Homogeneous Catalytic Photochemical Functionalization of Alkanes by Polyoxometalates

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Progress in the last 5 years toward the activation and functionalization of alkanes, the most abundant but least reactive class of organic compounds, has been substantial.[1-7] Thorough investigations of several homogeneous liquid-phase systems for alkane activation or functionalization at 25 °C have now been reported. These include organometallic systems[3,4] that effect stoichiometric alkane C–H bond activation with unusual C–H cleavage selectivities (least hindered positions most reactive) and metalloporphyrin systems[6,7] that effect catalytic alkane functionalization with conventional C–H cleavage selectivites (tertiary C–H most reactive). We report here, as part of our continuing efforts to develop soluble metal oxide species as superior catalysts for energetic and synthetic transformations of interest,[8,9] a new methodology for the homogeneous liquid-phase activation and functionalization of alkanes. This chemistry involves the irradiation of heteropolytungstic acids and alkanes in acetonitrile solution. The heteropolytungstic acids, unlike all alkane-activating organometallic and metalloporphyrin species in the literature, contain no oxidizable organic structure. The very high oxidative stability of the soluble and completely inorganic polyoxometalates, recently documented for catalytic thermal epoxidation processes,[9]
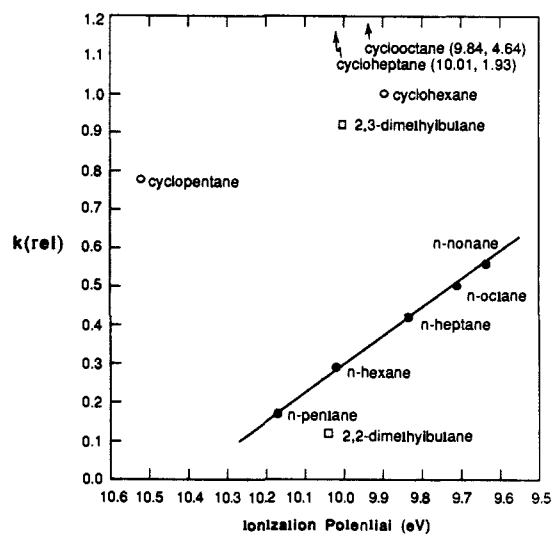

Figure 1. Plot of the relative reactivities ($k_{cyclohexane}$ = 1.00) vs. decreasing ionization potential for a variety of alkanes.[18] Normal alkanes (●), cycloalkanes (○), and branched alkanes (□). Only the normal alkanes show a linear correlation. Conditions for rate measurements: alkane 0.215 ± 0.001 M; catalyst, **1**, 3.384 mM; no Pt(0) or other hydrogen evolution catalyst present; irradiation by a 1000-W Xe lamp with $\lambda >$ 260 nm cutoff filter; temp = 22 °C. Data fit to the equation ln $(A_{\infty}/(A_{\infty} - A_{obsd}))$ = kt, where A_{obsd} is the absorption at λ_{max} for reduced **1** (740 nm); the A_{∞}, empirically determined, is 12.87. All reactions remained homogeneous at all times.

is now demonstrated for catalytic photochemical organic oxidation processes.

The charge-transfer excited states of a variety of polyoxomolybdates and polyoxotungstates, P_{ox}, accessible with UV or blue light are known to oxidize readily a variety of organic substrates usually resistant to homogeneous oxidizing conditions producing the well-characterized heteropoly blue complexes, P_{red} (eq 1 and 2).[8,10] When P_{ox} is a heteropolytungstic acid, such as H_3P-

$$P_{ox} + h\nu \rightarrow P_{ox}* \tag{1}$$

$$P_{ox}* + SH_2 \rightarrow P_{red} + S + 2H^+ \tag{2}$$

$$P_{red} + 2H^+ \rightarrow P_{ox} + H_2 \tag{3}$$

SH_2 = organic substrate =
alcohols, amides, ethers, many others.

$W_{12}O_{40}\cdot6H_2O$ (**1**), hydrogen evolution from the reduced form, P_{red}, is thermodynamically favorable and can be catalyzed by Pt(0) (eq 3).[8,10] Extensive screening revealed that only two common solvents, water and acetonitrile, are less reactive in these systems than the alkanes themselves; thus only these solvents can be used in this alkane functionalization chemistry. Under typical homogeneous reaction conditions (10.3 mmol of alkane, 0.030 mmol of **1**, and 2.0 mg of Pt(0) on carbon in 8.9 mL of acetonitrile under a rigorously anaerobic atmosphere (Ar), irradiated by a 1000-W Xe lamp using a Pyrex cutoff filter, $\lambda >$ 260 nm), alkane functionalization is not only achieved, but the products and other features of this chemistry are striking and distinct from those of the literature alkane activation systems cited above.

The following points pertain to this chemistry. (1) Different alkanes generate P_{red} at different rates and the early time dependence for the formation of P_{red} is consistent with loss of P_{ox}, **1**, by a first-order process. (2) Under pseudo-first-order conditions, the relative rates of production of P_{red} ($k_{cyclohexane}$ = 1.00) correlate to some extent with the ionization potential of the alkane (Figure 1). (3) The primary kinetic isotope effect $k(C_6H_{12})/k(C_6D_{12})$

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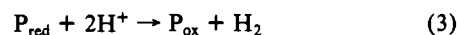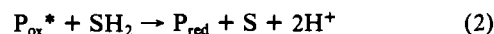
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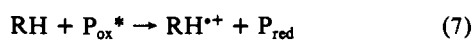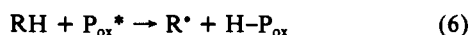
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is only 1.37 ± 0.03. (4) The principal products are methyl ketone, N-alkylacetamide, and alkene, and the product distributions vary greatly with the alkane structure. Substrates with tertiary C–H bonds produce alkene with very high selectivities ($\geq 90\%$) if the bond is adjacent to another tertiary C–H bond, N-alkylacetamide with very high selectivities ($\geq 90\%$) if the bond is adjacent only to primary centers, as in the case of isobutane (eq 4), and a mixture of products if the bond is adjacent to at least one secondary center. All substrates with only secondary C–H bonds (cycloalkanes) yield methyl ketone; in the case of cyclohexane, cyclohexyl methyl ketone (CMK) is the only major oxidation product detectable by GC and GC/MS analysis ($>90\%$ selectivity) (eq 5)! (5) Most alkanes give little if any alcohol or dimeric coupling products (RR).

NBA (4)

CMK (5)
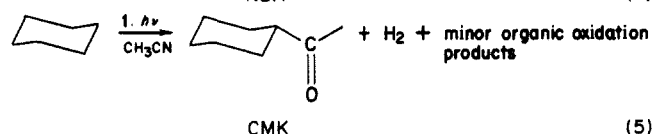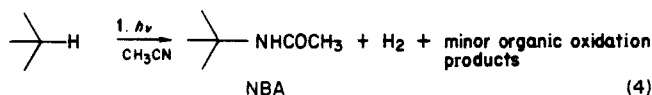
(6) For these processes, hydrogen, the only detectable reduction product, is generated in an amount approximately equal to the oxidizing equivalents represented by the organic products, providing a reasonable redox balance for the processes. (7) The quantum yields for the production of P_{red} by photooxidation of alkanes are quite high (~ 0.1 at 350 nm) for the most reactive alkanes, and several turnovers with respect to 1 can be achieved after several hours of irradiation with the light source noted above. (8) If the reactions are run in the presence of air, typical free-radical-chain autooxidation products (e.g., alkyl hydroperoxide, ketone, or alcohol, depending on the substrate) are produced at the expense of the other products.

The low and variable ratios for reaction at secondary vs. tertiary positions, the remarkable relative rates for the various cycloalkanes, and the very low primary kinetic isotope effect all argue against C–H bond activation by rate-determining hydrogen atom abstraction (eq 6). These lines of evidence coupled with the correlation of rates with ionization potential move us to propose that at least for the linear alkanes, the substrate activation process involves an initial electron transfer; rapid deprotonation of the cation radical then produces the radical (eq 7 and 8). Elec-

$$RH + P_{ox}{}^* \rightarrow R^\bullet + H\text{–}P_{ox} \qquad (6)$$

$$RH + P_{ox}{}^* \rightarrow RH^{\bullet+} + P_{red} \qquad (7)$$

$$RH^{\bullet+} \rightarrow R^\bullet + H^+ \qquad (8)$$

tron-transfer oxidation of strained alkanes by electrochemical methods and by photoexcited electron acceptors is well-known.[11] The most recent work on the stoichiometric oxidation of alkanes by Co^{III} and related species at elevated temperatures, however, suggests that these processes probably do not involve electron-transfer oxidation of the alkane.[12,13]

Whereas the regiochemistry is likely determined by eq 7 and 8, the actual functional groups produced are dictated by the fate of the radical, R$^\bullet$. The production of all three types of products, methyl ketone, N-alkylacetamide, and alkene, is compatible with alkyl radical intermediates. The generation of methyl ketones from alkanes (e.g., eq 5), an unprecedented process for saturated hydrocarbons, likely arises by reaction of alkyl radical with acetonitrile forming an iminium radical. Subsequent hydrolysis of the imine by the few equivalents of water present then yields ketone. In contrast, the production of N-alkylated acetamides

at tertiary positions (e.g., NBA in eq 4) is consistent only with nucleophilic capture of tertiary carbonium ion by acetonitrile followed by hydrolysis, a process analogous to the Ritter reaction. The rapid thermal oxidation of organic radicals by heteropoly-tungstates[14] as well as the production of N-alkylacetamides by electrooxidation of alkanes to carbonium ions in acetonitrile have both been reported.[15] Production of alkenes from alkyl radicals is a well-documented process.[16] In the systems reported here it is likely that alkyl radicals are generated from all alkanes but that subsequent oxidation of the radicals to the carbonium ions is important only for the readily oxidized tertiary radicals. Homogeneous alkane activation to produce radicals where only the tertiary radicals undergo subsequent oxidation to the carbonium ions competitive with capture is documented in two metalloporphyrin-based alkane functionalization systems.[6b,17]

Mechanistic and exploratory research on these new catalytic alkane functionalization processes is in progress.

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Mechanisms of Hemin-Catalyzed Oxidations: Rearrangements during the Epoxidation of *trans*-Cyclooctene

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The epoxidations of trichloroethylene,[3] styrenes,[4] and 1-phenyl-1-butenes[3b] are accompanied by hydride or chlorine migration to produce aldehydes and ketones, respectively. These results have been variously attributed to free-radical,[3] carbocation,[4] and metallooxetane[5] intermediates. We wish to report a he-

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