A New Catalytic System for the Direct Oxidation of Olefins to 1,2-Diols by Dioxygen in Aqueous Medium

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In aqueous medium, in the presence of dioxygen, metallic platinum is found to catalyse the oxidation of ethylene and propene to a mixture of ethane-1,2-diol and acetic acid, and propane-1,2-diol and acetone, respectively; only the 1,2-diol was formed, however, when carbon monoxide was added to the reaction mixture.

1,2-Diols derived from ethane and propane have a number of important industrial applications and are currently made from olefins primarily through a two-step procedure[1] involving, first, the synthesis of the corresponding epoxide,[2] and, second, the hydrolysis of the epoxide to the 1,2-diol. The silver catalysed formation of ethylene oxide from ethylene involves O_2 as the oxidant.[2] However, for the homogeneous Mo^{VI} catalysed epoxidation of propene, organic hydroperoxides rather than O_2 are used as oxidants.[2] In terms of direct conversion of olefins to 1,2-diols by O_2, we are aware of only two catalytic systems,[1] both homogeneous. The first uses a combination of TeO_2 and HBr in acetic acid and forms the diacetate and monohydroxyacetate as products. The second employs a combination of Os and Cu halides (or oxohalides). The 1,2-diol formation is believed to occur through the intermediacy of metallacyclic osmate esters.[1a] These processes have not been commercialized because of the problems of corrosion associated with the use of halide ions, especially under acidic conditions. Herein, we describe a new catalytic procedure for the direct oxidation of the lower olefins to 1,2-diols by O_2 in aqueous medium under relatively mild conditions.

Our results on the oxidation of ethylene and propene are summarized in Tables 1 and 2, respectively (the reaction conditions employed are described in the footnotes to the tables). Focusing on ethylene oxidation, several trends are immediately obvious. First, metallic Pd was not nearly as efficient a catalyst as was metallic Pt. Secondly, increase in reaction temperature from 100 to 180 °C greatly increased the ethane-1,2-diol to acetic acid ratio in the product mixture. Finally and most significantly, the addition of CO to the reaction mixture completely inhibited acetic acid formation resulting in ethane-1,2-diol being the sole organic product, even at 100 °C. The above trends persisted when $CuCl_2$ was used in place of O_2 as the oxidant (however, 2-chloroethanol was formed simultaneously with ethane-1,2-diol) or when propene was used as the substrate. In the latter case, acetic acid was formed by further oxidative degradation of propane-1,2-diol as verified by a control experiment.

While the mechanistic steps involved in the oxidation have not been elucidated in any detail, several points can be made. First, ethanol, the product of ethylene hydration, did not participate in the formation of ethane-1,2-diol. Thus, when ethanol was used as the substrate, acetic acid was the only observed product both in the presence and absence of added CO. It is noteworthy that, in this respect, the above oxidation differs from the oxidation of ethylene and ethanol by the Pt^{II} species, $PtCl_4^{2-}$, where ethane-1,2-diol is the common product.[3,4] Furthermore, labelling studies indicated that the conversion of ethanol to ethane-1,2-diol in the latter case proceeds through the intermediacy of ethylene.[3b,4b] While this difference in reactivity would appear to rule out the role of soluble Pt^{II} species in the present ethane-1,2-diol synthesis procedure, this was verified by performing an oxidation in the presence of excess Cl^- ions. Metallic Pt is more easily oxidized in the presence of Cl^- ions ($E°$/V: Pt^0/Pt^{2+}, −1.2; $Pt^0/PtCl_4^{2-}$, −0.73) and, furthermore, as stated above, the resultant Pt^{II} species, $PtCl_4^{2-}$, is effective in the oxidation of ethylene to ethane-1,2-diol. An increase in the formation of ethane-1,2-diol may, therefore, be anticipated if soluble Pt^{II} species were invovled but this was not observed.

Acetaldehyde appears to be an intermediate in the oxidation of ethylene to acetic acid and was observed when a lower temperature (100 °C) was employed for the oxidation in the absence of added CO. It is likely that the formation of acetaldehyde occurred through a parallel Wacker-type pathway[5] (Scheme 1); the subsequent metal catalysed oxidation to acetic acid is also well precedented.[3a,6]

We had earlier demonstrated the formation of hydrogen peroxide through Pt and Pd catalysed reaction of CO with water.[7] However, for the following reasons, it is most unlikely that hydrogen peroxide plays a significant role in olefin oxidations in the presence of CO. The decomposition of hydrogen peroxide to O_2 and water was previously found to be much faster in the presence of Pt when compared to Pd,[7] while Pt was the superior olefin oxidation catalyst in the present system. Also, the use of hydrogen peroxide in place O_2 as the oxidant did not result in a significantly enhanced yield of ethane-1,2-diol at 180 °C. It is certain that O_2, formed by hydrogen peroxide decomposition, was the oxidant at this elevated temperature.

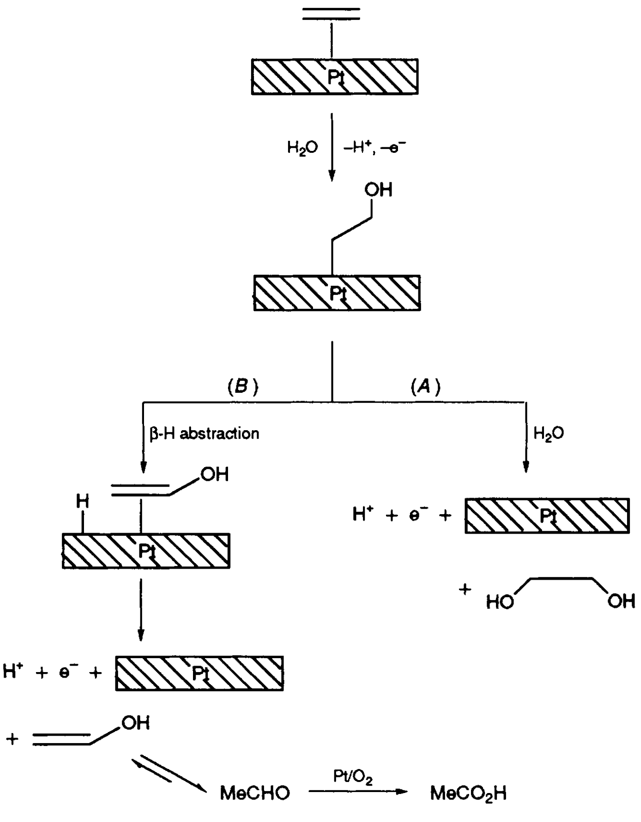
Table 1 Oxidation of ethylene[a]

Catalyst	Oxidant	CO[c]	T/°C	t/h	Turnovers[b] Ethane-1,2-diol	Turnovers[b] Acetic acid
Pt	O_2		180	22	320	340
Pt	O_2		180	52	1520	960
Pt	O_2		180	53	1460	700
Pt	O_2		100	24	15	50 (40)[d]
Pt	O_2	×	180	44	160	
Pt	O_2	×	100	49	100	
Pd	O_2		100	48	10	130 (90)[d]
Pd	O_2	×	180	44	150	
Pd	O_2	×	100	46	20	
Pt	$CuCl_2$[e]		180	26	620	60[d]
Pt	$CuCl_2$[e]		100	23	170 (110)[f]	40[d]
Pt	$CuCl_2$[e]	×	100	34	20 (110)[f]	

[a] *Reaction conditions*: 0.011 g of 5% Pt on carbon (70 μmol of surface Pt atoms per g of catalyst) or Pd on carbon (60 μmol of surface Pd atoms per g of catalyst); 10 ml of H_2O; C_2H_4, 300 psi; O_2, 35psi; Ar, 615 psi; stainless steel autoclave with glass liner (1 psi ≈ 6.89 × 10^3 Pa). [b] Turnover numbers were calculated assuming that only the surface metal atoms were active (the relative proportion of these was determined from H_2 chemisorption studies). [c] CO (100 psi) was added where indicated by ×. [d] Acetaldehyde. [e] 20 equiv. of $CuCl_2$ (relative to catalyst) was added in lieu of O_2. [f] 2-Chloroethanol.

Finally, in order to examine the possibility that ethane-1,2-diol was generated from an initially formed epoxide through a hydrolysis step, the ethylene oxidation was carried out in dimethyl sulfoxide. Neither ethylene oxide nor any other organic product was observed in significant amounts.

A likely mechanistic scenario for the oxidation of ethylene to ethane-1,2-diol and acetic acid is shown in Scheme 1. The formation of acetic acid *via* acetaldehyde follows the classic Wacker mechanism,[5] whereas ethane-1,2-diol is formed through two sequential nucleophilic attacks by water (or hydroxide ion) on the coordinated ethylene. The common intermediate is a surface-bound β-hydroxyethyl species. β-Hydrogen abstraction from this species would result in acetaldehyde formation while nucleophilic attack on the α-carbon would form ethane-1,2-diol. The observed change in product distribution upon the addition of CO now becomes understandable since the binding of CO[8] would eliminate vacant coordination sites necessary for β-hydrogen abstraction to take place. At the same time, back-bonding to coordinated CO will result in decreased electron density on the Pt resulting in higher susceptibility of the α-carbon of the β-hydroxyethyl moiety toward nucleophilic attack. The mechanism finds



Scheme 1

Table 2 Oxidation of propene[a]

Catalyst	Oxidant	CO[c]	T/°C	t/h	Propane-1,2-diol	Turnovers[b] Acetone	Turnovers[b] Acetic acid
Pt	O_2		180	24	960	310	
Pt	O_2		180	48	1930	330	640
Pt	O_2	×	180	24	240		
Pt	O_2	×	180	48	470		30
Pt	$CuCl_2$[d]		100	24	110 (50)[e] (30)[f]	300	50
Pt	$CuCl_2$[d]	×	100	24	40 (10)[e] (5)[f]	5	

Reaction conditions: 0.011 g of 5% Pt on carbon (70 μmol of surface Pt atoms per g of catalyst); 10 ml of H_2O C_3H_6, 150 psi; O_2, 30 psi; stainless steel autoclave with glass liner. [b] Turnover numbers were calculated assuming that only the surface metal atoms were active (the relative proportion of these was determined from H_2 chemisorption studies). [c] CO (100 psi) was added where indicated by ×. [d] 20 equiv. of $CuCl_2$ (relative to catalyst) was added in lieu of O_2. [e] 1-Chloropropan-2-ol. [f] 2-Chloropropan-1-ol.

parallel in the chemistry of the Pt^{IV} species, $[Cl_5Pt{-}CH_2CH_2OH]^{2-}$. In water, this species was found to decompose to ethane-1,2-diol (and some 2-chloroethanol) by nucleophilic attack on the α-carbon.[3b,4b,9] In this case, aldehyde formation did not occur due to the lack of Cl^- ion dissociation from the substitutionally inert, $18e^-$, d^6 metal species. Also of note is that our observation of the increase in ethane-1,2-diol + 2-chloroethanol to acetaldehyde + acetic acid ratio when $CuCl_2$ replaced O_2 as the oxidant closely parallels the increase in ethylene diacetate to vinyl acetate ratio in the oxidation of ethylene by the Pd^{II} ion in acetic acid.[10] The latter observation has been explained by invoking an interaction between Pd^{II} and Cu^{II} through bridging Cl^- ions resulting in the withdrawal of electron density on the Pd centre thereby aiding nucleophilic attack on the α-carbon bound to the metal.

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