

Deuterium kinetic isotope effects in homogeneous decatungstate catalyzed photooxygenation of 1,1-diphenylethane and 9-methyl-9H-fluorene: evidence for a hydrogen abstraction mechanism

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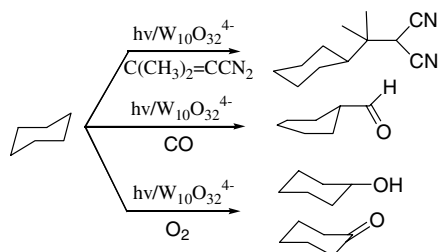
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Abstract—The homogeneous decatungstate $W_{10}O_{32}^{4-}$ catalyzed photooxygenation of 1,1-diphenylethane and 9-methyl-9H-fluorene has been studied mechanistically. The primary and β -secondary kinetic isotope effects provide strong evidence for a stepwise mechanism, with a hydrogen atom abstraction in the rate-determining step.
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The oxo-functionalization of saturated hydrocarbons, under mild oxidative conditions, represents a most important and synthetically useful transformation.^{1,2} During the last 20 years, important advances have been achieved in the use of polyoxometalates in the catalytic transformation of alkanes into the corresponding oxidation products.^{2,3} One of the most promising reagents is the decatungstate anion $W_{10}O_{32}^{4-}$, which appears to be particularly interesting with regard to the light-induced transformation of organic materials (Scheme 1).^{3–11} It is generally accepted that illumination of $W_{10}O_{32}^{4-}$ leads



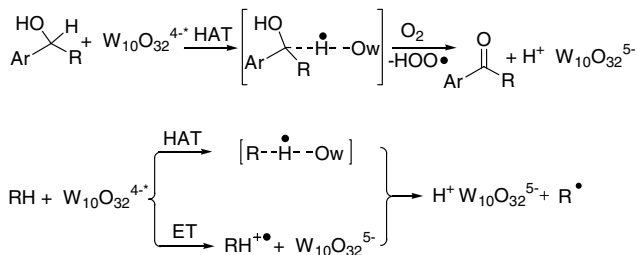
Scheme 1. Functionalization⁴ and oxidation⁵ of cyclohexane by decatungstate as a catalyst.

Keywords: Decatungstate; Polyoxometalate; Photooxygenation; Alkylarenes; Kinetic isotope effects.

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to the formation of a charge transfer excited state $W_{10}O_{32}^{4-*}$, which decays in less than 30 ps to an extremely reactive transient,^{7a} with a distorted geometry⁹ with respect to $W_{10}O_{32}^{4-}$, referred to as wO .^{6,7a,9}

Previous studies of the decatungstate^{4–11} ($W_{10}O_{32}^{4-}$) catalyzed photooxidation of alcohols,^{6,7a,9} 1-arylalkanol,^{11a} and alkanes^{4,5,7a} 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 an organic radical (Scheme 2). However, with easily oxidizable substrates, such as amines,⁹ aromatic hydrocarbons,¹⁰ and alkenes^{7b,c} direct electron transfer (ET) can compete with hydrogen atom transfer (HAT) and even become the dominant pathway. In any case, both mechanisms give rise to the same one-electron-reduced species ($W_{10}O_{32}^{5-}$), and to the corresponding substrate-derived radical R (Scheme 2).



Scheme 2.

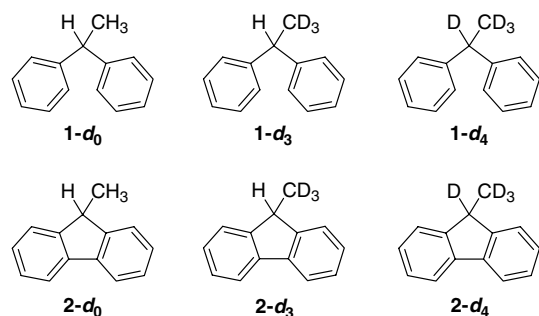


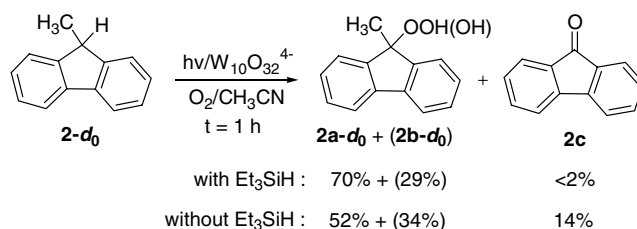
Figure 1. 1,1-Diphenylethane and 9-methyl-9H-fluorene and their deuterium-labeled analogues.

Following our recent interest in the selective oxo-functionalization of aryl alkanes by the decatungstate/ Et_3SiH system,^{11b} we report herein a mechanistic study of this catalytic system with 1,1-diphenylethane (**1-d₀**) and 9-methyl-9H-fluorene (**2-d₀**). These electron rich diaryl alkanes **1-d₀** and **2-d₀**, were the substrates of choice because they are potentially capable of reacting by both mechanisms (ET and/or HAT). In particular, we investigated the primary and the β -secondary kinetic isotope effects (KIEs) in the decatungstate catalyzed photooxygenation of **1-d₀** and **2-d₀** in the presence of Et_3SiH .¹² Kinetic isotope effect studies provide a powerful tool to probe the transition state of a reaction and led to useful conclusions on the bond making or bond breaking. In this work, the KIEs were determined by the decatungstate photocatalyzed oxygenation of 1,1-diphenylethane **1-d₀** and 9-methyl-9H-fluorene **2-d₀** and their deuterium-labeled analogues **1-d₃**, **1-d₄**, **2-d₃**, and **2-d₄** as shown in Figure 1.¹³

The homogeneous decatungstate catalyzed photooxygenations of the alkylarenes were carried out as follows: a solution of the alkane (0.03 M), Et_3SiH (0.06 M), and $\text{W}_{10}\text{O}_{32}^{4-}$ (5.5×10^{-5} M) in acetonitrile (4 ml) was irradiated in the presence of molecular oxygen with a Variac Eimac 300 W Xenon lamp ($\lambda = 300$ nm) as the light source. The extent of reaction and the product distribution were determined by ^1H NMR analysis. The corresponding tertiary alcohols produced after reduction of the initially formed tertiary hydroperoxides using triphenylphosphine were also measured by GC as were the carbonyl compounds.

In the photooxygenation of **2-d₀** in the absence of Et_3SiH ,^{11b,14} the corresponding 9-fluorenone **2c** was formed in a 14% relative yield, and the ratio of hydroperoxide (**2a-d₀**)/alcohol (**2b-d₀**) was found to be 1.5/1. However, in the presence of 2 equiv of Et_3SiH , the amount of 9-fluorenone decreased to less than 2% and the ratio of (**2a-d₀**)/(**2b-d₀**) increased to 2.3/1 (Scheme 3). The increase of the tertiary hydroperoxide has been attributed to trapping of the corresponding 9-methyl-9-fluorenoxy radical intermediate by Et_3SiH .^{11b,14}

The results of the decatungstate/ Et_3SiH catalyzed photooxygenations are summarized in Table 1. Irradiation of a mixture of equimolar quantities of analogous protio and deuterium labeled alkylarenes in acetonitrile at



Scheme 3. Decatungstate catalyzed photooxygenation of **2-d₀** in the presence or absence of Et_3SiH .

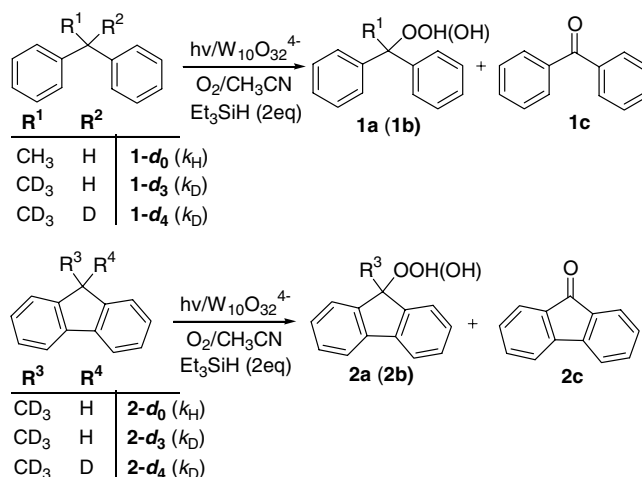
5–10 °C gave the tertiary hydroperoxides **1a** and **2a**, and the corresponding alcohols **1b** and **2b** as the major products, in more than 97% relative yield. The presence of 2 equiv of Et_3SiH suppressed substantially formation of aryl ketones **1c** and **2c**.^{11b,14,15} The observed isotope effects, which are proportional to the ratio of the corresponding tertiary alcohols **1b-d₀**/**1b-d₃** and **2b-d₀**/**2b-d₃** after reduction of initially formed hydroperoxides (**1a-d₀**/**1a-d₄** and **2a-d₀**/**2a-d₄**), were found to be $(k_{\text{H}}/k_{\text{D}})_{\text{obsd}} = 2.40 \pm 0.03$ and $(k_{\text{H}}/k_{\text{D}})_{\text{obsd}} = 1.90 \pm 0.02$, respectively.

These isotope effects are the summation of both the primary and β -secondary isotope effects as expressed by Eq. 1.^{12,16,17}

$$(k_{\text{H}}/k_{\text{D}})_{\text{obsd}} = [(k_{\text{H}}/k_{\text{D}})_{\text{pr}}] \cdot [(k_{\text{H}}/k_{\text{D}})_{\beta}]^3 \quad (1)$$

In order to measure the primary KIE in the photooxygenation of 1,1-diphenylethane and 9-methyl-9H-fluorene, their deuterated analogues **1-d₄** and **2-d₄** were used instead of their mono deuterated **1-d₁** and **2-d₁**. The reason for this was that after reduction of the tertiary hydroperoxides to the corresponding alcohols, the $(k_{\text{H}}/k_{\text{D}})_{\text{obsd}}$ values were determined accurately from the areas under the well-separated GC signals of the protio and the deuterium alcohols **1b-d₀**/**1b-d₃** and **2b-d₀**/**2b-d₃**, correspondingly. These isotope effect values may also be determined¹⁸ from the ratios of the remaining alkanes. It is interesting to mention here that the capillary column (60 m, 5% phenyl methylpolysiloxane) was capable of a baseline separation of the protio alcohols and the starting alkanes from their corresponding deuterium labeled analogues.

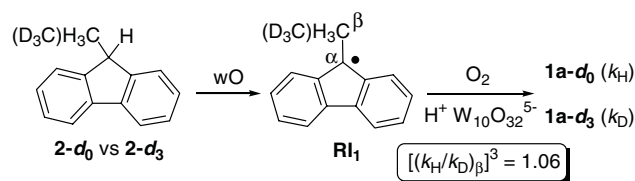
The β -secondary isotope effects were measured by the appropriate peaks of the corresponding tertiary alcohols **1b-d₀**/**1b-d₃** and **2b-d₀**/**2b-d₃** by GC and found to be $k_{\text{H}}/k_{\text{D}} = 1.05 \pm 0.01$ and $k_{\text{H}}/k_{\text{D}} = 1.06 \pm 0.01$, respectively. Therefore, the β -secondary isotope effect per deuterium is calculated to be, $(k_{\text{H}}/k_{\text{D}})_{\beta} = [k_{\text{H}}/k_{\text{D}}]^{1/3} \approx 1.02$ (2% per deuterium atom). This small value of the β -secondary isotope effect^{12c,19} is consistent with the formation of the tertiary radical intermediate **RI₁** in the rate-determining step of the reaction (Fig. 2). This result finds literature support from other systems, where the relatively small β -secondary isotope effect (2–3% per D, implies a radical intermediate, instead of the 5–10%, observed in ionic intermediates) was attributed to the formation of a radical intermediate.¹⁹

Table 1. Primary and β -secondary kinetic isotope effects of the decatungstate catalyzed photooxygenation for the equimolar mixtures of **1-d₀/1-d₄**, **1-d₀/1-d₃**, **2-d₀/2-d₄**, and **2-d₀/2-d₃** in the presence of O₂

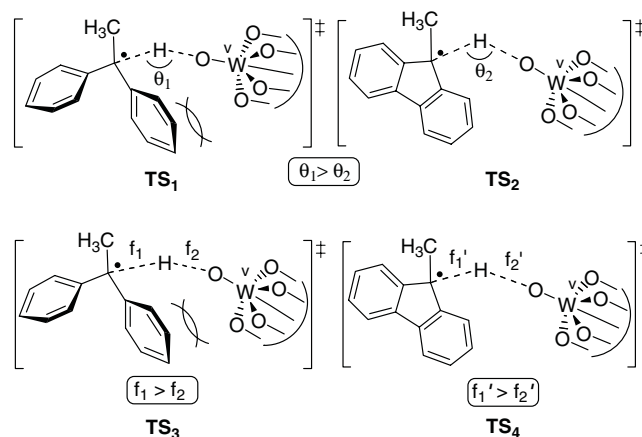
Alkanes	% Conv. ^a	% (a + b) ^b	% c ^b	(k_H/k_D) _{obsd}	(k_H/k_D) _{pr}
1-d₀/1-d₄	10	99	<2	2.40 ± 0.03	2.30
1-d₀/1-d₃	14	99	<2	1.05 ± 0.01	—
2-d₀/2-d₄	15	98	2	1.90 ± 0.02	1.78
2-d₀/2-d₃	18	97	3	1.06 ± 0.01	—

^a Alkylarene (0.03 M) was irradiated for 30 min with a 300 W Xenon lamp, in the presence of [Bu₄N]₄W₁₀O₃₂ (5.5 × 10⁻⁴ M), and Et₃SiH (0.06 M) in 4 mL acetonitrile, at 5–10 °C. The reaction conversion was kept to no more than 18%.

^b Determined by gas chromatography and ¹H NMR spectroscopy. The error was ±1% and ±4%, respectively.

**Figure 2.** β -Secondary kinetic isotope effect in the decatungstate photooxygenation of **2-d₀** versus **2-d₃**.

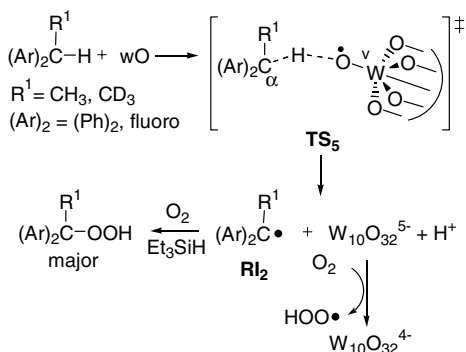
The primary KIEs of **1-d₀/1-d₄** and **2-d₀/2-d₄** were calculated using Eq. 1 and were found to be (k_H/k_D)_{pr} = 2.30 and (k_H/k_D)_{pr} = 1.78, respectively. Their significant primary isotope effect suggests that extensive C–H(D) bond cleavage occurs in the rate-determining step. It is useful to note here that the moderate value¹² of the primary isotope effect measured in these reactions ((k_H/k_D)_{obsd} = 1.78–2.30) may be attributed either to a bent transition state (i.e., non-linear hydrogen transfer)²⁰ or to an early transition state²¹ in which C–H(D) bond cleavage is not fully developed ($f_1 > f_2$ and $f'_1 > f'_2$) as shown in Figure 3. Moreover, the larger primary isotope effect determined for 1,1-diphenylethane, compared to that for 9-methyl-9H-fluorene (2.30 vs 1.78), may be attributed to a more linear hydrogen transfer from the former in the corresponding transition state (Fig. 3). The fact that $\theta_1 > \theta_2$ in the transition state **TS₁** compared to **TS₂** can be explained by steric interaction between the two laminating phenyl groups of 1,1-diphenylethane, which forces the two rings into a propeller-type conformation, and the incoming reactive decatungstate reactive intermediate.²²

**Figure 3.** Possible transition states of the hydrogen atom transfer from 1,1-diphenylethane and 9-methyl-9H-fluorene to the reactive decatungstate intermediate.

The primary and β -secondary isotope effects indicate that the W₁₀O₃₂⁴⁻ catalyzed photooxygenations of alkylarenes proceed via a hydrogen atom transfer (HAT) in the rate-determining step. In the case of an ET mechanism, the addition of a small amount (compared to the aryl alkanes) of an electron donor with an oxidation potential of less than that of **1-d₀** and **2-d₀** should retard the photooxidation by electron transfer from the donor molecule²³ to the alkylarenes radical cation, according to Eq. 2.



Trimethoxybenzene (TMB) with $E_{1/2\text{ox}}$ versus SCE 1.12 V²³ was used as the donor molecule. The oxidation potentials of **1-d₀** and **2-d₀** are in the range of



Scheme 4. The proposed mechanism in the decatungstate catalyzed photooxygenation of 1,1-diphenylethane and methyl-9H-fluorene in the presence of O_2 based on KIEs.

1.8–2.2 V.^{10,22} The presence of a small amount of TMB did not affect the rate of the decatungstate catalyzed photooxygenation of **1-d₀** and **2-d₀**. This result confirms that the hydrogen atom transfer mechanism is the predominant mechanism in the reaction of wO with **1-d₀** and **2-d₀**, as shown in Scheme 4.

In the first step, under irradiation conditions, decatungstate anion undergoes conversion into the well established long-lived intermediate wO.^{7–10} The substantial KIEs measured in this work ($k_{\text{H}}/k_{\text{D}} = 1.78\text{--}2.30$) suggest a hydrogen atom abstraction from the alpha carbon (C_{α}) of the alkylarene in the rate-determining step. Subsequently, a one-electron-reduced species $\text{H}^+\text{W}_{10}\text{O}_{32}^{5-}$ is produced along with a radical intermediate (**RI₂**), as shown in Scheme 4. The **RI₂**, in the presence of molecular oxygen, decomposes to the corresponding tertiary hydroperoxide. The one-electron-reduced species of the decatungstate re-oxidizes in the presence of molecular oxygen to give again $\text{W}_{10}\text{O}_{32}^{4-}$ and a molecule of hydrogen peroxide. This mechanism has support from previous kinetic results with aryl alkanols¹¹ and non-aromatic alkanes.^{4,5,7}

In conclusion, both primary and β -secondary kinetic isotope effects in the decatungstate catalyzed photooxygenation of alkylarenes support a hydrogen atom abstraction in the rate-determining step.

Acknowledgement

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- The ¹H NMR and ¹³C NMR data (in parts per million) of the alkylarenes are as follows: **1-d₀**: ¹H NMR (500 MHz, CDCl₃): δ 7.35 (t, 4H, $J = 7.7$ Hz), 7.30 (d, 4H, $J = 7.2$ Hz), 7.25 (t, 2H, $J = 7.3$ Hz), 4.21 (q, 1H, $J = 7.2$ Hz), 1.69 (d, 3H, $J = 7.2$ Hz). ¹³C NMR (125 MHz, CDCl₃): δ 146.4, 128.3, 127.6, 126.0, 44.7, 21.8. MS $m/z = 182$ (100, $m/z = 167$); **1-d₃**: ¹H NMR (125 MHz, CDCl₃): δ 7.35 (t, 4H, $J = 7.7$ Hz), 7.30 (d, 4H, $J = 7.2$ Hz), 7.25 (t, 2H, $J = 7.3$ Hz), 4.20 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 146.3, 128.3, 127.6, 126.0, 44.5, 21.0 (septet, $J_{\text{CD}} = 19$ Hz). MS $m/z = 185$ (100, $m/z = 167$); **1-d₄**: ¹H NMR (500 MHz, CDCl₃): δ 7.35 (t, 4H, $J = 7.7$ Hz), 7.30 (d, 4H, $J = 7.2$ Hz), 7.25 (t, 2H, $J = 7.3$ Hz). ¹³C NMR (125 MHz, CDCl₃): δ 146.3, 128.3, 127.6, 126.0, 43.9 (triplet, $J_{\text{CD}} = 19$ Hz), 20.9 (septet, $J_{\text{CD}} = 19$ Hz). MS $m/z = 186$ (100, $m/z = 168$); **2-d₀**: ¹H

- NMR (500 MHz, CDCl₃): δ 7.80 (d, 2H, $J = 7.4$ Hz), 7.55 (d, 2H, $J = 7.3$ Hz), 7.40 (t, 2H, $J = 7.3$ Hz), 7.36 (t, 2H, $J = 7.3$ Hz), 3.99 (q, 1H, $J = 7.4$ Hz), 1.57 (d, 3H, $J = 7.5$ Hz). ¹³C NMR (125 MHz, CDCl₃): δ 148.9, 140.5, 126.91, 126.89, 124.0, 119.8, 42.4, 18.2. MS $m/z = 180$ (100, $m/z = 165$). **2-d₃**: ¹H NMR (500 MHz, CDCl₃): δ 7.80 (d, 2H, $J = 7.4$ Hz), 7.55 (d, 2H, $J = 7.3$ Hz), 7.40 (t, 2H, $J = 7.3$ Hz), 7.36 (t, 2H, $J = 7.3$ Hz), 3.97 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 148.9, 140.5, 126.91, 126.89, 124.0, 119.8, 42.2, 17.3 (septet, $J_{CD} = 19$ Hz). MS $m/z = 183$ (100, $m/z = 165$). **2-d₄**: ¹H NMR (500 MHz, CDCl₃): δ 7.80 (d, 2H, $J = 7.4$ Hz), 7.55 (d, 2H, $J = 7.3$ Hz), 7.40 (t, 2H, $J = 7.3$ Hz), 7.36 (t, 2H, $J = 7.3$ Hz). ¹³C NMR (125 MHz, CDCl₃): δ 148.9, 140.5, 126.91, 126.89, 124.0, 119.8, 41.8 (triplet, $J_{CD} = 19$ Hz), 17.2 (septet, $J_{CD} = 19$ Hz). MS $m/z = 184$ (100, $m/z = 166$).
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