Alkane Oxidation with Peroxide Species Catalyzed by Osmium Tetroxide

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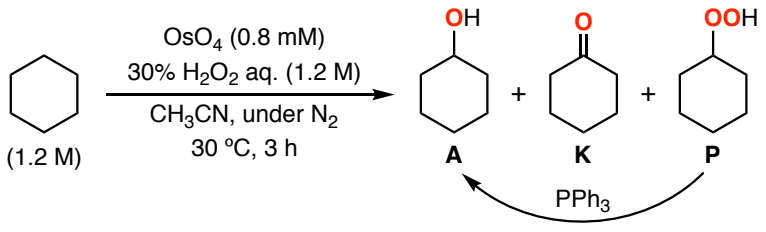
Osmium tetroxide (OsO_4) is known to catalyze oxidation of alkanes. Recently, alkane hydroxylation with $NaIO_4$ as a re-oxidant was reported, where the overoxidation proceeded exclusively to yield the corresponding carboxylic acids.[1] Since OsO_4 is easily re-produced after a reaction of the reduced Os^{VI} species with an appropriate oxidant, a simple catalytic reaction system can be developed by the use of OsO_4. In this study, we examined alkane oxidation catalyzed by OsO_4 with peroxide species such as hydrogen peroxide (H_2O_2) as an environmentally benign oxidant.

Oxidation of cyclohexane with H_2O_2 was carried out in the presence of a catalytic amount of OsO_4 in CH_3CN at 30 °C under N_2 atmosphere. GC-FID analysis of the products after 3 hours indicated that cyclohexanol (**A**) and cyclohexanone (**K**) were produced with turn over numbers (TONs) of OsO_4 as 16 and 20, respectively. On the other hand, upon a workup treatment of the reaction solution with triphenylphosphine (PPh_3), **A** was obtained selectively (A/K = 29) with TON of OsO_4 as 61, suggesting the generation of cyclohexyl hydroperoxide (**P**) *in situ* prior to formation of **A** (**Scheme 1**). The generation of **P** was suppressed under N_2 bubbling conditions, indicating that O_2 participated in the formation of **P**. Furthermore, the radical trap experiment with CCl_3Br obtained the corresponding brominated product. These results suggested that this oxidation reaction involves a cyclohexyl radical intermediate. The oxidation reaction of other substrates besides cyclohexane with H_2O_2 was also investigated. We, further, examined the catalytic oxidation reaction with other alkyl hydroperoxide species to compare the results in terms of product distribution and turnover number. The reaction mechanism was discussed on the basis of kinetic analysis on the catalytic alkane oxidation reactions.



Scheme 1. Reaction scheme on the oxidation of cyclohexane catalyzed by OsO_4

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