Sustained Catalytic Homogenous Oxo-transfer Oxidation of Alkanes. Interaction of Alkyl Hydroperoxides with Transition Metal-substituted Polyoxometalates

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The oxo-transfer oxidation of alkanes by t-butyl hydroperoxide can be catalysed by particular transition metal-substituted heteropolytungstates; the product yields and the stabilities of these systems are higher than those of other homogeneous catalytic alkane oxygenation systems reported in the literature.

Progress since 1980 toward the development of homogeneous catalysts for the selective hydroxylation of alkanes has been substantial.[1—3] The effective high yield oxo-transfer oxidation of alkanes from alkyl hydroperoxides, the most accessible and desirable class of oxygen donors, has yet to be achieved, however. Unfortunately, the well-known Halcon process and related heterolytic organic substrate oxidation processes based on hydroperoxides are not effective with respect to oxidizing saturated hydrocarbons.[2] We report here new homogeneous catalytic systems for the high yield oxo-transfer oxidation of alkanes by an alkyl hydroperoxide, and the first homogeneous catalytic alkane oxygenation systems of any kind that are of sufficient stability to sustain alkane functionalization for thousands of turnovers.

The tetra-n-hexylammonium salts of the transition metal-substituted heteropolytungstate complexes, $[PW_{11}(M)O_{39}]^{5-}$, (1-M),[4] catalyse the oxidation of alkanes by t-butyl hydroperoxide (TBHP). Product distributions for cyclohexane oxidation by typical catalysts in three different solvents along with the detailed reaction conditions are summarized in Table 1. In the best solvents, such as benzene, over 90% of the oxygen equivalents represented in the hydroperoxide can be accounted for by alkane oxidation products. Good to excellent yields of oxygenated products are obtained from several other alkanes examined. Adamantane, for example, produces the 1- and 2-alcohols and the 2-ketone in molar ratios 49 : 7 : 14 with a combined yield with respect to oxidant consumed as high as 90% in some systems. The product yields in these processes

**Table 1.** Homogeneous catalytic oxygenation of alkanes by t-butyl hydroperoxide (TBHP).[a]

M in catalyst[b] (1-M)	Substrate (RH)	Solvent benzene Product yields (%)[c]			TBHP[a] consumed	Turnovers[d] of catalyst
		ROH	R'=O	Bu'OH		
Co[II]	cyclo-C_6H_{12}	61	36	94	50	94
Mn[II]	cyclo-C_6H_{12}	47	40	88	78	125
Cu[II]	cyclo-C_6H_{12}	50	30	96	71	100
Fe[II]	cyclo-C_6H_{12}	59	31	98	45	72
Co[II]	$Me_2CHCHMe_2$	69	e	74	50	62
Co[II]	$C_6H_5Bu^t$	No detectable volatile products				
		Solvent 1,2-dichloroethane				
Co[II]	cyclo-C_6H_{12}	28	27	65	29	26
Mn[II]	cyclo-C_6H_{12}	18	19	55	23	14
Cu[II]	cyclo-C_6H_{12}	23	19	99	94	68
Fe[II]	cyclo-C_6H_{12}	19	17	60	29	17
Mn[II](OTf)$_2$	cyclo-C_6H_{12}	24	21	50	23	17
Co[II](OTf)$_2$	cyclo-C_6H_{12}	38	21	51	17	17
		Solvent acetonitrile				
Co[II]	cyclo-C_6H_{12}	1.0	4.9	f	f	10.6
Mn[II]	cyclo-C_6H_{12}	2.4	6.4	f	f	16
Cu[II]	cyclo-C_6H_{12}	7.4	9.9	f	f	30
Fe[II]	cyclo-C_6H_{12}	≪1	3.9	f	f	7.4
Mn[II](OTf)$_2$	cyclo-C_6H_{12}	4.7	≪1	f	f	6
Co[II](OTf)$_2$	cyclo-C_6H_{12}	≪1	≪1	f	f	f

[a] All reactions run with alkane (17 mmol), TBHP (0.284 mmol) (from 3.55 M solution in benzene solution), and (1-M) (1.6 × 10^{-3} mmol) in solvent (15 ml) at 65 °C under Ar [substrate/oxidant/catalyst (mol) 10600/177/1]. Product distributions quantified by g.l.c. and g.l.c.–mass spectrometric analyses after quantitative titration of residual TBHP with tri-n-butylphosphine. [b] The catalysts (1-M) were tetra-n-hexylammonium salts of [PW$_{11}$(M)O$_{39}$]$^{5-}$. OTf = trifluoromethanesulphonate. [c] Yields of alcohol and ketone, R'=O, based on TBHP consumed. The ketone yields are the molar yields multiplied by 2, since 2 equiv. of TBHP are required to make 1 equiv. of ketone. Yields of Bu'OH based on initial TBHP. [d] Moles of oxidizing equivalents in all products/moles of catalyst. [e] No primary alcohol or aldehyde detected. [f] Yields not determined.

are substantially higher than those seen for the most effective co-ordination complex or metalloporphyrin-based alkane oxidation systems[3] and the best metal-complex mediated homolytic hydroperoxide alkane oxidation processes.[5] The principal products in Table 1 are those derived from alkane functionalization and not the usual radical chain hydroperoxide decomposition products.[2,6] For example, di-t-butyl peroxide is not produced at all under the conditions given in Table 1. Not surprisingly, the initial kinetic products, the alcohols, are oxidized far more rapidly than the alkanes themselves in these reactions. No functionalization whatsoever takes place in the absence of either the catalyst (1-M) or TBHP, and benzene-soluble salts of [PW$_{12}$O$_{40}$]$^{3-}$, and the possible catalyst breakdown products [PW$_{11}$O$_{39}$]$^{7-}$ and [WO$_4$]$^{2-}$, display much lower or negligible reactivities for alkane oxidation by TBHP. The reactions summarized in Table 1 are not photochemical in nature. They are not influenced by stirring rate and appear to be homogeneous from start to finish. The trifluoromethane-sulphonate or nitrate salts of the transition metal salts most active for oxo transfer (e.g. Co[II], Cu[II], and Mn[II])[7] are not soluble in the nonpolar solvents such as benzene or chloroben-zene which lead to the production of high yields of the alkane functionalization products (Table 1).

The product distributions, the cleavage selectivities (e.g. $k_{tert.C-H}/k_{sec.C-H}$ for adamantane ≃ 9.8), the primary kinetic isotope effect [k_H/k_D = 6.5 for cyclohexane and (1-Co) under conditions in Table 1], the production of trans-9-decalol as the principal product derived from cis-decalin oxidation, and the production of chlorocyclohexane as the principal product

when an excess of CCl$_4$ is added to the systems in Table 1, all indicate that these reactions proceed in large part by radical processes. The lack of effect of several equivalents of the radical inhibitor 2,6-di-t-butyl-4-methylphenol (BHT) indicates that the radical chain component in these reactions is probably small or negligible, however. Spectroscopic examination of the catalysts before, during, and after alkane functionalization indicates that some of the catalytically active transition metal ions, e.g. Mn and Fe, change oxidation state during reaction, while others, e.g. Co and Cu, may not.

$$(1\text{-Co}^{III})O\cdot + RH \rightarrow (1\text{-Co}^{III})OH + \cdot R \rightarrow$$
$$(1\text{-Co}^{II}) + ROH \quad (1)$$
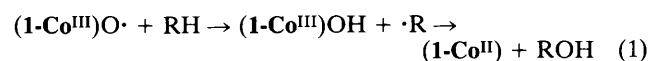
All data are compatible with equation (1) as a principal oxidative pathway for the (1-Co[II])/TBHP system as proposed by Mimoun and his co-workers for the analogous Co[II/III]BPI/TBHP [BPI = 1,3-bis(pyridylimino)isoindoline] and related systems[5] and by us and others for hydroxylation of alkanes by other oxometal complexes.[3] However, it is difficult to quantify at this stage the importance of substrate activation by Bu'O·, Bu'OO·, and other species, as well as the involvement of O$_2$, possibly generated in situ, in stoicheiometric or short-chain processes, with respect to these alkane functionalization reactions. The intermediate (1-Co[III])O· can be generated by homolytic O–O cleavage in (1-Co[III])OOR and by other routes.[5]

In contrast to metalloporphyrins or other catalysts contain-ing organic ligands, the oxide-W[VI] (d^0) frameworks of the

catalysts (**1-M**) render them stable to oxidation. In addition, the pentadentate ligand environment afforded by these frameworks prevents the $d^{\neq 0}$ transition metal active sites from being lost and hence deactivated by precipitation. These factors enable the reactions in Table 1 to be sustained for thousands of turnovers. There are problems with the attempted production of several thousand equivalents of alcohol and/or ketone relative to catalyst in one-pot reactions, however. The high concentration of reactant TBHP and the Bu^{t}OH that builds up under these conditions slows the reactions, and decreases the selectivity. Under these conditions, a large number of products, including di-t-butyl peroxide, are formed in addition to alcohol and ketone.

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