Hydrolysis of Acetonitrile, Catalyzed by Octaacetatotetraplatinum(II). — High Reactivity of Coordination Sites Trans to the Pt–Pt Bond —

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(Received May 2, 1994)

Synopsis. The platinum(II) cluster, $[Pt_4(CH_3COO)_8]$, catalyzes the hydrolysis of acetonitrile to acetamide in acetonitrile–water mixtures. Typical turnover number was 104 mol h^{-1} at 80 °C. The catalyst was slowly deactivated by the accumulation of the less active acetamide-substituted species, as well as by its decomposition.

Octaacetatotetraplatinum(II) $[Pt_4(CH_3COO)_8]$ (**1**) is a well-known cluster complex of divalent platinum, with unique structure[1] and reactivity (Chart 1).[2] It has a square-planar cluster core composed of four Pt(II) ions. The coordination geometry around each platinum(II) ion is a distorted octahedron if the Pt–Pt bonds are included. Previously, we reported that the acetate ligands which are in the plane of the square-planar cluster core are labile, whereas the out-of-plane ligands are inert to substitution.[2—4] While investigating reactivity of this cluster in solution, we found that **1** catalyzes the hydrolysis of acetonitrile to give acetamide. In this paper, we describe the catalytic activity under various conditions. We discuss how the catalytic activity is associated with the lability of coordination sites trans to the Pt–Pt bond.

Results and Discussion

When an aqueous acetonitrile solution of $[Pt_4(CH_3COO)_8]$ (**1**) was refluxed, a large amount of acetamide was produced.[5] The result shows that **1** has catalytic activity for hydration of acetonitrile to give acetamide (Eq. 1).

$$CH_3CN + H_2O \xrightarrow{\text{cat.}} CH_3CONH_2 \qquad (1)$$

Figure 1 shows an example of the amount of catalytically produced acetamide as a function of time under typical experimental conditions. The amount of acetamide increased linearly with time at the beginning of the reaction (at least for the first hour), and then the efficiency gradually decreased. The original pale orange color of the solution slowly changed to weakly bluish after ca. 5—6 h, and became blue green after the overnight reaction. The color change indicates the slow decomposition of the catalyst after the prolonged reaction time.

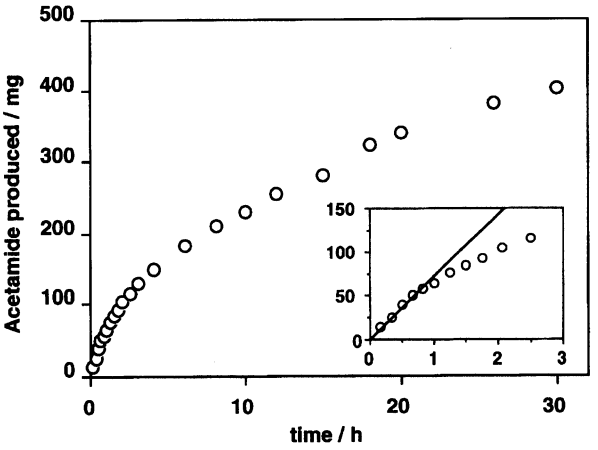

Fig. 1. Time dependence of the amount of acetamide catalytically produced in an aqueous acetonitrile solution of **1**. Experimental conditions: 10 mg of **1** in 20 cm^{-3} of aqueous–acetonitrile (1 : 1) solution at 80 °C. The inset shows the details of the initial 3 h.

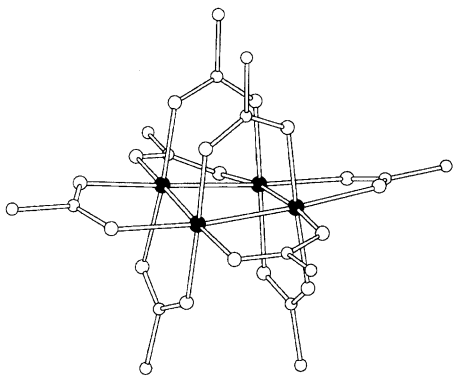

Chart 1.

The turnover number (N) was estimated from the initial linear portion of the time course. Throughout this paper, we will use turnover number (N) as defined by Eq. 2.

$$\text{turnover number}(N) = \frac{(\text{acetamide/mol})}{(\text{catalyst/mol})(\text{time/h})} \qquad (2)$$

The turnover number under the experimental conditions in Fig. 1 was 104 mol h^{-1}. The catalytic activity was increased with an increase in reaction temperature. Under the same conditions as those in Fig. 1, the turnover number was 17.1 mol h^{-1} at 60 °C, 32.4 at 70 °C, and 104 at 80 °C.

Figure 2 shows the amount of acetamide produced during the initial 1 h reaction time as a function of the catalyst concentration. There is a good linear relationship between them. This observation indicates that the rate of the acetamide formation depends linearly on the concentration of the catalyst.

Table 1. Comparison of Catalytic Activities for Hydrolysis of Acetonitrile to Acetamide

Cayalyst	Temp/°C	Turnovers	Ref.
trans-$[PtH(H_2O)(PMe_3)_2][OH]$	78	178.4	12)
$Pt_4(CH_3COO)_8$	80	104	This work
$Pt_4(CH_3COO)_4(CF_3COO)_4$	80	62.7	This work
$Pt_4(CH_3COO)_4(CH_3CONH)_4$	80	48.4	This work
trans-$[PtH(H_2O)(PEt_3)_2][OH]$	78	69.9	12)
trans-$[Rh(OH)(CO)(PPh_3)_2]$	78	50.0	7,13)
$PdCl(OH)(bipy)(H_2O)$	76	29.4	14)
$Pt[P(c\text{-}C_6H_{11})_3]_2$	80	26.7	15)
K_2PdCl_4, 2,2′-bipyridine; NaOH	76	8.8	14,16)
$Pt(PEt_3)_3$	80	2.7	15)

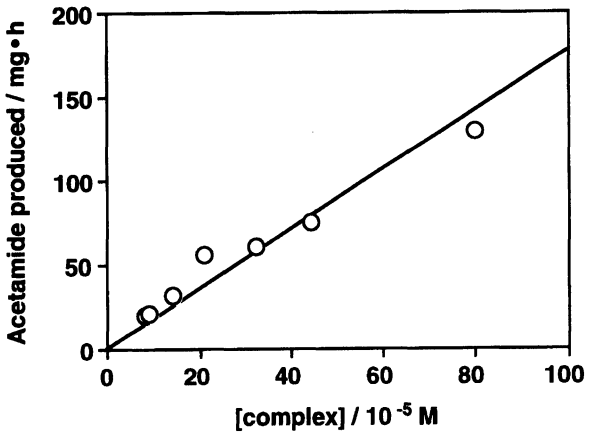

Fig. 2. Dependence of the amount of acetamide produced during the initial 1 h reaction time on the concentration of **1** in aqueous–acetonitrile (1 : 1) solution at 80 °C.

Figure 3 shows a plot of the turnover number vs. % volume of water in acetonitrile. The plot passes through the origin as expected from Eq. 1. The turnover number appears to increase almost linearly with the water content of the solution up to the water/acetonitrile ratio of 3/1.

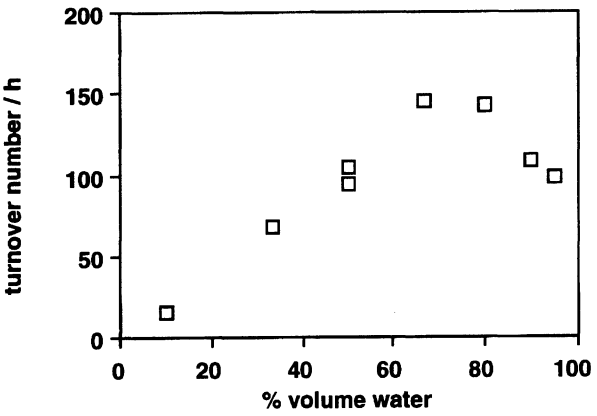

Fig. 3. Dependence of the turnover number of $[Pt_4(CH_3COO)_8]$-catalyzed hydrolysis of acetonitrile on the % volume of water. Experimental conditions: 20 mg of **1** in the solution of 20 cm^{-3} total volume at 80 °C.

As Fig. 1 and the color change during the prolonged reaction time show, catalyst **1** is slowly deactivated. The decomposition of the Pt_4 unit and the inhibition by the product are the two main factors responsible for the deactivation. We carried out experiments to find under what conditions the deactiviation is suppressed. We found that addition of acetate buffer (10—25 fold excess to the catalyst) prevented to some extent the decomposition of the catalyst without any loss of activity, and that the linear portion in the plot of acetamide produced vs. time lengthened with the same slope as the amount of added acetate buffer was increased. Without **1**, acetate buffer itself showed no catalytic activity. Addition of a simple inorganic acid or base did not enhance the catalytic activity of **1**. Rather, addition of a base caused an immediate color change of the solution to red brown, and thus the decomposition of the catalyst is evident.

Acetamide produced in the catalytic process suppressed the catalytic activity. Experiments were carried out by adding acetamide beforehand under otherwise the same conditions as those in Fig. 1. The turnover number was 90.3 and 25.8 mol h^{-1} in the presence of 89 and 890 fold excess of acetamide to the catalyst in molar ratio, respectively. The acetamidate complex $[Pt_4(CH_3COO)_4(CH_3CONH)_4]$ (**2**)[6a,6b] also exhibited the catalytic activity under the same conditions as those in Fig. 1. However, the efficiency was much lower than that of $[Pt_4(CH_3COO)_8]$, and the turnover number was 48.4 mol h^{-1}. The lesser catalytic activity of **2** and the above results suggest that the increase in the number of coordinated acetamides in place of acetate ligands at the in-plane coordination site is unfavorable for the catalytic activity. A similar tetranuclear platinum(II) cluster complex $[Pt_4(CH_3COO)_4(CF_3COO)_4]$ (**3**)[6a] again showed the lower activity of N=62.7 mol h^{-1}.

Nitriles coordinated to platinum are often hydrolyzed easily to corresponding amides.[7—10] It is very likely that acetonitrile substitutes for the in-plane acetate ligands in **1**, since the in-plane acetates are highly labile due to trans influence of the Pt–Pt bonds.[2,11] Coordinated acetonitrile is then attacked by a water molecule either directly or through its coordination at a neighboring platinum ion. The resulting acetamidate ion

would be detached easily due to the trans influence of the Pt–Pt bonds. Thus the catalytic cycle operates effectively. A similar mechanism has been proposed for the catalytic hydrolysis of acetonitrile by $[PtH(H_2O)(P(CH_3)_3)_2][OH]$, in which strong trans influence of the Pt–H bond is considered to be responsible for the catalytic reaction.[12] Table 1 summarizes the data of the catalytic hydrolysis of nitriles by some platinum complexes. The present tetra-platinum complex belongs to the group of those having efficient catalytic activity.

Experimental

Materials. $[Pt_4(CH_3COO)_8]$ (**1**),[1] $[Pt_4(CH_3COO)_4(CH_3CONH)_4]$ (**2**),[6a,6b] and $[Pt_4(CH_3COO)_4(CF_3COO)_4]$ (**3**),[6a] were prepared by the literature methods. Other commercially available materials were used as received.

Rate Studies. A mixture of 5 cm^3 of acetonitrile and 5 cm^3 of water containing 10 mg of **1** in a two neck flask with a condenser, was kept at 80 °C under nitrogen with stirring in a thermostated oil bath. At an appropriate time interval, 0.5 cm^3 each of the solution was withdrawn with a micro syringe through septum rubber cap. The collected sample was immediately cooled in an ice bath to stop the reaction and analyzed by gas chromatography (GC). GC measurements were performed with a Shimadzu GC-9A instrument using thermal conductivity detector and a 1.6 m Porapak-Q column. The flow rate of carrier gas was 50 $cm^3\ min^{-1}$. By using a time-temperature program, temperature was maintained at 120 °C for the initial 4 min and then increased at a rate of 15 $°C\,min^{-1}$ to a final temperature of 220 °C.

This work was supported by a Grant-in-Aid for Scientific Research No. 05235202 on Priority Area of "Activation of Inactive Small Molecules" and Grant-in Aids for Scientific Research Nos. 05403008 and 06740503 from the Ministry of Education, Science and Culture. We are grateful for research grant from Mitsubishi Foundation.

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5) For example, when a mixture of acetonitrile (10 cm^3), H_2O (10 cm^3) and 6 mg of **1** was refluxed for 3.5 h, 104 mg of white powder could be isolated from the resulting solution. The product can be purified by sublimation and was identified as acetamide by means of chemical analysis, ^1H NMR, and melting point measurement.

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11) We successfully isolated single crystals of a platinum complex formed during the catalytic process. Analytical and ^1H NMR data suggested that the compound is $[Pt_4(CH_3COO)_{8-n}\ (CH_3CONH)_n]$ and that n is close to 2. X-Ray analysis of this compound was not strainghtforward, since the structures of bridging acetate and bridging acetamidate ligands are X-ray crystallographically very similar and also because disorder occurs between their sites. It was evident, however, that the square-planar platinum cluster core and four out-of-plane acetate ligands remain essentially unchanged from **1**, that approximately two acetamidate ligands are in the plane of the cluster core, and that the disorder occurs only at the in-plane position. Crystal data: monoclinic, $C2/c$, $a=32.56(1)$, $b=10.727(3)$, $c=14.844(4)$ Å, $\beta=95.69(3)°$, number of observed reflections $(I>3\sigma(I))=2640$, $R=0.090$ for a model ($n=2$) without the disorder.[6a] It is also evident from ^1H NMR methyl proton chemical shifts that acetamidate ligands occupy the in-plane coordination sites.[6]

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