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Catalytic Carbon−Carbon and Carbon−Hydrogen Bond Cleavage in Lower Alkanes. Low-Temperature Hydroxylations and Hydroxycarbonylations with Dioxygen as the Oxidant

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Abstract: $RhCl_3$, in the presence of several equivalents of Cl^- and I^- ions, catalyzed the direct formation of methanol and acetic acid from methane, carbon monoxide, and dioxygen at 80−85 °C in a 6:1 mixture of perfluorobutyric acid and water (approximate turnover rate: 2.9/h based on Rh). It was possible to selectively form *either* methanol *or* acetic acid by a simple change in the solvent system. As might be anticipated, ethane was more reactive than methane, and under similar reaction conditions formed *methanol*, ethanol, and acetic acid (approximate turnover rate: 7.5/h based on Rh). For both methane and ethane, the product alcohols were *less* reactive than the starting alkanes. Methyl iodide was also *less* reactive than methane. *Most significantly, for ethane and higher alkanes products derived from C−C cleavage dominated over those derived from C−H cleavage on a per bond basis.* Indeed, C−C cleavage products were *virtually all* that were observed with butane, isopentane, and 2,3-dimethylbutane. While the mechanism of the C−H and C−C cleavage steps remains to be elucidated, preliminary indications are that outer-sphere electron transfer or bond homolysis resulting in the formation of alkyl radicals did not occur.

This report encompasses the highly catalytic, low temperature hydroxylations and hydroxycarbonylations of C−H and C−C bonds in lower alkanes with dioxygen as the oxidant.[1] The simultaneous cleavage of C−H and C−C bonds of alkanes, *as well as* O_2 activation, has been achieved. We are unaware of any report of such a highly catalytic system for the direct functionalization of methane and ethane by dioxygen at low to moderate temperatures (≤100 °C) although the use of other oxidants has been reported under these conditions.[2] Most significantly, our observations constitute the first examples of metal catalyzed oxidative functionalization of C−C bonds of simple alkanes in solution although several instances of C−C cleavage by metal complexes have been reported previously.[3]

The lower alkanes, such as methane and ethane, are the least reactive and most abundant of the hydrocarbon family with known reserves equal to that of petroleum.[4] Thus, the selective oxidative functionalization of these alkanes to more useful chemical products is of great practical interest.[5] For example, two of the highest volume functionalized organics produced commercially are methanol and acetic acid whose 1993 U.S. productions were 10.5×10^9 and 3.7×10^9 lbs, respectively.[6] The current technology for the conversion of alkanes to these products involves *multi-step* processes: (a) the high-temperature-steam reforming of alkanes to a mixture of H_2 and CO,[7] (b) the high-temperature conversion of the mixture of H_2 and CO to methanol,[7] and (c) the carbonylation of methanol to acetic acid,[8] mainly through the “Monsanto process”.[9] Clearly, the *direct*, low temperature conversion of the lower alkanes to methanol and acetic acid would be far more attractive from an economical standpoint. Of particular interest would be the formation of the *same* end product(s) from different starting alkanes, thus obviating the need to separate the alkanes. For example, natural gas is principally methane with 5−10% ethane. A system that converts both methane and ethane to the same C_1 product, such as methanol, would not require the prior separation of the alkanes. Of course, the formation of C_1 products from ethane and higher alkanes would require an *unprecedented* catalytic cleavage and oxidation of C−C bonds which we have now achieved. Additionally, catalytic C−C cleavage is the key step

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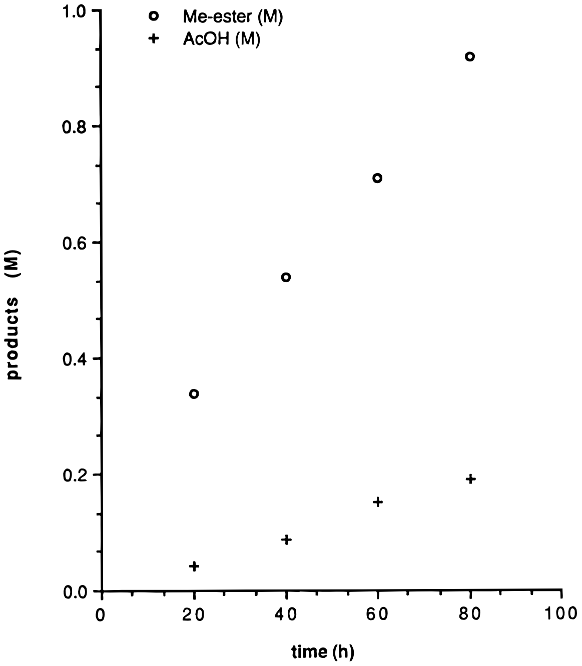

Figure 1. Plots of products formed from methane versus time. Reaction conditions: $RhCl_3{\cdot}3H_2O$ (5 mg, 0.005 M), KI (10 mg, 0.017 M), NaCl (15 mg, 0.073 M) in a 3.5 mL 6:1 (v/v) mixture of $C_3F_7CO_2H$ and D_2O, CH_4 (1000 psi), CO (300 psi), O_2 (100 psi), 80 °C. The reaction was run in a 125-mL stainless steel bomb equipped with a glass liner.

in petroleum cracking and a "one-pot" system for both cracking and subsequent oxidation of the light residues is of great interest in the context of the need for oxygenates in clean-burning gasoline.[10]

Results and Discussion

1. Catalyst. The catalyst system consists of $RhCl_3$ along with several equivalents of Cl^- and I^- ions dissolved in an acidic solvent, and the alkane functionalizations were carried out in the presence of O_2 and CO at 80−85 °C. The use of this system for the direct conversion of methane to acetic acid in aqueous medium was previously reported in a brief communication.[1]

2. Functionalization of Methane. The principal problem when water was used as the solvent was the low turnover rates (approximately 0.1 turnover/h based on Rh).[1] We now find that it is possible to both significantly increase the reaction rate and change the product specificity from acetic acid to methanol by the choice of appropriate solvents. Our results for the functionalization of methane in a 6:1 mixture (v/v) of perfluorobutyric acid and water as the solvent are summarized in Figure 1. Formic acid was the only significant byproduct observed. Starting with pure water as solvent, the reaction rate was found to increase steadily with increasing concentration of added perfluorobutyric acid. However, water was essential for the reaction since product formation was not observed in pure perfluorobutyric acid. For methane, when a 6:1 mixture (v/v) of perfluorobutyric acid and water was used as the solvent, the total concentration of acetic acid and methanol (and its ester) formed under reaction conditions similar to that used in pure water exceeded 1.1 M after the reaction was run for 80 h at 80 °C (approximate turnover rate: 2.9/h based on Rh). Along with an increase in rate, the product selectivity for methane functionalization was found to change from virtually all acetic acid to one in which the methanol derivative dominated. Since methyl perfluorobutyrate is both volatile and easily hydrolyzed back to the acid and methanol, it should be possible to design a system where the acid is recycled and methanol is the end product. With respect to product stability, control experiments using methanol (initial concentration: 0.45 M) and acetic acid (initial concentration 0.30 M) as substrates indicated that they were quite stable under the reaction conditions (14% of methanol reacted in 44 h; 5% of acetic acid reacted in 72 h). Furthermore, when $^{12}CH_4$ and ^{13}CO were employed, an analysis of the gas phase revealed only a trace of $^{12}CO_2$ ($^{13}CO_2$:$^{12}CO_2$ = 20). The relative rate of methane versus methanol oxidation *in the presence of the former* is given below.

A close examination of Figure 1 reveals that the methyl ester: acetic acid ratio decreased with time. One explanation for this trend would be that the methanol derivative was the initial product and that this was being carbonylated to acetic acid (the catalyst system consisting of a mixture of $RhCl_3$ and I^- ions resembles the "Monsanto system" for the carbonylation of methanol to acetic acid[9]). However, as in the aqueous system,[1] we were able to rule out this possibility through the following experiment. A 6:1 mixture (v/v) of perfluorobutyric acid and water was made 0.50 M in $^{13}CH_3OH$ (90% of which was converted to the methyl ester) and the methane functionalization reaction was run under conditions identical to those given in the caption of Figure 1. The products observed after 36 h were $C_3F_7CO_2{}^{12}CH_3$ + $^{12}CH_3OH$ (0.13 M), $^{12}CH_3CO_2H$ (0.22 M), $H^{12}CO_2H$ (0.02 M) and $C_3F_7CO_2{}^{13}CH_3$ + $^{13}CH_3OH$ (0.44 M), $H^{13}CO_2H$ (0.02 M). Clearly, methanol or its ester was *not* an intermediate in the formation of acetic acid from methane since no $^{13}CH_3CO_2H$ was formed. Note that at 1000 psi of pressure, the concentration of methane in pure water is 0.055 M. While the solubility of methane in a 6:1 mixture (v/v) of perfluorobutyric acid and water is expected to be higher, it is not likely to significantly exceed 0.5 M, the concentration of added $^{13}CH_3$-OH. Finally, the complementary labeling experiment was performed using 0.21 M $^{12}CH_3OH$ and 180 psi of $^{13}CH_4$, 100 psi of ^{12}CO, 50 psi of O_2, and 170 psi of N_2. After 18 h, the organic products observed in solution were $C_3F_7CO_2{}^{12}CH_3$ + $^{12}CH_3OH$ (0.21 M), $H^{12}CO_2H$ (0.05 M) and $C_3F_7CO_2{}^{13}CH_3$ + $^{13}CH_3OH$ (0.06 M), $^{13}CH_3CO_2H$ (0.01 M), $H^{13}CO_2H$ (0.04 M), thus confirming (a) that the products, methanol and acetic acid, were derived from methane and (b) that methane was significantly more reactive than methanol or its ester.

A second interesting result came out of the first of the two experiments described above that was run under standard conditions. There was a *switch* in product selectivity upon the addition of methanol to the solvent mixture: acetic acid rather than the methanol derivative was now the principal product and this was fully consistent with the gradual decrease in methyl ester:acetic acid ratio with time that is seen in Figure 1. Surmising that acetic acid became the favored product when perfluorobutyric acid present in the solvent mixture was converted to its ester, the methane functionalization was rerun in a solvent mixture in which part of the perfluorobutyric acid was replaced by 1,1,1,3,3,3-hexafluoro-2-propanol which would be expected to form an ester with the remaining acid. Indeed, acetic acid again became the predominant product. Thus, when a 4:2:1 (v/v/v) mixture of perfluorobutyric acid, 1,1,1,3,3,3-hexafluoro-2-propanol, and water was used as the solvent the products obtained after 34 h under the same conditions were $C_3F_7CO_2CH_3$ + CH_3OH (0.09 M), CH_3CO_2H (0.22 M), and HCO_2H (0.02 M).

While the detailed mechanism remains to be elucidated, the ratio of alcohol derivative to the corresponding higher acid may be assumed to be a function of the relative rates of nucleophilic attack versus carbon monoxide insertion into a common Rh−

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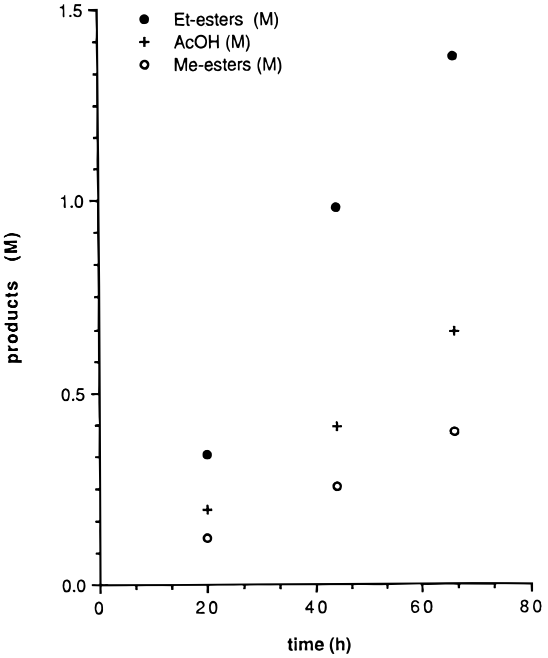
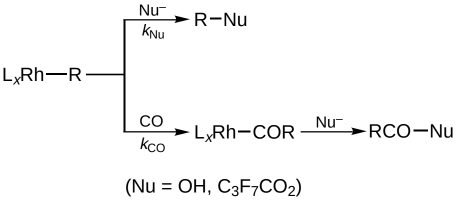


Figure 2. Plots of products formed from ethane versus time. Reaction conditions: $RhCl_3{\cdot}3H_2O$ (5 mg, 0.005 M), KI (10 mg, 0.017 M), NaCl (15 mg, 0.073 M) in a 3.5 mL 6:1 (v/v) mixture of $C_3F_7CO_2H$ and D_2O, C_2H_6 (550 psi), CO (150 psi), O_2 (50 psi), 80 °C. The reaction was run in a 125 mL stainless steel bomb equipped with a glass liner.

alkyl bond (i.e., k_{Nu}/k_{CO}, see eq 1). While, to a first-order approximation, k_{CO} is likely to be independent of the solvent, k_{Nu} will depend on the nature of the nucleophile derived from the solvent. Presumably, the perfluorobutyrate ion is a better nucleophile than water since more of the alcohol derivative was formed in a perfluorobutyric acid−water mixture than in pure water. This also explains why acetic acid was once again the major product when the perfluorobutyrate ion was tied up as the ester. In principle, nucleophiles stronger than the $C_3F_7CO_2^-$ ion should be able to compete with the latter when added to the reaction mixture. However, the addition of 7 equiv of acetate ion strongly retarded the reaction, *possibly* due to coordination to the metal center. In the same vein, the substitution of acetic acid for perfluorobutyric acid in the usual solvent mixture resulted in a drastic reduction in reaction rate (<10% of the original rate). Finally, consistent with the mechanistic scenario shown in eq 1 was also the observation that the ratio of acetic acid to methanol derivative formed from methane increased with increasing pressure of CO although the overall reaction was sharply inhibited at high CO pressures.



$$L_xRh{-}R \begin{cases} \xrightarrow[k_{Nu}]{Nu^-} R{-}Nu \\ \xrightarrow[k_{CO}]{CO} L_xRh{-}COR \xrightarrow{Nu^-} RCO{-}Nu \end{cases} \quad (Nu = OH,\ C_3F_7CO_2) \qquad (1)$$

3. Functionalization of Ethane. As might be anticipated, ethane was more reactive than methane and a higher reaction rate was observed for the conversion of ethane (Figure 2). Under similar reaction conditions, the total concentration of acetic acid, ethanol, and *methanol* (and their esters) exceeded 2.4 M after 66 h (approximate turnover rate: 7.5/h based on Rh).

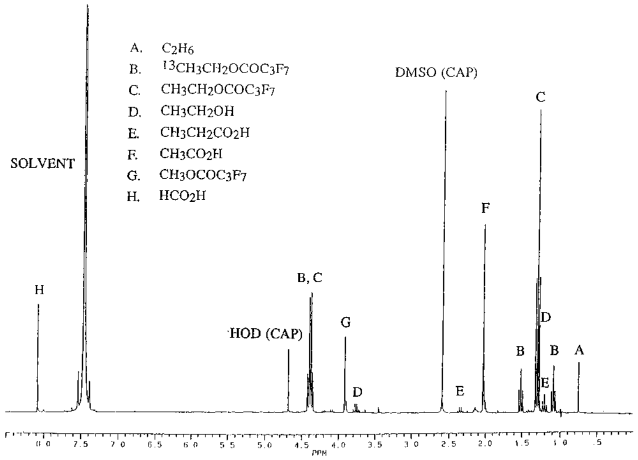


Figure 3. ^1H-NMR spectrum obtained after the following reaction conditions: $RhCl_3{\cdot}3H_2O$ (5 mg, 0.005 M), KI (10 mg, 0.017 M), NaCl (15 mg, 0.073 M), $^{13}CH_3CH_2OH$ (0.40 M) in a 3.5 mL 6:1 (v/v) mixture of $C_3F_7CO_2H$ and D_2O, C_2H_6 (550 psi), CO (150 psi), O_2 (75 psi), 80 °C, 20 h. A capillary containing a mixture of Me_2SO and D_2O was used as the internal standard.

Unlike methane, little hydroxycarbonylation was observed for ethane and higher alkanes. For example, no more than a trace of propionic acid was formed from ethane in a 6:1 mixture (v/v) of perfluorobutyric acid and water. The generally lower amount of hydroxycarbonylation observed for ethane may be due to a higher rate of nucleophilic attack on the $Rh{-}CH_2CH_3$ species when compared to the corresponding $Rh{-}CH_3$ species. This observation finds parallel in the rate of hydrolysis of the analogous Pt(IV) compounds $[Cl_5Pt{-}C_2H_5]^{2-}$ and $[Cl_5Pt{-}CH_3]^{2-}$, which can be synthesized through the reactions of $PtCl_4^{2-}$ with the corresponding alkyl iodide.[11] In pure water at ambient temperature, $[Cl_5Pt{-}C_2H_5]^{2-}$ was hydrolyzed within hours to ethanol whereas $[Cl_5Pt{-}CH_3]^{2-}$ was stable for days.

On a per bond basis, the ratio of products formed through C−H versus C−C cleavage of ethane was 0.6. Control experiments indicated that neither acetic acid nor ethanol was the source for the C_1 product, methanol. This is shown by the ^1H NMR spectrum obtained when both $^{13}CH_3{}^{12}CH_2OH$ (0.4 M) and $^{12}C_2H_6$ (550 psi) were present in the reaction mixture (Figure 3). Clearly, the labeled group of ethanol was *not* the source for either the methanol derivative or the acetic acid. Note that at 550 psi of pressure, the concentration of ethane in pure water is 0.03 M. While the solubility of ethane in a 6:1 mixture (v/v) of perfluorobutyric acid and water is expected to be higher, it is likely to be lower than 0.4 M, the concentration of added $^{13}CH_3{}^{12}CH_2OH$. In order to confirm that the observed methanol derivative was not formed in some way by CO hydrogenation, the ethane oxidation was repeated using $^{12}C_2H_6$ and ^{13}CO. No ^{13}C-containing organic products were observed except in acetic acid which was an approximate 4:1 mixture of $^{12}CH_3{}^{12}CO_2H$ and $^{12}CH_3{}^{13}CO_2H$. Thus, the experiment also confirmed that the majority of the acetic acid was derived from straightforward ethane oxidation rather than through C−C cleavage and carbonylation of a resultant $Rh{-}CH_3$ species. Interestingly, the results from the two labeling studies taken together showed that ethanol was not even an intermediate in the conversion of ethane to that fraction of acetic acid not formed via C−C cleavage. Finally, in order to conclusively demonstrate that ethane was indeed the source for methanol (and its ester), $^{13}C_2H_6$ was employed as the substrate (gas pressures: $^{13}C_2H_6$, 100 psi; CO, 200 psi; O_2, 100 psi; N_2, 800 psi) resulting in the exclusive formation of $C_3F_7CO_2{}^{13}CH_3 + {}^{13}CH_3OH$.

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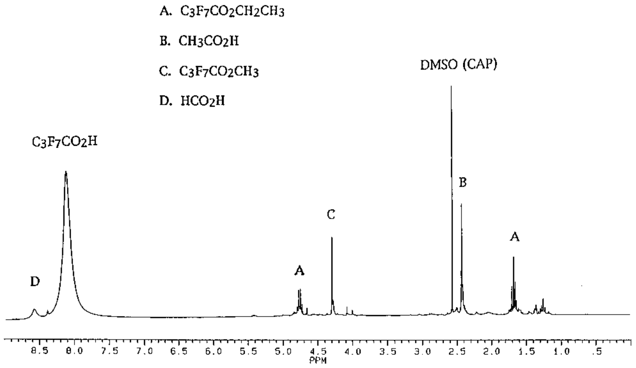

Figure 4. ^{1}H-NMR spectrum obtained after the following reaction conditions: $RhCl_3{\cdot}3H_2O$ (5 mg, 0.005 M), KI (10 mg, 0.017 M), NaCl (15 mg, 0.073 M), C_4H_{10} (5.6 mmol) in a 3.5 mL 6:1 (v/v) mixture of $C_3F_7CO_2H$ and D_2O, CO (300 psi), O_2 (100 psi), N_2 (800 psi), 90 °C, 66 h. A capillary containing a mixture of Me_2SO and D_2O was used as the internal standard.

The C−C cleavage of ethane was also observed when pure water was used as the solvent. For example, an approximate 3:1 mixture of $^{13}CH_3{}^{13}CO_2H$ and $^{13}CH_3{}^{12}CO_2H$ was also formed in water starting with $^{13}C_2H_6$, ^{12}CO, and O_2 (gas pressures: $^{13}C_2H_6$, 100 psi; CO, 200 psi; O_2, 100 psi; N_2, 600 psi). The complementary experiment with $^{12}C_2H_6$, ^{13}CO, and O_2 gave a 3:1 mixture of $^{12}CH_3{}^{12}CO_2H$ and $^{12}CH_3{}^{13}CO_2H$.

4. Functionalization of Higher Alkanes. When propane was used as the substrate, a mixture of *n*- and isopropyl esters and acetone were formed with a 5:1 preference for attack on the secondary C−H bond (on a per hydrogen basis). Thus, the reaction rate increased with decreasing C−H bond dissociation energy. In addition, significant quantities of acetic acid, ethanol, and methanol derivatives were formed through C−C cleavage.

A particularly striking example of catalytic C−C functionalization was obtained with *n*-butane. As shown in Figure 4, *virtually all* the products were derived through C−C cleavage! Especially noteworthy was the formation of ethanol derivative. Starting with 0.61 mmol of butane, the organic products observed after 20 h were $C_3F_7CO_2CH_2CH_3 + CH_3CH_2OH$ (0.18 mmol), CH_3CO_2H (0.34 mmol), CH_3CHO (0.04 mmol), $C_3F_7CO_2CH_3 + CH_3OH$ (0.17 mmol), HCO_2H (0.63 mmol), along with unreacted *n*-butane (0.05 mmol). The overall yield was 85.0% based on carbon content of *n*-butane. Note that the butane concentration was much higher for the reaction shown in Figure 4 and resulted in a slightly different product distribution. Finally, control experiments indicated that, like ethane, neither 1- or 2-butanol was the source of ethanol in the above reaction.

As with butane, products derived from C−C cleavage were *virtually all* that were observed with 2-methylbutane (isopentane). Starting with 0.42 mmol of substrate, the organic products observed after 20 h were $C_3F_7CO_2CH(CH_3)_2 + (CH_3)_2CHOH$ (0.03 mmol), $(CH_3)_2CO$ (0.07 mmol), $C_3F_7CO_2CH_2CH_3 + CH_3CH_2OH$ (0.07 mmol), CH_3CO_2H (0.20 mmol), $C_3F_7CO_2CH_3 + CH_3OH$ (0.14 mmol), HCO_2H (0.50 mmol), along with unreacted alkane (0.04 mmol). The overall yield was 87.2% based on carbon content of 2-methylbutane.

Finally, the hindered C−C bond of 2,3-dimethylbutane was also cleaved by the present system. Starting with 1.16 mmol of substrate, the organic products observed after 40 h were $C_3F_7CO_2CH(CH_3)_2 + (CH_3)_2CHOH$ (0.12 mmol), $(CH_3)_2CO$ (0.41 mmol), CH_3CO_2H (0.31 mmol), $C_3F_7CO_2CH_3 + CH_3OH$ (0.03 mmol), and HCO_2H (0.48 mmol). The overall yield was 40.0% based on carbon content of 2,3-dimethylbutane.

5. Mechanistic Considerations. The most significant aspect of the work described above is the observation of alkane C−C cleavage. Two reasons are usually cited for the general lack of C−C cleavage compared to corresponding C−H cleavage in reactions mediated by metal complexes in solution.[12] First, C−C bonds are sterically less accessible to transition metal centers surrounded by bulky ligands. Second, metal−carbon bonds tend to be weaker than metal−hydrogen bonds, again due to steric repulsions between the ligands surrounding the metal and the alkyl group bound to it. C−C cleavage is, however, commonly observed in the interaction of bare metal cations with alkanes.[13] In this case, there is no steric hindrance and the metal−carbon and metal−hydrogen bond strengths are comparable (approximately 60 kcal/mol).[13a,b,14]

Before a case is made for the cleavage of C−C and C−H bonds mediated by the metal center in the present instance, it is necessary to rule out alternative pathways. The possibility that a variation of oxychlorination[15] may be occurring in the gas phase (eq. 2) can be ruled out by the following experiment. The reaction involving methane was run in the absence of dissolved Rh salt, but in the presence of O_2, the promoters (KI, NaCl), *and* a large excess of dissolved Cl_2 (the solvent was saturated with Cl_2 prior to reaction). Such a reaction condition would be particularly favorable for oxychlorination since all the ingredients (Cl_2, HCl, and O_2) were present. No product formation was observed. Also note that in view of the inertness of CH_3I (see below) it is most unlikely that CH_3Cl, if formed, would convert to the observed products. Finally, simple alkyl radicals do not undergo C−C cleavage reactions.

$$2CH_4 + Cl_2 + {}^1\!/_2O_2 \rightarrow 2CH_3Cl + H_2O \qquad (2)$$

Another possibility is that a radical cation may form from the alkane by outer-sphere electron transfer and this species, in turn, would fragment some of the time by C−C cleavage (cf eq 3). For example, the 1e$^-$ oxidation of ethane leads to a

$$\begin{tikzcd}
C_2H_6 \arrow[r, "-e^-"] & {[C_2H_6^{\bullet+}]} \arrow[r, "-H^+"] \arrow[d] & C_2H_5^{\bullet} \arrow[r] & C_2\text{-products} \\
& CH_3^+ + CH_3^{\bullet} \arrow[r] & C_1\text{-products} &
\end{tikzcd} \qquad (3)$$

substantial weakening of the C−C bond (from 90 to 45−37 kcal/mol) resulting in fragmentation to $CH_3^{\bullet} + CH_3^+$.[16] The direct experimental precedent for such a step is Olah's observation of CH_3NO_2 as the principal product in the reaction of ethane with $NO_2^+PF_6^-$ in aprotic solvents (although the products may also arise from the direct attack of the electrophile on the C−C bond).[17] Additionally, we have shown that in 98% sulfuric acid, a variety of 1e$^-$ and 2e$^-$ oxidants will oxidize ethane to a mixture of C_1 and C_2 derivatives through a similar electron transfer pathway at 180°C.[18]

Several observations appear to rule out the involvement of free radicals formed by simple bond homolysis that would

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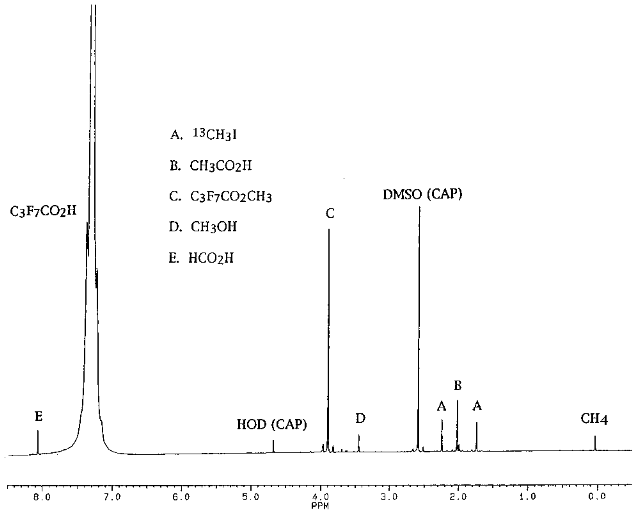

Figure 5. ^{1}H-NMR spectrum obtained after the following reaction conditions: $RhCl_3{\cdot}3H_2O$ (5 mg, 0.005 M), KI (10 mg, 0.017 M), NaCl (15 mg, 0.073 M), $^{13}CH_3I$ (0.22 M) in a 3.5 mL 6:1 (v/v) mixture of $C_3F_7CO_2H$ and D_2O, CH_4 (1000 psi), CO (300 psi), O_2 (100 psi), 80 °C, 20 h. A capillary containing a mixture of Me_2SO and D_2O was used as the internal standard.

follow electron transfer from the alkane. First, when the methane functionalization reaction was run under conditions identical to that shown in Figure 1 except that the reaction mixture was 0.22 M in $^{13}CH_3I$, the products observed were $C_3F_7CO_2{}^{12}CH_3$ + $^{12}CH_3OH$ ($^{13}CH_3I$ remained unchanged) (Figure 5), i.e., the significantly stronger CH_3-H bond (105 kcal/mol[19a]) was being broken in preference to the weak CH_3-I bond (57 kcal/mol[19a]); the ionization potential of CH_3I is also significantly lower than that of methane (9.5 vs 11.5 eV[19b]). The unusual reactivity pattern was further confirmed by the complementary labeling experiment involving $^{12}CH_3I$ and $^{13}CH_4$ which resulted in the formation of $C_3F_7CO_2{}^{13}CH_3$ + $^{13}CH_3OH$ only. Second, in the reaction run in the presence of $^{13}CH_3OH$ (vide supra), 0.21 mmol of $^{13}CH_3OH$ was oxidized at the same time as 1.23 mmol of $^{12}CH_4$ was converted to $C_3F_7CO_2{}^{12}CH_3$ + $^{12}CH_3OH$ + $^{12}CH_3CO_2H$. Thus, methane was *at least 5 times more reactive* than methanol and its derivative (note that an even higher selectivity for methane oxidation was observed in the reaction involving $^{13}CH_4$ and $^{12}CH_3OH$) although the homolytic C−H bond energy in the latter is 10 kcal/mol *lower*. However, this does not take into account the increase in the C−H bond energy when methanol is converted to the ester (the following C−H bond-energy data illustrate the point: $H-CH_2OH$, 94 kcal/mol; $H-CH_2OCOC_6H_5$, 100.2 kcal/mol[19c]). Finally, using a 1:1 mixture of C_2H_6 and C_2D_6 (250 psi each), a primary isotope effect (k_H/k_D) of 2.65(5) was observed for the formation of ethyl heptafluorobutyrate. This is inconsistent with the mechanism shown in eq 3 since electron transfer, which is expected to be the rate-limiting step, should exhibit only a very modest secondary isotope effect. Thus direct C−H bond cleavage within the coordination sphere of the metal is indicated. It should be noted that, due to the presence of excess I^- ions in the system, it is possible to have neither a radical more reactive than $I^{\bullet}$ nor an oxidant stronger than I_2. Since neither of these species is capable of reacting with methane, this provides additional support that the alkane functionalization is occurring within the coordination sphere of the metal.

In order to further delineate the reaction pathway followed by an 1e$^-$ oxidant/H-atom abstractor under the present reaction conditions, we examined the reaction of $S_2O_8^{2-}$ with methane and ethane. We had earlier demonstrated that in pure water, $S_2O_8^{2-}$ functionalized these alkanes through a hydrogen-abstraction step resulting in the formation of the corresponding alkyl radical as the intermediate (eq 4).[20] Additionally, we have shown that at 180 °C in 98% sulfuric acid, the $S_2O_8^{2-}$ ion will oxidize ethane to a mixture of C_1 and C_2 derivatives through an electron transfer pathway.[18] However, under the reaction conditions shown in Figure 1 except with $K_2S_2O_8$ replacing the Rh-based catalyst system, no product was formed from methane after 20 h. When ethane was used as the substrate (gas pressures: C_2H_6, 550 psi; CO, 150 psi; O_2, 50 psi), the following products were observed after 48 h: CH_3CO_2H (0.01 mmol), CH_3CHO (0.15 mmol), $HOCH_2CH_2OH$ and its mono- and diesters (0.13 mmol). Ethene, presumably formed by the deprotonation of the ethyl cation (see eq 4), may be an intermediate in the formation of the diol and its derivatives. This was demonstrated by replacing ethane by ethene (550 psi) in the above reaction, resulting in the formation of 0.71 mmol of $HOCH_2CH_2OH$ and its mono- and diesters in 20 h.

$$S_2O_8^{2-} \rightarrow SO_4^{\bullet -}$$

$$C_2H_6 \xrightarrow{SO_4^{\bullet -}} C_2H_6^{\bullet} \xrightarrow{SO_4^{\bullet -}} C_2H_5^{+} \overset{-H^+}{\rightleftharpoons} CH_2{=}CH_2 \rightarrow C_2\text{-products} \qquad (4)$$

A comparison of the reactivity pattern of the Rh-based catalyst system with that of $K_2S_2O_8$ further supports the proposition that the former does not simply function as an 1e$^-$ oxidant or a H-atom abstractor vis-a-vis alkanes. Clearly further studies are needed to elucidate the nature of the C−H and C−C cleavage steps. One should note that none of the experiments *establish* that the metal center is directly responsible for C−C cleavage. It is possible, for example, that the metal ion forms an alkyl species through C−H activation and that the C−C cleavage products are formed through a subsequent β-alkyl abstraction step. Such a sequence of steps has been reported in the reactions of bare metal cations with alkanes.[21] Still another possibility is that a metal alkoxide is formed initially from the alkane through a nonradical pathway and that a subsequent bond homolysis generates the alkoxy radical which then undergoes known fragmentations through C−C cleavage;[22] the fact that alcohols are unreactive in our system (see above) does not necessarily rule out this scenario.

The role of carbon monoxide in the rhodium-catalyzed alkane functionalizations is curious. Without CO there was no reaction even when the product was simply an alcohol derivative and, therefore, CO was not required by stoichiometry. One role of CO may simply be to serve as a stabilizing ligand, especially for Rh(I). Indeed, Rh(I) carbonyl complexes are formed under the reaction conditions.[1] However, it is likely that there is a second, more important, role of CO in the system. CO is also an essential reagent in a metallic palladium-catalyzed system for alkane functionalization that we reported earlier.[23] Our studies on that system showed that CO participates in the water-gas shift reaction to generate H_2 (together with CO_2) which, in turn, reacts with O_2 to form H_2O_2, the real oxidant involved in alkane functionalization. It is tempting to postulate a similar

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role for CO in the present rhodium-based system. Indeed, Rh salts in the presence of I^- ion as promoter have been shown to be active catalysts for the water-gas shift reaction.[24] Moreover, as with the metallic palladium based system, alkane functionalization does not occur if water is absent from the solvent mixture. Additionally, we observed the conversion CO to CO_2 in parallel with the alkane functionalization (see section 2 above). However, H_2O_2, if formed subsequent to the water-gas shift reaction, would be expected to react rapidly with the added I^- ions to generate I_2, a species that is thermodynamically not competent to react with methane or ethane. Nevertheless, we examined the effect of replacing O_2 in our system with a number of O-atom donor oxidants, such as H_2O_2, *m*-ClC_6H_4-COOOH, C_6H_5IO, and IO_4^-, both in the presence and absence of CO. In no case was product formation observed from methane. The role of CO must, therefore, await a more detailed analysis of the system.

6. Comparison with the Monsanto System. Finally, it is instructive to compare our reaction rates with that in the "Monsanto system" for the carbonylation of methanol—the currently preferred commercial process for the manufacture of acetic acid.[8,9] In a 6:1 mixture (v/v) of perfluorobutyric acid and water the rate of formation of acetic acid + methanol from methane was 3.2×10^{-4} M/min at 80 °C. In the Monsanto process, the rate of formation of acetic acid from methanol is 384×10^{-4} M/min at 180 °C.[25] Thus, the rate is 120 times faster in the latter system. However, the substrate concentration in the Monsanto system is typically 5 M. On the other hand, at the 1000 psi pressure that we employ, the aqueous concentration of methane is approximately 0.05 M. *If* the solution concentrations (more precisely, the activities) of methane in a 6:1 mixture (v/v) of perfluorobutyric acid and water are similar, then under similar substrate concentrations our rate of methane conversion is *comparable* to the rate of methanol conversion in the Monsanto system (this does not take into account the much higher reaction temperature employed for the latter).

Conclusion

We have discovered the first *catalytic* system that simultaneously cleaves C−H and C−C bonds of simple alkanes, as well as activates dioxygen, under mild conditions. For most of the alkanes studied, products derived from C−C cleavage dominated over those derived from C−H cleavage on a per bond basis. While the mechanism of the C−H and C−C cleavage steps remains to be elucidated, *preliminary* indications are that outer-sphere electron transfer or bond homolysis resulting in the formation of alkyl radicals does not occur.

A curious aspect of the previous metallic Pd[23] and now the homogeneous Rh-based systems is that, apart from their ability to activate both dioxygen and the alkane, both require a coreductant (carbon monoxide). Thus, there is a striking resemblance with monooxygenases.[26] In nature, while the dioxygenases utilize the dioxygen molecule more efficiently, it is the monooxygenases that carry out "difficult" oxidations, such as alkane oxidations. In the latter, one of the two oxygen atoms of dioxygen is reduced to water in a highly thermodynamically favorable reaction and the free energy gained thereby is employed to generate a high-energy oxygen species, such as a metal−oxo complex, from the second oxygen atom (eq 5).[26] The "Gif" system of Barton is also designed on this premise.[27] In at least the metallic Pd-based system,[23] the coreductant, carbon monoxide, is employed to generate dihydrogen (eq 6), the latter being formally equivalent to $2H^+ + 2e^-$ that is employed in the biological systems (cf eqs 5 and 7).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O + [O] \tag{5}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

$$O_2 + H_2 \rightarrow H_2O + [O] \tag{7}$$

How general is this requirement for a coreductant (e.g., CO or H_2) in achieving "difficult" catalytic hydrocarbon oxidations by dioxygen? Our work has provided two examples of catalytic systems, one homogeneous (this report) and the other heterogeneous,[23] that operate in this manner (i.e., as monooxygenase analogs). There have been other recent publications on catalytic systems for the oxidation of hydrocarbons, including olefins and aromatics, that also call for either CO or H_2 as the coreductant.[28] While, from a practical standpoint, it is more desirable for both oxygen atoms of O_2 to be used for substrate oxidation, there appears to be no known catalytic system that operates as an artificial "dioxygenase" under mild conditions toward "difficult" substrates, such as those possessing unactivated primary C−H bonds.

Experimental Section

General. The following chemicals were used as received: $RhCl_3 \cdot 3H_2O$ (Johnson Matthey); NaCl, KI, $^{13}CH_3I$, isopentane, 2,3-dimethylbutane (Aldrich); $K_2S_2O_8$ (Fisher Scientific Co); methane, ethane, propane, *n*-butane, nitrogen, oxygen, and carbon monoxide (Matheson); D_2O, ^{13}CO, $^{13}C_2H_6$, and C_2D_6 (Isotec, Inc.); and $^{13}CH_4$ (Cambridge Isotopes). Reactions under pressure were carried out in Parr general purpose bombs using glass liners. ^{1}H-NMR spectra were recorded on a Brucker AM 300 FT-NMR spectrometer using solvent resonance at the appropriate frequency or an external standard consisting of a capillary tube containing 1 μL of DMSO in 60 μL of D_2O for lock, reference, and as an integration standard. GC-MS was performed using a combination of Carls ERBA gas chromatograph equipped with a J & W Scientific DBS column (60 m × 0.255 mm) and a Kratos MS-25 mass spectrometer. In all cases, the products were identified by ^{1}H-NMR spectroscopy and confirmed by GC/MS and/or by comparison with authentic samples. The points in Figures 1 and 2 were generated by running a reaction for a certain time period, depressurizing, examining the reaction mixture by NMR spectroscopy, adding the reaction mixture back to the reactor, and resuming the reaction for the next time period.

Caution: Appropriate precautions should be taken while working with gases under high pressures. Particular attention should be paid to flammability limits of gas mixtures.

1. Functionalization of Alkanes with a Rhodium-Based Catalyst System. (a) Functionalization of Methane. $RhCl_3 \cdot 3H_2O$ (5.0 mg, 0.02 mmol), KI (10.0 mg, 0.06 mmol), and NaCl (15 mg, 0.26 mmol) were dissolved in 0.5 mL of D_2O in a glass container, 3 mL of C_3F_7-CO_2H was then added slowly, and a brownish mixture was formed. The glass container was placed in a high-pressure bomb which was then sealed. The bomb was purged and pressurized to 300 psi with CO, to 1300 psi with CH_4, then to 1400 psi with O_2. The contents were stirred at 80−85 °C for a certain time period. After venting, the products were examined by ^{1}H-NMR spectroscopy.

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(b) Functionalization of Methane in the Presence of CH_3I. The reaction was conducted as described above, except that 48 μL of $^{13}CH_3I$ (0.75 mmol) was added to the reaction mixture. The products formed were $^{12}CH_3OH$ and its ester (0.700 mmol), $^{12}CH_3{}^{12}CO_2H$ (0.140 mmol), $H^{12}CO_2H$(0.21 mmol), along with a trace of $^{13}CH_3CO_2H$.

In the reverse labeling experiment, 9 μL of $^{12}CH_3I$ (0.145 mmol) containing $^{12}CH_3OH$ (0.0026 mmol) was added to 1 mL of the reaction mixture. The bomb was then purged and pressurized to 250 psi with $^{13}CH_4$, to 350 psi with CO, to 450 psi with N_2, then to 500 psi with O_2. At the end of 18 h, 0.004 mmol of $^{13}CH_3OH$ and its ester were the only significant products observed; there was virtually no change in the amount of $^{12}CH_3OH$ and its ester (0.0023 mmol) that was present initially.

(c) Functionalization of Methane in the Presence of CH_3OH. The reaction was conducted as described in procedure (b), except that 73 μL of $^{13}CH_3OH$ (1.75 mmol) was added to the reaction mixture instead of $^{13}CH_3I$. The products observed were $^{12}CH_3OH$ and ester (0.46 mmol), $^{12}CH_3CO_2H$ (0.77 mmol), $H^{12}CO_2H$ (0.07 mmol), $^{13}CH_3OH$ and ester (1.54 mmol), and $H^{13}CO_2H$ (0.07 mmol).

In the reverse labeling experiment, 8.4 μL of $^{12}CH_3OH$ (0.21 mmol) was added to 1 mL of the reaction mixture. The bomb was then purged and pressurized to 180 psi with $^{13}CH_4$, to 280 psi with CO, to 450 psi with N_2, then to 500 psi with O_2. After 18 h, the organic products observed in solution were $^{12}CH_3OH$ and ester (0.21 M), $H^{12}CO_2H$ (0.05 M) and $^{13}CH_3OH$ and ester (0.06 M), $^{13}CH_3CO_2H$ (0.01 M), and $H^{13}CO_2H$ (0.04 M).

(d) Functionalization of Ethane. The reaction was conducted as described in procedure (a) except that 150 psi of CO, 550 psi of C_2H_6, and 50 psi of O_2 were added into the bomb.

(e) Functionalization of Ethane in the Presence of $^{13}CH_3CH_2OH$. $RhCl_3 \cdot 3H_2O$ (5.0 mg, 0.02 mmol), KI (10.0 mg, 0.06 mmol), NaCl (15 mg, 0.26 mmol), and $^{13}CH_3CH_2OH$ (80 μL, 1.4 mmol) were dissolved in 0.5 mL of D_2O in a glass container, and 3 mL of $C_3F_7CO_2H$ was then added slowly to the mixture. The glass container was placed in a high-pressure bomb which was then sealed. The bomb was pressurized to 500 psi with CH_3CH_3, to 700 psi with CO, to 1200 psi with N_2, to 1300 psi with O_2. The contents were stirred at 80−85 °C for 24 h. The products formed were $^{12}CH_3CO_2H$ (0.74 mmol), $^{12}CH_3CH_2OH$ (0.64 mmol), $^{12}CH_3OH$ and ester (0.15 mmol), and HCO_2H (2 mmol).

(f) Functionalization of *n*-Butane. The reaction was conducted as described in procedure (a), except that *n*-butane was bubbled through the solution in the glass container for 10 min following which the solution concentration of *n*-butane in the solution was measured by ^{1}H-NMR spectroscopy (0.173 M, 0.61 mmol). After the bomb was sealed, the contents were stirred under 300 psi of CO, 800 psi of N_2, and 100 psi of O_2 at 85 °C for 20 h. The products formed were CH_3CH_2OH and ester (0.18 mmol), CH_3CO_2H (0.34 mmol), CH_3CHO (0.04 mmol), CH_3OH and ester (0.17 mmol), HCO_2H (0.63 mmol), along with unreacted *n*-butane (0.05 mmol). The yield was 85.0% based on carbon content of butane.

(g) Functionalization of *n*-Butane under ^{13}CO. The reaction was conducted as described in procedure (f), except that 300 psi of ^{13}CO was used instead of ^{12}CO. Only ^{12}C-containing products were formed.

(h) Functionalization of Isopentane. The reaction was conducted as described in procedure (f), except that 0.420 mmol (0.120 M) of isopentane was used instead of *n*-butane. The products formed were 2-propanol and ester (0.03 mmol), CH_3COCH_3 (0.07 mmol), CH_3CH_2OH and ester (0.07 mmol), CH_3CO_2H (0.20 mmol), CH_3OH and ester (0.14 mmol), HCO_2H (0.50 mmol), along with unreacted isopentane (0.039 mmol). The yield was 87.2% based on carbon content of isopentane.

(i) Functionalization of 2,3-Dimethylbutane. The reaction was conducted as described in procedure (f), except that 1.16 mmol (0.330 M) of 2,3-dimethylbutane was used instead of *n*-butane. The organic products observed after 40 h were 2-propanol and ester (0.12 mmol), $(CH_3)_2CO$ (0.41 mmol), CH_3CO_2H (0.31 mmol), CH_3OH and ester (0.03 mmol), and HCO_2H (0.48 mmol). The overall yield was 40.0% based on carbon content of 2,3-dimethylbutane.

2. Functionalization of Alkanes with $K_2S_2O_8$. (a) Functionalization of methane. The reaction was conducted as described in procedure (a) in section 1, except that 272 mg of $K_2S_2O_8$ (1.0 mmol) was used instead of $RhCl_3 \cdot 3H_2O$ and its promoters. No product formation was observed after 20 h.

(b) Functionalization of Ethane. The reaction was conducted as described in procedure (a), except that 150 psi of CO, 550 psi of C_2H_6, and 50 psi of O_2 were added to the bomb and the reaction was carried out at 85 °C for 48 h. The products formed were CH_3CO_2H (0.01 mmol), CH_3CHO (0.15 mmol), and $HOCH_2CH_2OH$ and its mono- and diesters (0.13 mmol).

(c) Functionalization of Ethene. The reaction was conducted as described in procedure (b), except that 550 psi of ethene was used instead of ethane and the reaction was carried at 85 °C for 20 h. The products formed were $HOCH_2CH_2OH$ and its mono- and diesters (0.71 mmol).

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