SYNTHESIS OF HYDROGEN PEROXIDE

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Chemistry 671
Introduction

• **Oxidation**
  – Functionalize molecules (selective or partial oxidation)
  – Remove pollutant (complete oxidation)

• **Oxidizing Agents**
  – Oxygen gas
  – Other oxidants (Sodium perborate, metallic peroxide etc.)
  – **Hydrogen peroxide**

• **Problems with oxygen gas**
  • Triplet ground state (in oxygen)
  • Organic substrate (singlet ground state)

• **Problems with other oxidants**
  – Separation, poor atom efficiency, polluting

• **Hydrogen peroxide**
  \[ \text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + 2\text{H}_2\text{O} \]
Demand for hydrogen peroxide

- **Current market of H₂O₂**
  - Three million metric tons per year
  - As bleaching agent
  - As cosmetics, disinfectants
  - Chemical synthesis

- **In synthetic process**
  - Propylene oxide (PO)
    - polyurethanes
  - Annual Production of PO is > six million metric tons
  - Market of PO is increasing by 4-5% per year
  - Presently PO is produced by oxidation of propene by organic peroxide

\[
\text{C}_3\text{H}_6 + \text{organic peroxide} \rightarrow \text{C}_3\text{H}_6\text{O}
\]
  - Major PO producing company are designing a plant that produces 250,000 Metric tons/year of PO
  - Needs 180,000 Metric tons of H₂O₂

Synthesis

- Is synthesis process green?

2-alkyl anthraquinone $\rightarrow$ 2-alkyl anthrahydroquinone

$\text{Synthesis of hydrogen peroxide from Anthraquinone}$
Other problems:

- Feasible only on large scale production (in 4-6×10⁴ tones per annum)
- Should be transported and stored in large amount and used in small amount

Secondary reactions taking place in the presence of 2-alkylanthrahydroquinones.
• Direct synthesis

Two reasons

1. Green
2. Small scale production

H₂ + O₂ → H₂O₂

Hydrogen and oxygen both are environmentally friendly reagents/No waste/very cost effective
Historical overview of direct synthesis

• Dr. Hugo Henkel and Dr. Walter Weber June 16, 1913 filed a patent for direct combination of H₂ and O₂ to give H₂O₂

• Process claimed:
  • Porous pipe is impregnated with catalyst (Pd, Pt or Ni)
  • The pipe is placed under the water in a vessel under excessive pressure of oxygen (so the oxygen is in contact with outside of the pipe)
  • In to the interior of the pipe, gaseous H₂ is forced, the reaction occurs and hydrogen peroxide is produced.

• Pospelova, Kobozev, Eremin (1961)
  • Pd black, 0.001 N KCN, 0.1 N H₂SO₄, 20% H₂ – initial yield 80%
Problems with direct hydrogen peroxide synthesis

Which one is major route between these two?

The main problems with direct synthesis
• $\text{H}_2/\text{O}_2$ mixture is explosive
• Direct catalytic combination of $\text{H}_2$ with $\text{O}_2$ prefers to give $\text{H}_2\text{O}$ rather than $\text{H}_2\text{O}_2$ (selectivity)
• The catalyst active for production of $\text{H}_2\text{O}_2$ facilitates its decomposition

Fig. Various reactions during direct synthesis of hydrogen peroxide
• The favorable conditions
  – Lower temperature
  – Short reaction time
  – High pressure
  – Additive

• Catalyst
• Catalysts
  Au, Ag, Pd, Au-Pd, Pd-Pt,
• Promoters
  – Acids
  – Bromide ions (NaBr)
• Role of acids
  – H$_2$O$_2$ is more stable in acidic condition. When [H$^+$] is sufficient in the reaction medium, rxn 3 is suppressed
• Role of bromide ions
  • Small amount of bromide improves selectivity of H$_2$O$_2$
  • More bromide reduces the concentration of H$_2$O$_2$ severely
• Reasons: Br$^-$ is poison for Pd catalyst
  – Block very active water producing sites
    (Poison the catalytic sites active in breaking O-O bond)
  – At more concentration it destroys the catalyst
Mechanisms of synthesis of hydrogen peroxide

**Table 2**

Elementary steps involved in the reaction of hydrogen and oxygen on noble metal surfaces

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>(1) H$_2$(gas) $\rightarrow$ H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2) O$_2$(gas) $\rightarrow$ O$_2$</td>
</tr>
<tr>
<td>Dissociation</td>
<td>(3) H$_2$ $\rightarrow$ 2 H</td>
</tr>
<tr>
<td></td>
<td>(4) O$_2$ $\rightarrow$ 2 O</td>
</tr>
<tr>
<td>Radical formation</td>
<td>(5) O$_2$ + H $\rightarrow$ OOH</td>
</tr>
<tr>
<td></td>
<td>(6) O + H $\rightarrow$ OH</td>
</tr>
<tr>
<td></td>
<td>(7) O$_2$ + H $\rightarrow$ O + OH</td>
</tr>
<tr>
<td></td>
<td>(8) O + H$_2$ $\rightarrow$ OH + H</td>
</tr>
<tr>
<td>OOH reactions</td>
<td>(9) OOH + H $\rightarrow$ H$_2$O</td>
</tr>
<tr>
<td></td>
<td>(10) OOH + H$_2$ $\rightarrow$ H$_2$O$_2$ + H</td>
</tr>
<tr>
<td></td>
<td>(11) OOH + H $\rightarrow$ 2 OH</td>
</tr>
<tr>
<td></td>
<td>(12) OOH $\rightarrow$ O + OH</td>
</tr>
<tr>
<td>OH reactions</td>
<td>(13) OH + H $\rightarrow$ + H$_2$O</td>
</tr>
<tr>
<td></td>
<td>(14) OH + H$_2$ $\rightarrow$ H$_2$O + H</td>
</tr>
<tr>
<td></td>
<td>(15) 2 OH $\rightarrow$ H$_2$O + O</td>
</tr>
<tr>
<td></td>
<td>(16) 2 OH $\rightarrow$ H$_2$O$_2$</td>
</tr>
<tr>
<td></td>
<td>(17) OH + O$_2$ $\rightarrow$ OOH + O</td>
</tr>
<tr>
<td></td>
<td>(18) OH + OOH $\rightarrow$ H$_2$O$_2$ + O</td>
</tr>
<tr>
<td>Desorption</td>
<td>(19) H$_2$O$_2$ $\rightarrow$ H$_2$O$_2$ (gas)</td>
</tr>
<tr>
<td></td>
<td>(20) H$_2$O $\rightarrow$ H$_2$O (gas)</td>
</tr>
</tbody>
</table>

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**Mechanism of formation of H$_2$O$_2$**

12/13/2007
Definitions

• Conversion = (moles hydrogen consumed/moles hydrogen fed) x 100%

• Selectivity = \[\frac{[H_2O_2]}{[H_2O_2] + [H_2O]}\] x 100%
  = moles of \(H_2O_2\) produced/moles of hydrogen consumed x 100%

• Yield = Moles \(H_2O_2\) produced/moles \(H_2\) fed x 100

• Productivity = grams of \(H_2O_2\) produced / grams Pd / pt xhr

• The concentration of \(H_2O_2\) is determined by iodometric titration or titration with cerium sulfate or potassium permanganate

• The concentration of \(H_2O\) is determined by Karl-Fischer titration method
Solvent system used

- Methanol is better than water
- Solvent selection parameter (SSP)

- Solvent selection
  - Solvent selection parameter (ssp) = \( \sum (w_i s_i) \)
  - \( w_i \) = weight fraction of solvent component \( i \) in liquid reaction mixture
  - \( s_i \) = solubility of \( H_2 \) in pure component \( i \) expressed in mole fraction at 25 \(^\circ\)C and 1 atm

- As ssp increases \( H_2O_2 \) production increases
- Should have one phase, yield is high
- NaBr 3ppm to 200 ppm by wt of liq.rxn medium.
Effect of Solvent and Br⁻

1. Solvent selection parameter VS. Hydrogen peroxide yield

1. United States Patent 6576214


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### Effect of Liquid Solvent on Hydrogen Peroxide Synthesis

<table>
<thead>
<tr>
<th>Example Number</th>
<th>Liquid Mixture</th>
<th>Catalyst to liquid ratio</th>
<th>25 C. 10^-4 mole fraction</th>
<th>25 C. 10^-4 mole fraction</th>
<th>Weight fraction solvent</th>
<th>Average H₂ Solubility 10^-4 units</th>
<th>H₂ in Feed (vol.%)</th>
<th>H₂ Conversion (%)</th>
<th>H₂O₂ Concentration (wt %)</th>
<th>H₂O₂ Yield (g/gPd/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>1/100</td>
<td>0.14</td>
<td>0</td>
<td>0.14</td>
<td>3</td>
<td>24.3</td>
<td>2.9</td>
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<td>2</td>
<td>Methanol/Water</td>
<td>1/300</td>
<td>1.6</td>
<td>0.14</td>
<td>0.3</td>
<td>0.578</td>
<td>3</td>
<td>22</td>
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<tr>
<td>3</td>
<td>Acetonitrile/Water</td>
<td>1/300</td>
<td>1.76</td>
<td>0.14</td>
<td>0.3</td>
<td>0.626</td>
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<td>18.9</td>
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<td>4</td>
<td>Isopropanol/Water</td>
<td>1/300</td>
<td>2.7</td>
<td>0.14</td>
<td>0.3</td>
<td>0.908</td>
<td>3</td>
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<td>Acetone/Water</td>
<td>1/300</td>
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<td>0.14</td>
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<td>0.998</td>
<td>3</td>
<td>61.1</td>
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<td>6</td>
<td>Methanol</td>
<td>1/300</td>
<td>1.6</td>
<td>0.14</td>
<td>1</td>
<td>1.6</td>
<td>3</td>
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<td>DMF</td>
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<tr>
<td>8</td>
<td>Isopropanol</td>
<td>1/300</td>
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<td>0.14</td>
<td>1</td>
<td>2.7</td>
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<td>82.4</td>
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<td>750</td>
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<td>9</td>
<td>Hexane/Water *</td>
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<td>10</td>
<td>Formaldehyde/Water</td>
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<td>?</td>
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<td>0.3</td>
<td>?</td>
<td>3</td>
<td>11.8</td>
<td>0.3</td>
<td>64</td>
</tr>
</tbody>
</table>

**Comparative Example**

**Curve A Examples (with NaBr)**

**Curve B Examples (without NaBr)**

**Other Examples**
Effect of solvent in production of hydrogen peroxide

![Graph showing concentration profiles](image)

Fig. 3. $H_2O_2$ concentration profiles in different reaction media for TCM1. ■, 100% methanol; ◆, 100% water; ▲, 50% water and 50% methanol.
• The usefulness of solvent other than water
  – Most oxidation process involving H$_2$O$_2$ are carried out in organic solvent
  – Hydrogen and oxygen solubilities are higher in organic solvent than in water
  – Dry organic media helps to measure the produced water and measure the catalytic activity and selectivity.
Effect of catalyst mass and reaction time for the formation of $\text{H}_2\text{O}_2$

Conditions:
- 5.6 gm of MeOH
- 2.9 gm water
- 5% $\text{H}_2/\text{CO}_2$ and
- 25% $\text{O}_2/\text{CO}_2$

Fig. 2 Effect of catalyst mass on production of $\text{H}_2\text{O}_2$ using 0.6 wt.% Pd/sulfonated carbon. $\bullet$ = $\text{H}_2$ conversion, $\triangle$ = $\text{H}_2\text{O}_2$ selectivity, $\blacksquare$ = $\text{H}_2\text{O}_2$ yield.

Fig. 3 Progress as a function of time of the reaction between $\text{H}_2$ and $\text{O}_2$ using 0.6 wt.% Pd/sulfonated carbon. $\bullet$ = $\text{H}_2$ conversion, $\triangle$ = $\text{H}_2\text{O}_2$ selectivity, $\blacksquare$ = $\text{H}_2\text{O}_2$ yield.

Effect of temperature on hydrogen peroxide production

Fig. 4 Influence of temperature on H$_2$O$_2$ production using 0.6 wt.% Pd/sulfonated carbon $\bullet = $ H$_2$ conversion, $\triangle = $ H$_2$O$_2$ selectivity, $\blacksquare = $ H$_2$O$_2$ yield.

Bimetallic catalyst

Fig. 7. Catalytic performance of bimetallic samples (TCM3 and TCM4) compared to a monometallic sample (TCM1). Filled symbols, H$_2$O$_2$ concentration; open symbols, H$_2$O concentration.
Studies on possible decomposition route of hydrogen peroxide

Fig. 6 Decomposition of H₂O₂ under different experimental conditions using 0.6 wt.% Pd/sulfonated carbon, (A) = no catalyst, H₂, 1 °C, (B) = catalyst, O₂, 1 °C, (C) = catalyst, H₂, 1 °C, (D) = catalyst, H₂, HBr (1.8 × 10⁻⁵ mol l⁻¹), 1 °C, (E) = catalyst, H₂, HBr (1.8 × 10⁻⁵ mol l⁻¹), 17 °C, 3.7 MPa.
Direct synthesis of hydrogen peroxide
Direct synthesis of Hydrogen peroxide combined with organic synthesis
Selectivity is nearly 100% 

Rate of production - first order in hydrogen partial pressure

$D_2/O_2=0.2$

$H_2O_2$ produced  
$=0.2$ wt% 

$D_2$ conversion  $=3\%$ 

$T=293K, P=2\text{ MPa}, 0.05\text{N} \ H_2SO_4, H_3PO_4=0.015\text{N}, NaBr=5.1\times 10^{-4} \text{mol L}^{-1}$ 

SCCM=standard cubic centimeter per minute 

Figure 6. Comparison of formation of peroxide (open box) and water (filled box) on different catalyst supports, $\text{Pd/Al}_2\text{O}_3$ (13.3 mg), $\text{Pd-Pt/SiO}_2$ (29.0 mg), and $\text{Pd/C}$ (15.6 mg). Conditions were as follows: deuterium flow rate 1.6 sccm, oxygen flow rate 4.0 sccm, and liquid (reaction solution flow rate 0.1 mL min$^{-1}$.

12/13/2007
Conclusions:

- Direct synthesis of H$_2$O$_2$ from hydrogen and oxygen is convenient than anthraquinone process.
- Pd/gold or Pd/Pt catalyst is better than single metal.
- Short reaction time, high pressure and low temperature are favorable conditions.
- There is possibility of making portable hydrogen peroxide synthesis device for small scale production.
- Methanol/water mixture is good solvent system, NaBr is good additive and presence of acid are necessary conditions for maximizing the selectivity of hydrogen peroxide synthesis.
References
7. Benjamin E. Solsona et al., Chem. Mater. 2006, 18, 2689-2695
10. US patent 7,144,565
11. US patent 7,144,565
12. US patent 1108752