Activation of Water with Anionic Platinum Carbonyl Clusters †

Amitabha Basu, Sumit Bhaduri,* and Krishna R. Sharma
Alchemie Research Centre Private Limited, CAFI Site, P.O. Box 155, Thane-Belapur Road,
Thane 400 601, Maharashtra, India

Rate parameters have been determined for the oxidation of water to oxygen by $[Pt_{12}(CO)_{24}]^{2-}$. The cluster anion is found to catalyse the conversion of *p*-benzoquinone to benzene-1,4-diol with water or hydrogen. U.v.–visible and i.r. spectroscopy suggest the involvement of $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 3 or 4) anions as active intermediates in these catalytic reactions.

Activation of water with transition metal carbonyl clusters has been successfully used in catalytic processes such as the water-gas shift reaction,[1] the hydroformylation reaction,[2] the hydrogenation of nitrobenzene to aniline,[3] and very recently for the reduction of polynuclear aromatic and heteroaromatic nitrogen compounds.[4] However, in all these reactions the mode of activation is thought to be by the nucleophilic attack of a hydroxide ion onto a bonded carbonyl group. In this paper we describe a new approach for the activation of water which involves the oxidation of water to oxygen with anionic platinum cluster carbonyls. A preliminary account of this work has appeared recently.[5]

Results and Discussion

Spectrophotometric and Kinetic Studies.—Platinum cluster carbonyl anions of general formula $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 1—6 or 10) were synthesised by Longoni and Chini [6,7] and were characterised for n = 2, 3, and 5 by single-crystal *X*-ray diffraction studies. It has been found that all the clusters from the trimer to the hexamer have highly characteristic u.v.–visible spectra and these are shown along with some other relevant data in the Table.[5,8] The air sensitivity of the cluster anions necessitates the use of a special u.v. cell where a rigorously controlled atmosphere can be maintained (see Experimental section). No attempts have been made to record the u.v.–visible spectra of $[Pt_3(CO)_6]^{2-}$ and $[Pt_6(CO)_{12}]^{2-}$ since they cannot be produced by reducing the next-highest clusters (n = 2 and 3, respectively) either with water or hydrogen (see later).

The cluster anions are known to react with hydrogen and oxygen according to reactions (i) and (ii) and have been shown

$$(n-1)[\{Pt_3(CO)_6\}_n]^{2-} + H_2 \longrightarrow n[\{Pt_3(CO)_6\}_{n-1}]^{2-} + 2H^+ \quad \text{(i)}$$

$$n[\{Pt_3(CO)_6\}_{n-1}]^{2-} + 2H^+ + \tfrac{1}{2}O_2 \longrightarrow (n-1)[\{Pt_3(CO)_6\}_n]^{2-} + H_2O \quad \text{(ii)}$$

to be capable of catalysing the formation of water from the two gases.[5] Trace quantities of water have been found to increase the rate of reaction (i).[6] It has also been shown that an increase in the hydrogen pressure only, at moderate temperatures (⩽40 °C), cannot reduce $[Pt_9(CO)_{18}]^{2-}$ any further.[9]

Table. Spectroscopic data

Complex	Colour [a]	I.r. carbonyl bands (cm^{-1}) [a,b]	U.v.–visible spectrum [c]
$[Pt_{18}(CO)_{36}]^{2-}$	Olive-green	2 065vs, 1 900 (sh), 1 875s, 1 855 (sh), 1 840 (sh)	720 (37 500)
$[Pt_{15}(CO)_{30}]^{2-}$	Yellow-green	2 055vs, 1 890mw, 1 870s, 1 840mw, 1 830 (sh)	700 (28 600)
$[Pt_{12}(CO)_{24}]^{2-}$	Blue-green	2 040vs, 2 030 (sh), 1 880mw, 1 860s, 1 825mw	620 (23 000) 392 (65 600)
$[Pt_9(CO)_{18}]^{2-}$	Violet-red	2 030vs, 1 855 (sh), 1 840s, 1 830 (sh), 1 810m	560 (11 700) 368 (52 100)

[a] From ref. 6 and also observed in this work. [b] In tetrahydrofuran. [c] $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1}).

Reaction (i) and the forward reaction of (ii), conveniently monitored by spectrophotometry under a carefully controlled atmosphere, are both rate limited by the solubility of hydrogen and oxygen. Thus, under an atmosphere of hydrogen a *NN*-dimethylformamide (dmf) solution of $[Pt_{12}(CO)_{24}]^{2-}$ (1) exhibits spectral changes with clearly defined isosbestic points. Under these conditions, the changes in absorbance corresponding to the formation of $[Pt_9(CO)_{18}]^{2-}$ (2) are found to be linearly related to time, *i.e.* the order of the reaction with respect to the carbonyl cluster is suggested to be zero. Similar observations are made when, substituting hydrogen with oxygen, the oxidation of $[Pt_9(CO)_{18}]^{2-}$ is studied. However, under pseudo-first-order conditions, in solutions saturated with the appropriate gas, both reactions (i) and (ii) are rapid ($t_{\frac{1}{2}} < 5$ s). As expected trace quantities of water further enhance the rate of reaction (i). For the hexa- and penta-meric clusters the backward reaction of (ii), *i.e.* the reaction with water with evolution of oxygen, is also rapid ($t_{\frac{1}{2}} < 5$ s), but in the case of $[Pt_{12}(CO)_{24}]^{2-}$ (1) it shows excellent isosbesticity and reaches an equilibrium (Figure 1). However, by passing nitrogen through the solution, the liberated oxygen could be removed and reaction (iii) could be taken to completion. The

$$\underset{(1)}{3[Pt_{12}(CO)_{24}]^{2-}} + H_2O \longrightarrow \underset{(2)}{4[Pt_9(CO)_{18}]^{2-}} + 2H^+ + \tfrac{1}{2}O_2 \quad \text{(iii)}$$

evolution of oxygen from water has been experimentally established by carrying out the reaction under an inert atmosphere and analysing the evolved gas by g.c.–m.s. techniques.

An integrated rate equation that takes into account the equilibrium nature of reaction (iii) is far too complicated for any practical use. The kinetic data for the conversion of (1) to (2) have therefore been treated both on the basis of initial rates and also by an integrated pseudo-first-order rate equation. In the latter case linearity is observed for a little over one half-life. The infinity value could be calculated with moderate accuracy by substituting the nitrogen atmosphere in the special cell with a flow of hydrogen. Under these conditions

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† *Non-S.I. units employed*: cal = 4.184 J, lbf in^{-2} = 6.89 × 10^3 Pa.

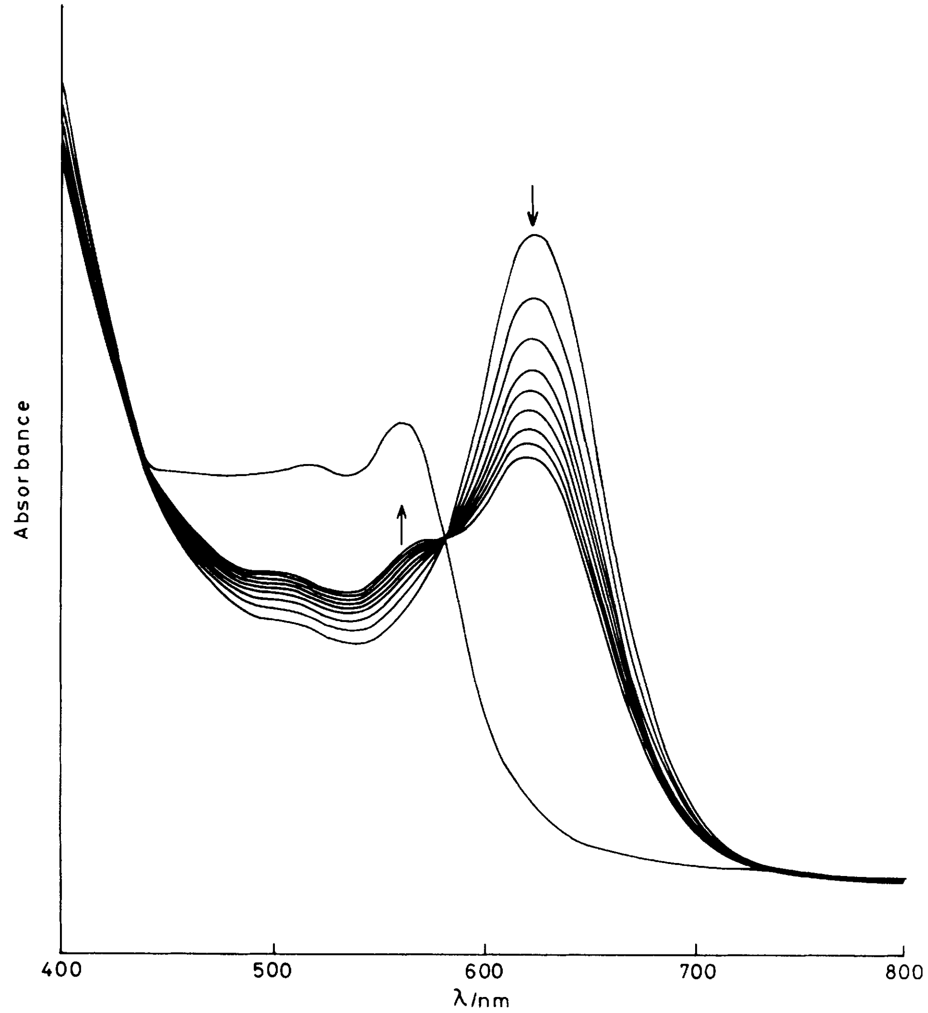


Figure 1. Final spectrum with band at 560 nm, after the conversion of (1) (5×10^{-4} mmol) to (2) in dmf (15 cm^3) in the presence of water (2.5×10^{-2} mmol) at 33 °C under nitrogen, obtained by driving the reaction to completion with hydrogen

(1) is rapidly and quantitatively converted to (2) and infinity values are obtained.

On the basis of the kinetic analysis (see Experimental section) the reaction of $[NBu^n_4]_2[Pt_{12}(CO)_{24}]$ with water in dmf appears to obey the rate law (iv). In this rate equation k is the rate constant and K the equilibrium constant for a rapid pre-equilibrium between water and (1). Plots of $k_{obs.}$ against

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

$[H_2O]$ shown in Figure 2 suggest a linear relationship between $k_{obs.}^{-1}$ and $[H_2O]^{-1}$. Since this indeed is found to be the case (Figure 3), k and K could be determined from the slopes and intercepts of the resultant straight lines. At 33 °C the rate parameters are $k = 2.7 \times 10^{-4}$ s^{-1}, $K = 0.8$ dm^3 mol^{-1}, $\Delta H^{\ddagger} = 13.1$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -20.5$ cal K^{-1} mol^{-1}. Substitution of water with D_2O yields $k(33\ °C) = 0.8 \times 10^{-4}$ s^{-1} making $k_{H_2O}/k_{D_2O} = 0.3$. A solvent isotope effect of the same order has been observed in the oxidation of formic acid by permanganate ion.[10]

Spectrophotometric studies showed that (2) could be cleanly oxidised back to (1) by uranyl or hexachloroplatinate salts. With excess $Na_2[PtCl_6]$, (1) is further oxidised to the pentamer. However the pentamer cannot be oxidised to the hexamer with $Na_2[PtCl_6]$. The syntheses of (1) and the pentamer from $Na_2[PtCl_6]$ show features of autocatalytic reactions,[11] which might well be the results of these facile redox reactions. Nitrobenzene fails to oxidise (2) but instantaneous oxidation is brought about by *p*-benzoquinone (Q) according to reaction (v).

$$4[Pt_9(CO)_{18}]^{2-} + 2H^+ + Q \longrightarrow H_2Q + 3[Pt_{12}(CO)_{24}]^{2-} \qquad \text{(v)}$$

Catalytic Conversion of p-*Benzoquinone to Benzene*-1,4-*diol*.—Combination of reactions (ii) and (v) leads to the catalytic cycle shown in Scheme 1. Although the overall catalytic reaction (vi) is endothermic, measurable quantities of benzene-

$$Q + H_2O \longrightarrow H_2Q + \tfrac{1}{2}O_2,\ \Delta H_{293}^{\ominus} = 27.1 \text{ kcal mol}^{-1} \qquad \text{(vi)}$$

1,4-diol (H_2Q) can be generated using (1) or (2) as the catalyst under the conditions described below. Water and *p*-benzoquinone were reacted in acetonitrile at 30 °C in the presence of $[NBu^n_4]_2[Pt_{12}(CO)_{24}]$ as the catalyst (mol ratio 50 : 1). A gentle stream of nitrogen was maintained through the solution. After 5 h the reaction mixture was analysed by high-pressure liquid chromatography (h.p.l.c.) and *ca.* 50% of the *p*-benzoquinone was found to have been converted to benzene-1,4-diol. The

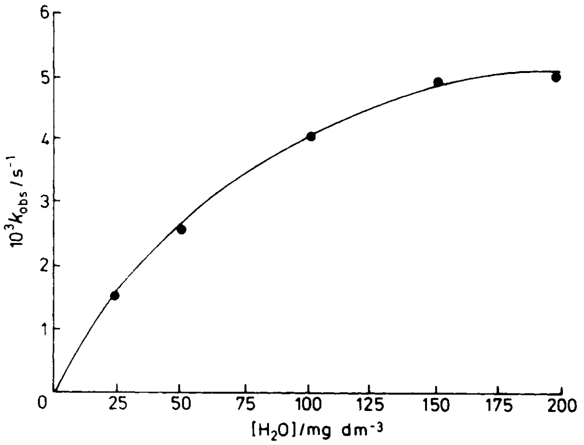


Figure 2. Plot of $k_{obs.}$ vs. $[H_2O]$ in dmf at 33 °C

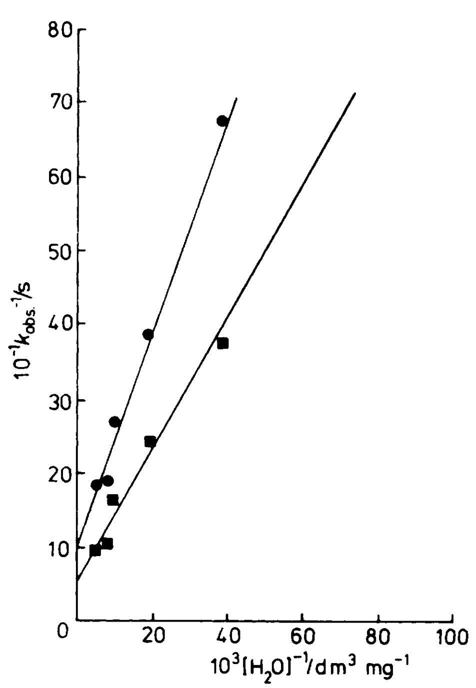
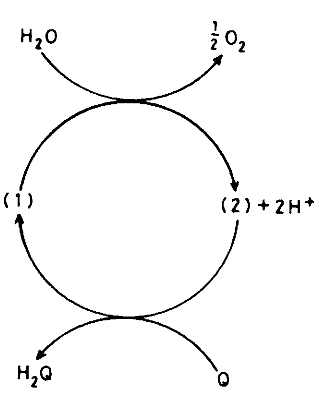
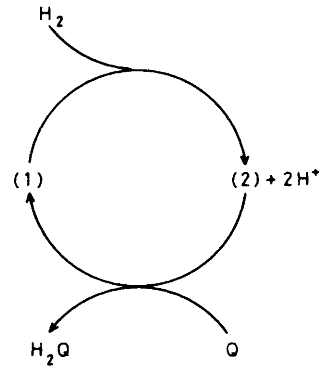


Figure 3. Plot of $k_{obs.}^{-1}$ vs. $[H_2O]^{-1}$ in dmf (●) and $[D_2O]^{-1}$ (■) at 33 °C



Scheme 1. Q = *p*-Benzoquinone, H_2Q = benzene-1,4-diol



Scheme 2. Q = *p*-Benzoquinone, H_2Q = benzene-1,4-diol

i.r. and u.v. spectra of the reaction mixture at this point showed the presence of (1) and (2). On the basis of the combined intensities of the characteristic u.v. bands it can be asserted with confidence that there was no observable loss of cluster concentration. However, in separate experiments it was found that prolonged (>16 h) reaction of (1) with quinone leads to the formation of as yet uncharacterised carbonyl cluster complex(es). In this connection it should be mentioned here that (1) also reacts slowly (>24 h) with acetonitrile under ambient conditions to give brown uncharacterised carbonyl complexes. This observation agrees well with the reported synthesis of $[Pt_{19}(CO)_{22}]^{4-}$ in acetonitrile.[12]

$[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 3—6) anions have been used as precursor material for the catalytic hydrogenation of benzaldehyde to benzyl alcohol.[9] However, in these reactions all the parent clusters are irreversibly reduced to some other common but uncharacterised cluster(s) considered to be the catalytically active species. Very little or no catalytic activity is observed until this common intermediate with characteristic i.r. bands is generated *in situ*. However, reactions (i) and (v) suggest that at least for the hydrogenation of *p*-benzoquinone (1) and (2) should be able to act as the active catalytic intermediates without undergoing any further reduction. The hydrogenation should proceed according to the catalytic cycle shown in Scheme 2. This indeed is found to be the case since *p*-benzoquinone could be hydrogenated quantitatively (acetonitrile solvent, 40 lbf in^{-2} H_2, 30 °C, 1 h) in the presence of (1) as the catalyst. Throughout the course of the reaction the i.r. and u.v.–visible spectra of the reactant solution show only the presence of (1) and (2).

Experimental

The platinum cluster carbonyl anions were prepared according to previously reported procedures.[6] I.r. and u.v.–visible spectra were recorded on Perkin-Elmer 377 and Pye-Unicam SP8 100 spectrophotometers respectively. The special cell used for anaerobic spectrophotometric work was purchased from Hellma GmbH. H.p.l.c. analyses were carried out on a Water Associates 440 HPLC unit with μ-Bondopack C_{18} column with methanol–water (60 : 40) as eluant. G.c.–m.s. analyses were carried out on a Hewlett-Packard 5992 unit.

Kinetic Experiments

These experiments were carried out in a special cell under a nitrogen atmosphere. The specially designated inlet and outlet near the cell mouth allowed the nitrogen atmosphere to be substituted by a flow of hydrogen. Water was circulated through the walls of the cell compartment to maintain constant temperature. Kinetic analyses based on initial rates were carried out by plotting absorbance against time and then determining the initial slopes. For the integrated rate equation, reactions were carried out with an excess but a fixed amount of water and ln ($A - A_\infty$) at 620 nm was plotted against time for about one half-life. Variation of the amount of water gave $k_{obs.}$ at different concentrations of water. The A_∞ values were measured by introducing a gentle flow of hydrogen. Since this reaction is fast and dmf has a high boiling point, solvent loss was negligible. Activation parameters were determined from plots of ln $k_{obs.}$ *vs.* $1/T$ at four different temperatures which showed good linearity. Seven $k_{obs.}$ values, each on the basis of one run, were determined of which two were discarded for poor fit.

Catalytic Reaction of p-*Benzoquinone with Water*.—Water (11.1 mmol) was reacted with *p*-benzoquinone (0.072 g, 0.67 mmol) in acetonitrile at 30 °C in the presence of (1) (0.047 g, 0.013 mmol) as the catalyst. The solution was stirred while maintaining a gentle stream of nitrogen through it. After 5 h the reaction mixture was analysed by h.p.l.c. and benzene-1,4-diol (0.0324 g, 0.29 mmol) was obtained.

Catalytic Reaction of p-*Benzoquinone with Hydrogen*.—*p*-Benzoquinone (0.072 g, 0.67 mmol) was hydrogenated in acetonitrile (20 cm^3) at 40 lbf in^{-2} hydrogen pressure for 1 h. Complex (1) (0.047 g, 0.013 mmol) was used as the catalyst; the temperature was maintained at 30 °C by a flow of water through the outer jacket of a double-jacketted pressure bottle.

Oxidation of (2) *with* $Na_2[PtCl_6]$.—Complex (1) (0.003 g, 0.001 mmol) in degassed dmf (20 cm^3) was reduced by hydrogen to quantitatively generate (2). Four drops of a solution of $Na_2[PtCl_6]$ (0.1 g, 0.22 mmol) in water (10 cm^3) were added to bring about quantitative conversion to (1) in 3 h.

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