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Oxidation of C-H compounds with peroxides catalyzed by polynuclear transition metal complexes in Si- or Ge-sesquioxane frameworks: A review[☆]

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This paper is dedicated with admiration to Professor Richard D. Adams in recognition of his notable contributions to the chemistry of polynuclear transition metal complexes and catalysis.

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ABSTRACT

Polynuclear transition metal complexes in Si- or Ge-sesquioxane frameworks synthesized in recent years turned out to be efficient catalysts in oxidation of organic compounds with peroxides: H_2O_2, *tert*-butyl hydroperoxide (TBHP), *meta*-chloroperoxybenzoic acid (MCPBA). This brief review describes oxygenations by peroxides of alkanes to alkyl hydroperoxides, alcohols and ketones and benzene to phenol as well as oxidation of alcohols to the corresponding ketones. Some reactions with MCPBA occur stereoselectively.

Contents

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1. Introduction

Siloxanes, organosilicon compounds containing Si–O–Si fragments, are very important substances both from academic and practical points of view [1]. Silsesquioxanes with chemical formula $[RSiO_{1.5}]_n$ (R is H, alkyl, aryl or alkoxyl) contain 1.5 atoms O per one atom Si (Latin “Sesqui” means “one-and-one-half times”).

Branched structural units of sesquioxane composition are known as a sophisticated instrument for bridging a gap between inorganic and organic chemistry. Mainly, such investigations were focused on silicon-containing ($RSiO_{1.5}$-based) sesquioxanes, capable to mimic natural silicates, modified due to the presence of an organic exterior [1]. Excellent ability of Si-sesquioxane frameworks to be a basement of metalladerivatives is also well-known and described in detail in several monographs, reviews and original papers [2]. Silsesquioxane fragments, acting as acyclic [2a], [2c], [2g] [3] cyclic [2g] [4] or condensed [2b] [2d], [2e] [2f], [2g] [5], ligands, provide enormous amount of metal-containing products. Cage-like metallasilsesquioxanes (CLMSs) $RXO_{1.5}$ (R – organic group, X = Si, Ge) constitute a large class of polycyclic compounds based on RSi–O–M structural fragment (M is a metal atom) [2–7].

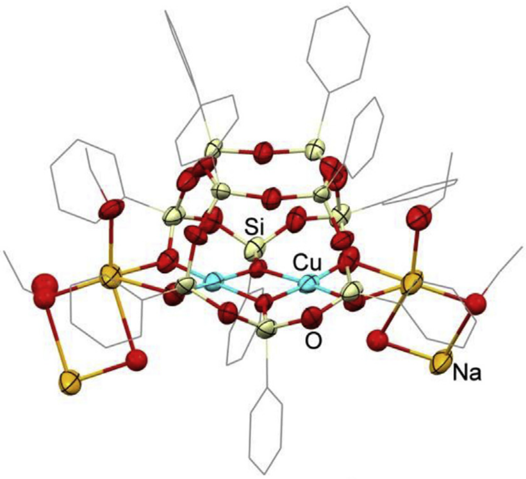

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Fig. 1. A simplified structure of complex $[(PhSi)_{10}O_{18}Cu_2Na_2]$ (**1**). Adapted from Ref. [17a] with permission of Wiley publishing company.

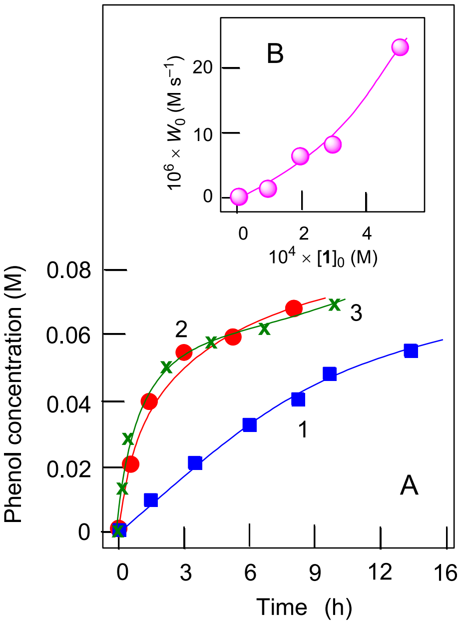
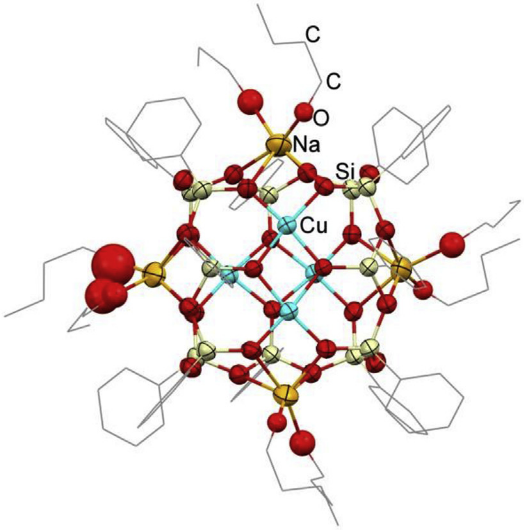


Fig. 2. Graph A: Accumulation of phenol during oxidation of benzene (0.45 M) with H_2O_2 (1.35 M; 35% aqueous) catalyzed by compound **1** at different concentrations of **1**: 1×10^{-4} M (curve 1), 2×10^{-4} M (2), 3×10^{-4} M (3). The reaction was carried out in acetonitrile in the presence of HNO_3 (0.05 M, 65% aqueous) at 70 °C. At $[\mathbf{1}]_0 = 1 \times 10^{-4}$ M (curve 1) after 14 h, TON was 530. Graph B: Dependence of initial reaction rate W_0 on initial concentration of **1** (for conditions of experiments presented in Graph A). Adapted from Ref. [17a] with permission from Wiley publishing company.



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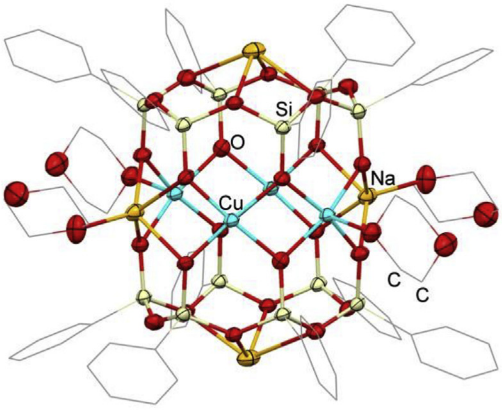

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Fig. 3. The structures of the “Globule”-like compound $[(PhSi)_{12}O_{24}Cu_4Na_4]$ (**2**) and “Sandwich”-like (or “Belt”-like) derivative $[(PhSi)_6O_{12}Cu_4Na_4(PhSi)_6O_{12}]$ (**3**). Adapted from Ref. [17c] with permission from the Royal Society of Chemistry.