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Decatungstate Photocatalyzed Oxidation of Aryl Alkanols. Electron Transfer or Hydrogen Abstraction Mechanism?

Ioannis N. Lykakis,[†] Charles Tanielian,[‡] and Michael Orfanopoulos*,[†]

Department of Chemistry, University of Crete, 71409 Iraklion, Greece, and
Laboratoire de Photochimie, Ecole Europeenne Chimie Polymeres Materiaux de
Strasbourg, 25, rue Becquerel, 67087 Strasbourg Cedex 2, France

orfanop@chemistry.uoc.gr

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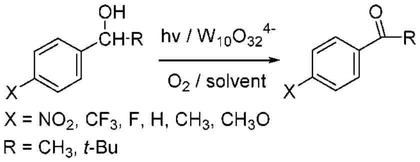
ABSTRACT



Decatungstate $W_{10}O_{32}^{4-}$ photosensitized oxidation of a series of para-X-substituted 1-aryl-1-alkanols was investigated. The only oxidation product of the side-chain of the 1-aryl-1-alkanol was the aryl ketone. The product analysis and kinetic data of the title reaction support a hydrogen atom transfer mechanism in the rate-determining step.

Polyoxometalates are efficient photocatalysts and exhibit a remarkable array of homogeneous oxidation reactions.[1] The most interesting and synthetically valuable properties of these metal−oxygen anion clusters are (a) the wide range of their redox potentials, (b) their oxidative and thermal stability, and (c) the reversibility in their multielectron reductions. Polyoxometalates such as $SiW_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$, $H_2W_{18}O_{62}^{6-}$, and $W_{10}O_{32}^{4-}$ catalyze the oxidation of a variety of organic substrates, for example, hydrocarbons, alcohols, substituted phenols, and amines.[2−15] In particular, decatungstate anion $W_{10}O_{32}^{4-}$ photocatalyzes the activation of the C−H bonds in saturated hydrocarbons and alcohols (eq 1).[3−15] Most of the recent work[3,5−14] has focused on the possible key intermediates that follow light absorption by the catalyst $W_{10}O_{32}$.[4−] For example, irradiation of $W_{10}O_{32}^{4-}$ in acetonitrile produces a short-lived excited-state intermediate $W_{10}O_{32}^{4-}$*, which is too short-lived (∼30 ps) to be responsible for bimolecular substrate−catalyst interactions.[10b,11]

[†] University of Crete.

[‡] Ecole Europeenne Chimie Polymeres Materiaux de Strasbourg.

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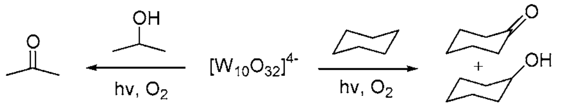
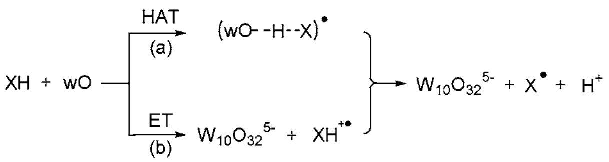


(1)

Laser flash photolysis studies are consistent with the decay of $W_{10}O_{32}^{4-}$* to a long-lived reactive intermediate.[10−14] This key intermediate, designated as wO, is formed with a quantum yield of ~0.6, has a lifetime of 65 ± 5 ns for $Na_4W_{10}O_{32}$ in aerated acetonitrile, and has attracted considerable oxygen to tungstate charge transfer.[12−14] On the basis of both spectroscopic and kinetic data, the reaction of the wO intermediate with organic substrates XH (Scheme 1) may occur either by (a) hydrogen abstraction transfer (HAT) and/or (b) electron transfer (ET), according to the proposed mechanism[3,10,12−14] shown in Scheme 1. Both mechanisms give rise to the same one-electron-reduced species and to the corresponding substrate-derived radical (Scheme 1).

Scheme 1

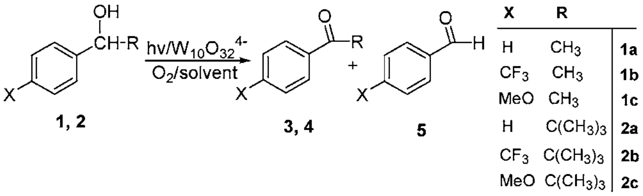


For substrates such as 1-aryl-1-alkanols, able to react by both mechanisms, it is difficult to predict the dominant one. The main objective of this work was precisely to determine for the first time the mechanism of reaction of wO with these substrates. For this purpose, we have investigated the $W_{10}O_{32}^{4-}$-catalyzed photooxidation of the following aromatic alcohols: 1-phenyl-1-ethanol (**1a**), 2,2-dimethyl-1-phenyl-1-propanol (**2a**) and the substituted derivatives 1-[4-(trifluoromethyl)phenyl]-1-ethanol (**1b**), 1-(4-methoxyphenyl)-1-ethanol (**1c**), 2,2-dimethyl-1-[4-(trifluoromethyl)phenyl]-1-propanol (**2b**), and 1-(4-methoxyphenyl)-2,2-dimethyl-1-propanol (**2c**) (Table 1).

It is known that in the side-chain oxidation of aromatic alcohols, which involves an ET mechanism, the intermediate is a radical cation[16,17] that fragments by undergoing C_α−H and/or C_α−C_β bond cleavage (Scheme 2). C_α−H bond cleavage leads to the corresponding aromatic ketones, while a C_α−C_β bond cleavage leads to the corresponding aldehydes. The product ratio formed from these cleavages is a powerful tool for distinguishing between ET or HAT in chemical and enzymatic oxidations.[18] A HAT mechanism leads only to the corresponding ketones.[18]

In this work, the decatungstate photosensitized oxidation of 1-aryl-1-alkanols was carried out as follows. A solution of 1-aryl-1-alkanols (0.05 M) and $W_{10}O_{32}^{4-}$ (5.5 × 10^{-5} M) in acetonitrile or acetone was irradiated in the presence of oxygen with a 300 W Xenon lamp (>300 nm) as the light source. Irradiation of **1a**, **1b**, and **1c** for 20 min at 5−10 °C gave exclusively the corresponding aryl ketones **3a**, **3b**, and **3c**. This result is consistent with a HAT mechanism and is in agreement with previously reported related studies.[16−18] The conversion, based on the recovered starting material, varied from 18 to 47% depending on the para substituent. The extent of the reaction was monitored by GC. The products were analyzed by ^{1}H NMR spectroscopy and GC−MS and compared with authentic samples.

Table 1. Product Analysis of Decatungstate-Sensitized Photooxidation of 1-Aryl-1-alkanols **1** and **2** in the Presence of O_2

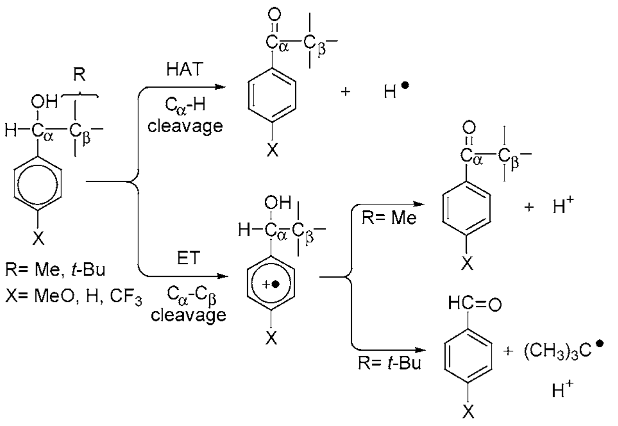


			relative product yield,[b] %	
substrate	solvent[a]	% conversion[b]	ArCOR	ArCHO
1a	CH_3CN	37	100	
1b	CH_3CN	47	100	
1c	CH_3CN	31	100	
2a	CH_3CN	35	97	3
2a	$(CH_3)_2CO$	20	99	1
2b	CH_3CN	40	97	3
2b	$(CH_3)_2CO$	24	98	2
2c	CH_3CN	30	97	3
2c	$(CH_3)_2CO$	18	99	1

[a] Aryl alkanol (0.05 M) was irradiated (20 min, Xenon lamp, 300 W, >300 nm) in the presence of $[Bu_4N]_4W_{10}O_{32}$ (5.5 × 10^{-4} M), in 4 mL of solvent, at 5−10 °C. [b] Determined by gas chromatography. The error was ±1%.

However, when R is *tert*-butyl (substrates **2a**−**c**), the $W_{10}O_{32}^{4-}$-sensitized photooxidations gave, in addition to the

Scheme 2



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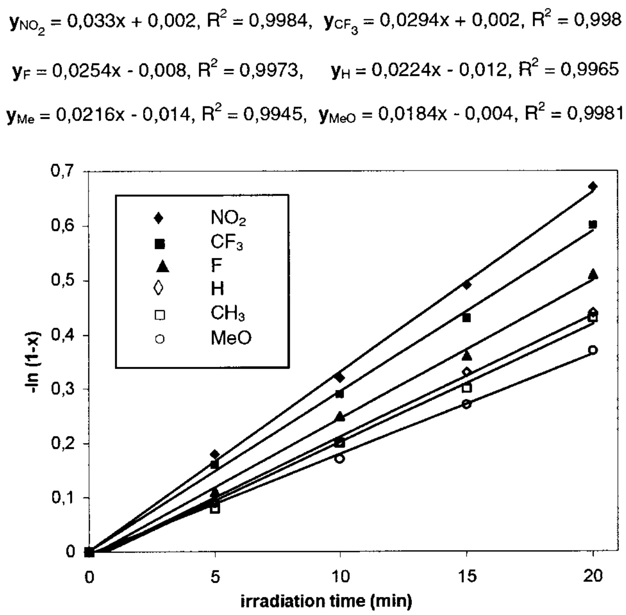


Figure 1. Time dependence of decatungstate (5.5×10^{-4} M)-sensitized photooxidation of 1-aryl-1-alkanols (0.05 M): 1-[4-nitrophenyl]-1-ethanol (◆) (**1d**), 1-[4-trifluoromethylphenyl]-1-ethanol (■) (**1b**), 1-[4-fluorophenyl]-1-ethanol (▲) (**1e**), 1-phenyl-1-ethanol (◇) (**1a**), 1-[4-methylphenyl]-1-ethanol (□) (**1f**), and 1-[4-methoxyphenyl]-1-ethanol (○) (**1c**) in oxygen-saturated acetonitrile solutions. Naphthalene was used as an internal standard. The measured rate constants were deduced from a pseudo first-order kinetics: $k_{NO_2} = 2.12 \times 10^8$ M^{-1}s^{-1}, $k_{CF_3} = 1.89 \times 10^8$ M^{-1} s^{-1}, $k_F = 1.63 \times 10^8$ M^{-1} s^{-1}, $k_H = 1.44 \times 10^8$ M^{-1} s^{-1}, $k_{CH_3} = 1.39 \times 10^8$ M^{-1} s^{-1}, $k_{MeO} = 1.18 \times 10^8$ M^{-1} s^{-1}.

major product aryl ketone, small amounts (1−3%) of the corresponding aryl aldehydes. This observation can be attributed to the formation of the relatively more stable *tert*-butyl radical followed the $C_\alpha - C_\beta$ bond cleavage (Scheme 2).

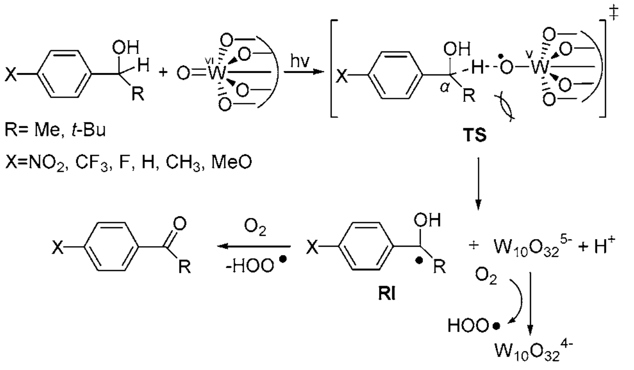
After the product study of the above photooxidation reaction (Table 1), a formal kinetic analysis of a series of para-X-substituted 1-aryl-1-ethanols (X = NO_2, CF_3, F, H, CH_3, MeO) was performed. Considering that during the photooxidation, the oxygen concentration remains constant in the reaction mixture and assuming a first-order dependence of the reaction rate on the 1-aryl-1-ethanol concentration, eq 2 can be applied.

$$kt = -\ln(1 - x) \qquad (2)$$

In eq 2, k, t, and x represent the rate constant, the irradiation time, and the conversion of 1-aryl-1-ethanol, respectively. According to eq 2, a plot of the conversion of 1-aryl-1-ethanols versus irradiation time should be linear with a slope equal to the rate constant k_X. The results in Figure 1 indeed show a good linear fit to eq 2. In all cases, the major product (>97%) was the corresponding aryl ketone.

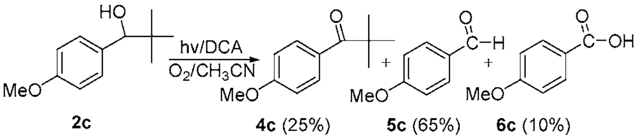
The plots in Figure 1 show that the rate constant depends on the para-substituent. As the electron-withdrawing ability of the substituent increases, the photooxidation reaction becomes faster. These results indicate that in the transition state (**TS**) of the rate-limiting step, a negative charge has been developed and it is better stabilized by electron-withdrawing substituents (Scheme 3). In the case of an ET mechanism forming a radical cation intermediate, the opposite kinetic results would have been expected. In that case, the *para*-methoxy substituent would lead to a faster reaction than electron-withdrawing substituents, because of a better stabilization of the radical cation intermediate.

Scheme 3. Proposed Mechanism for the Decatungstate Photocatalyzed Oxidation of 1-Aryl-1-alkanols in the Presence of O_2



For comparison reason, the para-substituted 1-aryl-1-alkanols **1c** and **2a**−**c** were photooxidized in the presence of 9,10-dicyanoanthracene (DCA). The results are summarized in the Table 2. DCA, at least for the oxidation of aryl alkenes[19] and ethers,[20] is a well-established electron-transfer photosensitizer. It is interesting to note that when the para-substituent was hydrogen (**2a**) or trifluoromethyl (**2b**), no reaction products were detected after irradiation for

Table 2. 9,10-Dicyanoanthracene (DCA)-Sensitized Photooxidation of 1-Aryl-1-alkanols in Oxygen Saturated Acetonitrile



		relative product yield,[b]%		
substrate[a]	% conversion	ArCOR	ArCHO	ArCOOH
2a		nd[c]	nd[c]	nd[c]
2b		nd	nd	nd
2c	30	25	65	10
1c	47	100	nd	nd

[a] 1-Aryl-1-alkanol (0.05 M) was irradiated (20 min, Xenon lamp, 300 W, >300 nm) in the presence of DCA (5.5×10^{-4}M), in oxygen-saturated acetonitrile, at 5−10 °C. [b] Determined by ^{1}H NMR. The error was ±4%. [c] Not detected

20 min. In contrast, when the para substituent was methoxy (**2c**), a 30% conversion was measured. In this case, the major scission product was the aryl aldehyde, its ratio to aryl ketone being 65/25, as shown in Table 2. Thus, the DCA oxidation of **2c** produces a product distribution completely different than that observed when the same substrate was photosensitized with $W_{10}O_{32}^{4-}$ (Table 1). Unlike decatungstate-sensitized photooxidation, this result is indicative of an extensive $C_\alpha - C_\beta$ bond cleavage and supports an electron-transfer process as the major mechanistic pathway.

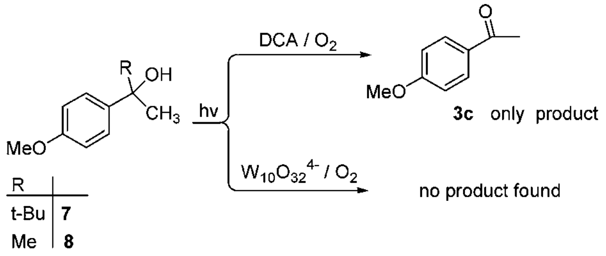
In the case of an ET mechanism, addition of a small amount (compared to 1-aryl-1-alkanol) of an electron donor molecule with oxidation potential less than that of the 1-aryl-1-alkanol should retard the photooxidation by electron transfer from the donor molecule to the 1-aryl-1-alkanol radical cation, according to the eq 3.

$$\text{aryl alkanol}^{+\bullet} + \text{D} \rightarrow \text{aryl alkanol} + \text{D}^{+\bullet} \qquad (3)$$

Trimethoxybenzene (TMB), with $E_{1/2ox}$ vs SCE 1.12 V,[19c] was used as the donor molecule. The oxidation potential of 1-aryl-1-alkanol **2c** is 1.6−1.7 V.[18] After 20 min irradiation of **2c** in the presence of DCA and small amounts of TMD, no photooxidation was observed. This result confirms that the electron-transfer mechanism is the predominant mechanism in the reaction of DCA with **2c**. However, in the case of $W_{10}O_{32}^{4-}$ as a photosensitizer, a small amount of TMB under the previous reaction conditions did not have any measurable effect on the photooxidation reaction of **2c**.

To probe further the HAT vs ET mechanism and obtain additional information on the photooxidative bond cleavage, we examined the photooxidation of 2-(4-methoxyphenyl)-3,3-dimethyl-2-butanol **7** and 2-(4-methoxyphenyl)-2-propanol **8** (Table 3). In these substrates no C_α−hydrogen is available for a HAT mechanism; only *tert*-butyl and methyl groups are available for oxidative $C_\alpha - C_\beta$ bond cleavage via an electron-transfer mechanism. Upon irradiation of 0.05 M solutions of **7** and **8** in oxygen-saturated acetonitrile and DCA as the sensitizer, the aryl ketone was the exclusive cleavage product (Table 3). However, under similar conditions in the presence of $W_{10}O_{32}^{4-}$ as the sensitizer, neither substrate gave a reaction. These results confirm unambiguously that the $W_{10}O_{32}^{4-}$ photosensitized oxidations of 1-aryl-1-alkanols proceed via a hydrogen abstraction mechanism. A reasonable mechanistic approach that may rationalize these and previous results is shown in Scheme 3. In the first step, under irradiation conditions, decatungstate anion undergoes in to the relatively long-lived intermediate wO.[3,10−14] In the transition state (**TS**), the developing radical between 1-aryl-1-alkanol and wO is better stabilized by electron-withdrawing substituents. 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**), as shown in Scheme 3. The **RI** in the presence of molecular oxygen decomposes to the corresponding aryl ketone through the possible formation of an 1-arylyl-peroxyl-ethanol intermediate. The one-electron-reduced species of decatungstate reoxidizes 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 transient spectroscopy.[12−14]

Table 3. Decatungstate- and DCA-Sensitized Photooxidation of **7** and **8** in Oxygen Saturated Acetonitrile



substrate	catalyst	irradiation time	% conversion[a]	$ArCOCH_3$
7	DCA	20 min	25	100
8	DCA	20 min	12	100
7	$W_{10}O_{32}^{4-}$	20 min	0	nd[b]
8	$W_{10}O_{32}^{4-}$	20 min	0	nd[b]

[a] Determined by 500 MHz ^{1}H NMR. The error was ±4%. [b] Not detected.

In conclusion, product analysis and kinetic data of the decatungstate-sensitized photooxidation of 1-aryl-1-alkanols support a hydrogen abstraction transfer mechanism in the rate-determining step.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for **2b**, **2c**, and **7**; photooxidation of **1b**,**d**−**f**, **2b**, **2c**, and **7** with $W_{10}O_{32}^{4-}$; photooxidation of **2c** and **7** with DCA; GC for the photooxidation of **2b** and **2a** with $W_{10}O_{32}^{4-}$; and GC−MS spectra of **2a**−**c** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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