

A novel route for *in-situ* H₂O₂ generation from selective reduction of O₂ by hydrazine using heterogeneous Pd catalyst in an aqueous medium

Vasant R. Choudhary,* Chanchal Samanta and Prabhas Jana

Received (in Cambridge, UK) 22nd July 2005, Accepted 5th September 2005

First published as an Advance Article on the web 3rd October 2005

DOI: 10.1039/b510543a

Hydrogen peroxide in high yields can be generated with high efficiency at mild conditions (25 °C and atmospheric pressure) with the formation of only environment-friendly by-products (N₂ and H₂O) by a reduction of O₂ by hydrazine from its hydrate/salt with its complete conversion in a short reaction period (≤0.5 h) using a easily separable supported Pd catalyst (Pd/Al₂O₃, Pd/Ga₂O₃ or Pd/C) in an acidic aqueous medium in the presence of bromide anions; the presence of both acid (protons) and bromide anions is essential for the selective reduction of O₂ by hydrazine to H₂O₂ and in their absence, the reaction leads only to the formation of water.

Hydrogen peroxide is an environmentally clean oxidizing agent; the by-product of its use is only water (which is environmentally benign). Because of the increasing environmental concerns, the use of H₂O₂ in a number of organic oxidation processes (e.g. epoxidation of olefins, hydroxylation of aromatics/olefins, oxidation of benzylic –CH₂OH to –CHO or –COOH, etc.) for the synthesis of fine/speciality chemicals is widely increasing.^{1–3} At present, H₂O₂ is produced commercially mainly by the autoxidation of hydroanthraquinone in a complex organic solvent, involving cyclic oxidation–hydrogenation steps.⁴ This process however, is cost effective only on a large scale (>20 000 tpa). The transport, storage and handling of bulk H₂O₂ are also quite hazardous. Hence, the use of *in-situ* generated H₂O₂ for organic oxidation reactions is not only of scientific interest but also of great practical importance. A few studies have been reported on the use of *in-situ* generated H₂O₂ in liquid-phase organic oxidation reactions.^{3,5–7}

The conventional method for *in-situ* H₂O₂ generation is based on the autoxidation of hydroanthraquinones by O₂ (hydroanthraquinone + O₂ → H₂O₂ + anthraquinone).³ However, the use of the autoxidation is limited because of the complex organic solvent system used to keep both the hydroquinone and quinone in their dissolved form. Moreover, the separation of the solvent, quinone and hydroquinone from the products of organic oxidation reaction is problematic. Direct oxidation of H₂ by O₂ using Pd catalyst is highly hazardous⁸ and hence its use for the *in-situ* H₂O₂ generation for organic oxidation reactions is dangerous. Sheriff and coworkers^{9,10} used Mn(II)/4,5-dihydroxybenzene-1,3-disulfonate as a homogeneous catalyst⁹ and Mn(II)-exchanged montmorillonite clay as a heterogeneous catalyst¹⁰ for the reduction of dioxygen by hydroxylamine to H₂O₂ with high turnover numbers (>10⁴). Recently, they have reported the use of Mn(III) and Mn(IV) complexes as homogeneous catalysts for the O₂-to-H₂O₂

reduction by hydroxylamine, using acetonitrile–water mixture as the reaction medium.¹¹ Because of separation problem, the use of homogeneous catalyst and/or organic solvent in the reaction is problematic. It is, therefore, of both scientific and practical interest to develop a new route for the *in-situ* H₂O₂ generation, which requires no organic solvent, produces only environment-friendly and easily separable by-product(s) and provides H₂O₂ with high yield under mild conditions, preferably using an easily separable heterogeneous catalyst. We have accomplished this difficult task. We report here our new route for the *in-situ* H₂O₂ generation from the selective reduction of O₂ by hydrazine (N₂H₄) from its hydrate/salt in an acidic aqueous medium, using Pd/C or Pd/Al₂O₃ (or Ga₂O₃) catalyst, in the presence of Br[–] in the medium or in the catalyst. The presence of both the mineral acid (protons) and Br[–] is a requirement for the selective oxidation of hydrazine to H₂O₂. In this method, the by-products formed are only N₂ and water, which are environmentally benign and pose no problem for their separation. Also, a complete conversion of hydrazine with high H₂O₂ yield can be accomplished in a short reaction period (≤30 min) at room temperature (25 °C) and atmospheric pressure.

Results (Tables 1–4) clearly show the formation of H₂O₂ with high rate in the reduction of O₂ by hydrazine from its sulfate or hydrate (N₂H₄ + 2 O₂ → 2 H₂O₂ + N₂) over the supported Pd catalysts¹² in an aqueous acidic medium in the presence of bromide anions in the medium or in the catalyst at 25 °C and atmospheric pressure. However, since the H₂O₂ formed per mole of N₂H₄ converted is less than 2.0, the non-selective conversion of N₂H₄ to water (N₂H₄ + O₂ → 2 H₂O + N₂) also occurs simultaneously, depending upon the reaction conditions. The procedure for carrying out the oxidation reaction is given elsewhere.¹³ No decomposition of N₂H₄ to N₂ and H₂ over the catalysts was observed at the reaction conditions employed for the reaction.

Table 1 H₂O₂ formed in the reduction of O₂ by hydrazine sulfate (at 25 °C) over Pd/Al₂O₃ in water as the reaction medium in the presence or absence of halide (reaction period = 0.5 h)

Halide in medium	Halide conc./mmol dm ^{–3}	H ₂ O ₂ formed ^c	H ₂ O ₂ yield (%)	Rate of H ₂ O ₂ generation ^d
None	0.0	0.0	0.0	0.0
KF or KCl	0.94	0.0	0.0	0.0
KI	0.94	0.0	0.0	0.0
KBr	0.94	1.17	59	53.8
KBr	4.7	1.22	61	56.1
MBr ^a	4.7	1.18 ± 0.04	57–61	54.3 ± 1.8
KBr ^b	2.7	0.65	33	29.9

^a M = H, Na or NH₄. ^b For Pd/C catalyst. ^c mol/mol of N₂H₄ converted. ^d mmol of H₂O₂ formed per gram of catalyst per hour.

Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune, 411008, India. E-mail: vrc@ems.ncl.res.in; vrc@che.ncl.res.in; Fax: + 91-20-2589.41

Table 2 H₂O₂ formed in the reduction of O₂ by hydrazine sulfate (N₂H₄·H₂SO₄) over halogenated Pd/Al₂O₃ (or Ga₂O₃) catalysts (halogen loading = 1.0 wt%) in water medium at 25 °C (reaction period = 0.5 h)

Halogen incorporated in catalyst	H ₂ O ₂ formed ^d	H ₂ O ₂ yield (%)	Rate of H ₂ O ₂ generation ^e
Catalyst: Pd/Al ₂ O ₃ with or without halogen			
None	0.0	0.0	0.0
F or Cl	0.0	0.0	0.0
I	0.0	0.0 ^f	0.0
Br	1.23	61.5	56.7
Br ^a	0.98	25.7 ^g	45.1
Br ^b	1.36	68.0	62.6
Br ^c	1.07	53.5	49.2
Catalyst: Pd/Ga ₂ O ₃ with or without halogen			
None	0.0	0.0	0.0
F or Cl	0.0	0.0	0.0
Br	1.01	50.5	46.5

^a Reaction period was 0.2 h. ^b 50 mmol H₃PO₄ was added to the reaction medium. ^c Hydrazine salt was N₂H₄·2HCl. ^d mol/mol of N₂H₄ converted. ^e mmol of H₂O₂ formed per gram of catalyst per hour. ^f Conversion of N₂H₄ was 10%. ^g Conversion of N₂H₄ was 52%; in all the other cases it was 100%.

Table 3 H₂O₂ formed in the reduction of O₂ hydrazine monohydrate over Pd/Al₂O₃ in aqueous reaction medium in the presence or absence of mineral acid (0.1 mol dm⁻³) and/or halide (0.94 mmol dm⁻³) at 25 °C (reaction period = 0.5 h)

Acid in medium	Halide in reaction medium	H ₂ O ₂ formed ^a	H ₂ O ₂ yield (%)
None	None	0.0	0.0
H ₃ PO ₄	None	0.0	0.0
H ₂ SO ₄	None	0.0	0.0
None	KBr	0.0	0.0
H ₃ PO ₄	KBr	0.85	42.5
H ₂ SO ₄	KBr	0.80	40.0
H ₃ PO ₄	KF or KCl	0.0	0.0
H ₂ SO ₄	KF or KCl	0.0	0.0
H ₃ PO ₄	KI	0.0	0.0 ^b
H ₂ SO ₄	KI	0.0	0.0 ^c

^a mol/mol of N₂H₄ converted. ^b Conversion of N₂H₄ was 10%.^c Conversion of N₂H₄ was 12%; in all the other cases it was 100%.

Results (Table 1) reveal that in the absence of any halide or in the presence of KF or KCl in the medium, the hydrazine from the hydrazine sulfate is completely converted to water (N₂H₄ + O₂ → 2 H₂O + N₂), without formation of any H₂O₂. The addition of KI to the medium also leads to similar results except that the hydrazine conversion is drastically reduced from 100 to 10% due to poisoning of the catalyst. However, in the presence of KBr in the medium at the same (0.94 mmol dm⁻³) or at higher concentration,

the H₂O₂ formed per mol of hydrazine was drastically increased from zero to 1.17 and 1.22, respectively, and also the hydrazine conversion was 100%. Influence of cations (H⁺, Na⁺, K⁺ or NH₄⁺) on the reaction as compared to that of the halide anions was found to be negligibly small.

The results, when the halogens (F, Cl, Br or I) are incorporated in the Pd/Al₂O₃ and Pd/Ga₂O₃ catalysts (Table 2), are quite similar to those observed for the halides in the reaction medium (Table 1). The results for the Pd/Al₂O₃ catalyst (Table 2) show that the addition of acid (H₃PO₄) in the medium causes an appreciable increase in the H₂O₂ yield (from 61.5 to 68.0%). It may be noted that the reaction medium containing the hydrazine salts is acidic (pH < 2) because of the release of associated acid molecules (H₂SO₄ or HCl) from the hydrazine salts after their dissolution in water.

When hydrazine hydrate was used instead of the hydrazine salts, in the absence of acid in the medium no H₂O₂ formation in the hydrazine oxidation is observed even though in the presence of bromide anions. In the absence of either bromide anions or mineral acid or both, the oxidation of hydrazine hydrate leads only to the formation of N₂ and water (Tables 3 and 4). With increasing the acid/hydrazine mole ratio, the H₂O₂ yield (or H₂O₂ formed per mol of hydrazine consumed) is increased appreciably. Among the mineral acids, the most preferable for the selective reduction of O₂ to H₂O₂ is sulfuric acid.

Table 4 H₂O₂ formed in the reduction of O₂ by hydrazine monohydrate over halogenated Pd/Al₂O₃ (halogen loading = 1.0 wt%) in aqueous reaction medium in the presence or absence of mineral acid (at 25 °C) (reaction period = 0.5 h)

Halogen in catalyst	Acid in medium	Conc. of acid/mol dm ⁻³	Acid/N ₂ H ₄ mole ratio	Conv. of N ₂ H ₄ (%)	H ₂ O ₂ formed ^b
None	H ₃ PO ₄	0.1	2.27	100 ^a	0.0
F or Cl	H ₃ PO ₄	0.1	2.27	100 ^a	0.0
I	H ₃ PO ₄	0.1	2.27	9.5 ^a	0.0
Br	None	0.0	0.0	100 ^a	0.0
Br	H ₃ PO ₄	0.02	0.45	100	0.30
Br	H ₃ PO ₄	0.2	4.5	60.2	0.88
Br	H ₂ SO ₄	0.04	0.91	100	1.16
Br	H ₂ SO ₄	0.02	0.45	87.3	0.84
Br	HCl	0.09	2.05	100	1.11
Br	HBr	0.09	2.05	39.5	0.7

^a Reaction period = 1.0 h. ^b mol/mol of N₂H₄ converted.

From the above results, it can be concluded that the reduction of O_2 by hydrazine (from hydrazine salt or hydrate) leads to H_2O_2 formation with high yields only in the presence of Br^- anions and protons (mineral acid). In their absence or in the presence of other halides and acid, only water (without even traces of H_2O_2) is formed in the reaction.

The hydrazine oxidation is not economically feasible for the large-scale production of H_2O_2 as a commodity chemical. However, although hydrazine is toxic and carcinogenic, since the reaction is fast and completed in a short period (<30 min), even at room temperature and atmospheric pressure, leaving no traces of unconverted hydrazine, it has high potential for providing an efficient route for the *in-situ* generation of H_2O_2 . It is environment-friendly, involving no objectionable by-products or organic solvent, unlike the hydroanthraquinone-to- H_2O_2 oxidation.

Chanchal Samanta and V. R. Choudhary are grateful to the CSIR (New Delhi) for the award of a Senior Research Fellowship and the Emeritus Scientist Scheme, respectively, and Prabhas Jana is grateful to UGC (New Delhi) for the award of a Senior Research Fellowship.

Notes and references

- 1 B. Notari, *Adv. Catal.*, 1996, **41**, 253.
- 2 G. Centi and M. Misino, *Catal. Today*, 1998, **41**, 287.
- 3 M. G. Clerici and P. Ingallina, *Catal. Today*, 1998, **41**, 351.
- 4 W. T. Hess, *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. J. K. Kroschwitz and M. Howe-Grant, Wiley, New York, 4th edn., 1995, vol. 13, pp. 961–995.
- 5 E. D. Park, Y.-S. Hwang and J. S. Lee, *Catal. Commun.*, 2001, 187.
- 6 S. Niwa, M. Eswaramoorthy, N. Jalajakumari, R. Anuj, I. Naotsugu, S. Hiroshi, N. Takemi and M. Fujio, *Science*, 2002, **295**, 105.
- 7 G. D. Vulpescu, M. Ruitenbeek, L. L. van Lieshout, L. A. Correia, D. Meyer and P. P. A. C. Pex, *Catal. Commun.*, 2004, **5**, 347.
- 8 V. R. Choudhary, S. D. Sansare and A. G. Gaikwad, *Angew. Chem., Int. Ed.*, 2001, **40**, 1776.
- 9 T. S. Sheriff, *J. Chem. Soc., Dalton Trans.*, 1992, 1051.
- 10 B. Hothi, V. Lechene, J. Robinson and T. S. Sheriff, *Polyhedron*, 1997, **16**, 1403.
- 11 (a) T. S. Sheriff, P. Carr and B. Piggott, *Inorg. Chim. Acta*, 2003, **348**, 115; (b) T. S. Sheriff, P. Carr, S. J. Coles, M. B. Hursthouse, J. Lesin and M. E. Light, *Inorg. Chim. Acta*, 2004, **357**, 2494.
- 12 The Pd (5%)/ Al_2O_3 and Pd (5%)/C catalysts in their reduced form were obtained from Lancaster (UK). The Ga_2O_3 (Aldrich) supported Pd (2.5%) catalyst was prepared by impregnating the support with palladium acetate from its acetonitrile solution, drying and calcining at 500 °C for 3 h and then reducing by ammoniacal hydrazine. The halogenation of the Pd catalysts was done by impregnating the catalyst with ammonium halide from its aqueous solution, drying and calcining in a flow of oxygen-free N_2 at 400 °C for 1 h.
- 13 The catalytic reduction of O_2 by hydrazine to H_2O_2 over the Pd catalysts was carried out in a magnetically stirred jacketed glass reactor (capacity: 100 cm^3) by passing continuously pure O_2 (99.5%) through an aqueous reaction medium in the presence or absence of different halide anions and/or mineral acids at the following reaction conditions: volume of reaction medium = 50 cm^3 , amount of catalyst = 0.1 g, hydrazine salt or hydrazine hydrate = 2.3 mmol, O_2 flow rate = 10 $cm^3\ min^{-1}$, temperature = 25 °C and pressure = atmospheric (0.95 atm). The initial concentration of hydrazine or its salt and catalyst was 46 $mmol\ dm^{-3}$ and 2.0 $g\ dm^{-3}$, respectively. The temperature of the reaction was controlled by passing continuously thermostated water maintained at desired temperature through the reactor jacket. The H_2O_2 from the reaction mixture (after separating the catalyst from the reaction mixture by filtration) was determined by iodometric titration and also by decomposing the H_2O_2 by MnO_2 and measuring the O_2 evolved quantitatively, according to the H_2O_2 decomposition reaction ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$); both the methods gave the same results. The unconverted hydrazine (if any) was determined by its titration against potassium iodate in a mixture of aqueous acidic (HCl) and $CHCl_3$ medium. The reactor effluent gas was analysed by gas chromatography. Only N_2 and O_2 are found in the gaseous products, indicating the formation of N_2 as the only other main product in both the selective and non-selective oxidation of hydrazine.