A Novel Hybrid System for the Direct Oxidation of Ethane to Acetic and Glycolic Acids in Aqueous Medium

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A combination of platinum(II) ion and metallic platinum is found to oxidise ethane to a mixture of acetic and glycolic acids in aqueous medium in the presence of oxygen; the platinum(II) ion is responsible for the initial C–H activation step leading eventually to the formation of ethanol and ethylene glycol, while metallic platinum catalyses the subsequent air oxidation of the alcohols to the corresponding acids.

The selective, oxidative functionalisation (preferably catalytic) of alkane C–H bonds is one of the most challenging chemical problems, in addition to being of great practical importance. Next to methane, ethane, which possesses only strong primary C–H bonds, is the least reactive member of the alkane family. Not surprisingly, the number of homogeneous or heterogeneous low temperature ($\leqslant$ 100 °C) procedures for the selective oxidation of ethane is extremely limited. For example, the photochemical chlorination of ethane is very unselective and invariably leads to multiple chlorinations.[1] To our knowledge, the only reported low temperature metal-mediated direct oxidation of ethane involves its conversion to ethyl chloride[2] (and ethanol[3]) in unknown yields by a mixture of K_2PtCl_4 and K_2PtCl_6. Herein, we report the first example of direct conversion of ethane to acetic and glycolic acids, under mild conditions [eqn. (1)]. Under appropriate conditions, hydroxycarbonylation of ethane to propionic acid was also achieved. In addition, the oxidation procedure is general as it appears that higher alkanes may be oxidised through a similar mechanism.

$$C_2H_6 + O_2 \xrightarrow[D_2O,\ 108\text{–}134\ ^\circ C]{PtCl_4{}^{2-} + \text{Pt black}} CH_3CO_2D + DOCH_2CO_2D \qquad (1)$$

The system employed consists of a homogeneous (Pt^{II}) and a heterogeneous (metallic Pt) component. As we shall demonstrate, the initial C–H activation occurs at the Pt^{II} centre culminating in the formation of ethanol and ethylene glycol. The role of the metallic Pt is to catalyse the subsequent oxidation of these alcohols to the corresponding carboxylic acids.

In a typical reaction, 0.1 mmol each of K_2PtCl_4 and Pt black (fuel cell grade) were added to 5 ml of D_2O and stirred at 122 °C for 68 h in the presence of a gas mixture consisting of 36.2% C_2H_6, 4.2% O_2 and 59.6% Ar [total pressure: 500 psi (1 psi $\approx 6.894757 \times 10^3$ Pa)]. At the end of this period, 0.084

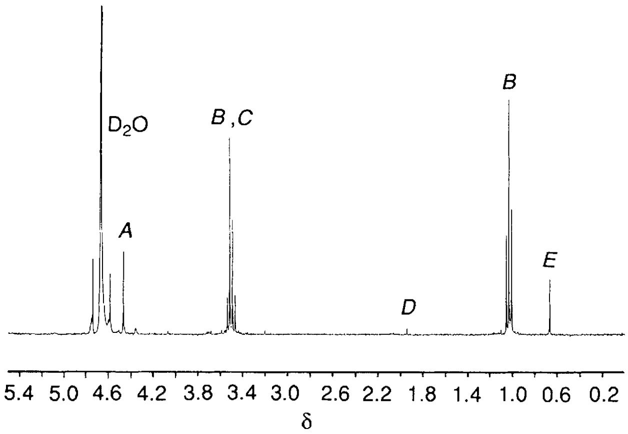
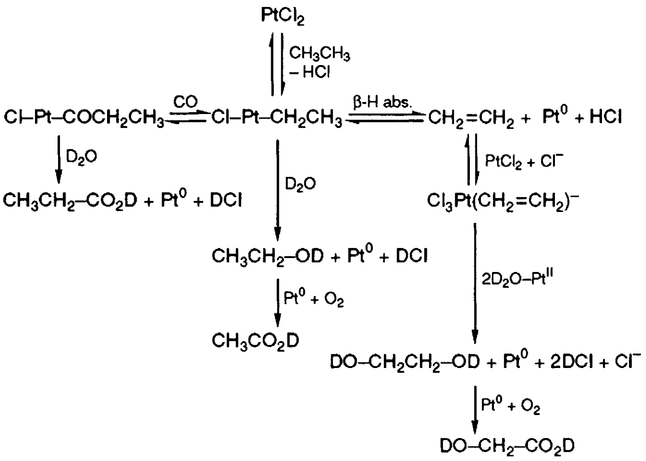


Fig. 1 ^1H NMR spectrum observed under the following reaction conditions: C_2H_6 (450 psi), O_2 (100 psi), K_2PtCl_4 (0.05 mmol), K_2PtCl_6 (0.05 mmol), D_2O (4 ml), 105 °C, 20 h. *A*; $PtCl_3(CH_2{=}CH_2)^-$, *B*; CH_3CH_2OD, *C*; $DOCH_2CH_2OD$, *D*; CH_3CO_2D, *E*; C_2H_6

mmol of CH_3CO_2D and 0.032 mmol of $DOCH_2CO_2D$ were observed. The organic products were analysed and quantitated by ^1H NMR spectrometry. Their identity was further verified by direct comparisons with the spectra of authentic samples. As the conversion of C_2H_6 to CH_3CO_2D and $DOCH_2CO_2D$ represents $6e^-$ and $8e^-$ oxidations, respectively, the overall transformation represented a net 0.76 mmol electron oxidation. On allowing the reaction to proceed for a longer time period, the yield of CH_3CO_2D continued to increase while that of $DOCH_2CO_2D$ decreased, presumably owing to its further oxidation, eventually to CO_2. Thus, after 109 h, the amounts of CH_3CO_2D and $DOCH_2CO_2D$ present were 0.100 mmol and 0.020 mmol, respectively, the yield of the former alone being equivalent to a net 0.60 mmol electron oxidation.

The following observations pertain to the mechanism of the above catalytic oxidation (see Scheme 1). The Pt^{II} ion was primarily responsible for the initial C–H activation step, since little or no reaction was observed in its absence. The electrophilic displacement step leading to the formation of a $Pt{-}CH_2CH_3$ species, as depicted in Scheme 1, is similar to that postulated earlier by us and others.[4] A $Pt{-}CH_2CH_3$ species appeared to be an intermediate since a significant quantity of $CH_3CH_2CO_2D$ was formed (*ca.* 15–20% relative to CH_3CO_2D at 50 psi CO) when CO was added to the system. As shown in Scheme 1, the carboxylic acid can form by the reaction of D_2O on a $Pt{-}COCH_2CH_3$ species, formed in turn by CO insertion into a $Pt{-}CH_2CH_3$ bond. This sequence of steps is observed in many catalytic reactions, such as the hydrocarboxylation of alkenes.[5] A second observation that implicated the intermediacy of a $Pt{-}CH_2CH_3$ species was the appearance of a resonance ascribable to $PtCl_3(CH_2{=}CH_2)^-$[6] in the ^1H NMR spectra of the reaction mixtures [^1H NMR: δ (D_2O) 4.48 (br s with ^{195}Pt satellites, $J_{Pt\text{-}H}$ 66 Hz]. This latter species was presumably formed by β-H abstraction from $Pt{-}CH_2CH_3$ followed by scavenging of the released $CH_2{=}CH_2$ by a Pt^{II} ion. Note that $PtCl_3(CH_2{=}CH_2)^-$ was also observed in the reaction of C_2H_6 with $PtCl_4{}^{2-}$ even in the absence of O_2. Also, no reaction was observed between C_2H_6 and K_2PtCl_6 under these conditions. Clearly, Pt^{IV} that might be present as an impurity or formed *in situ* by the oxidation of Pt^{II}, was not responsible for the C–H activation step.

The primary oxidised organic compounds formed were C_2H_5OD and $DOCH_2CH_2OD$. These could be detected in reactions carried out at lower temperatures and for shorter time periods. For example, when the reaction described above was conducted at 108 °C for 19 h, the products were: C_2H_5OD (0.004 mmol), CH_3CO_2D (0.002 mmol), $DOCH_2CH_2OD$ (0.002 mmol) and $DOCH_2CO_2D$ (0.0017 mmol). C_2H_5OD was presumably formed by attack of D_2O on $Pt{-}CH_2CH_3$. In order to find out whether this was a viable step, a $Pt^{IV}{-}CH_2CH_3$ species was generated by the reaction of $PtCl_4{}^{2-}$ with C_2H_5I [^1H NMR: δ (D_2O) 0.43 (3 H, t, $J_{H\text{-}H}$ 7 Hz), 3.98 (2 H, q with ^{195}Pt satellites, $J_{H\text{-}H}$ 7 and $J_{Pt\text{-}H}$ 86 Hz), a similar procedure has been reported by Shilov *et al.*[7]]. This species was found to react with D_2O at 25 °C over a period of several hours to form C_2H_5OD. Although this may not be an exact model since the oxidation state of the metal was different, it does lend support for the hydrolysis step in the catalytic reaction. $DOCH_2CH_2OD$ arose through the reaction of $PtCl_3(CH_2{=}CH_2)^-$ with D_2O and $PtCl_4{}^{2-}$ as was confirmed by an independent reaction involving the Zeise's salt,[6] $K[PtCl_3(CH_2{=}CH_2)]$ under the same conditions (the oxidative hydrolysis of Zeise's salt to ethylene glycol was previously reported[8]). In principle, ethylene glycol can also result from the oxidation of ethanol by Pt^{II}.[8] However, this reaction was found to be significantly slower than the Pt metal catalysed oxidation of ethanol to acetic acid.



Scheme 1

The acids, CH_3CO_2D and $DOCH_2CO_2D$, were formed by Pt metal catalysed oxidation of the corresponding alcohols by O_2. As has been demonstrated by first Cameron and Bocarsly[9] and then us,[10] the Pt^{II} ion, by itself, did not readily oxidise alcohols; rather, the reaction was catalysed by metallic Pt with the Pt^{II} ion, like O_2, acting merely as an oxidant. Evidence in favour of this hypothesis is the observation[9,10] of a prolonged induction period in the oxidation of alcohols by K_2PtCl_4; this induction period is eliminated upon the addition of metallic Pt. Also consistent with this scenario was the observation that only ethanol and ethylene glycol [together with $PtCl_3(CH_2{=}CH_2)^-$] were formed when K_2PtCl_6 was added to K_2PtCl_4 during the reaction of the latter with C_2H_6 and O_2 (Fig. 1). Note that a separate experiment indicated that K_2PtCl_6 was unreactive toward C_2H_6. The function of K_2PtCl_6 was to act as an oxidant and prevent the reduction of Pt^{II} to metallic Pt,[8] thus making the ethane to alcohol transformation truly catalytic in Pt^{II}, as has been observed previously for the remote C–H oxidation in aliphatic carboxylic acids.[11] Monitoring the reaction by ^{195}Pt NMR spectroscopy indicated that, as expected, the concentration of K_2PtCl_6 decreased with time. However, in the absence of added Pt^{IV} salt, the alcohol to acid oxidation step could not be stopped by excluding Pt^0 from the initial reaction mixture since Pt^0 was formed during the conversion of C_2H_6 to C_2H_5OD and $DOCH_2CH_2OD$ by Pt^{II}. Hence, CH_3CO_2D and $DOCH_2CO_2D$ were the ultimate products even in the absence of externally added metallic Pt. The advantage of adding O_2 to the reaction mixture was that it replaced Pt^{II} as the oxidant in the Pt metal catalysed oxidation of alcohols (the Pt metal catalysed oxidation of alcohols by O_2 is well-documented[9]). As a result, the role of the Pt^{II} ion remained confined to the initial oxidation of C_2H_6 to the two alcohols. On this basis, assuming no reoxidation of the reduced Pt^0, the total yield of the products should not exceed 100% relative to the Pt^{II} originally present. As described above, yields up to 116% relative to Pt^{II} were observed indicating some reoxidation to Pt^{II} under the reaction conditions. Since the Pt^{II} ion was no longer consumed in the alcohol to acid oxidation step, the overall effect of the addition of O_2 was that a greater yield of oxidised organic products was obtained from ethane. Consistent with this scenario was the observation that the reduction of Pt^{II} to Pt^0 was very much slower in the presence of O_2.

In conclusion, we have discovered the first metal-mediated procedure for the direct oxidation of ethane to acetic and glycolic acids. An attractive feature of the process is that it occurs in aqueous solution under mild conditions. From a mechanistic standpoint, the direct oxidative dehydrogenation of ethane to ethylene in homogeneous media is unprecedented (dehydrogenations under photochemical[12] and transfer hydrogenation[13] conditions are, however, known). Moreover, the reaction of propane with $PtCl_4^{2-}$ under similar conditions gave $PtCl_3(CH_3CH{=}CH_2)^-$ [^1H NMR: δ (D_2O) 1.55 (d with ^{195}Pt satellites, $J_{Pt\text{-}H}$ 40 and $J_{H\text{-}H}$ 6 Hz), 4.37 (d with ^{195}Pt satellites, $J_{Pt\text{-}H}$ 65, $J_{H\text{-}H}$ 13 Hz), 4.39 (d with ^{195}Pt satellites, $J_{Pt\text{-}H}$ 71 and $J_{H\text{-}H}$ 9 Hz), 5.33 (m with ^{195}Pt satellites, $J_{Pt\text{-}H}$ 69 and $J_{H\text{-}H}$ 6, 9 and 13 Hz); the resonances were identical to those observed for $K[PtCl_3(CH_3CH{=}CH_2)]$,[14] prepared independently from K_2PtCl_4 and C_3H_8] along with n- and iso-propanol and acetone. Thus, in principle, it should be possible to oxidise higher alkanes through a procedure similar to that used for ethane.

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