

## Dual-function Phase-transfer Catalysis in the Metal-assisted Oxidation by Hydrogen Peroxide of Styrene to Benzaldehyde or Acetophenone

Gabriela Barak and Yoel Sasson\*

Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

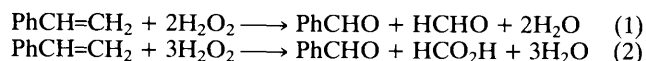
Quaternary ammonium salts assist the extraction of both hydrogen peroxide and metal salts, *e.g.* ruthenium or palladium chloride from the aqueous to the non-aqueous component of a two-phase system; the system has been used for the oxidation of styrene.

Hydrogen peroxide is an attractive oxidation agent in being cheap and easily available and, in addition, its products cause no pollution problems.<sup>1</sup> The direct synthetic application of hydrogen peroxide is, however, limited mainly to the epoxidation of active alkenes<sup>2</sup> and to the conversion of nitriles into amides.<sup>3</sup> This mild activity is significantly enhanced by the addition of various metal catalysts.<sup>4</sup> Typical examples are salts or oxides of V, Mo, W, Co, Mn, and Fe; all these catalysts function *via* the formation of intermediate oxo- or peroxo-metal complexes.<sup>4</sup> Combinations of hydrogen peroxide with transition metal compounds have been reported to oxidize terminal alkenes to methyl ketones,<sup>5</sup> to hydroxylate double bonds,<sup>4</sup> and to oxidize alcohols to aldehydes and carboxylic acids.<sup>6</sup> A common drawback in these systems is the low solubility of both the hydrogen peroxide and, in many cases, the metal catalyst in organic solvents. The usual solution is to use polar solvents like acetic or formic acid but this approach suffers from the inherent limitations of product separation and purification, solvent recycle, and side reactions with the solvent.

A few examples have demonstrated that the performance of hydrogen peroxide as oxidant in two-phase systems is remarkably improved by the addition of quaternary ammonium phase-transfer catalysts,<sup>7</sup> *e.g.* in alkene epoxidation,<sup>8</sup> and in the oxidations of alcohols,<sup>9</sup> aldehydes,<sup>10</sup> sulphides,<sup>11</sup> and ketones.<sup>12</sup> An extraction mechanism was proposed for these systems based on hydrogen bonding of H<sub>2</sub>O<sub>2</sub> to the lipophilic ammonium catalyst which transfers the peroxide into the organic phase.<sup>7</sup>

We have now observed that in the presence of certain metal salts the quaternary ammonium catalyst may have a dual role in that it extracts both the peroxide and the metal into apolar organic solvents, and modifies the nature of the metal by complexation, resulting in improved catalytic activity and in higher resistance of the metal towards reduction. A typical example is the ruthenium-catalysed oxidative cleavage of

alkenes to yield aldehydes; *e.g.* the oxidation of styrene proceeds according to reactions (1) and (2). 30% Hydrogen peroxide (300 mmol, 35 ml) was continuously added during 100 min to a solution of styrene (50 mmol) in 1,2-dichloroethane (10 ml) containing ruthenium chloride trihydrate (0.1 mmol) at 80 °C. No reaction took place except for some decomposition of hydrogen peroxide and precipitation of metal in the aqueous phase. Totally different behaviour was observed when didecyldimethylammonium bromide (DDAB) (1 mmol) was added to the system initially. The ruthenium salt was immediately and quantitatively extracted into the organic phase where it remained stable in solution throughout the process. The styrene was completely consumed yielding (based on g.c. analysis) benzaldehyde (64%), benzoic acid (6%), and styrene oxide (4%), together with other side products. The mass balance in the system was verified by titration of the formic acid in the aqueous phase; 60% of the reaction was found to proceed according to equation (1) and the rest according to equation (2). Complete decomposition of hydrogen peroxide was also observed.



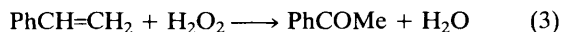
The system needs to be acidic (pH below 4–5). Attempts to neutralize the formic acid produced by sodium carbonate while the reaction proceeded resulted in total poisoning of the catalytic system.

Using tetrabutylammonium bromide (TBAB) as the phase-transfer catalyst also resulted in complete conversion but with somewhat lower selectivity for benzaldehyde formation (61%). More lipophilic quaternary ammonium salts accelerated the parallel decomposition of hydrogen peroxide and reduced the conversion of styrene. With the above procedure tetraheptylammonium bromide gave 87% and Aliquat 336 80% conversion.

Oxidation with total consumption of styrene takes place similarly in the absence of phase-transfer catalyst when the dichloroethane is replaced by the same volume of acetic acid. However the selectivity is different owing to the formation of 25% of styrene glycol [PhCH(OH)CH<sub>2</sub>OH] and its acetate esters.

The ruthenium salt is evidently responsible for the simultaneous rapid decomposition of hydrogen peroxide resulting in the need for the large excess of hydrogen peroxide. If the hydrogen peroxide is added initially in one portion uncontrollable decomposition takes place.

Interestingly, a different selectivity and general behaviour was observed when palladium chloride–Aliquat 336 was used as catalyst. With this system no hydrogen peroxide decomposition took place both in the presence and in the absence of a substrate. Here the oxidation of styrene, using the above procedure with the same stoichiometric quantities, took another course yielding mainly acetophenone (56%) [reaction (3)]<sup>5</sup> along with benzaldehyde (12%) and benzoic acid (14%). The palladium chloride was also quantitatively extracted into the dichloroethane solvent and remained there in solution throughout the reaction.



In the palladium-catalysed reactions the stoichiometric excess of hydrogen peroxide is used only to achieve reasonable reaction rates. At the end of the process the excess of the reagent could be recovered. Consequently, there is no advantage in gradual addition of the hydrogen peroxide.

Other metal and metal salt catalysts examined, *e.g.* rhodium, iridium, or cobalt(II) chloride showed much lower activity. Also ruthenium or palladium on carbon as well as palladium black were found to be inferior catalysts in comparison with their homogeneous counterparts.

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