by Bolland (*6*).

To achieve vigorous agitation of the

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reaction mixture a wrist action shaker was used. Reaction rate measurements were conducted at the highest temperatures of 120 and 130°C at various speeds and amplitudes of shaking. The oxygen absorption rate levelled off at a shaft speed of about 1000 strokes/min. All experiments in the present study were carried out at 1000 rpm shaker speed.

During every experiment, the amount of oxygen absorbed at various times was measured and formed the basis for the kinetic studies along with the composition of the reaction products.

At the conclusion of an experiment, the reactor contents were frozen, to arrest any further reaction and prior to analysis, 9 ml of benzene were added to wash out the catalyst from any precipitated oxidation products. The catalyst was separated by centrifugation and the clear liquid was analyzed for hydroperoxide by sodium thiosulphate titration of the liberated iodine, using the method of Wagner (*7*).

Aldehydes, alcohols, acids, and other oxidation products were determined by glc and infrared analysis as discussed in the analytical section.

Analytical Procedures

Preliminary qualitative and semiquantitative experiments in the oxidation of *p*-xylene in the presence of cobalt oxide in the temperature range 80–120°C gave evidence for the presence of carbonyl-containing compounds as the main reaction products. The infrared spectrum of an oxidized mixture showed a strong absorption band at a wave number of 1670 to 1740 cm^{-1}. No significant absorption band for an —OH group (in free or associated form) was observed when the concentration of the sample was in the range of 0.1 to 0.5% active compounds and a cell path length of 0.1 mm. The presence of more than one carbonyl group containing compound among the reaction products, aldehydes and acids, made impractical the quantitative resolution of the C–O band into the component contributions.

No absorption band characteristic of the presence of a hydroxide group was observed. This band around 3500 cm^{-1} was very evident in the case of the autoxidation of *p*-xylene at the boiling point (*8*).

There is little information in the literature about the analysis of the reaction products of *p*-xylene oxidation by glc. Frederick Baumann (*9*) reported the analysis of xylene oxidation products obtained in a high-temperature vapor-phase process, using an asphalt liquid phase on chromosorb P.

A more satisfactory gas chromatography column was developed for the analysis of the *p*-xylene oxidation products using a highly polar liquid phase available from Wilkens Research under the name FFAP.

Gaschrom Q, mesh 80/100 from Applied Science Laboratories was the inert support with 12% loading of FFAP. Two columns, 9 ft by ⅛ in. o.d. were made and conditioned for several hours at 240°C with a helium flow of 40 cm^3/min. The details for column preparation and the complete analysis conditions and column calibration are given elsewhere (*8*).

All five injected components, *p*-xylene, *p*-tolualdehyde, terephthalaldehyde and methyl esters of *p*-toluic and terephthalic acids have been successfully separated without significant tailing, with a total analysis time of 8 min. To improve the separation of the *p*-tolualdehyde and methyl-*p*-toluate peaks a helium flow rate of 46 ml/min was used with a temperature programming rate of 10°C/min starting at 190 up to 230°C.

The gas chromatographic analysis was carried out in two steps as follows:

1. The reaction products were analyzed directly after washing the catalyst-products mixture with benzene and catalyst separation, for aldehydes, hydrocarbons, and alcohols. The aromatic acids eluted very slowly and were obtained after 8 min with considerable tailing and had to be converted to esters for quantitative analysis.

2. The reaction products mixture was quantitatively esterified using an all-ethereal solution of diazomethane to give the methyl esters of any acids present. Diazomethane was found to react to a limited extent with the aldehydes in the oxidized mixture to give an apparently higher homolog. Thus a one-step analysis after product esterification was found to be inaccurate and was only used for qualitative identification purposes.

Chemicals used in the calibration of the gas chromatographic method were as follows:

p-Tolualdehyde from Aldrich Chemical Co., which was distilled three times in a nitrogen atmosphere and kept subsequently in a refrigerator. It was analyzed for aldehyde by a gravimetric precipitation method using 2,4-dinitrophenyl hydrazine as the precipitant. Its purity was found to be 97.5%.

Methyl *p*-toluate, an Eastman Kodak technical grade chemical, was found to be 98.7% pure, by determination of its saponification number.

p-Tolyl carbinol, was synthesized in the laboratory and was purified by recrystallization in heptane. Its melting point was 61°C (*8*).

4,4′-Dimethylbibenzyl, was synthesized using the procedure of C. Moritz (*10*).

The terephthalaldehyde and dimethyl terephthalate used were reagent grade chemicals from Eastman Kodak.

RESULTS

Initiation of the p-Xylene Oxidation

Most of the reported studies on homogeneous *p*-xylene oxidation in the liquid phase were carried out in the temperature range of 100–135°C; it was thus decided to investigate the heterogeneous catalytic effect of various metallic oxides on *p*-xylene oxidation between 100 and 130°C.

A series of preliminary runs with oxides such as CoO, Co_3O_4, MnO_2, NiO, Cu_2O, CuO, and V_2O_5 has shown that Co_3O_4 and to a lesser extent MnO_2 initiated the oxidation at 100–130°C. The induction periods for the other oxides were found to be very long; no oxygen absorption could be observed for several hours. Co_3O_4 was chosen on this basis for the main studies.

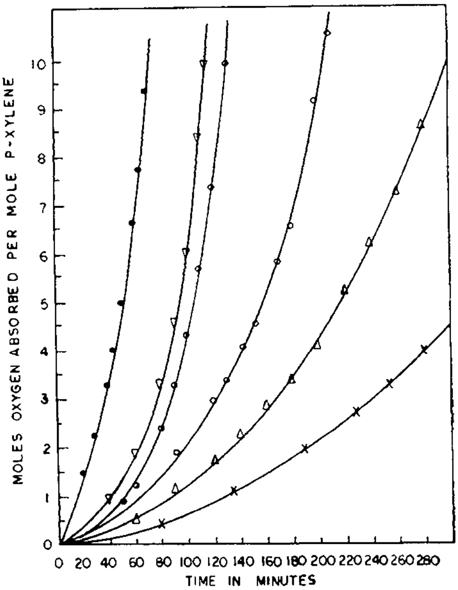


FIG. 1. Oxygen absorption curves at 120°C for *p*-xylene as a function of catalyst amount (g/ml): ●, 1.0, ▽, 0.2, ◐, 0.1, ○, 0.05, △, 0.025, ×, 0.01.

Figure 1 shows oxygen absorption curves obtained with the Co_3O_4 at 120°C as a function of catalyst amount per unit volume of *p*-xylene. The maximum absorption rates, as measured by the tangent to the absorption curve levelled off when more than 200 mg of catalyst were used per milliliter of *p*-xylene.

A plot of the average oxygen absorption rate vs catalyst amount (Fig. 2) on a logarithmic scale, gave a linear relationship for catalyst amounts up to 200 mg/ml. The slope was 0.5 ± 0.05. If we consider only the catalyst amounts up to 100 mg the slope is 0.60 ± 0.05.

Any catalyst amount above 200 mg had only the effect of shortening the induction period. At high catalyst amounts it might be considered that a less efficient use is made of the catalyst as a result of catalyst agglomeration.

The oxygen absorption rates measured in the present study with Co_3O_4 were higher by a factor of four than those reported by K. Kanai (*3*). In his studies of the liquid-phase oxidation of *p*-xylene

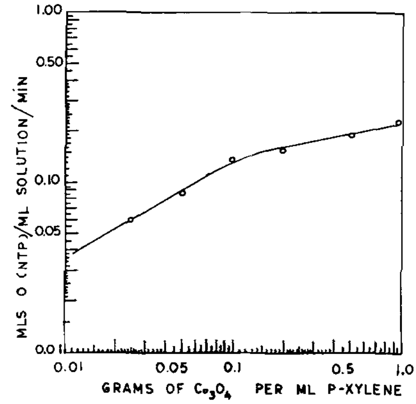


FIG. 2. Logarithmic plot of oxygen absorption rates vs catalyst amount for the Co_3O_4.

in the presence of Onium Salt-type catalysts, maximum rates of 0.025 moles O_2/mole *p*-xylene/hr were measured at 120°C.

The oxygen absorption rates with Co_3O_4 compare very well with those obtained in the cobalt stearate-catalyzed oxidations conducted in our laboratories (Fig. 3). The oxidation rates levelled off at catalyst concentrations of 10^{-3} moles/liter.

It is difficult to compare results obtained in homogeneous and heterogeneous catalysis due to lack of a term analogous to catalyst concentration in a homogeneous one-phase system which describes a two-phase solid–liquid system.

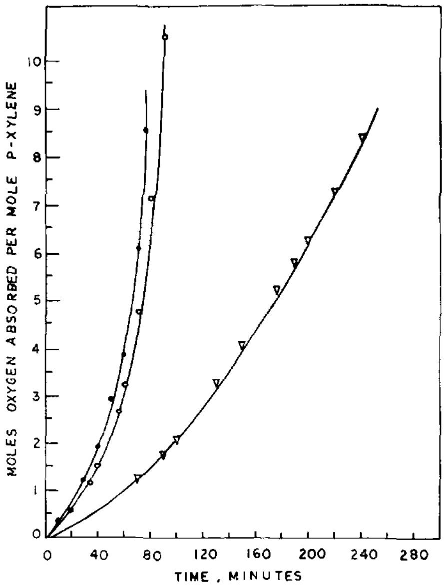


FIG. 3. Comparison of O_2 absorption curves at 120°C for *p*-xylene. Co Stearate, ●, $5/3 \times 10^{-3}$ g-mole/liter; ○, $5/3 \times 10^{-5}$ g-mole/liter; Co_3O_4, ▽, 0.5 g/ml.

Some authors (*4*) attempted to explain these analogies by suggesting that "homogeneous catalysts" were in fact, heterogeneous and in a colloidal state.

Importance of Catalyst Amount to Liquid Volume Ratio

Figure 4 shows O_2 absorption curves in which the catalyst amount and the volume of *p*-xylene were both varied while the ratio S/V of catalyst surface to liquid volume was constant. It can be seen that the rates of oxygen absorption given by the tangents to the curve are constant for the same S/V ratio. Since it was experimentally found that the oxygen absorption rate is of 0.5 to 0.60 order with respect to catalyst amount we can now express the rate of oxygen absorption in the form,

$$\frac{d(O_2)}{dt} = k\left(\frac{S}{V}\right)^{0.5}(RH)^{\alpha},$$

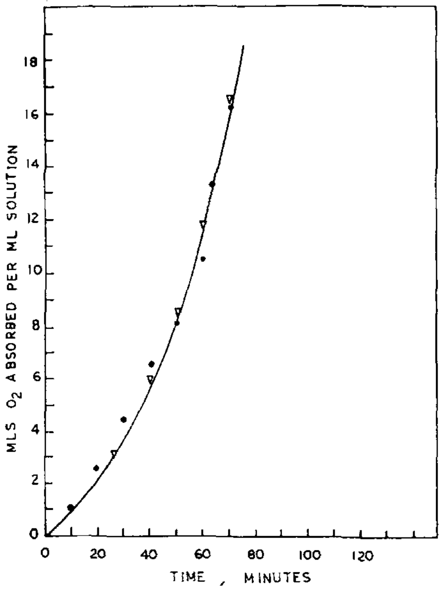


FIG. 4. Effect of catalyst amount to *p*-xylene volume on the O_2 absorption rate. ●, 0.5 g Co_3O_4/ 1 ml *p*-xylene, △, 2.5 g Co_3O_4/5 ml *p*-xylene.

where α is the reaction order with respect to the *p*-xylene concentration.

The significance of the fractional order with respect to catalyst surface area per unit hydrocarbon volume merits further discussion. For an entirely heterogeneous oxidation this order would be one while it would be zero for a homogeneous oxidation.

The fractional 0.5 order can be explained by assuming that the initiation reaction is of first order with respect to catalyst area while the termination of the chains occurs by bimolecular recombination of peroxy radicals and is homogeneous, thus independent of the presence of the Catalyst M.

$$RH + M \xrightarrow{k_1} R\cdot + (M - H),$$

$$RO_2\cdot + RO_2\cdot \xrightarrow{k_6} \text{reaction products}.$$

Using the Bodenstein-Semenov postulate of stationary radical concentrations we get

$$k_1(M)(RH) = k_6(RO_2\cdot)^2,$$

which when introduced in the classical equation for a propagation step gives

$$\frac{d(O_2)}{dt} = k(M)^{\frac{1}{2}}(RH)^{\alpha}$$

Here (M) stands for $\frac{S}{V}$.

A fractional order with respect to catalyst surface area was found by other workers (*11*) in their studies of cyclohexene and tetralin oxidation.

Effect of Catalyst Removal

Experiments were carried out in which the oxidation was allowed to proceed until varying amounts of oxygen were absorbed; then the reaction was discontinued and the catalyst separated by centrifuging.

Figure 5 shows the oxygen absorption before and after catalyst separation. It can be readily seen that in all cases the oxygen absorption rate decreased and after a time levelled off at some low value. When the extent of conversion was higher than 5–7%, the oxygen absorption continued at a rate equal to ¼ to ⅕ of the maximum rate observed before catalyst separation. The fact that no substantial catalytic effect was observed after catalyst separation discounted any possibility of homogeneous catalysis brought about by catalyst dissolution by the reaction medium.

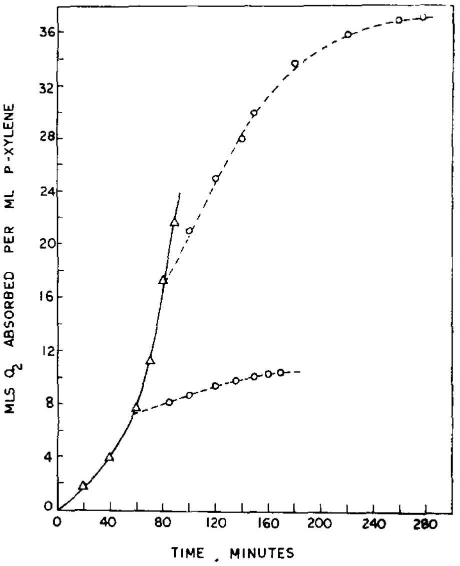


FIG. 5. Oxygen absorption rates after catalyst removal from a progressing oxidation at various stages: △, with catalyst, ○, after catalyst removal.

The sustaining of oxygen absorption after catalyst separation is probably due to the autoxidation of *p*-xylene catalyzed by the aldehyde and acid present after catalyst removal. This is in agreement with the results of Bradley (*12*) ,who found that *p*-toluic acid acts as a catalyst in the autocatalytic decomposition of *p*-methyl benzyl hydroperoxide.

Effect of Oxygen Pressure

Oxygen absorption data were obtained at 120 and 130°C under oxygen partial pressures ranging from 80 to 500 mm Hg. Figure 6 shows the results obtained at 120°C with 0.5 g of Co_3O_4/ml *p*-xylene. No dependence on oxygen pressure was found for pressures higher than 200 ± 25 mm Hg. This is in agreement with the results of Clement and Balaceanu (*11*). In their study of the heterogeneous initia-

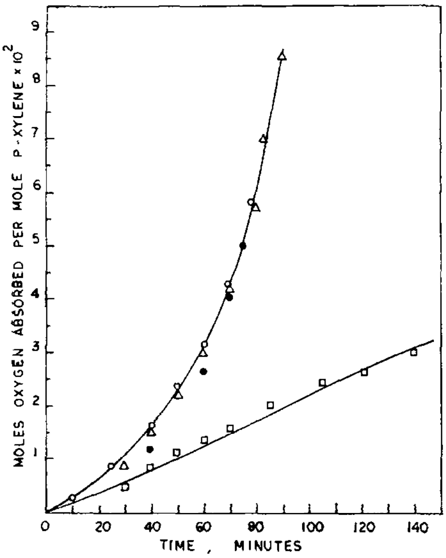


FIG. 6. Effect of oxygen partial pressure on the O_2 absorption curves of *p*-xylene at 120°C with Co_3O_4 (0.5 g/ml). O_2 partial pressures: ○, 500 mm Hg, △, 400 mm Hg, ○, 200 mm Hg, and □, 80 mm Hg.

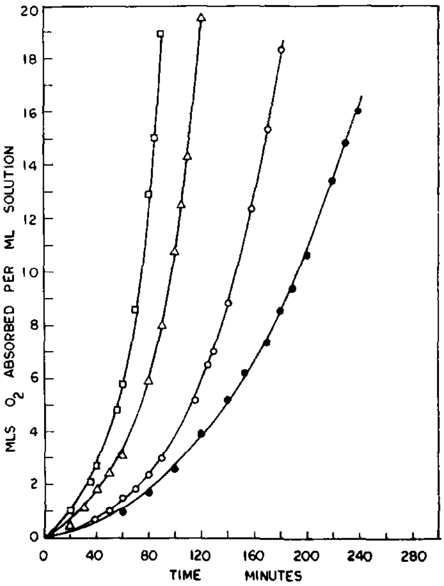


FIG. 7. Effect of *p*-xylene concentration (solvent: bromobenzene) on the O_2 absorption rate. Molarities: □, 8.15, ▽, 6.12, ○, 4.08, ●, 3.06.

tion of the oxidation of cyclohexene, tetralin and styrene with MnO_2 and Cr_2O_3, they found a zero order with respect to oxygen for O_2 pressure higher than 100 mm Hg.

The oxidation rate shows a dependence on oxygen pressure when the concentration of dissolved oxygen is low. This could be due either to a slow rate of dissolution of oxygen in which case the reaction is in the diffusion controlled range or due to a low partial pressure of oxygen. In the latter case, the rate of oxidation is proportional to the oxygen partial pressure. In Fig. 6, it can be seen that such a dependence on oxygen pressure is true for an oxygen partial pressure of 80 mm Hg.

Effect of p-Xylene Concentration

The dependence of the rate of oxidation on hydrocarbon concentration was studied using two inert diluents, *p*-dichlorobenzene and bromobenzene. The oxygen absorption data, as well as the dependence of the average oxidation rate on hydrocarbon concentration are shown in Figs. 7, 8. Due to the autocatalytic character of the reaction, in order to compare the rates at different *p*-xylene concentrations, it was necessary to obtain average values for oxygen absorption rates between intervals corresponding to the same amount of oxygen absorbed. In Fig. 8 the rates measured at varying degrees of oxidation are plotted versus the *p*-xylene concentration in bromobenzene. Each line in Fig. 8 connects points from Fig. 7 that correspond to the

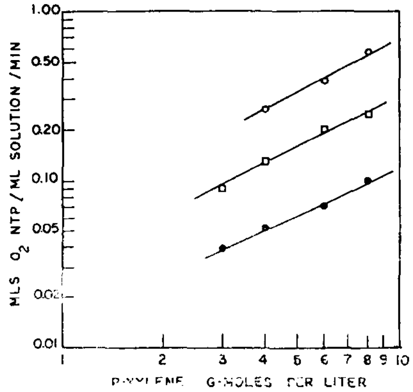


FIG. 8. Co_3O_4 activated oxidation of *p*-xylene at 120°C. Logarithmic plot of O_2 absorption rate vs *p*-xylene concentration. Each line connects points corresponding to the same amount of O_2 absorbed per ml solution. Average slope 0.96 ± 0.02.

same degree of oxidation. Thus the three lines represent three different degrees of oxidation. There is no correspondence of symbols between Figs. 7 and 8.

All lines are parallel with an average slope equal to 0.96 ± 0.02. With *p*-dichlorobenzene, the order was found to be 1.24. When the molarity of the *p*-xylene was 2 or less, the oxidation proceeded after very long induction periods. For this reason, measurements were limited to the concentration range 8.15–3.05 moles/liter.

Temperature Dependence of the Oxygen Absorption Rate

Experiments were carried out with pure *p*-xylene and Co_3O_4 (0.5 g/ml) in the temperature range 100–130°C. Temperatures below 100°C were not used due to the very long induction periods involved and the low oxygen absorption rates. The upper temperature was limited by the oxygen partial pressure requirement of 200–225 mm Hg which would have demanded a total pressure of 1000 mm Hg at 138°C. The manostatic apparatus was found to operate unsatisfactorily above 900 mm Hg.

For the calculation of the data necessary for the Arrhenius plot, average rates were calculated for different extents of O_2 absorption and plotted vs I/T on a semilogarithmic paper. The slope of the lines corresponding to the variation of average instantaneous rates with temperature, for varying conversions, varied between narrow limits, corresponding to an overall activation energy of 18 ± 2 kcal/mole (Fig. 9).

This is an apparent overall activation energy for the rate of oxygen absorption. Since all the experiments in this study were carried out in the kinetic control region the overall apparent activation energy of oxygen absorption is not a function of the rate of oxygen dissolution in the solvent phase.

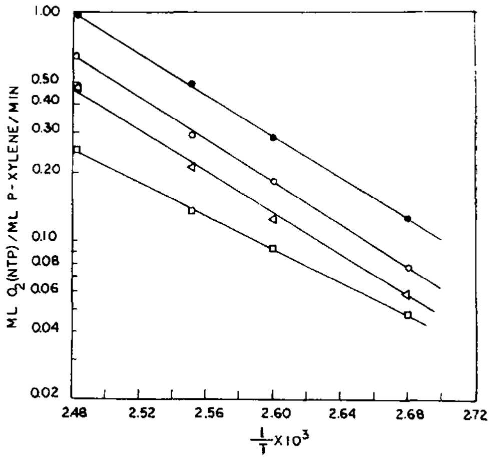


FIG. 9. Arrhenius plot of O_2 absorption rates for *p*-xylene with 0.5 g/ml Co_3O_4. Each line connects points corresponding to the same amount of O_2 absorbed per ml *p*-xylene.

It can be shown (*8*, *15*) that the overall activation energy, E_{ov} of a chain reaction in which chain termination occurs mainly by recombination of peroxy radicals, $RO_2\cdot$

$$E_{ov} = \tfrac{1}{2}E_i + E_p - \tfrac{1}{2}E_t,$$

that where E_i, E_p, and E_t are the activation energies for chain initiation, chain propagation, and chain termination, respectively.

Using bond-energy data, we can calculate E_p for *p*-xylene oxidation to be 8.0 kcal/g mole (*8*). E_t for the bimolecular recombination of radicals such as $R\cdot$, or $RO_2\cdot$ is very low, and according to Emanuel (*15*) of the order of 1–2 kcal/g-mole. The activation energy for the Co_3O_4-catalyzed initiation step of *p*-xylene oxidation is not known. To carry out the above estimation of E_{ov} we will assume E_i for the Co_3O_4-catalyzed oxidation of *p*-xylene to be close to the value obtained by C. E. Bawn (*16*) in his study of the cobalt-catalyzed oxidation of benzaldehyde, i.e., $E_i = 14.8$ kcal/g-mole.

Thus, $E_{ov} = (14.8)\tfrac{1}{2} + 8.0 - 2/2,$
$E_{ov} = 14.4$/kcals/g-mole.

This value is close to the experimentally determined value of 18 kcal/g mole.

Product Distribution Studies

Several experiments were carried out using the same catalyst, 0.5 g/ml Co_3O_4, at temperatures from 115 to 130°C. In every run the reaction was allowed to proceed until varying amounts of oxygen

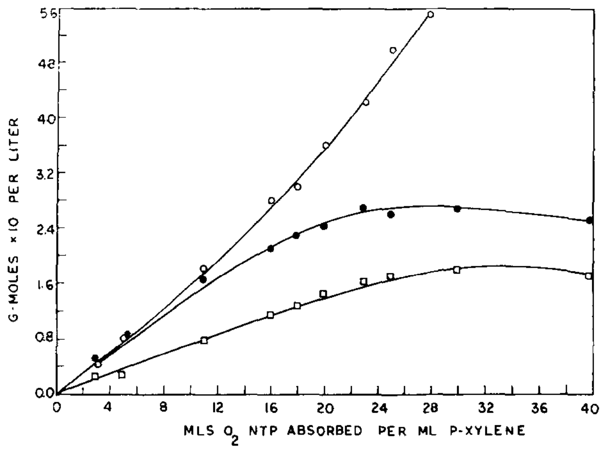


FIG. 10. Product distribution curves in the Co_3O_4-catalyzed oxidation of *p*-xylene (0.5 g Co_3O_4/ml; 120°C). ○, *p*-toluic acid, ●, *p*-tolualdehyde, and □, *p*-methyl benzyl alcohol.

were absorbed. Then the reaction was stopped, the reaction contents diluted with benzene to 10 ml, and analysis by gas chromatography was carried out. Titration with $Na_2S_2O_3$ revealed only traces of *p*-methyl benzyl hydroperoxide.

Some experiments were also carried using cobalt stearate as catalyst.

Examination of the product distribution curves (Figs. 10 and 11) reveals the following:

(a) There is a striking similarity between the homogeneous and heterogeneous reactions. The main difference between the two types of catalysis lies in the relative magnitudes of the rates of formation of the reaction products. A quantitative comparison can only be made if one could carry the oxidations with the same effective concentration of cobalt catalyst. This was not possible in our study.

(b) The alcohol and aldehyde appear to result from a parallel set of reactions.

(c) There is a steady-state concentration for the aldehyde which corresponds to the stage of the reaction at which the rate of formation of the aldehyde becomes

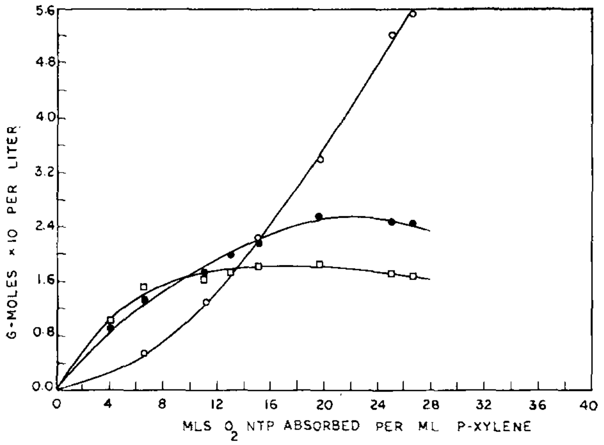


FIG. 11. Product distribution curves in the Co stearate-catalyzed oxidation of *p*-xylene (120°C). ○, *p*-toluic acid, ●, *p*-tolualdehyde, □, *p*-methyl benzyl alcohol. Co stearate concn ($5/3 \times 10^{-3}$ g-mole/liter).

equal to the rate of its further oxidation to *p*-toluic acid.

(d) The formation of the acid follows an *s*-shaped curve typical of an autocatalytic reaction.

(e) The concentration of hydroperoxide formed during the Co_3O_4-catalyzed oxidation of *p*-xylene, is very low and reached a maximum value before the attainment of maximum oxidation rate.

Chervinskii *et al.* (*13*), who studied *p*-xylene oxidation using cobalt stearate as a homogeneous catalyst, also reported low hydroperoxide concentrations. Their product distribution curves for 110°C show a maximum hydroperoxide concentration of 0.015 moles/liter attained 90 min after the start of the reaction.

To study the evolution of the concentration of hydroperoxide, experiments were carried out at low conversion levels. The experimental conditions and the results are summarized in Table 1.

TABLE 1

RESULTS OF THE STUDY OF THE EVOLUTION OF CONCENTRATION OF HYDROPEROXIDE[a]

Run No.	1	2	3	4	5	6
Reaction time (min)	5	10	15	30	45	60
Products	Concentration (g-mole/liter × 10^2)					
p-Tolualdehyde	1.000	1.625	2.170	3.420	4.000	5.000
p-Tolyl Carbinol	0.303	0.557	0.985	1.970	2.375	3.360
p-Toluic Acid	Trace	0.133	0.187	0.467	0.934	1.870
4,4′-DMBB (%)	Trace	Trace	0.011	0.020	0.024	0.040
Hydroperoxide	0.250	0.400	0.500	0.575	0.650	0.550
Total O_2 absorbed per ml *p*-xylene (ml NTP).	0.075	0.185	0.438	1.163	1.875	2.640

[a] Conditions of the experiment were as follows: Volume of *p*-xylene, 4 ml; weight of catalyst, 0.500 g; temperature, 120°C, oxygen pressure, 800 mm Hg; and shaker speed, 1050 rpm.

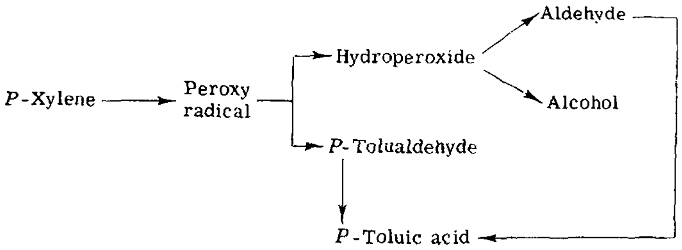
Thus, the maximum hydroperoxide concentration was obtained after 45 min reaction time, and was equivalent to 0.0065 mole/liter. This was about half of that reported by Chervinskii (*13*). His results were for 110°C and for soluble cobalt catalysis. Temperature could not account for the difference in maximum concentration, due to the high thermal stability of the hydroperoxide (*14*). The catalytic decomposition of *p*-methyl benzyl hydroperoxide appears to occur with a higher effectiveness on the cobalt oxide surface.

Aldehyde to Alcohol Ratio

At the very early stages of the reaction, when only trace amounts of acid were formed, the ratio of aldehyde to alcohol was close to 3 ± 0.5. The same ratio was found in another series of runs at 120°C with 0.1 g/ml of Co_3O_4, with conversions of 0.18–0.5% (based on *p*-xylene).

In experiments where *p*-methyl benzyl hydroperoxide was prepared by autoxidation (*8*), and then decomposed by the Co_3O_4 catalyst in a nitrogen atmosphere, the ratio of aldehyde to alcohol was very close to $\frac{1}{1}$. There is thus good evidence of a parallel route of aldehyde formation which proceeds independently from that of hydroperoxide decomposition. If alcohol was an intermediate for aldehyde formation, the ratio of concentrations of aldehyde to alcohol would have approached zero at very low conversions. This was not the case in the present investigations.

On the basis of the previous considerations, the following sequence of reaction steps is suggested:



Further oxidation of the alcohol to the aldehyde was found to proceed very slowly (*8*). The rate was found to be 0.2×10^{-4} g-mole/hr. Thus, aldehyde formation via further alcohol oxidation could account only for 10% of the total aldehyde formed (*8*).

Effect of Temperature

Increasing the temperature from 115 to 130°C resulted in an increase in the maximum concentrations of alcohol and aldehyde. Although the effect is small, it is significant. It shows that the activation energies of formation of those two products from *p*-xylene are slightly higher than those of the reactions of their further oxidation. This difference in activation energies of formation and consumption, is about 3 kcal/mole for the alcohol and 2.0 for the aldehyde.

CONCLUSIONS

1. Cobaltosic oxide (Co_3O_4) was found to be an effective heterogeneous catalyst for the oxidation of *p*-xylene in the liquid phase, in the temperature range 100–130°C.
2. The oxygen absorption curves showed similar characteristics in homogeneous and heterogeneous cobalt catalysis.
3. *p*-Methyl benzyl hydroperoxide was obtained only in trace quantities while *p*-toluic acid, *p*-tolyl carbinol, and *p*-tolualdehyde were the main products.
4. The alcohol and aldehyde appeared to result from a set of parallel reactions.
5. The oxygen absorption rate was found to be proportional to the square root of the ratio of catalyst amount to the volume of *p*-xylene; proportional to the first power of *p*-xylene concentration and independent of oxygen pressure in the range of 100 to 1000 mm Hg of oxygen partial pressure.
6. The apparent overall activation energy for the oxygen absorption was found to be 18 ± 2 kcal/g mole.

ACKNOWLEDGMENTS

The authors are indebted to the National Research Council, Ottawa and the President's Advisory Committee on Scientific Research, University of Toronto, for financial support.

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