438 © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 438—441 (1990) [Vol. 63, No. 2

Palladium Catalyzed Direct Oxidation of Benzene with Molecular Oxygen to Phenol

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(Received October 4, 1989)

Direct phenol synthesis from benzene is currently one of the most important problems in modern chemistry. We have reported new phenol synthesis from benzene and O_2 via direct activation of a C-H aromatic bond by the $Pd(OAc)_2$/phenanthroline catalyst system. The evidence for direct oxidation of benzene by O_2 was obtained using ^{18}O and ^{2}H isotopes. The mechanism was proposed on the basis of these results and the reactions of Ph-Pd σ complex intermediates.

In previous study,[1)] we developed new phenol synthesis from benzene and O_2 via direct activation of a C-H aromatic bond by the $Pd(OAc)_2$/phenanthroline catalyst system. There have been many investigations concerning the reactions via the C-H bond activation by transition metal catalysts,[2)] however, little is known on the direct phenol synthesis from benzene and O_2.[3)] Our phenol synthesis reaction proceeds under the conditions of 15 atm of O_2, 15 atm of CO, equimolar amounts of $Pd(OAc)_2$, and 1,10-phenanthroline (phen) and AcOH, at 180 °C. The addition of both CO and phenanthroline is essential to bring about the selective synthesis of phenol. We have obtained evidence for direct oxidation of benzene by O_2 from $^{18}O_2$ isotope experiments and investigated the mechanism using a Ph-Pd σ complex prepared directly from benzene and $Pd(OAc)_2$.[4)] In this paper we report these results.

Results and Discussion

Table 1 summarizes the results performed under various reaction conditions. In a typical experiment charging 8 cm^3 of benzene, 12 cm^3 of AcOH, 0.2 mmol of $Pd(OAc)_2$, 0.2 mmol of 1,10-phenanthroline, 15 atm of O_2, 15 atm of CO in an autoclave with stirring at 180 °C for 1 h, there were obtained phenol in 850% yield (yields are all based on Pd) with phenyl acetate (56%) as a by-product. The yield of phenol increased up to 1270% when O_2 and CO gases were repeatedly supplied to 30 atm, the initial pressure, every 1 h to replace those consumed during the 3 h period.

Table 1. Phenol Synthesis from Direct Oxidation of Benzene[a)]

Run	$Pd(OAc)_2$	Reaction time	Temp	Yield/%[b)]	
	mmol	h	°C	PhOH	PhOAc
1	0.2	1	180	850(3.8)	56
2	0.2	1	150	560(2.5)	40
3	0.2	1×3[c)]	180	1270(5.6)	120
4	0.1	1	180	1200(2.7)	115
5	0.5	1	180	381(4.2)	29

a) Benzene 8 cm^3, AcOH 12 cm^3, 1,10-phenanthroline 0.2 mmol, CO 15 atm, O_2 15 atm. b) Based on Pd and numbers in parenthesis are those based on the starting benzene. c) O_2 and CO gases were repeatedly supplied to 30 atm after removal of the residual gases in vacuo every 1 h.

$^{18}O_2$ Isotope Experiment. The reaction was done under the similar conditions using $^{18}O_2$ (95% purity) with stirring for 3 h at 180 °C, to give phenol in 780% yield. After the reaction, the total pressure decreased from 30 atm to 17 atm (at room temperature) and the composition of the gaseous phase was carbon monoxide (22.5%), oxygen (37.1%), and carbon dioxide (40.4%). The results are shown in Table 2. As can be seen from the material balance in the table, carbon dioxide, acetic anhydride, and water are also formed in addition to phenol with consumption of oxygen and carbon monoxide. On GLC mass analysis, it was found that phenol formed contained 92% of ^{18}O (Fig. 1) and that carbon dioxide and acetic acid formed, contained ^{18}O in the ratio of 33/100 and 3/100, respectively. This result clearly shows that phenol was formed via direct oxidation of benzene with molecular oxygen (Eq. 1).

^{2}H Isotope Experiment. In order to study isotope scrambling, the reactions using benzene-d_6 and acetic acid-d_4 (CD_3COOD) were carried out.

Table 2. Material Balance in the Reaction of Benzene and $^{18}O_2$[a)]

Charge		After the reaction	Balance
mmol		mmol	mmol
$Ph^{18}OH$	—	1.56	1.56
PhOAc	—	0.13	0.13
Ac_2O[b)]	—	0.36	0.36
CO	13.39	3.41	−9.98
CO_2	—	4.59	4.59
$CO^{18}O$	—	1.53	1.53
$^{18}O_2$	13.39	5.62	−7.77
$Ac^{18}OH$	—	6.00	6.00
H_2O[c)]	1.58	3.68	2.10

a) Benzene 8 cm^3, AcOH 12 cm^3, phen 0.2 mmol, CO 15 atm, O_2 15 atm, 180 °C, 3 h. b) Analyzed by GC after conversion to acetanilide. c) Analyzed by Karl-Fischer method.

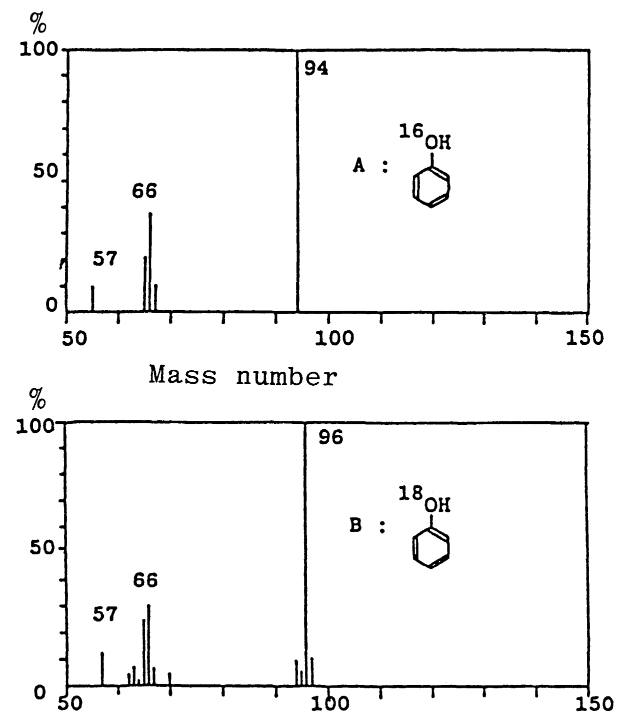


Fig. 1. Mass spectra of phenol. A: Obtained from the reaction with O_2. B: Obtained from the reaction with $^{18}O_2$.

$$C_6H_6 + {}^{18}O_2 + CO \rightarrow C_6H_5{}^{18}OH + CO^{18}O \qquad (1)$$

When the reaction was performed using benzene-d_6 instead of benzene, the phenol formed contained 100% of deuterium although the yield decreased (Eq. 2). On the other hand, when reaction was performed with benzene-d_6 using AcOH, both C_6D_5OD and C_6D_5OH were formed in molar ratio of 6:100 (Eq. 3). It was also found that when phenol (1.5 mmol) was treated in CD_3COOD (6 cm^3) under similar reaction conditions ($Pd(OAc)_2$, 0.2 mmol; phen, 0.2 mmol; N_2, 15 atm; 180 °C), C_6H_5OD and C_6H_5OH were obtained in ratio of 71:100 (Eq. 4). These results suggest that a Pd-OPh σ complex intermediate derived from O insertion to a Pd-Ph σ complex intermediate,[1)] reacts with AcOH to give phenol and an AcO-Pd which attacks benzene again to give the Pd-Ph intermediate (Eq. 5).[5)]

$$\underset{15\text{atm}}{C_6D_6 + O_2} \xrightarrow[180\,^\circ\text{C}]{Pd(OAc)_2/\text{phen}/CO(15\text{atm})} \underset{100\%\ D}{C_6D_5OD} \qquad (2)$$

$$\underset{15\text{atm}}{C_6D_6 + O_2} \xrightarrow[180\,^\circ\text{C, AcOH}]{Pd(OAc)_2/\text{phen}/CO(15\text{atm})} \underset{6\ :\ 100}{C_6D_5OD + C_6D_5OH} \qquad (3)$$

$$C_6H_5OH \xrightarrow[CD_3COOD,\ 180\,^\circ\text{C}]{Pd(OAc)_2/\text{phen}/N_2(15\text{atm})} \underset{71\ :\ 100}{C_6H_5OD + C_6H_5OH} \qquad (4)$$

$$C_6H_5O\text{-}Pd + AcOH \longrightarrow C_6H_5OH + AcO\text{-}Pd\text{-} \qquad (5)$$

Gas Balance. As is apparent from Table 2, O_2 and CO consumption is relatively high as compared with the quantity of phenol formed. We assumed that O_2 and CO both coordinated to a Pd/phen complex intermediate during and after the reaction. To test this, we performed gas recovery experiments using $CO/CO_2/O_2$ gas mixture (O_2 10.2 mmol, CO 5.6 mmol, CO_2 11.4 mmol) (Table 3). As can be seen from the table, CO, CO_2, and O_2 were recovered in 54, 100, and 75% yields after the treatment with the solution of $Pd(OAc)_2$ and phen in benzene/AcOH (at room temperature, stirring for 1 h under 30 atm). Contrary to this, in the absence of $Pd(OAc)_2$ and phen, these gases were recovered almost quantitatively. Since CO_2 can be recovered quantitatively,[6)] it can be concluded that CO and O_2 coordinate to a Pd/phen com-plex after the reaction. Two roles of CO can be thought in this reaction: one is to inhibit coupling of the Pd-Ph complex with benzene to give biphenyl by occupying the coordination site, and the other is to accept one oxygen atom of O_2, and another oxygen atom being incorporated into phenol, thus assisting the O-O bond cleavage.[1)] Thus, CO acts as a reducing agent of O_2 to give CO_2. Recently Sasaki et al. used H_2 as a reductant in direct phenol synthesis from benzene and O_2 by heterogeneous catalysts.[3c)]

Attempted Isolation of Pd/Phen/CO Complex. It is known that CO bubbling to $Pd(OAc)_2$ in AcOH gives Pd carbonyl complexes.[7)] We tried to isolate a Pd/phen/CO complex. The reaction of $Pd(OAc)_2$ with CO (0.5 atm), O_2 (0.5 atm) and phen in AcOH/benzene/chloroform at room temperature for 3 h, gave red-brown Pd/phen/CO complex (**1**) (2.8 g) with stoichiometry of $Pd_4(\text{phen})_4(CO)(OAc)_4$. The reaction of complex **1** at 180 °C for 3 h with O_2 (15 atm) or under N_2 (15 atm) gave rise to phenol in 680 and 95% yields, respectively, suggesting that **1** is an intermediate complex.

Reaction of Pd-Ph σ Complex with O_2. We have prepared a diphenyltripalladium(II) complex (**2**) from the reaction of $Pd(OAc)_2$ with benzene in the presence of dialkyl sulfides (Fig. 2).[4)] The complex **2** has been found to react with olefins and CO or CO_2 to give phenyl-substituted olefins and benzoic acid, respectively.[4c)] Then, reactions of **2** with O_2 were examined

Table 3. Recovery of Gas Phase Components[a)]

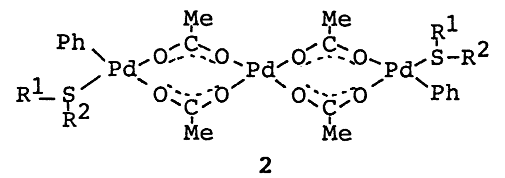
Benzene	AcOH	$Pd(OAc)_2$	phen	Recovered gas (mmol)			Recovery ratio		
cm^3	cm^3	mmol	mmol	O_2	CO	CO_2	O_2	CO	CO_2
4	6	—	—	10.2	5.6	11.4	100	100	100
4	6	0.2	0.2	7.6	3.0	11.4	75	54	100

a) Initially O_2 (10.2 mmol), CO (5.6 mmol), and CO_2 (11.4 mmol) were charged.

Table 4. Reaction of Diphenyltripalladium(II) Complex 2[a]

Run	Phen	AcOH	THF	CO	O_2	Temp	Time	Product yield/%[b]	
	mmol	cm^3	cm^3	atm	atm	°C	h	PhOH	PhCOOH
1	0.94	10	—	15	15	180	1	Trace	0
2	0.94	10	—	15	15	100	1	30	24
3	0.94	10	—	0.5	0.5	90	12	0.1	35
4	—	—	10	0.5	0.5	r.t.	12	1.2	60
5	0.94	—	10	0.5	0.5	60	12	0.9	55
6	0.94	—	10	0.5	0.5	r.t.	12	0.2	15

a) Complex **2** 0.32 mmol. b) Based on Pd.



2

$R^1=Bu^t$

$R^2=CH_2Bu^t$

Fig. 2.

under various conditions. The results are summarized in Table 4.

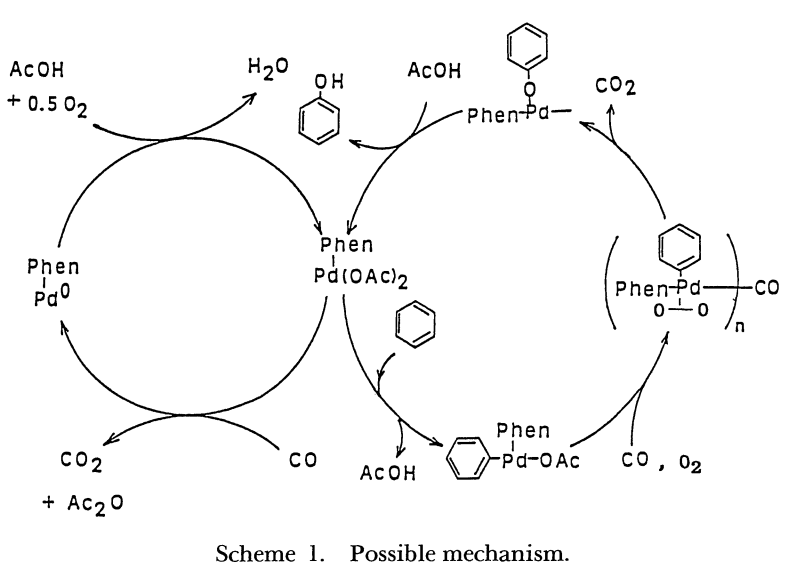
As can be seen from the table, under higher O_2 and CO pressure (15 atm each), phenol was formed in 30% yield from complex **2** with 24% of benzoic acid (Run 2) while benzoic acid was formed as a main product under lower pressure.[4] Furthermore, reaction of iodobenzene with O_2 in the presence of CO and Pd catalyst gave phenol in 10% yield. These results show that under high pressure of CO and O_2, O_2 could undergo activation and insert into a Pd-Ph σ bond.

Mechanism. On the basis of the results described above, we suggest the mechanism of formation of phenol from benzene and O_2 as depicted in Scheme 1. Main cycle (right) includes electrophilic attack of an active species $Pd(OAc)_2$/phen to benzene to form a Pd-Ph σ complex, activation of O_2 by a Pd/phen/CO complex to form a Pd-OPh complex, and its reaction with AcOH to form phenol and a $Pd(OAc)_2$/phen complex. Subcycle (left) includes oxidation/reduction of CO and O_2 by Pd to form CO_2, H_2O, and acetic anhydride. In the present reaction, ca. four times in mole of CO_2 are formed for every 1 mole formation of phenol. Therefore, it is very important to suppress the oxidation reaction of CO in the subcycle. Now attempt to make this reaction a practical chemical process which would substitute the cumene process, is currently underway.

Experimental

Materials and Method. $Pd(OAc)_2$ was prepared from Pd black and AcOH according to the procedure of Wilkinson and coworkers.[8] Diphenyltripalladium(II) complex (**2**) was prepared as described before.[4] GLC-mass analysis was performed on a Hitachi M-80B apparatus. The reaction of benzene with $^{18}O_2$ was performed as described before[1] charging $Pd(OAc)_2$ (0.2 mmol), phen (0.2 mmol), benzene (8 cm^3), AcOH (12 cm^3), CO (15 atm), and $^{18}O_2$ (15 atm) in a 30-cm^3 autoclave with stirring at 180 °C for 3 h. The reactions with benzene-d_6 and CD_3COOD were also conducted in similar method as described before.[1]

The Reaction of Diphenyltripalladium(II) Complex (2) with O_2. In a 200-cm^3 autoclave was placed a 50-cm^3 centrifuge tube containing complex **2** (0.32 mmol), phen (0.94



Scheme 1. Possible mechanism.

mmol), and AcOH (10 cm^3). The autoclave was closed and pressurized to 30 atm by CO and O_2 (15 atm each), and then the mixture was heated for 1 h at 100 °C with stirring. After the usual work-up, there were obtained phenol and benzoic acid in 30 and 24% yields, respectively. The results of the reactions done under various conditions were listed in Table 4.

Attempted Isolation of Pd/phen/CO Complex (1). A centrifuge tube containing a solution of $Pd(OAc)_2$ (2.0 g), AcOH (8 cm^3), benzene (12 cm^3), and chloroform (10 cm^3), was placed in an autoclave. After the autoclave was closed, CO and O_2 was introduced (0.5 atm, each). Then the mixture was stirred at room temperature for 3 h. After the reaction red-brown precipitates formed. The precipitates were filtered and washed with acetone and ether to obtain 2.8 g of the complex **2** which has IR spectrum at 1560 cm^{-1}. Found: C, 47.89; H, 3.32; N, 7.39; Pd, 29.45%. Calcd for $Pd_4phen_4(CO)(OAc)_4$: C, 48.58; H, 3.12; N, 7.95; Pd, 30.11%.

Reaction of Complex 1 with O_2. The complex **1** (0.5 g, 0.35 mmol as $Pd_4Phen_4(CO)(OAc)_4$) obtained as described above, was subjected to react with O_2 (15 atm) or under 15 atm N_2 in benzene (4 cm^3) and AcOH (6 cm^3) at 180 °C for 3 h to give phenol in 680 and 95% yields based on the complex.

This work was supported in part by grants from the Ministry of Education, Science and Culture of the Japanese Government.

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6) Almost quantitative CO_2 recovery from the reaction mixture was confirmed by the following experiment. CO_2 gas (10 atm, 8.9 mmol) was introduced in an autoclave containing $Pd(OAc)_2$ (0.2 mmol), phen (0.2 mmol), benzene (4 cm^3), and AcOH (6 cm^3) and the mixture was stirred at room temperature for 1 h. Then the CO_2 gas was released and gathered, and the solution was bubbled by N_2 to gather CO_2 residue. Of total gases recovered, CO_2 was 23.0% (8.2 mmol) and N_2 was 77.0%. Thus CO_2 recovery is 8.2/8.9=0.92.

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