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Mechanistic aspects of the oxidative functionalization of ethane and ethanol by platinum(II) salts in aqueous medium. Role of platinum(II)–olefin and platinum(IV)–alkyl intermediates

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Abstract

The relative rate of C–H bond activation by the Pt(II) ion decreased in the order $\text{H}-\text{CH}_2\text{CH}_3 > \text{H}-\text{CH}_2\text{CH}_2\text{OH} > \text{H}-\text{CH}(\text{OH})\text{CH}_3$. The platinum(II)–ethylene complex, $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, **1**, was the key intermediate in the oxidation of ethane, ethanol, and diethyl ether to 1,2-ethanediol by platinum(II) in aqueous medium. In particular, the intermediacy of **1** in the oxidation of ethanol to 1,2-ethanediol and 2-chloroethanol was verified through labelling studies. In D_2O , **1**, upon oxidation with one of a number of oxidants, converted to $[\text{PtCl}_5(\text{CH}_2\text{CH}_2\text{OD})]^{2-}$, **2**. **2** in turn decomposed to a mixture of 1,2-ethanediol and 2-chloroethanol on heating. The rate conversion of **1** was a function of pH, the anions present, and the oxidant used. While the conversion of **1** to **2** involved a nucleophilic attack by water (or hydroxide ion), such a step was not observed in the absence of an oxidant. In basic D_2O , the sequential replacement of Cl^- by OD^- in **1** occurred to successively form $[\text{PtCl}_2(\text{OD})(\text{C}_2\text{H}_4)]^-$, $[\text{PtCl}(\text{OD})_2(\text{C}_2\text{H}_4)]^-$ and $[\text{Pt}(\text{OD})_3(\text{C}_2\text{H}_4)]^-$. The process was reversed upon acidification. The species $[\text{PtCl}_5(\text{CH}_2\text{CHO})]^{2-}$, **3**, appeared to be the source for the small quantities of hydroxy- and/or chloroacetaldehyde formed during the oxidation of **1**. **3** was synthesized independently by the reaction of acetaldehyde with a mixture of PtCl_4^{2-} , and PtCl_6^{2-} in aqueous medium. When **1** was oxidized by Cl_2 in CD_3OD solution, the principal product was $[\text{PtCl}_5(\text{CH}_2\text{CO}_2\text{D})]^{2-}$, **4**, when a small amount of water was present, and $\text{CD}_3\text{OCH}_2\text{CH}_2\text{OCD}_3$ in the absence of water.

Keywords: Platinum complex; C–H activation; Oxidation; Ethane; Ethylene; Ethanol

1. Introduction

The selective oxidative functionalization of unactivated C–H bonds, such as those present in alkanes, is a subject of great current interest [1]. We [2], along with Bercaw and Labinger [3], have shown that platinum(II)–chloro complexes, when dissolved in water, will effect the conversion of ethane, ethanol, and diethyl ether to 1,2-ethanediol. Herein, we report on the mechanistic aspects of these functionalizations. The sequence of steps appears to be (a) the formation of a platinum(II)–alkyl species by electrophilic C–H activation (first proposed by Shilov and coworkers [4]), (b) the conversion of this species to a platinum(II)–olefin complex (e.g., by β -abstraction), (c) the oxidation of the platinum(II)–olefin complex to the corresponding

platinum(IV)– β -hydroxyalkyl compound and, finally, (d) the hydrolysis of this compound to the product 1,2-diol.

2. Results and discussion

When ethane was heated in the presence of an aqueous solution of K_2PtCl_4 and K_2PtCl_6 , the products observed were ethanol, 1,2-ethanediol, as well as Zeise's salt, $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, **1** (Fig. 1) [2b]. The function of the added Pt(IV) species, K_2PtCl_6 , was to act as a reoxidant and prevent the reduction of Pt(II) to metallic Pt [2,3]. The latter is known to catalyze the rapid oxidation of alcohols [2b,5]. A separate experiment indicated that K_2PtCl_6 was unreactive towards C–H bonds. Using ethanol as the substrate in place of ethane under similar conditions resulted in the exclusive oxidation of the methyl group and the formation of 1,2-

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ethanediol as the predominant product (along with a trace of 2-chloroethanol) (Fig. 2) [2a]. In view of these results, the question arises as to whether ethanol was an intermediate in the conversion of ethane to 1,2-ethanediol. This did not appear to be the case, since the formation of 1,2-ethanediol from ethane was significantly faster than from ethanol. That ethanol was not an intermediate in the conversion of ethane to 1,2-ethanediol was confirmed by the following experiment. When both $\text{CH}_3^{13}\text{CH}_2\text{OH}$ and CH_3CH_3 were present as substrates (respective solution concentrations 0.043 and 0.031 M), unlabeled 1,2-ethanediol and ethanol were the predominant products. This experiment clearly showed that the relative rate of C–H bond activation by the Pt(II) ion decreased in the order $\text{H}-\text{CH}_2\text{CH}_3 > \text{H}-\text{CH}_2\text{CH}_2\text{OH} > \text{H}-\text{CH}(\text{OH})\text{CH}_3$. Interestingly, this reactivity order was exactly opposite of that expected on the basis of homolytic C–H bond energies.

The common intermediate in the formation of 1,2-ethanediol from ethane and ethanol was $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, **1**. As we [2] and others [3] have shown, **1** was formed readily by the reaction of PtCl_4^{2-} with alkanes, alcohols, and ethers in aqueous medium and it was stable in the absence of added oxidants. However, it was converted to 1,2-ethanediol and related products at varying rates upon the addition of any one of a number of oxidants.

First, Halpern [6] and, more recently, Bercaw and Labinger [7] demonstrated this by using Cl_2 and PtCl_6^{2-} , respectively, as the oxidant. For example, the addition of PtCl_6^{2-} to a solution of **1** in D_2O at 85°C resulted in the near quantitative conversion of the latter to ethylene glycol and 2-chloroethanol. The relative ratio of the two products was found to depend on the Cl^- concentration, with almost exclusive formation of ethylene glycol being observed at low Cl^- concentrations. A trace of the known Pt(IV) species [6], $[\text{PtCl}_5(\text{CH}_2\text{CH}_2\text{OD})]^{2-}$, **2**, was also observed by $^1\text{H-NMR}$ spectroscopy in the above reaction. Compound **2** became the predominant reaction product when the above reaction was carried out at ambient temperature and, upon heating to 85°C , cleanly converted to ethylene glycol and 2-chloroethanol, thus establishing its intermediacy in the oxidation of **1**. Other oxidants that were effective for the conversion of **1** to **2** were $\text{S}_2\text{O}_8^{2-}$, O_2 in presence of metallic Pt and, more significantly, PtCl_4^{2-} . The last observation is consistent with the earlier report that Pt(II) salts alone (in the absence of other oxidants) were capable of converting appropriate hydrocarbons to 1,2-diols [2b]. Note that given the very similar values for the oxidation potentials of the $\text{Pt}^0/\text{PtCl}_4^{2-}$ and $\text{PtCl}_4^{2-}/\text{PtCl}_6^{2-}$ couples (E^0 (volts): $\text{Pt}^0/\text{PtCl}_4^{2-}$, -0.75 ; $\text{PtCl}_4^{2-}/\text{PtCl}_6^{2-}$, -0.68), it is not possible, however, to

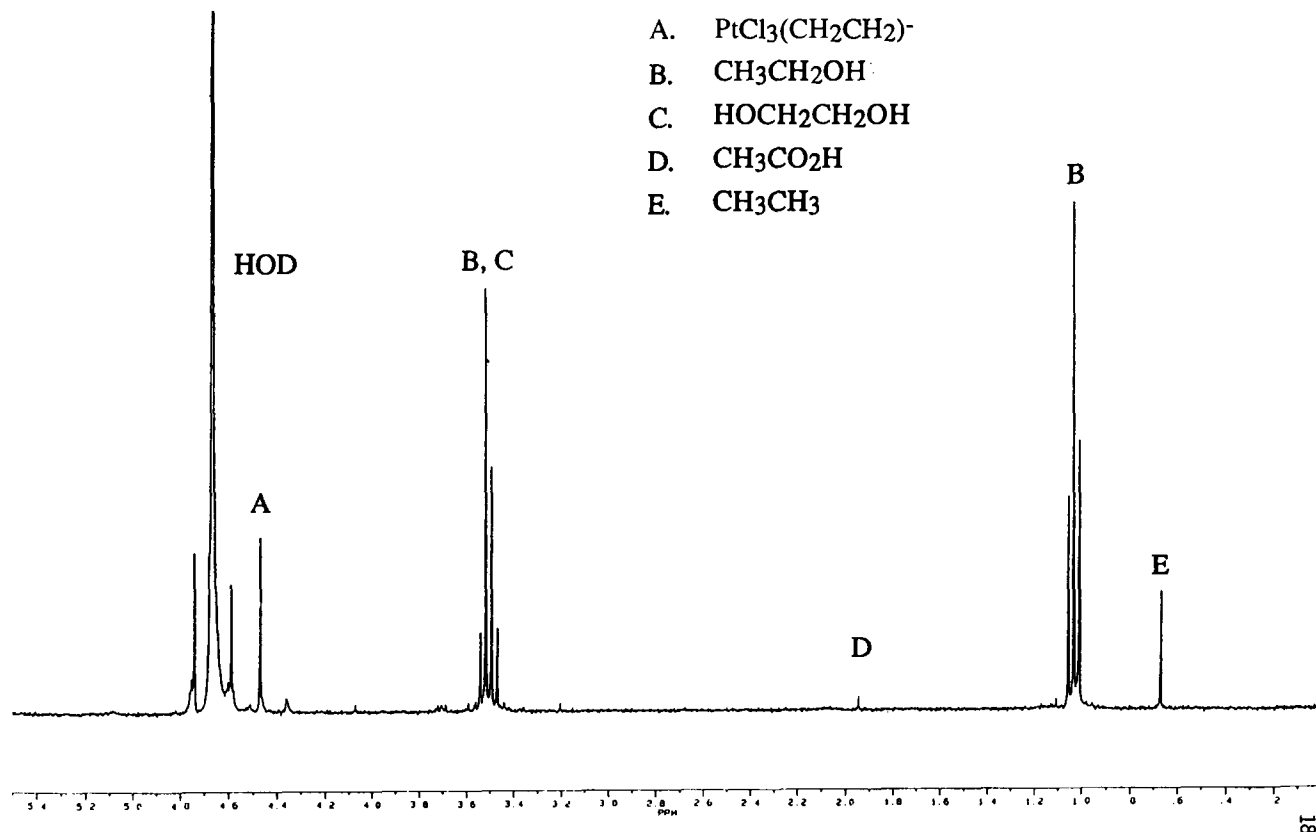


Fig. 1. $^1\text{H-NMR}$ spectrum obtained after the following reaction conditions: C_2H_6 (450 psi), O_2 (100 psi), K_2PtCl_4 (0.05 mmol), K_2PtCl_6 (0.05 mmol), D_2O (4 ml), 105°C , 20 h.

exclude the presence of PtCl_6^{2-} in PtCl_4^{2-} and vice-versa. As with **1**, the oxidation of the propylene complex, $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, with PtCl_6^{2-} at 85° C resulted in the formation of mostly propane-1,2-diol, some 1-chloro-2-propanol, and trace 2-chloro-1-propanol. Acetone was the only other significant product in the reaction.

The conversion of **1** to **2** obviously involves two steps: (a) nucleophilic attack by water (or hydroxide ion) on the coordinated olefin and (b) the oxidation of platinum(II) to platinum(IV). Studies on Wacker chemistry clearly demonstrate that nucleophilic attack by water on olefins coordinated to palladium(II) proceeds readily [8]. On the other hand, the oxidation potential for the Pt(II)/(IV) couple is significantly more positive than the corresponding Pd(II)/(IV) couple (E^0 (volts): $\text{Pd}^0/\text{PdCl}_4^{2-}$, -0.59 ; $\text{PdCl}_4^{2-}/\text{PdCl}_6^{2-}$, -1.29), making the oxidation step easier in the case of platinum(II) compounds and, of course, nucleophilic attack on an olefin coordinated to the highly electrophilic platinum(IV) center should be more facile. In a recent elegant study [7b], Bercaw and Labinger showed that the conversion of **1** to **2** involved external nucleophilic attack by water leading to inversion of stereochemistry, but

left open the question regarding the sequence in which the two steps occur. Our task, therefore, was to determine this sequence.

The addition of NaOD to a solution of **1** in D_2O at ambient temperature resulted in the disappearance of the ^1H NMR singlet (accompanied by its ^{195}Pt satellites) corresponding to **1** [^1H NMR (D_2O) (ppm): 4.60 (s, $J_{\text{Pt-H}} = 66$ Hz)] and the sequential formation of three new singlets (accompanied by their ^{195}Pt satellites) successively upfield of the previous one. From the general similarity of the chemical shifts and coupling constants, we ascribe the new resonances to species formed by sequential replacement of Cl^- by OD^- in **1** to successively form $[\text{PtCl}_2(\text{OD})(\text{C}_2\text{H}_4)]^-$, $[\text{PtCl}(\text{OD})_2(\text{C}_2\text{H}_4)]^-$, and $[\text{Pt}(\text{OD})_3(\text{C}_2\text{H}_4)]^-$ [^1H NMR (D_2O) (ppm): $[\text{PtCl}_2(\text{OD})(\text{C}_2\text{H}_4)]^-$, 3.90 (s, $J_{\text{Pt-H}} = 58.0$ Hz); $[\text{PtCl}(\text{OD})_2(\text{C}_2\text{H}_4)]^-$, 3.75 (s, $J_{\text{Pt-H}} = 60.0$ Hz); $[\text{Pt}(\text{OD})_3(\text{C}_2\text{H}_4)]^-$, 3.61 (s, $J_{\text{Pt-H}} = 60.9$ Hz)]. Since the trans effect of C_2H_4 is higher than that of Cl^- , the Cl^- trans to C_2H_4 was presumably the first to be replaced. This is also supported by the observation that the $^{195}\text{Pt-H}$ coupling constant decreased from 66 to 58 Hz upon the replacement of the first Cl^- but little change was observed on further substitution. Upon acid-

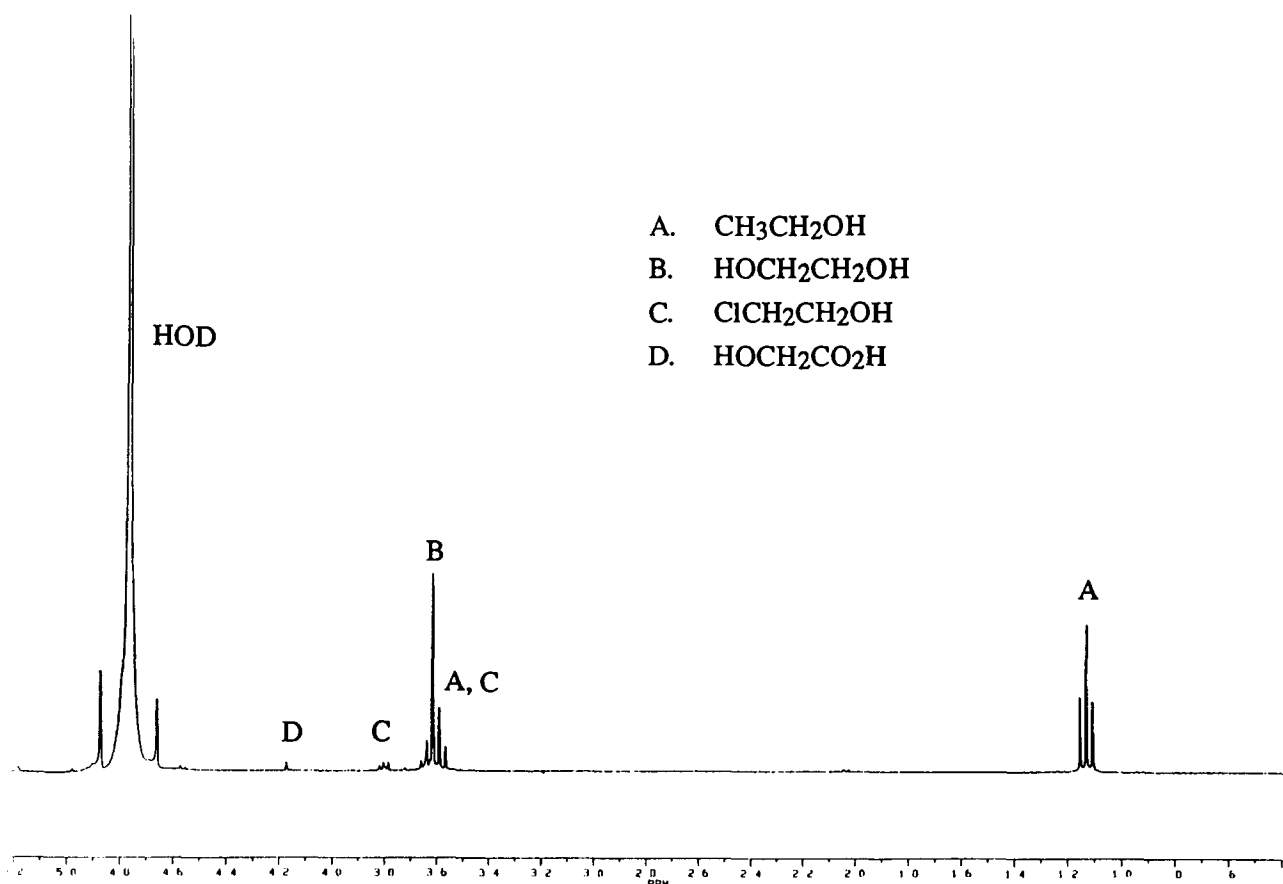


Fig. 2. ^1H -NMR spectrum obtained after the following reaction conditions: $\text{CH}_3\text{CH}_2\text{OH}$ (0.04 mmol), Na_2PtCl_4 (0.05 mmol), Na_2PtCl_6 (0.05 mmol), D_2O (0.6 ml), 85°.

ification of the solution with DCl all the above platinum(II) species were quantitatively (> 90%) reconverted to **1**.

The above platinum(II) complexes with coordinated hydroxide ion(s) and olefin are direct analogs of species postulated as intermediates in the oxidation of olefins by palladium(II) in water [8]. It is remarkable that the coordinated C_2H_4 in these platinum(II) compounds exhibited very little tendency at ambient temperature to undergo nucleophilic attack to form either a Pt(II)– CH_2CH_2OD species or organic species derived therefrom. To emphasize further the difference between the two systems, we note that the platinum complexes were formed and were stable at $pH > 10$ whereas nucleophilic attack on palladium(II) olefin complexes occurs even in neutral or acidic solutions. Moreover, the formation of **1** from $PtCl_4^{2-}$ and ethanol even at ambient temperature indicates that the reverse reaction, i.e., $Pt(II)–CH_2CH_2OD \rightarrow Pt(II)–(CH_2=CH_2) + OD^-$ is favored. Using $CH_3^{13}CH_2OH$ as substrate and a 1:1 mixture of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ as the oxidant combination, we observed the formation of 2-chloroethanol where the labelled carbon was distributed approximately equally between the two ends of the molecule [9]. This further confirmed that a symmetrical Pt–olefin species such as **1** was involved in the oxidation of ethanol to 2-chloroethanol (and 1,2-ethanediol) and that **2** did not arise by the direct oxidation of a Pt(II)– CH_2CH_2OD species formed by β -C–H activation of ethanol by Pt(II).

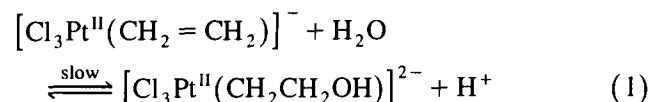
The above observations would appear to indicate that the nucleophilic attack on the coordinated olefin follows the oxidation of platinum(II) to platinum(IV). Nevertheless, a rate-limiting step involving nucleophilic attack on the olefin coordinated to the platinum(II) center is still possible provided that the equilibrium shown in Eq. 1 lies far to the left. Indeed, in a recent paper [7a], Bercau and Labinger have favored the latter conclusion based on the decrease in the rate of reaction of **1** with $PtCl_6^{2-}$ at lower pH. We have also examined the rate of conversion of **1** by two $2e^-$ -oxidants, $K_2S_2O_8$ and $PtCl_6^{2-}$, at ambient temperature starting at two different pH and our results are summarized in Table 1. Note that no buffer was used since none was found satisfactory and as a result there was a steady decrease in pH as the reactions progressed. Despite this experimental limitation, it is clear that while there was a decrease in rate when starting at a lower pH, the rate inhibition was not as sharp as would be expected on the basis of an inverse dependence on $[H^+]$. Moreover, if the step shown in Eq. 1 was rate-limiting, the nature of the oxidant or the (strong) acid employed should have had no influence on the rate and this was not the case. Thus, the sequence in which the two steps occur in the conversion of **1** to **2** must remain an open question. We believe that the problem is that the exact coordination environments are

Table 1
Oxidation of $K[PtCl_3(CH_2CH_2)]$

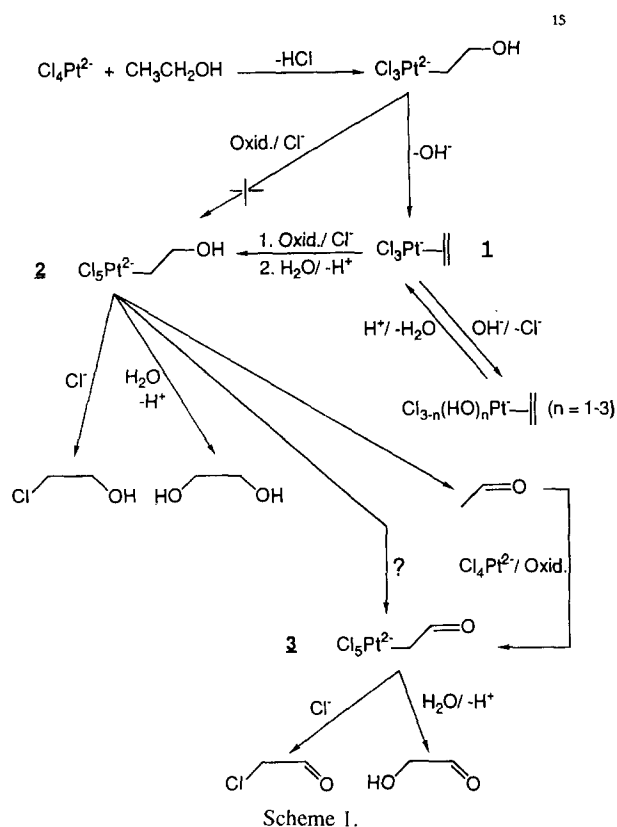
Oxidant	Time (h)	Yield ^a M (%) ^b		
		pH = 2 ^c		pH = 7
		HCl	HClO ₄	
$K_2S_2O_8$	50	0.012 (31)	0.016 (42)	0.018 (48)
	80	0.015 (41)	0.017 (46)	0.024 (65)
Na_2PtCl_6	50	0.010 (27)	0.014 (38)	0.017 (46)
	80	0.014 (40)	0.019 (52)	0.021 (57)

Typical conditions: $K[PtCl_3(CH_2CH_2)]$, 0.037 M; KCl, 0.037 M; $K_2S_2O_8$ or Na_2PtCl_6 , 0.037 M; 0.76 ml D_2O ; 25° C. ^a For $K[PtCl_3(CH_2CH_2OH)] + HOCH_2CH_2OH + ClCH_2CH_2OH$. ^b Based on $K[PtCl_3(CH_2CH_2)]$ consumed. ^c Achieved by adding either HCl or HClO₄.

not known for the metal complexes. Although we and others have generally depicted the compounds with chloro ligands, almost certainly species in which some of the chloro ligands have been replaced by water molecules coexist in solution. Moreover, as the chlorides are replaced by neutral water molecules, the susceptibility towards nucleophilic attack would increase while the ease of oxidation would decrease. Thus, it is conceivable that there may even be a switch in the sequence in which the steps occur upon a change in ligand environment around the metal.



Small quantities of hydroxy- and/or chloroacetaldehyde were usually formed during the oxidation of **1**. It is likely that the species $[PtCl_5(CH_2CHO)]^{2-}$, **3**, was an intermediate [¹H NMR (D_2O) (ppm): 9.80 (1H, t, $J_{H-H} = 4.5$ Hz); 4.42 (2H, d, $J_{H-H} = 4.5$ Hz, $J_{Pt-H} = 94$ Hz)]. The species **3** was observed as a minor organometallic product in the oxidation of **1** by either $PtCl_6^{2-}$ or $S_2O_8^{2-}$. Acetaldehyde, which was always formed as a minor side-product in the oxidation of **1**, may be the precursor to compound **3**, since the latter was the predominant product when acetaldehyde was allowed to react with a mixture of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ in D_2O at 90° C. Note that a small amount of $CH_3^{13}CH(OH)_2$ was also observed starting with $CH_3^{13}CH_2OH$. The distribution of the label indicates that this acetaldehyde hydrate was formed through an independent pathway that did not involve a symmetrical Pt–ethylene species (such as **1**) as intermediate. The acetaldehyde hydrate was probably a product of heterogeneous oxidation of ethanol catalyzed by trace metallic platinum [2b,5]. It is not possible at this point, however, to rule out the possibility that **3** may also be formed by further oxidation of the terminal carbon of **2**.



Finally, we also examined the oxidation of **1** by Cl_2 in CD_3OD at ambient temperature. Unlike in water, the reaction was complete within minutes at ambient temperature. In the presence of a small amount of water, the predominant product was $[\text{PtCl}_5(\text{CH}_2\text{CO}_2\text{D})]^{2-}$, **4**, together with traces of 1,2-ethanediol and 2-chloroacetic acid. Compound **4** could be synthesized independently [10] by the reaction of PtCl_4^{2-} with iodoacetic acid in water at ambient temperature [$^1\text{H NMR}$ (D_2O) (ppm): 4.21 (s, $J_{\text{Pt-H}} = 94$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O) (ppm): 21.5 ($J_{\text{Pt-C}} = 478$ Hz), 175.6]. When anhydrous CD_3OD was used, the principal product of the reaction of **1** with Cl_2 was $\text{CD}_3\text{OCH}_2\text{CH}_2\text{OCD}_3$; no intermediate organometallic species could be detected.

In conclusion, our results help to define further the mechanistic steps involved in the oxidative functionalization of ethane and ethanol to 1,2-ethanediol by $\text{Pt(II)}/\text{Pt(IV)}$ in aqueous medium. As an illustrative example, the mechanism for ethanol oxidation is summarized in Scheme 1.

3. Experimental section

3.1. General

Platinum salts were obtained from Johnson Matthey and were used as received. Ethane was purchased from Matheson. Chlorine was obtained from Union Carbide. The solvents D_2O (99.9% D, Cambridge Isotopes) and

CD_3OD (99.8% D, Cambridge Isotopes) were also used as received. Reactions under pressure were carried out in Parr general purpose bombs using glass liners. Reaction products were identified by their $^1\text{H-NMR}$ spectra recorded on a Bruker 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.

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, the reactions should be carried out in the absence of light [5b].

3.2. Synthesis of $\text{K}[\text{PtCl}_3(\text{olefin})]$

K_2PtCl_4 (0.1 g, 0.241 mmol) was dissolved in 2.0 ml D_2O in a glass liner, which was placed in a Parr high pressure vessel. The vessel was sealed and charged with either 500 psi of ethylene or 150 psi of propylene. After stirring at ambient temperature for 3 h, the vessel was depressurized, and a clear yellow solution removed from the liner. The olefin complex was isolated from this solution by removal of solvent: 1 equiv. of KCl formed in the reaction remained with the olefin complex. $^1\text{H NMR}$ (D_2O) (ppm): $\text{K}[\text{PtCl}_3(\text{CH}_2:\text{CH}_2)]$, 4.60 (s, $J_{\text{Pt-H}} = 66$ Hz); $\text{K}[\text{PtCl}_3(\text{CH}_3\text{CH}:\text{CH}_2)]$, 5.33 (1H, m, $J_{\text{Pt-H}} = 68.6$ Hz), 4.39 (1H, d, $J_{\text{H-H}} = 8.9$ Hz, $J_{\text{Pt-H}} = 71.0$ Hz); 4.38 (1H, d, $J_{\text{H-H}} = 12.7$ Hz, $J_{\text{Pt-H}} = 64.6$ Hz); 1.55 (3H, d, $J_{\text{H-H}} = 6.2$ Hz, $J_{\text{Pt-H}} = 40.4$ Hz).

3.3. Oxidation of ethane by Pt(II) and Pt(IV)

K_2PtCl_4 (0.021 g, 0.05 mmol) and K_2PtCl_6 (0.024 g, 0.05 mmol) were dissolved in 4 ml of D_2O in a glass container (K_2PtCl_6 was not completely soluble in D_2O). The glass container was placed in a high pressure bomb which was then sealed. The bomb was purged and pressurized to 100 psi with O_2 , then pressurized with CH_3CH_3 to 550 psi. The ratio of CH_3CH_3 to O_2 was below the explosion limit. The contents were stirred at 105°C for 20 h following which the $^1\text{H NMR}$ spectrum indicated that the products were $\text{K}[\text{PtCl}_3(\text{CH}_2:\text{CH}_2)]$, $\text{CH}_3\text{CH}_2\text{OD}$, $\text{DOCH}_2\text{CH}_2\text{OD}$ and a trace of CH_3COOD (Fig. 1).

3.4. Oxidation of ethanol to 1,2-ethanediol 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 (0.019 g, 0.05 mmol) and

$\text{Na}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$ (0.026 g, 0.05 mmol) in an NMR tube. The solution was heated at 85° C for 6 days. The $^1\text{H-NMR}$ spectrum indicated that the major oxidation product of ethanol was $\text{HOCH}_2\text{CH}_2\text{OH}$ along with a trace amount of $\text{ClCH}_2\text{CH}_2\text{OH}$ (Fig. 2).

3.5. Oxidation of ethane by Pt(II) and Pt(IV) in the presence of $\text{CH}_3^{13}\text{CH}_2\text{OH}$

$\text{CH}_3^{13}\text{CH}_2\text{OH}$ (10 μl , 0.172 mmol) was added to 4 ml of D_2O containing K_2PtCl_4 (0.042 g, 0.1 mmol) and $\text{Na}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$ (0.042 g, 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 $^1\text{H-NMR}$ spectrum revealed that the principal oxidation products were $\text{HOCH}_2\text{CH}_2\text{OH}$ (0.012 mmol) and $\text{CH}_3\text{CH}_2\text{OH}$ (0.036 mmol).

3.6. Formation of $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_{3-n}(\text{OH})_n]^-$

$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ (0.02 g, 0.054 mmol) was dissolved in 0.5 ml of D_2O to which was added 1 drop of concentrated NaOD in D_2O , and the solution was allowed to stand at ambient temperature for several days. Analysis by $^1\text{H-NMR}$ spectroscopy revealed three new singlets (accompanied by their ^{195}Pt satellites). Upon the addition of a sufficient amount of concentrated DCl such that the pH of the solution was below 7, only one singlet (accompanied by its ^{195}Pt satellites) was observed, corresponding to the original Pt(II)–olefin complex.

3.7. Oxidation of $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ by chlorine in methanol

$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ (0.01 g, 0.027 mmol) was dissolved in 0.8 ml CD_3OD (dried over molecular sieves) in an NMR tube. Cl_2 was then bubbled through the solution for 20 min at ambient temperature followed by N_2 for an additional 15 min. The products were examined by NMR spectroscopy.

3.8. Formation of $[\text{PtCl}_5(\text{CH}_2\text{CHO})]^{2-}$

K_2PtCl_4 (0.0167 g, 0.040 mmol) and $\text{Na}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$ (0.022 g, 0.042 mmol) dissolved in 0.5 ml D_2O were heated with excess CH_3CHO for 1 h at 90° C. At

the end of this period, a $^1\text{H-NMR}$ spectrum revealed the formation of $[\text{PtCl}_5(\text{CH}_2\text{CHO})]^{2-}$.

3.9. Formation of $[\text{PtCl}_5(\text{CH}_2\text{CO}_2\text{H})]^{2-}$

K_2PtCl_4 (0.048 g, 0.115 mmol) and iodoacetic acid (0.043 g, 0.23 mmol) were dissolved together in D_2O in an NMR tube. NMR spectrum was taken after 4 h at ambient temperature.

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- [10] (a) N. Basicckes and A. Sen, *Polyhedron*, 14 (1995) 197; (b) V.V. Zamashchikov, E.S. Rudakov, V.S. Garkusha-Bozhko, S.A. Mitchenko, S.L. Litvinenko and V.S. Chuprina, *Soviet J. Coord. Chem.*, 12 (1986) 474.