



Carbon–hydrogen bond activation of arenes and alkylarenes by electron transfer followed by oxygen transfer catalyzed by vanadium substituted polyoxometalates – A comparative study of the reactivity of different polyoxometalate compounds

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ABSTRACT

The reactivity of various vanadium-substituted polyoxometalates with different structures and oxidation potentials was compared for the electron transfer-oxygen transfer oxidation of anthracene and dihydroanthracene as model substrates. Electron transfer initiates the C–H bond activation. Analysis of reactivity via an outer sphere electron transfer model demonstrates that in addition to the oxidation potential, the polyoxometalate structure and charge are important parameters in the electron transfer reaction. A further comparative study for electron transfer and oxygen transfer reactivity showed that the eventual formation of the oxygenated product, although initiated by electron transfer was dependent on other factors.

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Introduction

The selective oxidation of hydrocarbons with molecular oxygen as terminal oxidant by activation of sp^3 and sp^2 carbon–hydrogen bonds remains a central objective and important research goal of our generation. Enzymes, notably of the cytochrome P-450 and methane monooxygenase families [1], exhibit exquisite activity and selectivity, but translation of this reactivity into simple relevant biomimetic analogues has been less successful, although much mechanistic knowledge has been gained. Such biomimetic oxidation reactions also require sacrificial electron donors or pre-reduced forms of O_2 such as peroxides [2]. From an entirely different perspective, molecular oxygen can be used for oxidation reactions that proceed by metal-catalyzed autooxidation pathways to yield many oxygenated products generally with low selectivity [3]. Already in the 1970's Shilov and coworkers put forward the concept of alkane oxidation, notably of methane, by electrophilic activation of C–H bonds using simple Pt(II) complexes; Pt(IV) salts

acted as the stoichiometric oxidant [4]. Subsequently, this now so called Shilov reaction, was extensively investigated towards a delineation of the reaction mechanism [5]. In parallel, there have been attempts to replace the Pt(IV) oxidant by more attractive oxidants. Sulfur trioxide introduced as oleum was found to be an especially suitable oxidant [6]. Use of O_2 as oxidant has been proven to be more complicated. Here polyoxometalates, notably the phosphovanadomolybdates, for example $H_5PV_2Mo_{10}O_{40}$, have significant potential due to their inherent stability to strongly oxidizing conditions [7], and their ability to catalyze reaction via electron transfer oxidation. Moreover, $H_5PV_2Mo_{10}O_{40}$ significantly inhibits autoxidation reactions that allows selective oxidative transformations [8]. Interestingly, a hybrid catalyst consisting of a Pt(II)bipyrimidine based complex combined with $H_5PV_2Mo_{10}O_{40}$ showed activity for the aerobic oxidation of methane, although the number of turnovers was limited and selectivity to methanol was compromised by formation of acetaldehyde and then formaldehyde [9]. More generally speaking we have found that $H_5PV_2Mo_{10}O_{40}$ can catalyze electron transfer-oxygen transfer (ET-OT) reactions [10]. These types of reactions can be considered as low temperature, homogeneous analogues of the high temperature, heterogeneous Mars-van Krevelen type oxygenations. This

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type of reactivity was first demonstrated for the oxygenation of activated arenes and alkylated arenes [11], and then later on for the oxidation of vicinal diols and primary alcohols [12], and sulfides [13]. More recently oxygen insertion into a metal–carbon bond has also been demonstrated [14]. There are three key features of these reactions: (1) initiation of C–H bond activation by electron transfer from the substrate to the polyoxometalate, (2) a sequence of reactions leading to oxygen transfer from the polyoxometalate to the substrate with formation of the oxygenated product and (3) the re-oxidation of the reduced and deoxygenated catalyst with O₂, although re-oxidation by electrolysis to form H₂ is also an intriguing option [15].

The initial electron-transfer oxidation of substrates with H₅PV₂Mo₁₀O₄₀ has an obvious limitation – the oxidation potential of the substrate cannot be too high relative to the oxidation potential of H₅PV₂Mo₁₀O₄₀, which is equal to 0.7 V vs SHE in water. In order to broaden the substrate scope of ET-OT type reactions one alternative is to use vanadomolybdates of improved redox properties so as to facilitate electron transfer activation of C–H bonds without compromising the other key features needed, oxygen transfer and re-oxidation with O₂. Here we present a comparative study between the reactivity of the well-studied H₅PV₂Mo₁₀O₄₀ and other vanadium substituted polyoxometalates of both the Keggin and Wells–Dawson type structures, where the polyoxometalates differ in charge, structure and the identity of heteroatoms, Fig. 1.

Results and discussion

Nine different polyoxometalates were synthesized and characterized according to published methods: two polyoxometalates with a Wells–Dawson structure Q₆H₂[V₃Mo₁₇O₆₂] [16], Q₅[S₂VMo₁₇O₆₂] [17], five polyoxomolybdates with Keggin structure Q₃SVMo₁₁O₄₀ [17], Q₄HVV₂Mo₁₀O₄₀ [18], H₅PV₂Mo₁₀O₄₀ [19], H₄PVMo₁₁O₄₀ [19], and Q₅PV₂Mo₁₀O₄₀ [11], and two polyoxotungstates with Keggin structure H₅PV₂W₁₀O₄₀ [20], and Q₄H₂SiV₂W₁₀O₄₀ [21]. In all cases Q is the tetrabutylammonium cation. In order to investigate the oxidation of active C–H bonds compounds, anthracene and dihydroanthracene were used as model substrates. Thus, either anthracene or dihydroanthracene (60 mM) and the polyoxometalate (1 mM) in acetonitrile were reacted in the presence of 50 mM of trifluoroacetic acid (TFA) at 1 atm O₂ at 50 °C for 18 h. The TFA was added so that all reactions

would be acidic and have a sufficient oxidation potential to enable C–H bond activation and catalysis [22]. The non-acidic polyoxometalates did not catalyze oxidation reactions in the absence of TFA. Analysis of the reaction mixture showed the selective oxidation of anthracene to anthraquinone and also the oxidation dihydroanthracene to anthracene (~90%) as a major product and anthraquinone (~10%) as minor product.

As noted above it was previously shown that H₅PV₂Mo₁₀O₄₀ initiated oxidation of anthracene and dihydroanthracene by electron transfer (ET) that was then followed by proton transfer (PCET) as opposed to hydrogen atom transfer or hydride transfer [11]. The research question is therefore – do all vanadium containing polyoxometalates initiate C–H bond activation by ET processes, that is, is this a general characteristic of these compounds? In order to answer this question the various vanadium(V) containing polyoxometalates (V^V-POM) were reacted anthracene or dihydroanthracene under Ar. The appearance of the signature reduced blue polyoxometalate species (V^{IV}-POM) at 750 nm in the visible spectrum was observed. Kinetic profiles for the reaction dependence on the polyoxometalate concentration were obtained under pseudo-first order conditions from the reaction of 0.25 mM of V^V-POM and 25 mM of hydrocarbon in 2 mL of acetonitrile containing 50 mM of TFA under argon at 50 °C. Further, reaction with the hydrocarbons at limiting concentrations demonstrated that the reactions were first order in both V^V-POM and in the substrate. The second order rate constants were calculated for the oxidation of anthracene and dihydroanthracene, Fig. 1. As one may observe neither of the vanadium containing polyoxotungstates were active and activity of vanadium containing polyoxomolybdates depended on their structure. In all cases anthracene was more reactive than dihydroanthracene. This observation is in correlation with the relative gas-phase ionization potentials as a measure of the oxidation potential, which are 7.4 eV and 8.3 eV for anthracene and dihydroanthracene respectively [23]. Since the reactive C–H bond of anthracene is stronger than that of dihydroanthracene, 105 versus 76 kcal/mol, it appears clear that there was no correlation of the rate as a function of the C–H bond strength. These initial results appear to support an initial electron-transfer reaction rather than a hydrogen atom transfer process for the activation of hydrocarbon by the V^V-POMs.

In order to support this conclusion, the dependence of rate constant of reaction of anthracene oxidation on redox potential of the various vanadium containing polyoxometalates was studied,

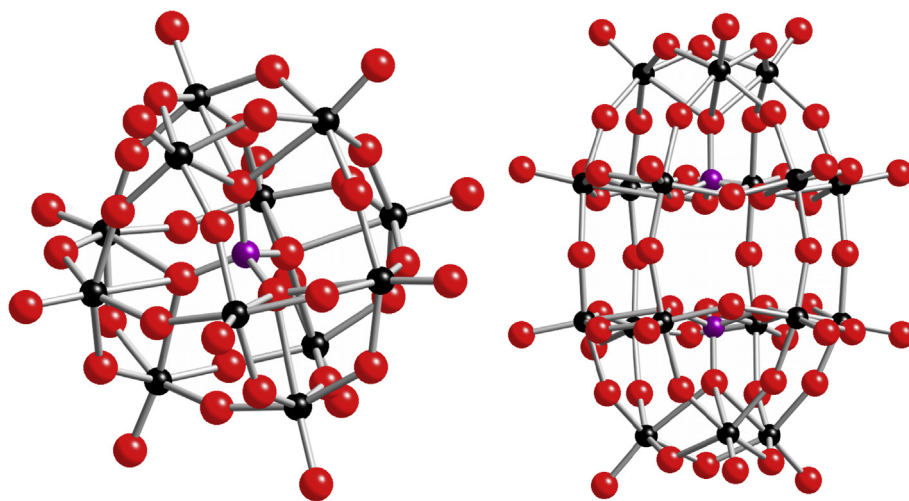


Fig. 1. Ball and stick models of Keggin, XM₁₂O₄₀⁹⁻ (left), and Wells–Dawson, X₂M₁₈O₆₂¹²⁻ (right), polyanions where X is the central heteroatom (purple); X = P, Si, S or V. M are the addenda atoms (black); M is a combination of V, Mo and W with one or two vanadium atoms whose position is not specifically known. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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