companying the dimensionality transitions are expected, eventually approaching on-off switching, once efforts are taken to orientate the nanostructures.

The implications of the present work on nanotechnology seem manyfold. The present methods to construct zero-, one-, and two-dimensional nanostructures suggest controllable nanostructures in conjugated electronically conducting polymers. P4VP is a semiconducting side-chain–conjugated polymer. In this case, conductivity appears to proceed through a protonic mechanism (*19*); this mechanism is not a serious limitation to the generality of the concepts, which are based on a control of the morphology. Chemically, P4VP resembles in several ways main-chain–conjugated polymers such as polyaniline, poly(*p*-pyridine), poly(*p*-pyridine vinylene) (*20, 21*), and possibly even polypyrrole. These materials are inherently difficult to process because of their rigidity. However, in polyaniline, for example, methods have been demonstrated to introduce processibility by the use of amphiphilic dopants (*22*) or amphiphilic oligomers capable of molecular recognition with the polyaniline chain (*23*). Such concepts easily provide the short length scale discussed above.

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Platinum Catalysts for the High-Yield Oxidation of Methane to a Methanol Derivative

Roy A. Periana,* Douglas J. Taube, Scott Gamble,
Henry Taube, Takashi Satoh, Hiroshi Fujii

Platinum catalysts are reported for the direct, low-temperature, oxidative conversion of methane to a methanol derivative at greater than 70 percent one-pass yield based on methane. The catalysts are platinum complexes derived from the bidiazine ligand family that are stable, active, and selective for the oxidation of a carbon-hydrogen bond of methane to produce methyl esters. Mechanistic studies show that platinum(II) is the most active oxidation state of platinum for reaction with methane, and are consistent with reaction proceeding through carbon-hydrogen bond activation of methane to generate a platinum-methyl intermediate that is oxidized to generate the methyl ester product.

More efficient methods for the oxidation of low-value, light alkane feedstocks, such as natural gas, to the corresponding alcohols or other useful liquid products would accelerate the use of natural gas feedstocks as a complement to petroleum. Current technologies for the conversion of natural gas to liquid products proceed by generation of carbon monoxide and hydrogen (syn-gas) that is then converted to higher products through Fischer-Tropsch chemistry (*1*). The initial formation of syn-gas in these processes is energy intensive and proceeds at high temperatures, typically 850°C. In contrast, direct methods partially oxidize the alkane molecule, functionalizing one C–H bond, and in principle can proceed more efficiently and cost-effectively through lower temperature routes.

Given the potential for high payoff, the goal of direct, selective alkane oxidation has been the focus of substantial effort since the 1970s (*2, 3*). Despite these extensive efforts, very few selective alkane oxidation processes are known. Except in a few special cases (*4*), the basic chemistry for the selective, low-temperature, direct, oxidative conversion of alkane C–H bonds to useful functional groups in high one-pass yield (*5*) has not yet been developed. Such development is challenging, because alkane C–H bonds are among the least reactive known and the desired products of oxidation are typically more reactive than the starting alkanes and are consumed before recovery. Consequently, only uneconomically low one-pass yields can be obtained with direct alkane oxidation chemistries available today without prohibitively expensive separations and recycle.

We developed a catalytic system for the direct, low-temperature, selective oxidation of methane to generate an ester of methanol in 72% one-pass yield at 81% selectivity based on methane (*5*). Recently, we reported the selective oxidation of methane to an ester of methanol in ~43% one-pass yield catalyzed by mercuric salts (*6*). We now show that selected Pt complexes are more effective catalysts for this reaction. These Pt complexes are stable and selectively activate (*7*) and oxidize a C–H bond of methane at temperatures as low as 100°C to generate a methyl ester product that is chemically "protected" from overoxidation

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Catalytica Advanced Technologies Inc., 430 Ferguson Drive, Mountain View, CA 94043, USA.

*To whom correspondence should be addressed. E-mail: rap@mv.catalytica-inc.com

to combustion products.

Earlier (6), we noted that the inorganic salts of Tl, Au, Pd, and Pt promoted oxidation of methane in strong oxidizing acids such as concentrated H_2SO_4. Only stoichiometric oxidations were observed with Au and Tl salts, because reoxidation of the reduced forms of these salts is not possible with suitable oxidants. Catalysis was observed with the Pd and Pt salts, with Pt being the more efficient. However, catalyst life as well as reaction selectivities were poor with these metal salts because of the irreversible bulk-metal formation that occurs with the use of noble metals. Control studies show that the poor selectivity arises because the bulk noble metals catalyze the complete combustion of the desired products. This issue has been documented in the Wacker system (8) as well as the Shilov Pt system for alkane oxidation (3).

The best documented solution to minimizing irreversible reduction of the group VIII noble metals is the use of chloride ligands to stabilize Pd(II) catalysts in the Wacker process (8). Unfortunately, the addition of chloride as well as other well-established methods to prevent metal ion reduction, such as the use of heteropoly acids, were not useful for our methane oxidation system.

To address this issue, we focused our efforts on the use of ligands that might stabilize cationic Pt species in concentrated H_2SO_4 at temperatures >100°C without inhibiting C–H activation (7). The primary issues considered in catalyst design were the stability of the ligand-Pt bond and the ligand itself in the hot, strongly acidic and oxidizing environment as well as the availability of open coordination sites for C–H activation. In view of the high kinetic lability of O-based ligands and the known, poor oxidative and thermal stability of P-based ligands, we focused our efforts on N-ligated complexes.

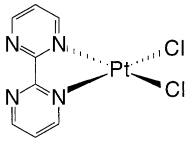
Initial reactions with simple, σ-donor, amine Pt complexes confirmed the validity of this approach. *cis*- or *trans*-$Pt(NH_3)Cl_2$ was soluble and persisted in concentrated H_2SO_4, decomposing at 180°C with a half-life of ~15 min. During this time, this material was an active catalyst [turnover frequency (TOF; extrapolated to the beginning of the reaction) = 10^{-3} s^{-1} (9)] for the oxidation of methane by concentrated H_2SO_4 to generate methyl bisulfate at >90% selectivity (10)

$$CH_4 + 2\,H_2SO_4 \rightarrow CH_3OSO_3H + 2\,H_2O + SO_2 \qquad (1)$$

The short life of the catalyst in concentrated H_2SO_4 solutions resulted from the expected irreversible protonation of the NH_3 ligands to generate insoluble $PtCl_2$ and NH_4HSO_4 (Eq. 2). However, the stability of solutions of this simple di-ammine complex in hot, concentrated, H_2SO_4 for even a limited time illustrated the hoped-for kinetic stability and oxidation activity of N-ligated complexes in the reaction environment.

$$Pt(NH_3)_2Cl_2 + 2\,H_2SO_4 \rightarrow (PtCl_2)_n + 2\,NH_4HSO_4 \qquad (2)$$

To develop more stable catalysts, π-acidic, chelating, N-based ligands were examined with the expectation that π-acid ligands could be expected to have both lower proton affinity as well as higher affinity for Pt(II), a π-donor metal, than σ-donor ligands such as NH_3. Several Pt complexes were identified that were less susceptible to both protolytic ligand loss and irreversible reduction to Pt metal while still facilitating methane oxidation. Among the most effective catalysts is dichloro(η-2-{2,2′-bipyrimidyl})platinum(II) [(bpym)$PtCl_2$; **1**]. Control experiments show that a 50 mM solution of this material in 20% oleum, even after 200°C for 50 hours, shows no evidence of ligand attack as monitored by nuclear magnetic resonance (NMR) spectroscopy. Even though some free ligand (unbound to Pt) is observed, the solution remained homogeneous, and no insoluble $(PtCl_2)_n$ formation or decomposition to Pt metal is observed (11). Chloride loss was observed (as evidenced by HCl gas formation), presumably generating mixtures of the corresponding bis-bisulfate or mixed bisulfate chloride Pt–bipyrimidine (bpym) complex.



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Scheme 1. Structure of (bpym)$PtCl_2$.

The reaction of methane (3400 kPa, 115 mmol) with 80 ml of 102% H_2SO_4 containing a 50 mM concentration of **1** at 220°C for 2.5 hours resulted in ~90% methane conversion and the formation of ~1 M solutions of methyl bisulfate at 81% selectivity (10, 12). Control experiments confirm that no significant methane oxidation occurs without added catalyst. In separate experiments, catalyst TOFs of 10^{-2} s^{-1}, volumetric productivities of 10^{-6} mol cm^{-3} s^{-1} and turnover numbers (9) of >500 (13) have been demonstrated with this ligated Pt catalyst system. Kinetic analyses of typical reaction profiles and control experiments on the oxidation of solutions of methyl bisulfate show the rate constant for oxidation of methane to be at least 100 times greater than that for methyl bisulfate (14).

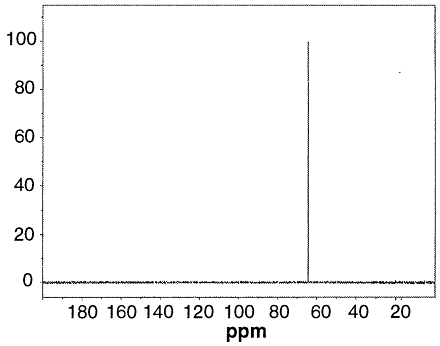

Fig. 1. Carbon-13 NMR spectrum of the crude solution from the reaction of methane with 102% H_2SO_4 containing 50 mM of (bpym)$PtCl_2$ that shows that the only liquid-phase products are CH_3OSO_3H and CH_3OH.

The solution remained active after reaction with methane, and formation of Pt black or other insoluble materials was not observed (11). Analyses of the crude reaction mixtures by ^{13}C NMR from oxidation of ^{13}C-enriched methane confirmed that the only liquid-phase carbon product is methyl bisulfate (with some free methanol) and that it was produced from the added methane (Fig. 1). In contrast to the Hg(II) system (6), methane sulfonic acid (CH_3SO_3H) is not produced in the presence of excess SO_3. Greater than 95% of the C has been accounted for, and the only observable C-based side products are gas-phase CO_2 and trace levels of methyl chloride. In addition to H_2SO_4, other strong acids, such as CF_3SO_3H or $HB(HSO_4)_4$, can be used as solvent and reactant for methane oxidation to methyl esters catalyzed with **1** by using oxidants other than SO_3 or H_2SO_4.

The high stability of complex **1** to strong acid and oxidizing conditions has been traced to the high affinity of the bpym ligand for Pt(II). Remarkably, unlike the simple NH_3 ligands that are irreversibly lost by protonation (Eq. 2) resulting in formation of insoluble $(PtCl_2)_n$ or Pt black, similar loss of the bpym ligand from the Pt center is reversible. Evidence for this reversibility is the "self-assembling" characteristics of **1**, whereby treatment of insoluble $(PtCl_2)_n$ with 1 equivalent (equiv.) of bpym (50 mM) in concentrated H_2SO_4 at 150°C leads to complete dissolution of $(PtCl_2)_n$ and formation of a homogeneous solution of **1**. By comparison, treatment of $(PtCl_2)_n$ in hot, concentrated H_2SO_4 with >100 equiv. of NH_3 does not lead to Pt dissolution. The affinity of bpym for Pt(II) is also sufficiently high so that a solution of bpym (20 mM) in hot, 96% H_2SO_4 leads to the oxidative dissolution of Pt metal (added as Pt black) to produce a homogeneous solution of (bpym)$Pt(HSO_4)_2$ (Eq. 3). Control experiments show that no such dissolution occurs in the absence of the bpym ligand. These experiments show the effectiveness of the bpym ligand for maintaining the homogeneity of Pt cations in strong acids under strongly oxidizing, high-temperature conditions.

$$\mathrm{Pt(0)} + \mathrm{bpym} + 3\ \mathrm{H_2SO_4} \rightarrow \mathrm{(bpym)Pt(HSO_4)_2} + \mathrm{SO_2} + 2\ \mathrm{H_2O} \tag{3}$$

A key characteristic of the methane oxidation system described above is that the system is catalytic in the Pt complex, and a potentially practical scheme can be developed based on known, facile hydrolysis of the methyl bisulfate and reoxidation of SO_2 (Scheme 2). Other systems that catalyze the oxidation of methane to methyl species (*2, 3, 6*) have been reported. However, except for our earlier work (*6*), the highest yield of methyl product (based on added methane) claimed for any of the reported systems is <3%. Additionally, none of the reported systems use efficiently recyclable oxidants or afford efficient catalysis in the expensive, metal-based complexes.

Step 1

$$\mathrm{CH_4 + HX + SO_3 \rightarrow CH_3X + H_2O + SO_2}$$

Step 2

$$\mathrm{CH_3X + H_2O \rightarrow CH_3OH + HX}$$

Step 3

$$\mathrm{SO_2 + 1/2\ O_2 \rightarrow SO_3}$$

$$\mathrm{Net\ CH_4 + 1/2\ O_2 \rightarrow CH_3OH}$$

Scheme 2. Process scheme for the net oxidation of methane to methanol. X = OSO_3H.

The N-ligated Pt oxidation systems are mechanistically related to our earlier system based on Hg (*6*), as well as to the Shilov aqueous Pt(II)/(IV) system (*3, 15*), in that the same three key steps—C–H activation, oxidation, and functionalization—are proposed for the catalytic sequence (Fig. 2).

In the case of the C–H activation step, the data are consistent with this step proceeding through the Pt(II) oxidation state rather than bulk metal, homogeneous Pt(0) or the Pt(IV) oxidation states. The proposed C–H activation step can be conveniently monitored in isolation from the remaining two steps shown in Fig. 2 by carrying out the reaction of methane with **1** in a nonoxidizing, deuterated acid solvent such as CF_3SO_3D or in D_2SO_4 at temperatures below 150°C (*16*). Under these conditions, the rate of C–H activation can be measured over a 30-min period by the rate of H/D exchange between methane and the solvent (*17*). The extent of H/D exchange of gas-phase methane with time was measured by gas chromatography–mass spectroscopy (GC-MS). Extensive H/D exchange (5 to 10% of the gas-phase methane at a TOF of $\sim 10^{-2}\ s^{-1}$) was observed with Pt(II) [added in the form of $(bpym)PtSO_4$] without net reduction or oxidation of the Pt (*18*). However, replacement of Pt(II) with Pt(IV) [added in the form of $H_2Pt(OH)_6$ or $(bpym)Pt(HSO_4)_4$] or Pt(0) (added as Pt black) led to no measurable H/D exchange (*19*). Ruling out soluble Pt(0) is more difficult, because we did not examine the chemistry of homogeneous Pt(0) species of bpym. However, the observation that added Pt(II) catalyzes H/D exchange without any observable reduction to Pt(0) (*18*) would tend to rule out this possibility.

An interesting question is whether the C–H activation reaction by $(bpym)PtCl_2$ in H_2SO_4 occurs by an oxidative addition mechanism (to generate a methyl hydrido Pt intermediate that loses a proton) or by electrophilic substitution (via a metal-methane complex that loses a proton) as was proposed for the Hg(II) system (*6, 20*). Recent work by Bercaw and Labinger (*15*) on the Shilov system (*2, 3*) showed that C–H activation by oxidative addition with Pt(II) complexes must be considered. We do not have sufficient data to differentiate between these closely related possibilities. However, whatever the exact molecular details of the reaction, we believe that the process is electrophilic in character and occurs with the cationic, highly electrophilic, coordinatively unsaturated, 14-electron, T-shaped complex (Fig. 2). This belief is based on the observation that although H/D exchange can be observed with gas-phase methane, no H/D exchange could be observed with the methyl C–H bonds of perprotio methyl bisulfate when a D_2SO_4 solution of methyl bisulfate was treated with **1** (*21*). Although alternative explanations can be advanced, such as increased steric hindrance with methyl bisulfate, we prefer the explanation that the electron-withdrawing bisulfate group inhibits electrophilic reaction between the metal complex and the C–H bonds of methyl bisulfate relative to those of methane. Similar explanations are advanced for the retarding effect of the nitro group on the rate of electrophilic substitution of nitrobenzene relative to benzene. The mechanism of this reaction deserves more detailed consideration, because factors that control reactivity of C–H bonds in C–H activation systems could lead to greater control of reaction selectivity.

As in the Hg(II) system (*6*), the oxidation step is rate-determining in the catalytic sequence. As noted above, H/D exchange can be observed below 150°C without formation of CH_3OSO_3H occurring at an observable rate when methane is treated with D_2SO_4 containing **1** in a 30-min period. This observation shows that the C–H activation step must be faster than either the oxidation step or the functionalization step, or both. As a model of the oxidation step, treatment of **1** with H_2SO_4 is observed to result in oxidation to Pt(IV) (Eq. 4) at appreciable rates only at temperatures above 150°C.

$$\mathrm{(bpym)Pt^{II}Cl_2} + 3\ \mathrm{H_2SO_4} \rightarrow \mathrm{(bpym)Pt^{IV}Cl_2(HSO_4)_2} + \mathrm{SO_2} + 2\ \mathrm{H_2O} \tag{4}$$

To examine the feasibility of the functionalization step, as well as to establish the relative rates of the steps, we carried out the reaction with methane below 150°C (where only C–H activation occurs) in the presence of both **1** and Pt(IV) [added as $H_2Pt(OH)_6$]. Under these conditions, in addition to H/D exchange with methane, quantitative formation of methyl bisulfate [relative to added Pt(IV)] was observed. These results are consistent with C–H activation and functionalization steps occurring faster than the oxidation step. Consistent with the proposal that the oxidation step is the rate-determining step, Pt(II) complexes that have been shown to undergo faster oxidation to Pt(IV) also catalyze faster methyl bisulfate formation from methane. Thus, the $(NH_3)_2PtCl_2$ complex, which has been shown to be oxidized much more rapidly to Pt(IV) species than is the $(bpym)PtCl_2$ complex, also catalyzes the oxidization of methane to methyl bisulfate at a faster rate (albeit with a shorter lifetime; see below). Similarly, **1** is more rapidly oxidized to Pt(IV) than is $(bpym)PtSO_4$ and likewise catalyzes the oxidation of methane

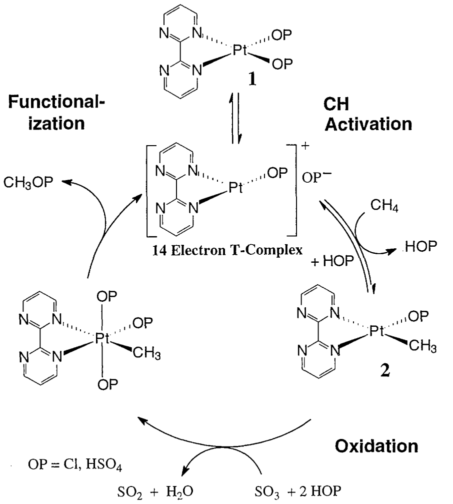

Fig. 2. Proposed reaction mechanism for the oxidation of methane.

to methyl bisulfate at a faster rate.

Unlike the Hg(II) system reported earlier (6), a key intermediate in the reaction mechanism, the proposed Pt^{II}-CH_3 species (2) obtained from the C–H activation step, was not observed in the crude reaction mixtures. We believe that the Pt^{II}-CH_3 species has a substantially lower acid stability compared to methyl mercury bisulfate (CH_3HgOSO_3H). The methyl mercury compound was shown to be stable in 96% H_2SO_4 for days at room temperature (it eventually decomposes to form methyl bisulfate and methane) and could be quantitatively generated by treatment of methyl mercury hydroxide and H_2SO_4 at room temperature (6). However, treatment of synthesized (bpym)Pt(CH_3)(Cl) with concentrated H_2SO_4 at room temperature led to rapid evolution of methane with the stoichiometry shown in Eq. 5.

$$\text{(bpym)PtCl(CH}_3\text{)} + H_2SO_4 \rightarrow \text{(bpym)PtCl(HSO}_4\text{)} + CH_4 \quad (5)$$

Fortunately, decomposition to methane was sufficiently slow at room temperature to enable a transient methyl Pt species to be observed by ^1H NMR spectroscopy, showing that a CH_3-Pt species in H_2SO_4 is a plausible intermediate. However, at typical reaction temperatures for methane oxidation (180° to 220°C), loss of methane from synthesized (bpym)Pt(CH_3)(Cl) was immediate and complete upon addition to H_2SO_4. The primary product was methane (>95%), but methyl bisulfate [~1 to 5% yield based on added (bpym)Pt(CH_3)(Cl)] was also produced. These observations are consistent with the lack of observable CH_3-Pt species, because only a very low steady-state level of such species would be expected during catalysis. The formation of low levels of methyl bisulfate also provides evidence for the conversion of 2 to product, as proposed in the functionalization step (Fig. 2). As expected on the basis of our experiments with added Pt(IV), the addition of 2 to solutions of H_2SO_4 containing Pt(IV) [as $H_2Pt(OH)_6$] led to increased methyl bisulfate production [relative to H_2SO_4 solutions not containing added Pt(IV)] along with methane. This result is consistent with Shilov's (3) and Bercaw and Labinger's (15) proposal that Pt(IV) can be an oxidant for conversion of a CH_3-Pt species into product.

Another important piece of evidence in support of the methyl Pt intermediate, **2**, as a key intermediate is the observation of multiple D incorporation into the methane produced upon reaction of a synthesized sample of (bpym)Pt(CH_3)(Cl) with D_2SO_4 at room temperature. Similar observations of multiple D incorporation into gas-phase methane as well as the solution-phase methyl bisulfate product are made when the reaction of methane is examined using solutions of **1** in D_2SO_4. A key observation in this case is that the extent of D incorporation into the product methyl bisulfate is several times higher than into the gas-phase methane even though (*21*) no H/D exchange is observed when methyl bisulfate alone is treated with a D_2SO_4 solution of **1**. These results strongly suggest, as shown in Fig. 3, that a single C–H activation can lead to multiple H/D exchange, possibly via a methane complex (**3**) before methane loss or oxidation of the methyl Pt to methyl bisulfate occurs (*20, 22*).

A key role of the bpym ligand is maintaining the solubility of the Pt(II) species. This, coupled with the observations that simple, nonligated Pt salts also catalyze methane oxidation (albeit at significantly lower selectivities and rates) and that the bpym ligand can be reversibly lost [see above; (*11*)], raises the important question of whether the bpym ligand is attached to the Pt center in the transition state for C–H activation. This is useful information, because the presence of the ligand in the transition state for C–H activation could enable the selectivity of the C–H activation reaction to be controlled. More detailed experiments are required to completely address this point, but initial competition experiments, which show that the relative rates of H/D exchange between D_2SO_4 solvent and the methyl C–H bonds of two co-dissolved substrates (methane and ethyl phosphonic acid) are dependent on the identity of the ligand on the Pt(II) catalyst, strongly suggest that the bpym ligand is attached to the metal during C–H activation.

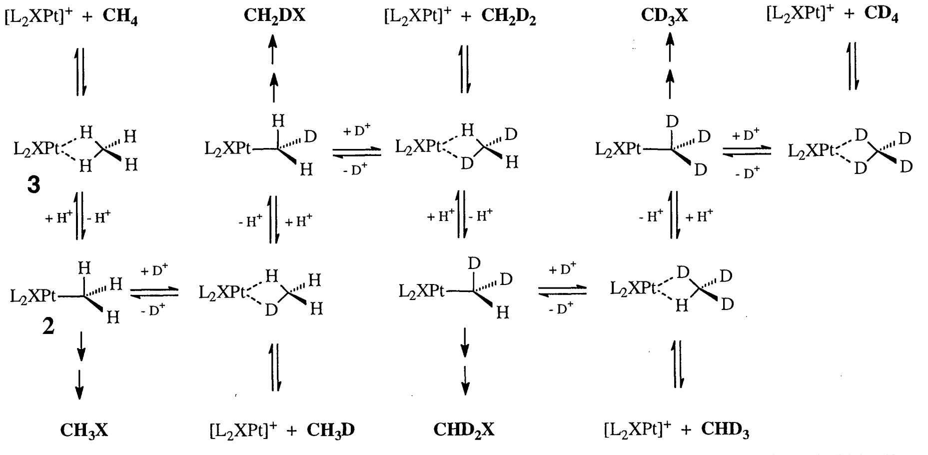

Fig. 3. Proposed mechanism accounting for multiple H/D exchange into methane and methyl bisulfate by a single C–H activation event through a methane complex.

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4. The oxidation of butane to maleic anhydride or acetic acid, propane to acrylonitrile, or isobutane to *t*-butyl hydroperoxide are atypical, free-radical–based alkane autooxidation reactions that proceed in reasonable selectivities and yields (>10% per pass) because either the products are uniquely stable, as in the case of maleic anhydride, acetic acid, and acrylonitrile, or in the case of isobutane, the reactivity of the tertiary C–H bond is significantly higher than those in the products.
5. The phrase "one-pass yield" is used to describe the yield of product generated without separation and recycle of the starting materials. This is analogous to the yield from a batch process. Conversion, selectivity, and yield are defined as

   % conversion ≡
   $$\left(\frac{[CH_4]\text{initial} - [CH_4]\text{final}}{[CH_4]\text{initial}}\right) \times 100$$
   % selectivity to CH_3OH ≡
   $$\left(\frac{[CH_3OH]}{[CH_4]\text{initial} - [CH_4]\text{final}}\right) \times 100$$
   % yield ≡ (% conversion) × (% selectivity)
6. R. A. Periana *et al.*, *Science* **259**, 340 (1993); U.S. Patents 5,233,113 and 5,306,855.
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8. P. M. Henry, *Palladium Catalyzed Oxidation of Hydrocarbons*, (Reidel, Dordrecht, Netherlands, 1980).
9. Turnover frequency = [(mol of product produced)/(mol of added catalysts)] per second; Turnover number = [(mol of product produced)/(mol of added catalysts)] when reaction is stopped.

10. The data we report were obtained from the following typical experimental procedures. All data has been shown to be reproducible with an error of ~5%. The oxidation of methane was conducted in a 300-ml high-pressure, stirred autoclave from Autoclave Engineers. The reactor was modified so that all the internal parts were either glass-lined or made from tantalum. The reactor was equipped with baffles, a hollow shaft/impeller, and was stirred at 1500 rpm to insure thorough gas-liquid mixing during the reaction. The reactor was loaded with the Pt catalyst (typically 20 to 50 mM) along with 80 to 120 ml H_2SO_4 (at desired concentration), and the system was degassed with N. The reactor was heated to the desired reaction temperature (typically between 180° and 220°C), and a mixture of 97% methane and 3% neon was added to a total pressure of 500 psig. The methane/neon feed was added to the reactor from a known-volume reservoir in which the temperature and pressure of the gas was measured before and after addition so that the total moles of methane/neon added to the reactor could be accurately determined. The reaction was typically allowed to proceed for 1 to 3 hours. Cooling to near room temperature with an external, water-cooled line stopped the reaction, and the gas phase was vented into a 20-liter pressure vessel. After allowing several hours for thorough gas mixing, the vented gas was analyzed with a Hewlett-Packard 5880 GC equipped with a Hayesep D column and a thermal conductivity detector. The molar composition in the vented gas (primarily CH_4, CO_2, SO_2, and CH_3Cl) was determined on the basis of the reference neon internal standard; molar ratios of the gases; and the temperature, pressures, and volume of the vented gas. The liquid phase remaining in the 300-ml high-pressure reactor was analyzed by ^1H and ^{13}C NMR and high-pressure liquid chromatography (HPLC) analyses. For NMR analysis, a known amount of acetic acid was added to an aliquot of the reaction solution as an internal standard. Methyl bisulfate (and any free methanol) was determined from the ratio of the ^1H NMR methyl resonances of methyl bisulfate (3.4 ppm) to acetic acid (2.02 ppm). The methyl products were also quantified by HPLC analysis of the liquid phase. Known volume aliquots of reaction solution were first hydrolyzed by the addition of three parts water to one part crude reaction solution and heated to 90°C for 4 hours in a sealed vial. The hydrolyzed solution was analyzed with a Hewlett-Packard 1050 HPLC equipped with an HPX-87H column (Bio-Rad) and a refractive index detector. The eluent was 0.1 volume % H_2SO_4 in water. Methanol eluted at 16.2 min. The gas phase (CH_4, CO_2 and CH_3Cl) and liquid phase (CH_3OSO_3H and CH_3OH) analyses allowed >90 to 95% mass balance on methane.
11. Oxidation of the Pt(II) center to Pt(IV) occurs as evidenced by changes in the solution NMR spectra. Free ligand is generated, but no reaction at the C–H bonds is observed.
12. Calculated volumetric productivity based on the liquid phase for this reaction is $\sim 10^{-7}$ mol ml^{-1} s^{-1}; Catalyst turnover number (~20) and catalyst TOF ($\sim 10^{-3}$ s^{-1}) were values obtained over the integrated reaction time.
13. The catalyst was still active after 500 turnovers. The reaction was stopped at this point. The actual number of turnovers before the regeneration would be required has not been determined.
14. The exact value depends on the value for the solubility of methane in H_2SO_4 used in the calculations.
15. M. W. Holtcamp, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **119**, 848 (1997) and references therein.
16. At temperatures below 150°C, negligible methane oxidation (<1%) is observed with concentrated H_2SO_4 containing **1** under typical reaction conditions over a 30-min period.
17. Assuming the microscopic reverse of the C–H activation step, protonolysis of the methyl Pt bond is significantly more rapid than the C–H activation step.
18. The lack of any redox change in the Pt center is evidenced by the stability of the (bpym)PtX_2 complex, absence of reduced Pt, lack of methyl bisulfate or overoxidation products such as CO_2, and lack of reduction products such as SO_2.
19. If H/D exchange is occurring with these oxidation states the rates must be at least three orders of magnitude slower than with Pt(II).
20. C. Hall and R. N. Perutz, *Chem. Rev.* **96**, 3125 (1996); J. J. Schneider, *Angew. Chem. Int. Ed. Engl.* **35**, 1068 (1996) and references therein. Methane complexes are now generally accepted intermediates in C–H activation reactions. To date, extensive indirect data have been obtained to support the intermediacy of such species. However, none have been isolated and characterized.
21. No H/D exchange is observed between D_2SO_4 and the methyl C–H bonds of methyl bisulate when a solution of CH_3OSO_3H (0.2 M) containing 50 mM (bpym)$PtCl_2$ is heated to 220°C for 2 hours. However, a slow rate of oxidation of methyl bisulfate to CO_2 is observed and can be considered to be a limiting rate of H/D exchange of methyl bisulfate (if we assume that all C–H activation events of methyl bisulfate lead to rapid CO_2 formation). In this case, we can estimate that the rate C–H activation of methane is at least 100 times greater than that of methyl bisulfate (*13*). No methane formation is observed in these reactions indicating that the oxidation of methane to methyl bisulfate occurs irreversible as expected.
22. Similar scrambling had been observed by Shilov (*3*) who proposed a carbene-hydride intermediate to explain the results.

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The Lost Colony and Jamestown Droughts

David W. Stahle,* Malcolm K. Cleaveland, Dennis B. Blanton,
Matthew D. Therrell, David A. Gay

Tree-ring data from Virginia indicate that the Lost Colony of Roanoke Island disappeared during the most extreme drought in 800 years (1587–1589) and that the alarming mortality and the near abandonment of Jamestown Colony occurred during the driest 7-year episode in 770 years (1606–1612). These extraordinary droughts can now be implicated in the fate of the Lost Colony and in the appalling death rate during the early occupations at Jamestown, the first permanent English settlement in America.

The network of moisture-sensitive tree-ring chronologies now available for the United States has recently been used to reconstruct summer drought and wetness on a continent-wide basis from 1700 to 1978 A.D. (*1*). Much longer chronologies are available for some areas, including a network of 800-year-long baldcypress (*Taxodium distichum*) chronologies for the southeastern United States. These exactly dated tree-ring proxies of growing-season climate can provide unique information on environmental conditions during the early colonial history of the eastern United States. Here, we use two long baldcypress chronologies to reconstruct the Palmer hydrological drought index (PHDI) (*2*) for the Tidewater region of southeastern Virginia and northeastern North Carolina (Fig. 1) and show that extreme drought afflicted the first English attempts to colonize the New World at Roanoke and Jamestown Island.

Centuries-old baldcypress trees survive locally along the Blackwater and Nottoway rivers in southeastern Virginia (Fig. 1), and exactly dated tree-ring chronologies were developed nondestructively for each location (*3*). Both chronologies are directly correlated with precipitation and are inversely correlated with temperature during the growing season (April to July), in spite of the frequently flooded riparian habitat of the sample trees (*4*). A regional baldcypress tree-ring chronology was computed as the arithmetic mean of the Blackwater and Nottoway rivers' chronologies for the common period 1185 to 1984 A.D. (variance trend due to low sample size in the early years was removed). The regional chronology is well replicated (>26 cores from 12 trees after 1225, and 62 cores at 1600) and was used to reconstruct regionally averaged July PHDI for the Tidewater and eastern Piedmont climatic divisions of Virginia and the northern and central coastal plain divisions of North Carolina (*5*). This large homogeneous climatic province includes Jamestown, Roanoke Island, and most of the drainage basins of the Blackwater and Nottoway rivers. The PHDI is closely related to the Palmer drought severity index, and both are used by the National Weather Service to monitor drought and wetness conditions across the United States (*6*). The July PHDI integrates the effects of spring and summer precipitation and temperature anomalies on the soil water balance (*2*) and is an excellent measure of

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D. W. Stahle, M. K. Cleaveland, M. D. Therrell, D. A. Gay, Tree-Ring Laboratory, Department of Geography, University of Arkansas, Fayetteville, AR 72701, USA.
D. B. Blanton, Center for Archaeological Research, The College of William and Mary, Williamsburg, VA 23187-8795, USA.

*To whom correspondence should be addressed. E-mail: dstahle@comp.uark.edu