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Reaction Networks in the Catalytic Vapor-Phase Oxidation of Toluene and Xylenes

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A reaction network for catalytic oxidation of toluene is constructed from a collection of product patterns over a variety of metal oxide catalysts, and by also considering known organic reactions. The treatment is extended to *o*-, *m*-, and *p*-xylene with data from the literature. The reaction mechanisms of the initial steps in oxidation of toluene are discussed. © 1986 Academic Press, Inc.

INTRODUCTION

The catalytic oxidation of aromatic hydrocarbons over metal oxides involves complex processes showing a variety of products under different conditions. For example, in the catalytic oxidation of *o*-xylene about 15 products were identified (*1*, *2*) and for toluene about 10 (*3*). Other papers provide evidence for even more products and in the case of toluene oxidation 23 products were identified in the work to be described in this paper. Thorough discussions of complete reaction schemes, however, seldom appear in the literature. One reason is that in most practical cases, in kinetic studies for example, only the major occurring species need be considered. In addition much attention is paid to the catalyst itself, concerning its physical and chemical properties in relation to the catalytic effects. The catalytic processes, however, also contain much that is organic chemistry. Knowledge on feasible reactions for various intermediates allows construction of reaction paths and networks for these complex reactions. Such information is valuable in the selection of feasible schemes in kinetic studies and in studies on reaction mechanisms.

In the present study reaction networks based on products identified in the catalytic oxidation of toluene and known reactions for intermediates are constructed. The complete networks of feasible reactions are then based on data for different catalysts and process conditions. It should be noted that this gives no quantitative information as to the occurrence of different products under various conditions. To illustrate the general complexity in the oxidation of alkylaromatics, the xylenes are also considered. Finally, the initial step reaction mechanisms are discussed on the basis of knowledge both from heterogeneous catalysis and organic chemistry.

EXPERIMENTAL

Details of the catalytic studies are reported elsewhere (*4*). Condensates collected from several experiments of oxidation of toluene over metal oxides were analyzed on a conventional Finnegan GLC-MS system. The analytical column was as reported elsewhere (*5*) and the identification of the compounds by their mass spectra was performed with the computer, except for products 8, 10, 11, and 12 of Fig. 1, which were identified by their retention times.

RESULTS

In Fig. 1 23 products of vapor-phase catalytic oxidation of toluene, identified by GLC-MS, are shown. It was not possible to identify product 1 definitively, because of

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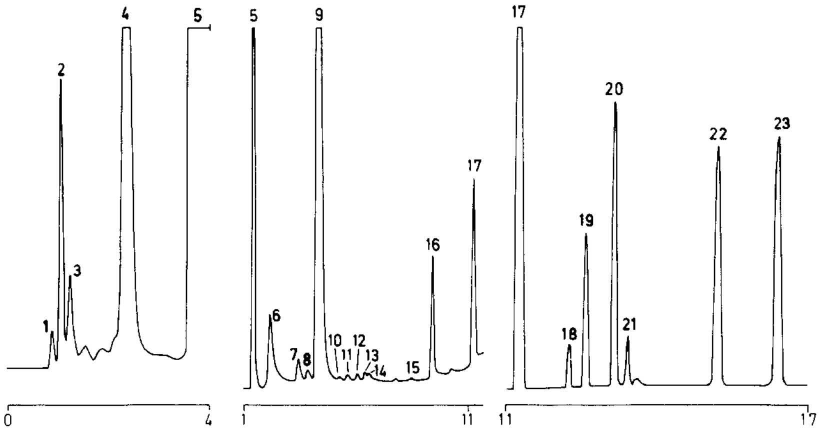

FIG. 1. Chromatogram assembled from injections of three different product condensates obtained from the catalytic oxidation of toluene over various metal oxides. (1) Unidentified, (2) pentadiene, (3) furan, (4) benzene, (5) toluene, (6) maleic anhydride, (7) benzoquinone, (8) citraconic anhydride, (9) benzaldehyde, (10) phenol, (11) toluquinone, (12) benzylic alcohol, (13) *o*-cresol, (14) *m*-, *p*-cresol, (15) benzoic acid, (16) phthalic anhydride, (17) *o*-methyl-diphenylmethane, *p*-methyl-diphenylmethane, and bibenzyl, (18) benzophenone, (19) *o*-methyl-diphenylmethanone, (20) *p*-methyl-diphenylmethanone, (21) diphenylethanone, (22) diphenylethandione, (23) anthraquinone.

interference with contaminants of the vacuum in the mass spectrometer. It was, however, quite clear from the catalytic studies that components 1, 2 (pentadiene), and 3 (furan) were formed in measurable quantities only when component 4 (benzene), was formed in large quantities, that is at higher temperatures over some catalysts (*4*). In these cases ethylene was identified in samples of the gas phase leaving the condensers. It is apparent that components 1,2,3,ethylene and benzene are connected in some way. Some of these are likely to form under "cracking" conditions and are not included in the present discussion on oxidation schemes. The other components formed are given in Fig. 1.

Concerning the isomers *o*- and *p*-methyl-diphenylmethane and bibenzyl these could not be identified separately. Unfortunately, both the retention time and the mass spectra of these three are almost identical. However, the oxidation products of these compounds were identified and their formation is probable. Some products not found in this study have been reported elsewhere. These are: acetic acid, (*6, 7*) (identified with MS); bibenzyl and stilbene (*8*); trans-stilbene (*9*); and *o*-formyl-diphenylmethane (*3*).

DISCUSSION

Reaction Network in Toluene Oxidation

In the catalytic oxidation of toluene three parallel reaction paths have been recognized earlier (*3*). The first and most important reaction path (Route 1) is the one initiated by attack on the methyl group with subsequent oxidation steps. The second path is also initiated by attack on the methyl group but with subsequent oxidative coupling (Route 2) forming dimers that are oxidized further. This path may give up to 30% of the products (*4*). The third reaction path (Route 3) is due to direct oxidation in the aromatic nucleus and occurs to a very low extent, less than 1% (*4*), and is almost negligible.

Route 1. The various products of Route 1 are arranged in a set of subsequent reactions as shown in Fig. 2. These appear in a logical order and the scheme is consistent with the known products from the various intermediates as shown in Table 1. Route 1 is presented as a "rake" mechanism which seems to be of some validity in hy-

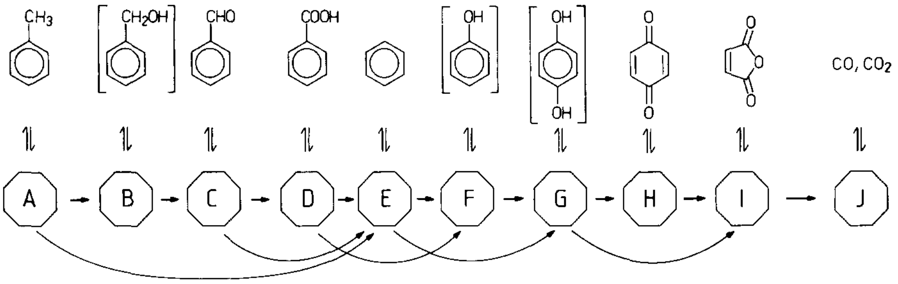

FIG. 2. "Rake" mechanism of Route 1 in the catalytic oxidation of toluene. Compounds within parentheses have only been observed in trace quantities.

drocarbon oxidation reactions (*16, 17*). The various surface intermediates may desorb forming the corresponding product or react further to a higher oxidized adsorbed intermediate, and so on. The adsorption–desorption arrows for the various products are drawn merely to underline the importance of the adsorbed species. Under reaction conditions no true adsorption–desorption equilibria are expected. The stability of the various products should also be considered. For example, benzene is a fairly stable compound compared with the other intermediates and it is uncertain to what extent desorbed benzene reacts further in this system. Van der Wiele and van den Berg (*18*) obtained negligible conversion of benzene at the same conditions as giving 50% toluene conversion. Furthermore, the multitude of combination of sites and intermediates indicates a more complex picture and Fig. 2 shows probably a rough simplification.

TABLE I

Products Obtained from Various Intermediates of Routes 1 and 3 in the Catalytic Oxidation of Toluene over Metal Oxides

Reactant	Partial oxidation products	Ref.
Route 1		
Maleic anhydride	None	(*10*)
Furan	Maleic anhydride	(*10, 11*)
Benzoquinone	Maleic anhydride	(*13*)
Hydroquinone	Maleic anhydride, benzoquinone	(*13*)
Phenol	Benzoquinone, maleic anhydride	(*15*)
Benzene	Maleic anhydride, benzoquinone, phenol	(*12*)
Benzene	Same plus hydroquinone	(*14*)
Benzylic alcohol	Benzaldehyde, benzoic acid, benzoquinone, maleic anhydride	(*15*)
Benzaldehyde	Benzoic acid, benzoquinone, maleic anhydride	(*15*)
Route 3		
o-, *m*-, *p*-Cresol	Citraconic anhydride, maleic anhydride, acetic anhydride, salicylic aldehyde	(*7, 27*)
Citraconic anhydride	Acetic acid	(*27*)
Maleic anhydride	None	(*10*)

Some comments should be made concerning the reaction sequence of Route 1. There are some alternative reactions indicated by bent arrows in Fig. 2.

The first represents dealkylation of toluene which could occur to some extent considering the detection of "cracking" products as ethylene and pentadiene, but should perhaps not be included in an oxidation scheme.

The second arrow shows the decarbonylation of benzaldehyde to benzene which was observed in pulse experiments with toluene/N_2 mixtures producing benzene, CO, and water almost stoichiometrically (*19*).

The third arrow is made by analogy with metal-ion-catalyzed decarboxylation of fatty acids in the liquid phase (*20*). It is then assumed that phenyl radicals are produced at the decarboxylation. The phenyl radical may then take up a hydrogen atom forming benzene (species E in Fig. 2) or a hydroxyl radical forming phenol (species F in Fig. 2). The last two arrows are based on a benzene oxidation study (*13*) indicating the initial formation of hydroquinone which then reacts to *p*-benzoquinone or maleic anhydride, whereas oxidation of *p*-benzoquinone gives a low yield of maleic anhydride.

Route 2. The second reaction path, Route 2, is the most diversified one (see Fig. 3). The initial step is an oxidative coupling of two toluene molecules producing three isomers. Of these, *o*-methyl-diphenylmethane appears to be the most important one and *p*-methyl-diphenylmethane the least. For some catalysts giving oxidative coupling, only this first step is obtained, whereas for other catalysts a subsequent oxidation in a stepwise manner is also obtained (*4*). Then various partially oxidized products are formed as shown in Fig. 3.

The methyl-diphenylmethanes both appear to react initially at the methylene groups forming the corresponding ketones. Thereafter, the methyl groups are oxidized and decarboxylated due to the activating effect of the keto group in the *ortho* and *para* positions. The benzophenone is assumed to decompose into molecules belonging to Route 1 upon further oxidation. In this work partially oxidized diphenylmethanes containing keto groups were the only intermediate products observed. However, occasionally a few other small peaks that were not identified appeared in the chromatograms at positions corresponding to compounds of 200–300°C boiling point. Possibly, these were due to traces of other partially oxidized diphenylmethanes containing hydroxy and aldehyde functions.

The third isomer, bibenzyl, first forms diphenylethanone, which is oxidized further to benzil (diphenylethandione). Formation from benzaldehyde by benzoin condensation, as known in organic chemistry (*21*), is of no importance in vapor-phase catalysis. Otherwise it should have been formed when starting with benzaldehyde as reactant (*15*). The next step is probably a splitting of some bond in the ethanedione part giving benzaldehyde and benzoic acid (*15*) passing to Route 1.

The route to anthraquinone (upper part

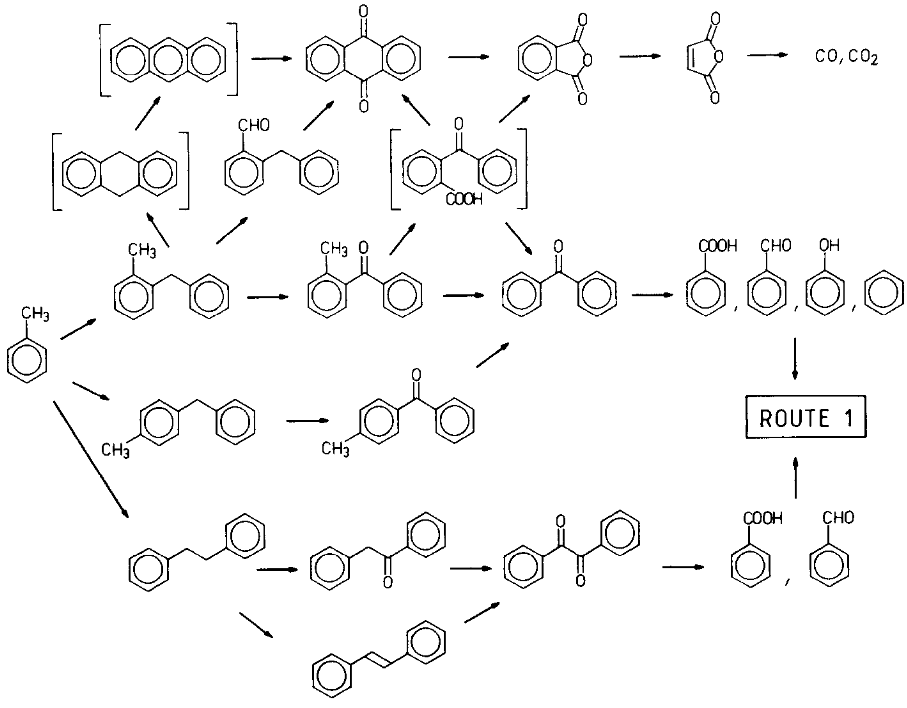

FIG. 3. Oxidative coupling reactions in toluene oxidation, Route 2. Compounds within parentheses have not been identified.

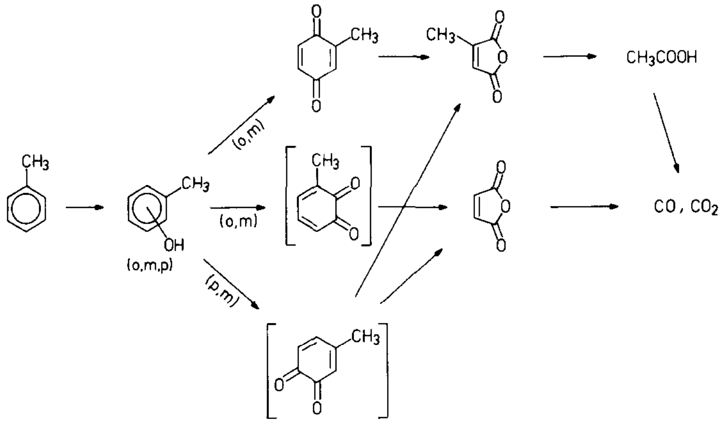

FIG. 4. Reaction scheme of Route 3 in the catalytic oxidation of toluene. The *o*-toluquinones have not been observed.

of Fig. 3) is a matter of discussion. It is well known that it is not easily formed by condensation from simpler molecules. It could not be identified in the catalytic oxidation of benzylic alcohol (*22*), benzaldehyde (*22*), or *o*-cresol (*7*), but there are contradictory results reporting anthraquinone in benzaldehyde oxidation products (*19*). Consequently, it is assumed that a small part of anthraquinone may be due to condensation from benzaldehyde and that the main part is from the oxidative coupling route. Since anthracene is easily oxidized to anthraquinone in large yields (*23*) it seems natural to assume that one path is from *o*-methyl-diphenylmethane by an oxidative cyclization to form dihydroanthracene, which is the precursor to anthracene. These species may be very reactive (*23, 3*), which would explain why they have never been reported in the literature. However, there is a second possibility which in fact is suggested to be of major importance. Acid-catalyzed formation of anthraquinone from *o*-benzoylbenzoic acid is known in organic syntheses (*24*). It is very plausible that this reaction is also occurring in vapor-phase catalysis. Morita (*25*) observed that when increasing the length of the side chain of alkylbenzene to three or more carbon atoms, phthalic anhydride was formed in the catalytic oxidation. Evidently, a cyclization is obtained if a side chain carbon atom is geometrically allowed to come close to the *ortho* position without to much force. Most likely this is the case for *o*-methyl-diphenylmethanone. In fact, a very recent patent (*26*) claims yields of 91.8% anthraquinone, 4.5% phthalic anhydride, and 4% carbon oxides in vapor phase oxidation of *o*-methyldiphenylmethanone over a vanadium oxide catalyst at 380°C. This compound is also the natural intermediate for the formation of benzophenone.

Finally, the paths to phthalic and maleic anhydride are well known. Phthalic anhydride is obtained from anthraquinone (*23*) and phthalic anhydride is in turn oxidized to maleic anhydride (*1*) which finally forms carbon oxides (*10, 11*). An additional path to phthalic anhydride could be directly from *o*-benzoyl-benzoic acid by splitting of one benzene ring leaving a natural precursor to phthalic anhydride. This completes the network of reactions in the oxidative coupling route shown in Fig. 3.

Route 3. The third reaction path, Route 3 (see Fig. 4), is drawn in consistency with the known products of the various intermediates (see Table 1). Route 3, which is the least important one, is initiated by an attack in the aromatic nucleus. Since the methyl substituent has a weak *ortho* and *para* directing effect, the *o*- and *p*-cresols should be the dominating products. The cresols will react further in a more complex manner. Since the hydroxy substituents of the cresols are strongly ring-activating and *ortho-para* directing, oxidation in the nucleus will be dominating with side chain oxidation occurring only to a low extent. This is in agreement with the low amount of salicylic aldehyde formed from cresols (see Table 1).

Due to the *ortho-para* directing effect, the three different cresol isomers will produce certain products as shown in Fig. 5. These are *p*-toluquinone and in theory two different *o*-toluquinones, although the *o*-quinones have not been reported. The hydroquinones in Fig. 5 are postulated intermediates. Data on the oxidation of the (in toluene oxidation) dominating isomers *o*- and *p*-cresol (*27*) (products are maleic and citraconic anhydride) indicate a main difference in a lower selectivity for citraconic anhydride from *p*-cresol. Thus, it follows that *o*-toluquinone, the product of *p*-cresol, is oxidized to maleic anhydride mainly. Citraconic anhydride, on the other hand, is likely to be formed mainly from *p*-toluquinone, which is a product of *o*-cresol. This is also consistent with the observed products and makes it possible to suggest the complete reaction network of Route 3 as presented in Fig. 4.

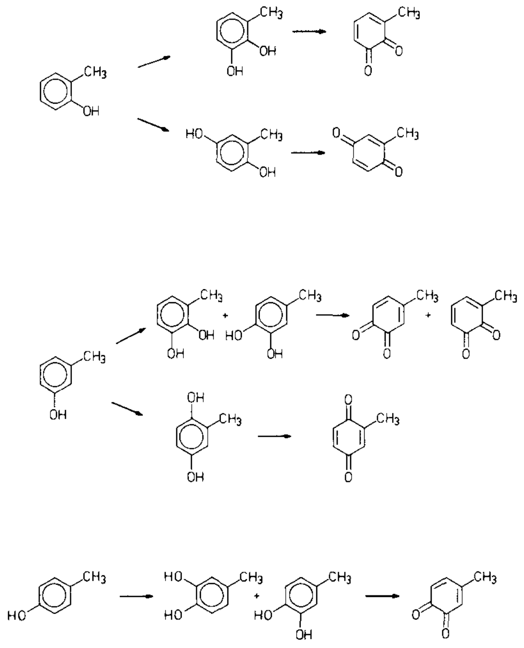

FIG. 5. Possible intermediates in cresol oxidation due to *ortho-para* directing effects.

Reaction Network in o-Xylene Oxidation

A very detailed analysis of o-xylene oxidation products was given by Bernardini *et al.* (*1, 2*) and a reaction scheme with a stepwise successive oxidation of *o*-xylene was suggested. In spite of the detail there were still a few missing products needed to complete the picture some of which are actually reported in later literature. Vrbaški and Mathews (*28*) found traces of *o*-formylbenzylalcohol. Erlandsson and Lundin (*29*) found phenol and phthalan (*o*-oxylene-oxide). Levin (*30*) mentions the presence of *o*-methylol-benzoic acid and finally Vanhove and Blanchard (*31*) report dimethyl-maleic anhydride. All these products reported so far are summed up in the reaction scheme shown in Fig. 6. Compounds shown within parentheses have never been identified in *o*-xylene oxidation but are postulated as logical intermediates. Other products not shown in the scheme and not discussed here are C_1, C_2, and C_3 aldehydes and acids identified in traces (*1, 31*). Their presence as intermediates seems very likely since the overall picture is that the oxidation occurs in a stepwise manner.

The reaction scheme (Fig. 6) has a very systematic structure. Along each row or column one substituent is oxidized successively. Thus, starting from *o*-xylene, one of the methyl groups is oxidized to the alcohol, aldehyde, and carboxylic acid, which finally decarboxylates. The toluene thereby formed will follow the oxidation route described above, explaining the appearance of benzaldehyde, benzoic acid, and so on. This route should also produce benzaldehyde, benzoic acid and benzene due to decarboxylation of the dicarboxylic acid and the *o*-formyl-benzoic acid. Each one of the products in the first row (Fig. 6) may be oxidized at the other methyl group in a stepwise manner. The reaction sequences

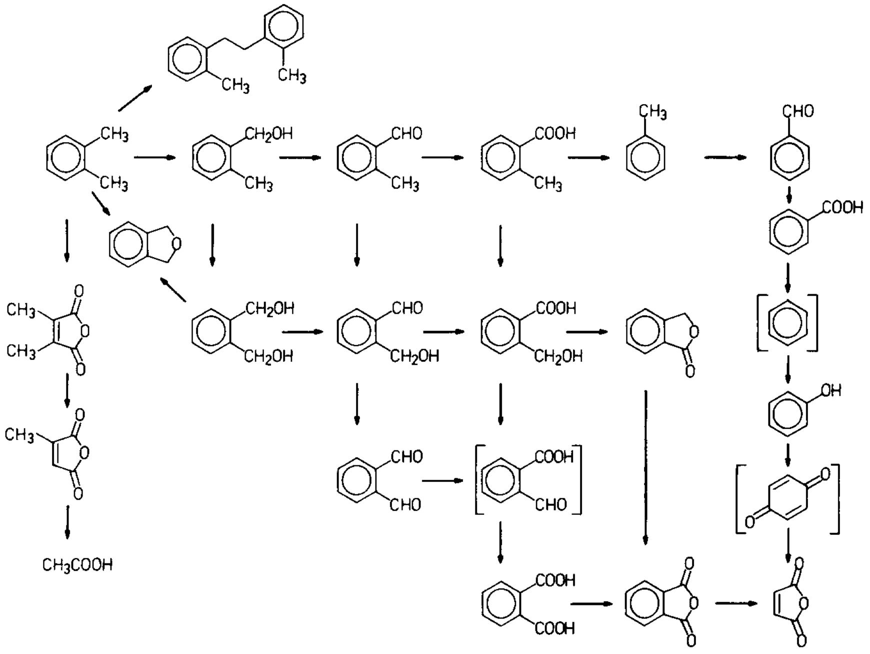

FIG. 6. Reaction scheme of *o*-xylene oxidation. Compounds within parentheses have not been reported.

in the scheme (Fig. 6) are also supported by studies of the oxidation products of several of the intermediates (*1, 28, 32*). However, there seems to be reason for some doubt concerning the appearance of phthalan since it may be formed in homogeneous vapor-phase oxidation of *o*-xylene at higher temperatures (*33*).

Reaction Networks in m- and p-Xylene Oxidation

Concerning the reactions of *m*-xylene the information is very rare. Van der Wiele (*19*) has studied the oxidation of all three xylene isomers and reports in *m*-xylene oxidation the products tolualdehyde, toluene, benzene, and benzaldehyde. One could assume that the stepwise oxidation occurs as for *o*-xylene in an analogous manner and from this construct a detailed reaction scheme.

Several studies on the oxidation of *p*-xylene have been reported. In Fig. 7 a reaction scheme is shown based on the products identified by Mathur and Viswanath (*34, 35*) and the formation of toluene, benzaldehyde and benzene as shown by van der Wiele (*19*). Intermediates missing in the *p*-xylene oxidation scheme may be derived by analogy with the *o*-xylene oxidation scheme. In studies of liquid-phase oxidation of *p*-xylene it has been shown that alcohols are also formed (*36*).

Reaction Mechanisms in Toluene Oxidation

Hydrogen transfer mechanism. The rate-limiting step in many hydrocarbon oxidation reactions is in general thought to be the initial attack on the hydrocarbon (*17*). The detailed mechanism of this first step is unknown, but is generally considered as a hydrogen abstraction step (*12, 37–43*). Also in the oxidation of toluene to benzaldehyde (*18*) and in the oxidative coupling of toluene (*8*) the initial toluene activating step seems to be rate-determining. No information about the nature of these intermediate species are to be found, except possibly in an IR study (*44*) on toluene adsorption on basic ZnO, where dissociative adsorption

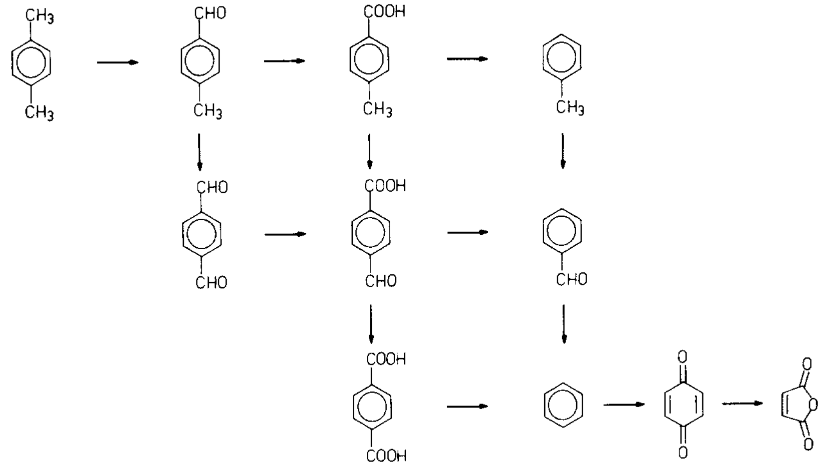

FIG. 7. Reaction scheme of *p*-xylene oxidation.

with formation of new OH groups and adsorbed benzyl species is reported. Such species should certainly be very favorable for the oxidative coupling route at least. Associatively adsorbed toluene (more loosely bound) is also reported (*44*). The latter is probably hydrogen-bonded to terminal surface hydroxyl groups through the π-electron system (*45*).

Considering the common features for the different routes it is tempting to suggest the formation of a common intermediate, which determines the partition between the various routes. This is analogous to the findings of Burrington *et al.* (*46*) that the selectivity of allylbenzene oxidation is determined by the decomposition of a σ-complex. Furthermore, studies of the adsorption of alkylpyridines on vanadium oxide catalysts revealed strongly bonded species retained at 400°C under vacuum (*47, 48*). It was suggested that these were probably σ-bonded through the methyl group to terminal oxygens of the metal oxide. It has also been shown that these are an essential prerequisite in the selective ammoxidation of 3-picoline (*49*).

In Fig. 8, a possible reaction mechanism for the initial steps in toluene oxidation is shown. Details of the metal oxide surface and the restructuring of the surface, i.e., the dehydration and reoxidation steps, are not considered for reasons of simplicity (The redox model was screened out from 17 other reaction models for toluene oxidation (*50*)). In the first step, loosely bound, physically adsorbed or hydrogen-bonded toluene is subjected to a rate-determining hydrogen abstraction forming an OH group and π-complexed benzyl species of radical character. If the benzyl radicals react with neutral toluene molecules the coupling products of Route 2 will be obtained. A high concentration of the benzyl radicals would favor the formation of dibenzyl by recombination of two radicals (*51*). The same reactions will also occur to some extent in the vapor phase due to desorption of benzyl radicals. As a parallel path we find Route 3 since the benzylic species will form resonance structures with the charge or radical character to some extent delocalized to the ring system in preferentially *ortho* and *para* positions. A direct hydrogen abstraction in the nucleus requires a much higher energy than in the methyl position (*52*) and the total process is thought to be unfavorable. As mentioned above, Route 3 is almost negligible. Route 1 is obtained if the benzylic radical reacts in the benzylic position. Thus, when the π-complexed benzylic radical is transferred into a σ-complex the key intermediate determining the selectivity is formed. It is possible, at least from a geometrical point of view, that these two subsequent steps occur in a more or less concerted reaction. In that case the benzylic radicals will not appear as separate intermediates. Routes 2 and 3 will then be inhibited and the catalyst will be completely selective for side chain oxidation.

As indicated in Fig. 8, one may consider the breaking of four different bonds in the σ-complex. The one that will be favored depends on the molecular orbital energies and geometries in the reaction center, i.e., the σ-complex with surroundings. Breakage of bond d will simply be a reversal of the σ-complex formation. If, however, bond c is broken, the precursor to benzylic alcohol is formed. It seems that the favored and faster reaction is the dissociation of bond b (hydrogen abstraction) forming an activated species (bottom of Fig. 8). If this species decomposes with dissociation of bond c the aldehyde will be formed. If instead bond a is broken, benzene is desorbed and CO follows subsequently.

Electron transfer mechanism. It is possible that the first step of Fig. 9 should in principle be divided into several processes. There are analogies with liquid-phase metal-ion-catalyzed oxidation reactions, where the initial step often consists of separate electron transfer and proton abstraction steps (*53*). There are of course also other mechanisms that can occur in liquid-phase oxidations (*53, 54*). Some of the more reasonable paths (from the standpoint of vapor-phase catalysis) are: (1) electron transfer, (2) electrophilic substitution, (3) nucleophilic substitution within the coordination sphere of "soft" metal ions, for example, Pd(II). These mechanisms de-

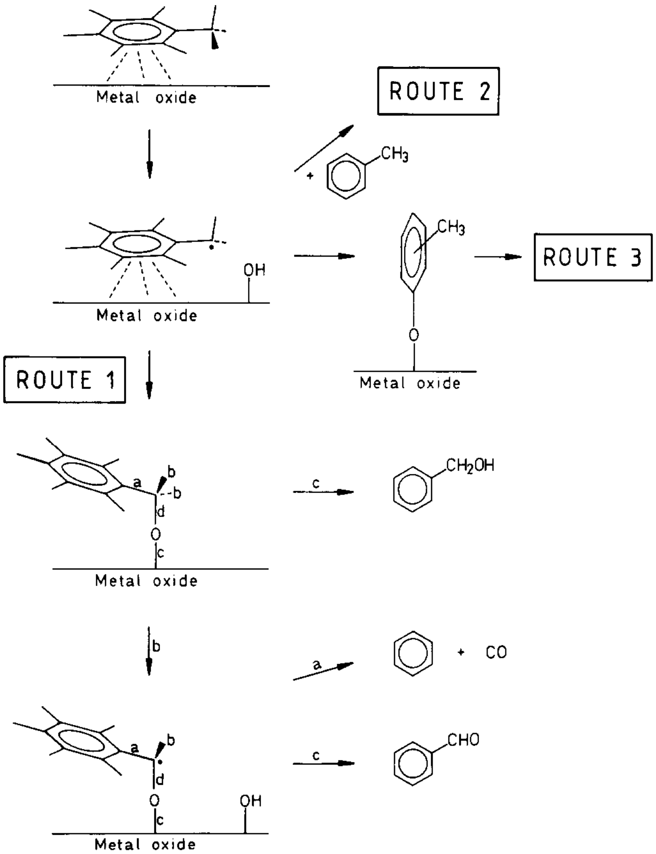

FIG. 8. Hydrogen transfer mechanism for the initial steps in catalytic oxidation of toluene.

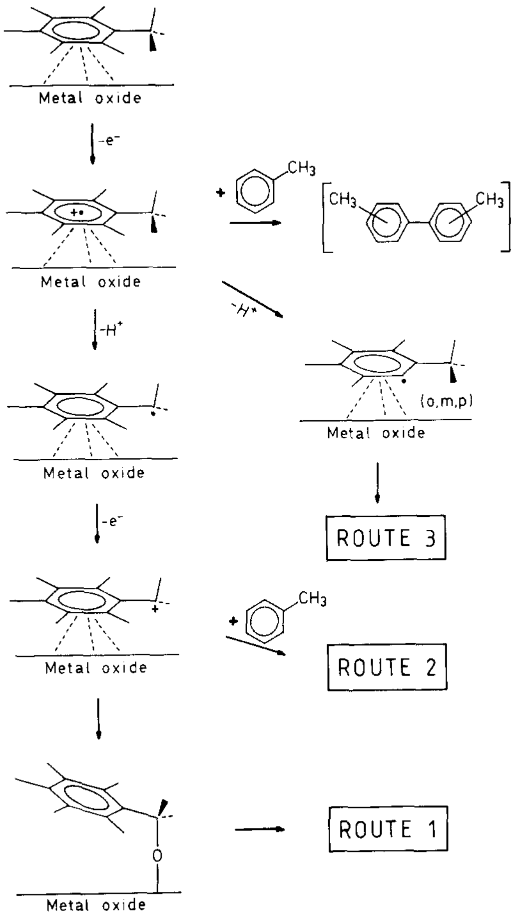

FIG. 9. Electron transfer mechanism for the initial steps in catalytic oxidation of toluene. The compound within parentheses (bitolyl) has never been observed.

pend on the nature of the metal compound and the ionization potential of the aromatic compound. On arranging oxidants in order of decreasing oxidation potential, a continuous change from electron transfer to electrophilic substitution will be observed (*55*). In process (1) the first step is a reversible transfer of one electron to the metal oxidant with the formation of a cation radical, in our case $PhCH_3^{+\cdot}$ (see Fig. 9). This is considered to be a slow, rate-determining step which is followed by a faster one in which the cation radical subsequently releases one proton forming the benzyl radical. The benefit of this mechanism is that the methyl hydrogen dissociation energy is lower by 28 kcal/mole for the cation radical than for toluene (*56*). In vapor-phase catalysis the cation radicals apparently do not react with other toluene molecules in an electrophilic substitution process. Bitolyls would be expected in such reactions (*55*), but these could not be found in the products. The reason may be that the cation radicals are too short-lived due to a fast proton release. The benzyl radicals formed will pass on to Routes 1 and 2 (see Fig. 9). Since the positive charge on the benzyl cation-radical is to some extent located at the *ortho* and *para* positions (*57*), there is a certain probability for a direct substitution reaction with nucleophilic oxygen, which will lead to Route 3. A proton release (vide supra) from the nucleus as a competing process to methyl proton release is also feasible. The methyl-phenyl radical thus formed will also lead to Route 3.

In the hydrogen transfer mechanism (vide supra) the benzyl radical species were assumed to lead to all three routes. In the electron transfer mechanism, however, it is thought that these have too short a lifetime for these reactions to occur to any appreciable extent. Thus, with electron transfer catalysts a strongly competing process will be the release of a second electron. The ionization potential of the benzyl radical is 7.76 eV, which is considerably lower than 8.82 eV for toluene (*52*). Therefore, the second electron transfer should be a faster process than the first one. In this step benzyl cations are formed and these will lead to products of Routes 1 and 2 (see Fig. 9).

The benzyl cation intermediate will react further with either a second toluene molecule or alternatively with an oxide ion of the catalyst surface. By analogy with liquid-phase metal-ion-catalyzed oxidation, the first case will lead to diphenylmethanes (*55*), thus initiating Route 2. In the second case, the σ C–O bonded key intermediate for Route 1 is obtained. It is identical to that formed also in the hydrogen transfer mechanism (see Fig. 8). Clearly, a high toluene concentration will favor Route 2 and a low concentration Route 1.

ACKNOWLEDGMENT

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