Activation of Water with Anionic Platinum Carbonyl Clusters

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The platinum cluster carbonyl anion $[Pt_{12}(CO)_{24}]^{2-}$ catalyses the reaction between water and *p*-benzoquinone to give *p*-dihydroxybenzene and oxygen; rate parameters have been determined for the reaction between $[Pt_{12}(CO)_{24}]^{2-}$ and water.

Activation of water with transition metal carbonyl clusters has been successfully used in various catalytic processes.[1–4] However, there is no example of a cluster-catalysed reaction where water as one of the reactants is oxidised to oxygen. We report here a new approach for the activation of water which involves this redox reaction of water with anionic platinum cluster carbonyls.

Platinum cluster carbonyl anions of the general formula $[Pt_3(CO)_6]_n^{2-}$ (n = *ca.* 10, 6, 5, 4, 3, 2, 1) have been synthesised by Longoni and Chini and reported[5] to catalyse the formation of water from hydrogen and oxygen† by combining reactions (1) and (2). All the clusters from the trimer (n = 3)

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† The reaction of all the platinum cluster carbonyl anions with water to give oxygen has been reported by Longoni *et al.*,[5] but according to a referee's suggestion we confirmed this by g.c.–mass spectrometric analyses of the evolved gas.

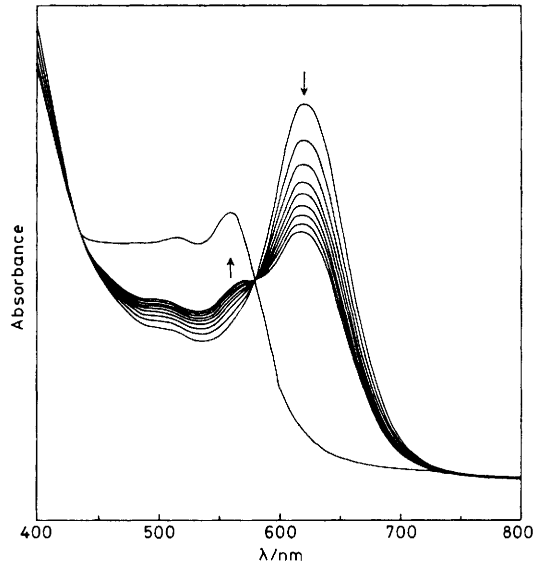


Figure 1. Conversion of (**1**) (5×10^{-4} mmol) into (**2**) in dimethylformamide (15 ml) in the presence of water (25×10^{-3} mmol) at 33 °C under nitrogen. The final spectrum with a band at 560 nm was obtained by driving the reaction to completion with hydrogen.

$$(n-1)\ [\mathrm{Pt_3(CO)_6}]_n^{2-} + \mathrm{H_2} \rightarrow n\ [\mathrm{Pt_3(CO)_6}]_{n-1}^{2-} + 2\mathrm{H^+} \qquad (1)$$

$$n\ [\mathrm{Pt_3(CO)_6}]_{n-1}^{2-} + 2\mathrm{H^+} + \tfrac{1}{2}\mathrm{O_2} \rightleftharpoons (n-1)\ [\mathrm{Pt_3(CO)_6}]_n^{2-} + \mathrm{H_2O} \qquad (2)$$

to the hexamer ($n = 6$) have characteristic u.v.–visible spectra and their interconversions according to reaction (1) and (2) could be conveniently monitored by spectrophotometry.‡ For these clusters, both reaction (1) and the forward reaction of reaction (2) are rate limited by the solubility of hydrogen and oxygen. Under pseudo-first-order conditions, in solutions saturated with the appropriate gas, both these reactions are rapid ($t_{\frac{1}{2}}$ <5 s). For the hexamer ($n = 6$) and the pentamer ($n = 5$) the back reaction of (2) is also rapid ($t_{\frac{1}{2}} < 5$ s) but excellent isobesticity, leading to an equilibrium, is observed in the reduction of $[\mathrm{Pt_{12}(CO)_{24}}]^{2-}$ to $[\mathrm{Pt_9(CO)_{18}}]^{2-}$ by water (Figure 1).

$[\mathrm{Pt_3(CO)_6}]_n^{2-}$
(**1**), $n = 4$
(**2**), $n = 3$

Since an integrated rate equation that takes into account the equilibrium nature of this reaction is far too complicated for any practical use, the kinetic data for the conversion of (**1**) into (**2**) have been treated both on the basis of initial rates and also by an integrated pseudo-first-order rate equation which shows linearity for a little over one half-life. Fortunately, in the latter case, the infinity value could be calculated with accuracy by substituting the nitrogen atmosphere in the special cell with hydrogen, thereby making the forward reaction go to completion. This is in accordance with the reported reaction of the cluster carbonyl anions with hydrogen in the presence of water.[5]

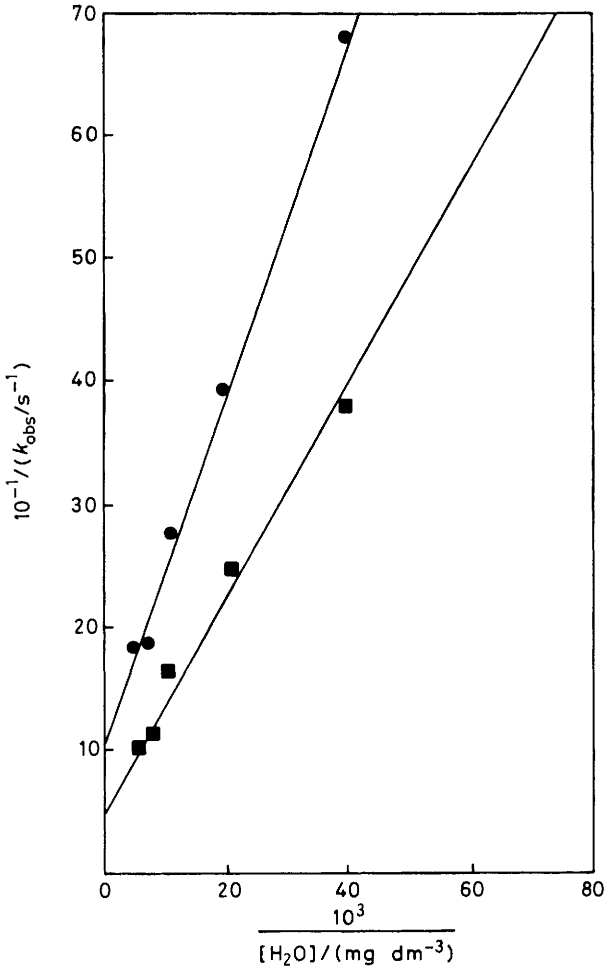
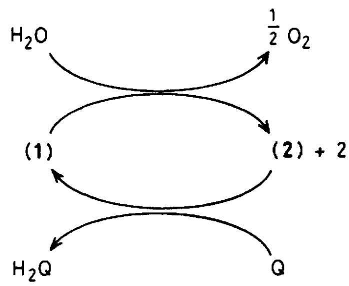


Figure 2. k_{obs}^{-1} *vs.* $[\mathrm{H_2O}]^{-1}$; ●, for water; ■, for $\mathrm{D_2O}$, at 33 °C.



Q = *p*-benzoquinone, $\mathrm{H_2Q}$ = *p*-dihydroxybenzene.

Scheme 1

The reaction of (**1**) with water in dimethylformamide appears to obey the rate law (3). In this rate equation k is the

$$\text{Rate} = kK[\text{complex}][\mathrm{H_2O}]/(1 + K[\mathrm{H_2O}]) \qquad (3)$$

rate constant, K is the equilibrium constant for a rapid pre-equilibrium between water and (**1**). Plots of k_{obs}^{-1} $\{k_{obs} = k[\mathrm{H_2O}]/(1 + K[\mathrm{H_2O}])\}$ against $[\mathrm{H_2O}]^{-1}$ yield reasonably good straight lines (Figure 2). At 33 °C the rate parameters are $k = 2.67 \times 10^{-4}\ \mathrm{s^{-1}}$, $K = 0.815\ \mathrm{mol^{-1}}$ ($\Delta H^{\ddagger} = 13.13$ kcal mol^{-1}; $\Delta S^{\ddagger} = -20.46$ cal K^{-1} mol^{-1}).§ Substitution of

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‡ All spectrophotometric work was carried out in a special cell under a controlled atmosphere: λ_{max}: $[\mathrm{Pt_{18}(CO)_{36}}]^{2-}$, 720 nm ($\epsilon$ 37 500); $[\mathrm{Pt_{15}(CO)_{30}}]^{2-}$, 700 (28 600); (**1**) 620 (23 000) and 392 (65 600); (**2**), 560 (11 700) and 368 (52 100).

§ 1 cal = 4.184 J.

water with D_2O yields $k(33\ ^\circ C) = 0.77 \times 10^{-4}\ s^{-1}$ making $k(H_2O)/k(D_2O)$ = *ca.* 0.3. Solvent isotope effects of the same order have been observed in the oxidation of formic acid by permanganate ion.[6]

Complex (**2**) undergoes instantaneous oxidation with *p*-benzoquinone, suggesting the possibility of a catalytic cycle as shown in Scheme 1.

Although the overall reaction (4) is endothermic,¶ much more than stoicheiometric quantities of *p*-dihydroxybenzene could be generated by using complex (**1**) as the catalyst. Thus,

$$Q + H_2O \rightarrow H_2Q + \tfrac{1}{2}O_2 \qquad (4)$$

$$\Delta H^\circ\,(293\ K) = +\,27.1\ \text{kcal mol}^{-1}$$

in a typical catalytic run, water (11.1 mmol) reacted with *p*-benzoquinone (0.67 mmol) in acetonitrile at 30 °C in the presence of (**1**) (0.013 mmol) as the catalyst. A gentle stream of nitrogen was maintained through the solution. After 5 h, the mixture was analysed by high-pressure liquid chromatography (Waters Associates 440 HPLC unit with μ-Bondapak C_{18} column with methanol–water, 60:40, as eluant) and *p*-dihydroxybenzene (0.29 mmol) was obtained. The i.r. and u.v. spectra of the mixture at this point show the presence of both (**1**) and (**2**).

On the basis of the combined intensities of the u.v. peaks due to (**1**) and (**2**), it is clear that cluster decomposition has not taken place. If the reaction is continued for a longer time ($\geq$20 h), partial conversion of the catalyst into some other deactivated carbonyl species is evident on the basis of the u.v. and i.r. spectra. This is not surprising; complex (**1**) has been found to react slowly ($t_{\frac{1}{2}}$>8 h) with *p*-benzoquinone or acetonitrile to give other as yet uncharacterised carbonyl products.

The potential of (**1**) to catalyse the direct oxidation of water in systems for the photochemical activation of water is being further investigated.

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¶ ΔH° (293 K) calculated from heat of combustion values given in 'Handbook of Chemistry and Physics,' 48th Edn., The Chemical Rubber Co., Ohio.

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