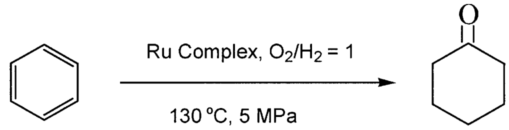
One-step synthesis of cyclohexanone from benzene with O_2/H_2 catalyzed by ruthenium diaminodiphosphine complex

Wei-Xiong Pan[a], Wai-Kwok Wong[b,*], Xian-Qing Qiu[a], and Fu-Wa Lee[b]

[a]*Department of Chemistry, Tsinghua University, Beijing, 100084, P.R. China*
[b]*Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P.R. China*

Received 31 May 2003; accepted 11 October 2003

Cyclohexanone can be one-step synthesized from benzene catalyzed by a ruthenium diaminodiphosphine complex with 65% selectivity (35% phenol as by-product) and TOF = 63 h^{-1} at 130 °C and 5 MPa (O_2/H_2 = 1) pressure.



This shows that hydroxylation (oxidation) and hydrogenation (reduction), which normally required totally noncompatible conditions and catalysts, can proceed in a "one-pot" manner by using one metal complex catalyst.

KEY WORDS: cyclohexanone; Ru complex; one-step synthesis.

1. Introduction

The synthesis of cyclohexanone is of commercial significance in the manufacture of caprolactum, a monomer used in the synthesis of Nylon-6. There are two routes, one via cyclohexane and the other via phenol as intermediate, to produce cyclohexanone from benzene feedstock in industry. Both routes are two-step processes. In the cyclohexane route, benzene is first hydrogenated to cyclohexane catalyzed by supported Ni, Pd [1], Pt [2], amorphous Ni-P [3], ultrafine Ni-Co-W-B [4] and Ru complex [5]. This is followed by the oxidation of cyclohexane with O_2 to cyclohexanone using boric acid or catalyzed by molecular sieves containing Ti [6], Cr [7], Ce [8] and CrCoAPO-5(AFI) [9]. For the first step the yield can be quantitative, while in the second step there are 15% by-products, which are mainly adipic, glutaric and tartaric acids.

In the phenol route, benzene is first hydroxylated to phenol, which then hydrogenates to cyclohexanone. Direct hydroxylation of benzene can be accomplished by nitrous oxide [10–14] and hydrogen peroxide [15,16]. Molecular oxygen can also be used as the oxidant; however, a reductant such as hydrogen [17–21], ammonia [22] and alkyl- or halo-substituted hydroquinone is required. Hydroxylation of benzene with molecular oxygen in the absence of a reductant usually gives a low yield of phenol [17,23–25]. The catalysts used are various molecular sieves such as nonsubstituted or transition metal-substituted MCM-41 [16], ZSM-5 [1], TS-1 [2,20]; mixed metal oxides [18,19,22]; salts of heteropolyacids [23,25] and metal organic complexes [24]. The hydrogenation of phenol mainly uses Pd catalysts supported by MgO [26], Al_2O_3 [27], SiO_2 [28] or modified Pd [29]. In this process, cyclohexanone is the partially hydrogenated product. To avoid further hydrogenation to cyclohexanol, the catalyst and reaction conditions must be carefully chosen.

It is worth noting that hydroxylation (oxidation) and hydrogenation (reduction) require totally noncompatible conditions and quite different catalysts. It is unlikely that the formation of cyclohexanone from benzene could proceed in a "one-pot" manner or employ only one catalyst. In fact, to our knowledge, there has not yet been any report on the one-step synthesis of cyclohexanone from benzene.

Recently, we have reported the catalytic oxidation of olefins with O_2 using a ruthenium complex with a tridentate diaminodiphosphine ligand, *trans*-$RuCl_2[\kappa^3$-1*R*,2*R*-P(NH)(NH)P](PPh_3) [1*R*,2*R*-P(NH)(NH)P = *N*,*N'*-bis[2-(diphenylphosphino)benzyl]-1*R*,2*R*-diaminocyclohexane] as catalyst [30]. Herein we report the one-step synthesis of cyclohexanone from benzene and O_2/H_2 catalyzed by *trans*-$RuCl_2[\kappa^3$-1*R*,2*R*-P(NH)(NH)P](PPh_3). The catalyst loading for each run was 1.6 mg or about 1.46 μmol. The reactor used was a 50-cm^3 stainless steel autoclave with a temperature-controlling unit and a magnetic stirrer. Aliquots of samples were withdrawn from the reactor at fixed time

---

* To whom correspondence should be addressed.
E-mail: wkwong@hkbu.edu.hk

1011-372X/04/0100–0025/0 © 2004 Plenum Publishing Corporation

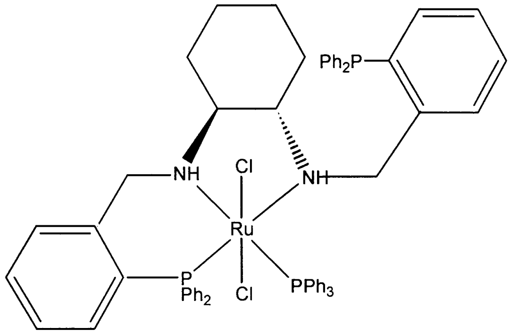


Figure 1. Ruthenium diaminodiphosphine complex catalyst.

intervals and analyzed by a HP-5890 GC (a HP-5 capillary column) equipped with an FID or a HP-6890 GC coupled with a HP 5973 MSD.

The results of the catalytic reactions are summarized in table 1. In the absence of H_2, neither cyclohexanone nor phenol was formed at 130 °C and 2.5-MPa O_2 (entry 1). However, an introduction of 0.6-MPa H_2 led to only production of phenol at the same temperature and pressure (entry 2). Doubling the total pressure to 5 MPa while keeping the O_2/H_2 mole ratio at 3 increased the conversion by onefold (from 0.1 to 1.25%) and produced cyclohexanone with 12% selectivity (entry 3). A further increase in the hydrogen partial pressure to $O_2/H_2 = 1$ inhibited the formation of the dihydroxylation products catechol [o-$C_6H_4(OH)_2$] and hydroquinone [p-$C_6H_4(OH)_2$], but augmented the cyclohexanone selectivity to 65% with phenol as the only detectable by-product (entry 4). Apparently, a higher hydrogen partial pressure favors the formation of cyclohexanone.

The solvent dependence of the catalytic reactions has also been investigated. Under similar conditions, addition of acetonitrile increased the selectivity for cyclohexanone by more than three times (entries 3 & 5), while that of methanol reduced it by a half (entries 3 & 6). It appeared that the use of acetonitrile increased the benzene conversion, presumably due to an increase in catalyst/substrate ratio, but significantly reduced the TOF (turnover frequency) from 63 to 15 h^{-1}.

To identify the pathway for the formation of cyclohexanone, phenol and cyclohexane were chosen as substrates. Under similar reaction conditions, phenol gave catechol and hydroquinone as the only detectable products (entry 7), while cyclohexane gave cyclohexanone as the major product along with cyclohexanol and cyclohexyl hexanedioate (entry 8). The results showed that both benzene and cyclohexane selectively gave cyclohexanone and implied that benzene be hydrogenated to cyclohexane followed by oxidation to cyclohexanone.

One advantage of the present one-step synthesis is that phenol is the only by-product in the reaction. Presumably, the formation of deep oxidized products such as adipic, glutaric and tartaric acids could be inhibited by H_2, whereas the production of cyclohexanol from the oxidation of cyclohexane could be minimized by O_2. By changing the reaction conditions, the product ratio of cyclohexanone to phenol could be varied widely.

Normally, hydrogenation using metal, metal oxide or metal complex catalysts involves the dissociation of H_2 molecule, which occurs with difficulty when the O_2 to H_2 mole ratio exceeds unity. To have some insight into the hydrogenation mechanism, Pt on activated charcoal (Pt/C), over which H_2 should be dissociated easily, was added as a cocatalyst to the ruthenium catalytic system under the same conditions. The result showed that the conversion, TOF and the selectivity of the catalytic

Table 1
Results of catalytic reactions of benzene, phenol and cyclohexane with O_2/H_2 at 130 °C for 6 h[a]

Entry	1	2	3	4	5	6	7	8
Substrate	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Phenol	Cyclohexane
Total pressure (MPa)	2.5	2.5	5.0	5.0	4.6	5.5	5.0	5.0
H_2 partial pressure (MPa)	0	0.6	1.2	2.4	1.2	1.2	1.2	0
Substrate (cm^3/mmol)	3/33.6	3/33.6	3/33.6	3/33.6	0.46/5.15	1.5/16.8	3[d]/31.9	3/27.6
Solvent/amount (cm^3)	–	–	–	–	[b]/2	[c]/1.5	–	–
Conversion (mol%)	0	0.1	1.25	1.8	2.7	3.53	9	1
TOF (h^{-1})	0	3.5	44	63	15	62	316	25
Selectivity (mol%)								
Cyclohexanone	0	0	12	65	41	7	0	40
Cyclohexanol	0	0	0	0	0	0	0	25
Phenol	0	99	86	34	59	92	–	0
Catechol	0	0	1.5	0	0	0.7	35	0
Hydroquinone	0	0	0.5	0	0	0.2	34	0

[a] Catalyst: *trans*-$RuCl_2[\kappa^3$-1R,2R-P(NH)(NH)P](PPh_3), 1.6 mg, 1.46 μmol.

[b] Acetonitrile.

[c] Methanol.

[d] 3.0 g of phenol.

system were nearly unaffected except that an immiscible layer of water, that presumably resulted from the catalytic reaction of H_2 with O_2, was observed. The side reaction, production of water from H_2 and O_2, has not been found for the ruthenium complex catalyst. This suggested that the mechanism for H_2 activation by ruthenium complex would be very different from that over a Pt catalyst and no Ru metal has been found from complex decomposition.

Acknowledgments

We acknowledge the Hong Kong Baptist University and the Hong Kong Research Grants Council (HKBU 2053/97P) for financial support of this work.

References

[1] A. Horvath, A. Beck, Z. Koppany, A. Sarkany and L. Guczi, J. Mol. Catal A: Chem. 182 (2002) 295.
[2] L.J. Simon, J.G. van Ommen, A. Jentys and J.A. Lercher, Catal. Today 73 (2002) 105.
[3] H.X. Li and Y.P. Xu, Mater. Lett. 51 (2001) 101.
[4] M.H. Qiao, S.H. Xie, W.L. Dai and J.F. Deng, Catal. Lett. 71 (2001) 187.
[5] P.J. Dyson, K. Russell and T. Welton, Inorg. Chem. Commun. 4 (2001) 571.
[6] T. Sooknoi and J. Limtrakul, Appl. Catal. A: Gen. 233 (2002) 227.
[7] R.S. da Cruz, J.M.D.E. Silva, U. Arnold and U. Schuchardt, J. Mol. Catal. A: Chem. 171 (2001) 251.
[8] E.L. Pires, J.C. Magalhaes and U. Schuchardt, Appl. Catal. A: Gen. 203 (2000) 231.
[9] A.F. Masters, J.K. Beattie and A.L. Roa, Catal. Lett. 75 (2001) 159.
[10] B. Louis, C. Tezel, L. Kiwi-Minsker and A. Renken, Catal. Today 69 (2001) 365.
[11] R. Leanza, I. Rossetti, I. Mazzola and L. Forni, Appl. Catal. A: Gen. 205 (2001) 93.
[12] L.V. Pirutko, A.K. Uriarte, V.S. Chernyavsky, A.S. Kharitonov and G.L. Panov, Micropor. Mesopor. Mat. 48 (2001) 345.
[13] G.I. Panov, A.K. Uriarte, M.A. Rodkin and V.I. Sobolev, Catal. Today 41 (1998) 365.
[14] J.L. Motz, H. Heinichen and W.F. Hölderich, J. Mol. Catal. A: Chem. 136 (1998) 175.
[15] M. Stockmann, F. Konietzni, J.U. Notheis, J. Voss, W. Keune and W.F. Maier, Appl. Catal. A: Gen. 208 (2001) 343.
[16] V. Parvulescu and B.L. Su, Catal. Today 69 (2001) 315.
[17] I. Yamanaka, T. Nabeta, S. Takenaka and K. Otsuka, Stud. Surf. Sci. Catal. 130: (International Congress on Catalysis, 2000, Pt. A), (2000) 809–815.
[18] K. Sasaki, A. Kunai, S. Ito, F. Iwasaki and M. Hamada Japanese Patient 02138233 (1990) Tosoh Corp.
[19] T. Miyake, M. Hamada, Y. Sasaki and K. Sekizawa Japanese Patient 03178946 (1991) Tosoh Corp.
[20] T. Tatsumi, K. Yuasa and H. Tominaga, J. Chem. Soc., Chem. Commun. (1992) 1446.
[21] W. Laufer and W.F. Hoelderich, Chem. Commun. (2002) 1684.
[22] B. Liptakova, M. Hronec and Z. Cvengrosova, Catal. Today 61 (2000) 143.
[23] Y.J. Seo, Y. Mukai, T. Tagawa and S. Goto, J. Mol. Catal. A: Chem. 120 (1997) 149.
[24] G.A. Gamidov, M.M. Aguseinova and U.A. Gasanova, Zh. Obshch. Khim. 66 (1996) 974.
[25] L.C. Passoni, F.J. Luna, M. Wallau, R. Buffon and U. Schuchardt, J. Mol. Catal. A: Chem. 134 (1998) 129.
[26] P. Claus, H. Berndt, C. Mohr, J. Radnik, E.J. Shin and M.A. Keane, J. Catal. 192 (2000) 88.
[27] N. Mahata, K.V. Raghavan and V. Vishwanathan, Appl. Catal. A: Gen. 182 (1999) 183.
[28] S.G. Shore, E.R. Ding, C. Park and M.A. Keane, Catal. Commun. 3 (2002) 77.
[29] G. Neri, A.M. Visco, A. Donato, C. Milone, M. Malentacchi and G. Gubitosa, Appl. Catal. A: Gen. 110 (1994) 49.
[30] W.K. Wong, X.P. Chen, W.X. Pan, J.P. Guo and W.Y. Wong, Eur. J. Inorg. Chem. (2002) 231.