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Radical Carbonylation of Alkanes via Polyoxotungstate Photocatalysis

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The catalytic functionalization of alkanes remains a research area of intense interest because of the low cost and wide availability of these substrates, as well as the scientific challenges posed by selective C−H bond activation.[1−4] The photochemical carbonylation of alkanes and arenes (hydrocarbon + CO) to yield aldehydes has recently been achieved by both organometallic and radical type mechanisms. Carbonylation of benzene via organometallic intermediates using Rh(I) or Ir(I) catalysts under 1 atm of CO has produced up to 74 turnovers of benzaldehyde with modest chemoselectivity, but carbonylation of alkanes has resulted in lower turnover numbers and poor selectivity for the aldehyde products.[5−7] Goldman found that photolysis of aromatic ketones in the presence of an Ir(I) or Rh(I) cocatalyst and cyclohexane produced the carbonylated alkane via a hydrogen abstraction mechanism with up to 9.5 catalyst turnovers.[8,9] Crabtree has generated alkyl radicals via mercury photosensitization in the presence of CO to produce some aldehyde products (chemoselectivities <60%).[10] Recently we described the selective radical addition reaction of alkanes to ethylene and acetylene yielding ethylated and vinylated products, respectively.[11] These radical chain reactions were catalytically photoinitiated by soluble, stable polyoxotungstate (P_{ox}) complexes. We now report the selective radical carbonylation of alkanes under 1 atm of CO photocatalyzed by $Q_4[W_{10}O_{32}]$ and $Q_3[PW_{12}O_{40}]$ [Q = $(n\text{-Bu})_4N$] (see Figure 1) to give aldehydes, with turnover levels and selectivities that exceed those of previously reported systems.

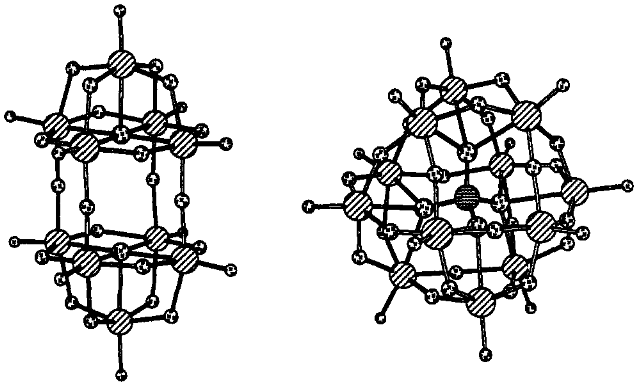
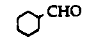
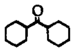
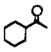
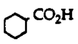
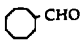
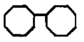
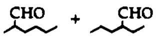
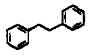


Figure 1. Ball and stick diagrams of the isopolytungstate, $[W_{10}O_{32}]^{4-}$, (left), and the heteropolytungstate, $[PW_{12}O_{40}]^{3-}$ (right): W and P, large circles; O, small circles.

Table 1. Organic Products from the Radical Addition of Alkanes to CO, Catalyzed by Polyoxotungstates[a]

substrate	catalyst	aldehyde; turnovers (selectivity[b])	other products; turnovers		
					
	$[W_{10}O_{32}]^{4-}$	54 (68)	4.1	2.7	c,d
		51 (93)[e]	c	c	c
	$[PW_{12}O_{40}]^{3-}$	3.6 (84)	c	c	0.7
					
	$[W_{10}O_{32}]^{4-}$	18 (69)	5.7		2.5
		12 (81)[e]	1.6		<1
	$[PW_{12}O_{40}]^{3-}$	1.8 (85)	c		c
			unidentified		
	$[W_{10}O_{32}]^{4-}$	12 (79)			
		-			
	$[W_{10}O_{32}]^{4-}$	c	2		

[a] Acetonitrile solutions of $[W_{10}O_{32}]^{4-}$ (0.75 mM) or $[PW_{12}O_{40}]^{3-}$ (1.5 mM) {cation = $[(n\text{-Bu})_4N]$} and alkane (0.5 M) were saturated with 1 atm of CO (~9 mM), magnetically stirred, and irradiated for 16 h using a 550-W medium-pressure Hg lamp with Pyrex filter ($\lambda > 280$ nm) at 25 °C. [b] [Moles of aldehyde/total moles of all organic products] × 100 as determined by GC using an internal standard. Identification of organic products was confirmed by GC/MS or by comparison to authentic samples. [c] Below detectable limit. [d] Less than 1 turnover of dicyclohexyl and cyclohexene was observed. [e] Benzene solvent {cation = $[(n\text{-heptyl})_4N]$}; solutions irradiated 24 h.

Results and experimental conditions for the carbonylation of cyclohexane, cyclooctane, and *n*-hexane in acetonitrile are reported in Table 1. The carbonylation of cyclohexane catalyzed by $Q_4[W_{10}O_{32}]$ was most facile, producing 54 turnovers in 16 h with a selectivity of 68% for the aldehyde product (8% overall yield). Other products formed in the reaction include dicyclohexyl ketone, cyclohexylmethyl ketone, and traces of dicyclohexyl and cyclohexene. In benzene solvent (Q = $[n\text{-heptyl}]_4N$), selectivity for cyclohexanecarboxaldehyde increased to 93% with 51 turnovers. Carbonylation of cyclooctane and *n*-hexane by $Q_4[W_{10}O_{32}]$ was slower, producing 18 and 12 turnovers, respectively, in 16 h in acetonitrile, but the aldehyde was the major product in each case. Reactions photoinitiated by the Keggin complex, $Q_3[PW_{12}O_{40}]$, were significantly slower than those using $Q_4[W_{10}O_{32}]$, as the latter complex absorbs more light and, in addition, exhibits higher quantum yields for attack on hydrocarbon than the Keggin complex under these conditions.[12,13] The selectivities for aldehydes in the $Q_3[PW_{12}O_{40}]$-catalyzed reactions were greater than 80% and were limited by overoxidation to the corresponding carboxylic acid.

Selective activation of the secondary over primary C−H bonds in *n*-hexane as well as the formation of the radical recombination products dicyclohexyl ketone and dicyclooctyl strongly supports a radical mechanism for the carbonylation reactions. As described in eqs 1−4, the photoexcited species P_{ox}^* abstracts a hydrogen atom from the alkane substrate, producing an alkyl radical and the protonated, reduced catalyst, $H^+[P_{red}]$.[12−15] The resulting alkyl radical is subsequently

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$$P_{ox} \xrightarrow{h\nu} P_{ox}^{*} \tag{1}$$

$$RH + P_{ox}^{*} \rightarrow R^{\bullet} + H^{+}[P_{red}] \tag{2}$$

$$R^{\bullet} + CO \rightleftharpoons R\dot{C}O \tag{3}$$

$$R\dot{C}O + RH \rightleftharpoons RCHO + R^{\bullet} \tag{4}$$

$$R\dot{C}O + H^{+}[P_{red}] \rightarrow RCHO + P_{ox} \tag{5}$$

trapped by CO, yielding an acyl radical (eq 3) in a reversible process ($\Delta H^\circ = -8$ kcal/mol).[10,16,17] The acyl radical is then converted to aldehyde either by an endothermic H$^\bullet$ abstraction ($\Delta H^\circ = \sim +8$ kcal/mol),[18] a chain-propagating step (eq 4), or by reductive H$^\bullet$ donation from $H^+[P_{red}]$, a chain-terminating step (eq 5). However, as ΔH° for the sum of eqs 3 and 4 is approximately 0 kcal/mol and $T\Delta S^\circ$ for the two steps is ~ -10 kcal/mol,[16] the radical chain process is strongly disfavored thermodynamically and cannot be a dominant pathway for aldehyde formation. Consequently, aldehyde must be formed via eq 5, in which the reduced catalyst is reoxidized to complete the catalytic cycle. The deep blue $H^+[P_{red}]$ ($\lambda_{max} = 630$ nm; $\epsilon = 11\,400$ M^{-1} cm^{-1}) forms rapidly at early times under the reaction conditions, allowing facile reduction of the acyl radical to give the aldehyde product (eq 5). Production of $H^+[P_{red}]$ slows at longer times, however, reaching a maximum of only 15% catalyst reduction after 2 h for cyclohexane substrate, while aldehyde formation continues unaffected.[19] The initial rate of formation of $H^+[P_{red}]$ (4.2×10^{-10} mol/s) is independent of the concentration of CO, consistent with H$^\bullet$ abstraction (eq 2) as the rate-determining step for the process. In addition the ratio of the initial rate of cyclohexanecarboxaldehyde formation (2.7×10^{-10} mol/s) to that of $H^+[P_{red}]$ formation is only 0.67, a further indication that a radical chain process is not the dominant mechanism.

Examination of the secondary products listed in Table 1 gives insight into the relative stabilities of the radical species described in the equilibrium in eq 3. The principal byproduct of cyclohexane carbonylation in acetonitrile is dicyclohexyl ketone, indicating that a relatively large amount of acyl radical is present which is able to couple with additional substrate-derived radical. In contrast, the primary byproducts of the cyclooctane carbonylation are the dimer, dicyclooctyl, and the disproportionation product, cyclooctene, suggesting that eq 3 lies more to the left, resulting in secondary products derived from cyclooctyl radicals. These observations are consistent with the lower bond dissociation energy of cyclooctane[18] and, hence, the greater stability of cyclooctyl radical with respect to cyclohexyl radical. The attempted carbonylation of toluene, for example, resulted in only the coupling product, bibenzyl, reflecting the well-known stability of the benzyl radical. The cyclohexylmethyl ketone formed in the cyclohexane reaction derives from reductive capture of the cyclohexyl radical by P_{red} and subsequent reaction with acetonitrile.[12,20]

Carbonylation rates and selectivities are quite high at early reaction times (25 turnovers in 90 min with 85% selectivity for cyclohexanecarboxaldehyde) and decrease gradually over the course of the reaction, reaching maximum aldehyde concentrations (~40 mM for CyCHO) after 12–20 h in acetonitrile, depending on the substrate. Initial rates of catalyst reduction are 3.8 times faster in acetonitrile than in benzene for cyclohexane substrate, but final turnover numbers are only slightly lower in benzene. Interestingly, selectivity for aldehyde product was significantly higher in the slower benzene reactions, although it is unclear whether this is directly related to the rate of catalyst reduction. Previously reported alkane carbonylation reactions were typically limited by catalyst attack on the aldehyde, since the aldehydic C–H bond is considerably more reactive than the alkane C–H bonds in both organometallic and radical-based systems.[7,8,10] When the carbonylation of cyclooctane in acetonitrile was carried out in the presence of 30 mM cyclohexanecarboxaldehyde in our system (0.75 mM $Q_4[W_{10}O_{32}]$), 9 turnovers of cyclohexane were formed in addition to 12 turnovers of cyclooctanecarboxaldehyde. Furthermore, when cyclohexane was replaced by cyclohexanecarboxaldehyde as a "substrate" under standard reaction conditions, initial rates of catalyst reduction increased by 4.3 in acetonitrile and 5.3 in benzene. Thus, decarbonylation of aldehyde products is facile and is clearly yield limiting under these conditions.

Efficient radical trapping of CO in synthetically useful reactions (from functionalized starting materials) has traditionally required high pressures as a consequence of the equilibrium in eq 3.[21,22] In contrast, the effective trapping of radicals by low-pressure CO in this work apparently results from the relatively efficient production of radicals by P_{ox}^*, coupled with the rapid trapping of the acyl radical by eq 5. $[W_{10}O_{32}]^{4-}$ was previously shown to be a considerably more efficient photoinitiator of alkane autoxidation than the conventional radical initiators azobis(isobutyronitrile) (AIBN) and benzoyl peroxide under photolytic conditions ($\lambda > 280$ nm).[23] Use of AIBN or benzoyl peroxide in place of $[W_{10}O_{32}]^{4-}$ under the carbonylation conditions listed in Table 1 in the presence of cyclohexane resulted in no formation of aldehyde. Control reactions without polyoxometalate produced no aldehyde in either solvent, and in addition, no benzaldehyde or aryl ketones, previously shown to be active H-abstraction photocatalysts,[8] were detected in any of the benzene reactions.

In contrast to previous solution phase alkane carbonylation reactions,[6–8] reaction rates and turnover numbers in this work are not limited by decomposition of the catalyst. Isolation of the $Q_4[W_{10}O_{32}]$ catalyst after reaction yielded a material that was unchanged by IR and UV–visible spectroscopy. We are now exploring techniques to continually separate the aldehyde from the reaction mixture in order to develop a high turnover system that maintains good product selectivity.

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[15] "P_{red}" rapidly disproportionates to $[W_{10}O_{32}]^{6-}$ and $[W_{10}O_{32}]^{4-}$ under these conditions.

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[19] $H^+[P_{red}]$ was monitored by UV–vis for a CO-saturated acetonitrile solution of $Q_4[W_{10}O_{32}]$ (1.0 mM) and cyclohexane (0.5 M) in a Schlenk quartz cuvette irradiated with a Xe lamp fitted with a 320-nm interference filter.

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