

## Anaerobic Functionalization of Remote Unactivated Carbon-Hydrogen Bonds by Polyoxometalates

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**Abstract** The excited states of a representative heteropolytungstate,  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ , and a representative isopolytungstate,  $\text{W}_{10}\text{O}_{32}^{4-}$ , accessible with near UV or blue light, oxidize alkanes and conventionally far more reactive organic molecules including alcohols, alkenes, *N*-alkylacetamides, and ketones, at comparable rates. One or more of the latter three types of compounds are produced upon irradiation of acetonitrile solutions containing the polyoxotungstate and alkane substrate under anaerobic conditions. Comparison of alcohol versus alkane reactivities under absolute and competitive kinetic conditions indicates that alcohol-polyoxotungstate preassociation can be important in these processes. Reaction of *cis*- and *trans*-2-decalones in these systems indicates that functionalization of unactivated positions (primarily incorporation of the olefinic unit) remote from the usually activating ketone group can be accomplished.

### Introduction

Despite the intense activity in the last 5 or 6 years toward the development of methods to functionalize unactivated C-H bonds in alkanes and other organic molecules, few methods exist that are catalytic and show interesting selectivities.<sup>1-10</sup> Several organometallic alkane activation systems display nonclassical carbon-hydrogen bond cleavage selectivities (primary C-H most reactive), but few of these systems are catalytic. The organometallic systems that are catalytic are inactivated rapidly by ligand degradation.<sup>1</sup> Superacids and other extremely electrophilic media can effect alkane oxidation with interesting selectivities.<sup>2,3</sup> The oxygenation of alkanes by oxygen atom donors (e.g. peroxides, peracids, hypochlorite, iodosylarenes, amine *N*-oxides, etc.) can be catalyzed by transition metal metalloporphyrins,<sup>4-5</sup> Schiff base or macrocyclic complexes,<sup>6</sup> nitrate(triflate) salts,<sup>7</sup> zeolite-encapsulated phthalocyanine and related complexes,<sup>8</sup> and transition metal-substituted polyoxometalate (TMSP) complexes.<sup>9</sup> The inherent kinetic C-H bond cleavage selectivities in all these systems are conventional (tertiary C-H most reactive). Furthermore, all but the TMSP catalysts, and perhaps the zeolite-encapsulated species are susceptible to inactivation either by oxidative degradation of the ligand or by precipitation of the transition metal active site as the metal oxide. Few if any methods for the cleavage of unactivated carbon-hydrogen bonds demonstrate broad spectrum tolerance of other functional groups, present either in the same molecule or in other molecules in the reaction system. In other words, cleavage of unactivated carbon-hydrogen bonds in the presence of molecules that already contain functional groups, particularly those functional groups that activate proximal bonds, remains very difficult to achieve. We report here a systematic approach to this problem using polyoxometalates.

Polyoxometalates are a large class of inorganic cluster-like compounds composed only of certain  $d^0$  transition metal ions (e.g.  $\text{V}^{\text{V}}$ ,  $\text{Nb}^{\text{V}}$ ,  $\text{Ta}^{\text{V}}$ ,  $\text{Mo}^{\text{VI}}$ , and  $\text{W}^{\text{VI}}$ ) and oxide ions and held together only by metal-oxygen bonds.<sup>11</sup> They are accessible in quantity and their redox, solubility, and other key properties can be systematically altered in a rational fashion. The thermodynamic resistance of polyoxometalates to oxidation and other features of this class of molecules attracted us in context with difficult organic transformations and other processes, including the selective catalytic functionalization of alkenes and alkanes.<sup>9,12-14</sup> Figure 1 illustrates the structure of the most common and one of the most thermodynamically stable polyoxometalate structures, the heteropoly "Keggin" ion.

Recently our research group developed photochemical methods for the homogeneous selective catalytic functionalization of alkanes by polyoxometalates.<sup>13</sup> The alkane derived products in these processes are alkenes, *N*-alkylacetamides and alkyl methyl ketones (equation 1). The oxidation equivalents represented in these products are balanced well in most cases by the quantity of the reduction product, hydrogen gas, that is evolved. The product distributions generated in these reactions depend on the nature of the alkane substrate, the polyoxometalate catalyst, and the presence or absence of a co-catalyst for the evolution of hydrogen, e.g.  $\text{Pt(0)}$ . Subsequent research

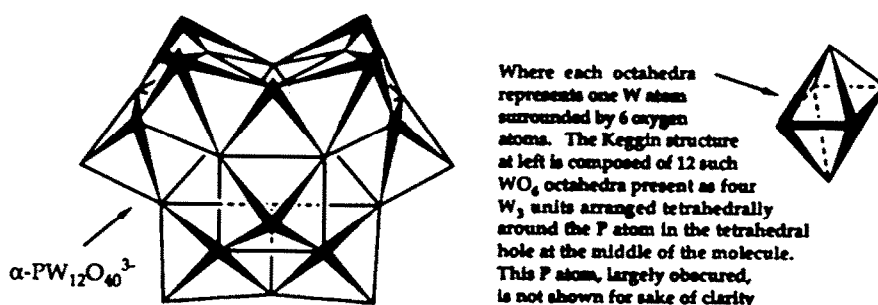
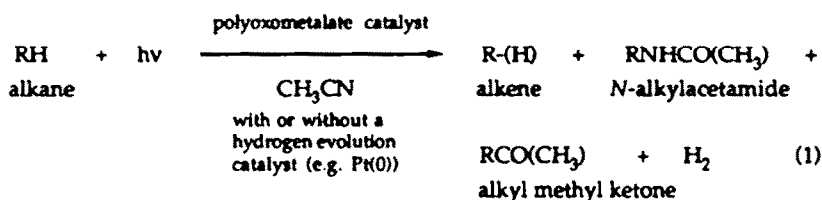


Figure 1. The structure of the  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$ , one representative of a large class of heteropoly complexes,  $(\text{X}^{(n+)})\text{M}_{12}\text{O}_{40}^{(8-n)-}$ , shown in polyhedral notation.

led to establishment of many of the energetic and mechanistic features of this catalytic photochemistry and systematic development of systems that produce alkenes and hydrogen gas catalytically and directly from alkanes with high selectivity.<sup>14</sup> These latter processes are endothermic by up to 35 kcal/mol in the dark.



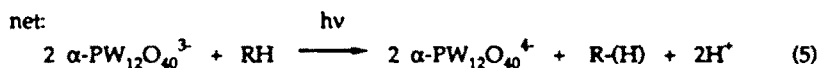
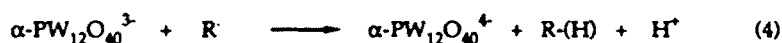
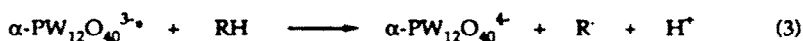
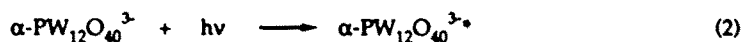
It was the highly unusual if not unprecedented relative substrate reactivities encountered in kinetics investigations of the homogeneous system constituted by  $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$ /alkane (or other organic substrate)/acetonitrile solvent/light ( $\lambda > 270 \text{ nm}$ )<sup>14a</sup> that led us to the present study. Cyclohexane and cyclooctane, the corresponding cyclic alcohols, and the products derived from the reaction in equation 1, the cycloalkenes, *N*-cycloalkylacetamides, and cycloalkyl methyl ketones, all display remarkably similar rates of reaction with respect to the excited state of  $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$  (all within a factor of 10 of each other).<sup>14a</sup> In contrast, alkanes are *substantially* less reactive toward strong bases, radicals, carbenes, and most other reactive species than these other classes of organic compounds. Alcohols are typically hundreds to millions of times more reactive than the corresponding alkanes.<sup>15</sup> The potential ability to modify unactivated hydrocarbon skeletons in the presence of functional group bearing moieties has compelled us to conduct two types of kinetic experiments. The first type of kinetic experiment entails a comparison of the relative reactivities of alkanes and structurally related alcohols in separate reactions with the reactivities of these two types of compounds when present in the same reaction. The second type of kinetic experiment involves the attempted functionalization of unactivated hydrocarbon backbones in molecules *that already contain a functional group elsewhere in the molecule*. The fact that, in previous work, it was shown that alkanes react at comparable rates to alcohols, or the organic products in equation 1, does not demand that these different substrates will react at similar rates when *competing* for the same population of polyoxotungstate excited states. These experiments addressed here are of central importance with regard to further establishment of the mechanism of polyoxometalate-catalyzed photochemical processes, and the ultimate use of such processes in synthesis.

## Results and Discussion

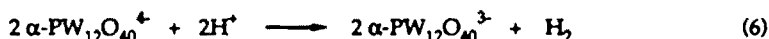
### Competitive Reactions - Alkanes versus Alcohols.

The reactions of an exemplary alkane, cyclooctane, and an exemplary alcohol, 2-butanol with

respect to the excited states of both  $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$  and  $(\pi\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ , have been examined under both absolute and competitive kinetics conditions. The principal products under the reaction conditions used here (large molar excess of alkane,  $\lambda > 320$  nm near-UV light, acetonitrile solvent,  $25^\circ\text{C}$ ), cyclooctene and 2-butanone, from cyclooctane and 2-butanol, respectively, are produced with nearly quantitative selectivities. In other words, the reaction conditions are highly selective for the net dehydrogenation of the substrates, and eqs 2-5 (using the complex  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$  for sake of illustration), summarize the chemistry.<sup>14</sup> The reoxidation of the reduced polyoxotungstate,  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ , eq 6 is often facile rendering the dehydrogenation process catalytic in polyoxotungstate. For the kinetics and product studies reported here, however, conditions were



$\text{RH}$  = alkane or alcohol;  $\text{R(H)}$  = alkene or ketone



purposely chosen (no  $\text{Pt(0)}$  or other hydrogen evolution catalyst present) under which the net processes were stoichiometric (eq 5). That is, eq 6, did not proceed to an appreciable degree over the lifetime of the kinetic measurements and effectively the rates of the rate-determining<sup>14</sup> substrate activation process, only, were examined. These experimental conditions facilitated monitoring the rate of production of both the reduced polyoxotungstate product,  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$  or protonated  $\text{W}_{10}\text{O}_{32}^{6-}$ , for the reactions involving  $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$  and  $(\pi\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ , respectively, and the oxidized organic product,  $\text{R(H)}$ . In addition, experimental conditions were found, principally through the use of appropriate reactant concentrations and cut-off filters, under which only the photochemistry associated with the polyoxometalates and not the organic reactants or products was operable.

Figure 2 illustrates the rates of production of  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ , using only cyclooctane, only 2-butanol, and a 50:50 molar mixture of the two compounds as substrates. At early reaction times, (Figure 2-B), the alkane reproducibly produces  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$  with a faster but similar rate relative to 2-butanol, (initial rates = 0.09, 0.07, and 0.08  $\text{mM m}^{-1}$  for 100% alkane substrate, 100% alcohol substrate and the 50:50 mixture, respectively). The relative rates of production of the organic products were monitored independently and agreed with the relative rates of production of the  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$  product. To the best of our knowledge, there is no other set of reaction conditions in the literature under which alkanes are oxidized more rapidly than primary or secondary alcohols. Oxidative titration of the reduced polyoxometalates with  $\text{Ce}^{\text{IV}}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and  $\text{O}_2$  established that the increased quantity of the reduced chromophore generated at later reaction times for the 2-butanol reaction relative to the cyclooctane reaction, as is apparent in Figure 2-A, results from partial reduction of the one-electron reduced polyoxotungstate to the two-electron reduced complex. In other words, the initial polyoxotungstate reduction product,  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ , has a finite, albeit low, quantum yield for further reduction in alcohol/acetonitrile solution, but a negligible quantum yield for further reduction in the alkane/acetonitrile solution. The initial

rates for photoreduction of  $W_{10}O_{32}^{4-}$  using only cyclooctane, only 2-butanol and a 50:50 mixture of the two compounds as the substrate(s), are, respectively, 0.02, 0.06, and 0.05  $\text{mM s}^{-1}$ . The  $W_{10}O_{32}^{4-}$

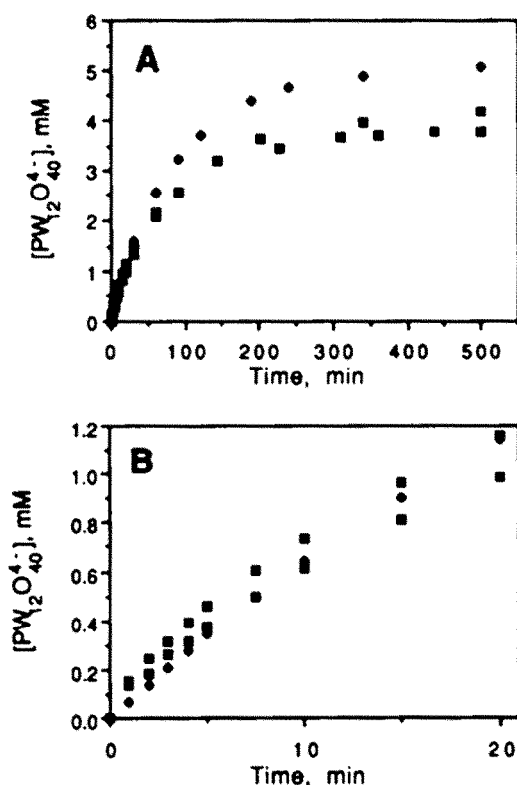


Figure 2. Photochemical production of  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$  by cyclooctane ( $\square$ ), 2-butanol ( $\blacklozenge$ ), and a 50:50 molar mixture of cyclooctane and 2-butanol ( $\blacksquare$ ) from  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$  in acetonitrile solution. Reactions monitored at  $\lambda_{\text{max}}$  of  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$  (730 nm). The top plots (A) show the entire time course of the reactions; the bottom plots (B) show the behavior at early times.  $[\alpha\text{-PW}_{12}\text{O}_{40}^{3-}]_0 = 3.3 \text{ mM}$  and  $[\text{organic substrate}] = 0.48 \text{ M}$  for cyclooctane or butanol reactions and  $0.24 \text{ M}$  in each substrate for the 1:1 reactions; all reactions run at  $25^\circ\text{C}$ . Additional conditions given in Experimental section.

complex is reduced 51 times as rapidly as the  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$  complex in the 2-butanol/acetonitrile solution, but only 13 times as rapidly as the latter complex in the cyclooctane/acetonitrile solution.

The most valuable information derives from an examination of the product distributions in these reactions and a comparison of this data with the kinetics data in Figure 2. Table I summarizes the product distributions obtained from the reactions recorded in Figure 2. The product yields in excess of 100%, based on the quantity of reduced polyoxotungstate generated, for some of the reactions in Table I result in part from the evolution of a small quantity of hydrogen gas from the reduced complex. It should be pointed out that the product yields in Table I based on the reactant  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$  are different by a factor of 2 from those reported, that is, those based on  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ , by virtue of the stoichiometry – 2 equivalents of the one-electron reduction product,  $\alpha\text{-PW}_{12}\text{O}_{40}^{4-}$ , are produced per 1 equivalent of the two-electron oxidation product, alkene or ketone. The data in this table establish clearly that the relative quantities of the various products obtained under competitive conditions, (a 1:1 mole ratio of both substrates present) are not directly proportional to the relative rates of oxidation of the two substrates separately. If the product distributions were proportional to the absolute rates, then, for the  $\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$  system, more cyclooctene derived from cyclooctane oxidation relative to ketone derived from alcohol oxidation would be produced in the competitive reactions. In fact, however, the ketone product is formed in preference to the alkene product. Given that other recent investigations have established that the substrate is present in the rate determining activated complex in both alkane and alcohol

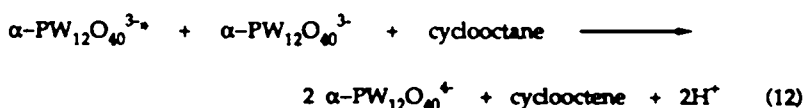
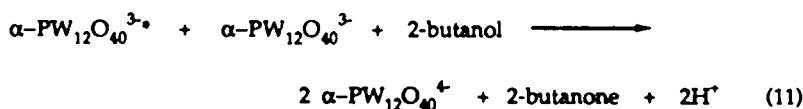
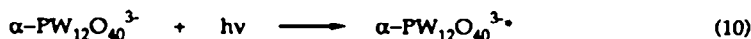
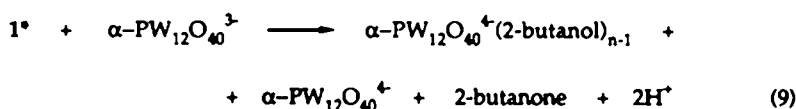
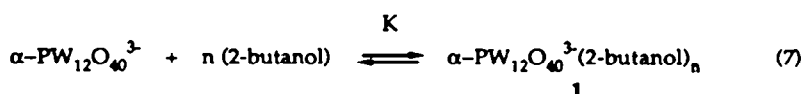
oxidations by a range of polyoxometalates,<sup>13,14,16-22</sup> a reasonable rationale for the predominance of ketone over alkene product under competitive conditions involves a rapid preequilibrium association between the polyoxotungstate and the alcohol substrate, eq 7, followed by slower substrate oxidation processes. For the alcohol reactions, substrate oxidation could derive from an association complex, eqs 8 and 9, or from a diffusive bimolecular encounter with the unassociated excited state, eq 11. Alkane is effectively oxidized solely by diffusive encounter with the polyoxometalate excited state, eq 12. Equations 7-12 have been written not to imply detailed mechanism, as much of this information has yet to be gleaned from experiment, but rather to represent overall balanced processes of general applicability in this chemistry. Although equations 7-12 have been specifically written using  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> they pertain, in principal, to any polyoxometalate that is photochemically active with respect to these two substrates. The association numbers (mole ratio of polyoxometalate to alcohol substrate in the complex(es)), and

**Table I. Yields of Organic Oxidation Products from the Photochemical Oxidation of Cyclooctane and 2-Butanone by  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> and W<sub>10</sub>O<sub>32</sub><sup>4-</sup>.<sup>a</sup>**

polyoxotungstate photocatalyst	organic substrate <sup>b</sup>	Products Yields, (% based on $\alpha$ -PW <sub>12</sub> O <sub>40</sub> <sup>4-</sup> )
$\alpha$ -PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	cyclooctane	cyclooctene (85)
$\alpha$ -PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	2-butanol	2-butanone (113)
$\alpha$ -PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	1:1	cyclooctene (22), 2-butanone (105)
W <sub>10</sub> O <sub>32</sub> <sup>4-</sup>	cyclooctane	cyclooctene (56), dimer (39)
W <sub>10</sub> O <sub>32</sub> <sup>4-</sup>	2-butanol	2-butanone (107)
W <sub>10</sub> O <sub>32</sub> <sup>4-</sup>	1:1	cyclooctene (11), 2-butanone (87), dimer (5)

<sup>a</sup> Conditions for  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> reactions: [ $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>]<sub>0</sub> = 3.3 mM; for W<sub>10</sub>O<sub>32</sub><sup>4-</sup> reactions: [W<sub>10</sub>O<sub>32</sub><sup>4-</sup>]<sub>0</sub> = 1.8 mM; all reactions run at 25°C. <sup>b</sup> 1:1 = equal amounts of both cyclooctane and 2-butanol; [organic substrate] = 0.48 M for cyclooctane or butanol reactions and 0.24 M in each substrate for the 1:1 reactions.

association constants are not known quantitatively at this time for any system involving polyoxometalate solvation by alcohols. The effect of alcohol-polyoxometalate preassociation on polyoxometalate photochemistry has been specifically cited by Fox and co-workers.<sup>17</sup> We provide here kinetic evidence for the significance of such interactions.



The proximity of the alcohol substrates to the polyoxometalates can be facilitated by hydrogen-bonding, or, as we have demonstrated in several structurally characterized complexes containing both photochemically active polyoxometalates and organic substrates, by weak but electronically significant noncovalent intermolecular interactions.<sup>23,24</sup>

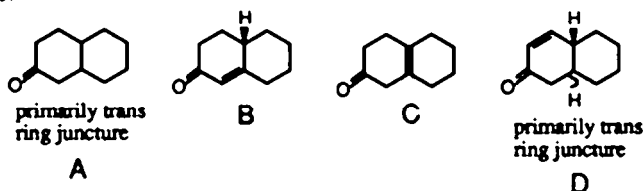
### Competitive Intramolecular Processes - Reactions of 2-Decalone

The next set of exploratory experiments address the possibility of using the minimal differences in reactivity between unactivated hydrocarbon skeletons and functional group bearing moieties observed in the polyoxometalate photochemistry, to see whether the former could be functionalized in the presence of the latter *within the same molecule*. For the initial experiments, we chose 2-decalone as the substrate. This compound has a well-defined functional group with a proximal region of enhanced reactivity, principally the  $\alpha$ -C-H bonds, and several of its likely oxidation products are readily obtained in high states of purity.

The products resulting from the photochemical oxidation of a 82:18 molar mixture of *cis*- and *trans*-2-decalones by four different polyoxometalate systems are summarized in Table II. The products generated in these reactions vary dramatically with the polyoxometalate and the reaction conditions. Although gc and gc/ms analyses have confirmed the presence of the dimeric products, the particular isomers have not been unequivocally established at this time. The reactions in Table II were examined under conditions of low catalyst turnover to minimize production of compounds derived from subsequent reaction of the initial kinetic products (< 10% conversion for reactions 1, 2 or 4; < 70% conversion for reaction 3). The first reaction, that involving  $\alpha$ -H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, produces no detectable isomerization of the thermodynamically less stable *cis*-decalone starting material to the corresponding *trans* isomer, but does produce the olefinic

Table II. Functionalization of 2-Decalone<sup>a</sup>

Products:



Complex<sup>b</sup>

Product Yields, %<sup>c</sup>

based on total organic products (turnovers of complex)

	A	B	C	D	others(dimers)
$\alpha$ -H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0	28(0.13)	11(0.05)	0	61(0.3)
$\alpha$ -Li <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0	48(0.21)	25(0.11)	0	26(0.12)
Q <sub>4</sub> W <sub>10</sub> O <sub>32</sub>	100(1.7) <sup>d</sup>	0	0	0	0
Q <sub>4</sub> W <sub>10</sub> O <sub>32</sub> /TFA <sup>e</sup>	0	40(0.6)	25(0.4)	0	35(0.5)

<sup>a</sup> Reaction conditions: [2-decalone] = 0.15 M in all reactions; [polyoxometalate] = sufficient to absorb >99% of incident radiation: [ $\alpha$ -H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>] = 8.4 mM, [ $\alpha$ -Li<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>] = 8.4 mM, [W<sub>10</sub>O<sub>32</sub><sup>4-</sup>] = 8.4 mM.  $\lambda$  > 270-nm cut-off filter used for  $\alpha$ -H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and  $\alpha$ -Li<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> reactions;  $\lambda$  > 320-nm cut-off filter used for W<sub>10</sub>O<sub>32</sub><sup>4-</sup> reactions. All reactions run at 25°C; additional reaction conditions given in Experimental. Isomeric ratio of reactant 2-decalones = 82:18 *cis*/*trans*. <sup>b</sup>Q = tetra-*n*-butylammonium ion. <sup>c</sup>Yields before parenthesis based on total detectable organic products; yields in parenthesis (turnovers of catalyst) are moles of product per mol complex. <sup>d</sup>see text. <sup>e</sup>250 eq trifluoroacetic acid (TFA) used per eq W<sub>10</sub>O<sub>32</sub><sup>4-</sup>.

ketones, B and C, (common name = octalones), and a mixture of dimers. In contrast, Q<sub>4</sub>W<sub>10</sub>O<sub>32</sub> in the absence of acid produces no octalones and does isomerize the *cis*-decalone starting material to the *trans* isomer with very high selectivity. The third reaction, (Q<sub>4</sub>W<sub>10</sub>O<sub>32</sub> / no acid) produces only the isomerized starting material. The selectivity drops from 100% to 63% after several

turnovers of the  $W_{10}O_{32}^{4-}$  in this system, yet under these conditions, still no octalones are detectable. (It should be pointed out that the only products other than the *trans*-2-decalone in the latter reaction are those derived from photochemical degradation of the tetra-*n*-butyl ammonium counterion. The selectivity after many turnovers with respect to products derived only from the decalone remains very high). Independent experiments with authentic octalones indicated that catalytic amounts of toluene sulfonic acid,  $H_2SO_4$ , or the acidic complex,  $\alpha-H_3PW_{12}O_{40}$  itself, in the dark, produced the same thermodynamic distribution of octalones B and C (85:15 on a molar basis) and that rapid acid-catalyzed equilibration would disguise any kinetic behavior producing unusual or thermodynamically unstable products in the reaction involving  $\alpha-H_3PW_{12}O_{40}$ . Interestingly, the acids that equilibrated B and C did not equilibrate all three octalones, B, C and D. A kinetic barrier for converting either B or C into D exists under the acidic conditions sufficient to equilibrate B and C. Experimental conditions were sought under which production of the thermodynamically less stable octalone C, a product resulting from functionalization of C-H bonds remote from the ketone group, was enhanced over production of the more stable conjugated isomer, B. The conditions in both the second and fourth reactions in Table II did produce a nonequilibrium mixture of octalones enriched in the remote product, C. The effect of trifluoroacetic acid was noteworthy. The rate of isomerization of the octalones by this acid was slow compared to the rate of photochemical functionalization and the presence of this acid dramatically altered the products produced by the  $W_{10}O_{32}^{4-}$  system.

These preliminary results indicate that under appropriate conditions, functionalization of unactivated moieties by polyoxometalate excited states can be observed in molecules bearing functional groups. This research area warrants in-depth investigation to establish the origins of such nonclassical reactivities and the mechanisms of the highly complex processes involved in modification of organic species by polyoxometalates.

## Experimental

### Materials

The acetonitrile was Burdick and Jackson glass distilled grade and stored over 4Å molecular sieves. The complexes,  $\alpha-H_3PW_{12}O_{40}$ ,<sup>25</sup>  $(n-Bu_4N)_4W_{10}O_{32}$ ,<sup>26</sup>  $\alpha-Li_3PW_{12}O_{40}$ ,<sup>27</sup> and the 2-octalones,<sup>28</sup> were all prepared and purified by literature methods.

### Methods

All procedures were carried out under inert atmosphere, except some of the product analyses. In the latter cases control experiments established that there was no effect of the analysis procedures on the product distributions. The kinetic studies were conducted using quartz cuvette reaction vessels equipped with teflon stopcocks and standard-taper fittings. These vessels facilitated manipulation on dual manifold vacuum lines, monitoring of the photochemical reactions by UV-visible spectroscopy via a Hewlett-Packard (HP) multidiode array 8451A instrument, and ready sampling of the liquid and gas phases inside the vessel. The photochemical reaction apparatus used for both the kinetics and product studies was an Oriel 1000-W Xe lamp assembly equipped with infrared and various cut-off filters interfaced with a thermostated cell holder. The samples were stirred magnetically during irradiation. Product analyses were conducted by gas chromatography and gas chromatography/mass spectrometry. The gc analyses were performed using HP 5890 gas chromatographs equipped with 5% phenyl methyl silicone fused silica capillary columns and interfaced with HP 3390A electronic integrators. The gc/ms analyses were done both in house on a VG 70S instrument and out of house by Wan Industries, Atlanta, GA. The identity of the octalone products were established not only by gc and gc/ms analysis but also by comparison with independently synthesized authentic octalones.<sup>28</sup>

For all reactions, conditions were established using the appropriate concentrations of alkane, alcohol or ketone substrates and polyoxometalate catalysts such that >99% of the light in all cases was being absorbed by the polyoxometalate chromophore and not by the chromophores of the organic reactants or products.

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