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Mechanism of decatungstate photocatalyzed oxygenation of aromatic alcohols
Part II. Kinetic isotope effects studies

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Abstract

A combination of time-resolved techniques (part I) with kinetic isotope effects studies (part II) has been used to investigate the mechanism of the decatungstate ($W_{10}O_{32}{}^{4-}$) photocatalyzed oxidation of aromatic alcohols, in acetonitrile. It is demonstrated that aromatic alcohols exclusively react by hydrogen atom transfer (HAT) mechanism, like to that proposed for the analogous alkane oxidations, and not by an electron transfer (ET) which is predominant in alkenes. The primary and β-secondary isotope effects provide strong evidence for a stepwise mechanism, in which the hydrogen atom abstraction occurs in the rate-determining step of the reaction. The positive slope in Hammett kinetics suggests a radical intermediate for this reaction and supports an early transition state.

Keywords: Decatungstate; Polyoxometalate; Photocatalytic oxygenation; Aromatic alcohols; Kinetic isotope effects; Hammett kinetic

1. Introduction

During the last 20 years, important advances have been achieved in the use of polyoxometalates in the catalytic transformation of organic compounds to the corresponding oxidative products [1]. The most interesting and synthetically valuable properties of these metal–oxygen anion-clusters are the wide range of their redox potentials, as well as the reversibility in their multi-electron reductions. One of the most promising systems is the decatungstate anion $W_{10}O_{32}{}^{4-}$, which has been especially considered for its very important photocatalytic properties (Scheme 1) [2–16]. It is generally accepted that illumination of $W_{10}O_{32}{}^{4-}$ leads to the formation of a locally excited state $W_{10}O_{32}{}^{4-*}$ that decays in less than 30 ps [3] to an extremely reactive transient, designated as wO [4]. This latter intermediate is most likely the reactive species in the decatungstate photocatalytic reactions with several organic compounds [2–20].

Previous studies of the decatungstate catalyzed photooxidation of aliphatic alcohols [4,6,7,18] and alkanes [4,5,8,11,12] suggests that the reactive intermediate wO is quenched by a hydrogen atom transfer (HAT) to give the one-electron-reduced form ($H^+W_{10}O_{32}{}^{5-}$) and oxidative products (Scheme 2). It was proposed that the reduced form (RF) can be oxidized back to $W_{10}O_{32}{}^{4-}$ in the presence of oxygen with parallel formation of peroxy compounds [4]. Therein, in the decatungstate catalyzed photooxidation of propan-2-ol, a quantitative conversion of acetone and hydrogen peroxide under continuous photolysis was obtained:

$$(CH_3)_2CHOH + O_2 \xrightarrow[W_{10}O_{32}{}^{4-}]{h\nu} (CH_3)_2CO + H_2O_2$$

However, with easily oxidizable substrates, such as amines [6], aromatic hydrocarbons [10] and alkenes [19,20] it was proposed that a direct electron transfer (ET) can compete with hydrogen atom transfer. Thus, the reaction of the wO intermediate with organic substrates XH may occur either by: (a) hydrogen abstraction transfer (HAT) and/or (b) electron transfer, according to the proposed mechanism shown in Scheme 3.

In this work we report a detailed mechanistic study of the decatungstate photocatalyzed oxidation of reaction of aromatic

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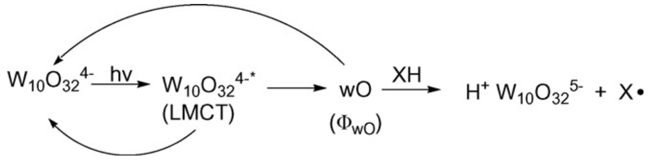
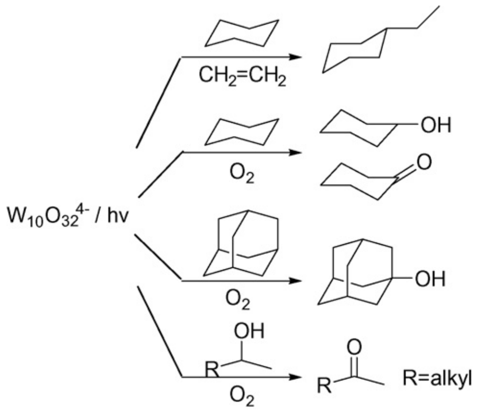


Scheme 1.



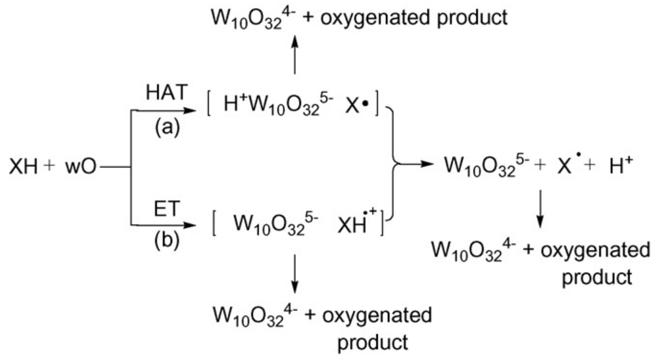
Scheme 2.

alcohols. Because these substrates are potentially capable of reacting by both HAT and/or ET mechanisms, it is difficult to predict the dominant one. In particular, we investigated the primary and the β-secondary kinetic isotope effects (KIEs), in the decatungstate catalyzed photooxygenation of 1-phenylethanol (**1-*d*$_0$**) and 2,2-dimethyl-1-phenyl-1-propanol (**2-*d*$_0$**) in the presence of O_2. In general, deuterium kinetic isotope effects are a powerful tool to probe the transition state and provide valuable information on the extent of bond breaking and bond making of a reaction. We also report herein a Hammet kinetic study of a series of *para*-substituted-1-phenyethanols and discuss mechanistic possibilities. A combination of kinetic isotope effects studies (this paper, part II) and time-resolved techniques with continuous photolysis and laser flash photolysis studies (part I), allow us to evaluate the hydrogen abstraction transfer and/or the electron transfer mechanisms to the overall process.

2. Experimental

2.1. Apparatus and general procedure of decatungstate photooxidation

^{1}H NMR and ^{13}C NMR spectra were recorded on 500 MHz spectrometers, in $CDCl_3$, except for the ^{1}H NMR spectra of some catalytic photooxidation products, which were run in CD_3CN solutions. Chemical shifts are reported in ppm. The catalytic photooxidations were monitored using gas chromatography (GC), HP 5890 series, equipped with a 60 m of 5% phenyl methyl silicone capillary column and ^{1}H NMR spectroscopy. Catalytic photooxidations were achieved with a Xenon Variac Cermax 300 W lamp. Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, SDS, 230–400 mesh ASTM). The solvent used was HPLC grade acetonitrile, sample size was 2 mL, and the concentrations of $Na_4W_{10}O_{32}$ or $[Bu_4N]_4W_{10}O_{32}$ and aromatic alcohol were 5.5×10^{-4} and 0.05 M, respectively. The photooxidations were carried out in a quartz cell. Samples irradiated for period of 1–90 min while molecular oxygen was continuously bubbled through the solution. During irradiation, the reaction mixtures were cooled with ice bath and the reaction was monitored by gas chromatography.



Scheme 3.

Sodium decatungstate [3a] and tetrabutylamonium decatungstate [13] were synthesized and purified by literature procedures. All time-resolved techniques are reported in details in part I.

2.2. Materials and ^{1}H and ^{13}C NMR spectroscopic data

2.2.1. 1-Phenylethanol (**1-*d*$_0$**)

This compound was purchased from Aldrich. ^{1}H NMR (500 MHz): δ 7.37 (m, 4H), 7.30 (m, 1H), 4.91 (q, *J* = 6.5 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H).

2.2.2. 1-Deuterium-1-phenylethanol (**1-*d*$_1$**)

To a mixture of $LiAlD_4$ (0.42 g, 10 mmol) in dry ether 40 mL under argon atmosphere at 0 °C was added dropwise a solution of acetophenone (3.6 g, 30 mmol) in dry ether (15 mL). The mixture was heated under reflux for 1 h. The reaction was quenched at 0 °C by addition of 0.4 mL H_2O, 0.4 mL of 15% NaOH and 1.2 mL H_2O, followed by filtration. The mixture was washed with 5% $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated to give the 1-deuterium-1-phenylethanol (3.3 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (m, 4H), 7.29 (m, 1H), 1.51 (s, 3H).

2.2.3. 2,2,2-Trideuterium-1-phenylethanol (**1-*d*$_3$**) and 1,2,2,2-tetradeuterium-1-phenylethanol (**1-*d*$_4$**)

These compounds were prepared according to the synthetic scheme shown below: