Selective Decomposition of Tetralin Hydroperoxide Catalysed by Quaternary Ammonium Salts

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Tetralin hydroperoxide decomposes to 1-tetralone *via* a hydrogen bond complex with quaternary ammonium salt catalysts.

While the standard conditions for the catalytic autoxidation of alkyl aromatic compounds require the presence of a cobalt(II) catalyst and a bromide promoter[1] there are some reports on the catalytic activity of onium salts in the absence of a metal.[2–6] Ohkubo proposed direct activation of oxygen by interaction with d-orbitals of an onium cation.[2–4] Harustiak *et al.* suggested that the ammonium cation functions only as a phase transfer agent for the bromide ion, which is the true catalyst.[5,6] In order to elucidate the role of quaternary salts in autoxidation reactions we have examined the catalytic decomposition of 1,2,3,4-tetrahydronaphthalene 1-hydroperoxide (tetralin hydroperoxide, THOP[7]) to 3,4-dihydronaphthalene-1(2*H*)-one 1-tetralone and 1,2,3,4-tetrahydro-1-naphthol (1-tetralol).[8] Fig. 1 presents conversion–time profiles for the decomposition of THOP at 110 °C in the presence of 0.5 mole% of tetra-n-hexylammonium halide catalysts (THAX where X = Cl, Br or I). Also shown is the control reaction in the absence of a catalyst and the reaction with THAC when an aqueous phase is present. The order of decreasing reactivity is clearly $Cl^- > Br^- > I^-$ and water reduces the catalytic activity. The tetralone : tetralol ratio was found to be 0.9 in the control experiment while in the catalytic runs it was 1.4 for THAC, 1.6 for THAB and 1.5 for THAI. We propose that the scission of the O–O bond in THOP is achieved *via* a hydrogen bond complex formation between the substrate and the onium catalyst [eqn. (1)].

$$R_2CHOOH + Q^+X^- \rightarrow R_2CHOOH\cdot\cdot X^-Q^+ \quad (1)$$

Adducts of this type are formed due to hydrogen bonding between the acidic hydrogen of the peroxide and the electron-rich, naked anion of the catalyst. This interaction is stronger for the smaller and harder anions. However, solvation of the anion, as in the presence of water, reduces the strength of this hydrogen bond. It should be noted that ammonium salts–hydroperoxide adducts have been previously isolated and characterized.[9] This hydrogen bonding weakens the O–O bond in the adduct which decomposes as in eqn. 2.

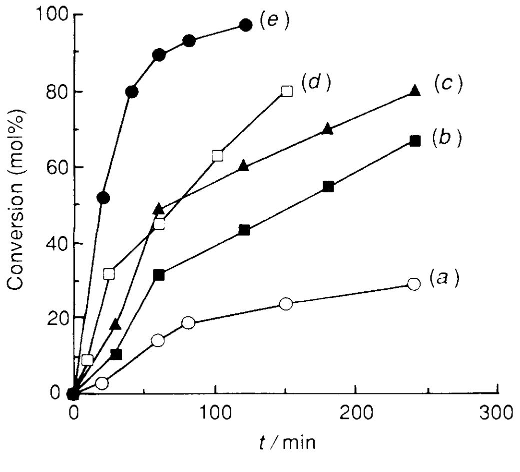

Fig. 1 Decomposition of tetralin hydroperoxide (THOP) in presence of tetrahexylammonium halides.

Reaction conditions: 20 g of 40% THP solution in tetralin, 0.5 mol% of THAX at 110 °C. In the run containing water the THAC:water ratio was 4 : 1. Analysis of samples by titration of THP.[11] (*a*), control; (*b*), THAI; (*c*), THAB; (*d*), THAC–H_2O; (*e*), THAC.

$$R_2CHOOH\cdots\cdots X^-Q^+ \rightarrow R_2CHO^\bullet + Q^+OH^- + X^\bullet \quad (2)$$

The alkoxyl radical formed *via* eqn. 2 can then react in two parallel routes: (*a*) hydrogen abstraction from an available donor (*e.g.* the hydrocarbon) to yield an alcohol (tetralol) and an alkyl radical [eqn. (3)]. (*b*) Reaction with another radical (*e.g.* the halide radical) to yield a ketone (tetralone) and hydrogen halide [eqn. (4)]. In a final step the onium hydroxide formed in reaction 2 is neutralized by the acid formed in reaction 4 to regenerate the original catalyst and complete the catalytic cycle [eqn. (5)].

$$R_2CHO^\bullet + R_2CH_2 \rightarrow R_2CHOH + R_2CH^\bullet \quad (3)$$

$$R_2CHO^\bullet + X^\bullet \rightarrow R_2C{=}O + HX \quad (4)$$

$$Q^+OH^- + HX \rightarrow Q^+X^- + H_2O \quad (5)$$

The validity of the key step 2 was confirmed by conducting a stoichiometric reaction between THOP and THAB in tetralin in the presence of added toluene. 5 mol% of benzyl bromide (based on toluene) was identified in the mixture, indicating the presence of a bromide radical. In a second experiment, solid sodium hydroxide was added in order to neutralize the hydrobromic acid formed in step 4. In this experiment 20% of the ammonium salt was converted to hydroxide THAOH as in eqn. 2. We verified that this is not a result of direct anion exchange between the solid hydroxide and THAB. Such an exchange, carried out separately, yielded less than 0.5% conversion. THAOH is therefore a proven intermediate in the catalytic decomposition of alkyl hydroperoxides.

In step 2 an O–O bond is ruptured homolytically followed by a one electron transfer from the halide anion to the hydroxide radical. Examining different ammonium cations, we found no variation in the activity or the selectivity of the two structurally dissimilar ammonium catalysts THAC and di-n-decyldimethylammonium chloride (DDAC). This result indicates that the ammonium cation has no active role in the transition state of reaction 2. Examining the two competing reactions 3 and 4, we concluded that if the ketone (1-tetralone) is the desired product, as is usually the case,[10] one should enhance the rate of step 4 and minimize the occurrence of reaction 3. This can be achieved by applying the following conditions: (*a*) use of a catalyst to release a more potent radical $X^\bullet$, thus chloride catalysts are preferred over bromide or iodide catalysts; (*b*) increasing the catalyst concentration which will result in a higher concentration of the halide radical and faster hydrogen radical abstraction; (*c*) avoiding hydrogen donor solvents.

In exercising these principles we realized that a significant improvement in the selectivity can be achieved by replacing tetralin with chlorobenzene as a solvent and applying a large quantity of catalyst. Therefore, reaction of 1 g of THOP with 1 g of THAC in chlorobenzene (30 ml) at 110 °C yielded, after 1 h, 100% conversion with 95% selectivity to 1-tetralone. An additional increase in the selectivity to greater than 99.5% was achieved when an Amberlyst A-26 anion exchanger in chloride form was applied instead of THAC. We mixed 6 g of THOP (24 mequiv.) and 20 g of A-26 (44 mequiv. Cl^-) in chlorobenzene (60 ml) at 110 °C for 1 h. Filtration, followed by evaporation of the solvent *in vacuo*, yielded practically pure 1-*tetralone*. We believe that the reason for the exceptional selectivity in this case is the very high catalyst : substrate ratio at the microenvironment reaction site, which results in a complete supression of reaction 3.

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