February, 1991] © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 641—643 (1991) 641

Oxidation of *trans*-1,2-Cyclohexanediaminetetraacetatocobaltate(II) by Peroxodiphosphate Catalyzed by Ag(I) in Acetate Buffers. A Kinetic Study

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(Received April 9, 1990)

The kinetics of oxidation of *trans*-1,2-cyclohexanediaminetetraacetatocobaltate(II) by peroxodiphosphate (PDP) in acetate buffers was studied in the presence of Ag(I). For the first time, this study gives a clear evidence for the involvement of Ag(I)/Ag(II) cycle in the Ag(I)-catalyzed PDP oxidation reactions in acetate buffers. A plausible mechanism consistent with the observed kinetic features is proposed.

Peroxodiphosphate (PDP) is the structural and electronic analogue of peroxodisulfate (PDS). The Ag(I)-catalyzed reactions of PDP are scanty[1,2] when compared with those of PDS.[3] In acid medium, the PDP reactions are liable to occur via a hydrolytic path and the reactivity was ascribed to the hydrolytic product. In acetate buffered medium, the hydrolysis of PDP is negligible and the reactive species is PDP itself. In this medium, the uncatalyzed reactions were reported to be slow[4] and Ag(I) is recently proposed as an efficient catalyst for these reactions.[4–7] But these studies could not clearly establish whether the reaction occurs through an Ag(I)/Ag(II) cycle or via complexation of PDP with Ag(I). We report in this communication the results of our studies to clarify the role played by Ag(I) in the Ag(I)-catalyzed oxidation of *trans*-1,2-cyclohexanediaminetetraacetatocobaltate(II), $[Co(cydta)]^{2-}$ by PDP in acetate buffers.

Experimental

All the aqueous solutions were prepared afresh with double distilled deionized water. Peroxodiphosphate is a gift sample from FMC Corporation, USA and was used as such. Its aqueous solutions were standardized iodometrically.[8] *trans*-1,2-Cyclohexanediaminetetraacetic acid (H_4cydta) is an Aldrich sample and the aqueous solutions of its disodium salt were standardized against standard zinc sulfate solution in ammonical buffers (pH=10) using Eriochrome Black T as indicator. All other reagents were either AR or GR grade as the case may be. Ionic strength of the medium was maintained by using E. Merck's 'p.a.' grade sodium nitrate. The pH of the medium was maintained by varying [AcOH] and fixing [AcONa]. In all the kinetic runs, the ligand was in 10% excess to that of [Co(II)].

The kinetics of the reaction were monitored spectrophotometrically by measuring the increase in absorbance of the product, $[Co(cydta)]^-$ at 545 nm using a Carl Zeiss 'Spekol' spectrocolorimeter in conjunction with an EK_5 attachment and a Cenco circulation cum immersion thermostat. Toshniwal's CL-46 digital pH meter was used for adjusting the pH of the reaction mixtures. The reaction was initiated by adding the temperature-equilibrated Ag(I) solution to the rest of the reaction mixture kept at 30.0±0.1 °C in a black coated reaction vessel. The reaction mixture was immediately transferred to the optical cell of the spectrocolorimeter and the increase in optical density (OD) at 545 nm against the reagent blank was noted from time to time.

Results

When the spectrum of the reaction mixture in a typical kinetic run was recorded with time on a Shimadzu UV-260 spectrophotometer in the range 360—600 nm, two absorption maxima (380 and 545 nm) were noticed all through the reaction time unlike in earlier reports using other oxidants[9] where the former peak was noticed after a certain period of time since the commencement of the reaction.

The stoichiometry of the reaction was determined under the conditions: $[Co^{II}(cydta)^{2-}] \gg [PDP]$ at 30.0±0.1 °C. The amount of $[Co^{III}(cydta)^-]$ formed

Table 1. Kinetic Data for the Oxidation of $[Co(cydta)^{2-}]$ by Peroxodiphosphate Catalyzed by Ag(I) in Acetate Buffers[a)]

$[Co(cydta)^{2-}]$	[PDP]	[Ag(I)]	$[H^+]$	$k_0 \times 10^7$
$\times 10^4$ M	$\times 10^3$ M	$\times 10^4$ M	$\times 10^6$ M	$M\,s^{-1}$
5.0	30.0	10.0	10.0	7.96
10.0	30.0	10.0	10.0	8.33
15.0	30.0	10.0	10.0	8.05
20.0	30.0	10.0	10.0	8.23
25.0	30.0	10.0	10.0	8.55
30.0	30.0	10.0	10.0	8.50
20.0	5.0	10.0	10.0	1.0
20.0	10.0	10.0	10.0	2.06
20.0	15.0	10.0	10.0	3.56
20.0	20.0	10.0	10.0	4.18
20.0	30.0	10.0	10.0	7.33
20.0	30.0	5.0	10.0	3.68
20.0	30.0	10.0	10.0	7.80
20.0	30.0	15.0	10.0	12.88
20.0	30.0	20.0	10.0	18.21
20.0	30.0	10.0	1.78	11.06
20.0	30.0	10.0	5.62	9.73
20.0	30.0	10.0	10.0	8.45
20.0	30.0	10.0	22.38	6.96
20.0	30.0	10.0	56.23	5.31

a) I=0.3 mol dm^{-3}: Temp=30.0±0.1 °C.

was estimated by measuring the optical density of the reaction mixture at the end of the reaction (D_∞) as indicated by its constancy with time and the molar absorbance of the $[Co^{III}(cydta)^-]$. It was observed that 2 moles of $[Co^{II}(cydta)^{2-}]$ required one mole of PDP for its complete oxidation.

The progress of the reaction was monitored at 545 nm upto 80% completion of the reaction. The plots of $(D_\infty$-$D_t)$ versus time (where D_∞ and D_t are the optical densities of the reaction mixture after completion of the reaction and at time '*t*' respectively) were linear. From the slopes of these plots, the zero-order rate constants (k_0) were evaluated and are given in Table 1. The zero-order rate constants were found to be independent of $[Co(cydta)^{2-}]$, suggesting the independence of the reaction rate on the $[Co(cydta)^{2-}]$. When the substrate was varied in the range $(5.0$—$30.0)\times10^{-4}$ mol dm^{-3}, keeping all other parameters constant, the D_∞ values were plotted against $[Co(cydta)^{2-}]$, a straight line passing through origin was obtained. From the slope of this plot, the molar extinction coefficient (ε) was found to be 310 ± 8 mol^{-1} dm^3 cm^{-1}, which is in good agreement with that reported earlier[10] for $[Co(cydta)^-]$ under similar experimental conditions, thus supporting our view that the product is exclusively $[Co(cydta)^-]$. The zero-order rate constants (k_0) were found to increase with increasing [PDP] and a plot of k_0 versus [PDP] was a straight line passing through the origin, suggesting the first-order dependence of the reaction rate on [PDP]. When the kinetic runs were carried out by varying [Ag(I)] in the range $(5.0$—$20.0)\times10^{-4}$ mol dm^{-3}, keeping all other parameters constant, the zero-order rate constants were found to increase linearly with [Ag(I)] and a plot of k_0 versus [Ag(I)] was a straight line passing through the origin confirming that the reaction is also first-order in [Ag(I)]. Increase in pH of the reaction medium increased the rate. A plot of $k_0\{K_a+[H^+]\}$ versus $[H^+]$, where K_a is the third acid dissociation constant of PDP,[11] was a straight line with a positive slope and positive intercept on the ordinate (Fig. 1). Sodiumacetate and disodiumhydrogenphosphate were found to have no effect on the reaction rate at fixed $[H^+]$ where as increasing $[H_2cydta^{2-}]$ and ionic strength had inhibitory effect on the reaction rate. The reaction mixture initiated polymerization of acrylonitrile monomer suggesting the involvement of free radical intermediates in the reaction. Although at $[H^+]$ used in the kinetic runs, the characteristic test for Ag(II)[12] was not observed, perhaps due to unfavorable conditions for the formation of the orange red colored precipitate of Ag(II)-bipyridyl complex, it was positive when the reaction mixture was acidified.

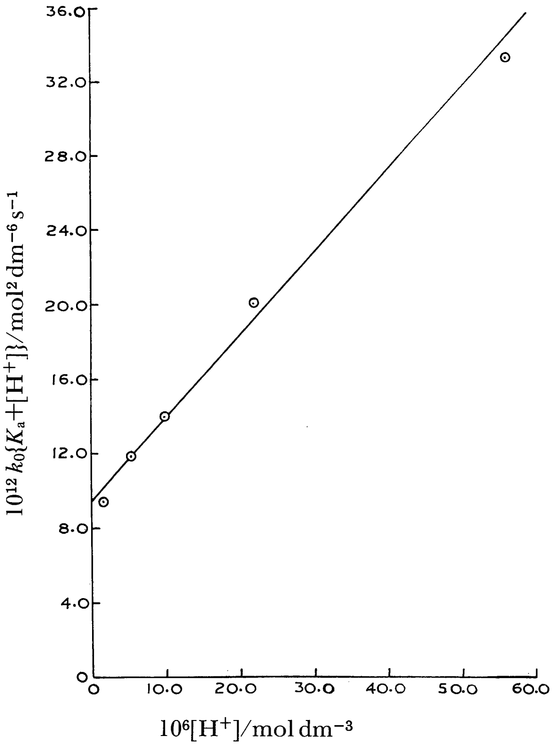

Fig. 1. Plot of $k_0\{K_a+[H^+]\}$ vs. $[H^+]$. $[Co^{II}(cydta)^{2-}]=2.0\times10^{-3}$ M; $[PDP]=3.0\times10^{-2}$ M; $[Ag(I)]=1.0\times10^{-3}$ M; I=0.3 M; Temp=30.0 ± 0.1 °C.

Discussion

The earlier studies on the oxidation of $[Co^{II}(cydta)^{2-}]$ by various oxidants[9,10,13,14] point out to its direct oxidation by the oxidant via the formation of an innersphere complex or in a direct step. In the oxidation of $[Co^{II}(cydta)^{2-}]$ by PDS, clear first-order dependence on each [reactant] was reported.[10] With periodate as the oxidant,[13] the order in $[Co^{II}(cydta)^{2-}]$ was found to vary between **1** and **2**. In the present study, the direct oxidation of $[Co^{II}(cydta)^{2-}]$ by PDP was not observed, thus making the presence of Ag(I) as a catalyst mandatory. This is interesting because the oxidation of metal ions and their complexes by PDP was reported to follow an innersphere path way[15] and Co(II) complexes are known to be labile. Despite this, the reaction doesnot occur in absence of a catalyst like Ag(I).

In the earlier reports[4—7] on the Ag(I) catalyzed oxidation reactions of PDP in acetate buffers, the catalytic role of Ag(I) was ascribed to its complexation with PDP rather than to the formation of higher oxidation states of Ag(I). The earlier investigators could not obtain any experimental evidence for the existence of Ag(II) or Ag(III) in the reaction, but at the same time they could not also rule out the possibility of Ag(II) or Ag(III) being involved in the reaction. In the present case, the zero-order dependence of the reaction rate on $[Co(cydta)^{2-}]$ and the positive test for Ag(II) unequivocally suggests that Ag(II), which is formed as an active intermediate, is responsible for the oxidation of the substrate. Further it was observed that in absence of either PDP or Ag(I), the reaction was negligible, thus ruling out the possibility of oxidation of $[Co(cydta)^{2-}]$ by either PDP or Ag(I) alone. In the earlier studies on Ag(I) catalyzed oxidation reactions of PDP in acid media, the formation of Ag(II) as an intermediate was reported.[1,2] In the present study also in absence of the substrate, when PDP is added to Ag(I) in acetate buffers (pH=5.0) a black precipitate which slowly changes to a pale yellow was noticed. It is interesting to recall that Edwards[11] reported that this black precipitate is a peroxodiphosphate complex of silver which rapidly oxidizes water to form Ag(I). When Ag(II) generated electrolytically is added to $[Co(cydta)^{2-}]$, an intense pink color characteristic of $[Co(cydta)^{-}]$ was immediately noticed. A perusal of the redox potentials of the couples: PDP/PO_4^{3-} (2.01 V); Ag(II)/Ag(I) (1.98 V) and $[Co(cydta)^{-}]/[Co(cydta)^{2-}]$ (0.62 V)[#] shows that the oxidation of $[Co(cydta)^{2-}]$ is readily feasible. The quantitative nature of the reactions with Ag(II) either as a reactant or a product could not be established unequivocally as it is highly unstable under the experimental conditions. Although in the mechanism now proposed, the $HPO_4^{-\cdot}$ was also shown to be the reactive species responsible for the oxidation, it may be noted that it is formed along with Ag(II) in step(3). Further Michaelis-Menten type kinetic pattern characteristic of the precomplexation equilibrium was not observed. This may be due to the fact that even if the Ag(I)PDP complex is formed, it immediately decomposes to give the reactive intermediates, thus escaping its identification kinetically.

Under the experimental conditions, $H_2P_2O_8^{2-}$ and $HP_2O_8^{3-}$ are the active oxidizing species of PDP. The linearity of the plot of $k_0\{K_a+[H^+]\}$ versus $[H^+]$ suggests that both the species are reactive. Keeping in view these facts, the following mechanism is proposed.

$$H_2P_2O_8^{2-} \overset{K_a}{\rightleftharpoons} HP_2O_8^{3-} + H^+, \qquad (1)$$

$$H_2P_2O_8^{2-} + Ag^+ \xrightarrow{k_1} Ag^{2+} + HPO_4^{-\cdot} + HPO_4^{2-}, \qquad (2)$$

$$HP_2O_8^{3-} + Ag^+ \xrightarrow{k_2} Ag^{2+} + HPO_4^{-\cdot} + HPO_4^{3-}, \qquad (3)$$

$$[Co^{II}(cydta)]^{2-} + Ag^{2+}/HPO_4^{-\cdot} \xrightarrow{\text{fast}} \text{products}. \qquad (4)$$

This mechanism leads to the rate law:

$$k_0 = \frac{[PDP]_t[Ag(I)]_t\{k_1[H^+]+k_2K_a\}}{\{K_a+[H^+]\}},$$

where $[PDP]_t$, $[Ag(I)]_t$ represent the total analytical concentrations of the respective reagents and K_a is the third acid dissociation constant of PDP. This rate law explains all the observed facts. From the slope and intercept values of the $k_0\{K_a+[H^+]\}$ versus $[H^+]$, the k_1 and k_2 were calculated to be: $(14.2\pm0.5)\times10^{-3}$ $mol^{-1}\,dm^3\,s^{-1}$ and (43.5 ± 0.8) $mol^{-1}\,dm^3\,s^{-1}$ at 30.0±0.1 °C. This shows that $HP_2O_8^{3-}$ is ca. 10^3 times more reactive than $H_2P_2O_8^{2-}$ towards Ag(I). From the Arrhenius plot the activation parameters for the two steps were calculated to be: $E_{act}=(96.9\pm0.6)$ and (58.1 ± 0.5) $kJ\,mol^{-1}$ and $\Delta S^*=+(68\pm4)$, and $-(29\pm0.2)$ $J\,K^{-1}\,mol^{-1}$ respectively at 30.0±0.1 °C.

Two of us (PSS and KAK) are thankful to the CSIR and DAE, India for the financial assistance. Our special thanks are due to Frank Caropreso of FMC Corporation, USA for the free gift of a PDP sample.

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[#] Experimentally determined by the authors in the present study.