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TITANIUM DIOXIDE PHOTOCATALYZED OXIDATION OF AROMATIC HYDROCARBONS: THE ROLE OF WATER AND OXYGEN TO INDUCE AROMATIC HYDROXYLATION

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Careful examination of the effects of oxygen and water on titanium dioxide photocatalyzed oxidation of benzene and toluene has revealed that electron transfers from water and toluene to the photogenerated positive holes, synchronized with electron transfer from the photoexcited titanium dioxide to oxygen, result, respectively, in aromatic nuclear hydroxylation giving phenolic products and in oxidation of the side chain of toluene affording benzyl alcohol and benzaldehyde.

Currently photocatalytic actions of semiconductor have extensively been investigated mostly for water cleavage; however, attention has recently been paid to its actions to organic compounds to extend the new scope of photochemistry of semiconductor.[1-5]

Irradiation of powdered titanium dioxide suspended in solution containing aromatic compounds and water under oxygen has recently been shown to induce hydroxylation of aromatic nuclei giving phenolic compounds and oxidation of side chains of the aromatic compounds.[6,7] These reactions have been assumed to proceed through hydroxyl and other radical intermediates; however, the mechanism for their generation, whether reactive free radicals result from oxidation of water, from reduction of oxygen, or from oxidation of the substrates on the surface of the photoexcited titanium dioxide, is not clear. This paper attempts to reveal the mechanism for the formation of free radicals on irradiation of titanium dioxide in the presence of benzene and toluene by carefully examining the effects of oxygen and water, and to show that the presence of oxygen is essential for the reaction

and that under oxygen oxidation of water contributes to aromatic hydroxylation and oxidation of toluene as a substrate leads to oxidation of its side chain.

In the present investigation, powdered titanium dioxide (30 mg, anatase from Ventron, treated with hydrogen stream at 600°C for 5 h) was suspended in an acetonitrile solution (2 ml) containing benzene or toluene (16 vol%) and varying amounts of water (0 - 8 vol%) and irradiated with light longer than 350 nm (through Toshiba UV-35 glass filter) from a 1 kW high pressure mercury lamp for 15 h at 20°C, and the resulting products were determined by GLPC.

In the runs under oxygen, titanium dioxide powder was suspended in the sample solution in a Pyrex tube containing a magnetic stirring bar and oxygen stream was passed through the mixture, and then the tube was connected to an oxygen reservoir and irradiated with continuous stirring. In the runs under careful removal of air, an acetonitrile solution of an aromatic substrate with or without water was put in a Pyrex tube with a side arm which contained powdered titanium dioxide and a stirring bar, degassed by freeze and thaw cycles, and sealed, and then all the contents were mixed in the tube and irradiated.

Figure 1 depicts typical results of the oxidation of benzene under oxygen and under degassing with varying concentrations of water. As Fig. 1 clearly shows,

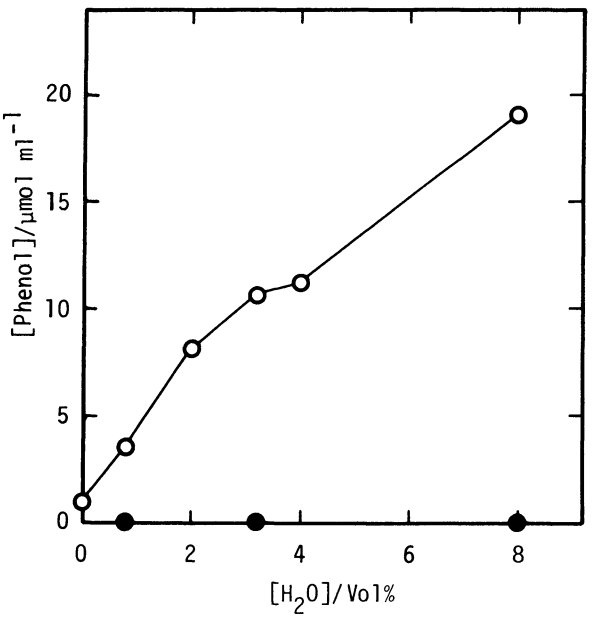


Fig. 1. Hydroxylation of Benzene in MeCN under Degassing (●) and under Oxygen (○).

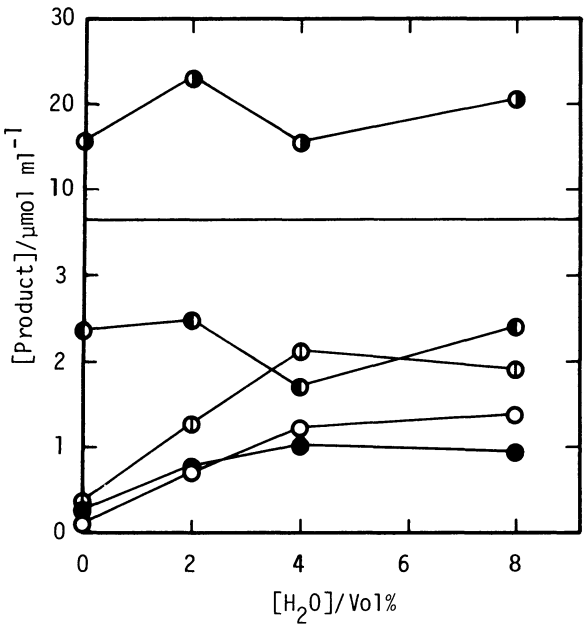
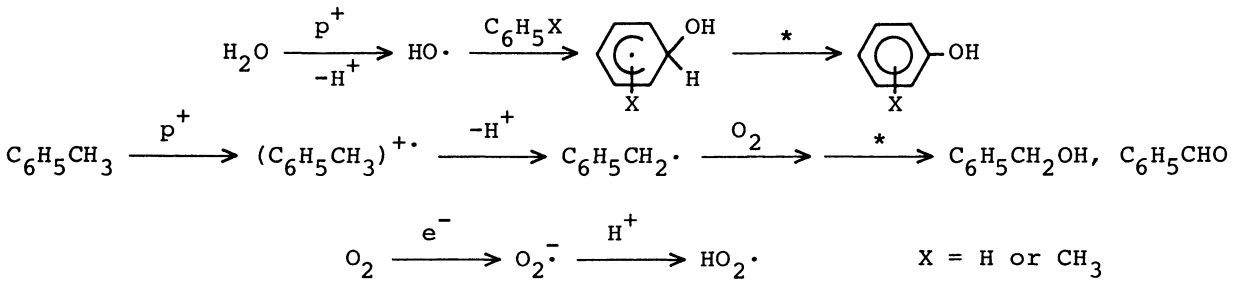


Fig. 2. Oxidation of Toluene in MeCN under Oxygen; products: PhCHO (◑), $PhCH_2OH$ (◐), o-cresol (○), m-cresol (●), p-cresol (◍).

under degassing only a trace amount of phenol was produced even in the presence of water, and under oxygen its yield is still low in the absence of water, but increases with increasing concentration of water.[8] For the reaction of toluene under careful removal of oxygen only trace amounts of oxidation products were produced even in the presence of water as found for benzene.

It is noticeable that in the oxidation of toluene under oxygen (Fig. 2) o-, m-, and p-cresol resulting from nuclear hydroxylation of the substrate are produced in very low yields in the absence of water, but tend to increase with increasing concentration of water; on the contrary, benzaldehyde and benzyl alcohol arising from oxidation of the side chain are produced in much higher yields than cresols in the absence of water, but their yields are not considerably varied with water concentration.

The above results concerning benzene and toluene show that the presence of oxygen is necessary for the formation of oxidation products; however, the presence of only water is not enough to induce the oxidation of the substrates. These facts indicate that water can be oxidized into hydroxyl radicals on the photogenerated positive holes with concurrent removal of electrons in the conduction band by oxygen probably adsorbed on the semiconductor surface. The resulting hydroxyl radicals will hydroxylate the aromatic nuclei.



* Detailed mechanisms are omitted since the processes following the initial generation of free radicals are nearly the same as proposed for the reactions of Fenton's reagent with aromatic substrates.[9]

Under oxygen in the absence of water toluene will transfer an electron to the positive hole, concurrently with electron transfer from the conduction band to oxygen, to give toluene radical cation;[5,10] on the other hand, in the presence of water both toluene and water will transfer electrons to the positive hole. The resulting toluene radical cation may subsequently lose a proton affording a benzyl radical, which will be oxidized with oxygen or superoxide anion finally into

benzyl alcohol and benzaldehyde as proposed for the reactions of Fenton's reagent with toluene.[9]

Therefore, it is reasonable to conclude that on irradiation of titanium dioxide under oxygen, the electron transfer from water to the positive hole mainly results in hydroxylation of the aromatic nuclei and the electron transfer from toluene mainly leads to oxidation of its side chain, and that oxygen contributes to these reactions by concurrently accepting an electron from the conduction band of semiconductor.

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8) Irradiation under argon in the presence of water did not completely suppress the formation of phenol, indicating that under this condition oxygen could not satisfactorily be removed from the reaction mixture.

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10) The oxidation potential of toluene is slightly lower than that of water. For this reason, toluene can be oxidized by the photogenerated positive hole of titanium dioxide.

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