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Selective Ethylation and Vinylation of Alkanes via Polyoxotungstate Photocatalyzed Radical Addition Reactions

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General interest in radical addition reactions derives from their flexibility and mildness relative to ionic reactions.[1,2] Carbon radical chain addition to unsaturated species, in particular, has been extensively utilized to produce useful organic products.[2–6] The general process, eq 1, thoroughly documented to proceed via eqs 2–4,

Net

$$RH + H_2C{=}CHR' \rightarrow RH_2C{-}CH_2R' \qquad (1)$$

Mechanism

$$R^{\bullet} \text{ (from initiation process)} \qquad (2)$$

$$R^{\bullet} + H_2C{=}CHR' \rightarrow RH_2C{-}{}^{\bullet}CHR' \qquad (3)$$

$$RH_2C{-}{}^{\bullet}CHR' + RH \rightarrow RH_2C{-}CH_2R' + R^{\bullet} \qquad (4)$$

often affords high yields of addition products while avoiding high concentrations of radical species that lead to undesirable coupling and disproportionation reactions. Unfortunately, such radical addition reactions have so far been limited to C–H bonds which are activated toward H abstraction, such as those α to heteroatoms or in benzylic or allylic positions. Unactivated C–H bonds have only been observed to react under severe conditions such as high temperatures and pressures[7] or high-energy radiation.[5] In this work we take advantage of the diverse photoredox chemistry of unactivated C–H bonds by robust and oxidatively resistant d^0 polyoxometalates, including the efficient generation of intermediate organic radicals by some systems.[8–10] It is motivated in part by the need for versatile and mild methodologies to transform surfaces of high-technology plastics, diamond, and composites with unactivated C–H bonds. We now report the application of polyoxotungstates (P_{ox}), $(n\text{-}Bu_4N)_4W_{10}O_{32}$ and $(n\text{-}Bu_4N)_3PW_{12}O_{40}$ (Figure 1), as effective catalytic photoinitiators of highly selective radical addition reactions of unactivated C–H bonds to both ethylene and acetylene at ambient temperature and pressure.

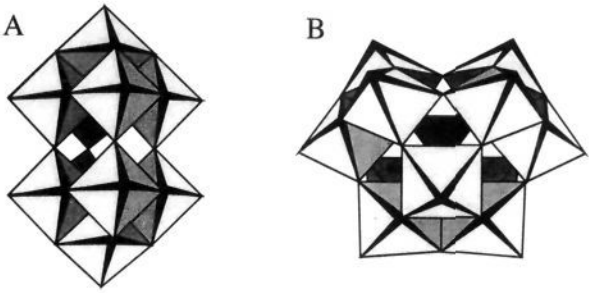
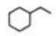
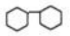
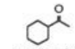
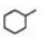
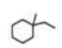
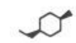
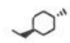
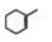
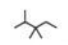
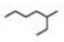
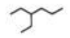
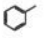
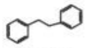
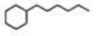
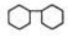
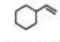
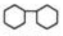
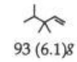


Figure 1. Polyhedral structures of the two polyoxotungstate catalysts used in this study. (A) $[W_{10}O_{32}]^{4-}$ (a D_{4h} isopolyanion); (B) $[PW_{12}O_{40}]^{3-}$ (a T_d heteropolyanion).

Table I. Organic Product Distributions from the Radical Addition of Alkanes to Unsaturated Substrates Initiated by Polyoxotungstates[a]

poly-oxotungstate	substrate	organic products, % of detected products[b] (turnovers, based on P_{ox})				
I. Additions of Substrate to Ethylene[c]						
						
$Q_4W_{10}O_{32}$		82 (8.1)	<1	2 (0.2)	11 (1.1)[d]	
$Q_3PW_{12}O_{40}$		87 (1.6)[d]				
						
$Q_4W_{10}O_{32}$		37 (4.1)	24 (2.6)	25 (2.7)[d]		
$Q_3PW_{12}O_{40}$			10 (0.2)	5 (0.1)	85 (1.5)	
						
$Q_4W_{10}O_{32}$		100 (3.2)				
$Q_3PW_{12}O_{40}$			100 (2.6)			
		 + 				
$Q_4W_{10}O_{32}$		100 (3.1)[e]				
						
$Q_4W_{10}O_{32}$		N.R.				
						
$Q_4W_{10}O_{32}$		100 (0.5)				
II. Addition of Substrate to 1-Hexene[f]						
						
$Q_4W_{10}O_{32}$		54 (0.4)	10 (0.1)[g]			
III. Additions of Substrate to Acetylene[h]						
						
$Q_4W_{10}O_{32}$		99 (8.6)	1 (0.1)			
						
$Q_4W_{10}O_{32}$		93 (6.1)[g]				

[a] Acetonitrile solutions of polyoxotungstate (1.5 mM) and alkane (0.5 M) were irradiated for 15 h using a 550-W medium-pressure Hg lamp with Pyrex filter ($\lambda > 280$nm) at 25 °C. [b] Moles of product/total moles of all organic products as determined by GC. N.R., no reaction. [c] Acetonitrile solutions were saturated with C_2H_4 at 1 atm; $[C_2H_4] \sim 0.07$ M. [d] Remaining organic products are doubly ethylated substrate. [e] Ethylated products could not be separated by GC. [f] [Alkane] = 0.25 M; [1-hexene] = 0.09 M. [g] Remaining organic products were unidentified. [h] Solutions were saturated with C_2H_2 at 1 atm; $[C_2H_2] \sim 0.27$ M.

Table I summarizes the results for the photocatalytic ethylation or vinylation of a variety of hydrocarbon substrates by P_{ox} and gives the reaction conditions. The chemoselectivities and regioselectivities (including relative C–H bond reactivities, 3° > 2° ≫ 1°) are all consistent with H atom abstraction from alkane followed by radical addition (e.g., eq 3). Conversions were kept low (2–5%) for these reactions to minimize the obscuring effect of subsequent reactions of the initial products and, hence, to accurately assess the kinetic selectivity and mechanism. Furthermore, the kinetics of representative reactions (ethylation and vinylation of cyclohexane by $[W_{10}O_{32}]^{4-}$) implied kinetic product

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distributions. Thus, the relative yields in Table I approximate the relative rates of the intermediate radical trapping processes, radical addition (k_{add}, eq 3), the desired process leading to ethylated or vinylated products, versus the undesired and selectivity-limiting side reactions. For $[W_{10}O_{32}]^{4-}$, undesired reactions are radical coupling (k_c) and reduction of the radical via $[W_{10}O_{32}]^{6-}$ to a carbanion (k_{red}) with subsequent attack at the nitrile carbon of the solvent and hydrolysis of the imine to yield alkyl methyl ketone.[11-13] For $[PW_{12}O_{40}]^{3-}$, it is radical oxidation to a carbocation (k_{ox}), a process consistent with the products (1-methylcyclohexene from methylcyclohexane and 2,3-dimethyl-2-butene from 2,3-dimethylbutane)[14] and with the ground-state potentials of P_{ox} ($E°$ vs $Ag/AgNO_3$ for $[PW_{12}O_{40}]^{3-/4-}$ and $[W_{10}O_{32}]^{4-/5-}$ is –0.670 and –1.270 V, respectively, in acetonitrile). Selective 1:1 addition of alkane to ethylene was found to occur for cyclohexane, methylcyclohexane, 2,3-dimethylbutane, and *n*-hexane. Yields of addition product were highest for cyclohexane, with 8–9 effective turnovers of the polyoxotungstate and selectivity for ethylcyclohexane of >80% ($k_{add}/(k_c + k_{red}) \sim 6.3$). Selectivity for ethylation of 2,3-dimethylbutane and *n*-hexane was 100%, although the rates of reaction for both were less than half that for cyclohexane. Addition of cyclohexane to 1-hexene was far less effective and selective than addition to ethylene or acetylene ($k_{add}/k_c \sim 41$ and 4.5 for ethylene and 1-hexene, respectively). Toluene yielded only bibenzyl, indicating that the addition of the relatively stable benzyl radical to ethylene is slow compared to coupling ($k_{add}/k_c \sim 0$). Interestingly, attempted addition of secondary alcohols to ethylene gave only ketones with either polyoxotungstate, reflecting the thermodynamic and kinetic facility of radical oxidation ($k_{ox} \gg k_{add}$).

Addition of C–H bonds to acetylenes is less common than that to olefins because attack of the radical on the triple bond is relatively slow.[4,6] Furthermore, when addition does occur, the olefinic products tend to be more reactive toward a second addition, with the net result of two substrate molecules added across the acetylenic bond.[6] In contrast, radicals photocatalytically generated from alkanes under the conditions in Table I add to acetylene to give the vinylated products with remarkable selectivity ($k_{add}/k_c \sim 99$ and 93 for vinylation of cyclohexane and 2,3-dimethylbutane, respectively) and equal or greater turnovers than in the addition to ethylene. The unexpectedly fast rate of addition of acetylene results principally from a higher solubility of acetylene (0.27 M) versus ethylene (0.07 M) in acetonitrile under 1 atm at 25 °C.

Several long-term reactions were conducted, and the results indicated that high selectivity can be maintained even when substantial amounts of substrate are converted. For example, the addition of cyclohexane to acetylene yielded vinylcyclohexane with 91% selectivity and 6–7% conversion of alkane after 62 h, while addition to ethylene gave ethylcyclohexane with 83% selectivity and 8–9% conversion after 78 h. No attempt was made to optimize high substrate conversion reactions, but conversions higher than 10% were difficult to attain because the reactions slowed considerably after 20 h. Significantly, no oligomeric or polymeric products resulting from consecutive addition of unsaturated substrates were observed in any of the reactions. Therefore, while turnover levels are modest, increased reaction rates without loss of selectivity may be possible by increasing the pressure of ethylene or acetylene.

Initial rate kinetics indicate that the rate of formation of reduced catalyst is completely independent of ethylene or acetylene concentration, which is consistent with the mechanism established previously for $[W_{10}O_{32}]^{4-*}$/alkane systems involving rate-limiting H atom abstraction (eqs 5 and 6; $P_{red} = [W_{10}O_{32}]^{5-}$);[9,11]

$$P_{ox} \xrightarrow{h\nu} P_{ox}^{*} \tag{5}$$

$$P_{ox}^{*} + RH \xrightarrow{slow} P_{red} + R^{\bullet} + H^{+} \tag{6}$$

$$H^{+} + P_{red} + RCH_2CH_2^{\bullet} \rightarrow RCH_2CH_3 + P_{ox} \tag{7}$$

radical capture by alkene or alkyne (eq 3) is a fast subsequent step. Total yields of radical-derived organic products in reactions between cyclohexane and ethylene or acetylene were approximately 4 times greater than those in the absence of ethylene or acetylene. These values indicate an average radical chain length of 4 over the course of the addition reaction in the case of $[W_{10}O_{32}]^{4-}$. In addition to the termination processes previously discussed, short radical chains may result from chain termination by H atom donation accompanied by reoxidation of the catalyst (eq 7), which can compete effectively with the dominant chain-transfer step in conventional organic radical chain addition reactions (eq 4). The application of the title reactions to insoluble materials with surface C–H functions, in progress in our laboratory, will further address the complex termination chemistry in these photocatalytic addition reactions.

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[11] The reduced catalyst, upon equilibration, is a mixture of $[W_{10}O_{32}]^{5-}$ and $[W_{10}O_{32}]^{6-}$ (refs 9 and 10).

[12] Prosser-McCartha, C. M.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 3671.

[13] Products resulting from H· abstraction from CH_3CN were not observed. CH_3CN was previously shown to be relatively inert toward H· abstraction because the electron-withdrawing nitrile group disfavors any polar contribution to the transition state. See: Naguib, Y. M. A.; Steel, C.; Cohen, S. G.; Young, M. A. *J. Phys. Chem.* **1987**, *91*, 3033.

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