A Highly Catalytic Bimetallic System for the Low-Temperature Selective Oxidation of Methane and Lower Alkanes with Dioxygen as the Oxidant

Minren Lin, Terrence Hogan, and Ayusman Sen*

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received December 20, 1996[⊗]

Abstract: This report describes a highly catalytic bimetallic system for the low temperature selective oxidation of methane, ethane, and butane with dioxygen as the oxidant. The catalytic system consists of a mixture of copper chloride and metallic palladium and operates in a 3:1 mixture (v/v) of trifluoroacetic acid and water in the presence of dioxygen and carbon monoxide. Methane was selectively converted to methanol. The dependence of the reaction rate on the partial pressure of methane was measured, and saturation kinetics was observed. The dependence of the rate on the partial pressure of carbon monoxide was measured at two different pressures of methane, and a first-order dependence on the partial pressure of carbon monoxide was observed in both instances. The activation parameters for the overall reaction were obtained under the reaction conditions when the rate was first order in both methane and carbon monoxide. The values obtained were $A = 2 \times 10^4$ s^{-1} and $E_a = 15.3$ kcal mol^{-1}. Both C−H and C−C cleavage products were observed for ethane and *n*-butane, resulting in the formation of methanol, ethanol, and acetic acid. The rate of formation of methanol from methane with the bimetallic system was ca. 65×10^{-4} M/min at 145−150 °C. This rate may be compared to the rate of formation of acetic acid from methanol in the benchmark Monsanto process: 380×10^{-4} M/min at 180 °C.

Methane is the least reactive and the most abundant member of the hydrocarbon family. Ethane comes second in both categories. Together, their known reserves equal that of petroleum.[1] Thus, the selective oxidative functionalization of these alkanes to more useful chemical products is of great practical interest.[2] For example, one of the highest volume functionalized organics produced commercially is methanol whose 1995 U.S. production was 11.3×10^9 lbs.[3] The current technology for the conversion of alkanes to methanol involves a ***multi-step*** process:[4] (a) the high temperature steam reforming of alkanes to a mixture of H$_2$ and CO and (b) the high temperature conversion of the mixture of H$_2$ and CO to methanol. Clearly, the ***direct***, low temperature conversion to methanol would be far more attractive from an economical standpoint. Of particular interest would be the formation of the ***same*** end product 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 a catalytic cleavage and oxidation of C−C bonds which has little precedence under mild

conditions.[5,6] Additionally, catalytic C−C cleavage is the key step 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.[7]

We previously reported a catalytic system for methane and ethane functionalization that consisted of RhCl$_3$ along with several equivalents of Cl$^-$ and I$^-$ ions dissolved in an acidic solvent.[5] This Rh-based catalytic system is superior to other reported systems for the low temperature functionalization of methane and ethane with dioxygen;[8] nevertheless, it has several drawbacks from a practical standpoint. First, rhodium is relatively expensive and the efficient postseparation of the catalyst poses a problem because of the homogeneous reaction system. More importantly, in the reaction of methane, while methanol could be made the principal product by the appropriate

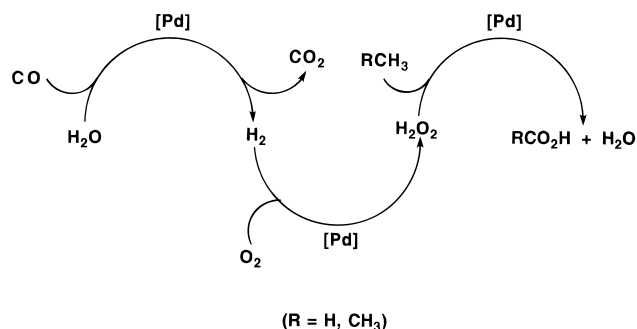⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

(1) (a) Axelrod, M. G.; Gaffney, A. M.; Pitchai, R.; Sofranko, J. A. In *Natural Gas Conversion II*; Curry-Hyde, H. E.; Howe, R. F., Eds.; Elsevier: Amsterdam, 1994; p 93. (b) Masters, C. D.; Root, D. H.; Attanasi, E. D. *Science* **1991,** *253,* 146. (c) Starr, C.; Searl, M. F.; Alpert, S. *Science* **1992,** *256,* 981.

(2) Recent reviews: (a) Olah, G. A.; Molnár, A. *Hydrocarbon Chemistry*; Wiley: New York, 1995. (b) Crabtree, R. H. *Chem. Rev.* **1995,** *95,* 987. (c) Labinger, J. A. *Fuel Process. Technol.* **1995,** *42,* 325. (d) Fierro, J. L. G. *Catal. Lett.* **1993,** *22,* 67. (e) Srivastava, R. D.; Zhou, P.; Stiegel, G. J.; Rao, V. U. S.; Cinquegrane, G. *Catal. (London)* **1992,** *9,* 183.

(3) *Chem. Eng. News* **1996,** *April 8,* p 17.

(4) (a) Cheng, W.-H.; Kung, H. H., Eds.; *Methanol Production and Use*; Marcel Dekker: New York, 1994. (b) Wade, L. E.; Gengelbach, R. B.; Trumbley, J. L.; Hallbauer, W. L. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1981; Vol. 15, p 398.

(5) Lin, M.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996,** *118,* 4574.

(6) Examples of *noncatalytic* C−C cleavage by metal species under mild conditions: (a) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994,** *116,* 3647. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994,** *116,* 10015. (c) Chiang, H. J.; Liu, C.-S. *J. Organomet. Chem.* **1993,** *458,* 167. (d) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994,** *370,* 42. (e) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993,** *364,* 699. (f) Rondon, D.; Chaudret, B.; He, X.-D.; Labroue, D. *J. Am. Chem. Soc.* **1991,** *113,* 5671. (g) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989,** *111,* 2717. (h) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988,** *110,* 976. (i) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986,** *108,* 7222. (j) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986,** *108,* 4679. (k) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982,** *104,* 6471.

(7) Unzelman, G. H. *Oil Gas J.* **1991,** *89,* 44, 62.

(8) (a) Yamanaka, I.; Soma, M.; Otsuka, K. *Chem. Lett.* **1996,** 565. (b) Nishiguchi, T.; Nakata, K.; Takaki, K.; Fujiwara, Y. *Chem. Lett.* **1992,** 1141. (c) Goldstein, A. S.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1991,** 21. (d) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991,** *113,* 700. Examples at higher temperatures (~200 °C): (e) Vargaftik, M. N.; Stolarov, I. P.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1990,** 1049. (f) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Löffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993,** *259,* 340. Also: Snyder, J. C.; Grosse, A. V. U.S. Patent 2,493,038, 1950.

Scheme 1

(R = H, CH₃)

choice of the reaction medium, there was always a significant amount of acetic acid formed as a coproduct.[5] This was, of course, undesirable if the goal was the production of methanol only. Given these disadvantages of the Rh-based catalytic system, we sought a new catalytic system that (a) was based on less expensive metals, (b) was insoluble in the reaction medium and could be separated by simple filtration, and (c) converted methane to methanol, *only*.

Results and Discussion

We previously discovered[9,10] a Pd-based catalytic system for the oxidation of methane and ethane. In this system, metallic palladium was found to catalyze the oxidation of methane and ethane by dioxygen in aqueous medium at 70–110 °C in the presence of carbon monoxide. Formic acid was the observed oxidation product from methane while acetic acid, together with some formic acid, was formed from ethane. *No* alkane oxidation was observed in the absence of added carbon monoxide. The essential role of carbon monoxide in achieving "difficult" alkane oxidation was shown by a competition experiment between $^{12}CH_3^{12}CH_3$ and $^{13}CH_3^{12}CH_2OH$, in both the presence and absence of carbon monoxide.[11] In the absence of added carbon monoxide, only $^{13}CH_3^{12}CO_2H$ was formed by the oxidation of $^{13}CH_3^{12}CH_2OH$. When carbon monoxide was added, almost half of the products were derived from $^{12}CH_3^{12}CH_3$. The products from this reaction were $^{12}CH_3^{12}CH_2OH$, $^{12}CH_3^{12}CO_2H$, and $^{13}CH_3^{12}CO_2H$. Thus, the more inert ethane was oxidized *only* in the presence of added carbon monoxide. The requirement of a coreductant (carbon monoxide) makes the overall reaction formally analogous to the monooxygenases in which only one of the two oxygen atoms in the dioxygen molecule is used for substrate oxidation.[12]

Studies indicated that the overall transformation encompassed three catalytic steps in tandem (Scheme 1).[9] The first was the water gas shift reaction involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. The second catalytic step involved the combination of dihydrogen with dioxygen to yield hydrogen peroxide.[13]

The final step involved the metal-catalyzed oxidation of the alkane by hydrogen peroxide.

The following pieces of evidence support the mechanism shown in Scheme 1.[9] The use of ^{13}CO resulted in the formation of $^{13}CO_2$ as the *only* ^{13}C-containing product. Water was also necessary since no oxidation was observed in a dry trifluoro-acetic acid–nitromethane mixture. The above observations were consistent with a metal-catalyzed water gas shift reaction. It was possible to bypass this first catalytic reaction by replacing carbon monoxide with dihydrogen. In the latter instance it was possible to run the reaction in a non-aqueous medium such as a dry trifluoroacetic acid–nitromethane mixture.

That hydrogen peroxide (or its equivalent) was formed in this system, starting with carbon monoxide and dioxygen in the presence of water, was verified by running the reaction in the *absence* of alkane. Titration of the resultant solution with a standard solution of $KMnO_4$ indicated a hydrogen peroxide concentration of 0.002 M. In an independent experiment we observed the slow Pd-catalyzed oxidation of ethane to ethanol, acetic acid, and formic acid by hydrogen peroxide at 30 °C. A lower reaction temperature was chosen in order to avoid the observed metal-catalyzed decomposition of hydrogen peroxide to water and dioxygen. It is this latter undesirable reaction that made carbon monoxide a more effective coreductant than dihydrogen. Starting with carbon monoxide, hydrogen peroxide was formed at a low steady rate through the first two catalytic reactions and was used efficiently for alkane oxidation. On the other hand, starting with dihydrogen, hydrogen peroxide was formed rapidly (as evidenced by a relatively rapid drop in gas pressure), but most of it underwent subsequent metal-catalyzed decomposition at the reaction temperature (85–100 °C).

While acetic acid was formed in good yields from ethane, the analogous formation of formic acid from methane proceeded only in low yields because of the general instability of the latter acid under the reaction conditions. Since formic acid is a much less desirable product from methane than is methanol, we have now examined the possibility of halting the oxidation of methane at the methanol stage.

Simply changing the solvent in the Pd-based catalytic system from water to a mixture of water and either perfluorobutyric acid or trifluoroacetic acid (some water was necessary for the reaction, see Scheme 1) had no significant effect on product composition: formic acid was still the principal product from methane. However, the addition of $CuCl_2$ to the reaction mixture had a dramatic effect. ***Methanol and its ester now became the preferred products, with virtually no acetic acid and little formic acid being formed (Figure 1)!*** Typical reaction conditions and product yields are shown in Table 1. High pressure stainless steel reactors equipped with glass liners were employed. The products were quantified by ^1H-NMR spectroscopy with use of an external standard consisting of a capillary tube containing 1 μL of DMSO in 60 μL of D_2O. Table 1 also shows that as little as 1 mg of 5% Pd on carbon (60 μmol of surface Pd atoms/g of catalyst, as determined from dihydrogen chemisorption studies) was effective; no reaction was observed when Pd was omitted. Since methyl trifluoro-acetate 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.

Table 2 shows the effect of varying the concentration of $CuCl_2$. Within the range studied, the amount of Cu(II) ion present did not appear to make a significant difference in the rate of product formation, although in its absence formic acid became the preferred product (see above). The fate of $CuCl_2$ in the course of the reaction was briefly examined. As expected,
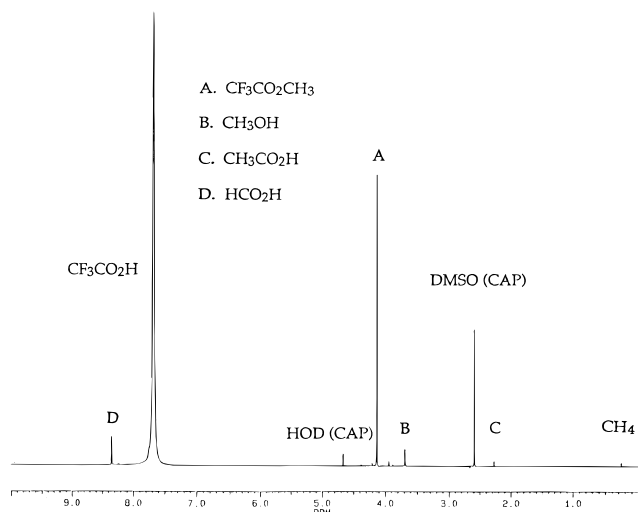
(9) Lin, M.; Sen, A. *J. Am. Chem. Soc.* **1992**, *114*, 7307.

(10) Sen, A.; Lin, M. U.S. Patent 5,393,922, 1995.

(11) Hogan, T.; Simpson, R.; Lin, M.; Sen, A. *Catal. Lett.* **1996**, *40*, 95.

(12) Reviews on monooxygenases and their synthetic analogs: (a) Valentine, J. S. in *Bioinorganic Chemistry*; Bertini, I., Gray, H. B., Lippard, S. J., Valentine, J. S., Eds.; University Science Books: Mill Valley, CA, 1994; p 253. (b) Que, L. in *Bioinorganic Catalysis*; Reedijk, J., Ed.; Marcel Dekker: New York, 1993; p 347. (c) Mansuy, D.; Battioni, P. In *Bioinorganic Catalysis*; Reedijk, J., Ed.; Marcel Dekker: New York, 1993; p 395. (d) Groh, S. E.; Nelson, M. J. In *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990; p 305. (e) Ortiz de Montellano, P. R. In *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986; p 217. (f) Groves, J. T. *J. Chem. Ed.* **1985**, *62*, 928. (g) Guegerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.

(13) Gosser, L. W. U.S. Patent 4,681,751, 1987.

Figure 1. ^{1}H-NMR spectrum obtained with the following reaction conditions: $CuCl_2$, 0.1 mmol; 5% Pd/C, 1.0 mg; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; CH_4, 900 psi; CO, 200 psi; O_2, 100 psi; 85−95 °C; 90 h.

Table 1. The $CuCl_2$/[Pd/C] Catalyst System in H_2O/CF_3CO_2H for Methane Oxidation[a]

time (h)	[5% Pd/C] (mg)	CH_3OH (+ester) (M)
20	0.0	tr
	1.0	0.12
	6.0	0.16
	12.0	0.07
50	1.0	0.48
	6.0	0.46
	12.0	0.22
90	1.0	0.75
	6.0	0.69
	12.0	0.39

[a] Standard reaction conditions: $CuCl_2$, 0.1 mmol; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; CH_4, 900 psi; CO, 200 psi; O_2, 100 psi; 85−95 °C.

Table 2. The $CuCl_2$/[Pd/C] Catalyst System in H_2O/CF_3CO_2H for Methane Oxidation[a]

time (h)	$CuCl_2$ (mmol)	CH_3OH (+ester) (M)
18	0.05	0.16
	0.10[b]	0.12
	0.15	0.10
50	0.05	0.47
	0.10	0.48
	0.15	0.48
90	0.05	0.73
	0.10	0.75
	0.15	0.63

[a] Standard reaction conditions: [5% Pd/C], 1.0 mg; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; CH_4, 900 psi; CO, 200 psi; O_2, 100 psi; 85−95 °C. [b] For 20 h.

the initial reaction mixture was blue due to the presence of Cu(II) ion in solution. However, when the reactor was opened after the partial oxidation of methane was allowed to proceed for several hours, the solution was found to be colorless and a white precipitate was found at the bottom of the glass liner employed. Upon exposure to air this precipitate dissolved to regenerate the blue solution. An elemental analysis of the white precipitate revealed it to be CuCl. Presumably, the Cu(II) salt added initially to the reaction mixture was reduced by CO in the course of the reaction. Essentially identical amounts of methanol and its derivative (0.09 M) were formed in 1 h starting with either $CuCl_2$ (0.0074 M) or CuCl + Cl$^-$ (0.0074 M each) under the following reaction conditions: K_2PdCl_4, 0.02 mg (3.0 × 10^{-5}

Table 3. The Cu(II) + Cl$^-$/[Pd/C] Catalyst System in H_2O/CF_3CO_2H for Methane Oxidation[a]

NaCl (mmol)	time (h)	CH_3OH (+ ester) (M)
0.00	42[b]	0.02
0.05	48	0.42
0.10	48	0.45
0.15	48	0.42

[a] Standard reaction conditions: $Cu(CF_3CO_2)_2$, 0.1 mmol; [5% Pd/C], 3.0 mg; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; CH_4, 900 psi; CO, 200 psi; O_2, 100 psi; 85−95 °C. [b] The solution was homogeneous after reaction.

M); H_2O, 0.5 mL; CF_3CO_2H, 1.5 mL; CH_4, 800 psi; CO, 150 psi; O_2, 75 psi; 90−95 °C. The comparable yields of product obtained from the two reactions in 1 h also indicated that there was no significant induction period during which Cu(II) was being reduced to Cu(I) in the first reaction. Whether CuCl remains in the solid state through the course of the reaction cannot be addressed unequivocally since it is quite possible that under high pressure of CO, soluble Cu(I)−carbonyl complexes were being formed.[14]

The recycling of catalyst was carried out in one experiment. Following the oxidation of methane under the standard reaction conditions, the reactor was opened and the precipitated CuCl, together with metallic Pd, was filtered off and used in a second methane oxidation reaction. The yield obtained in the latter reaction was comparable to that in the first.

As Table 3 illustrates, the presence of Cl$^-$ ion was essential for the conversion of methane to methanol and its ester to occur. An alternative way to add both Cl$^-$ ion and metallic Pd to the system was by starting with K_2PdCl_4 which was rapidly reduced to the metallic Pd by CO with the simultaneous release of Cl$^-$ ion. A direct comparison between K_2PdCl_4 and 5% Pd/C in the oxidation of ethane revealed similar product distributions and yields (see below).

The effect of varying the halide ion in the copper salt employed was examined. With the following conditions—Cu salt, 0.06 mmol; 5% Pd/C, 20 mg; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; CH_4, 1000 psi; CO, 100 psi; O_2, 100 psi; temperature, 85−95 °C—the yields of methanol and its ester in 20 h were 0.27, 0. 12, and 0.04 M for $CuCl_2$, $CuBr_2$, and CuI, respectively. Thus, the yield decreased in the order Cl$^-$ > Br$^-$ > I$^-$.

While many of the catalytic studies were carried out with 5% Pd on carbon, Pd black was also effective for the reaction. Additionally, control experiments indicated that carbon itself did not catalyze methane oxidation in the absence of metallic Pd.

The relative rates of methane oxidation to methanol derivative versus further oxidation of methanol were examined by carrying out the oxidation of $^{12}CH_4$ in the presence of $^{13}CH_3OH$. A 3:1 mixture (v/v) of trifluoroacetic acid and water was made 0.19 M in $^{13}CH_3OH$ (most of which was converted to the methyl ester) and the methane functionalization reaction was run under conditions identical with those shown in Figure 1. The methanol and its derivatives observed after 48 h were as follows: $CF_3CO_2^{13}CH_3$ + $^{13}CH_3OH$ (0.05 M), and $CF_3CO_2^{12}CH_3$ + $^{12}CH_3OH$ (0.88 M). The data indicated that the rate of methanol formation was at least 6.5 times greater than the overoxidation of methanol. The unusually high selectivity toward methanol formation is striking. Given that the C−H bond energy of methane is 10 kcal/mol higher than that in methanol, any oxidation procedure that involved hydrogen atom abstraction from the substrate C−H bond would have resulted in up to six

(14) (a) Jagner, S.; Håkansson, M. *Inorg. Chem.* **1990**, *29*, 5241. (b) Busch, M. A.; Franklin, T. C. *Inorg. Chem.* **1979**, *18*, 521. (c) Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, *8*, 2533.

Selective Oxidation of Methane and Lower Alkanes

J. Am. Chem. Soc., Vol. 119, No. 26, 1997 6051

Table 4. Effect of Temperature on Methane Oxidation with the CuCl$_2$/K$_2$PdCl$_4$ Catalyst System in H$_2$O/CF$_3$CO$_2$H[a]

temp (°C)	time (min)	CH$_3$OH (+ester) (M)	turnover/min based on Cu	turnover/min based on Pd
85−90	360	0.34	0.13	31.5
95−100	270	0.42	0.21	52.2
110−115	225	0.58	0.35	86.2
125−130	90	0.30	0.45	110.8
140−145	85	0.45	0.72	176.1
145−150	85	0.55	0.88	216.7

[a] Standard reaction conditions: CuCl$_2$, 2.0 mg (7.4 × 10^{-3} M); K$_2$PdCl$_4$, 0.02 mg (3.0 × 10^{-5} M); H$_2$O, 0.5 mL; CF$_3$CO$_2$H, 1.5 mL; CH$_4$, 1000 psi; CO, 200 psi; O$_2$, 100 psi.
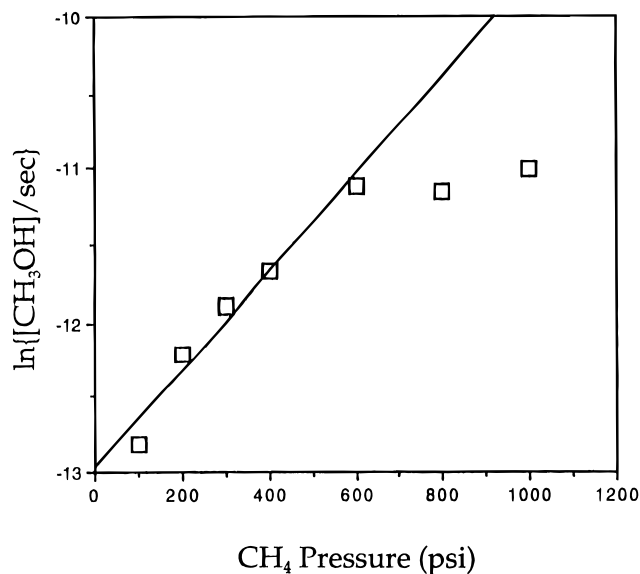
Figure 2. Rate dependence on the partial pressure of methane. Reaction conditions: CuCl$_2$, 0.015 mmol; K$_2$PdCl$_4$, 0.06 μmol; H$_2$O, 0.5 mL; CF$_3$CO$_2$H, 1.5 mL; CO, 200 psi; O$_2$, 100 psi; CH$_4$ + N$_2$, 1000 psi; 77−85 °C; 1 h.

orders of magnitude higher rate for methanol overoxidation when compared to its rate of formation from methane (however, see below). Note that at 900 psi of pressure, the concentration of methane in pure water is 0.045 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 0.19 M, the concentration of added ^{13}CH$_3$OH. The activity of methane at constant pressure should not, of course, vary with solvent composition.

The most interesting aspect of the chemistry described above was the significant increase in the rate of methane to methanol conversion with an increase in reaction temperature. This is illustrated in Table 4. It should be noted that because of the experimental setup, it required 20−40 min for the reaction mixture to reach the indicated temperature. Thus the actual rate of reaction at a given temperature was invariably higher than that shown in Table 4.

The dependence of the reaction rate on the partial pressures of methane and carbon monoxide was examined. In order to avoid the lag time associated with the stainless steel bomb and the reaction mixture reaching the designated reaction temperature, the bomb and its contents (except for the reactant gases) were preheated. The reaction was then initiated by adding the reactant gases (see Experimental Section for details). Saturation kinetics was observed for methane (Figure 2). Thus, a first-order dependence on methane partial pressure was obtained up to a pressure of 700 psi. However, the reaction rate became

CO Pressure (psi)
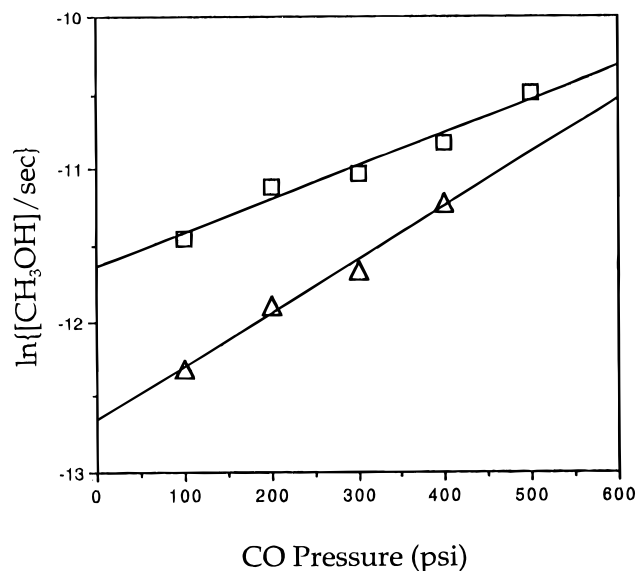
Figure 3. Rate dependence on the partial pressure of carbon monoxide at 300 psi CH$_4$ (△) and 600 psi CH$_4$ (□). Reaction conditions: CuCl$_2$, 0.015 mmol; K$_2$PdCl$_4$, 0.06 μmol; H$_2$O, 0.5 mL; CF$_3$CO$_2$H, 1.5 mL; CH$_4$, 300 (△) or 600 (○) psi; CO + N$_2$, 900 (△) or 600 (□) psi; O$_2$, 100 psi; 77−85 °C; 1 h.

$$y = 9.9175 - 7.6949x \quad R^2 = 0.970$$

1/T (× 1000 K)
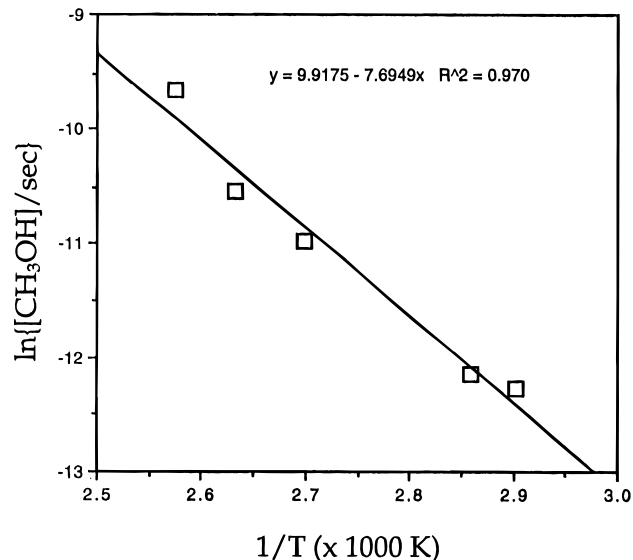
Figure 4. Arrhenius plot for the oxidation of methane. Reaction conditions: CuCl$_2$, 0.015 mmol; K$_2$PdCl$_4$, 0.06 μmol; H$_2$O, 0.5 mL; CF$_3$CO$_2$H, 1.5 mL; CH$_4$, 500 psi; CO, 200 psi; O$_2$, 100 psi; N$_2$, 500 psi; 1 h.

zero order in methane when its partial pressure exceeded 700 psi. The dependence of the rate on the partial pressure of carbon monoxide was measured at two different pressures of methane (Figure 3). A first-order dependence on the partial pressure of carbon monoxide was observed in both instances.

We have obtained the activation parameters for the overall reaction under the reaction condition when the rate was first order in both methane and carbon monoxide. The Arrhenius plot obtained is shown in Figure 4 and gave the following values: $A = 2 \times 10^4$ s^{-1}; $E_a = 15.3$ kcal mol^{-1}. For comparison, the activation energy for hydrogen abstraction from methane in the oxidative coupling reaction catalyzed by Li/MgO varies from 25 to 50 kcal mol^{-1}.[15]

The ability of metal salts, other than CuCl$_2$, as cocatalysts in halting the functionalization of methane at the methanol stage

(15) Lunsford, J. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 970.

Table 5. Fe(II)/[Pd/C] and Fe(III)/[Pd/C] Catalyst Systems in H_2O/CF_3CO_2H for Methane Oxidation[a]

cocatalyst	time (h)	CH_3OH (+ester) (M)
$FeCl_2$	48	0.12
	84	0.11
$FeCl_3$	48	0.07
	84	0.16

[a] Standard reaction conditions: [5% Pd/C], 3.0 mg; cocatalyst, 0.10 mmol; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; CH_4, 900 psi; CO, 200 psi; O_2, 100 psi; 85−95 °C.
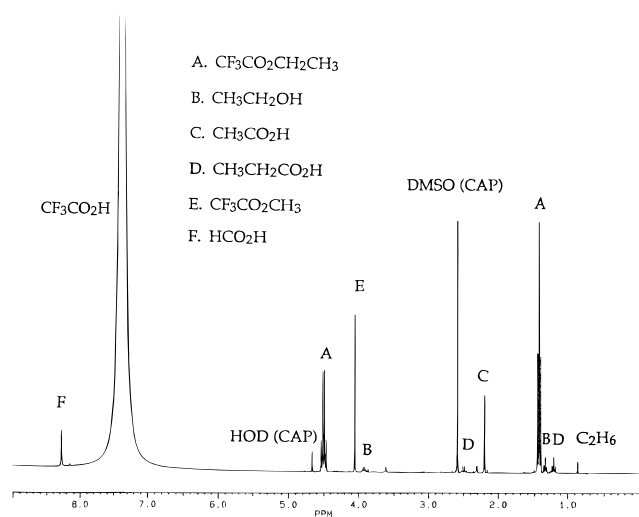

A. $CF_3CO_2CH_2CH_3$
B. CH_3CH_2OH
C. CH_3CO_2H
D. $CH_3CH_2CO_2H$
E. $CF_3CO_2CH_3$
F. HCO_2H

Figure 5. ^{1}H-NMR spectrum obtained with the following reaction conditions: $CuCl_2$, 0.1 mmol; 5% Pd/C, 1.0 mg; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; C_2H_6, 400 psi; CO, 150 psi; O_2, 75 psi; N_2, 400 psi; 85−95 °C; 90 h.

was briefly examined. As shown in Table 5, methanol and its ester were also the dominant products in the presence of either $FeCl_2$ or $FeCl_3$, but the rate of methane conversion was lower compared to that observed in the presence of $CuCl_2$.

We have also briefly examined ethane and *n*-butane as substrates in the $CuCl_2$/Pd catalytic system. As expected, the rate of ethane conversion was significantly higher than methane conversion with the products being ethanol (and its ester), methanol (and its ester), and acetic acid (see Figure 5). Thus, 0.75 M ethanol and its ester, 0.30 M methanol and its ester, and 0.14 M acetic acid were formed in 16 h under the following reaction conditions: $CuCl_2$, 0.1 mmol; [5% Pd/C], 3.0−5.0 mg; H_2O, 1.0 mL; CF_3CO_2H, 3.0 mL; C_2H_6, 400 psi; CO, 150 psi; O_2, 75 psi; N_2, 400 psi; temperature 85−95 °C. For comparison, a similar product distribution was obtained when K_2PdCl_4 was used in place of 5% Pd/C. For example, 0.72 M ethanol and its ester, 0.22 M methanol and its ester, and 0.15 M acetic acid were formed in 18 h under the following reaction conditions: $CuCl_2$, 2.0 mg (7.4×10^{-3} M); K_2PdCl_4, 0.02 mg (3.0×10^{-5} M); H_2O, 0.5 mL; CF_3CO_2H, 1.5 mL; C_2H_6, 400 psi; CO, 150 psi; O_2, 75 psi; N_2, 400 psi; temperature 90−95 °C. In the case of n-butane, 0.14 M ethanol and its ester, 0.14 M methanol and its ester, and 0.15 M acetic acid were formed in 20 h under the following reaction conditions: $CuCl_2$, 2.0 mg (7.4×10^{-3} M); K_2PdCl_4, 0.02 mg (3.0×10^{-5} M); H_2O, 0.5 mL; CF_3CO_2H, 1.5 mL; C_4H_{10}, 30 psi; CO, 150 psi; O_2, 75 psi; N_2, 800 psi; temperature 85−95 °C.

Unlike the "classical" Fenton-type systems,[16] *free* alkyl radicals appear not to be intermediates in our system unless they are rapidly trapped by O_2 (however, a non-radical mechanism for Fenton chemistry has also been suggested recently[17]). Thus, the rate of methanol formation was at least 6.5 times greater than the overoxidation of methanol. Given that the C−H bond energy of methane is 10 kcal/mol higher than that in methanol, any oxidation procedure that involved hydrogen atom abstraction from the substrate C−H bond would have resulted in up to six orders of magnitude higher rate for methanol overoxidation when compared to its rate of formation from methane. However, this argument 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: $H-CH_3$, 104 kcal/mol; $H-CH_2OH$, 94 kcal/mol; $H-CH_2OCOC_6H_5$, 100.2 kcal/mol[18]). A further evidence against the participation of *free* radicals was that acetic acid was not formed from methane even though carbon monoxide was present in the reaction mixture. Note that carbon monoxide is a trapping agent for alkyl radicals (e.g., rate constant in water for trapping of $CH_3^•$ by CO:[19] 2×10^6 L mol^{-1}s^{-1}) and we have observed the formation of acetic acid in good yields from methyl radical and carbon monoxide in water under oxidizing conditions.[20] Nevertheless, the lack of carbon monoxide trapping does not rule out radical formation and recombination *within* a solvent cage.

We now turn to the catalytic C−C cleavage reactions. From the data given above on ethane oxidation, the ratio of products derived from initial C−H cleavage versus C−C cleavage was approximately 1, on a per bond basis. No methanol was observed when ethane was omitted from the reaction mixture, indicating that methanol was not being formed from carbon monoxide (e.g., by hydrogenation). Experiments with ethanol, acetaldehyde, and acetic acid as substrates indicated that all three formed methanol in varying degrees (acetaldehyde > ethanol ≫ acetic acid). However, control experiments involving $^{13}CH_3CH_2OH$ and $^{12}C_2H_6$, as well as $^{13}CH_3CO_2H$ and $^{12}C_2H_6$, showed that in the presence of the alkane both ethanol and acetic acid were unreactive, with all the products formed being derived from ethane.

For *n*-butane, virtually all of the observed products were derived by C−C cleavage. Note that the formation of methanol from ethane and ethanol from *n*-butane would appear to rule out metal-assisted cleavage of vicinal diols as the source of C−C cleavage products.

Finally, it is instructive to compare our reaction rate with that in the "Monsanto system" for the carbonylation of methanol—an enormously successful solution-phase commercial process.[21] In a 3:1 mixture (v/v) of trifluoroacetic acid and water, the rate of formation of methanol from methane with use of the bimetallic system was ca. 65×10^{-4} M/min at 145−150 °C. In the Monsanto process, the rate of formation of acetic acid from methanol is 380×10^{-4} M/min at 180 °C.[22] Thus, the rate is 6 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 of pressure that we employ, the aqueous concentration of methane is approximately

(16) Reviews: (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; p 35, 171, 329. (b) Edwards, J. O.; Curci R. In *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Strukul, G., Ed.; Kluwer Academic: Dordrecht, 1992; p 97.

(17) Sawyer, D. T.; Sobkowiak, A.; Matsushita, T. *Acc. Chem. Res.* **1996**, *29*, 409.

(18) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press: Boca Raton, 1991; pp 9−114.

(19) Bakac, A.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1497.

(20) Lin, M.; Sen, A. *J. Chem. Soc., Chem. Commun.* **1992**, 892.

(21) (a) *Acetic Acid and Its Derivatives*; Agreda, V. H., Zoeller, J. R., Eds.; Marcel Dekker: New York, 1993. (b) Wagner, F. S. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1978; Vol. 1, p 124. (c) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255.

(22) Hjortkjaer, J.; Jensen, V. W. *Ind. Eng. Chem., Prod. Res. Dev.* **1976**, *15*, 46.

0.05 M. *If* the solution concentration (more precisely, the activity) of methane in a trifluoroacetic acid/water mixture is similar, then under *similar* substrate concentrations our rate of methane conversion is significantly *higher* than the rate of methanol conversion in the Monsanto system (this does not take into account the higher reaction temperature employed for the latter). Our results, therefore, strongly suggest that the low temperature direct partial oxidation of methane and lower alkanes by dioxygen is commercially feasible.

Conclusion

We have discovered a highly catalytic system that simultaneously cleaves C−H and C−C bonds of simple alkanes, as well as activates dioxygen, under mild conditions. For ethane and *n*-butane, products derived from C−C cleavage competed with or dominated over those derived from C−H cleavage on a per bond basis.

The present bimetallic system is similar to the previously described homogeneous Rh-based system[5] in its ability to activate both dioxygen and the alkane and requiring a coreductant (carbon monoxide). However, there are important differences in reactivity. First, in the case of methane, the bimetallic system specifically forms methanol whereas the latter system produced both methanol and acetic acid (albeit in varying amounts) under *all* reaction conditions. Second, while both systems gave C−C cleavage products from ethane and *n*-butane, only the former also yielded C−C cleavage products from the corresponding alcohols.

On a more general theme, the requirement of a coreductant (carbon monoxide) by the above two catalytic systems is striking and resembles the monooxygenases.[12] How general is this requirement for a coreductant (e.g., CO or H₂) in achieving "difficult" catalytic hydrocarbon oxidations by dioxygen? 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 H₂ as the coreductant.[23] 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: 5% Pd/carbon (Johnson Matthey); $CuCl_2$, CuCl, $CuBr_2$, CuI, $Cu(CF_3CO_2)_2$, $FeCl_3$, $FeCl_2$, NaCl, H_2O_2, and $K_2S_2O_8$ (Aldrich); methane, ethane, dioxygen, and carbon monoxide (Matheson); $^{13}CH_3CH_2OH$, $^{13}CH_3OH$, D_2O, ^{13}CO, and $^{13}C_2H_4$ (Cambridge Isotope). For the 5% Pd/carbon employed, dihydrogen chemisorption studies indicated the presence of 60 μmol of surface Pd atoms/g of sample. Reactions under pressure were carried out in Parr general purpose bombs with glass liners. Reaction products were identified by their ^1H- and ^{13}C-NMR spectra recorded on a Bruker AM 300 FT-NMR spectrometer with the 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. The identity of the

products was further confirmed by GC/MS and/or by comparison with authentic samples.

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

A. Cu/Pd Based Catalytic System. 1. Oxidation of Methane. In a typical reaction, $CuCl_2$ (13.5 mg, 0.1 mmol) and 5% Pd on carbon (1.0 mg) were added to 1.0 mL of H_2O in a glass container; 3 mL of CF_3CO_2H was then added slowly. The glass container was then placed in a high pressure bomb that was then sealed. The bomb was purged and pressurized to 200 psi with CO, to 1200 psi with CH_4, then to 1300 psi with O_2. The contents were stirred at 80−85 °C for 20 h following which the reactor was cooled and the pressure slowly released. The reaction mixture was then directly analyzed by NMR spectroscopy.

2. Oxidation of Ethane. The reaction was conducted as described in procedure A.1, except that 150 psi of CO, 400 psi of C_2H_6, 75 psi of O_2, and 400 psi of N_2 were added to the bomb.

B. Fe/Pd Based Catalytic System: Oxidation of Methane. The reactions were conducted as described in procedure A.1, except that $FeCl_3$ (0.1 mmol) or $FeCl_2$ (0.1 mmol) instead of $CuCl_2$ was added to the system.

C. Determination of Activation Energy. To a glass liner was added 0.5 mL of 0.03 M $CuCl_2$(aq) solution, 1.5 mL of CF_3CO_2H, and 10 μL of 0.006 M K_2PdCl_4(aq) solution. The glass liner was then placed in a 125-mL high-pressure bomb that was then sealed. The bomb was pressurized to 500 psi with N_2 and preheated to reaction temperature. The reactor was then pressurized to 1000 psi with CH_4, to 1200 psi with CO, and finally to 1300 psi with O_2. The contents were stirred at the reaction temperature for 1 h following which the reactor was cooled and the pressure slowly released. The reaction mixture was then directly analyzed by NMR spectroscopy.

D. Rate Dependence on Methane Pressure. The reactions were conducted as described in procedure C, except that the reactor was charged with 100 to 1000 psi of CH_4 and then to 1000 psi with N_2 and preheated to reaction temperature for 1 h. The reactor was then pressurized with 200 psi of CO and with 100 psi of O_2. The contents were stirred at 77−85 °C for 1 h following which the reactor was cooled for 1 h, and the pressure slowly released. The reaction mixtures were then directly analyzed by NMR spectroscopy.

E. Rate Dependence on Carbon Monoxide Pressure. 1. At 300 psi of Methane. The reactions were conducted as described in procedure C, except that the reactor was charged with 300 psi of CH_4 and 400 to 800 psi of N_2. The reactor was then preheated to reaction temperature for 1 h. To the hot reactor was then added 100 to 500 psi of CO (total pressure of N_2 + CO = 900 psi) and 100 psi of O_2. The contents were stirred at 77−85 °C for 1 h following which the reactor was cooled for 1 h, and the pressure slowly released. The reaction mixtures were then directly analyzed by NMR spectroscopy.

2. At 600 psi of Methane. The reactions were conducted as described in procedure C, except that the reactor was charged with 600 psi of CH_4 and 100 to 500 psi of N_2. The reactor was then preheated to reaction temperature for 1 h. To the hot reactor was then added 100 to 500 psi of CO (total pressure of N_2 + CO = 600 psi) and 100 psi of O_2. The contents were stirred at 77−85 °C for 1 h following which the reactor was cooled for 1 h, and the pressure slowly released. The reaction mixtures were then directly analyzed by NMR spectroscopy.

(23) Representative examples: (a) Otake, M. *Chemtech* **1995**, 36. (b) Miyake, T.; Hamada, M.; Sasaki, Y.; Oguri, M. *Appl. Catal. A: General* **1995**, *131*, 33. (c) Teranishi, T.; Toshima, N. *J. Chem. Soc., Dalton Trans.* **1995**, 979. (d) Wang, Y.; Otsuka, K. *J. Catal.* **1995**, *155*, 256. (e) Benvenuto, M. A.; Sen, A. *J. Chem. Soc., Chem. Commun.* **1993**, 970.