Activation of Methane and Ethane and Their Selective Oxidation to the Alcohols in Protic Media

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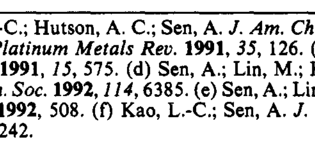
Abstract: The selective oxidation of methane and ethane to the alcohols in solvents ranging from strong acids to neutral aqueous medium has been studied. In 98% sulfuric acid, methane is oxidized to CH_3OSO_3H by a variety of 1e⁻ and 2e⁻ oxidants, such as $S_2O_8^{2-}$, Ce(IV), Pd(II), and Hg(II). In the case of ethane, the observed products are CH_3OSO_3H and $HO_3SCH_2CH_2OSO_3H$. These oxidations appear to proceed through a series of electron-transfer steps involving the intermediacy of radicals and carbocations. We have determined the ratio of rate constants for methane versus methanol oxidation by the Pt(II) ion in water and an average value of 0.17(2) was obtained. The similarity in rate constants for methane and methanol oxidations under such mild conditions is remarkable. Moving to substrates with C–H bonds somewhat weaker than that in methane results in actual ***reversal*** of commonly observed selectivity. As an example, we have observed the ***exclusive*** oxidation of the methyl group in ethanol resulting in the formation of 1,2-ethanediol as the predominant product. In addition, when ethane was included as a substrate, the relative rate of C–H bond activation by the Pt(II) ion ***decreased*** in the order $H–CH_2CH_3 > H–CH_2CH_2OH > H–CH(OH)CH_3$. Another example of unusual selectivity was the observation of 1,3-propanediol as the predominant product in the oxidation of 1-propanol by the Pt(II) ion in water.

In this paper, we delineate the scope and the limitations of the activation of methane and ethane and their selective oxidation to the alcohols in protic media.[1] Methane is the most abundant and the least reactive member of the hydrocarbon family. Ethane comes second in both categories. Together, they constitute >95% of natural gas, with known reserves approaching that of petroleum.[2] A significant portion of the methane and ethane produced is not utilized because of the difficulty associated with the transportation of a flammable, low-boiling gas. Their possible use as automobile fuels is also limited by the intrinsic disadvantages of gaseous fuels, i.e., low-energy content per unit volume and the hazards associated with handling and distribution. Thus, the selective conversion of methane and ethane to more useful chemical products is of great practical interest.

The lack of reactivity of these two molecules stems from their unusually high bond energies (C–H bond energy of methane: 104 kcal/mol), and most reactions involving the homolysis of a C–H bond occur at fairly high temperatures or under photolytic conditions. Moreover, the selectivity in these reactions is usually low because of the subsequent reactions of the intermediate products which tend to be more reactive than the alkane itself. Using methane as an example, its C–H bond energy is 10 kcal/mol higher than that in methanol. Therefore, unless methanol can be removed as soon as it is formed, any oxidation procedure that involves hydrogen–atom abstraction from the substrate C–H bond would ***normally*** (vide infra) cause rapid overoxidation of methanol. The radical initiated chlorination of methane invariably leads to multiple chlorinations[3] (chlorination, however, is more specific in the presence of superacids[4]). In order to achieve the selective functionalization of methane and ethane, it is therefore necessary to design a pathway that does ***not*** involve C–H bond homolysis as one of the steps.

Our approach[5] to the problem builds upon earlier work by Shilov and co-workers[6] and is schematically outlined in eq 1. The critical C–H bond cleavage step involves attack by an electrophilic metal ion. This is followed by a 2e⁻ oxidation of the bound alkyl group by the metal in the presence of a nucleophile. The net result is the formation of a functionalized alkyl compound together with a reduced metal species. The reoxidation of the metal by a cooxidant completes the cycle and the system becomes catalytic in the metal. Using this approach, we had earlier observed turnovers in the Pd(II) catalyzed oxidation of methane by hydrogen peroxide in trifluoroacetic acid at 90 °C.[5a,b] The Co(III) ion has also been demonstrated to be effective.[7] The observed organic product in each case was the ester, $CF_3CO_2CH_3$, a readily hydrolyzable derivative of methanol. Because of the electron-withdrawing nature of the CF_3CO_2 substituent, the C–H bonds of the methyl group in the ester are less susceptible to electrophilic attack than those in the parent alcohol. Thus a key role of the solvent is to bind the methanol formed as the ester, thereby retarding its further oxidation.[5a,b]



(1)

(Ox = 2e⁻ oxidant, Nu = Nucleophile)

Results and Discussion

A. C–H Activation in Sulfuric Acid Medium. Recently, a new high-yield system for the oxidation of methane to methanol

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⊛ Abstract published in *Advance ACS Abstracts*, January 1, 1994.

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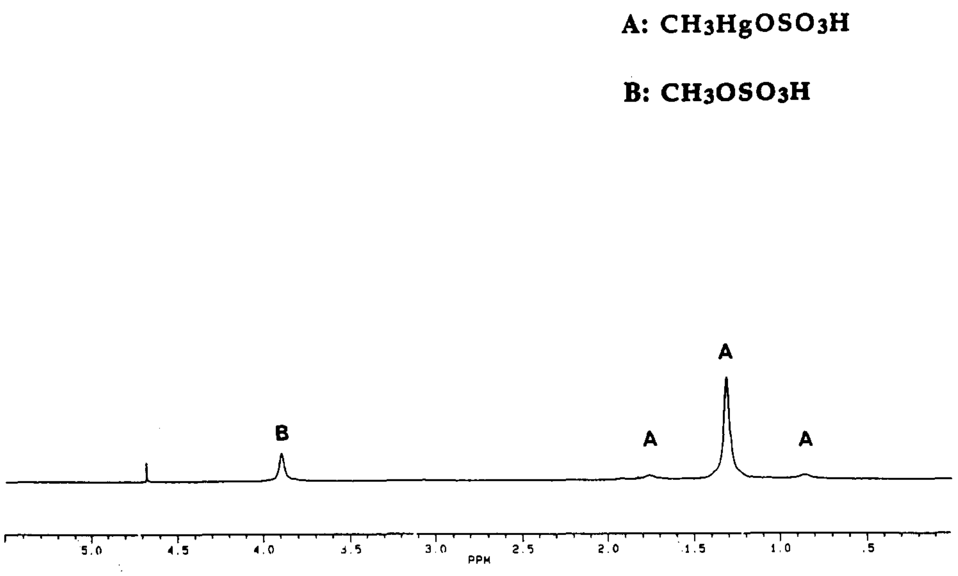
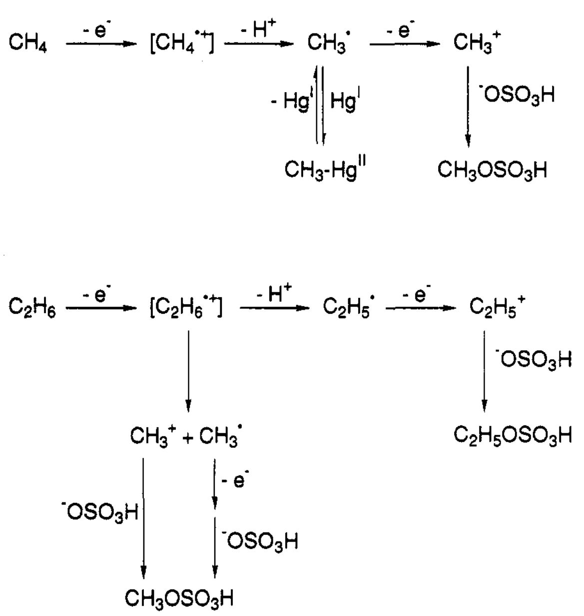


Figure 1. ^{1}H NMR spectrum obtained after the following reaction conditions: CH_4 (1000 psi), $HgSO_4$ (0.2 mmol), D_2SO_4 (2 mL), 150 °C, 24 h.

derivatives was reported.[8] The system consists of Hg(II) ion in 100% sulfuric acid and operates at 180 °C. A mechanistic scenario closely analogous to that shown in eq 1 was proposed with the Hg(II) ion acting as the electrophile and an 1e$^-$ oxidant and sulfuric acid serving both as the nucleophile and the reoxidant. As in our system, further oxidation of methanol was prevented by its conversion to the ester, CH_3OSO_3H. However, despite the superficial similarity between the two systems, there appear to be several key differences. For example, we have observed that a number of unrelated 1e$^-$ and 2e$^-$ oxidants that are highly unlikely to activate methane through the above pathway will also oxidize it to CH_3OSO_3H in this solvent system. Moreover, when ethane is used as the substrate, C–C bond cleavage occurs to a significant extent.

The formation of CH_3OSO_3H was observed by ^{1}H NMR spectroscopy when methane at 1000 psi was contacted at 150–180 °C with a 0.1 M solution of any one of the following oxidants in 98% sulfuric acid (yield based on **2e$^-$** oxidation in 24 h): $K_2S_2O_8$ (150 °C, 25%; 180 °C, 39%), $Ce(SO_4)_2$ (150 °C, 24%; 180 °C, 38%), $PdSO_4$ (180 °C, 95%), and $HgSO_4$ (150 °C, 28% (+64% CH_3HgOSO_3H); 180 °C, 690%). CH_3SO_3H was formed as a minor side-product in several instances; however, control experiments using both $HgSO_4$ and $K_2S_2O_8$ indicated that it was not converted to CH_3OSO_3H under the reaction conditions. When $HgSO_4$ was present, CH_3HgOSO_3H was observed as an additional product. This organometallic species became the predominant or even the ***exclusive*** product when the reaction was carried out at lower temperatures. For example, when the reaction was run at 150 °C for 24 h, the observed products (yield relative to Hg) were CH_3OSO_3H (14%) and CH_3HgOSO_3H (64%) (see Figure 1). CH_3HgOSO_3H, in turn, was found to generate CH_3OSO_3H on heating to 180 °C. While these observations are certainly consistent with the mechanism outlined in eq 1, alternative C–H activation and oxidation pathways cannot be ruled out since other 1e$^-$ and 2e$^-$ oxidants gave comparable stoichiometric yields (i.e., under conditions where mercury is not reoxidized by sulfuric acid). $K_2S_2O_8$ is an interesting case in point. We had earlier demonstrated that in water at 110 °C, SO_4^- (generated from $S_2O_8^{2-}$) abstracts a hydrogen atom from methane or ethane to form the corresponding alkyl radical which is then converted to, inter alia, the alcohol and the sulfate.[9] In the presence of added carbon monoxide, this radical is trapped efficiently, and the resultant acyl radical is ultimately converted to a carboxylic acid. It is therefore possible that, as shown in Scheme 1, the role of ***all*** the oxidants in sulfuric acid was to generate a methyl radical from methane by outer-sphere electron transfer followed by proton loss. The methyl radical was eventually converted to CH_3OSO_3H. In the special case of Hg(II) as the oxidant, CH_3HgOSO_3H was formed by (reversible) recombination of methyl and Hg(I) radicals. Consistent with this mechanism was our failure to synthesize CH_3HgOSO_3H in sulfuric acid from CH_3OSO_3H and either Hg(II) or Hg(I) sulfate even under conditions where CH_3HgOSO_3H can be made from methane and is stable (see above). It may also be noted that the proposed mechanism is similar to those suggested for methane monooxygenase where both the methyl radical and the methyl cation, formed by electron transfers to high-valent iron–oxo species, have been implicated as intermediates.[10]

Scheme 1



The mechanistic scenario outlined above finds support in the reactivity pattern observed with ethane. The radical cation formed from ethane by electron transfer would be expected to fragment some of the time by C–C cleavage[11] (Scheme 1). The direct precedent for such a step is Olah's observation of CH_3NO_2 as the principal product in the reaction of ethane with $NO_2^+PF_6^-$.[12]

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[8] Periana, R. A.; Taube, D. J.; Evitt, E. R.; Löffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340. There is an earlier report on a similar system involving oxidation of methane by SO_3 catalyzed by group IIB metal ions, including Hg^{II}, see: Snyder, J. C.; Grosse, A. V. *U.S. Patent* 2,493,038 (1950). We thank a referee for the citation.

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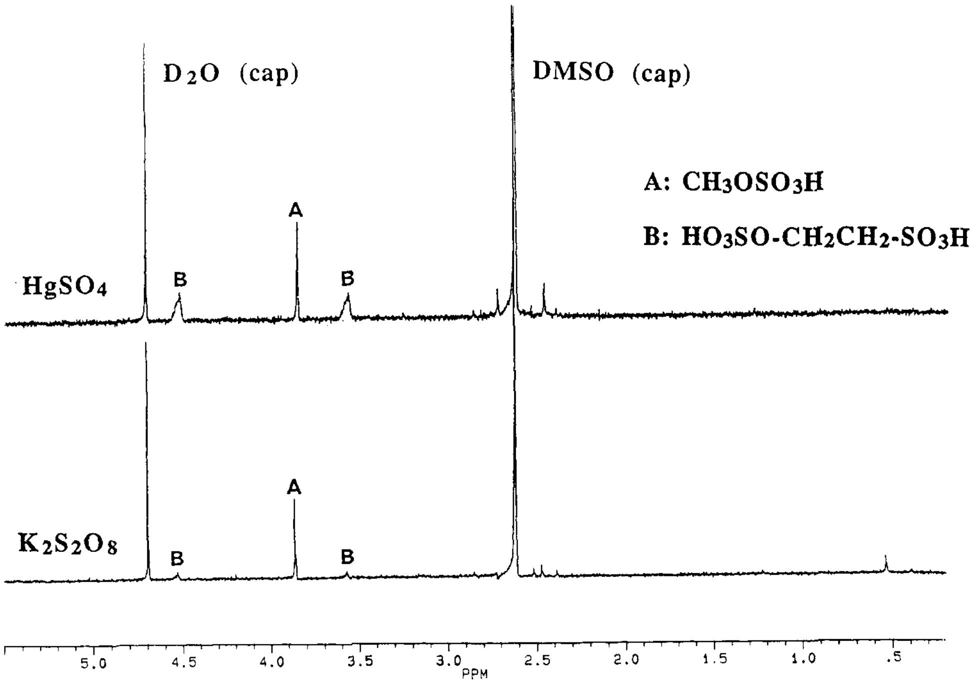
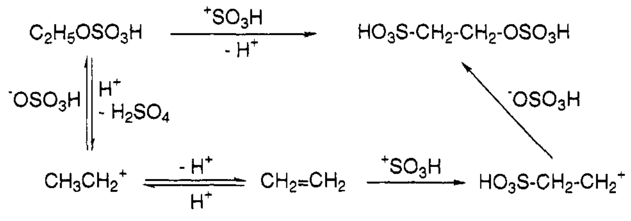


Figure 2. ^{1}H NMR spectrum obtained after the following reaction conditions: top spectrum C_2H_6 (550 psi), $HgSO_4$ (0.1 mmol), D_2SO_4 (1 mL), 180 °C, 24 h; bottom spectrum C_2H_6 (550 psi), $K_2S_2O_8$ (0.1 mmol), D_2SO_4 (1 mL), 180 °C, 24 h. For calibration, a capillary containing a mixture of D_2O and DMSO was inserted into the NMR tube.

Scheme 2



Indeed, the formation of CH_3OSO_3H was observed (up to 25% yield relative to oxidant in 24 h) when ethane at 550 psi was contacted at 150–180 °C with a 0.1 M solution of any one of the following oxidants in 98% sulfuric acid: $K_2S_2O_8$, $Ce(SO_4)_2$, and $HgSO_4$ (see Figure 2). Trace amounts of CH_3CO_2H were also observed; however, control experiments showed that CH_3OSO_3H was not derived from CH_3CO_2H through a decarboxylation step. The only other product observed in the reaction of ethane was $HO_3SCH_2CH_2OSO_3H$ (see Figure 2). This compound appears to be derived from the initially formed $C_2H_5OSO_3H$. Heating $C_2H_5OSO_3H$ in sulfuric acid for as little as 15 min at 180 °C resulted in its conversion to $HO_3SCH_2CH_2OSO_3H$. Scheme 2 shows two possible pathways for this transformation. Adding $CH_3{}^{13}CH_2OH$ to sulfuric acid at ambient temperature resulted in the immediate formation of $CH_3{}^{13}CH_2OSO_3H$. Heating $CH_3{}^{13}CH_2OSO_3H$ in sulfuric acid at 125 °C for 30 min resulted in the formation of $C_2H_5OSO_3H$ where the labeled carbon was distributed equally between the the two ends of the ethyl group. Further heating at 180 °C for 15 min caused the quantitative transformation to $HO_3SCH_2CH_2OSO_3H$ where the labeled carbon remained distributed equally between the the two ends of the molecule. The scrambling of the labeled carbon presumably occurred through the intermediacy of either the ethyl cation (via rapid 1,2-H shift) or ethylene or both. The possible role of ethylene in the conversion of $C_2H_5OSO_3H$ to $HO_3SCH_2CH_2OSO_3H$ was supported by the observation of the formation of $HO_3SCH_2CH_2OSO_3H$ when 1 atm of ethylene was heated at 180 °C in the presence of sulfuric acid.

It is clear from the above discussion that, at least with the oxidants studied, a significant pathway for the oxidation of methane and ethane in sulfuric acid involved discrete outer-sphere electron-transfer steps. An additional parallel pathway involving direct electrophilic attack on the substrate was still possible for some oxidants. In the latter case, for ethane, the observed formation of CH_3OSO_3H would imply a direct attack on the C–C bond by the incoming electrophile (e.g., Hg(II) or HO_3SO^+). However, it is difficult to see, given its large size, how a Hg(II) ion could approach the C–C bond without first encountering and activating a C–H bond. On the other hand, it is known that an 1e$^-$ oxidation of ethane leads to a substantial weakening of the C–C bond (from 90 to 45–37 kcal/mol) resulting in fragmentation to $CH_3^{\cdot} + CH_3^+$.[11] In preliminary experiments, the formation of CH_3OSO_3H was also observed when propane was used as the substrate. In general, however, the use of higher alkanes led to complex mixtures of products as well as carbonaceous residues.

It is noteworthy that ***all*** the oxidants exhibited unusually high selectivity for methane versus CH_3OSO_3H oxidation. Using calculations similar to that described in the section on C–H activation in aqueous medium and assuming that the steady-state concentration of CH_3OSO_3H was greater or equal to that observed at the end of a 24-h reaction period, the rate constant for the oxidation of methane was found to be equal to or significantly greater than that for CH_3OSO_3H oxidation.[13] In addition, for both $HgSO_4$ and $K_2S_2O_8$, very little oxidation of added $^{13}CH_3OSO_3H$ was observed under reaction conditions

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(12) Olah, G. A.; Lin, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1259.

(13) Due to the lack of appropriate solubility data for methane, a number of crude assumptions have been made. These are (a) that the solubility of methane in 98% sulfuric acid is similar to that in water and (b) that the solubility at 180 °C is similar to that at 100 °C. The solubility at 180 °C will almost certainly be substantially lower than at 100 °C. In addition, for all or most of the oxidants, the steady-state concentration of CH_3OSO_3H may be much greater than that observed at the end of the 24 h reaction period. For these two reasons the ***actual*** ratio of methane to CH_3OSO_3H oxidation rate constants at 180 °C is almost certainly much higher than what our data indicate.

employed for the oxidation of methane. At first glance, the unusual selectivity would appear to contradict any mechanism involving the formation of free radicals since the homolytic bond strength of methane exceeds that of methanol by 10 kcal/mol. However, the presence of an electron-withdrawing substituent makes the methanol C–H bonds less susceptible to ***both*** electrophilic attack ***and*** H-atom abstraction. The latter phenomenon can be accounted by the destabilizing inductive effect of the substituent on the electron-deficient trivalent carbon. The following C–H bond-energy data[14] serve to illustrate the point: H–CH_2CH_3, 100.3 kcal/mol; H–CH_2CF_3, 106.7 kcal/mol; H–CH_2OH, 94 kcal/mol; and H–$CH_2OCOC_6H_5$, 100.2 kcal/mol. Thus, given that the –OSO_3H group is significantly more electron withdrawing than the –$OCOC_6H_5$ group (cf. $HOSO_3H$ is a strong acid while $HOCOC_6H_5$ is quite weak), the bond energy of H–CH_2OSO_3H may be comparable to that of methane. The protonation of the oxygen lone pairs in sulfuric acid would, of course, further augment the electron-withdrawing ability of the sulfate functionality.

B. C–H Activation in Aqueous Medium. The great advantage of using a strong acid as solvent is that the alcohol formed is protected either as the ester[5a,b,7,8] or by protonation.[4] However, from a practical as well as environmental standpoint, it is most desirable that the oxidations be carried out in an innocuous solvent. Water is ideal in this respect. As demonstrated by us[5d–f] and others,[6,15,16] in aqueous medium, the Pt(II) ion will activate the C–H bonds of various substrates including alkanes, resulting in their oxidation, through the electrophilic pathway shown in eq 1. Of note is the lack of products derived from C–C cleavage as was observed in sulfuric acid. A problem associated with alkane oxidations in water is that the primary product, alcohol, is not protected and is therefore very susceptible to overoxidation. Thus, it is of some importance to determine the relative rates of methane versus methanol oxidation by the Pt(II) ion in water.

Figure 3 summarizes our results on the Pt(II) oxidation of methane versus methanol. The function of the added Pt(IV) species, Na_2PtCl_6, was to act as an oxidant and prevent the reduction of Pt(II) to metallic Pt.[5d–f,15] The latter is known to catalyze the rapid oxidation of alcohols.[5d,e,17] Note that a separate experiment indicated that Na_2PtCl_6 was unreactive toward methane. Under conditions where the pressure (and hence the concentration) of methane was kept constant, a steady-state concentration of methanol was reached both in the presence and absence of initially added methanol. Under these reaction conditions, $d[CH_3OH]/dt = 0 = k_1[Pt(II)][CH_4] - k_2[Pt(II)][CH_3OH]$; therefore, the ratio of methane to methanol oxidation rate constants $(k_1/k_2) = [CH_3OH]/[CH_4]$. From the data in Figure 3, an average value of 0.17(2) was obtained. Since the formation of metallic Pt cannot be ***rigorously*** excluded, the above value represents the ***lower*** limit for the reactivity of Pt(II). It should be noted that the results shown in Figure 3 are not vitiated by the loss of oxidizing ability of the Pt(II)/Pt(IV) combination after long reaction times. For example, when methanol alone was used as the substrate, its concentration dropped well below the steady-state concentrations shown in Figure 3. When after 160 h methane was added to the system, the concentration of methanol increased again and approached the expected steady-state concentration. Finally, the source of oxygen in the methane to methanol transformation appears to be water since the oxidation was found to occur even in the absence of added O_2.

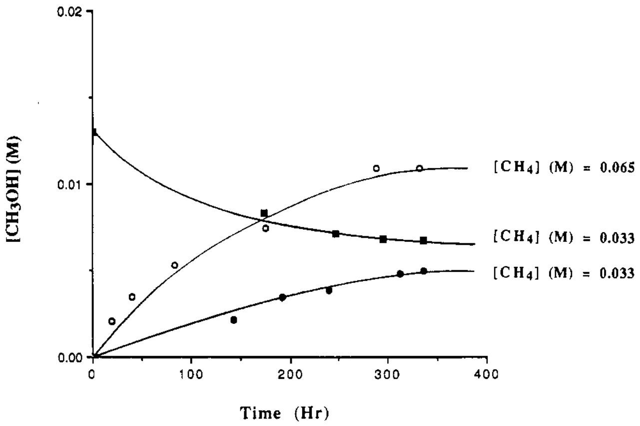

Figure 3. Plots of CH_3OH formation from CH_4 versus time obtained under the following reaction conditions: CH_4 (600 or 1200 psi), O_2 (200 psi), CH_3OH (0 or 0.013 M), Na_2PtCl_4 (0.1 mmol), Na_2PtCl_6 (0.1 mmol), and D_2O (5 mL), 100–105 °C.

It is indeed very remarkable that the Pt(II) ion in water will oxidize methane and methanol at similar rates under such mild conditions. The observed similarity in rates is even more striking because of the expected much higher binding ability of methanol to the Pt(II) center. In contrast, given that the C–H bond energy of methane is 10 kcal/mol higher than that in methanol, any oxidation procedure that involves hydrogen-atom abstraction from the substrate C–H bond would have resulted in up to six orders of magnitude difference in rate constants for methane and methanol oxidations. Thus, our results on relative oxidation rates further support the electrophilic C–H activation mechanism for alkane oxidations by Pt(II).

Moving to substrates with C–H bonds somewhat weaker than that in methane results in actual ***reversal*** of commonly observed selectivity. For example, although the methyl C–H bonds in ethanol are significantly stronger than those in the methylene group, Bercaw and Labinger observed that the former group was oxidized at a higher rate by the Pt(II)/Pt(IV) combination in water at 90 °C.[15] Indeed, under conditions where the precipitation of metallic Pt (an excellent catalyst for the oxidation of the alcohol functionality[5d,e,17]) was avoided, we have observed the ***exclusive*** oxidation of the methyl group in ethanol resulting in the formation of 1,2-ethanediol as the predominant product (along with a trace of 2-chloroethanol) (Figure 4). When both $CH_3{}^{13}CH_2OH$ and CH_3CH_3 were present as substrates (respective solution concentrations, 0.043 and 0.031 M), the products observed were 1,2-ethanediol that was predominantly unlabeled as well as unlabeled ethanol. The above set of experiments clearly shows that the relative rate of C–H bond activation by the Pt(II) ion ***decreased*** in the order H–CH_2CH_3 > H–CH_2CH_2OH > H–CH(OH)CH_3, i.e., an order that is exactly ***opposite*** of that expected on the basis homolytic C–H bond energies. On a practical level, our observations show that the direct conversion of ethane to 1,2-ethanediol was possible.

A final example of unusual selectivity involves 1-propanol where by far the strongest C–H bonds belong to the methyl terminus. As shown in Figure 5, the oxidation of 1-propanol by the Pt(II)/Pt(IV) combination led to the formation of 1,3-propanediol as the predominant product. In an earlier study, Bercaw and Labinger had estimated that the ratio of attack on the α, β, and γ C–H bonds of 1-propanol by the same metal ion combination was 2:3:3.[15b] It is possible that the significantly lower selectivity reported by them was due to the presence of metallic platinum which would favor the oxidation of α C–H bonds in particular[5d,e,17] (see Experimental Section).

While the selectivity with respect to C–H activation by the Pt(II) ion in aqueous medium is without precedent, in some instances it is still short of what is desirable from a practical standpoint. For example, in the case of selective oxidation of

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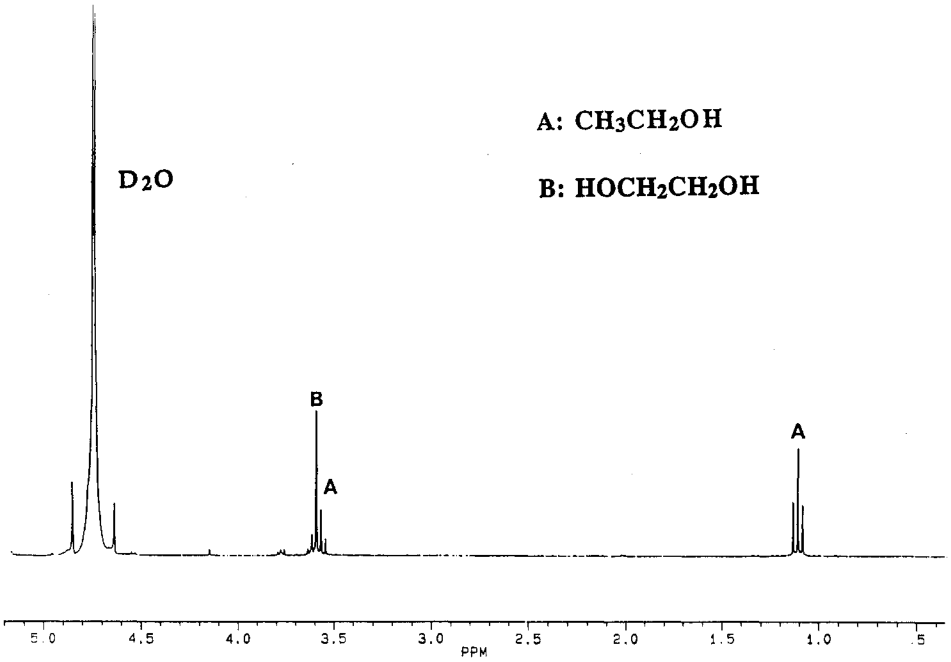

Figure 4. ^1H NMR spectrum obtained after the following reaction conditions: CH_3CH_2OH (0.04 mmol), Na_2PtCl_4 (0.05 mmol), Na_2PtCl_6 (0.05 mmol), D_2O (0.6 mL), 85 °C, 6 days.

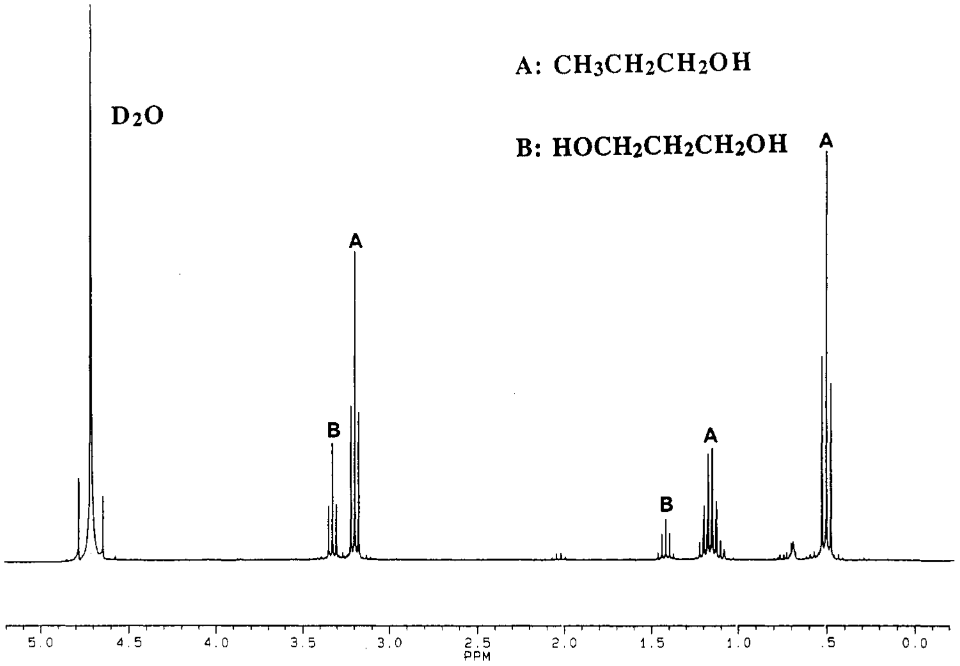

Figure 5. ^1H NMR spectrum obtained after the following reaction conditions: $CH_3CH_2CH_2OH$ (0.21 mmol), K_2PtCl_4 (0.077 mmol), K_2PtCl_6 (0.115 mmol), D_2O (1 mL), 115 °C, 1 days.

methane to methanol, as Figure 3 shows, the maximum concentration of methanol that is attainable in solution is quite low. Clearly, a system that shows an even higher methane to methanol oxidation selectivity is required.

Experimental Section

General Methods. The reagents $K_2S_2O_8$ (Fischer Scientific), $HgSO_4$ (Aldrich), and $Ce(SO_4)_2$ (Aldrich) were used as received. Palladium and platinum salts were obtained from Johnson Matthey and were used as received. Methane and ethane were purchased from Matheson. The solvents D_2SO_4 (98 wt%, Aldrich) and D_2O (99.9% D, Aldrich) were also used as received. Reaction vessels were Parr general purpose bombs. Reaction products were identified by their ^1H NMR spectra recorded on a Brucker AM 300 FT-NMR spectrometer using solvent reference at the appropriate frequency, or an external standard consisting of a capillary tube containing 1 μL of DMSO in 60 μL of D_2O used for lock, reference, and as an integration standard when sulfuric acid was used as the solvent.

Caution: (a) Appropriate precautions should be taken while working with gases under high pressures. Particular attention should be paid to flammability limits of gas mixtures. (b) The presence of metallic Pt has an adverse effect on selectivity in the oxidations by Pt(II) ion, and aqueous solutions of platinum salts should be carefully filtered prior to use. In addition, since light induces the autocatalytic decomposition of platinum salts to metallic Pt,[17b] the reactions should be carried out in the absence of light.

Methane Oxidation in Sulfuric Acid. Dry oxidant ($K_2S_2O_8$, $HgSO_4$, $Ce(SO_4)_2$, or $PdSO_4$, 0.1 mmol) was added to a glass scintillation vial, followed by the addition of 1.0 mL of D_2SO_4. The vial was then inserted into a Parr high pressure reactor and the reactor sealed. The reactor was pressurized to 1000 psi with CH_4 and then immersed in an oil bath heated to 180 °C. After 24 h, the reactor was cooled in an ice bath for approximately 30 min, depressurized, and opened. A liquid sample was taken from the scintillation vial and examined by ^1H NMR spectroscopy. The predominant product of the oxidation of methane was CH_3OSO_3H (δ, ppm 3.90, (s)).

A similar reaction using $HgSO_4$ (0.1 mmol) was conducted at 150 °C for 24 h. The ^1H NMR spectrum indicated that the major products were CH_3HgOSO_3H (δ, ppm 1.32 (s), ^2J(Hg–H) = 270.7 Hz) and CH_3OSO_3H. The yields of these two products were 64% and 14%, respectively, based on the Hg salt. After heating the same sample at 180 °C for 2 h, the ^1H NMR spectrum indicated that the CH_3HgOSO_3H had converted to CH_3OSO_3H.

Oxidation of Methane in the Presence of $^{13}CH_3OSO_3H$. $^{13}CH_3OH$ (30 μL) was added to a glass scintillation vial containing $HgSO_4$ (0.2 mmol) in 2 mL of H_2SO_4. $^{13}CH_3OH$ was instantly converted to $^{13}CH_3OSO_3H$, the concentration of which was measured by integration of the ^1H NMR spectrum versus the capillary tube external standard. Then, following the previous procedure, the methane oxidation experiment was carried out at 165 °C for 20 h. The concentration of $^{13}CH_3OSO_3H$ remained essentially constant while the oxidation products of methane, CH_3OSO_3H (0.084 mmol) and CH_3HgOSO_3H (0.12 mmol), were formed. Very little oxidation of added $^{13}CH_3OSO_3H$ was also observed in the oxidation of methane by $K_2S_2O_8$.

Ethane Oxidation in Sulfuric Acid. The experiments was conducted in a manner analogous to that described for methane, except that 550 psi of CH_3CH_3 was substituted for CH_4. The major oxidative products of ethane were CH_3OSO_3H and $HO_3SCH_2CH_2OSO_3H$ as shown in Figure 2.

Conversion of $CH_3CH_2OSO_3H$ to $HO_3SCH_2CH_2OSO_3H$. Ethyl sulfate (4 μL) was added to an NMR tube containing 0.5 mL of H_2SO_4, and the tube was sealed with a rubber septum. After heating at 180 °C for 15 min, the sample was cooled to room temperature. The ^1H NMR spectrum indicated that $CH_3CH_2OSO_3H$ was quantitatively converted to $HO_3SCH_2CH_2OSO_3H$ (δ, ppm 4.45 (t), ^3J(H,H) = 5.3 Hz, (–CH_2O–); 3.50 (t), ^3J(H,H) = 5.3 Hz, (–CH_2S–).

Oxidation of $CH_3{}^{13}CH_2OH$ in H_2SO_4. $CH_3{}^{13}CH_2OH$ (20 μL) was added to 0.5 mL of H_2SO_4 in an NMR tube which was sealed with a rubber septum. The ^1H NMR spectrum indicated that $CH_3{}^{13}CH_2OH$ was quantitatively converted to $CH_3{}^{13}CH_2OSO_3H$ (δ, ppm 4.25 (dq), ^1J(C,H) = 156.1 Hz, ^3J(H,H) = 7.8 Hz; 1.18 (dt), ^2J(C,H) = 4.5 Hz).

After heating the sample at 125 °C for 30 min, the ^1H NMR spectrum indicated that the ^{13}C-carbon was distributed equally between the two positions ($^{13}CH_3CH_2OSO_3H$, δ, ppm 1.18 (dt), ^1J(C,H) = 129.5 Hz). After heating the sample at 180 °C for 15 min, the ^1H NMR spectrum indicated that $HO_3S^{13}CH_2CH_2OSO_3H$ and $HO_3SCH_2{}^{13}CH_2OSO_3H$ were formed in equal amounts (–$S^{13}CH_2CH_2$–, ^1J(C,H) = 141.0 Hz, ^2J(C,H) = 2.3 Hz; –$CH_2{}^{13}CH_2O$–, ^1J(C,H) = 157.0 Hz, ^2J(C,H) = 3.8 Hz).

Oxidation of Ethanol to Ethylene Glycol by Pt(II) and Pt(IV). Ethanol (2.5 μL, 0.043 mmol) was added to 0.6 mL of D_2O containing Na_2PtCl_4 (0.05 mmol) and Na_2PtCl_6 (0.05 mmol) in a NMR tube. The solution was heated at 85 °C for 6 days. The ^1H NMR spectrum indicated that the major oxidation product of ethanol was $HOCH_2CH_2OH$ along with a trace amount of $ClCH_2CH_2OH$ (Figure 4).

Oxidation of Ethane by Pt(II) and Pt(IV) in the Presence of $CH_3{}^{13}CH_2OH$. $CH_3{}^{13}CH_2OH$ (10 μL, 0.172 mmol) was added to 4 mL of D_2O containing K_2PtCl_4 (0.1 mmol) and Na_2PtCl_6 (0.08 mmol) in a glass scintillation vial. The vial was then inserted into a Parr high-pressure reactor, and the reactor was sealed. The reactor was then pressurized with 550 psi of C_2H_6 and 100 psi of O_2 and heated at 100 °C for 20 h. At the end of this period, the ^1H NMR spectrum revealed that the predominant oxidation products were $HOCH_2CH_2OH$ (0.012 mmol) and CH_3CH_2OH (0.036 mmol).

Oxidation of 1-Propanol to 1,3-Propanediol by Pt(II) and Pt(IV). Propanol (17 μL) was added to 1 mL of D_2O containing 0.0319 g of K_2PtCl_4 (0.077 mmol) and 0.0755 g of K_2PtCl_6 (0.115 mmol) in an NMR tube. The tube was evacuated, sealed, and heated at 115 °C in an oil bath for 24 h. The ^1H NMR spectrum indicated that the major oxidation product of 1-propanol was 1,3-propanediol (δ, ppm 3.30, 4H, t, ^3J(H,H) = 6.8 Hz); 1.41, 2H, q, ^3J(H,H) = 6.8 Hz) (Figure 5).

Relative Rates of CH_4 vs CH_3OH Oxidation by Pt(II). Na_2PtCl_4 (0.1 mmol) and Na_2PtCl_6 (0.1 mmol) were dissolved in 5 mL of 0.013 M $^{13}CH_3OH$ in D_2O in a glass container. The glass container was placed in a high-pressure bomb which was pressurized to 600 psi with methane and then pressurized with oxygen to a total of 800 psi. The contents were stirred and heated at 100–105 °C. The ^1H NMR spectrum indicated that the concentration of $^{13}CH_3OH$ decreased, while that of CH_3OH (the oxidation product of methane) increased. The total amount of methanol was measured, and the results are plotted in Figure 3. Two similar reactions were conducted under 600 and 1200 psi of methane without adding $^{13}CH_3OH$. The amounts of CH_3OH formed were measured, and the results are also plotted in Figure 3.

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