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Catalytic Oxidation of o-Xylene

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Oxidation of *o*-xylene to phthalic anhydride over V_2O_5-TiO_2 catalyst has been studied in order to detect the intermediates of this conversion. The oxidation of alcohols such as *o*-methylbenzyl alcohol and *o*-xylene-α,α'-diol yields the same compounds as those obtained from the hydrocarbon in the same conditions, whereas oxidation of *o*-toluic acid yields mainly the lactone, phthalide. Moreover, a competitive oxidation of inactive *o*-methylbenzyl alcohol, and *o*-xylene (methyl-^{14}C) results in the formation of *o*-tolualdehyde, phthalide, and phthalic anhydride, having different specific radioactivities, and demonstrates that different reaction paths are involved.

A mechanism is proposed in which the selective incorporation of oxygen occurs after abstraction of one hydrogen atom so as to produce a surface alcoholate ion, whereas degradation into maleic anhydrides and carbon oxides arises from substitution of hydrogen atoms of the aromatic nucleus by oxygen.

INTRODUCTION

The main product of *o*-xylene catalytic oxidation is phthalic anhydride, but the formation of this compound involves many steps resulting in the successive formation of *o*-tolualdehyde, *o*-toluic acid, and phthalide (C_6H_4—COO—CH_2—) (*1–5*). Together with this selective oxidation there is a degradation of the C_8 molecule into di- and monomethyl maleic anhydrides, maleic anhydride, and carbon oxides. In these last reactions the aromatic system is directly involved since the carboxylic groups of maleic anhydride are inactive when *o*-xylene (methyl-^{14}C) is oxidized (*11*).

Although *o*-tolualdehyde appears to be the primary product, there is still the possibility that alcohol could in fact be the first intermediate of the incorporation of oxygen, but it would not be detected in the gas phase if it is strongly adsorbed. In order to establish the scheme of this conversion and confirm preliminary kinetic studies (*6*), we have studied the oxidation of some oxygenated compounds in the *o*-xylene series—mainly, *o*-methylbenzyl alcohol, *o*-xylene-α,α'-diol, *o*-tolualdehyde, and *o*-toluic acid. In *o*-toluic acid there is a methyl group next to a carboxylic function. Should oxygen be incorporated via a surface alcoholate ion, this could react with the neighboring acid group so as to produce a lactone—namely, phthalide.

EXPERIMENTAL

The apparatus and experimental method have been described in previous communications (*6*, *11*). The Pyrex reactor contained a small amount of V_2O_5–TiO_2 coprecipitated catalyst (composition: 12.5% mol TiO_2), whose selectivity in *o*-xylene oxidation is 74%. Liquid compounds were directly injected into the reactor and vaporized in a preheating helix. The specific radioactivity of labeled compound was measured with a Loenco Radiochromatograph.

Ortho-xylene, *ortho*-tolualdehyde, and

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ortho-toluic acid have been obtained commercially. *o*-Methylbenzyl alcohol has been prepared by reduction of toluic acid with lithium aluminum hydride. It has been purified by distillation at a pressure of 17 mm Hg and 116°C. *o*-Xylene-α,α'-diol has been synthesized by hydrolysis of *o*-xylene-α,α'-dibromide obtained by the method of Stephenson (*12*). *o*-Xylene (methyl-^{14}C) has been prepared from *o*-bromotoluene and [^{14}C]barium carbonate.

RESULTS

A. Oxidation of o-Methylbenzyl Alcohol

At 450°C and with a *W/F* ratio of 1 (*W* = weight of catalyst, *F* = feed rate of hydrocarbon, moles/hr) the conversion of the alcohol is total, the reaction being realized with solutions containing 10, 30, or 50% of *o*-methylbenzyl alcohol in *o*-xylene. The main products are *o*-tolualdehyde, (*o*-methylbenzaldehyde), phthaldialdehyde, phthalide, and phthalic anhydride; thus the alcohol could be an intermediate in the stepwise oxidation of *o*-xylene since the products involved are identical. Oxidation of the alcohol is very fast, as previously demonstrated (*4*, *5*), and it cannot be detected in the gas phase products of *o*-xylene conversion.

In another experiment, *o*-methylbenzyl alcohol was oxidized at 400°C together with *o*-xylene (methyl-^{14}C). Under these conditions, and with solutions containing 30% alcohol, some alcohol is recovered; it is completely inactive, whereas *o*-tolualdehyde possesses an appreciable activity. If alcoholate ions are formed in *o*-xylene oxidation, they are adsorbed on the catalyst surface and rapidly form aldehyde, so that the equilibrium with gas phase *o*-methylbenzyl alcohol is not achieved.

TABLE 1

OXIDATION OF *o*-METHYLBENZYL ALCOHOL (METHYL-^{14}C) AND *o*-XYLENE MIXTURE

Compound	Radioactivities of products	
	Radioactivity $\bar{a}$ mCi/mole	$\bar{a}/\bar{a}_{o\text{-TA}}$
o-Xylene	4	11.1
o-Methylbenzyl alcohol	0	0
o-Tolualdehyde	0.36	1
o-Phthalaldehyde	0.36	1
Phthalide	0.175	0.49
Phthalic anhydride	0.31	0.86

The radioactivities of the products are reported in Table 1. Tolualdehyde is formed ten times faster from the alcohol than from *o*-xylene. The radioactivity of phthalide produced in this competitive reaction is less than that of *o*-tolualdehyde. It can be concluded that *o*-methylbenzyl alcohol is oxidized into phthalide via two reaction paths, one giving rise to *o*-tolualdehyde and the other to the lactone via some undesorbed intermediate which could be a primary diol —namely, *o*-xylene-α,α'-diol. In drawing this conclusion, we proceed from the assumption that undesorbed *o*-tolualdehyde originating from *o*-methylbenzyl alcohol and *o*-tolualdehyde originating from *o*-xylene will behave similarly, both in desorbing and in reacting to phthalide and phthalic anhydride.

B. Oxidation of o-Xylene-α,α'-diol

By oxidation of this diol at 400°C, phthalan [C_6H_4 (—CH_2—O—CH_2—)], phthalide, and phthalic anhydride are obtained, so that *o*-xylene-α,α'-diol, or the corresponding adsorbed alcoholate, is the possible intermediate of a second reaction of *o*-methylbenzyl alcohol giving rise to phthalide. These results are in agreement with the formal scheme previously proposed (*6*). There are two methyl groups on the aromatic ring, presupposing the possibility of alternative abstraction of hydrogen, and thus branching in the reaction path.

C. Oxidations of o-Tolualdehyde

This reaction yields the same products as those obtained in *o*-xylene oxidation. In Fig. 1, data for the formation of each compound are plotted as a function of hydrocarbon conversion. Both the formation of phthalide and phthalic anhydride occur initially with measurable rates, whereas in *o*-xylene oxidation the initial rates for the

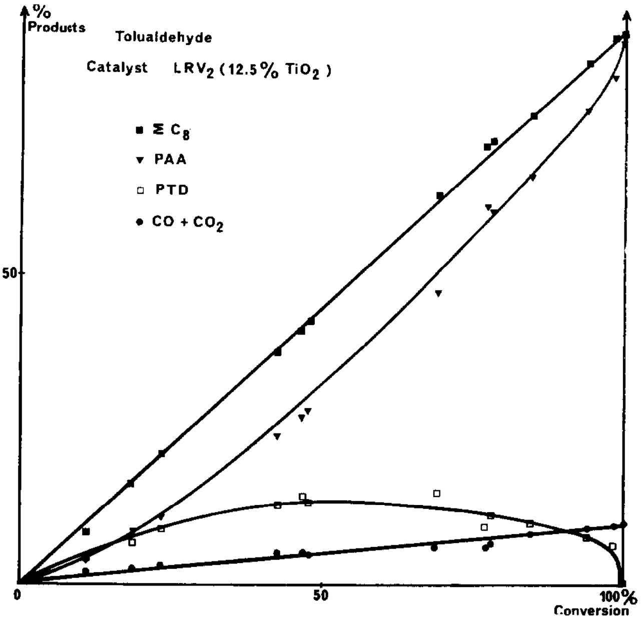


FIG. 1. Oxidation of *o*-tolualdehyde, showing products as a function of conversion at 450°C (PAA—phthalic anhydride; PTD—phthalide).

production of these intermediates is negligible (*6*). Consequently, they are obtained from *o*-tolualdehyde by two competitive processes according to the kinetic scheme previously established.

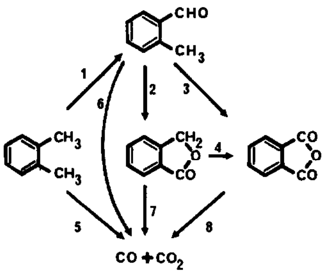


TABLE 2

Comparison between Selectivities for *o*-Xylene and *o*-Tolualdehyde Oxidation on V_2O_5–TiO_2 Catalyst (T = 450°C)

Catalyst V-Ti mol% TiO_2	12.5	35	96
o-Xylene oxidation selectivity	0.74	0.62	0.83
o-Tolualdehyde oxidation selectivity	0.90	0.85	0.94
$(k_1/k_2)_{o\text{-X}} = X$	2.85	1.63	4.9
$(k_1/k_2)_{o\text{-TA}} = Y$	9	5.65	15.7
$\frac{X}{Y}$	0.32	0.29	0.31

The initial selectivity S has been studied on three V–Ti coprecipitated catalysts, and the variation of S with the composition of the mixed oxides is reported in Table 2. It is similar to the one observed for *o*-xylene oxidation. The competition between selective oxidation and degradation can be related to the initial selectivity:

$$\frac{k_1}{k_5} = \frac{S_{o\text{-X}}}{1 - S_{o\text{-X}}} \qquad \frac{k_2 + k_3}{k_6} = \frac{S_{o\text{-TA}}}{1 - S_{o\text{-TA}}},$$

where *o*-X stands for *o*-xylene and *o*-TA for *o*-tolualdehyde. These ratios are different according to the reactant, but whatever the catalyst may be, the relation

$$k_1/k_5 = 0.3(k_2 + k_3)/k_6$$

is verified. The low selectivity observed with some V–Ti catalysts does not result from considerable degradation of one special intermediate (for example, *o*-tolualdehyde). This effect interferes with all the elementary steps.

D. *Oxidation of o-Toluic Acid and Phthaldialdehyde*

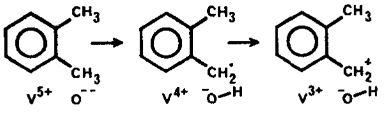
These two compounds are detected in small quantity during the oxidation of *o*-xylene and *o*-tolualdehyde. Their conversion is total when injected into the reactor together with *o*-xylene (the solution containing 80 or 90% of the compound to be oxidized). This demonstrates that these intermediates are strongly adsorbed, so their formation in the gas phase will be negligible under all conditions.

In initial conditions where o-xylene yields only *o*-tolualdehyde, *o*-toluic acid yields phthalide together with phthalic anhydride. Phthaldialdehyde yields phthalic anhydride.

DISCUSSION

Oxidation of *o*-methylbenzyl alcohol and oxidation of *o*-xylene-α,α'-diol yield the same products as those obtained from *o*-xylene in the same conditions. They could be the primary products of the hydrocarbon conversion, but, as demonstrated by experiments with labeled *o*-xylene, they are not detected in the gas phase because their oxidation is very fast. Nevertheless, from experiments made with *o*-toluic acid, it can be concluded that oxygen is incorporated via surface alcoholate ions. In this particular case, the surface ion reacts with the ortho acid group to give an ester—namely, phthalide—detected also in the gas phase products arising from the *o*-xylene oxidation.

The incorporation of oxygen, then, involves the reaction of the oxygen ion with a chemisorbed species formed by abstraction of one hydrogen atom and the transfer of one or two electrons to produce a radical (*7*) or a carbocation.



$$\left[\begin{array}{l} V^{3+} \longrightarrow V^{5+} + 2e \\ 2OH^{-} \longrightarrow H_2O + O^{--} + \square \end{array}\right.$$

The nature of this adsorbed species is difficult to define, but, according to the conclusions of Weiss (*8*), the hypothesis of a positively charged intermediate could be retained if the reductant character of the radical is taken into account. The reaction of an oxygen anion of the catalyst (*16*) with this carbocation then yields the adsorbed alcoholate ion. The same process could be repeated in order to produce *o*-tolualdehyde, water, and an anionic vacancy where the oxygen adsorption will take place owing to the reduced state of the catalyst. In fact, the reduction of the surface cations could be scrambled all over several atoms since the rates of electron transfer is large. The V^{4+} ions often observed on these catalysts would then be obtained (*13*).

By repetition of this process (abstraction of hydrogen, electron transfer, and incorporation of ionic oxygen) phthalic anhydride could be produced, but at every step there is the possibility of reaction on each of the side-chain carbon atoms.

The degradation into maleic anhydrides, CO, and CO_2 occurs at the same time as the selective oxidation, and, according to the results of *o*-xylene (methyl-^{14}C) oxidation, the carboxylic function of maleic anhydride originates from the aromatic ring (*11*). Consequently, there is a competitive reaction of oxygen ions on the unsaturated part of the molecule, presumably π-complexed by surface cations (*14, 15*). The products so obtained (oxygenated aromatic compounds) give rise to the compounds mentioned above.

According to these assumptions, the selectivity of catalytic oxidation would increase as the bond strength of the π-complex decreases. This agrees with the observation that the best selectivity in phthalic anhydride is obtained when the most oxidized intermediate is involved (*o*-tolualdehyde, phthalide) (*4, 9*). It agrees also with measurements of the bond strength of oxygen. In the V_2O_5–TiO_2 series, the most selective catalysts are those for which the oxygen bond is the strongest (*10*).

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