

Reaction Network and Kinetics for the Catalytic Oxidation of Toluene over V_2O_5

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The oxidation of three methyl-diphenylmethane isomers and of bibenzyl, benzyl alcohol, and benzaldehyde, which are intermediates in the catalytic oxidation of toluene over V_2O_5 , has been studied to elucidate the reaction network and relative importance of various reactions. Selectivity dependences reveal that the network is composed mainly of three parallel reaction routes: (1) side-chain oxidation with consecutive reactions, (2) oxidative coupling with both parallel and consecutive reactions, and (3) carbon oxide formation. Coupling products are not negligible, with an initial selectivity of 29% (400°C). Anthraquinone is produced mainly from *o*-methyl-diphenylmethane through *o*-methyl-diphenylmethanone. Initial ring oxidation products were not found with the conditions and catalyst used. Selectivity dependences suggested product lumping and a simplified network. Kinetic analysis of this reaction network indicates that higher temperatures favor route 2 over route 1. The same initial intermediates for route 1 of side-chain oxidation and for route 2 of oxidative coupling are suggested. © 1990 Academic Press, Inc.

INTRODUCTION

Catalytic oxidation of toluene over metal oxides is a complex reaction system consisting of a variety of parallel and consecutive reactions (1, 2), and 23 products identified by GC-MS have been reported (2). Among the three parallel routes for selective oxidation, those for oxidative coupling and aromatic nucleus oxidation are generally neglected in studies of the mechanism and kinetics of toluene oxidation (3-8), although anthraquinone was reported as one of the major products over V_2O_5 as early as 1941 (9). The origin of anthraquinone is not clear. It could not be identified as a product of oxidation of benzylic alcohol or benzaldehyde (10), but contradictory results for benzaldehyde are reported (11). The reason may be that the partitioning between the

side-chain oxidation route and the oxidative coupling route depends on the properties of the catalyst and on the process conditions. In later studies on vanadium-based catalysts it was found that the partitioning between these two routes could be affected by additions to the catalyst (12, 13). It therefore seems important to investigate the oxidation of coupling products to clarify the reaction pathways of toluene oxidation over V_2O_5 and to elucidate the origin of anthraquinone formation. Since the earlier network was based mainly on identified products and possible products of the intermediates of side-chain oxidation (route 1), the work presented here was also performed to verify some parts of the network and mechanisms by investigating the oxidation of intermediates not studied earlier and by a kinetic analysis of toluene oxidation.

EXPERIMENTAL

The catalyst was as-received V_2O_5 from Aldrich-Chemie (99.6 + %) and was sieved to obtain a fraction of particles of particle

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size 200–300 μm for use in the catalytic measurements. The BET surface area was measured to be 3.45 m^2/g . A conventional flow apparatus operated at atmospheric pressure was used as described elsewhere (14). The gas flow was 6–55 dm^3/h . Toluene was introduced with a saturator to give 1.2 vol% toluene, 15.7 vol% oxygen, and the balance nitrogen. The other compounds were also introduced with saturators. The concentration of benzaldehyde was 0.10–0.13 vol% and the gas flow was 12 dm^3/h . The concentration of *o*-methyl-diphenylmethane (*o*-MDPM) was 0.02 vol% and gas flow, 9 dm^3/h . The other compounds, *m*-methyl-diphenylmethane (*m*-MDPM), *p*-methyl-diphenylmethane (*p*-MDPM), and bibenzyl (BB) were run at 0.01 vol% and 6 dm^3/h . The catalyst bed contained 0.4 g of catalyst diluted with 0.69 of inert quartz to avoid adverse thermal effects. All measurements were performed on the same catalyst bed. The on-line analytical methods have been described elsewhere (15). During the kinetic studies the reactor was operated at conversions between 0.2 and 10% and reaction rates were directly calculated from these differential data. During experiments for product identification conversions were varied up to 100%.

RESULTS AND DISCUSSION

Oxidation of Toluene

The effect of temperature on conversion and product distribution was determined under standard conditions and the results are shown in Figs. 1 and 2. The selective oxidation products found after reaction over V_2O_5 were benzaldehyde (BA), benzoic acid (BzA), maleic anhydride (MA), benzoquinone (BQ), phthalic anhydride (PA), MDPM, *o*- and *p*-methyl-diphenylmethanone, (*o*-MDPMO and *p*-MDPMO), diphenyl-ethanone (DPE), diphenyl-ethandione (DPED), biphenylmethanone (BPM), and anthraquinone (AN). The changes in selectivities of these products with increased conversion fit well with the suggested side-chain oxidation route (route 1) and oxidative

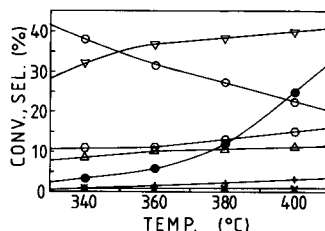


FIG. 1. Conversion of toluene and selectivities for various products in oxidation over vanadium oxide versus reaction temperature. Conversion (●). Selectivity for benzaldehyde (○), carbon oxides (▽), benzoic acid (◊), anthraquinone (△), maleic anhydride (+), and benzoquinone (×).

coupling route (route 2). The sum of selectivities for coupling products, as high as 29%, shows that the oxidative coupling route is not negligible. No products arising from oxidation in the aromatic nucleus were identified. With the reaction network shown earlier (2) only selective products were discussed, but it could be interesting also to consider the carbon oxides. Substantial amounts of CO and CO_2 formed at low conversions indicate a third parallel reaction route for direct oxidation to carbon oxides (route 3). These are also formed in the final step of the selective routes. Production of carbon oxides can be explained by that adsorbed species either give selective products or carbon oxides depending on intrinsic reactivities and supply of reactive oxygen

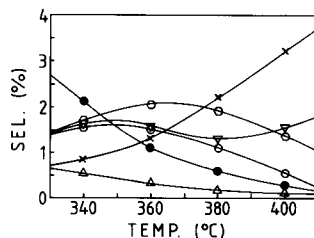


FIG. 2. Selectivity for coupling products (anthraquinone in Fig. 1) in oxidation of toluene over vanadium oxide versus reaction temperature. Selectivity for methyl-diphenylmethane isomers (●), *o*-methyl-diphenylmethanone (○), *p*-methyl-diphenylmethanone (◊), diphenylethanone plus diphenylethandione (▽), biphenylmethanone (△), and phthalic anhydride (×).

species. It could also be explained by the presence of different sites active for selective products or active for carbon oxides. The present study was not directed toward this question but we have noted that the catalytic properties of vanadium pentoxide are strongly affected by the preparation method and *in situ* treatment. This could cause a variation in the mean valence state of vanadium, a variation in the defect concentration and type, and a variation in the concentration of different crystal planes. These are all factors which would contribute to changed selectivities. The reason could be changes in concentration of electrophilic oxygen species, which lead to carbon oxide formation (16), and of lattice oxygen species, which result in selective oxidation (17, 18). The (010) plane containing the nucleophilic double-bonded oxide ions has been correlated with selective oxidation, whereas formation of carbon oxides has been correlated with the other planes probably holding more electrophilic oxygen species (19).

Oxidation of Benzyl Alcohol and Benzaldehyde

It was found that benzyl alcohol is very easily oxidized over vanadium oxide catalysts. At 100°C a conversion of 17% was obtained and complete conversion was obtained at 200°C. The only product found was benzaldehyde. The further oxidation of benzaldehyde, observed over Cu-zeolites at higher temperatures (20), does not occur over vanadium oxide at 200°C. The higher temperature also resulted in large quantities of carbon oxides, not observed here. These results show that the high activity and selectivity of V_2O_5 for oxidation of benzyl alcohol are in agreement with the results observed by FTIR (8), where almost exactly the same spectrum is obtained by adsorption of benzyl alcohol and benzaldehyde at room temperature over monolayer vanadia-titania catalysts. Note that the temperature at which complete conversion of benzyl alcohol is obtained is much lower than that normally used in catalyst screening and kinetic

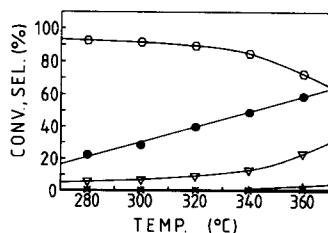


FIG. 3. Conversion of benzaldehyde and selectivity for various products in oxidation over vanadium oxide versus reaction temperature. Conversion (●). Selectivity for benzoic acid (○), CO + CO₂ (∇), benzene (×), and benzoquinone + maleic anhydride (+).

studies of toluene oxidation. Therefore, it is hardly observed as a product of toluene oxidation over vanadium oxides. Its appearance as a short-lived free intermediate is not impossible, although it seems more likely that the precursor to benzyl alcohol is further oxidized instead. The presence of small quantities of benzyl alcohol in product condensates for different catalysts was previously suggested based on identification by retention time only (2). It has, however, not been identified by mass spectrometry. Photochemical oxidation of benzyl alcohol (21) produces considerable quantities of coupling products that could fit into the reaction network for toluene oxidation. It is therefore interesting to note that these coupling products are not formed during catalytic oxidation over vanadium oxide, showing that no condensation occurs.

Catalytic oxidation of benzaldehyde over vanadium oxide was found to produce mainly benzoic acid, with minor production of carbon oxides and benzene and, at high conversion, also benzoquinone and maleic anhydride (see Fig. 3). The selectivity for benzoic acid is 90% even at a conversion level as high as 40%. Extrapolation of the lines in Fig. 3 to a temperature at which the conversion is 0% gives an initial selectivity at this temperature for benzoic acid of about 96% and of about 0.5% for benzene. The extrapolation performed is reasonable, considering the rather small changes in selectivity with temperature and conversion. The very low initial selectivity for carbon oxides

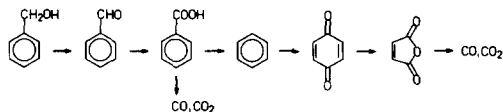


FIG. 4. Major reactions in the sequential oxidation of benzyl alcohol over vanadium oxide.

shows that a parallel route to carbon oxides is negligible and the initial selectivity for benzene points toward a competing decarbonylation mechanism. The further oxidation of the initial product, benzoic acid, is observed at higher conversion levels as an increased selectivity for CO and CO₂ as well as in the appearance of benzoquinone and maleic anhydride. Whether the benzoic acid is first desorbed and then readsorbed for continued oxidation is not known. Probably there is a competition between benzoic acid desorption and further oxidation of the adsorbed precursor. The coupling products observed in toluene oxidation are completely absent in oxidation of benzaldehyde. This confirms that the coupling products originate at an earlier stage in the oxidation process. On the whole the data support the earlier model (2) for the reaction network of route 1, except for the omission of benzyl alcohol as a free intermediate. The reactions shown to occur by the present data are given in Fig. 4.

Oxidation of MDPM Isomers and Bibenzyl

The intermediates investigated were the three methyl-diphenylmethane isomers and bibenzyl. Results for conversion and selectivity of oxidation of *o*-methyl-diphenylmethane are presented in Fig. 5. The main products are *o*-methyl-diphenylmethanone (*o*-MDPMO), anthraquinone (AN), and carbon oxides. Extrapolation of the selectivities to a temperature at which the conversion is 0% shows that *o*-MDPMO is the primary product, with an initial selectivity of about 70% at this temperature. At higher conversion *o*-MDPMO is further oxidized with formation of phthalic anhydride, an-

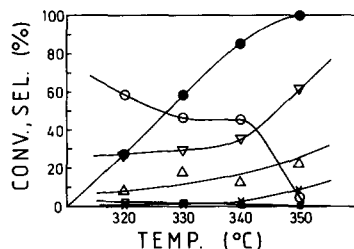


FIG. 5. Conversion of *o*-methyl-diphenylmethane and selectivity for various products in oxidation over vanadium oxide versus reaction temperature. Conversion (●). Selectivity for *o*-methyl-diphenylmethanone (○), anthraquinone (△), phthalic anhydride (×), biphenylmethanone (□), carbon oxides (▽). Selectivities for the remaining products (benzoic acid, maleic anhydride, and two isomer oxidation products), which totaled less than 2%, are not shown. (Small amounts of MDPM isomers were present in the reactant.)

thraquinone, and carbon oxides. Minor amounts of biphenylmethanone (BPM) are also formed, showing that during oxidation of the side chain it may either decarboxylate or couple with the ring forming anthraquinone or phthalic anhydride. The increased formation of benzoic acid (not shown in Fig. 5) with decreased selectivity for BPM indicates one product of BPM oxidation. The presence of two parallel reactions of the postulated intermediate (*o*-benzoyl-benzoic acid) forming anthraquinone or phthalic anhydride was seen earlier by the influence of potassium additions to the catalyst (12). Figure 6 shows the reaction network indicated by the data in conformity with earlier results.

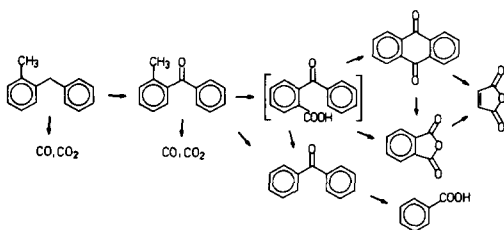


FIG. 6. Major reactions in oxidation of *o*-methyl-diphenylmethane over vanadium oxide. Compound within brackets is postulated intermediate (*o*-benzoyl-benzoic acid).

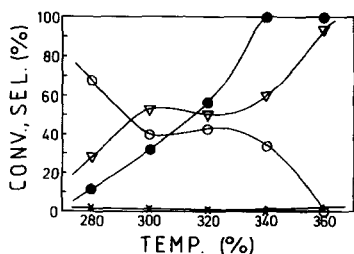


FIG. 7. Conversion of *m*-methyl-diphenylmethane (*m*-MDPM) and selectivity for various products in oxidation over vanadium oxide versus reaction temperature. Conversion (●). Selectivity for *m*-methyl-diphenylmethanone (○), biphenylmethanone (×), benzoic acid (+), carbon oxides (∇). Selectivities for the remaining products, which totaled less than 5%, are not shown. These products were formed by oxidation of MDPM isomers that were present in the reactant.

Conversion and selectivity in oxidation of *m*-MDPM is shown in Fig. 7. The main products are *m*-MDPMO and carbon oxides. Extrapolation of the selectivities to a temperature at which the conversion is 0% gives about 85% initial selectivity (at this temperature) for *m*-MDPMO, evidently the primary product. A low selectivity for BPM decreasing with increased conversion is observed. Simultaneously the selectivity for benzoic acid increases. These data indicate that *m*-MDPMO is oxidized to BPM, which is further oxidized to benzoic acid. The initial selectivity for carbon oxides, seen in Fig. 7, indicates the presence of a parallel route. At high conversion a sharp drop in the *m*-MDPMO selectivity and a sharp rise in the selectivity for carbon oxides indicate that there is a parallel route for combustion in this case also. The reaction scheme is shown in Fig. 8.

The *p*-MDPM isomer contained considerable quantities of bibenzyl (BB) and these

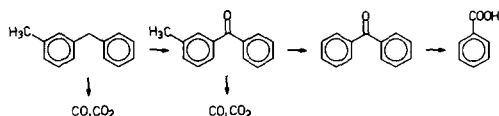


FIG. 8. Major reactions in oxidation of *m*-methyl-diphenylmethane over vanadium oxide.

were therefore oxidized together. The results are shown in Fig. 9. The major selective oxidation product of *p*-MDPM is *p*-methyl-diphenylmethanone (*p*-MDPMO) and for bibenzyl it is diphenylethanedione (DPED). Extrapolation to a temperature at which the conversion is 0% gives a rather low initial selectivity for carbon oxides at this temperature and these compounds react preferentially to selective oxidation products. The extrapolation method adopted for the isomers is probably not as accurate as that for benzaldehyde (see Fig. 3), where smaller differences in selectivities were obtained. *p*-MDPMO reacts further to BPM and from the decreased selectivity for the latter and the appearance of benzoic acid at increased conversion, the sequential formation of these is plausible. In oxidation of bibenzyl, the primary product is diphenylethanone (DE), which reacts further to the major product diphenylethanedione. The data for both reactants show that these follow the earlier given reaction network for the coupling products (2). In the gas chromatographic analysis used, the three MDPM isomers, bibenzyl and *cis*-stilbene come in one peak with only a very small difference in the retention times. *trans*-Stilbene, however, is completely separated

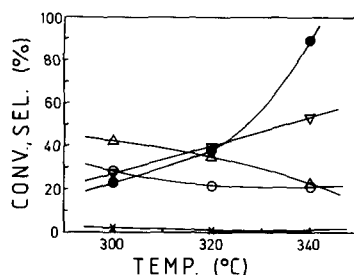


FIG. 9. Conversion of a mixture of *p*-methyl-diphenylmethane and bibenzyl and selectivity for various products in oxidation over vanadium oxide versus reaction temperature. Conversion (●). Selectivity for *p*-methyl-diphenylmethanone (○), diphenylethanedione (Δ), biphenylmethanone (×), benzoic acid (+), carbon oxides (∇). Selectivities for some products (diphenylethanone and some products of MDPM isomer oxidation), which totaled less than 2%, are not shown.

TABLE 1

Apparent Activation Energies for Oxidation of Toluene and Some Intermediates over Vanadium Oxide

Compound	E_{app} (kJ/mol)
Benzyl alcohol	26
Benzaldehyde	55
<i>o</i> -MDPM	93
<i>m</i> -MDPM	82
<i>p</i> -MDPM	91
Toluene	124

from these, but comes very close to *o*-MDPMO. A large quantity of *trans*-stilbene is definitely not formed. To prevent the stilbenes from further oxidation it is necessary to use a less active catalyst material and different process conditions, but then the side-chain products are not formed (22–23). It can be concluded that the initial oxidation products of the four isomers are the corresponding ketones and carbon oxides. The results clearly show that anthraquinone originates from *o*-MDPM only and not from any of the other isomers.

In comparison with toluene the oxidations of the isomers are temperature sensitive, with complete conversion occurring within a temperature interval of 40°C under the present conditions. The temperature required for 50% conversion of the different compounds over vanadium oxide is 314–327°C for the four isomers, 341°C for benzaldehyde, and 427°C for toluene. The apparent activation energies are given in Table 1.

Kinetics of Toluene Oxidation

To give hints about how to simplify the kinetic analysis we investigated systematics in selectivities. Thus we divide the 14 products of the three parallel routes into three groups. The main side-chain oxidation products, benzaldehyde and benzoic acid, together form one group. Carbon monoxide and carbon dioxide form a second group. All other products together form the last

group: these are mainly the oxidative coupling products. We have also placed benzoquinone and maleic anhydride into this group, although they are also products of route 1. The reason is that the selectivity for these is low and that the MDPM isomers are more easily oxidized over the vanadium oxide catalyst than benzoic acid. A considerable quantity of these may thus originate from the coupling products and the kinetic analysis is considerably simplified. Further indications are given in Fig. 10, which shows selectivities as a function of space time at four different temperatures. It is evident that the selectivity for the first group does not change with space time, whereas the increased selectivity for carbon oxides is matched by the decreased selectivity for the coupling products. This third group will henceforth be called "CP." It should be mentioned that the apparently unchanged selectivity for the first group does not seem to be in agreement with the results found in oxidation of benzaldehyde, where the oxidation of benzoic acid to carbon oxides is visible. However, benzoic acid formation from the oxidation of coupling products is verified in the present study of oxidation of MDPM isomers. Therefore, the unchanged selectivity indicates that the rate of formation of benzoic acid from coupling products

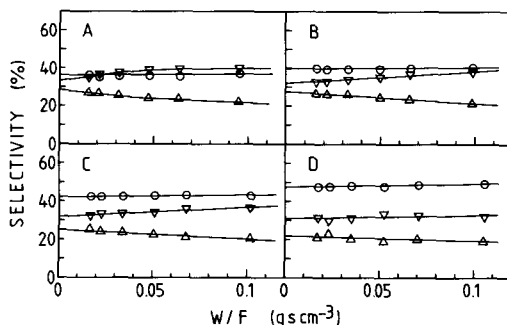


FIG. 10. Selectivity for product groups in oxidation over vanadium oxide as a function of space time at different temperatures. (A) 400°C, (B) 380°C, (C) 360°C, (D) 340°C. Selectivity for group 1, benzaldehyde + benzoic acid (○); group 2, coupling products + BQ + MA (△); group 3, carbon oxides (▽).

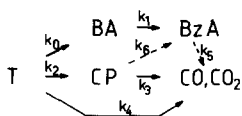


FIG. 11. Simplified reaction network for kinetic analysis. Toluene (T), benzaldehyde (BA), benzoic acid (BzA), coupling products (CP).

is approximately equal to the rate of oxidation of benzoic acid to carbon oxides under present reaction conditions.

Figure 11 shows the simplified reaction network for kinetic analysis, which now only contains five rate constants to be estimated. In the kinetic investigation the oxygen was in excess and kept constant at 0.2 atm and toluene was maintained constant at 1.2 vol%. The only variable was space time. It is then assumed that the reaction under the present conditions is pseudo-first order in toluene as shown for other catalysts producing mainly side-chain oxidation products (4, 24). For the formation of the coupling products we also assume a first-order dependence, since this was found in studies on oxidative dehydrodimerization of toluene (22, 23). The kinetics were evaluated by the differential reactor model since conversions were in most measurements below 10%. It is also assumed that product inhibition is not important at these low conversions. The rate equations for the simplified network are

$$r_T = (k_0 + k_2 + k_4)P_T \quad (1)$$

$$r_{BA} = k_0P_T - k_1P_{BA} \quad (2)$$

$$r_{BzA} = k_1P_{BA} + k_6P_{CP} - k_5P_{BzA} = k_1P_{BA} \quad (3)$$

$$r_{CP} = 0.5k_2P_T - k_3P_{CP} - k_6P_{CP} = 0.5k_2P_T - k'_3P_{CP} \quad (4)$$

$$r_{CO_x} = 7k_4P_T + 14k'_3P_{CP} \quad (5)$$

where $k_6P_{CP} \approx k_5P_{BzA}$ and $k'_3 = k_3 + k_6$.

The rate constants were evaluated by least-squares analysis with the Marquardt algorithm, and the Arrhenius plots are

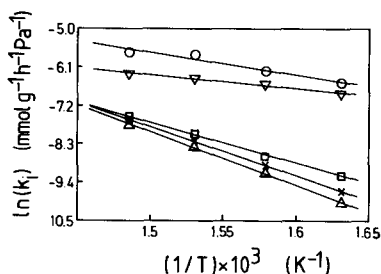


FIG. 12. Arrhenius plots for the rate constant of the simplified network of toluene oxidation over vanadium oxide. k_0 (\square), k_1 (\circ), k_2 (\triangle), k_3 (∇), k_4 (\times).

shown in Fig. 12. The combined good fit of these validates the analysis and the calculated rates deviate from measured rates by less than 5%. The rate constants and the derived activation energies and preexponential factors are shown in Table 2. From the activation energies one can predict that higher temperatures favor the coupling route and the formation of carbon oxides. The results confirm the presence of three parallel routes. The initial selectivities for benzaldehyde, MDPM, and carbon oxides were estimated from the respective rate constants k_0 , k_2 , and k_4 . The results are shown in Fig. 13, and it is clear that benzaldehyde formation is increased at lower temperatures, and the selectivity for MDPM increases with increased temperature. It is notable that the initial selectivity for carbon oxides is not changed much compared with those of BA and MDPM and are almost constant at high temperatures. The data suggest

TABLE 2

Activation Energies and Preexponential Factors Determined for the Various Rate Constants		
Rate constant	E_a (kJ/mol)	A (mmol/(g _{cat} h · Pa))
k_0	98	2.4×10^4
k_1	53	50
k_2	130	5.2×10^6
k'_3	32	0.60
k_4	117	6.5×10^5

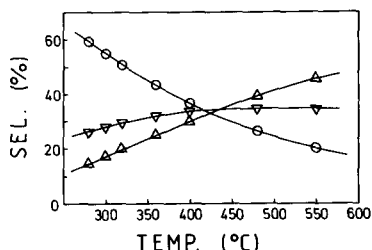


FIG. 13. Initial selectivities for oxidation of toluene calculated from the rate constants as $k_1/(k_0 + k_2 + k_4)$. Route 1 (○), route 2 (△), route 3 (▽).

that routes 1 and 2 share the same intermediate. Higher temperatures favor the coupling of this intermediate species over its reaction with oxide ions for benzaldehyde formation. It has been suggested that the initial species is a benzylic radical-like species (1, 2, 8). We have calculated the distribution of the radical character over the molecule with simple LCAO-MO theory, only considering π electrons. The result is that the spin density is 0.571 on the CH₂ carbon, 0.143 on the *ortho* and *para* carbons, and 0.0 on the *meta* carbon. If it is assumed that the reactivity is proportional to the spin density, it is clearly seen that the reactivity of the species is greatest for the CH₂ carbon, much lower in the *ortho* and *para* positions, and zero in the *meta* position. Considering only this argument one would obtain 57% side-chain products, 28.6% *ortho* products, and 14.3% *para* products. Recombination of two such radical species would favor bibenzyl and methyl-diphenylmethane formation. We have not detected any methyl-biphenyl products, which could be caused by their instability or that ring coupling is unfavorable because the absence of a vacant site in the attacking species greatly decreases the reaction rate. Recombination reactions do seem plausible considering the formation of bibenzyl products. However, the benzyl radical appears to react more frequently with a neutral toluene molecule. In this case the attacking radical preferably reacts in a ring position, forming MDPM. This was shown for phenyl radicals reacting with toluene, where meth-

yl-biphenyls were the main products (25). The frontier electron density for the ground-state toluene was calculated by the HMO method as *ortho* 0.382, *meta* 0.301, and *para* 0.301 (25). This gives a product distribution of 46% *o*-MDPM, 36% *m*-MDPM, and 18% *p*-MDPM. The high selectivity of coupling products at high temperature (see Fig. 13) suggests that recombination of these radical-like species and reaction with toluene molecules dominate over reaction with oxide ions. At lower temperatures, the latter dominates. The activation energy for the formation of benzoic acid is rather low, suggesting that at low temperatures, where benzaldehyde formation is favored, the further oxidation will be more important. Production of benzoic acid should thus be favored by low temperature and low space velocity. This explains some literature results (26, 27) where high benzoic acid production may be explained by the lower temperatures and space velocities used, in comparison with our results on similar catalysts, but operated under the different conditions mentioned (28).

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