Oxidation of Hydrocarbons by Aqueous Platinum Salts: Mechanism and Selectivity[†]

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Water-soluble organic compounds are selectively oxidized by aqueous solutions of chloroplatinum(II) and chloroplatinum(IV) salts. *p*-Toluenesulfonic acid undergoes stepwise hydroxylation to the corresponding alcohol and aldehyde, with no further oxidation to the carboxylic acid; *p*-ethylbenzenesulfonic acid is functionalized at both the benzylic and methyl positions. Ethanol is converted to a spectrum of C_2 (chloro)oxygenates, including ethylene glycol and 2-chloroethanol, products resulting from methyl functionalization. *n*-Propanol is also significantly attacked at the methyl position. ^{13}C labeling and kinetics studies were used to elucidate mechanistic pathways. The reactivity of a methyl group C–H bond is at least as high as that of a C–H bond α to oxygen, in contrast to most alkane conversion systems.

Introduction

The selective functionalization of saturated hydrocarbons is among the most attractive and elusive challenges facing chemists today. Transformations such as the hydroxylation of methane to methanol, or of linear alkanes to terminal alcohols, would be of immense potential importance for production of chemicals and fuels; yet to date no very efficient example has been reported. The primary hurdle to be overcome is that of selectivity: with most methods for hydrocarbon oxidation, whether by homogeneous or heterogeneous catalysts, the products formed are considerably more reactive than the starting alkane, so that high conversion and selectivity cannot be simultaneously achieved. Furthermore, in most hydroxylations the terminal position is generally the *least* reactive. Both of these trends are consequences of the reaction mechanism, which generally involves homolytic C–H bond cleavage as the initial step.

An approach that has received a great deal of attention over the past 10 years is activation of alkanes by organometallic species.[1] C–H bond activation by such species can be remarkably facile, and selectivity patterns, while not definitely established, tend to run *opposite* to those described above: less substituted positions are often the most reactive.[2] Unfortunately, the vast majority of examples do not appear to lead to viable catalysts for alkane functionalization. Most fall into one of two categories: low-valent, electron-rich, coordinatively unsaturated complexes of late transition metals, which react by oxidative addition of a C–H bond (eq 1), and early-transition-metal (including lanthanides and actinides) complexes with d^0 configurations, which undergo σ-bond metathesis (eq 2). In either case, the species involved are highly sensitive to oxidizing agents and/or the desired oxygenation products and hence would not survive catalytic conditions.

$$L_nM + R\text{–}H \rightarrow L_nM(R)(H) \qquad (1)$$

$$L_nM\text{–}X + R\text{–}H \rightarrow L_nM\text{–}R + H\text{–}X \qquad (2)$$

A third category, one that is not nearly so well characterized, is the reaction of alkanes with simple Pt^{II} and Pd^{II} complexes. In contrast to the previous examples, stable organometallic complexes are not obtained; instead, C–H activation is manifested by observation of catalytic H–D exchange or of (generally stoichiometric, not catalytic) alkane functionalization.[3,4] These reactions are thought to proceed via a step such as eq 3 and have been termed electrophilic substitution.

$$L_nM^{2+} + R\text{–}H \rightarrow L_nM\text{–}R^+ + H^+ \qquad (3)$$

Of particular interest is the report of alkane hydroxylation by a combination of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ salts in aqueous solution.[3] This system seems applicable to *catalytic* functionalization—the metal complexes involved are certainly capable of tolerating O_2 or other oxidants—and yet catalytic hydroxylation has not been achieved. (The homogeneous catalytic chlorination of methane to

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[1] See, for example: Hill, C. L., Ed. *Activation and Functionalization of Alkanes*; Wiley-Interscience: New York, 1989, and references therein.

[2] Jones, W. D. In ref 1, pp 128–132, and references cited therein.

[3] Shilov, A. E. In ref 1, pp 3–11, and references cited therein. Recent work on this topic is also reported in ref 16 and: Kao, L.-C.; Sen, A. *J. Chem. Soc., Chem. Commun.* 1991, 1242. Sen, A.; Lin, M. *J. Chem. Soc., Chem. Commun.* 1992, 508.

[4] Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* 1987, *109*, 8109.

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methyl chloride, by chlorine in the presence of aqueous platinum chloride salts, was recently reported.[5]) Furthermore, little detailed information is available about mechanism and consequent selectivity trends. Most of the earlier work employed hydrocarbons of low solubility in the aqueous medium, precluding the use of NMR to monitor reaction products, intermediates, and kinetics. We have examined, and here report upon, the hydroxylation of *water-soluble* organic substrates, which has enabled us to further delineate the mechanism of this system, as well as to discover novel and potentially valuable selectivity patterns. A preliminary communication of parts of this work has appeared previously.[6]

Experimental Section

General Considerations. ^{1}H NMR spectra were recorded on Varian EM390, GE 300, JEOL FX90Q, JEOL FNM400, and Bruker AM500 spectrometers. All other nuclei (^{2}H, ^{13}C, ^{195}Pt) were observed on JEOL FX90Q, GE 300, and Bruker AM500 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. Gas chromatograms were recorded on a Perkin-Elmer 8410 gas chromatograph (Carbowax, 20 m). Platinum salts were obtained from Aldrich (with the exception of Na_2PtCl_4, which was obtained from Aesar). These commercial samples are always somewhat impure: ^{195}Pt NMR spectroscopy reveals that the Pt(II) salts are contaminated with small concentrations of Pt(IV) and vice versa. Furthermore, the aqueous solutions usually exhibited small amounts of platinum metal and/or other insoluble species; these were filtered prior to use. p-$HO_3SC_6H_4COOH$ (**5**) was prepared according to ref 7. All other reagents were obtained commercially and used without further purification.

Oxidation of *p*-Toluenesulfonic Acid (1). Reactions were typically carried out on solutions of 0.2–0.4 M **1**, 0.2–0.4 M Na_2PtCl_6, and 0.02–0.05 M Na_2PtCl_4 in 0.5 cm^3 of D_2O. Samples were loaded (in air) into 5-mm NMR tubes, frozen with liquid nitrogen, and sealed in vacuo. The tubes were fully immersed in a stirred, thermostated silicon oil bath (120 °C) in an inverted position (to avoid interference with NMR by platinum mirrors); after heating, they were centrifuged to concentrate any platinum particles at the base of the tube. Stepwise formation of the alcohol p-$HO_3SC_6H_4CH_2OH$ (**2**) and aldehyde p-$HO_3SC_6H_4CHO$ (**3**) were monitored by following the growth of the corresponding ^{1}H NMR signals. H/D exchange could be detected in both unreacted **1** and product **2** by the appearance of multiplets slightly upfield from the main signal; however, these never amounted to more than a few percent of the total intensity. Under some conditions significant amounts of the chloride p-$HO_3SC_6H_4CH_2Cl$(**4**) were also detected, but the diacid p-$HO_3SC_6H_4COOH$ (**5**) was never observed. Compounds **2**–**5** are all known.[7] For determination of absolute yields reactions were run in ordinary H_2O (to eliminate H/D exchange; vide infra) in a small bomb reactor; after reaction, the solvent was removed in vacuo and the residue redissolved in D_2O containing a weighed amount of glycine as NMR reference standard. In tests for catalytic oxidation, no Pt(IV) salt was used; instead, varying amounts of either $K_2S_2O_8$ or $H_3PMo_{12}O_{40}$ were added to the solutions containing **1** and the Pt(II) salt.

Oxidation of *p*-Ethylbenzenesulfonic Acid (6) and Its Salt. Reaction of **6** under the above conditions resulted in NMR signals assigned to one major product (**7**) and a number of minor products. By NMR, **7** is also the sole product formed from the reaction of sodium p-styrenesulfonate and Na_2PtCl_4; from this fact and comparison of NMR parameters[8] to those of known Pt(II)–styrene complexes, **7** was assigned as $[(\eta^2\text{-}p\text{-}HO_3SC_6H_4CH{=}CH_2)PtCl_3]^-$. ^{1}H NMR: δ 4.42 d ($^3J_{HH}$ = 8 Hz), 4.95 d ($^3J_{HH}$ = 12 Hz), 6.28 dd ($^3J_{HH}$ = 8 Hz, 12 Hz); broad ^{195}Pt satellites ($J_{^{195}Pt^1H} \approx$ 60–70 Hz) were also observed. When the sodium salt of **6** was treated similarly, no **7** was obtained. Products were identified from the aliphatic region of the NMR (data are in the Supplementary Material), on the basis of comparison to known compounds and close analogs. The aromatic region was too complex to assign completely; hence, the exact nature of the ring-oxidized product **11** could not be determined.

Reactions of Ethanol and Other Alcohols. The oxidations of alcohols were studied under the above standard conditions, using either Na or K salts of the chloroplatinate ions. Reactions were carried out at 120 °C in sealed NMR tubes or small ampules. The organic diacid **5** (approximately 0.030 M) was employed in many cases to provide an internal NMR reference signal; the presence of variable amounts of **5** or H_2SO_4 did not influence reactions. Products were identified by ^{1}H and ^{13}C NMR and/or GC. In the case of ethanol, mono- and di-^{13}C-labeled as well as unlabeled ethanol were used to provide all needed shifts and coupling constants. All parameters agreed with literature values (note that aldehydes exist primarily as hydrates under these conditions[9]). Reactions were monitored in time by ^{1}H and ^{13}C NMR spectroscopy and/or by GC. Since the β-hydrogens of aldehydes and ketones readily exchange with the solvent, the relative concentrations were determined from integrated ^{13}C NMR signals (scaled by comparison with other compounds) and from GC. Carbon dioxide was determined on larger scale reactions (0.45 mmol of alcohol, standard conditions) carried out in small glass bombs; the solutions were thoroughly degassed by three freeze–pump–thaw cycles before reaction. After completion, the gas was transferred by Toepler pump into a gas bulb of known volume, or to a 10-cm gas cell for IR identification (CO_2 yields are given on a moles of carbon basis). Products quantified by these methods generally accounted for at least 80% of the consumed alcohol; a few (mostly quite weak) signals in the ^{1}H and ^{13}C NMR remain to be assigned. Reactions of other C_2 (chloro) oxygenates, such as chloroacetaldehyde, were carried out under the same conditions as for ethanol.

Reaction of Zeise's Salt and Na_2PtCl_6. A 15-mg portion of $KPt(C_2H_4)Cl_3{\cdot}H_2O$ (0.038 mmol) and 50 mg of $Na_2PtCl_6{\cdot}6H_2O$ (0.088 mmol) were dissolved in 0.5 mL of D_2O, and this solution was heated for 20 min at 120 °C in a sealed NMR tube under vacuum (p-$HO_3SC_6H_4COOH$ (**5**) added as internal reference). Ethylene glycol (0.012 mmol, 31%) and chloroethanol (0.020 mmol, 52%) were formed, plus trace amounts of acetaldehyde (<0.5%).

Results

Oxidation of *p*-Toluenesulfonic Acid (1). p-Toluenesulfonic acid (**1**) is oxidized cleanly at the methyl position, leading to alcohol **2** and aldehyde **3** (eq 4). The

$$\underset{1}{p\text{-}HO_3SC_6H_4CH_3} \rightarrow \underset{2}{p\text{-}HO_3SC_6H_4CH_2OH} \rightarrow \underset{3}{p\text{-}HO_3SC_6H_4CHO} \quad (4)$$

NMR spectrum shows clearly that no more than a trace of any other product is formed (Figure 1); in particular,

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(5) Horváth, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, *12*, 8.

(6) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 5628.

(7) **2**: Hubbuch, A.; Bindewald, R.; Fohles, J.; Nuithani, V. K.; Zuhn, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 394. **3**: Bollag, W. *Eur. J. Med. Chem.* **1983**, *18*, 394. **4**: Amagasa, M.; Hida, M.; Kamoi, Y. *Kogyo Kagasku Zasshi* **1949**, *52*, 116; *Chem. Abstr.* **1951**, *45*, 2149. **5**: Smiles, S.; Harrison, D. C. *J. Chem. Soc.* **1922**, *21*, 2023. NMR parameters have not been reported for all of these compounds; data are provided in the supplementary material.

(8) (a) Kinugasa, T.; Nakamura, M.; Yamada, H.; Saika, A. *Inorg. Chem.* **1968**, *7*, 2649. (b) Cooper, D. G.; Powell, J. *Inorg. Chem.* **1976**, *15*, 1959.

(9) Chastrette, F.; Bracoud, C.; Chastrette, M.; Mittioda, G.; Christidis, Y. *Bull. Soc. Chim. Fr.* **1985**, 66.

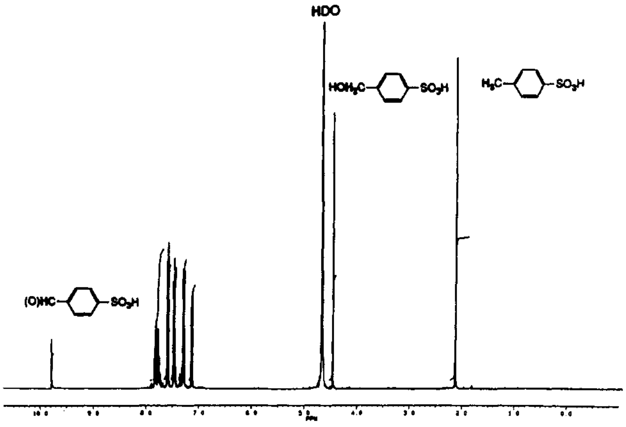

Figure 1. ^{1}H NMR spectrum of oxidation of *p*-toluenesulfonic acid after 2 h at 120 °C (D_2O; standard concentrations (see text)).

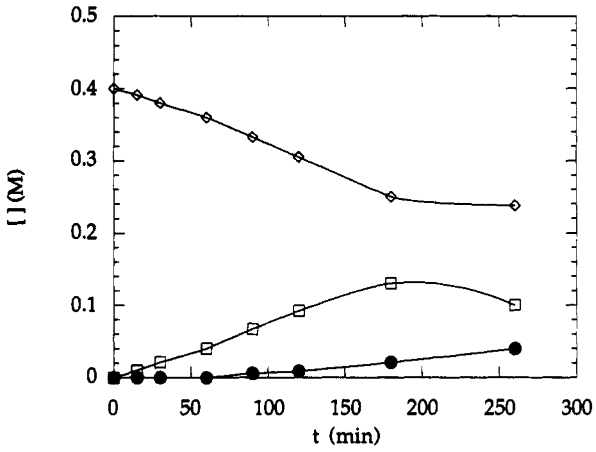

Figure 2. Oxidation of *p*-toluenesulfonic acid (0.40 M) at 120 °C ($[Pt(IV)]_0$ = 0.18 M, $[Pt(II)]_0$ = 0.026 M): (◇) $HSO_3C_6H_4CH_3$ (1); (□) $HSO_3C_6H_4CH_2OH$ (2); (●) $HSO_3C_6H_4CHO$ (3).

there is no further oxidation to the carboxylic acid 5. There is also no evidence for oxidation at aromatic ring positions, although slow competing H/D exchange is observed at both methyl and ring sites. Products 2 and 3 are formed sequentially, as can be seen by monitoring their formation over time (Figure 2) and by the direct reaction of 2, prepared by literature methods,[7] under the standard conditions. Small amounts of the chloride 4 are also formed when the initial total chloride/1 ratio is higher than the standard values. Solutions remain visibly homogeneous for the majority of the reaction time (typically around 6 h for standard conditions), but deposition of platinum metal is always eventually observed. As shown in Table I, the degree to which 1 is converted to 2 and 3 as a number of factors are varied has been examined. Note in particular that oxidation is observed even if only one oxidation state of Pt is initially added, although, as noted in the Experimental Section, small amounts of the other will always be present as impurities. The dependence of rate on concentration of the two oxidation states was examined in more detail. Whereas the kinetics of these reactions are complex (vide infra), they are roughly first order at low (<20%) conversions of 1 under the conditions employed (0.4 M 1, 0–0.4 M Na_2PtCl_6, and 0–0.2 M Na_2PtCl_4 in D_2O). The first-order rate constants for disappearance of 1 estimated in this manner are shown in Table II. Although there is no simple dependence discernible, it does appear that the rate increases with [Pt(II)], although not linearly, whereas the rate decreases with [Pt(IV)]. The last entry in Table IV suggests that 1 is about 1.5 times as reactive as 2 under otherwise identical conditions. This conclusion is also supported by examining the relative amounts of the two products, which in Table I can be seen to depend primarily on the degree of conversion, as would be expected for a stepwise sequence. Fitting the ratio of products to a simple model of two successive pseudo-first-order reactions gives rate constants whose ratio is also close to 1.5:1.

The appearance of platinum metal raises the issue of possible heterogeneously catalyzed reactions. No oxidation at all is observed on exposing 1 to colloidal platinum under standard conditions; of course, no obvious oxidant is present. Addition of colloidal platinum to a standard reaction does not affect the rate. Addition of elemental mercury, a standard test for heterogeneous activity,[10] decreases but does not suppress activity (Table I). The decrease may be attributed to the fact that Hg(0) reduces both Pt(II) and Pt(IV).

For reactions in D_2O, H/D exchange competes with oxidation, as shown by both isotopically shifted multiplets in the ^{1}H spectrum and growth of the corresponding new peaks in the ^{2}H spectrum. At early stages the extent of exchange is relatively minor; however, at later stages it becomes more significant. Furthermore, while at early stages exchange takes place about equally at all positions, later the degree of exchange at the methyl group of 1 increases substantially relative to that at the aromatic positions, beginning just about the same time that deposition of Pt metal becomes significant, suggesting that at least a part of the exchange may be catalyzed heterogeneously. We have not explored this issue in any more detail. Although no ring oxidation was detected for 1, treatment of sodium *p*-toluate under the same conditions led mostly to a ring-hydroxylated product, along with a smaller amount of *p*-(hydroxymethyl)benzoate. H/D exchange was much more extensive than with 1. The reasons for this difference are not entirely clear but may be related to deposition of Pt metal, which appears to accelerate ring oxidation as well as H/D exchange.

Oxidation of *p*-Ethylbenzenesulfonic Acid (6). In order to test the possible role of benzylic activation in reactions of 1, ethyl analog 6 was oxidized under the same conditions. While the expected products 8 and 9 (eq 5)

$$\underset{6'}{^-O_3SC_6H_4CH_2CH_3} \rightarrow \underset{8'}{^-O_3SC_6H_4CHOHCH_3} + \underset{9'}{^-O_3SC_6H_4CH_2CH_2OH} + \underset{10'}{^-O_3SC_6H_4CH_2CH_2Cl} + \underset{11'}{^-O_3SC_6H_3XCH_2CH_3} \quad (5)$$

did appear to be present by NMR, the major product was assigned as styrene complex $[(\eta^2\text{-}p\text{-}HO_3SC_6H_4CH{=}CH_2)PtCl_3]^-$ (7), presumably formed by (acid-catalyzed) dehydration of the alcohol(s). Replacing 6 with its sodium salt 6′ eliminated this pathway, giving the results shown in Table III. The aromatic region of the ^{1}H NMR spectrum is too complex to assign completely; hence, the exact nature of the ring-oxidized product 11 could not be determined.

Under standard conditions the ratio of substitution at $\alpha:\beta$ positions is 0.46:1. The fact that hydroxylations at the terminal methyl and benzylic methylene positions of 6′ occur at comparable rates indicates that the factors

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[10] Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

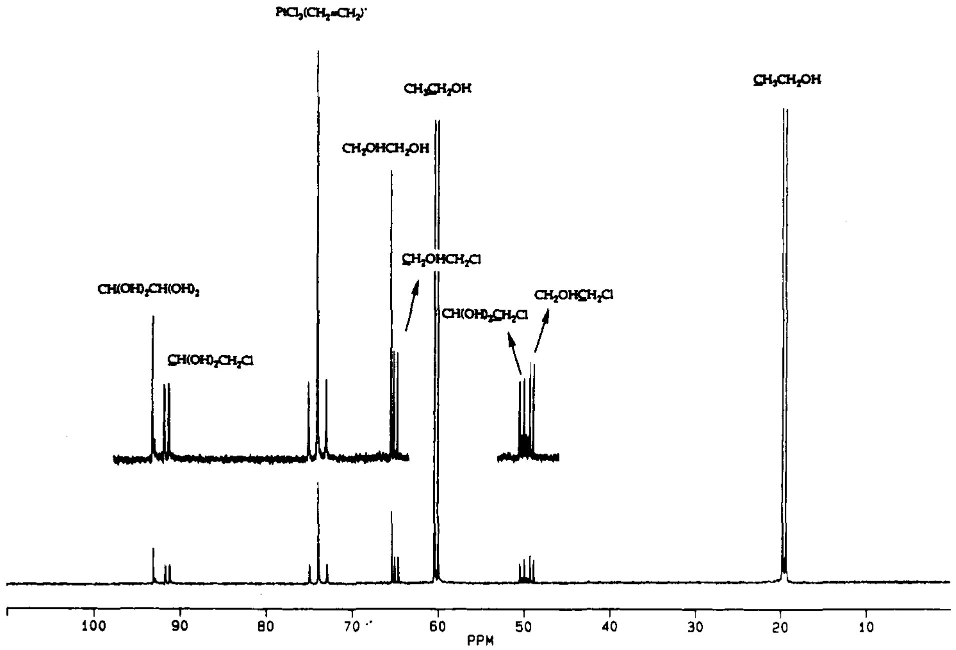

Figure 3. Oxidation of 1,2-$^{13}C_2$-ethanol at 120 °C after 30 min. Satellite signals upfield indicate H/D exchange with D_2O ($[Pt(IV)]_0$ = 0.22 M, $[Pt(II)]_0$ = 0.028 M, $[ethanol]_0$ = 0.42 M).

Table I. Oxidation of 1 under Different Conditions

[1], M	[Pt(IV)], M	[Pt(II)], M	other	*t*, h	*T*, °C	% converted	2:3
0.406	0.22	0.026		1	122	11	8:1
0.406	0.22	0.026		6	100	14	12:1
0.406	0.22	0.026		83	80.4	15	7:1
0.406	0.22			3.3	122	14	10:1
0.406		0.183		1.5	122	14	5:1
0.155	0.11	0.013		39	115	46	2:1
0.155	0.11	0.013	light excluded	39	115	49	1:1
0.155	0.11	0.013	5 M HCl	85	115	0	
0.155	0.11	0.013	0.009 M bpy	39	115	13	5:1
0.155	0.11	0.013	Hg	23	115	16	11:1
0.394	0.22	0.026		14.5	122	60	1:1
0.394			Pt metal	20	122	0	

Table II. Dependence of Oxidation Rate on Pt Concentration[a]

[Pt(IV)], M	[Pt(II)], M	k_{init}, s^{-1}
0.178	0.020	3.7×10^{-5}
0.178	0.080	6.5×10^{-5}
0.356	0.020	1.5×10^{-5}
0.178		3.7×10^{-6} [b]
	0.183	1.4×10^{-5} [c]
0.178	0.020	2.4×10^{-5} [d]

[a] Conditions: [1] = 0.40 M; *T* = 122 °C. [b] *k* increases after an induction period of about 1.5 h. [c] Deposition of Pt metal begins immediately. [d] **2** used as substrate.

Table III. Oxidation of Sodium *p*-Ethylbenzenesulfonate[a]

[Pt(IV)], M	[Pt(II)], M	*t*, h	[8], M	[9], M	[10], M	[11], M	α:β[b]
0.22	0.026	4	0.013	0.021	0.019	0.014	0.46
0.22	0.000	6	0.009	0.028	0.012	0.030	0.33
0.00	0.22	6	0.010	0.005	0.000	0.011	2.0

[a] Conditions: [6] = 0.22 M; *T* = 122 °C. [b] [8]/([9] + [10]).

governing reactivity are quite different from those in radical reactions. In comparison to 1, here there is (i) greater formation of chloride, but only in the β-position, (ii) considerably more ring oxidation, and (iii) no detectable subsequent oxidation to aldehyde. Oxidation occurs at the α- and β-positions at comparable rates, but the apparent relative reactivity of the two positions depends strongly on the relative concentrations of the Pt species: higher concentrations of Pt(IV) favor β-attack, while α is favored by higher [Pt(II)].

Table IV. Reactions Catalytic in Pt[a]

$ArCH_3$	Pt^{II}	$K_2S_2O_8$	$ArCH_2OH$	ArCHO	ArCOOH	2e$^-$/Pt	2e$^-$/S_2O_8
1.0	0.1	0	0.08			0.8	
1.0	0.1	1.0	0.42	0.05	0.05	6.8	0.71
1.0	0.1	2.0	0.50	0.12	0.24	14.7	0.72
1.0	0	1.0	0.12	0.03	0.06		0.42

$ArCH_3$	Pt^{II}	PMo_{12}	$ArCH_2OH$	ArCHO	2e$^-$/Pt	2e$^-$/PMo
1.0	0.1	0.1	0.14	0.05	2.5	1.7
1.0	0.1	1.0	0.2	0.12	4.5	0.5
1.0	0	0.1				

[a] Standard conditions (see text); Ar = p-$HO_3SC_6H_4$–. Entries in the first six columns are equivalents relative to the $ArCH_3$; entries in the last two columns are total oxidizing equivalents represented by the three products, relative to Pt or to oxidant, respectively.

Catalytic Oxidation. Reactions of *p*-toluenesulfonic acid were run with Pt(II) and either peroxydisulfate or phosphomolybdic acid as oxidant to determine whether Pt(IV) is an *obligatory* stoichiometric oxidant; results are shown in Table IV. With the stronger oxidant $S_2O_8^{2-}$, up to 15 turnovers could apparently be achieved; however, this is somewhat misleading, as some oxidation takes place even in the absence of Pt, and oxidation all the way to the carboxylic acid is observed here as well. Phosphomolybdic acid gave only 4–5 turnovers, but there was no blank

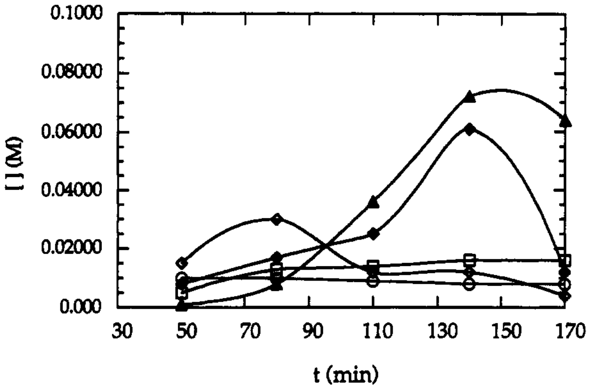

Figure 4. Oxidation of ethanol in D_2O at 120 °C ($[Pt(IV)]_0 = 0.18$ M, $[Pt(II)]_0 = 0.026$ M, $[\mathbf{5}] = 0.030$ M, $[\text{ethanol}]_0 = 0.30$ M): (○) CH_2OHCH_2OH; (□) CH_2OHCH_2Cl; (◆) Pt(ethene); (◇) $CH_2ClCH(OH)_2$; (▲) $CH(OH)_2CH(OH)_2$.

reaction and no carboxylic acid. Other cooxidants tried (O_2, $CuCl_2$) showed no increase in conversion compared to the Pt system alone.

Oxidation of Ethanol. The reaction of ethanol with chloroplatinum complexes was first studied as long ago as 1827, when Zeise's salt, $(\eta^2\text{-}C_2H_4)PtCl_3^-$ (**12**), was first reported. More recently, such reactions have been found to give acetaldehyde, possibly via formation and hydrolysis of Zeise's salt.[11] The fact that the methyl group in **1** is more reactive than the hydroxymethyl group in **2** suggests that the Pt(IV)/Pt(II) system, in contrast, might oxidize ethanol directly to ethylene glycol. Such transformations are, of course, very desirable in organic synthesis, provided the reactions have some selectivity.

Reaction of ethanol with the Pt(IV)/Pt(II) mixture does indeed yield ethylene glycol.[6] In fact, a spectrum of C_2 (chloro) oxygenates is formed. In the initial phase of the oxidation, chloroacetaldehyde (hydrate), ethylene glycol, 2-chloroethanol, and Zeise's salt were the dominant species; in later stages glyoxal (hydrate) and acetic, glycolic, glyoxalic, and chloroacetic acids were detected.[12] Products were identified from the ^{13}C NMR spectra of species obtained from doubly ^{13}C labeled ethanol and by comparison to authentic samples. Carbon dioxide is also produced. Under standard conditions (0.18 M K_2PtCl_6, 0.026 M K_2PtCl_4, 0.298 M ethanol, 0.25 mL of D_2O) about 50% of the ethanol is eventually converted into products, with a typical final distribution shown in eq 6.

$$\begin{aligned} CH_3CH_2OH \rightarrow\ & \underset{3\%}{HOCH_2CH_2OH} + \underset{5\%}{ClCH_2CH_2OH} + \\ & \underset{1\%}{ClCH_2CH(OH)_2} + \underset{21\%}{CH(OH)_2CH(OH)_2} + \\ & \underset{4\%}{(\eta^2\text{-}C_2H_4)PtCl_3^-} + \underset{6\%}{CH_3CO_2H} + \underset{4\%}{HOCH_2CO_2H} + \\ & \underset{\text{trace}}{CH(OH)_2CO_2H} + \underset{\text{trace}}{ClCH_2CO_2H} + \underset{>8\%}{CO_2} \quad (6) \end{aligned}$$

The reaction starts off slowly; virtually no product is formed in the first 30 min (see Figure 4), followed by a rapid increase in rate. This initial period of slow reaction is independent of [Pt(II)] (between 0.026 and 0.06 M) and the concentration of $p\text{-}HO_3SC_6H_4COOH$ (normally added as an inert internal reference) or small amounts of H_2SO_4. Preheating the Pt(IV)/Pt(II) solution before adding ethanol also has no effect. Higher initial concentrations of Pt(II) result in a decrease in reaction rate and in formation of a larger amount of chloroethanol relative to glycol. Both effects are presumably caused by the higher $[Cl^-]$, which parallels the observations made for the oxidation of *p*-toluenesulfonic acid. In contrast, rapid initial appearance of product was observed when Zeise's salt was substituted for $PtCl_4^{2-}$ (vide infra). Lowering the initial concentration of ethanol leads to a sharp decrease in rate; at 0.15 M (standard conditions otherwise), the reaction takes over 6 h for completion.

Formation of Ethylene Glycol and 2-Chloroethanol. Some additional aspects concerning the reaction pathway for ethanol oxidation to ethylene glycol or 2-chloroethanol were investigated using various labeled ethanols. The carbon label in 1-^{13}C-ethanol and the deuterium labels in either 1,1-dideuterio- or 2,2,2-trideuterioethanol do not exchange between α- and β-positions in ethanol. No kinetic isotope effect on the oxidation of the deuterium-labeled ethanols 1,1-dideuterio- or 2,2,2-trideuterioethanol was observed; to within experimental uncertainty (±5%), rates for both labeled compounds as well as nonlabeled ethanol were equal.[13]

The 2-chloroethanol produced from 1-^{13}C-ethanol has the carbon label *equally* distributed over both positions, indicating that a symmetric intermediate has been formed along the reaction pathway. An obvious candidate, ethylene glycol, is *not* a precursor for 2-chloroethanol. Reaction of equal amounts of glycol and 1,2-$^{13}C_2$-ethanol with the Pt(IV)/Pt(II) system gives only labeled (no unlabeled) 2-chloroethanol. Conversely, the amount of ethylene glycol formed cannot be explained by simple hydrolysis of chloroethanol. In a control experiment, only about 10% of 2-chloroethanol is converted into glycol under standard conditions with Pt(II)/Pt(IV).[14]

A more likely candidate is Zeise's salt, $Pt(C_2H_4)Cl_3^-$, which is also present in the reaction mixture. The possible intermediacy of Zeise's salt was tested as follows: it is known that oxidation of $Pt(C_2H_4)Cl_3^-$ by Cl_2 results in the formation of ethylene glycol and chloroethanol (but not 1,2-dichloroethane).[15] Indeed, we observed that the reaction between Zeise's salt and $PtCl_6^{2-}$ yields these same products.[16] Reaction was complete within 20 min at 120 °C, and no other products were formed.[17] In addition, Zeise's salt may be substituted for $PtCl_4^{2-}$ as catalyst for the oxidation of ethanol by $PtCl_6^{2-}$. When a mixture of 1,2-$^{13}C_2$-ethanol and nonlabeled $Pt(C_2H_4)Cl_3^-$ is oxidized, in the early stages, *unlabeled* glycol and chloroethanol are formed, and the concentration of $Pt(C_2H_4)Cl_3^-$ decreases close to zero. After 25 min, the concentration of *labeled* $Pt(^{13}C_2H_4)Cl_3^-$ starts to build up.

Formation of More Oxidized Products. Chloroacetaldehyde (hydrate) formed from 1- or 2-^{13}C-ethanol

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[11] Hass, D.; Hauthal, T. *Z. Chem.* **1975**, *15*, 33.

[12] Some minor signals in the NMR (^1H and ^{13}C) could not be assigned; the only "missing" products, hydroxyacetaldehyde and oxalic acid, were separately shown to be consumed rapidly under standard reaction conditions. The mass balance of the reaction is further obscured by extensive H/D exchange with the solvent.

[13] Kinetic deuterium isotope effects were measured by internal competition with mixtures of the isotopomers under the standard reaction conditions.

[14] The hydrolysis rate for chloroethanol is unaffected by the addition of ca. 0.15 M 1,2-^{13}C-ethanol.

[15] Halpern, J.; Jewsbury, R. A. *J. Organomet. Chem.* **1979**, *181*, 223.

[16] See also: Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.

[17] Some trace amounts of acetaldehyde are also present, probably due to reaction of $Pt(C_2H_4)Cl_3^-$ with water via the Wacker mechanism. Reaction of Zeise's salt with $PtCl_6^{2-}$ at room temperature slowly gives the same products as Cl_2 oxidation,[15] $PtCl_5(CH_2CH_2OH)^{2-}$ and $PtCl_5(CH_2CH_2Cl)^{2-}$, by ^1H NMR.

is found to have label almost entirely in the carbonyl or chloromethyl position, respectively. This excludes chloroethanol as an important precursor to chloroacetaldehyde. Independently it was shown that oxidation of chloroethanol is too slow to account for the amount of chloroacetaldehyde present. Chloroacetaldehyde may arise from *rapid* oxidation of acetaldehyde; the rate of conversion of acetaldehyde to chloroacetaldehyde plus some glyoxal under standard conditions was shown separately to be fast enough to account for the amounts of chloroacetaldehyde obtained from ethanol. Alternatively, chloroacetaldehyde could originate from a (vinyl alcohol)platinum adduct, $Pt(CH_2{=}CHOH)$ (see Discussion).

Glyoxal presumably results from oxidation and subsequent hydrolysis of chloroacetaldehyde: the concentration of the latter compound builds up to a maximum value and then decreases, concomitant with the appearance of glyoxal. Oxidation of chloroacetaldehyde with the Pt(II)/Pt(IV) system under standard conditions does indeed give glyoxal as the major product, together with some acetic, glycolic, and glyoxalic acids at a rate consistent with the proposal that chloroacetaldehyde mediates formation of glyoxal. Glyoxal is also formed by oxidation of ethylene glycol under standard reaction conditions.

Substantial amounts of acids, particularly acetic acid, are observed *only* when Pt metal is present. Glycolic acid is a secondary product, mainly originating from glycol. This was concluded from the distribution of carbon labels when starting from 1-^{13}C-ethanol: the ^{1}H NMR spectrum for the products shows two doublets for $HOCH_2CO_2H$, with J(CH) = 145 and 4.3 Hz, assigned to $HO^{13}CH_2CO_2H$ and $HOCH_2{}^{13}CO_2H$, respectively. The intensity ratio is close to 1:1 (53:47), implying a symmetric intermediate (glycol) and excluding β-oxidation of acetic acid or hydrolysis of chloroacetic acid as a major route. In a separate experiment it was observed that oxidation of acetic acid is slow under standard conditions; no detectable amounts of products were formed after 1.5 h. Hydrolysis of chloroacetic acid is also slow. The β-hydrogen atoms in both acetic and glycolic acid show extensive H/D scrambling with the solvent.

The carbon dioxide obtained from the same mono-^{13}C-labeled ethanol consists of 40% $^{12}CO_2$ and 60% $^{13}CO_2$ (from intensities of the IR peaks). The most probable immediate precursor of CO_2 is oxalic acid. Independently, it was shown that oxalic acid is completely converted to CO_2 under reaction conditions. On the other hand, if oxalic acid is the sole precursor to CO_2, equal amounts of the two isotopomers are expected. An additional path (such as oxidative decarboxylation of acetic acid) that converts only the labeled carbon to CO_2 must be responsible for about 25% of the total. The other C_1 product implied by this result was not completely accounted for, but ^{13}C NMR shows the presence of some formic acid.

Selectivity. The selectivity for attack at the β- and α-positions is estimated by the ratio of products (Zeise's salt + chloroethanol + ethylene glycol): chloroacetaldehyde, measured at early stages of the reaction before substantial conversion to secondary products has taken place. This ratio was found to be approximately 1.5:1. The selectivity again is strongly dependent on the Pt species present. Oxidation at the α-carbon is favored when elemental platinum is present. Either adding metallic platinum at the start of the reaction (standard conditions in Pt(IV)/Pt(II), ethanol) or using only Pt(II) (where deposition of Pt accompanies reaction from the beginning) results only in the production of acetaldehyde and acetic acid; no methyl oxidation products are observed.

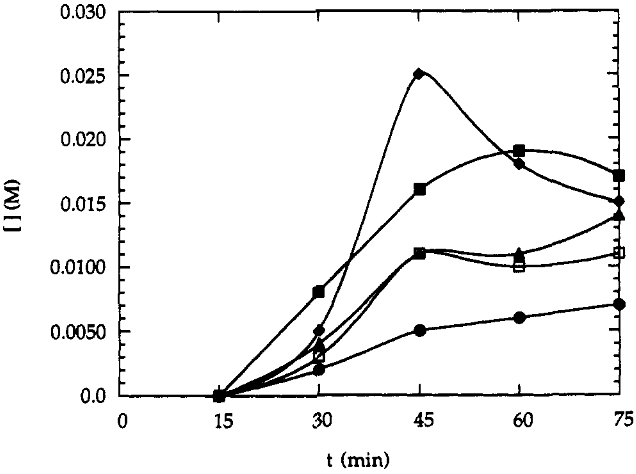


Figure 5. Oxidation of 1-propanol in D_2O at 120 °C ($[Pt(IV)]_0$ = 0.18 M, $[Pt(II)]_0$ = 0.026 M, [**5**] = 0.030 M, $[\text{1-propanol}]_0$ = 0.30 M): (■) $CH_3CH_2CH(OH)_2$; (◆) Pt(propene); (▲) $CH_2ClCH_2CH_2OH$; (□) $CH_2OHCH_2CH_2OH$; (●) CH_3COCH_3.

Reactions of Other Alcohols. The water-soluble alcohols methanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol were examined under standard conditions. Methanol appears to be the least reactive, with carbon dioxide as the only significant product detected. The oxidation of 1-propanol gives initially a number of products (Figure 5) which can be classified (see Discussion) as arising from γ-(1,3-propanediol, 1-chloropropan-3-ol), β-(propene–$PtCl_3^-$, acetone), or α-attack (1-propanal (hydrate)). From the respective yield of these products, the ratio for initial attack at the α:β:γ positions was estimated as 2:3:3. Toward the end of the reaction some new products are formed, probably higher oxygenates which are the result of further oxidations; none of them was identified positively. Carbon dioxide is also produced (eq 7). The

$$CH_3CH_2CH_2OH \rightarrow \underset{8\%}{ClCH_2CH_2CH_2OH} + \underset{4\%}{HOCH_2CH_2CH_2OH} + \underset{>6\%}{CH_3COCH_3} + \underset{\mathbf{13},\ <1\%}{(CH_3CH{=}CH_2)PtCl_3^-} + \underset{10\%}{CO_2} \quad (7)$$

reaction is complete within 1.5 h (conversion 35–40%), somewhat faster than the oxidation of ethanol. In contrast, the oxidation of 2-propanol gives only acetone and carbon dioxide (eq 8); the propene–Pt adduct **13** is observed in

$$CH_3CH(OH)CH_3 \rightarrow \underset{60\%}{CH_3COCH_3} + \underset{11\%}{CO_2} \quad (8)$$

intermediate stages (Figure 6). This reaction is somewhat slower than ethanol oxidation (complete in 3.5 h, conversion 70–75%). The fastest oxidation was observed with 2-methyl-2-propanol as substrate: reaction was complete within 40 min. The major oxidation product is carbon dioxide, accounting for approximately 85% of the electrons available. The remaining alcohol is dehydrated to 2-methylpropene (partially deuterated). During the reaction extensive H/D exchange between unreacted 2-methyl-2-propanol and D_2O takes place.

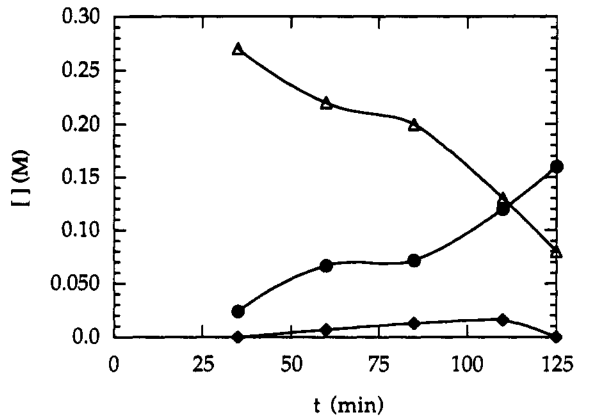
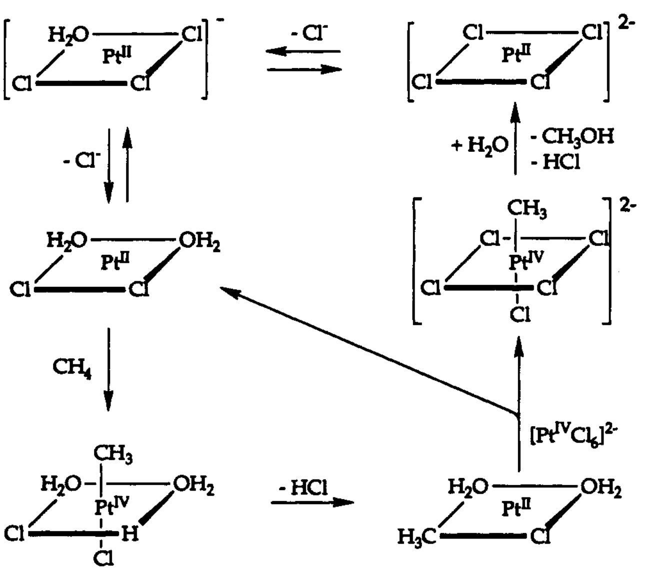


Figure 6. Oxidation of 2-propanol in D_2O at 120 °C ($[Pt(IV)]_0$ = 0.18 M, $[Pt(II)]_0$ = 0.026 M, [**5**] = 0.030 M, $[2\text{-propanol}]_0$ = 0.30 M): (▲) $CH_3CH_2OHCH_3$; (●) CH_3COCH_3; (◆) Pt(propene).

Scheme I



Discussion

Mechanism of Alkane Oxidation. Shilov's original proposal for the mechanism of alkane oxidation is shown in Scheme I.[3] The first, key step is oxidative addition of a C–H bond to a Pt(II) center, followed by loss of proton to give an alkyl–Pt(II) complex. According to this proposed mechanism, in the absence of Pt(IV), only H/D exchange (by reversal of this sequence) is observed, but with Pt(IV) also present the alkyl–Pt(II) complex is transformed into a alkyl–Pt(IV) species (by either alkyl or electron transfer). The resulting alkyl–Pt(IV) complex undergoes nucleophilic attack by water (or chloride) to form the alcohol (or alkyl chloride) and Pt(II).[3,18] The net stoichiometry is that of eq 9.

$$RH + L_4Pt^{IV}Cl_2 + H_2O \rightarrow ROH + L_4Pt^{II} + 2HCl \quad (9)$$

$$L = Cl^-, H_2O$$

Our results with *p*-toluenesulfonic acid are consistent with a modified version of this mechanistic proposal. The fact that oxidation is observed even in the absence of added Pt(IV) can be rationalized by the fact that the reduction potentials of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ are very similar, and hence, alkyl–Pt(II) compounds could be oxidized to alkyl–Pt(IV) species by Pt(II) as well as by Pt(IV). In that case, immediate deposition of Pt metal would accompany the reaction—as is observed. This modified mechanistic pathway would strongly imply that the reaction of alkyl–Pt(II) with Pt(IV) involves electron transfer, not alkyl transfer.

Another possibility is that the entire scheme for oxidation of *p*-toluenesulfonic acid—C–O bond formation as well as C–H activation—is mediated by Pt(II), with the sole role of Pt(IV) being to intercept Pt(0) before it aggregates to deposit metal, as shown in eqs 10 and 11, a

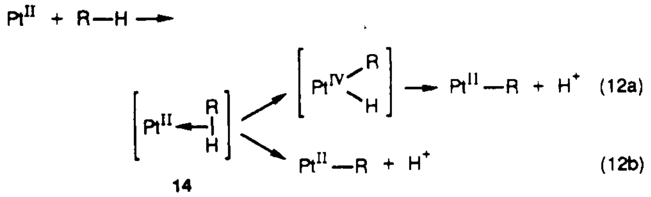
$$RH + L_2Pt^{II}Cl_2 + H_2O \rightarrow ROH + Pt^0 + 2HCl + 2L \quad (10)$$

$$Pt^0 + Pt^{IV} \rightarrow 2Pt^{II} \quad (11)$$

reaction sequence reminiscent of Wacker oxidation of ethylene, as well as the analogous functionalization of hydrocarbons by Pd(II).[4] This pathway may not be significant in the case of a *general* C–H bond, as Pt(II) alone generates little or no methyl oxidation products from ethanol, but rather α-oxidation products, probably catalyzed by Pt metal (see below). However, it might be more favorable for *benzylic* positions, as in *p*-toluenesulfonic acid. This possibility is suggested by the dependence of regioselectivity on Pt oxidation state in reactions of *p*-ethylbenzenesulfonic acid (Table III). Much more of the β-oxidized products are found when Pt(IV) is added, in agreement with the postulate that complete functionalization can be accomplished by Pt(II) alone at the benzylic position, but not at the terminal, non-benzylic methyl group.

A rigorous distinction between these two possibilities—Scheme I vs eqs 10 and 11—is not possible at present, and indeed both may be operating in any given case. It may be noted that there is precedent for formation of C–O and C–Cl bonds by attack of water or Cl^- on isolated alkyl–Pt(IV) complexes such as $[CpCo(PO(OR)_2)_3]Pt(CH_3)_3$[19] and $[(CH_3)PtCl_5]^{2-}$,[20] but no such reaction of an alkyl–Pt(II) complex is known.

Nature of C–H Activation. Shilov's proposal involves oxidative addition followed by deprotonation (eq 12a);[3] however, oxidation of Pt(II) to $Pt^{IV}(R)(H)$ does not appear very attractive (and even less so for the analogous Pd chemistry[4]). Furthermore, it is difficult to see why



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activation of C–H should be competitive with that of C–Cl, as implied by some of the secondary ethanol reactions (see below), if oxidative addition is operating. A more

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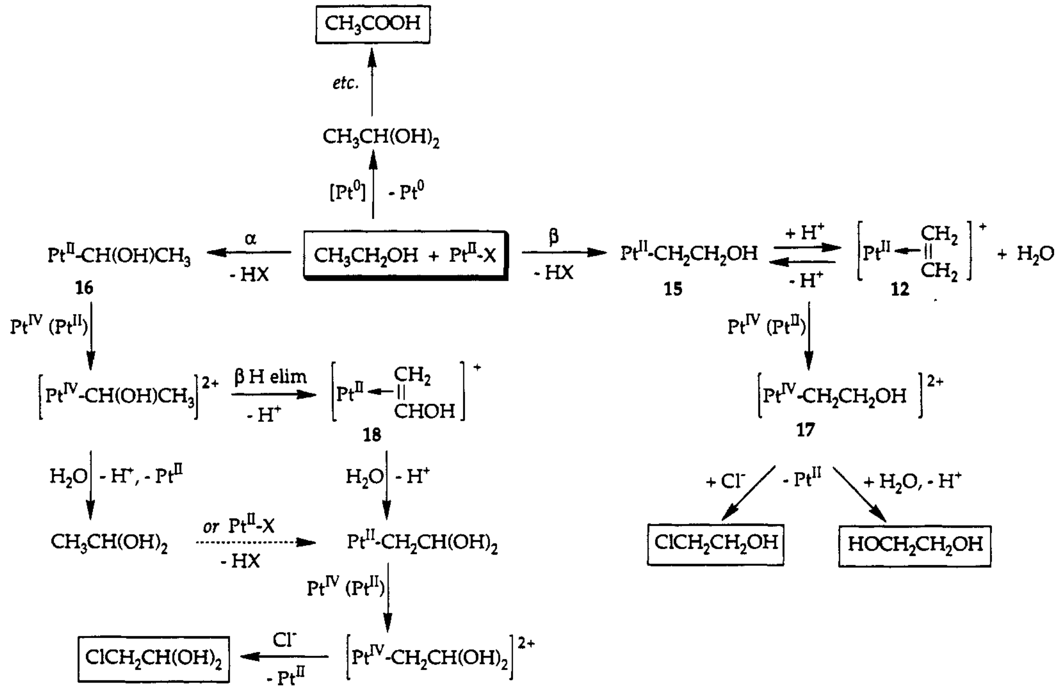
(18) (a) Zamashchikov, V. V.; Kitaigorodskii, A. N.; Litvinenko, S. L.; Rudakov, E. S.; Uzhik, O. N.; Shilov, A. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, *8*, 1730. (b) Zamashchikov, V. V.; Litvinenko, S. L.; Shologon, V. I. *Kinet. Katal.* **1987**, *28*, 1059 and references cited therein.

(19) Marsh, R. E.; Schaefer, W. P.; Lyon, D. K.; Labinger, J. A.; Bercaw, J. E. *Acta Crystallogr., Sect. C*, in press. Bercaw, J. E.; Labinger, J. A.; Lyon, D. K., unpublished results.

(20) Luinstra, G.; Labinger, J. A.; Bercaw, J. E., submitted for publication.

Scheme II



reasonable alternative is shown in eq 12b. There is increasing evidence for an intermediate involving the C–H bonding pair as donor to a vacant metal orbital, the "σ complex" 14. This evidence primarily arises from studies on oxidative-addition reactions (eq 1),[21] but there are good reasons for believing that it also applies to the σ-bond metathesis case of eq 2,[22] and it appears entirely reasonable to propose a similar intermediate for the present system.

Electrophilic displacement by eq 12b would be analogous to the related chemistry of dihydrogen complexes, which have been shown to be quite acidic; in fact, deprotonation of a ruthenium complex that exists as an equilibrium mixture of dihydrogen and dihydride forms has been shown to occur exclusively via the former.[23] Still another precedent is the deprotonation of an agostic cobalt complex—an intramolecular analog of 14—to give a cobalt alkyl.[24] Unfortunately, unlike the cases of dihydrogen and agostic complexes, no example of a stable *intermolecular* σ-alkane complex has yet been found; therefore, distinction between these mechanisms is not yet possible. Still, this picture is attractive in that it leads to a rather unified picture of C–H activation by metal centers, where the initial interaction is the formation of the σ complex, while the subsequent path depends on the nature of the complex: oxidative addition for a low-valent, electron-rich center; σ-bond metathesis for a d^0 complex with a suitable leaving group X; loss of H^+ for an electrophilic Pt(II) or Pd(II) complex.

Mechanism of Alcohol Oxidation. Our proposed mechanism that accounts for the initial products in the oxidation of ethanol is shown in Scheme II. C–H activation as discussed above can take place at either the α- or β-position, leading to the alkyl–Pt(II) species 15 and 16, respectively. Although direct oxidation and functionalization of 16 analogous to the reaction of 1 would appear possible, labeling studies show clearly that a symmetric intermediate, presumably 12, intervenes. Apparently, dehydration of $Pt^{II}–CH_2CH_2OH$ is a very facile process under reaction conditions. Formation of the β-oxidation products, glycol and chloroethanol, arise from oxidation of 12 (or 16, if it is in equilibrium with 12) by Pt(IV), giving hydroxyethyl–Pt^{IV} (17), which is cleaved by water or Cl^-. This parallels the formation of the same products from 12 plus Cl_2.[15]

An analogous pathway from 15, the product of initial α-C–H bond activation, would produce acetaldehyde, only traces of which are usually observed. Subsequent conversion to chloroacetaldehyde was shown to be rapid under reaction conditions, however. Alternatively, chloroacetaldehyde could be obtained from 15 without the intermediacy of free acetaldehyde, via vinyl alcohol complex 18 in a sequence reminiscent of Wacker chemistry.[25] The Wacker intermediate 18 should in principle be accessible from 16 as well, but this route must be slow relative to the other paths available to 16, as it would lead to acetaldehyde (and subsequent products) with labels in *both* positions starting from 1-^{13}C-ethanol, which was not observed.

Yet another possible route to products derived from attack at the α-position is oxidation catalyzed by metallic platinum[16] (which forms more rapidly in the absence of Pt(IV)). Under standard conditions, however, this does not seem an important reaction route, since little acetic acid is formed; it is found when Pt metal is present (see below).

Details concerning the formation of more oxidized products are less clear, and probably a combination of homogeneous and heterogeneous processes are involved. The most reasonable path for conversion of chloroacetaldehyde to glyoxal, the major product, is shown in eq 13. Two of the minor products, glyoxalic acid and chloroacetic

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[21] Jones, W. D. In ref 1, pp 140–147, and references cited therein.

[22] Rothwell, I. P. In ref 1, pp 180–182, and references cited therein.

[23] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865.

[24] Kanamori, K.; Broderick, W. E.; Jordan, R. F.; Willett, R. D.; Legg, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 7122. Broderick, W. E.; Kanamori, K.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1991**, *30*, 3875.

[25] For an example of a stable vinyl alcohol complex, see: (a) Tsutsui, M.; Ori, M.; Francis, J. *J. Am. Chem. Soc.* **1972**, *94*, 1414. (b) Francis, J.; Tsutsui, M. *Chem. Lett.* **1972**, 663.

$$\mathrm{ClCH_2CH(OH)_2} \xrightarrow[-\mathrm{H^+}]{\mathrm{Pt^{II}}} \mathrm{Pt^{II}\text{-}CHClCH(OH)_2} \xrightarrow{\mathrm{Pt^{IV}}\ \mathrm{H_2O}} \rightarrow$$
$$\mathrm{HOCHClCH(OH)_2} \xrightarrow[-\mathrm{HCl}]{\mathrm{H_2O}} \mathrm{(HO)_2CHCH(OH)_2} \quad (13)$$

acid, presumably arise from direct α-oxidation of glyoxal and chloroacetaldehyde, respectively, very possibly involving heterogeneous catalysis.[26]

Three positions for attack are available in the oxidation of 1-propanol. Although no labeling studies were carried out to establish the actual reaction pathways, a similar scheme (Scheme III) may be constructed that accounts for the products observed and is consistent with the chemistry of **1** as well as the other alcohols. Propionaldehyde is formed by initial attack at the α-position; it accumulates to a much higher degree than does acetaldehyde from ethanol. Initial attack at the γ-position gives $\mathrm{Pt^{II}\text{–}CH_2CH_2CH_2OH}$; unlike **16**, there is no leaving group in the β-position, so it is functionalized directly to either 1,3-propanediol or 1-chloropropan-3-ol, analogous to **1**. Attack at the β-carbon gives a product that *does* have a β-hydroxy group and dehydrates like **16**, giving propene–Pt(II) adduct **13**. However, the product that would be expected by analogy to **16**, propane-1,2-diol, is *not* observed; instead, acetone is the major product. Acetone was also the only product from the oxidation of a propene–Pt(II) adduct by Cl_2 in water.[15,27] Apparently, β-hydrogen elimination from the presumed intermediate $\mathrm{Pt^{IV}\text{–}CH_2CH(OH)Me}$ (again, a Wacker-like step) is faster than attack by water or Cl^- to give 1,2-propanediol and 1-chloropropane-2-ol, whereas the reverse is true for $\mathrm{Pt^{IV}\text{–}CH_2CH_2OH}$. This reversal might be explicable in terms of relative steric hindrance as well as stabilization of a vinyl alcohol complex by methyl substitution.

The formation of acetone from 2-propanol could involve direct attack at the methine C–H bond, but it probably proceeds primarily via attack at one of the methyl groups and dehydration to $\mathrm{PtCl_3(CH_2{=}CHCH_3)^-}$, which is observed as an intermediate (Figure 6). There should be a strong statistical and steric preference for attack at the terminal methyl group.

Selectivity of C–H Attack. As noted in the Introduction, selectivity is a crucial factor in determining the practical potential of an alkane activation system: the common situation, where C–H bonds of products are much more reactive than those of the starting alkane, is highly undesirable. For oxidation of *p*-toluenesulfonic acid (**1**), this is clearly not the case: although strictly quantitative comparison is ruled out by the complications discussed below, both initial rates of conversion and relative amounts of sequential products vs time indicate that hydroxylation of the methyl group in **1** is around 1.5 times as fast as oxidation of the hydroxymethyl group of **2**. Under the same conditions, oxidation of the corresponding aldehyde **3** is not observed at all. Still unexplained is the competition between attack at aliphatic and aromatic ring positions; the latter is significant with *p*-ethylbenzenesulfonic acid and with *p*-toluic acid but not with **1**. No reasons for these differences are obvious.

The selectivity for attack at the methyl or hydroxymethyl group in ethanol compares nicely with the results obtained from **1**, the ratio being approximately 1.5(1). The selectivity for attack at a methyl or methylene group vs attack at the hydroxymethyl in 1-propanol is again close to 1.5, and also there is little preference for attack at methyl: methylene C–H bonds (ratio 1:1). For 2-propanol the ratio of attack at the α- or β-position cannot be determined, since both routes give the same products. (The oxidation of 2-methyl-2-propanol is an exception: total oxidation to carbon dioxide is found. The underlying mechanism is not understood.) Apparently, the Pt(IV)/Pt(II) system is not highly sensitive to electronic or steric effects: all selectivities are within experimental uncertainty of statistical values.

It should be noted, though, that these selectivities apply only at early stages of the reaction, when no (visible) Pt metal has formed. In contrast, Pt metal appears to be an excellent catalyst for oxidation by Pt(IV) at "activated" positions α to oxygen; this is consistently seen in this work as well as by other workers.[16,28] It is difficult to exclude the possibility that small amounts of colloidal Pt are responsible for some of the chemistry even at fairly early stages, and therefore, these selectivities should be taken as lower limits; the relative reactivity of methyl vs hydroxymethyl toward soluble Pt complexes might actually be significantly higher. This is an important prerequisite for the development of catalytic systems for hydrocarbon functionalization based on this chemistry; it suggests, for example, that methane could be converted to methanol at a rate at least as high as the subsequent overoxidation of methanol.

The Active Pt Complex. The above mechanisms would suggest that the rate of oxidation should depend upon Pt(II); qualitatively this is, in fact, observed, but no straightforward quantitative dependence could be elucidated. With **1**, in some cases, the rate was found to vary *inversely* with Pt(IV). Furthermore, the mechanism implies that oxidation of **1** should continue until *all* added platinum, Pt(II) as well as Pt(IV), has been reduced to Pt metal. This is not what is observed: reaction generally comes to a halt before all Pt(IV) is consumed, and usually before visible formation of Pt metal has occurred. These observations can be understood by recognizing that (i) the reaction produces 2 mol of Cl^-/mol of RH oxidized and (ii) the form in which the Pt(II) is added, $[PtCl_4]^{2-}$, is *not* the active species. This conclusion was also reached by Russian workers, who in fact propose that $PtCl_2(H_2O)_2$ is the most active.[3,29] In the initial reaction mixture, the equilibrium of eq 14 is established, as readily demonstrated

$$\mathrm{PtCl_4^{2-}} \rightleftarrows \mathrm{PtCl_3(H_2O)^-} + \mathrm{Cl^-} \rightleftarrows \mathrm{PtCl_2(H_2O)_2} + 2\mathrm{Cl^-}\ \text{etc.} \quad (14)$$

by ^{195}Pt NMR.[30] As the reaction proceeds, liberation of Cl^- shifts the equilibrium position increasingly to the left;

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[26] The appearance of acetic acid, the third minor product, suggests that C–Cl bond activation can compete with C–H activation under certain circumstances, albeit not very effectively.

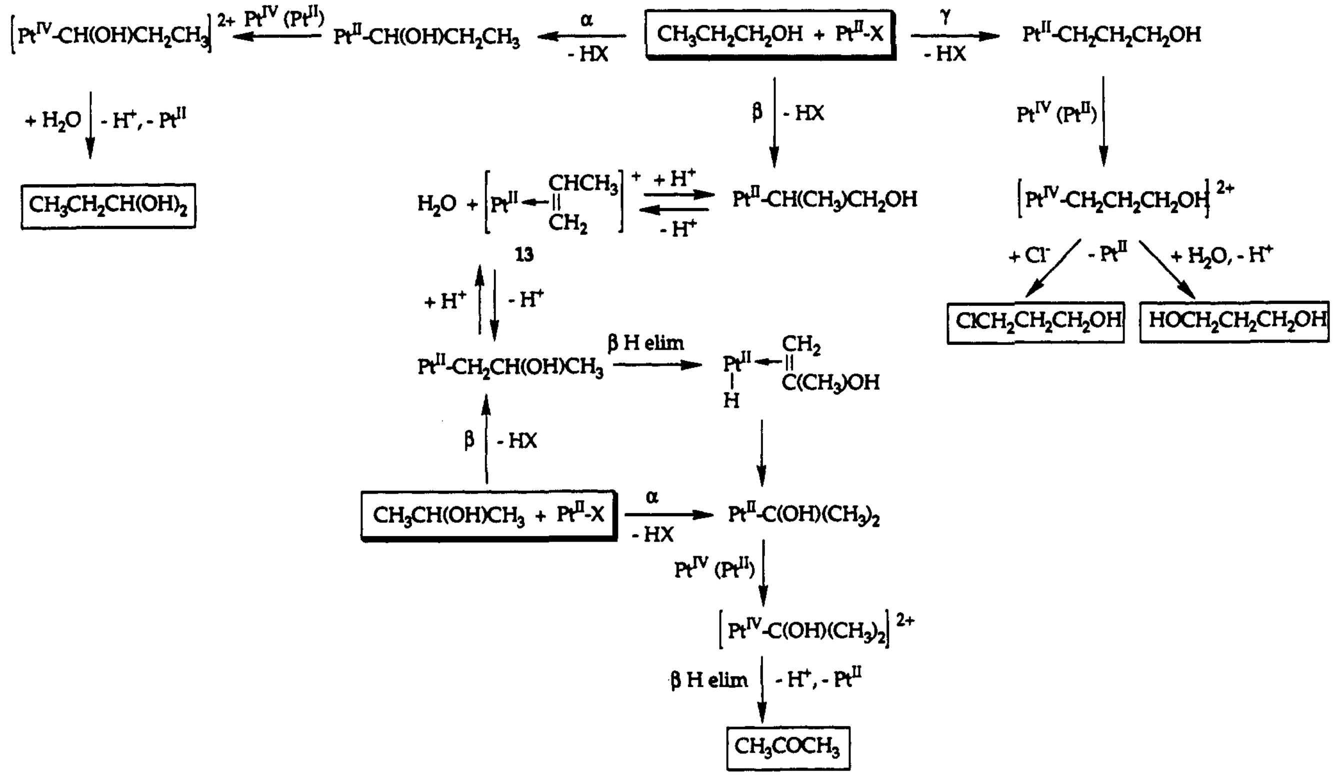
[27] Stark, F. O.; Falender, J. R.; Wright, A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Stone, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 2, p 313.

[28] Camerson, R. E.; Bocarsly, A. B. *Inorg. Chem.* **1986**, *25*, 2910. Compare also oxidation of methane and other hydrocarbons by Fe^{3+}/Pt^0 (König, G. Ger. Offen. DE 3,101,024, 1982; *Chem. Abstr.* **1982**, *97*, 127040. Stenberg, P. J.; King, C. M.; Whitesides, G. M.; Kool, L. R., personal communication) as well as the well-known oxidation of alcohols by O_2 catalyzed by Pt metal (Nicoletti, J. W.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 759 and references cited therein).

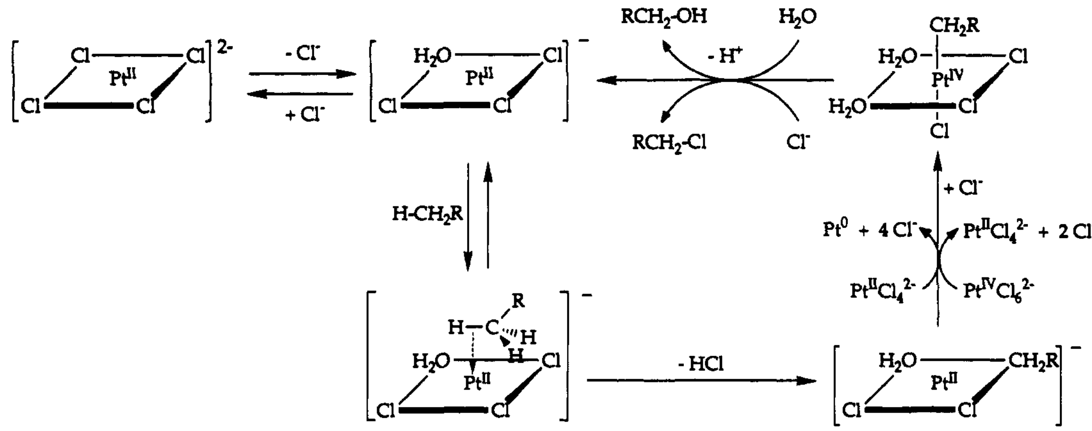
[29] Zamashchikov, V. V.; Rudakov, E. S.; Yaroshenko, A. P. *React. Kinet. Catal. Lett.* **1983**, *22*, 39.

[30] Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *Adv. Chem. Ser.* **1992**, *No. 230*, 221.

Scheme III



Scheme IV



alternatively, increasing the initial amount of $[PtCl_6]^{2-}$ (while keeping [Pt(II)] the same) has the same effect. When $[PtCl_4]^{2-}$ has become the predominant Pt(II) species in solution (by ^{195}Pt NMR), reaction effectively ceases. Note that oxidation may be inhibited completely from the outset by addition of excess Cl^- (Table III). The simplest conclusion is that a more aquated, less abundant, but highly reactive species is responsible for the catalysis.

The possibility that C–H activation is actually catalyzed heterogenously, by small amounts of colloidal Pt metal formed from reaction mixtures, needs to be considered—especially since visible metal deposition is always eventually observed. Poisoning by metallic mercury is usually considered the most reliable test of heterogeneous activity: reactions taking place at surface sites should be *completely* inhibited in this test.[10] We find that addition of Hg slows the reaction somewhat, which is not surprising as Hg readily reduces both Pt(II) and Pt(IV), so that the concentration of active complex is thus lowered. Since reaction still proceeds, this test implies a homogeneously catalyzed reaction. As discussed earlier, there *is* a mechanism for oxidation catalyzed by Pt metal, but it operates primarily on C–H bonds α to oxygen.

Conclusions and Prospects for Catalytic Hydrocarbon Oxidation. Our proposed overall general mechanism for hydroxylation by Pt(II)/Pt(IV) is shown in Scheme IV. It would appear that reaction could be made catalytic in Pt, if a suitable oxidant can be found that will recycle Pt(II) to Pt(IV) (or Pt(0) to Pt(II), since Pt(II) is apparently capable of taking alkyl-Pt(II) to alkyl–Pt(IV) in some cases). Of course, there are rather severe constraints on such a system: the oxidant must not be so efficient as to rapidly convert *all* Pt to the +4 oxidation state, as Pt(II) is essential.

We have demonstrated some success in this area: as shown in Table IV, more than one turnover per Pt(II) can be observed when Pt(IV) is replaced by $S_2O_8^{2-}$ or phosphomolybdic acid. The former is somewhat misleading, as there is significant oxidation of *p*-toluenesulfonic acid even without Pt, as well as some complete oxidation to the carboxylic acid; however, even if only initial product, the alcohol *p*-$HO_3SC_6H_4CH_2OH$, is considered, it is clear that more is produced in the $Pt^{II}/S_2O_8^{2-}$ system than with either component alone, considerably more than stoichiometric oxidation by Pt alone would account for. Nonetheless, a catalytic reaction could not be sustained; only about 70% of the oxidizing equivalents provided could be utilized. Since no free Cl^- is being generated here, termination of oxidation must be due to a different reason than in the Pt(II)/Pt(IV) system; this is under investigation.

Phosphomolybdic acid is a milder oxidant and does not oxidize *p*-toluenesulfonic acid in the absence of Pt, but it is also capable of turning over the Pt(II)/*p*-toluenesulfonic acid system, although not so effectively as $S_2O_8^{2-}$. Since reduced (blue) phosphomolybdic acid is known to be reoxidizable by O_2, the reactions were also run in the presence of 1 atm of O_2, but no increases in product formation were detected. Separately, we found that the blue color generated in these reactions could *not* be discharged by O_2 under our standard reaction conditions, suggesting that the reoxidation is somehow being inhibited.

Although no practical oxidation scheme has yet been demonstrated, the unusual and often very high selectivities for oxidation at what are more commonly the least reactive positions, coupled with the (admittedly severely limited) ability to make reactions catalytic in Pt, suggest that this approach to hydrocarbon functionalization has significant potential.

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Supplementary Material Available: Tables of ^1H NMR data for oxidation products of 1 and 6′ and for the oxidation of ethanol, 1-propanol, and 2-propanol, ^{195}Pt NMR data for Pt(II) and Pt(IV) complexes, and ^1H and ^{13}C NMR data for ethanol oxidation products (8 pages). Ordering information is given on any current masthead page.

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