The Liquid Phase Oxidation of Tetralin and *p*-Xylene in the Presence of Onium Salt Type Catalysts*

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Summary: In one of our early works, it was found that some onium salt type compounds exerted a strong catalytic effect on the oxidation of hydrocarbons. In the present work, the liquid phase oxidation of tetralin and *p*-xylene with oxygen was carried out in details in the presence of the onium salt type catalysts such as tetra-*n*-butylphosphonium, triphenylsulfonium, and tetraphenylphosphonium chlorides or bromides. By the use of these catalysts, tetralin was oxidized to tetralin hydroperoxide and *p*-xylene was converted to *p*-toluic acid and *p*-toluic aldehyde in mild conditions. The effect of triphenylsulfonium halides was more active than that of tetraphenylphosphonium halides and in particular the chlorides indicated an excellent ability in the oxidation.

Introduction

The catalyst in liquid phase oxidation of hydrocarbons with oxygen or air has widely been investigated from an industrial point of view.

In the low temperature liquid phase oxidation of hydrocarbons, transition metal compounds^{1),2)} such as cobalt acetate, cobalt naphthenate, copper naphthenate, manganese acetate, and bromine compounds³⁾ such as alkali bromides, hydrogen bromide and tetra-bromoethane were generally used as catalysts. And for practical purpose, two or more of the compounds mentioned above were combined and the complexes or mixtures⁴⁾ were extensively used in petrochemical industry. Recently, Brederick and coworkers^{5),6)} demonstrated some organic ammonium salts containing halogen anion were useful catalysts for some oxidation processes, and the application of ammonium salts was more effective to the reaction than alkali halides.

In our previous report⁷⁾, catalytic activities of some onium salt type compounds containing nitrogen, sulfur and phosphorus atoms were tested by the liquid phase oxidation of tetralin with oxygen, and this indicated that

they were better catalyst than Brederick's ammonium catalysts. Sulfonium and phosphonium halides were stable crystalline compounds for storage and easily purified by recrystallization.

The oxygen absorption to tetralin and *p*-xylene was observed by reading the change of a mercury scale of an oxygen buret described in one of our previous reports⁷⁾, which was cooperated with a mercury receptacle by an electrical method to keep an ordinary pressure of oxygen in reaction system. In the oxidation of tetralin, the effect of triphenylsulfonium chloride related to the reaction temperature. The oxygen absorption to tetralin was recognized already at about 30°C and the absorption velocity was observed to be ca. 4.74×10^{-4} mole min.⁻¹ at 50°C, 5.40×10^{-3} mole min.⁻¹ at 65°C, and 1.36×10^{-2} mole min.⁻¹ at 80°C after 10 minutes per one mole of tetralin employed. The absorption velocity for tetraphenylphosphonium chloride was found to be about 1.65×10^{-3} mole min.⁻¹ at 65°C and 7.45×10^{-3} mole min.⁻¹ at 80°C after 10 minutes per one mole of tetralin, respectively. In the reaction of tetralin, tetralin hydroperoxide was isolated by distillation as the main product of the reaction under reduced pressure.

In the experiment for xylene isomers, tetra-*n*-butylphosphonium chloride and tri-

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phenylsulfonium chloride were used as catalyst, and the susceptibility to oxidation of xylene isomers was in the following order: *o*-xylene > *p*-xylene > *m*-xylene and their reaction products consisted mainly of corresponding toluic aldehyde and toluic acid in all of the three cases.

In an attempt to screen useful catalysts for the oxidation of *p*-xylene, three groups of catalysts which were tetra-*n*-butylphosphonium (I), triphenylsulfonium (II) and tetraphenylphosphonium halides (III) containing chlorine and bromine anions were used.

These onium salts were almost insoluble to *p*-xylene, and the reaction started in a suspended state of catalysts, and then the amount of absorbed oxygen was measured continuously.

Tetra-*n*-butylphosphonium bromide had a stronger catalytic effect for the oxidation of *p*-xylene than the chloride. Triphenylsulfonium chloride also indicated an effective action. For instance, in the use of this compound, the oxygen absorption velocity to *p*-xylene at 110°C was 6.4×10^{-5} mole min.⁻¹ after 30 minutes, 1.8×10^{-4} mole min.⁻¹ after 60 minutes and 4.80×10^{-4} mole min.⁻¹ after 120 minutes, while, in the case of tetra-*n*-butylphosphonium bromide, the absorption velocity was 1.4×10^{-4} mole min.⁻¹ after 30 minutes, 2.7×10^{-4} mole min.⁻¹ after 60 minutes, and 4.6×10^{-4} after 120 minutes per one mole of *p*-xylene.

In the reaction catalysed by tetraphenylphosphonium halides, the induction period was longer in the case of chloride than that of the bromide. However, the chloride exhibited a more enduring catalytic ability than the bromide.

Ohta and Marumo¹⁾ reported the liquid phase oxidation of *p*-xylene catalysed by several transition metal naphthenates at 135°C for 4–10 hours without polar solvent. The reaction condition and the yield of main products, *p*-toluic aldehyde and *p*-toluic acid, seemed to be similar to the present experiment using onium catalyst for *p*-xylene oxidation. In the oxidation of tetralin, however, our onium salt catalyst was found to give a

better result.

From the above-mentioned observations, certain onium compounds containing phosphorus or sulfur atom and chlorine anion proved to be generally useful catalysts for low temperature reaction of hydrocarbons with oxygen. Similar results have also been obtained in the use of air instead of oxygen, which will be reported in future.

The catalytic activity of onium salts was generally in the following order: triphenylsulfonium chloride > tetra-*n*-butylphosphonium chloride > tetraphenylphosphonium chloride and these onium catalysts could be recovered from a mixture reacted below 115°C. The catalysts recovered were used repeatedly and behaved as effectively as the fresh onium compounds in subsequent oxidation reactions.

Experimental

1. Apparatus

The amount of absorbed oxygen during the reaction was measured by a modified apparatus described in the previous paper⁷⁾. The apparatus mainly consisted of an oxygen reservoir buret (200 ml), a reaction vessel (50 ml) and a mercury receptacle (200 ml). The buret was surrounded by a water jacket to keep the temperature constant, the upper side of the buret was introduced to the reaction vessel through a manometer and the lower side was connected to the mercury receptacle. The buret and the mercury receptacle were operated simultaneously to maintain a constant pressure of oxygen by an electrical method. The reaction vessel fitted with a magnetic stirrer was automatically controlled to keep desired conditions. After the catalyst and the hydrocarbon were placed in the reaction vessel, oxygen was brought into the buret and the air in the reaction system was removed by moving the mercury receptacle up and down. When the air escaped completely, oxygen was charged into the buret and the reaction mixture was stirred magnetically. The amount of oxygen absorbed was measured.

2. Materials

Oxygen: Oxygen (J. P. grade) from a bomb was dried with sulfuric acid and silica gel, and the purity was minimum 99.0% by

Table 1

Catalyst	Chemical formula	Appearance	Melting point (°C)
Di- <i>n</i> -butylammonium chloride	(<i>n</i> -C ₄ H ₉) ₂ H ₂ NCl	Colorless crystals	283-284
Tetra- <i>n</i> -butylphosphonium bromide	(<i>n</i> -C ₄ H ₉) ₄ PBr	Colorless crystals	112-113
Tetra- <i>n</i> -butylphosphonium chloride	(<i>n</i> -C ₄ H ₉) ₄ PCl	Colorless crystals	67-68
Tetraphenylphosphonium bromide	(C ₆ H ₅) ₄ PBr	Colorless needles	288-289
Tetraphenylphosphonium chloride	(C ₆ H ₅) ₄ PCl	Colorless needles	271-272
Triphenylsulfonium bromide	(C ₆ H ₅) ₃ SBr	Colorless needles	291-292
Triphenylsulfonium chloride	(C ₆ H ₅) ₃ SCl	Colorless needles	297-298

volume.

Tetralin: Commercial pure tetralin was shaken with concentrated sulfuric acid, neutralized with 10% sodium hydroxide solution, washed with water, dried and distilled to afford pure tetralin (b.p. 206-207°C).

***o*-Xylene and *m*-Xylene:** Commercial pure xylenes were dried and rectified by the Podbielniak apparatus to give pure samples: *o*-xylene boiled at 144.0-144.2°C (n_D^{20} 1.5055) and *m*-xylene boiled at 139.0-139.1°C (n_D^{20} 1.4972).

***p*-Xylene:** *p*-Xylene (98%) was washed repeatedly with concentrated sulfuric acid to give a colorless acid layer. The oil was washed with water, dried over anhydrous sodium carbonate and then fractionated through an efficient column. The fraction boiled at the range of 136-137°C was chilled to afford pure crystals of *p*-xylene (m.p. 13°C, b.p. 138.1-138.2°C, n_D^{20} 1.4958).

Catalyst: Catalysts were prepared by our earlier method^{7,8)}, purified by recrystallization and their properties were listed in Table 1.

3. Oxidation of tetralin

In the reaction vessel were placed 10 ml (0.073 mole) of tetralin and 10 mg of onium salts listed in Table 1 as the catalyst. The reaction vessel was immersed in an oil bath kept at a desired temperature and the reaction started with vigorous stirring. The absorbed oxygen was measured continuously. The results were shown in Fig. 1.

4. Tetralin hydroperoxide

The reaction mixture in Experiment 3. was transferred into a distillation flask and unreacted tetralin was then distilled off under nitrogen stream of diminished pressure below 4 mmHg. The residue was cooled to give crude tetralin hydroperoxide (slight yellowish needles m.p. 50-52°C) and the crystals were

- (1) Tetralin 10 ml + (C₆H₅)₃SCl 10 mg
- (2) Tetralin 10 ml + (C₆H₅)₄PCl 10 mg
- (3) Tetralin 10 ml + (*n*-C₄H₉)₂H₂NCl 10 mg
- (4) Tetralin 10 ml + (*n*-C₄H₉)₄PCl 10 mg
- (5) Tetralin 10 ml + (C₆H₅)₃SBr 10 mg
- (6) Tetralin 10 ml + (*n*-C₄H₉)₄PBr 10 mg
- (7) Tetralin 10 ml + (C₆H₅)₄PBr 10 mg

Fig. 1 Oxidation of tetralin at 80°C

Table 2

Catalyst	Reaction Time (min.)	Temp. (°C)	Oxygen (ml)	Yields of tetralin hydroperoxide (%)
(C ₆ H ₅) ₄ PCl	360	80	595	64
(C ₆ H ₅) ₄ PBr	360	80	319	64
(<i>n</i> -C ₄ H ₉) ₄ PCl	360	80	546	62
(<i>n</i> -C ₄ H ₉) ₄ PBr	360	80	334	58.5
(C ₆ H ₅) ₃ SCl	360	80	612	71.5
(C ₆ H ₅) ₃ SBr	360	80	582	63

recrystallized from toluene to give pure sample melting at 54°C, which was identified as an authentic specimen. The results were listed in Table 2.

5. Oxidation of xylene isomers

In the reaction vessel 10 ml (0.080 mole)

- (1) *o*-Xylene 10 ml + $(C_6H_5)_3SCl$ 70 mg
 (2) *p*-Xylene 10 ml + $(C_6H_5)_3SCl$ 70 mg
 (3) *m*-Xylene 10 ml + $(C_6H_5)_3SCl$ 70 mg

Fig. 2 Oxidation of xylene isomers in the presence of triphenyl sulfonium chloride at 110°C

of xylene and 90 mg of triphenylsulfonium chloride as the catalyst were placed and the reaction vessel was heated at 110°C. The results were shown in Fig. 2. After the reaction mixture was cooled and then treated with cold anhydrous ether to form white mass, the precipitates were collected by filtration, washed with ether and dried. The recovered materials were found to be unchanged catalyst. The recovered catalysts could be

- (1) *p*-Xylene 10 ml + $(C_6H_5)_3SCl$ 50 mg
 (2) *p*-Xylene 10 ml + $(n-C_4H_9)_4PBr$ 50 mg
 (3) *p*-Xylene 10 ml + $(n-C_4H_9)_4PCl$ 50 mg
 (4) *p*-Xylene 10 ml + $(n-C_4H_9)_2H_2NCl$ 50 mg
 (5) *p*-Xylene 10 ml + $(C_6H_5)_3SBr$ 50 mg
 (6) *p*-Xylene 10 ml + $(C_6H_5)_4PCl$ 50 mg
 (7) *p*-Xylene 10 ml + $(C_6H_5)_4PBr$ 50 mg

Fig. 3 Influence of onium salts in *p*-xylene oxidation at 110°C

employed to further oxidation experiments as well as newly prepared catalysts.

6. Influence of the composition of onium salts in *p*-xylene oxidation

10 ml (0.080 mole) of *p*-xylene was placed in the reaction vessel and 50 mg of onium salt shown in Fig. 3 was added as the catalyst. Reactions were greatly influenced by the composition of onium salts indicated in Fig. 3.

7. The amount of triphenylsulfonium chloride in *p*-xylene oxidation

The oxidation of *p*-xylene with oxygen in the presence of triphenylsulfonium chloride was also carried out similarly to Experiment 6. The amount of the catalyst used was changed from 10 mg to 90 mg for 10 ml of *p*-xylene. The results were shown in Fig. 4.

- p*-Xylene 10 ml + $(C_6H_5)_3SCl$: (1) 90 mg, (2) 80 mg, (3) 50 mg, (4) 30 mg, (5) 20 mg, (6) 10 mg

Fig. 4 Oxidation of *p*-xylene catalyzed by triphenylsulfonium chloride at 110°C

The oxygen absorption curve versus reaction time at each experiment was of definite characteristic shape and the total amount of oxygen in the reaction was paralleled with that of the catalyst employed, but a recommendable amount was more than 50 mg with respect to triphenylsulfonium chloride for 10 ml of *p*-xylene.

8. Oxidation temperature of *p*-xylene

In the oxidation of tetralin (Experiment

3), the reaction was carried out at 50–80°C to collect tetralin hydroperoxide, but the separation of pure *p*-xylene hydroperoxide was rather difficult in the oxidation of *p*-xylene carried out at 100–130°C. In the reaction vessel, 10 ml of *p*-xylene and 90 mg of triphenylsulfonium chloride were placed and the reaction vessel was immersed into an oil bath maintained at a desired temperature. The oxygen absorption was continuously measured and the results were shown in Fig. 5.

p-Xylene 10 ml + (C₆H₅)₃SCl 90 mg: (1) at 120°C, (2) at 115°C, (3) at 110°C, (4) at 130°C, (5) at 100°C

Fig. 5 Effect of temperature on *p*-xylene oxidation

The *p*-xylene oxidation without polar solvent was not rapid at 100°C, but remarkably rapid at 115–120°C. The reaction at 130°C showed a very short induction period and a decreasing of catalytic ability. Although triphenylsulfonium chloride was so stable on heating below its melting point, 297–298°C, that the catalyst remained unchangable in boiling *p*-xylene in the absence of oxygen, the catalytic action was slowly depressed during the reaction.

9. Products of *p*-xylene oxidation

To the reaction mixture was added 5 ml of 1-N sodium hydroxide solution and the mixture was titrated with 0.1-N hydrochloric acid to measure the amount of toluic acid. The resultant solution was mixed with 50 ml of ethyl alcohol and 100 ml of 2,4-dinitrophenylhydrazonium sulfate solution (2,4-DNPH 40 g + H₂SO₄ 200 ml + H₂O 300 ml + C₂H₅OH 1 l). The mixture was shaken for several hours to precipitate an orange red hydrazone. The precipitate was filtered, washed with 10 ml of 50% aq. alcohol and dried in vacuum to

weigh the hydrazone. The acidic substance from the oxidation mixture was found to be the almost pure *p*-toluic acid. The hydrazone recrystallized from nitrobenzene was identified to be that of *p*-toluic aldehyde with authentic specimen, which melted at 234.0°–234.5°C. Some examples of the oxidation of *p*-xylene (10 ml) catalysed by triphenylsulfonium chloride at several reaction conditions were listed in Table 3.

Table 3 Oxidation products of *p*-xylene*

Catalyst (C ₆ H ₅) ₃ SCl (mg)	Reaction		The amount of absorbed oxygen (mole)	Products	
	Temp. (°C)	Time (min.)		Toluic acid (mole)	Toluic** aldehyde (mole)
10	110	190	0.0025	0.00065	0.00097
20	110	190	0.0031	0.00084	0.00114
30	110	210	0.0043	0.00130	0.00150
40	110	240	0.0071	0.00258	0.00200
50	110	260	0.0081	0.00321	0.00214
80	110	300	0.0088	0.00362	0.00244
90	110	300	0.0100	0.00451	0.00251
10	115	180	0.0029	0.00073	0.00119
20	115	190	0.0051	0.00146	0.00186
50	115	190	0.0074	0.00262	0.00238
90	115	280	0.0105	0.00443	0.00283
10	120	110	0.0029	0.00071	0.00082
20	120	160	0.0046	0.00127	0.00121
40	120	200	0.0075	0.00252	0.00197
90	120	310	0.0105	0.00430	0.00244
10	130	140	0.0035	0.00089	0.00115
30	130	150	0.0042	0.00108	0.00133
50	130	200	0.0050	0.00164	0.00174
70	130	200	0.0053	0.00174	0.00181
90	130	230	0.0062	0.00193	0.00205

* *p*-Xylene of 0.080 mole was used in each experiment.

** Calculated from the weight of 2,4-dinitrophenylhydrazone.

Discussion

In the present work the low temperature liquid phase oxidation of tetralin with oxygen in the presence of onium salt catalysts exhibited the typical characteristics of an autoxidation process, and the observation was confirmed by comparing the yields of tetralin hydroperoxide in the use of several catalysts indicated in Table 2. The oxygen was absorbed by tetralin without induction period and triphenylsulfonium and tetraphenylphosphonium chlorides showed a superior catalytic behavior.

The action of onium salt catalysts appeared

to depend on both of the cationic part and the halogen anion. The effect of onium chloride was noteworthy, notwithstanding the order (iodine > bromine > chlorine) of the easiness of halogen radical formation from halides in the presence of oxygen⁷. The difference in activity of these catalysts might be caused by their heat stability and solubility to the reaction mixture of oxidation products such as hydroperoxide and other by products, and also by the easiness of abstraction of a hydrogen atom in the hydrocarbon molecule by the halogen radical preformed.

In the liquid phase oxidation of xylene isomers, *m*-xylene had a short induction period (about 20 min.) for oxygen absorption shown in Fig. 2, and *o*-xylene absorbed the oxygen rapidly to form *o*-toluic acid and aldehyde as main products. After the oxidation of xylene isomers was carried out at 110°C, the catalyst was collected, identified by ultraviolet spectroscopy with the initial triphenylsulfonium chloride and repeatedly employed for the same purpose, indicating a similar catalytic effect to the second batch of reaction.

The catalyst used in the reaction above 130°C was gradually decomposed during the reaction, and it was unsuccessful to recover it. The decomposition of the catalyst became appreciable at the boiling points of xylene isomers. Triphenylsulfonium chloride in Fig. 3, showed an excellent effect as much as that of the oxidation of tetralin in Fig. 1, and two curves with respect to tetra-*n*-butylphosphonium chloride and bromide crossed over 300 min. In this experiment (Fig. 3) tetraphenylphosphonium chloride was expected to give a good result but the chloride had little effect for reason of its unstable property on heating in the reaction medium of *p*-xylene. Tetraphenylphosphonium halides underwent decomposition accompanied by a color change in the oxidation mixture at 110°C to form triphenylphosphine oxide and phenolic materials owing to the decomposition of *p*-xylene hydroperoxide as an initial oxidation product.

From the Experiment 6, the effect of the amount of triphenylsulfonium chloride on *p*-xylene oxidation was examined in Fig. 4. The increase in the volume of absorbed oxygen

reached the limit at the amount of 80–90 mg of the chloride employed to 10 ml of *p*-xylene. The total amount of oxygen in Fig. 4 appeared to be proportional to 2/3rd power of the amount of triphenylsulfonium chloride catalyst and this relation was shown in Fig. 6.

$M_{(C_6H_5)_3SCl}$: mole of triphenylsulfonium
 M_{O_2} : mole of total absorbed oxygen

Fig. 6 Relation of the amount of triphenylsulfonium chloride to the total amount of absorbed oxygen in *p*-xylene oxidation at 110°C

In Experiment 8, the increase of oxygen absorption at the initial reaction step was ascribed to an increase of reaction temperature. However, the best result was obtained in 115–120°C because the triphenylsulfonium chloride partially decomposed at 130°C through the reaction (Fig. 5). These observations suggested the necessity of a careful selection of reaction conditions such as the catalyst amount and the reaction temperature in the liquid phase oxidation of *p*-xylene catalysed by triphenylsulfonium chloride.

The formation of *p*-toluic acid at 110–130°C was greatly influenced by the amount of the absorbed oxygen but that of *p*-toluic aldehyde was not so affected. The relation of the amount of *p*-toluic acid determined in Experiment 9, against the total amount of oxygen absorbed appeared to be proportional to a three-second order in Table 3.

Further experiments of other alkyl benzenes such as cumene or *p*-cymene in the liquid phase oxidation, catalysed by triphenylsulfonium chloride below 95°C indicated similar tendency of oxygen absorption as in the case of *p*-xylene oxidation.

Conclusion

The liquid phase oxidation of tetralin and *p*-xylene with oxygen under ordinary pressure was carried out in the presence of onium

salts as new catalysts. The main catalysts were tetra-*n*-butylphosphonium, triphenylphosphonium, triphenylsulfonium and tetraphenylphosphonium chlorides and bromides. Tetralin was smoothly oxidized by these catalysts to afford tetralin hydroperoxide. In the oxidation of *p*-xylene, the oxygen absorption was greatly affected by the composition, the amount of catalysts, and the reaction temperature. The main products of *p*-xylene oxidation were *p*-toluic acid and *p*-toluic aldehyde and the best result was obtained by the use of triphenylsulfonium chloride as the catalyst. Catalytic activities of onium compounds showed generally in the following order: sulfonium chloride > phosphonium chloride > ammonium chloride. The onium salt catalysts were prepared easily and their activities did not decrease on storage for a long period of time. In the field of liquid phase oxidation studies, attention for an effective catalyst has been centered in the petrochemical industry and further interesting developments are expected.

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