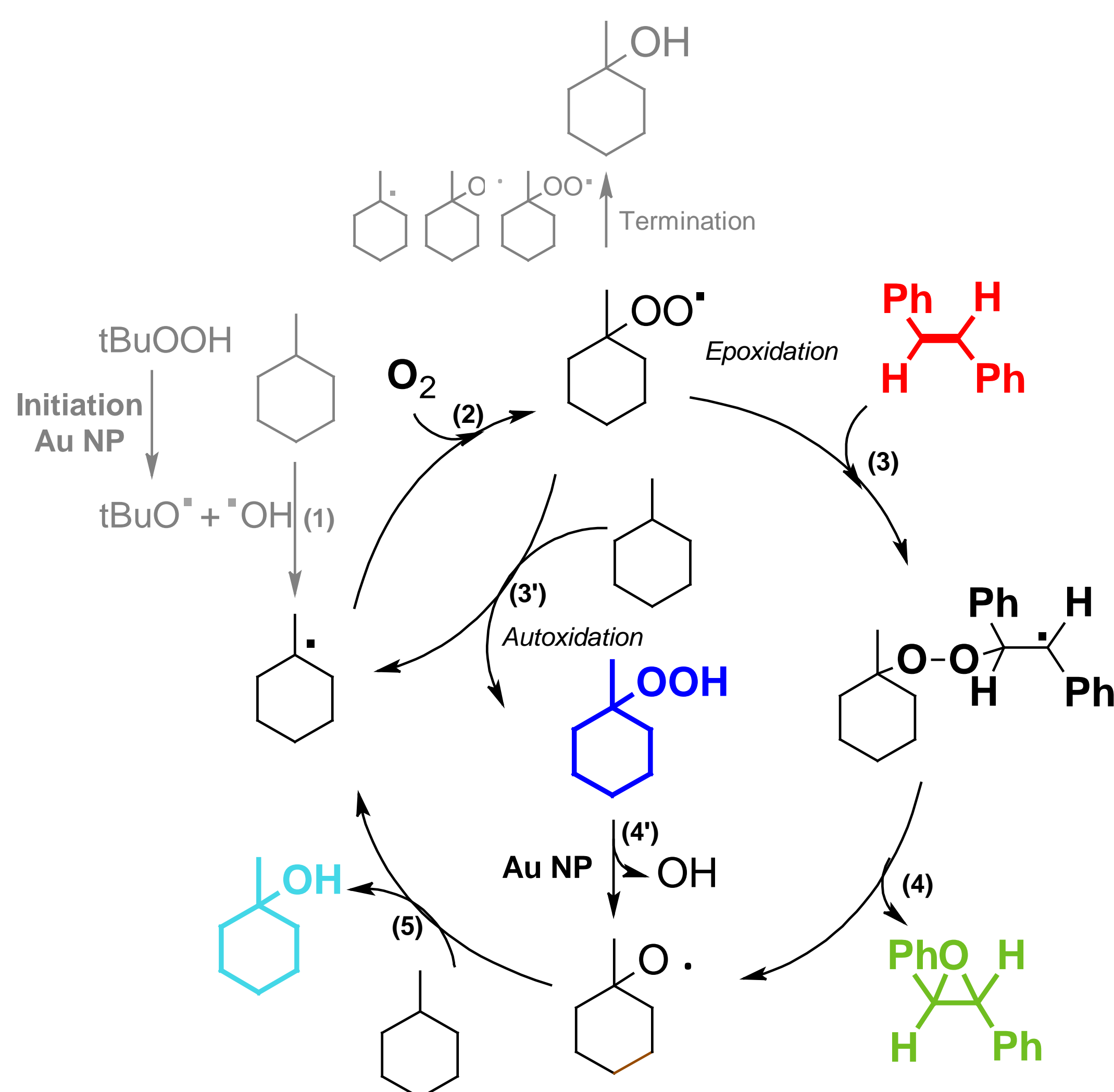


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Potential of aerobic reactions in petrochemistry

Selective oxidations allow the synthesis of high added value oxygenated molecules from petrochemicals. They currently play an essential role in fine chemical manufacturing. Moving from toxic acids and hazardous peroxides towards air as oxidant would thus significantly improve sustainability. The challenge is to activate the particularly inert oxygen molecule, at sub-ambient pressure and mild temperature (< 100° C), in order to perform these aerobic transformations.

The exceptional activity of 2 nm gold sols stabilized with octylsilane ligands and of passivated 1.8 nm Au NP dispersed on silica (resulting from multi-step syntheses developed at C2P2, Lyon; collaborations C. Thieuleux and C. Copéret) indicated that gold was the kinetically active component of the catalyst and that the support was essentially controlling the dispersion of the active phase in the medium, i.e. mass-transfers. The idea was thus to produce Au NP directly on hydrophobic supports. Their surface chemistry however excluded the possibility of using the conventional preparations in aqueous phase. After screening various approaches starting from the triphenylphosphine complex of gold, AuPPh₃Cl, a simple chemical reduction in a ethanol/dichloromethane mixture containing a suspension of commercially available methylated silica finally led to the targeted 3 nm supported gold particles (L. Burel). This Au/SiO₂_R972 material, resulting from a straight-forward, easily reproducible, potentially scalable protocol, became the reference catalyst for the aerobic co-oxidation of methylcyclohexane (MCH) and stilbene (tS) and allowed a complete macro-kinetic study of the reaction.



Hydrophobic gold catalysts

Gold particles (Au NP) with diameters below 5 nm have proven unique in molecular oxygen at low temperature, when associated with reducible oxides as support in particular. These gold catalysts have also proven uniquely selective in catalyzing the mild co-oxidation of a tertiary alkane and a bulky alkene with air, leading to the corresponding alcohol and epoxide. However, to reach kinetic regime and improve reaction rates, hydrophobic catalysts, exhibiting enhanced affinity with the apolar reaction media, had to be developed.

Understanding the reaction mechanism

The identification (GC-MS, S. Mangematin) and quantification (triphenylphosphine titration followed by ³¹P NMR) of the central methylcyclohexyl hydroperoxide (MCOOH) intermediate indicated that the radical reaction mechanism involved a methylcyclohexane autoxidation pathway and a stilbene epoxidation pathway, both leading to the production of the alcohol (MCOH). The effect of the MCH/tS/Au ratios on the MCOH, MCOOH and epoxide apparent production rates clearly showed that:

- gold is involved in the degradation of hydroperoxides as well as in radical recombination (termination);
- both reactants can act as a promoter for the selective oxidation of the other by enhancing propagation (MCH) or inhibiting termination (tS).

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