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.
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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:

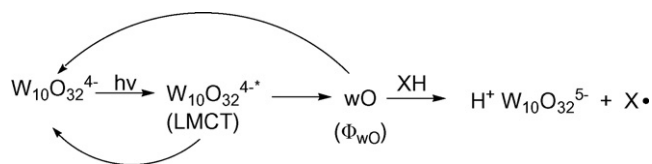$$(CH_3)_2CHOH + O_2 \xrightarrow[W_{10}O_{32}^{4-}]{h\nu} (CH_3)_2CO + H_2O_2$$
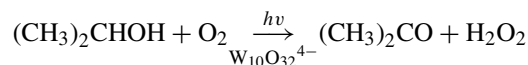
However, with easily oxidizable substrates, such as amines [6], aromatic hydrocarbons [10] and alkenes [19,20] it was proposed that a direct electron transfer (ET) can compete with hydrogen atom transfer. Thus, the reaction of the wO intermediate with organic substrates XH may occur either by: (a) hydrogen 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
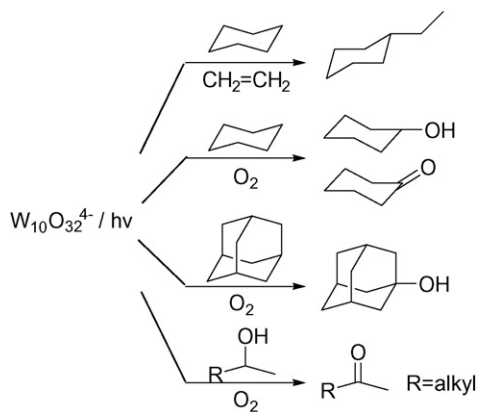
Scheme 1.

Scheme 2.

Scheme 3.

tions 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.

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 ^1H and ^{13}C NMR spectroscopic data

2.2.1. 1-Phenylethanol (1-d₀)
This compound was purchased from Aldrich. ^1H 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-d₁)
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%). ^1H 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-d₃) and 1,2,2,2-tetradeuterium-1-phenylethanol (1-d₄)
These compounds were prepared according to the synthetic scheme shown below:
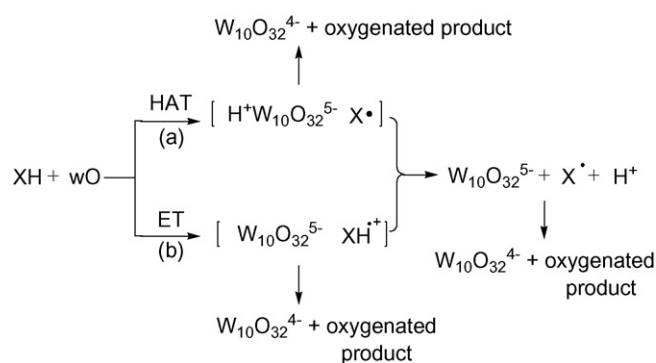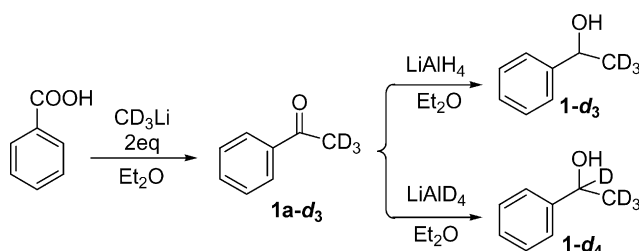

alcohols. Because these substrates are potentially capable of reacting by both HAT and/or ET mechanisms, it is difficult to predict the dominant one. In particular, we investigated the primary and the β-secondary kinetic isotope effects (KIEs), in the decatungstate catalyzed photooxygenation of 1-phenylethanol (1-d₀) and 2,2-dimethyl-1-phenyl-1-propanol (2-d₀) 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

^1H NMR and ^{13}C NMR spectra were recorded on 500 MHz spectrometers, in $CDCl_3$, except for the ^1H 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 ^1H 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 concentra-

2.2.4. 2,2,2-Trideuterium-1-phenylethanone (1a-d₃)

A cold ($-78\,^\circ$C), argon-blanketed solution of the benzoic acid (3.7 g, 30 mmol) in anhydrous ether (40 mL) was treated slowly with CD$_3$Li (65 mL of 1 M in hexane, 65 mmol) [21]. After 15 min, the reaction mixture was warmed to $0\,^\circ$C, stirred for 3 h and carefully treated with water. The ether phase was separated, washed with water, dried over MgSO$_4$ and evaporated. The residue was purified by medium pressure liquid chromatography on silica gel (elution with 10% ethyl acetate in hexane) to give 2.9 g (80%) of **1a-d₃**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.99 (d, 2H, $J = 7.8$ Hz), 7.59 (t, 1H, $J = 7.4$ Hz), 7.48 (t, 2H, $J = 7.7$ Hz).

2.2.5. 2,2,2-Trideuterium-1-phenylethanol (1-d₃)

To a mixture of LiAlH$_4$ (0.19 g, 5 mmol) in dry ether (40 mL) under argon atmosphere was added dropwise a solution of 2,2,2-trideuterium-1-phenylethanone (1.9 g, 15 mmol) in dry ether (10 mL), at $0\,^\circ$C. The mixture was heated under reflux for 1 h. The reaction was quenched at $0\,^\circ$C by addition of 0.2 mL H$_2$O, 0.2 mL of 15% NaOH and 0.6 mL H$_2$O, followed by filtration. The mixture was washed with 5% NaHCO$_3$ and brine, dried over MgSO$_4$ and concentrated to give the **1-d₃** (1.7 g, 90% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 (m, 4H), 7.29 (m, 1H), 4.91 (s, 1H), 1.99 (s, OH).

### 2.2.6. 1,2,2,2-Tetradeuterium-1-phenylethanol (1-d₄)

To a mixture of LiAlD$_4$ (0.21 g, 5 mmol) in dry ether (40 mL) under argon atmosphere at $0\,^\circ$C was added dropwise a solution of 2,2,2-trideuterium-1-phenylethanone (1.9 g, 15 mmol) in dry ether (10 mL). The mixture was heated under reflux for 1 h. The reaction was quenched at $0\,^\circ$C by addition of 0.2 mL H$_2$O, 0.2 mL of 15% NaOH and 0.6 mL H$_2$O, followed by filtration. The mixture was washed with 5% NaHCO$_3$ and brine, dried over MgSO$_4$ and concentrated to give the **1-d₄** (1.7 g, 89% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 (m, 4H), 7.29 (m, 1H), 1.99 (s, OH).

2.2.7. 2,2-Dimethyl-1-phenyl-1-propanol (2-d₀)

To a cooled solution ($0\,^\circ$C) of 1.6 g (15.0 mmol) benzaldehyde in 30 mL dry Et$_2$O was added dropwise 22.5 mL t-BuLi (1.4 M in hexane) under Ar atmosphere. The reaction mixture was stirred at room temperature for 1 h. The reaction was quenched at $0\,^\circ$C by addition of 1 mL of H$_2$O, followed by filtration. The mixture was washed with saturated solution of NaHCO$_3$ and brine, dried over MgSO$_4$ and concentrated to give the **2-d₀** (1.90 g, 77% yield). ^{1}H NMR (500 MHz, CD$_3$CN): δ 7.27 (d, 4H, $J = 4.3$ Hz), 7.21 (m, 1H), 4.29 (d, 1H, $J = 3.8$ Hz), 3.12 (d, OH, $J = 3.8$ Hz), 0.84 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 142.2, 127.6, 127.5, 127.3, 82.4, 35.6, 25.9. MS $m/z = 164$ (100, $m/z = 107$).

2.2.8. 1-Deuterium-2,2-dimethyl-1-phenyl-1-propanol (2-d₁)

This compound was prepared according to the synthetic scheme shown below:
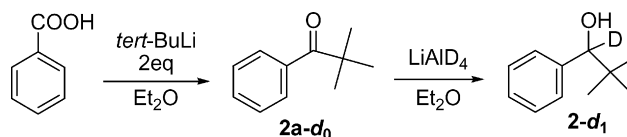
2.2.9. 2,2-Dimethyl-1-phenyl-1-propanone (2a-d₀)

A cold ($-78\,^\circ$C), argon-blanketed solution of the benzoic acid (3.7 g, 30 mmol) in anhydrous ether (60 mL) was treated slowly with t-BuLi (65 mmol). After 15 min, the reaction mixture was warmed to $0\,^\circ$C, stirred for 3 h and carefully treated with water. The ether phase was separated, washed with water, dried over MgSO$_4$ and evaporated. The residue was purified by medium pressure liquid chromatography on silica gel (elution with 10% ethyl acetate in hexane) to give 2.9 g (60% yield) of **2a-d₀**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.65 (d, 2H, $J = 7.3$ Hz), 7.42 (t, 1H, $J = 7.3$ Hz), 7.36 (t, 2H, $J = 7.3$ Hz), 1.32 (s, 9H). MS $m/z = 162$ (100, $m/z = 105$).

2.2.10. 1-Deuterium-2,2-dimethyl-1-phenyl-1-propanol (2-d₁)

To a mixture of LiAlD$_4$ (0.17 g, 4 mmol) in dry ether (40 mL) under argon atmosphere at $0\,^\circ$C was added dropwise a solution of **2a-d₀** (1.2 g, 10 mmol) in dry ether (15 mL). The mixture was heated under reflux for 1 h. The reaction was quenched at $0\,^\circ$C by addition of 0.2 mL H$_2$O, 0.2 mL of 15% NaOH and 0.6 mL H$_2$O, followed by filtration. The mixture was washed with 5% NaHCO$_3$ and brine, dried over MgSO$_4$ and concentrated to give the **2-d₁** (1.5 g, 91% yield). ^{1}H NMR (500 MHz, CD$_3$CN): δ 7.27 (d, 4H, $J = 4.3$ Hz), 7.21 (m, 1H), 3.10 (s, OH), 0.84 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 142.2, 127.6, 127.5, 127.3, 81.9 (triplet, $J_{CD} = 19$ Hz), 35.5, 25.9. MS $m/z = 165$ (100, $m/z = 108$).

2.2.11. 1-(4-Nitrophenyl)ethanol (3)

This compound was prepared by triethylsilane and etherated boron trifluoride reduction of 4-nitroacetophenone [22]. To a solution of 0.5 g (5 mmol) of 4-nitroacetophenone in anhydrous dichloromethane, at $0\,^\circ$C, was added 3 mL (20 mmol) Et$_3$SiH and 2.5 mL (10 mmol) of the solution BF$_3$/Et$_2$O. The reaction mixture was stirred for 15 min and then was added 1.5 mL of 10% NaOH at $0\,^\circ$C and the organic layer was extracted with ether. The corresponding alcohol **3** was isolated in pure by flash column chromatography (2/1, hexane/ethyl acetate eluent solvent), in 90% yield, 2.00 g. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.21 (d, 2H, $J = 8.6$ Hz), 7.55 (d, 2H, $J = 8.7$ Hz), 5.03 (q, H, $J = 6.5$ Hz), 1.54 (s, 3H, $J = 6.5$ Hz).

2.2.12. 1-[4-(Trifluoromethyl)phenyl]ethanol (4)

This compound was prepared by Grignard reaction of 1.75 g (10.0 mmol) 4-(trifluoromethyl)benzaldehyde, 1.7 g or 0.75 mL (12 mmol) MeI and 0.36 g (15 mmol) Mg in dry ether (60 mL) under argon atmosphere at $0\,^\circ$C. Was isolated 1.7 g of the alcohol **4** (90% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.63 (d, 2H, $J = 8.1$ Hz), 7.51 (d, 2H, $J = 6.4$ Hz), 4.98 (q, 1H, $J = 6.4$ Hz), 1.53 (d, 3H, $J = 6.5$ Hz). MS $m/z = 190$ (100, $m/z = 175$).

2.2.13. 1-(4-Fluorophenyl)ethanol (5)

This compound was prepared by Grignard reaction of 1.3 g (10.0 mmol) of 4-fluorobenzaldehyde, 1.7 g or 0.75 mL (12 mmol) of MeI and 0.4 g (17 mmol) of Mg in dry ether (70 mL) under argon atmosphere at $0\,^\circ$C. Was isolated 1.3 g the alcohol **5** (93% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 (dd, 2H, $J_1 = 8.4$ Hz, $J_2 = 5.5$ Hz), 7.05 (t, 2H, $J = 8.7$ Hz), 4.92 (q, 1H, $J = 6.4$ Hz), 1.51 (d, 3H, $J = 6.4$ Hz).

2.2.14. 1-(4-Methylphenyl)ethanol (6)

This compound was prepared by Grignard reaction of 2.4 g (20.0 mmol) of 4-methylbenzaldehyde and 3.4 g or 1.5 mL (24 mmol) methyl iodide and 0.7 g (30 mmol) Mg, in dry ether (60 mL) under argon atmosphere at $0\,^\circ$C. Was isolated 2.4 g of the alcohol **6** (88% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.29 (d, 2H, $J = 7.5$ Hz), 7.18 (d, 2H, $J = 7.5$ Hz), 4.90 (q, 1H, $J = 6.4$ Hz), 2.37 (s, 3H), 1.50 (d, 3H, $J = 6.4$ Hz). MS $m/z = 136$ (100, $m/z = 93$).

2.2.15. Benzyl alcohol (7-d$_0$)

This compound was purchased from Aldrich. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.39 (m, 4H), 7.32 (m, 1H), 4.63 (d, 2H, $J = 4.9$ Hz), 3.42 (t, 1H, $J = 5.5$ Hz).

3. Results and discussion

3.1. Primary and β-secondary kinetic isotope effects

In preliminary study of the homogeneous decatungstate oxidation of 1-aryl-1-alkanols [23a], it was shown that the only oxidation product of the side-chain of the 1-aryl-1-alkanols was the aryl ketone. The product analysis of the decatungstate catalyzed photooxidation of 1-aryl-1-alkanols, support a hydrogen atom transfer mechanism [23a]. The product ratio formed from these cleavages is a powerful tool to distinguish between electron transfer and hydrogen abstraction transfer in chemical and enzymatic oxidations [23,24]. For substrates such as 1-aryl-1-alkanols which are able to react by both mechanisms, it is difficult to predict the dominant one (Scheme 4) [24]. However, the photooxidation of 1-aryl-1-alkanols with 9,10-dicyanoanthracene (DCA) [23b] – a well established photosensitizer that promotes an electron transfer mechanism in polar
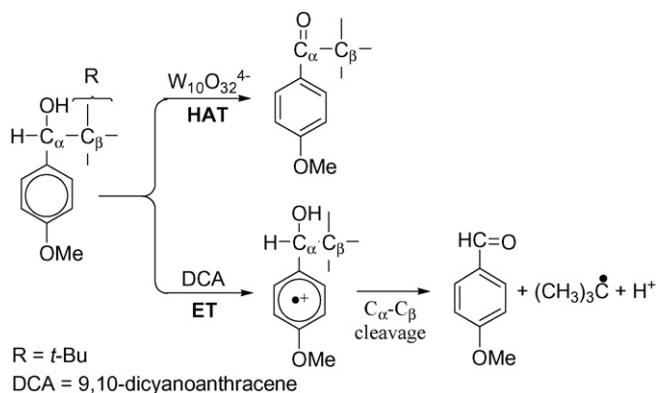
solvents [25] – gave the corresponding aryl aldehydes, as the only or major product (Scheme 4). This result supports an electron transfer between DCA and substrate, forming the radical cation intermediate, which undergoes heterolytic C_α–C_β bond cleavage [23b].

Also, the quantitative production of hydroperoxides in the decatungstate catalyzed photooxidation of 1-phenylethanol, reported in the first part of this study, suggests the formation of the one-electron-reduced species under illumination conditions, which support a hydrogen atom abstraction from the substrate by wO, followed by rapid deprotonation of the resultant radical. Since the initially formed charge transfer excited state of decatungstate has a very short lifetime, the longer-lived intermediate wO is most likely the reactive intermediate in subsequent photocatalytic reactions.

In order to learn more about the nature and reactivity of wO intermediate and to study further the mechanism of the decatungstate photooxidation reaction of the aromatic alcohols, we measured the primary and β-secondary kinetic isotope effects [26]. The KIEs were determined by both: (a) measuring the absolute rate constants by laser flash photolysis techniques and (b) analysis of the photooxidation products of the 1-phenylethanol and 2,2-dimethyl-1-phenyl-1-propanol and their deuterium-labelled analogues by ^{1}H NMR and gas chromatography. Kinetic isotope effect study is a powerful tool to probe the transition state of the reaction and to obtain useful information on the bond making or bond breaking [26].

The absolute rate constants of the decatungstate photooxidation of 1-phenylethanol **1-d$_0$** and 2,2-dimethyl-1-phenyl-1-propanol (**2-d$_0$**) and their deuterium-labelled analogues **1-d$_4$** and **2-d$_1$** by continuous photolysis (Fig. 1) were determined as follows: the decays of wO transient are well fitted via first-order kinetics either in the absence of any substrates with a lifetime of $\tau = 65 \pm 5$ ns and in the presence of 1-phenylethanols, from which the values of molecular rate constant can be derived: $k_{XH} = 14.4 \times 10^7$, 9.4×10^7, 9.5×10^7 and 7.08×10^7 M^1 s^{-1},

Scheme 4. Compared photooxidation of 1-aryl-1-alkanol with decatungstate and DCA as catalysts.
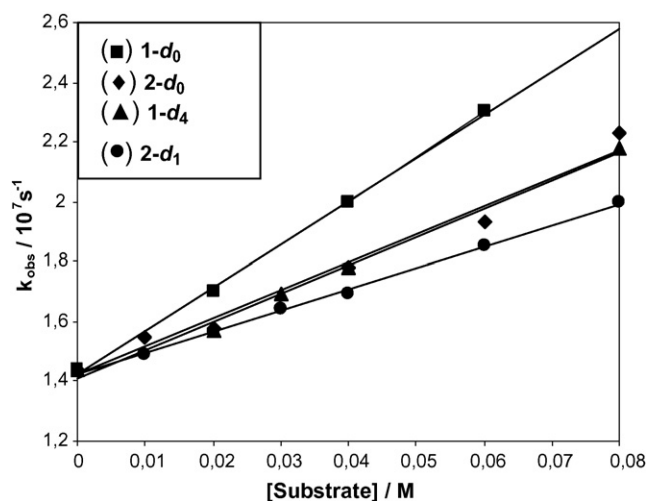

Fig. 1. Dependence of the pseudo-first-order rate constant of decay of wO measured at 780 run on 1-phenylethanol (**1-d$_0$**) (■), 2,2-dimethyl-1-phenyl-1-propanol (**2-d$_0$**) (♦), 1,2,2,2-tetradeuterium-1-phenylethanol (**1-d$_4$**) (▲) and 1-deuterium-2,2-dimethyl-1-phenyl-1-propanol (**2-d$_1$**) (●).
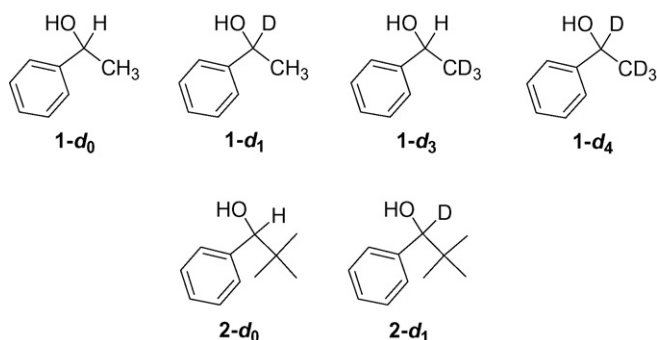
Fig. 2. 1-Phenylethanol and 2,2-dimethyl-1-phenyl-1-propanol and their deuterium-labelled analogues.

respectively, for **1-d_0**, **2-d_0**, **1-d_4** and **2-d_1** (Fig. 1). The ratio of the values of k_{XH} obtained for **2-d_0/2-d_1** is proportional to a primary isotope effect and found to be $(k_H/k_D)_{pr} = 1.34$, whereas the ratio **1-d_1/1-d_4** is the summation of a primary and β-secondary isotope effects designated by the ratio $(k_H/k_D)_{obs} = 1.53$. The substantial primary isotope effects found here suggest that an C−H(D) bond cleavage occurs in the rate-determining step.

To secure these results, the primary and the β-secondary kinetic isotope effects were also determined by ^{1}H NMR product analysis the decatungstate photocatalyzed oxidation of 1-phenylethanol **1-d_0** and 2,2-dimethyl-1-phenyl-1-propanol **2-d_0** and their deuterium-labelled analogues **l-d_1**, **l-d_3**, **1-d_4** and **2-d_1** (Fig. 2), as shown in Table 1.

These intermolecular competitions were carried out as follow: a solution of an equimolar mixture of protio and deuterium-labelled alcohols (0.05 M) and $W_{10}O_{32}^{4-}$ (5.5×10^{-5} M) in acetonitrile (2 mL) was irradiated in the presence of molecular oxygen with a Variac Eimac 300 Watt Xenon lamp ($\lambda \geq 300$ nm) as the light source. The extent of reaction and the product distribution were determined by ^{1}H NMR and gas chromatography. The results are summarized in Table 1.
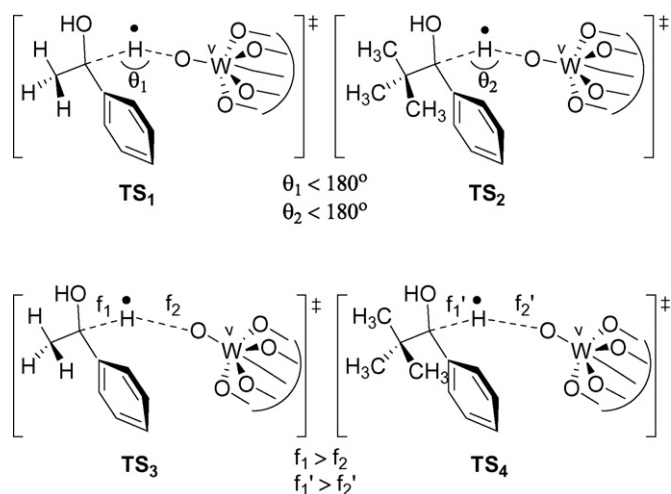
For a high accuracy in determining the ratio k_H/k_D, the reaction conversions were kept less than 40%. In all cases the corresponding aryl ketones **1a-d_0**, **1a-d_3** and **2a-d_0** were observed as the only products. The observed kinetic isotope effects k_H/k_D are proportional either to the ratio of the corresponding arylketones, or to the ratio of the remaining starting alcohols. Therefore, the KIEs were determined by ^{1}H NMR integration of the signals of the remaining starting alcohols and the k_H/k_D values were calculated according to Eq. (1) [27]. For example, H_r and D_r are the amounts of protio and deuterium-labelled products and H_i and D_r are the amounts of protio and deuterium-labelled starting amount of alcohols.

$$\frac{k_H}{k_D} = \frac{\log((1 - H_r)/H_i)}{\log((1 - D_r)/D_i)} \quad (1)$$

In the decatungstate catalyzed photooxidation of the equimolar mixtures of **1-d_0/1-d_1** and **2-d_0/2-d_1** in separate experiments, the only oxidative products observed, were the acetophenone **1a-d_0** and 2,2-dimethyl-1-phenyl-1-propanone **2a-d_0**, respectively. In both reactions, the protio and deuterium-labelled alcohols gave the same ketone as the product. In this case, the primary kinetic isotope effects $(k_H/k_D)_{pr}$ were propotional to the ratio of the remaining protio and deuterium alcohols. The KIEs were fount to be $(k_H/k_D)_{pr} = 1.45 \pm 0.05$ and $(k_H/k_D)_{pr} = 1.46 \pm 0.05$, respectively (Table 1). The ratio **1-d_0/1-d_1** was measured by integration of the ^{1}H NMR signals at 1.50 and 1.51 ppm of the methyl groups of the remaining alcohols **1-d_0** and **1-d_1**, and the quartet at 4.91 ppm which correspond to the benzylic proton of **1-d_0**. For the mixture of **2-d_0/2-d_1** the value of $(k_H/k_D)_{pr}$ was measured by integration of the ^{1}H NMR signals of the aromatic protons of the remaining alcohols **2-d_0** and **2-d_1** at 7.2 and 7.3 ppm and the single peak at 4.30 ppm which correspond to the benzylic proton of the remaining alcohol **2-d_0**.

The significant primary isotope effects suggests that an extensive C−H(D) bond cleavage occurs in the transition state of the decatungstate catalytic oxidation of the secondary benzyl alcohols **1-d_0** and **2-d_0**. It is useful to note here that the moderate value [26] of the primary isotope effect measured in these reactions $[(k_H/k_D)_{obs} = 1.45$ and $1.46]$ may be attributed either to a bent transition state (i.e. nonlinear hydrogen transfer) [28] or to an early transition state [29,30] in which C−H(D) bond cleavage is not fully developed. If this is the case, and according to the theory [26,29], the force constant f_1 is expected to be larger than f_2 and subsequently $f_1' > f_2'$ (Scheme 5).

It is interested to note here that for the determination of the primary KIE of the decatungstate catalyzed photooxidation of 1-phenylethanol, its deuterated analogue **1-d_4** was used instead of its mono deuterated **1-d_1**. The reason is that after the oxidation reaction the $(k_H/k_D)_{obs}$ value was accurately determined by the integration of the areas under the well-separated GC signals of the protio from the deuterium arylketones **1a-d_0/1a-d_3**. This isotope effect value may also be determined from the ratio of remaining protio and deuterium alcohols [27]. It is also interesting to mention here that the capillary column (60 m, 5% phenyl methylpolysiloxane) was capable of separating of the protio acetophenone **1a-d_0** and starting alcohol **1-d_0**, from their corresponding deuterium-labelled analogues

Table 1
Primary and β-secondary kinetic isotope effects of the decatungstate catalyzed photooxidation for the equimolar mixtures of **1-d_0/1-d_1**, **1-d_0/1-d_3**, **1-d_0/1-d_4** and **2-d_0/2-d_1**, in the presence of O_2

	R_1	R_2	
	H	CH_3	**1-d_0**
	D	CH_3	**1-d_1**
	H	CD_3	**1-d_3**
	D	CD_3	**1-d_4**
	H	$C(CH_3)_3$	**2-d_0**
	D	$C(CH_3)_3$	**2-d_1**

Alcohols	Time (min)	Conversion[a] (%)	$(k_H/k_D)_{obs}$
1-d_0/1-d_1	10	22	1.45 ± 0.05[b]
1-d_0/1-d_4	10	22	1.60 ± 0.02[c]
1-d_0/1-d_3	9	18	1.09 ± 0.03[b]
1-d_0/1-d_3	11	23	1.08 ± 0.01[c]
2-d_0/2-d_1	10	20	1.46 ± 0.05[b]
2-d_0/2-d_1	20	37	1.47 ± 0.05[b]

[a] Based on the remaining alcohols.
[b] Determined by ^{1}H NMR spectroscopy with [Bu₄N]$W_{10}O_{32}$ as a catalyst; the error was ±3%.
[c] Determined by gas chromatography with Na₄$W_{10}O_{32}$ as a catalyst; each value is the average of three consecutive measurements; the error was ±1%.
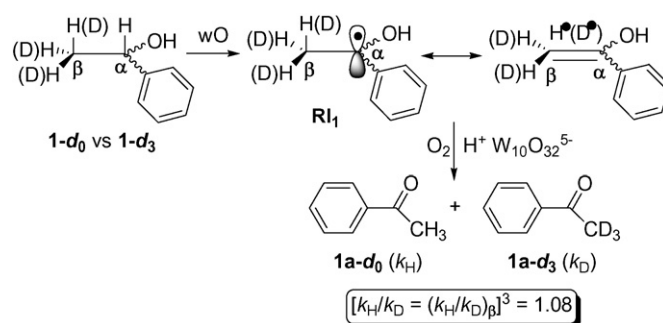
Scheme 5. Possible transition states of the hydrogen atom transfer from 1-phenylethanol and 2,2-dimethyl-1-phenyl-1-propanol to decatungstate reactive intermediate.

Scheme 6. β-Secondary kinetic isotope effect in the decatungstate photooxidation of 1-d_0 vs. 1-d_3.

2,2,2-trideuteriumacetophenone **1a-d_3** and **1-d_4** (Fig. 3A) with baseline resolution. The reaction of the mixture of **1-d_0/1-d_4**, was carried out in less than 22% conversion to products, with naphthalene as internal standard (Table 1). The observed isotope effects which are proportional to the ratio of the corresponding arylketones **1a-d_0/1a-d_3** or to the ratio of the corresponding 1-phenylethanols **1-d_0/1-d_4** (using Eq. (1)), was fount to be $(k_H/k_D)_{obs} = 1.60 \pm 0.02$ (Table 1). This isotope effect value is the summation of both primary and β-secondary isotope effects expressed by Eq. (2) [26,31,32].

$$\left(\frac{k_H}{k_D}\right)_{obs} = \left(\frac{k_H}{k_D}\right)_{pr} \left[\left(\frac{k_H}{k_D}\right)_{\beta}\right]^3 \qquad (2)$$

In order to measure the β-secondary isotope effect, the decatungstate catalyzed photooxidation of an equimolar mixture of **1-d_0** and **1-d_3** was carried out under similar conditions to those described previously. After 11 min of irradiation, the two

arylketones **1a-d_0** and **1a-d_3** are detected in 23% yield, based on the remaining alcohols. The β-secondary isotope effects were measured by the integration of the well GC-separated signals of the corresponding arylketones **1a-d_0/1a-d_3**, and found to be $k_H/k_D = 1.08 \pm 0.01$ (Fig. 3B) and also, by the integration of the appropriate ^{1}H NMR absorptions. In this case the isotopic ratio was found to be $k_H/k_D = 1.09 \pm 0.03$, very similar with the value from GC measurement. The GC response factors for the deuterated and nondeuterated substances have been measured against methyl benzoate as internal standard; the relative response factors were in the range 1.00–1.01 [31c]. Therefore, the β-secondary isotope effect per deuterium is calculated to be $(k_H/k_D)_{\beta} = [k_H/k_D]^{1/3} \approx 1.026$–1.03 (2.6–3% per deuterium atom). The small normal value of the β-secondary isotope effect [26,33] may indicate the formation of the benzylic (C_α) radical intermediate (**RI$_1$**) in the rate-determining step of this reaction. In the case of the non deuterated phenylethanol, the transition state, leading to **RI$_1$** intermediate, is expected to have lower energy than transition state of the deuterated analogue, because the developing radical is stabilized better in the former, by hyperconjugation from the three hydrogens of the methyl group, than in the later case by the three deuteriums of the methyl group (Scheme 6) [34,35]. This result found
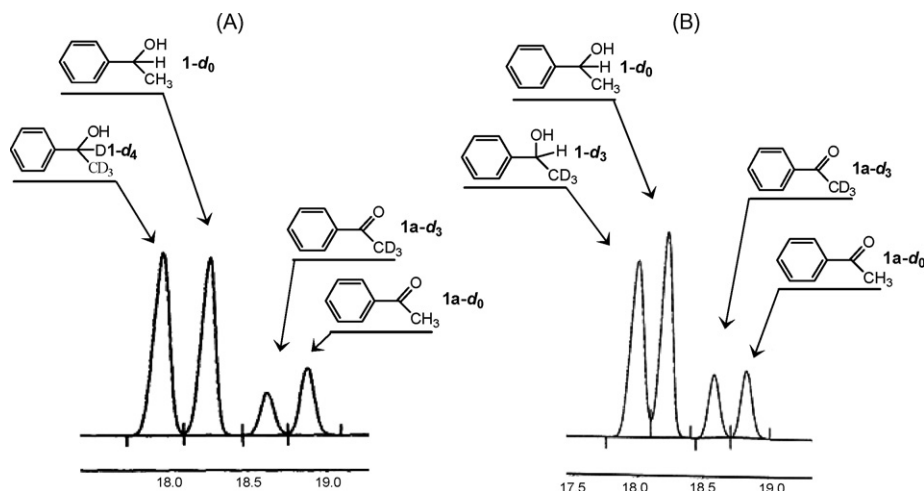

Fig. 3. Gas chromatographs from the decatungstate catalyzed photooxidation of the equimolar mixture of: (A) **1-d_0** and **1-d_4** and (B) **1-d_0** and **1-d_3**. Determination of the primary and β-secondary isotope effects by integration of the areas under the appropriate product or the remaining alcohol signals.

literature support from other systems, where the relatively small β-secondary isotope effect (2–3% per D), attributed to a radical formation [33], whereas values of 5–10% per D atom, were more indicative for the formation of an ionic intermediate.

As we mentioned before, the observed KIEs $(k_H/k_D)_{obs} = 1.6$ (Table 1) from the **1-d_0** versus **1-d_4** isotopic competition is the summation of both, primary and β-secondary isotope effects. In order to calculate the primary IE $(k_H/k_D)_{pr}$ free of β-secondary isotopic contribution, Eq. (2) was applied and the calculated value was $(k_H/k_D)_{pr} = 1.47$–1.48. This value, free of β-secondary isotopic contribution, is in a good agreement with those values measured in the oxidation of the mixture of **1-d_0** versus **1-d_1** as well as of the **2-d_0** versus **2-d_1**, which are also free of β-secondary isotopic contribution (Table 1). It is interesting to note here, that a good agreement between the two methods for determining kinetic isotope effect values was found: (a) from absolute rate kinetics following wO decay and (b) from ^{1}H NMR product analysis. For example, the intermolecular primary kinetic isotope effect between **2-d_0** versus **2-d_1** measured from ^{1}H NMR product analysis, was found to be $(k_H/k_D)_{pr} = 1.46$, whereas from absolute rate kinetics by continuous photolysis experiment $(k_H/k_D)_{pr} = 1.34$. Similarities were also found between the intermolecular kinetic isotope effect of **1-d_0** versus **1-d_4** (summation of both primary and β-secondary isotope effects), by product analysis $(k_H/k_D)_{obs} = 1.60$ and $(k_H/k_D)_{obs} = 1\,53$ by continuous photolysis.

3.2. Hammett kinetic

To examine further the extent of the electronic effect on the rates of the reactions, and obtain valuable information for the transition state of the decatungstate photocatalyzed reaction of 1-phenylethanol, we studied the Hammett kinetics of the oxidation of a series of *para*-substituted-1-phenylethanols, expressed by Eq. (3) [36,37]:

$$\log\left(\frac{k}{k_0}\right) = \sigma\rho \tag{3}$$

where k is the rate constant of the *para*-substituted 1-phenylethanol, k_0 the rate constant of the 1-phenylethanol, σ the Hammett substituent constant and ρ is the slope of the line.

The Hammett kinetics of **1-d_0** versus 1-(4-nitrophenyl) ethanol (**3**), 1-[(4-trifluoromethyl)phenyl]ethanol (**4**), 1-(4-fluorophenyl)ethanol (**5**) and 1-(4-methylphenyl)ethanol (**6**) were measured. Competitive photooxidations of equimolar mixtures of *para*-substituted 1-phenylethanol and 1-phenylethanol with [Bu$_4$N]$_4$W$_{10}$O$_{32}$, as the photocatalyst, were carried out at three different temperatures: 25, 5 and −10 °C under the conditions described previously (Table 2). In all cases the corresponding arylketones (**1a** and **3a–6a**) were observed as the only products and characterized by ^{1}H NMR and GC–MS. All the oxidations were carried at the same irradiation time intervals, in which 1-phenylethanone (**1a-d_0**) was formed in about 10% with respect to the phenylethanol, and using naphthalene as internal standard.

The Hammett plot in the competition of *para*-substituted 1-phenylethanols versus 1-phenylethanol (Fig. 4a), gave a small

Table 2
Hammett kinetic ratios k/k_0 of the oxidation of *p*-substituent 1-phenylethanols

1 vs **3-6**
X=NO$_2$(**3**), CF$_3$(**4**), F(**5**), CH$_3$(**6**)
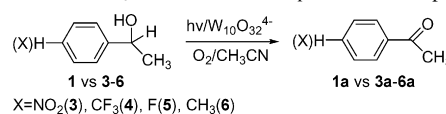
T (°C)	k/k_0 [a]					ρ (R^2)
	p-Me	*p*-H	*p*-F	*p*-CF$_3$	*p*-NO$_2$	
−10	0.85	1	1.22	1.38	2.13	0.36 (0.931)
5	0.87	1	1.23	1.34	1.72	0.28 (0.909)
25	0.98	1	1.23	1.55	2.15	0.32 (0.989)

[a] Error limits were less than 2% being average deviations of three runs unless otherwise stated.

positive slope with $\rho = 0.32$ ($R^2 = 0.989$). This small value, indicates the development of negative charge or a radical intermediate in the transition state, which is better stabilized by an electron-withdrawing substituent [38]. For example, the ratio of k_{NO_2}/k_H was found to be between 1.72 and 2.15, whereas of the ratio of k_{Me}/k_H which was in the range of 0.85–0.98 (Table 2). In contrast, in the case where a positive charge (e.g.
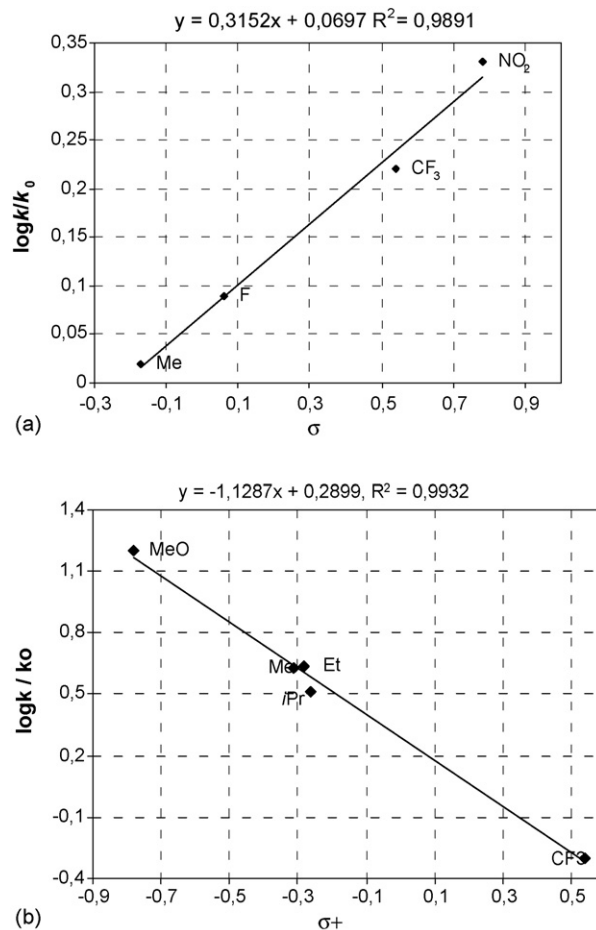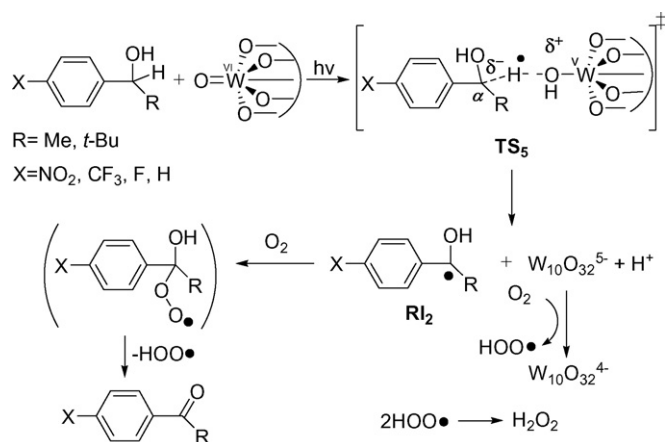

(a)

(b)

Fig. 4. (a) Hammett plot of the decatungstate catalyzed photooxidation of *para*-substituted 1-phenylethanols. The values for σ were taken from ref. [41]. (b) Hammett plot of the DCA sensitized photooxidation of *para*-substituted 1-phenylethanols (ref. [23b]). The values for σ^+ were taken from ref. [41].

Scheme 7. Proposed mechanism in the decatungstate oxidation of 1-phenylethanol and 2,2-dimethyl-1-phenyl-1-propanol and their *para*-substituted derivatives, in the presence of O_2.

a radical cation) is developed in the transition state, electron-donating substituents stabilize better the TS of the reaction [23b,39,40]. For example, we have shown recently [23b] that 9,10-dicyanoanthracene catalyzed photooxidations of substrates similar to these in this work, gave negative Hammett slope ($\rho^+ = -1.12$), opposite to the one observed when decatungstate was the photocatalyst (Fig. 4b). We should note here that DCA is a well known electron transfer sensitizer in polar solvents. In that case, the methoxy substituent of the *para*-substituted 1-phenylethanol stabilizes better the radical cation which is developing in the transition state, affording a negative Hammett slope. It is interesting to note here that the small positive Hammett slope found in this work, confirms also the formation of an asymmetric transition state (early transition state), where the C_α–H bond cleavage is not extended. This result is also consistent with the small value of the primary kinetic isotope effect.

The results of this study, based on KIEs, Hammett kinetics, as well as on the O_2 consumption and wO decay, confirm unambiguously that the $W_{10}O_{32}{}^{4-}$ photocatalyzed oxidations of 1-phenylethanol and 2,2-dimethyl-1-phenyl-1-propanol proceed via a hydrogen abstraction mechanism. A reasonable mechanistic approach that may rationalize these and previous results, is shown in Scheme 7. Firstly, under irradiation conditions, decatungstate anion undergoes decay to the relatively long-lived intermediate wO [3,4,6,7]. Subsequent hydrogen atom abstraction from the α-carbon (C_α) of the alcohol produces the one-electron-reduced species $H^+W_{10}O_{32}{}^{5-}$ and a radical intermediate (**RI$_2$**), as it is shown in Scheme 7. In the transition state (**TS$_5$**), the developing radical between 1-phenylethanol and wO is better stabilized by electron-withdrawing substituents. The **RI$_2$** in the presence of molecular oxygen decomposes to the corresponding aryl ketone through the possible formation of 1-aryl-1-peroxyl-ethanol intermediate. The one-electron-reduced species of decatungstate re-oxidizes in the presence of a molecule of oxygen to give again $W_{10}O_{32}{}^{4-}$ and a molecule of hydrogen peroxide. This mechanism has found support from laser flash kinetic photolysis, pulse radiolysis studies and product analysis with aliphatic alcohols, alkanes and alkylarenes in previous studies [4,7,19,20,30].

4. Conclusion

In this collaborative work the use of complementary techniques such as time-resolved and steady-state techniques (part I) as well as kinetic isotope effects studies and Hammett kinetics (part II), have been devoted to study the mechanism of the decatungstate photocatalyzed oxidation of aromatic alcohols in air or oxygen saturated acetonitrile. In part I, based upon a series of observations (quantitative formation of peroxide and deuterium-labelled effect) and the detailed examination of kinetic parameters derived from complete kinetic study, it is concluded that benzyl alcohols react with the reactive intermediate wO by a hydrogen abstraction transfer mechanism. In part II, the values of the KIEs obtained from ^{1}H NMR product analysis confirm a HAT mechanism. Also, Hammett kinetics with *para*-substituted 1-phenylethanols suggest the formation of a radical intermediate and together with KIEs, support an early transition state of this photooxidation reaction.

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