Liquid Phase Oxidation of *p*-Xylene:
Effects of Potassium with Various Reaction Conditions

Sung Hwa Jhung

Samsung General Chemicals Co., Ltd., San 222-2, Dokgod-Ri, Daesan-Up, Seosan-Si, Chungnam 356-711, Korea
Received August 31, 2001

Introduction

Terephthalic acid (TPA) is one of the most important chemicals, with an annual production capacity of more than 24,000,000 tons in the year 2000. The annual production capacity of Korea, 4,540,000 tons, is the highest in the world.[1] TPA, the raw material of polyester, is usually produced commercially by liquid phase oxidation of *p*-xylene (pX) with air, using a catalyst combination of cobalt, manganese and bromide ions in acetic acid at around 170-210 °C.[2,3]

Because of the huge production capacity of TPA, even small improvements in the process are very important from the economic view. The desirable improvements in the TPA process are described elsewhere,[3] and the studies to improve the liquid phase oxidation of alkyl aromatics with catalysts of metal/bromine have been reviewed in detail by Partenheimer.[4]

An alkali metal cannot be excluded from the production of TPA in a commercial reactor because a sodium hydroxide solution is used to dissolve precipitated materials that cause line plugging. On the other hand, as a bromine source, alkaline bromine such as sodium bromide or potassium bromide can be utilized instead of hydrobromic acid or an organic bromide, such as tetrabromoethane.

However, the effects of alkali metals on the oxidation of alkyl aromatic compounds, including *p*-xylene are not very well known. Apparently just one article[5] has been published, which focuses on the effect of alkali metal acetates on *p*-xylene oxidation, to explain the elimination of an induction period for oxidation with the CoBr$_2$. Several patents[6,7] claim the improvement of color properties of produced TPA and the reduction of reactor corrosion caused by the bromine and acetic acid. One paper[8] describes the accelerating effect of alkali metal on the oxidation of *p*-toluic acid, an intermediate of TPA from *p*-xylene.

The effects of alkali metals on *p*-xylene oxidation are very important, considering the capacity of TPA and the inevitable incorporation of alkali metals in a commercial plant, especially after the start up of a plant, even though it is inadvertent.

---

*Tel: +82-41-660-6361; Fax: +82-41-660-6369; e-mail: shjhung @samsung.co.kr

Recently, we have reported the effects of alkali metals on the liquid phase oxidation of xylenes.[9,10] The reaction rate can be eventually accelerated, even though the rate is decelerated a bit initially, with the addition of a suitable concentration of alkali metal. The formation of poisonous materials has been postulated to explain these effects. Side reactions forming carbon dioxide can also be decreased with the addition of an alkali metal.

In the present report, the decelerating and accelerating effects of alkali metals on the oxidation of alkyl aromatics are discussed based on the results with various catalyst and water concentrations and reaction temperature. The effects of alkali metal in the catalyst system of Co/Br without manganese were also determined. The oxidation of toluene and p-toluic acid was studied to check the change of mechanism with the functional groups of the benzene ring.

Experimental Section

Apparatus. The apparatus for the oxidation reaction is explained elsewhere.[9] The reaction rate and cumulated conversion were monitored continuously by the consumption rate of oxygen.

Procedure. The procedure for the oxidation reaction is explained elsewhere.[9] 200 g of reactants (15% *p*-xylene, 7.5% water and 77.5% acetic acid) were charged in a 450 mL titanium reactor. The expected oxygen consumption was 848 mmol, based on the stoichiometry of *p*-xylene oxidation only. Reactants of 30% toluene (expected oxygen consumption: 848 mmol) and 19.23% *p*-toluic acid (expected oxygen consumption: 424 mmol) were used instead of 15% *p*-xylene to study the effects of substrate, and the amount of acetic acid was changed accordingly. Based on the total weight of the reaction mixture, the catalyst comprised 100 ppm of cobalt, 200 ppm of manganese and 300 ppm of bromine as a base condition. The concentration of each catalyst component was changed by 15% to study the effect of catalyst concentration on the potassium effect (K effect). In other words, the cobalt, manganese and bromine concentrations were 85-115, 170-230 and 255-345 ppm in that order. In this report, the terms Z, N and P mean the concentration of each catalyst component is zero level (Z), negative level (N) or less than 15% from Z and positive level (P) or more than 15% from Z, and the order of components is cobalt,

manganese, bromine. In other words, for example, NNP and ZPN mean Co 85, Mn 170, Br 345 ppm and Co 100, Mn 230, Br 255 ppm, respectively. The concentrations of cobalt and bromine for the case of the Co/Br system were 100 or 200 ppm for cobalt and 300 ppm for bromine. The effects of K were investigated with the addition of 98 ppm of K (147 ppm for the case of p-toluic acid oxidation).

Unless otherwise stated, the reaction temperature was 185 °C in the oxidation with the Co/Mn/Br catalyst system and 190 °C with the Co/Br catalyst system.

Reagents. Cobalt acetate tetrahydrate, manganese acetate tetrahydrate, hydrogen bromide and potassium acetate were used to prepare the catalyst solution. All other chemicals including p-xylene, acetic acid, toluene and p-toluic acid were guaranteed reagent grades.

Analysis. The detailed analysis methods for solid and liquid products are reported elsewhere.[9] The K effect is represented with the relative increase in the oxidation rate from the catalyst system without potassium.

Results and Discussion

Dependence of K effects on catalyst concentration. The effect of alkali metals on p-xylene oxidation, an initial deceleration that gives way to an acceleration is explained elsewhere.[9,10] From Figure 1, for the case of changing the

manganese concentration, this effect occurs for every catalyst condition, even though the degrees of effect vary slightly. The results, including the case of changing the cobalt and manganese concentration (Figures similar to Figure 1 are not included.) when the oxygen conversion is 88.4% or 750 mmol are summarized in Table 1. Clearly, the K effect is high when the concentration of manganese or bromine is low. However, the effect is not highly dependent on the concentration of cobalt. In summary, the effect dominates the condition of PNN, NNN and probably ZNN. Actually, the K effect for the case of PNN and NNN are 11.2% and 9.6%, respectively.

The effect decreases with an increase in catalyst concentration: The effects are 9.6 for NNN, 6.5 for ZZZ and 4.1% for PPP.

To check the fact that the K effect is large when the manganese concentration is low, the effect of potassium with the Co/Br catalyst system (the effect is largest when the concentration of manganese is lowest) was checked. The K effect when manganese is excluded is extremely high, up to 50% for the case of 100 ppm of cobalt or 80% for the case of 200 ppm of cobalt, as shown in Figure 2. However, this tremendous effect diminished up to nearly zero as the conversion increased, and the typical deceleration in the beginning of the reaction did not prevail. To confirm this diminishing pattern, it is necessary to perform an experiment
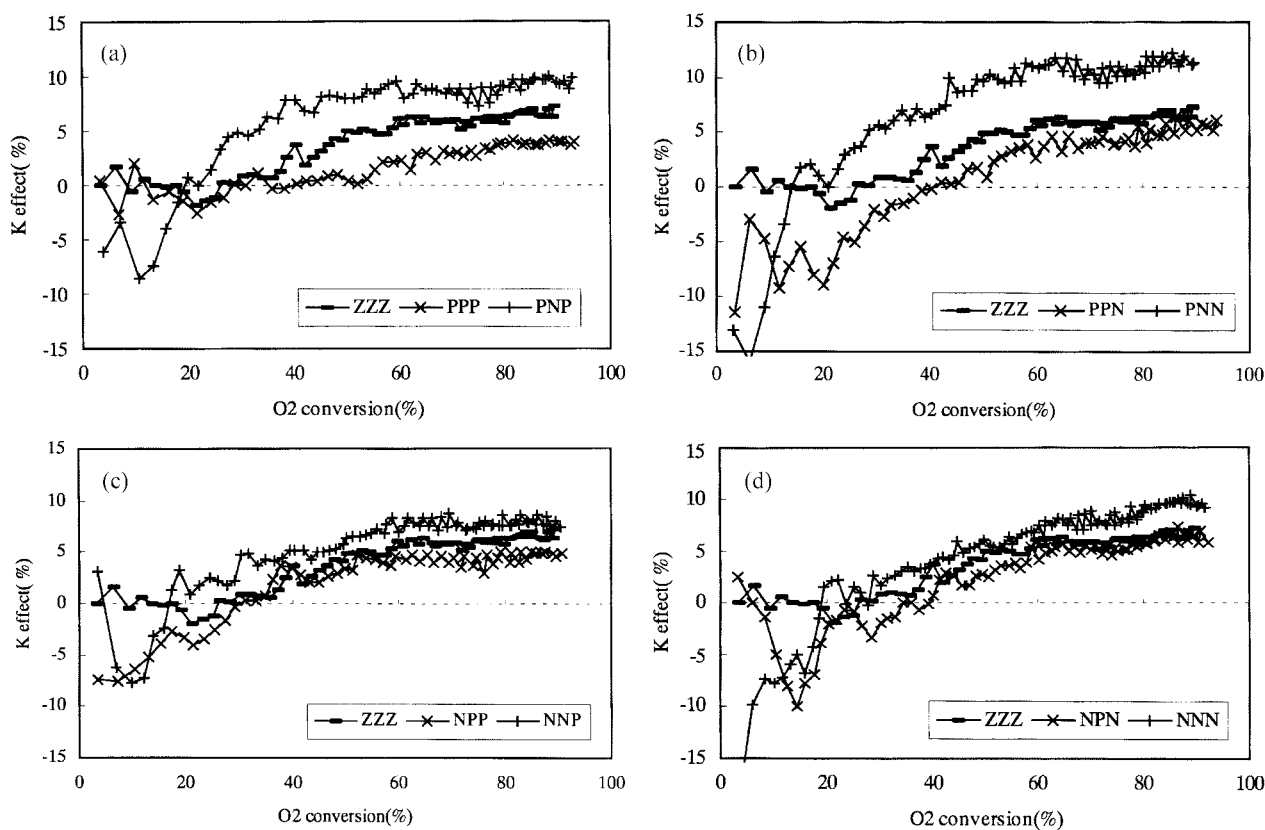

Figure 1. The effect of added potassium on the rate of p-xylene oxidation. (a) In the condition of high cobalt and high bromide concentration. (b) In the condition of high cobalt and low bromide concentration. (c) In the condition of low cobalt and high bromide concentration. (d) In the condition of low cobalt and low bromide concentration.

Table 1. The dependence of K effect on the concentration of catalyst

No.	Catalyst concentration[a]	K effect (%)[b]	Dependence of the K effect on catalyst concentration
1	ZZZ	6.5	1) Dependence on manganese concentration:
2	PPP	4.1	- high Mn : average of 2,3,6,7 = 21.6/4=5.40
3	PPN	6.0	- low Mn : average of 4,5,8,9 = 37.7/4=9.43
4	PNP	9.0	2) Dependence on bromine concentration:
5	PNN	11.2	- high Br : average of 2,4,6,8 = 26.0/4=6.50
6	NPP	5.0	- low Br : average of 3,5,7,9 = 33.3/4=8.33
7	NPN	6.5	3) Dependence on cobalt concentration:
8	NNP	7.9	- high Co : average of 2,3,4,5 = 30.3/4=7.58
9	NNN	9.6	- low Co : average of 6,7,8,9 = 29.0/4=7.25

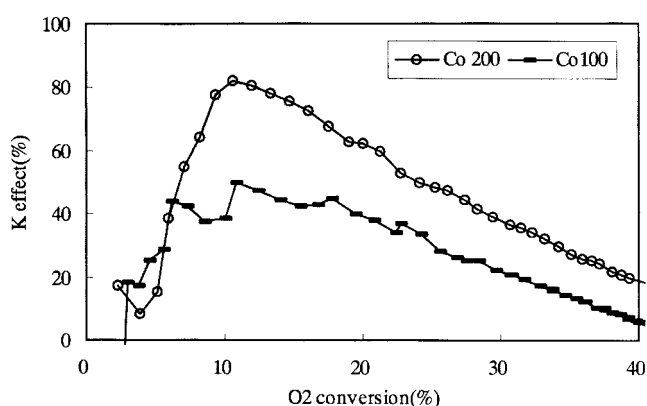[a]See text. [b]K effect at 88.4% of oxygen conversion (750 mmol).

Figure 2. The effect of added potassium to the Co/Br (300 ppm) catalyst system on the rate of *p*-xylene oxidation.

under the condition of a continuous flow of oxygen or air because the reactor in this study is operated in a batch mode and the oxygen can be deficient for the case of low selective reactions, such as p-xylene oxidation with Co/Br catalyst.

In summary, the deceleration and subsequent acceleration in activity when potassium is added to the Co/Mn/Br catalyst system in various compositions has been confirmed. As reported in a previous reference,[10] the acceleration increases generally to the same degree of deceleration. The K effect is large when the concentration of manganese or bromide is low and the K effect for the case of the Co/Br catalyst system is as high as 50-80%.

Dependence of K effect on the substrate. One may imagine the situation of deceleration in the oxidation of *p*-xylene and acceleration in the oxidation of *p*-toluic acid, because initially the reaction is decelerated (oxidation of *p*-xylene) and is later accelerated (oxidation of *p*-toluic acid). However, the effects with the substrates of *p*-xylene, toluene and *p*-toluic acid are very similar, as shown in Figure 3, even though the degrees of the K effect differ slightly. The typical deceleration and acceleration pattern occurred in all substrates investigated. Therefore, the mechanism of the K effect seems does not depend on a functional group on the benzene ring or the electronic environment but on the oxidation reaction itself. The K effect does not depend on the type of substrate and, as suggested elsewhere,[10] this effect may be explained as stemming from the formation of
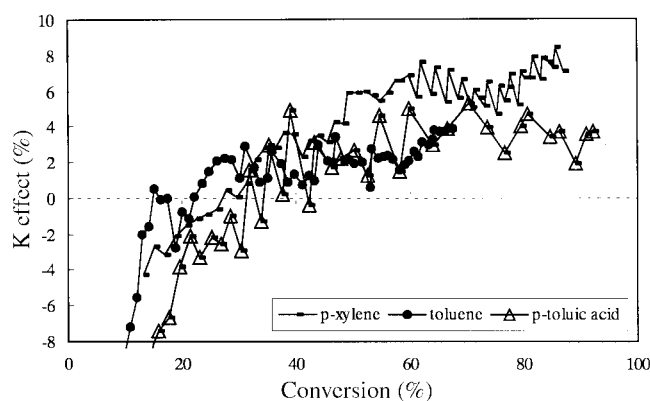

Figure 3. The effect of added potassium on the rate of oxidation of *p*-xylene (concentration: 15%), toluene (concentration: 30%) and *p*-toluic acid (concentration: 19.23%). The catalyst composed of 100 ppm of Co, 200 ppm of Mn and 300 ppm of Br. The added potassium concentration was 98 ppm for the oxidations of *p*-xylene and toluene and 147 ppm for the oxidation of *p*-toluic acid.

poisonous species and the interaction of them with the added potassium in the latter stage of reaction. The added potassium (which retards the reaction in the beginning of the reaction) may interact with poisonous materials that may be formed as the reaction progresses, and, therefore, the potassium may decrease the negative effects of the poisonous species. This proposed mechanism is already reported in a reference.[10]

Dependence of K effect on the water concentration and reaction temperature. Checking the K effect for various conditions of water concentration and reaction temperature is important because the oxidation reaction can be varied not only in catalyst concentration but also in water concentration and reaction temperature. In Figure 4 and Figure 5, the effect increases as the water concentration decreases and the reaction temperature decreases. This means that the effect does not depend merely on the reaction rate, because the oxidation rates are high when the water concentration is low and the reaction temperature is high. We can surmise that the effect decreases to zero or negative when the reaction temperature is higher than 190 °C. Therefore, the selection of suitable reaction conditions and catalyst concentrations is necessary to achieve a positive K effect.
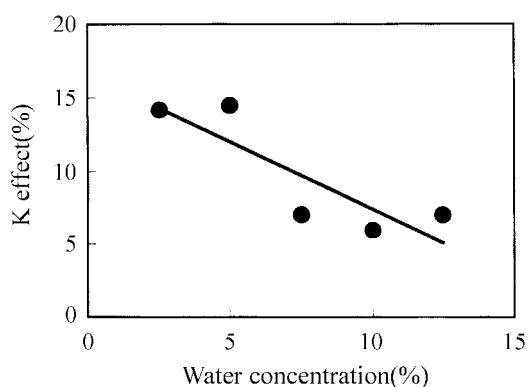
Figure 4. The effect of added potassium on the rate of *p*-xylene oxidation with various water concentrations. The O_2 conversion was 60%.
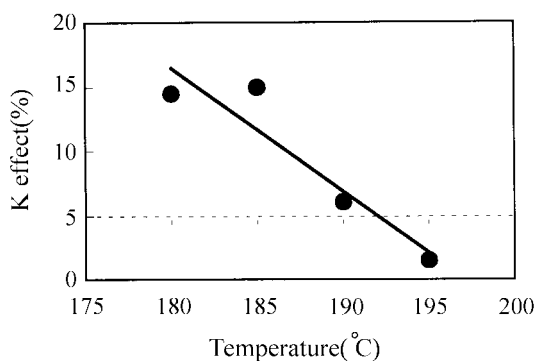

Figure 5. The effect of added potassium on the rate of *p*-xylene oxidation with various reaction temperatures. The O_2 conversion was 60%.

Conclusions

The K effect increases as the concentration of manganese or bromine decreases. The effect also increases as the total catalyst concentration, water concentration or reaction temperature decreases. The K effect in the case of oxidation with Co/Br is as high as 80%; this case should be investigated in detail. The oxidation of *p*-xylene, toluene and *p*-toluic acid shows patterns quite similar in K effect, which may show that the K effect is not highly dependent on the electronic environment of the substrates.

References

1. http://www.hyosungchemical.com/english/
2. http://www.utm.edu/departments/artsci/chemistry/Terephthalic Acid.html
3. Chavan, S. A.; Halligudi, S. B.; Srinivas, D.; Rantnasamy, P. *J. Mol. Catal. A* **2000**, *161*, 49.
4. Partenheimer, W. *Catal. Today* **1995**, *23*, 69.
5. Sheldon, R. A.; Kochi, J. K. *Metal-catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Ch. 5 and Ch. 10.
6. Jpn. Open Pat. 52-97929 (1977), to Toyobo co. Ltd.
7. US Pat. 4 158 738 (1979), to E. I. Du Pont de Nemours and Company.
8. Ohta, N.; Koie, T.; Sakata, S. *Kogyo Kagaku Zasshi* **1965**, *68*, 2239.
9. Jhung, S. H.; Lee, K. H.; Park, Y.-S. *Bull. Korean Chem. Soc.* **2002**, *23*, 59.
10. Jhung, S. H.; Lee, K. H.; Park, Y.-S. *Appl. Catal. A* **2002**, *230*, 31.