

Direct selective oxidation of benzene to phenol using molecular oxygen in the presence of palladium and heteropolyacids¹

Luis Cesar Passoni, Alexandre Tadini Cruz, Regina Buffon, Ulf Schuchardt *

Instituto de Química, Universidade Estadual de Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil

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Abstract

The use of heteropolyacids as a reoxidant for palladium in the direct oxidation of benzene to phenol with molecular oxygen was studied as a function of the variables involved. It was shown that the oxidation system is very effective even if a molar ratio of HOAc:H₂O of 1:2 is used. After 4 h at 130°C the benzene conversion is 15% and the selectivity for phenol is above 70%. The quantity of palladium acetate can be drastically reduced allowing turnover numbers as high as 800.

Keywords: Palladium; Heteropolyacids; Benzene oxidation; Dioxygen; Phenol

1. Introduction

Palladium catalyzed oxidation of aromatic compounds has been known since 1965, when, based on the Wacker process, Helden and Verberg [1] described the oxidative coupling of benzene to biphenyl in acetic acid, catalyzed by palladium chloride in the presence of sodium acetate. In 1971 Henry [2] obtained the same results using palladium acetate in acetic acid in the presence of an alkaline metal acetate. However, when the copper/dioxygen reoxidation system was replaced by a strong oxidant, such as potassium dichromate or permanganate in the presence of dioxygen, the product distribution changed completely and the reaction began to show nucleophilic substitution rather than aromatic ring coupling products, although with a low turnover number of 5 [2]. Jintoku et al. showed that the use of 1,10-phenanthroline as a stabilizing ligand for palladium and carbon monoxide to avoid biphenyl formation, produces phenyl acetate with the increased turnover number of 12 [3,4]. Matveev and Kozhevnikov [5] proposed the use of vanadium-containing heteropolyacids (HPAs) as a reoxidant for palladium in Wacker-type reactions. These authors were able to perform oxidative coupling and oxidative acetoxylation of benzene in water/acetic acid, to give phenyl acetate and biphenyl with a turnover number of 4.4 [6].

* Fax: +55-19-2393805; e-mail: ulf@iqm.unicamp.br.

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In a recent paper [7] we discussed the possibility of selectively producing phenol from benzene using palladium acetate as catalyst, in the presence of an alkaline metal acetate and a strong oxidant, such as dichromate, in water/acetic acid, using molecular oxygen as the oxidant. Such a system is able to obtain a turnover number of 40 with a selectivity for phenol of about 70%. However, potassium dichromate, the best reoxidant for this catalytic system, is slowly reduced, causing deactivation of the oxidation system. The search for a better reoxidant was thus warranted. We wish to describe here our results on the use of heteropolyacids as the reoxidant for palladium in the direct oxidation of benzene to phenol.

2. Experimental

All chemicals were commercial grade and used without further purification, except for acetic acid which was distilled. Palladium acetate was purchased from Aldrich (analytical grade), benzene from Merck (UV solvent) and lithium acetate from Aldrich (98%). The heteropolyacids were prepared according to the method described by Tsigdinos et al. [8] and were analyzed by X-ray diffraction and X-ray fluorescence.

The oxidation reactions were carried out in a PTFE-lined Parr 4042 pressure reactor. In a typical experiment the reaction vessel was loaded with 0.07 mmol of palladium acetate, 0.3 g of HPA, 10 mmol of lithium acetate, a mixture of 400 mmol of acetic acid and 100 mmol of water, 100 mmol of benzene and approximately 40 bar of dioxygen at room temperature, which was adjusted to 60 bar at 100°C. The reaction mixture was heated to 130°C for 4 h, with 600 rpm mechanical stirring. After this time the reactor was quenched with cold water, the reaction mixture was filtered and the solids washed with acetic acid to complete 100.0 mL of total volume.

The products were analyzed by HPLC using a Waters system equipped with two model 510 piston pumps, a 100 mm × 5 mm i.d. C-18 Radial Pak Cartridge and a PDA 991 detector to record the UV–VIS spectra. A methanol/water gradient, starting at 60/40 (v/v) and reaching 100% methanol within 9 min was used for elution. The samples were prepared by solubilization in methanol/water 60/40 (v/v). Their UV–VIS spectra were recorded and compared with authentic samples. Identification of the reaction products was carried out by GC–MS. The products were quantified using calibration curves. The quantity of phenol produced was determined in four independent experiments, under the same conditions, giving a maximum deviation of ±0.5 mmol.

3. Results and discussion

The synthesis of molybdovanadophosphoric heteropolyacids (HPAs) with 0, 2, 3, 4 and 6 vanadium atoms resulted in HPAs with the general formula $H_{3+x}[PMo_{12-x}V_xO_{40}]$, where x was 0, 2.6, 3.3, 3.6, or 4.5, respectively. Their Keggin type structure was confirmed by X-ray diffraction. These HPAs were tested for the direct oxidation of benzene to phenol. It was found that the presence of vanadium atoms is essential for performing the reaction. When no vanadium was present only biphenyl is formed. On the other hand, when using vanadium-containing HPAs, 6 mmol of phenol with 75% selectivity were produced, independent of the number of vanadium atoms in the HPAs. In the subsequent studies an HPA with 3.3 vanadium atoms was employed as a large amount was available. Benzaldehyde, benzoic acid, benzophenone, acetophenone, hydroxybenzaldehyde, biphenyl

and a solid residue with the minimum formula C_3H_3O , determined by elemental analysis, were observed as by-products.

The effect of temperature was studied and the results are shown in Fig. 1. At lower temperatures only a small amount of biphenyl is observed. At temperatures above 100°C the phenol yield increases continuously up to 145°C . Higher temperatures are needed to perform this oxidation since C–H bonds in benzene are difficult to be activated. A considerable decrease in selectivity above 130°C is also observed. This might be due to the fact that phenol is more reactive than benzene and is consumed more rapidly than it is produced above 130°C . It is also observed that with higher temperatures the formation of a solid residue increases significantly.

Fig. 2 shows the behavior of the phenol yield with increasing dioxygen pressure. An almost constant increase in benzene conversion with increasing O_2 pressure is observed, reflected by an increase in phenol yield, which reaches a maximum at 60 bar, with a constant selectivity of about 75%. Above 60 bar a slight decrease in phenol yield, but a drastic decrease in selectivity, to 54% at 80 bar, is observed. Further increase of the O_2 pressure results in an even lower selectivity and, at 100 bar, deep oxidation is noticed. The subsequent studies were carried out with 60 bar oxygen pressure, which gives the best phenol yield under the reaction conditions.

As shown in Fig. 3, the phenol production reaches a maximum in 4 h. However, the reaction is not over after this time, as a slight decrease in the selectivity is observed with increasing reaction times. This is due to over-oxidation of the reaction products and to an increase in the formation of solid residue. After 4 h of reaction time the HPA is irreversibly reduced to dark brown compounds which do not precipitate as ammonium salts. Furthermore, the major part of the palladium acetate (approximately 80%) is also reduced to palladium black. These reductions may be caused by the benzaldehyde [9] formed as a side product: if benzaldehyde (10 mmol) is added to the initial reaction mixture, it is almost completely oxidized to benzoic acid and the phenol production drops to 3 mmol. On the other hand, addition of a new portion of HPA after 4 h and pressuring the reaction mixture with 60 bar of O_2 allows to restart the oxidation reaction at 130°C . However the reaction is no longer selective: after a total reaction time of 8 h the benzene conversion is 26%, but 50% of the products are the solid residue and only 27% is phenol.

Fig. 4 shows the dependence of the phenol yield and selectivity on the quantity of benzene used. Increasing the quantity of benzene to 130 mmol increases both phenol yield and selectivity, implying a benzene conversion of approximately 15%. The conversion decreases slightly for higher benzene

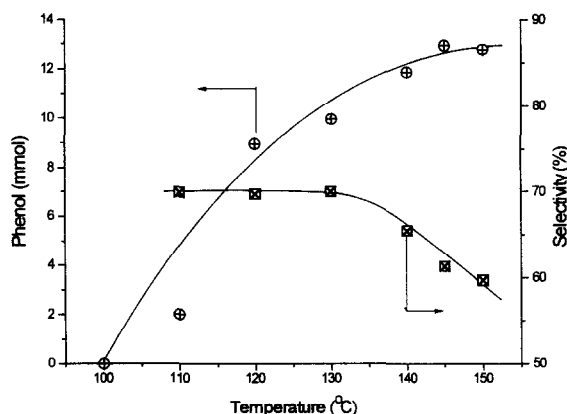


Fig. 1. Quantity of phenol and selectivity of the reaction as a function of temperature. Conditions: 0.07 mmol of palladium acetate, 0.3 g of HPA, 10 mmol of lithium acetate, 100 mmol of benzene, 400 mmol of acetic acid, 100 mmol of water, 60 bar O_2 , 4 h.

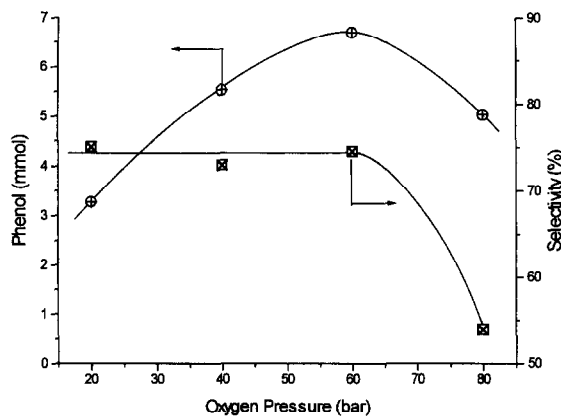


Fig. 2. Quantity of phenol and selectivity of the reaction as a function of dioxygen pressure. Conditions: 0.07 mmol of palladium acetate, 0.2 g of HPA, 10 mmol of lithium acetate, 100 mmol of benzene, 400 mmol of acetic acid, 100 mmol of water, 3 h at 130°C.

quantities as the phenol yield and selectivity remain constant above 130 mmol of benzene. A certain amount of benzene in the reaction mixture is necessary to reduce coordination of the formed phenol to the palladium atoms, which leads to over-oxidation products, thus lowering the selectivity. In the subsequent experiments 150 mmol of benzene were used to ensure the maximum production of phenol.

The solvent composition also has a major influence on the phenol yield and selectivity as shown in Fig. 5. Up to a HOAc:H₂O molar ratio of 1:2 both selectivity and phenol yield increase. This is probably due to the easier solubilization of benzene in the reaction medium with the increasing organic character of the solvent. A further increase in the HOAc:H₂O molar ratio causes a slight decrease in the phenol yield and selectivity, due to increasing side reactions caused by radical processes.

The influence of the HPA concentration in the reaction medium was also studied. It was observed that varying the HPA quantity from 0.10 to 0.30 g only slightly increased the yield of phenol and the selectivity of the process. On the other hand, varying the quantity of palladium acetate from 0.02 to 0.07 mmol only increases the phenol produced by 20%, as shown in Fig. 6. We believe there are two major concerns: first, as the HPA concentration is the same, there may be not enough HPA to

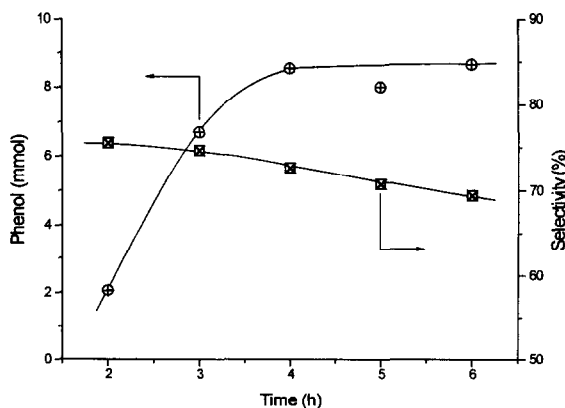


Fig. 3. Quantity of phenol and selectivity of the reaction as a function of reaction time. Conditions: 0.07 mmol of palladium acetate, 0.2 g of HPA, 10 mmol of lithium acetate, 100 mmol of benzene, 400 mmol of acetic acid, 100 mmol of water, 60 bar O₂ at 130°C.

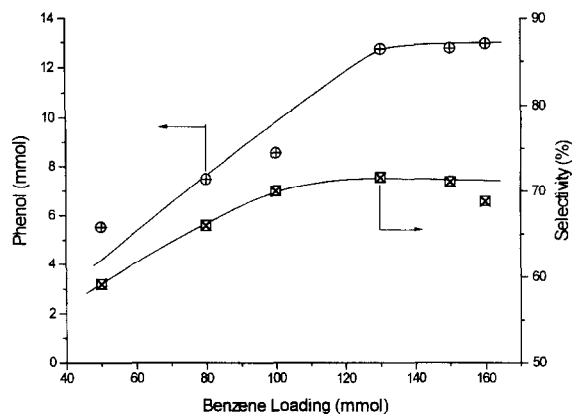


Fig. 4. Quantity of phenol and selectivity of the reaction as a function of benzene loading. Conditions: 0.07 mmol of palladium acetate, 0.3 g of HPA, 10 mmol of lithium acetate, 400 mmol of acetic acid, 100 mmol of water, 60 bar O_2 , 4 h at 130°C.

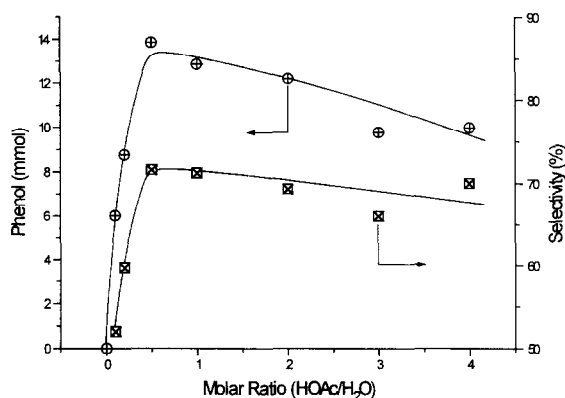


Fig. 5. Quantity of phenol and selectivity of the reaction as a function of HOAc/ H_2O molar ratio. Conditions: 0.07 mmol of palladium acetate, 0.3 g of HPA, 10 mmol of lithium acetate, 150 mmol of benzene, 60 bar O_2 , 4 h at 130°C.

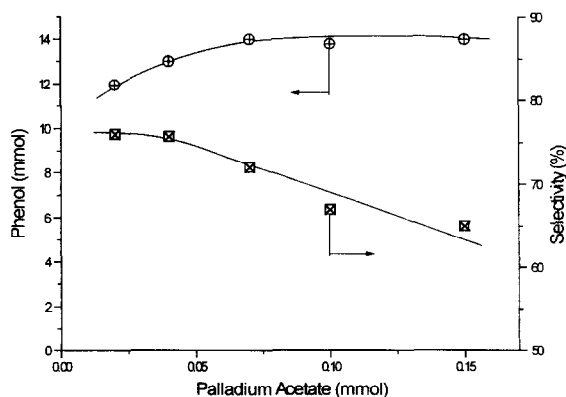
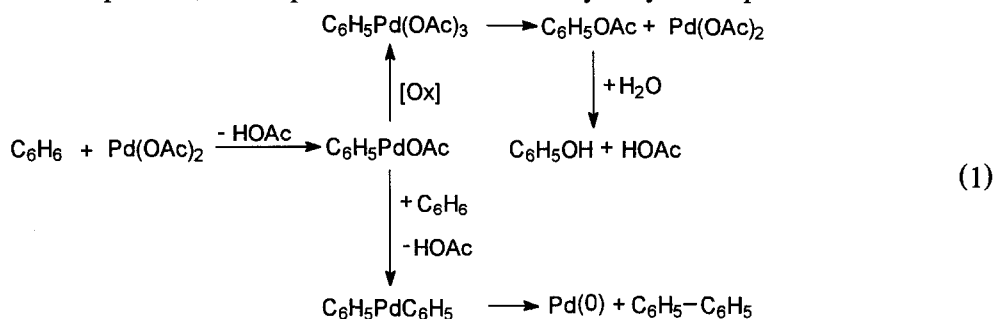


Fig. 6. Quantity of phenol and selectivity of the reaction as a function of the quantity of palladium acetate. Conditions: 0.3 g of HPA, 10 mmol of lithium acetate, 150 mmol of benzene, 200 mmol of acetic acid, 400 mmol of water, 60 bar O_2 , 4 h at 130°C.

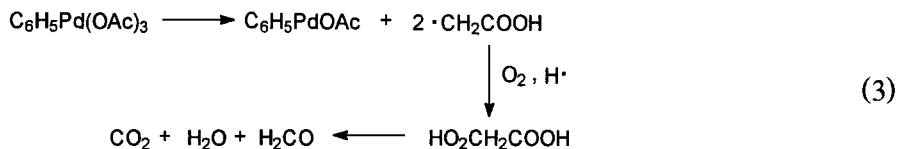
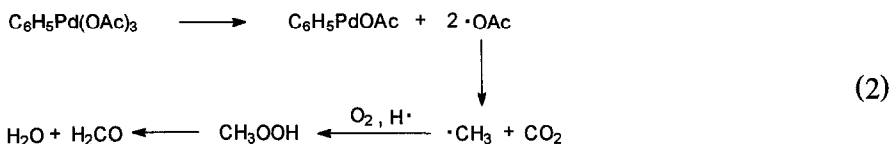
reoxidize the catalyst if larger quantities are used. Second, a large excess of benzene over palladium is necessary to perform the reaction selectively, as shown in the reduced phenol selectivity for higher quantities of catalyst. This is in agreement with the results observed when varying the benzene quantity and with a constant lowering of the selectivity observed for increasing quantities of palladium in the reaction mixture.

4. Considerations on the reaction mechanism

As proposed by Lyons [10] the benzene is electrophilically attacked by palladium acetate. In the absence of a strong oxidant the phenylpalladium(II) acetate thus formed reacts to give diphenyl and palladium(0). In the presence of a strong oxidant, phenylpalladium(IV) triacetate is formed which then undergoes reductive elimination to produce phenyl acetate (Eq. (1)). In the absence of water, phenol acetate is the main product; in the presence of water it is hydrolyzed to phenol.



The intermediate palladium(IV) complex is shown by the by-products. As observed in the oxidation of *p*-xylene to terephthalic acid by the Amoco process [11], the palladium(IV) complex may undergo thermolysis, resulting in the oxidation of an acetate ligand to form a methyl radical (Eq. (2)) or a CH_2COOH radical (Eq. (3)) which immediately react with molecular oxygen to form, principally, formaldehyde [12].



The formaldehyde attacks benzene electrophilically to form benzaldehyde, benzoic acid, benzophenone and other by-products. The acetophenone is probably obtained in an acid catalyzed acetylation of benzene. The solid residue is observed in larger amounts if phenol is used as a substrate of the oxidation under the reaction conditions [13]. According to infrared and elemental analyses, this

is a mixture of polynuclear phenolic compounds with oxygen and CO groups linking the aromatic nuclei.

5. Conclusions

When 0.02 mmol of palladium acetate was used 12 mmol of phenol, with 75% selectivity, is produced, meaning a turnover number of 800. This is, to the best of our knowledge, the highest turnover number ever reported for this reaction. This high turnover number, combined with a conversion of benzene of more than 10%, makes this reaction industrially interesting. However, after 4 h of reaction time, the HPA is irreversibly reduced as well as most of the palladium acetate. Addition of a new portion of HPA promotes unselective oxidations, mostly to overoxidize the products to polynuclear phenolic compounds.

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References

- [1] R. Van Helden and G. Verberg, *Rec. Rev.* 84 (1965) 1263.
- [2] P.M. Henry, *J. Org. Chem.* 36 (1971) 1886.
- [3] T. Jintoku, H. Taniguchi and Y. Fujiwara, *Chem. Lett.* (1987) 1865.
- [4] T. Jintoku, Y. Fujiwara, K. Takaki, Y. Fuchita and K. Huaki, *Bull. Chem. Soc. Jpn.* 63 (1990) 139.
- [5] K.I. Matveev and I.V. Kozhevnikov, *Kinet. Catal.* 21 (1980) 1189.
- [6] L.N. Pachkovskaya, K.I. Matveev, G.N. Il'inich and N.K. Eremenko, *Kinet. Catal.* 18 (1977) 1040.
- [7] U. Schuchardt, A.T. Cruz, C.H. Collins and L.C. Passoni, *Stud. Surf. Sci. Catal.* 82 (1994) 551.
- [8] G.A. Tsigdinos and C.J. Hallada, *Inorg. Chem.* 7 (1968) 437.
- [9] A.W. Stobbe-Kreemers, M. van der Zon, M. Makkee and J.J.F. Scholten, *J. Mol. Catal. A* 107 (1996) 247.
- [10] J.E. Lyons, in: A.E. Martell and D.T. Sawyer (Eds.), *Oxygen Complexes and Oxygen Activation by Transition Metal Complexes* (Plenum Press, New York, 1988) p. 233.
- [11] W. Partenheimer, *J. Mol. Catal.* 67 (1991) 35.
- [12] T.P. Kenigsberg, N.G. Ariko, N.I. Mitskevich and V.F. Nazimov, *Kinet. Catal.* 26 (1985) 1279.
- [13] U. Schuchardt, A.T. Cruz and C.H. Collins, unpublished results.