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Kinetics of demetallation and oxidation of tetrakis-(*p*-(trimethylammonio)phenyl)porphine–silver complex*

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Abstract

Kinetics of the acid-catalyzed disproportionation, followed by demetallation of [tetrakis(*p*-(trimethylammonio)phenyl)porphinato]silver(II) was studied at 25 °C and $\mu = 0.1$ mol dm^{-3} [NaNO$_3$]. Under the conditions of study, the silver porphyrin exists as dimers in solution. The reaction was found to be first order in dimer and second order in [H_3O^+], with k, the third-order rate constant $= 1.28 \pm 0.02$ mol^{-2} dm^6 s^{-1}. Kinetics of aquasilver(I) oxidation of the silver(I) and silver(II) porphyrins are also reported. Oxidation of silver(I) porphyrin by aquasilver(I) is found to be first order each in aquasilver(I) and porphyrin with the overall second-order rate constant $= (10.7 \pm 0.3) \times 10^{-2}$ mol^{-1} dm^3. Plausible mechanisms for all these reactions are presented.

Introduction

Earlier Krisnamurthy [2] reported on the unique mode of demetallation involving disproportionation of [tetrakis(*p*-sulfonato)phenyl)porphinato]silver(II), Ag(tpps)†. It was proposed that upon protonation the mixed valent dimer formed by disproportionation dissociates into trivalent and monovalent silver porphyrins. The monovalent silver porphyrin undergoes demetallation in a fast reaction. Subsequent to this report electrochemical [3] and radiolysis studies [4] confirmed the instability of monovalent monosilver porphyrins In this report, a mechanism for the demetallation reaction of [tetrakis(*p*-(trimethylammonio)phenyl)porphinato]silver(II), Ag(tapp), a peripherally positive charged analogue of Ag(tpps) is discussed.

Experimental

Synthesis of Ag(tapp)

A pure sample (1.0 g) of the iodide form of H$_2$tapp [(H$_2$tapp)I$_4$] [5] was converted to the acetate form in solution by anion exchange using Rexyn 202 (Fisher, 30×2 cm column). Silver nitrate (0.5 g) was added to the eluate, ($\approx$80 ml) which was adjusted to 7.0 pH, in a 200 ml beaker. The resulting solution, initially green in color turned red on warming to about 60 °C (higher temperatures hastened the process). Completion of the Ag(tapp) formation was monitored by spectral changes at 421 and 473 nm. At the end of the reaction, a few magnesium turnings (*c.* 0.5 g) were added. The contents of the reaction vessel were stirred and then left for about 15 min. The Ag(tapp) solution was centrifuged and sodium perchlorate crystals (*c.* 10 g) were added to the centrifugate. The precipitate thus formed was filtered, washed thoroughly with cold distilled water and dried for 24 h. *Anal.* Found: C, 44.11; H, 3.97; N, 7.40. Calc. for $C_{56}H_{60}N_8Cl_4O_{16}Ag \cdot 9H_2O$: C, 44.43; H, 5.16; N, 7.41%. The hydration number was chosen to fit the analysis. The synthesis was started with a pure porphyrin sample. The carbon to nitrogen ratio in the pure porphyrin was well established. Therefore in the newly synthesized complex, the carbon to nitrogen ration in combination with carbon and nitrogen analysis was taken as the basis for calculation. Since no solvent other than water was used, the formula was chosen with waters of hydration to fit the analysis. No explanation could be offered for the low value observed for hydrogen analysis. Elemental analyses were performed by MicAnal of Arizona.

Ag(tapp) (0.3 g) thus prepared was converted into the acetate form in solution by ion exchange. The

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†For all the porphyrin species, the peripheral charges are omitted for clarity. The oxidation state of silver is shown in the abbreviations only if it is other than two.

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eluate was made up to 500 ml with distilled water and stored as stock. The concentration of the stock solution, determined spectrophotometrically was 3.023×10^{-4} mol^1 dm^{-3}. The extinction coefficient of Ag(tapp) at 540 nm was calculated to be 1.10×10^4 mol^{-1} dm^3 cm^{-1}.

Materials and methods

Kinetic runs were made employing a Beckmann model CIII Acta UV–Vis spectrophotometer with thermostatted cell compartments (25.0 ± 0.1 °C). Kinetics of the solvolysis and oxidation of Ag(tapp) were monitored at 414 (the isobestic point between monomer and dimeric forms of Ag(tapp)) and 420.6 (Soret of $Ag^{III}(tapp)^+$ dimer) nm, respectively. $AgNO_3$ (Matheson Coleman and Bell) was standardized by the Vollhard method. HNO_3 (A.R. Mallenckrodt) was standardized by titration with NaOH. KI (AR, Mallinckrodt), $NaNO_3$(Alfa products) and CH_3COOH (Fisher) were used as obtained.

Results and discussion

Among water soluble porphyrins, it was found that those metalloporphyrins which contain a four coordinated metal ion in the center and anionic substituents at the periphery dimerized depending on ionic strength [6]. One of the porphyrins found to dimerize was Ag(tpps). The spectral changes observed in the titration of Ag(tapp) with $NaNO_3$ showed the existence of a monomer/dimer equilibrium as in the case of $Ag^{III}(tapp)^+$ [7] in solution. The monomer Soret is at 421 nm while the dimer Soret is at 410 nm.

At $\mu = 0.1$ mol dm^{-3} ($NaNO_3$) and complex concentration of 3.02×10^{-6} mol dm^{-3}, Ag(tapp), the peripherally positively charged analogue of Ag(tpps), was completely dimerized in solution.

Formation of Ag(tapp)

Earlier the kinetics of the formation of $Ag_2^I(tapp)$ [8] were reported. This complex is green colored. As noted in the synthesis, this green solution becomes red (the color of Ag(tapp)) on standing. Kinetics of this disproportionation were also investigated employing a 10.00-cm path-length thermostatted cuvette. The appearance of Ag(tapp) was monitored at 420 nm with porphyrin concentration $= 1.8\times10^{-7}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3} [$NaNO_3$] and pH = 7.00 [tris], and silver(I) concentration ranging from 1.07×10^{-3} to 5.71×10^{-2} mol dm^{-3}. The reaction was first order each in Ag(I) and porphyrin. The plot of pseudo-first-order rate constants, k_o, versus $[Ag^+]$ is presented in Fig. 1. The following pre-equilibrium mechanism is proposed for this reaction:

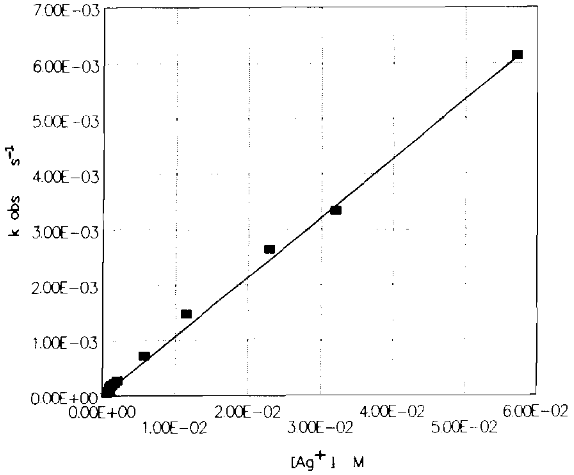

Fig. 1. Plot of pseudo-first-order rate constant, k_o vs. $[Ag^+]$ for the oxidation of $Ag_2(tapp)$ by Ag^+. (Points are experimental and the line calculated by regression analysis).

$$Ag^+ + H_2tapp \rightleftharpoons HAg(tapp) + H^+ \qquad K_1, k_1, k_{-1} \quad (1)$$

$$HAg(tapp) + Ag^+ \longrightarrow Ag(tapp) + Ag^0 + H^+ \qquad k_2 \quad (2)$$

For such a mechanism, the derived rate expression is

$$d[Ag(tapp)]/dt = k_2[HAg(tapp)][Ag^+];$$

$$[HAg(tapp)] = K_1[Ag^+][H_2tapp]_e/[H^+] \text{ and}$$

$$[H_2tapp]_T = [H_2tapp]_e + [HAg(tapp)]$$

where $[H_2tapp]_e$ and $[H_2tapp]_T$ stand for the equilibrium and total concentration of free base porphyrin. Therefore $d[Ag(tapp)]/dt = k_2K_1[Ag^+]^2[H_2tapp]_T/\{[H^+]+K_1[Ag^+]\}$. If $K_1\ [Ag^+] \gg [H^+]$, then rate $= k_2[Ag^+][H_2tapp]_T$. This rate expression is consistent with the experimentally observed rate law. The rate step is that described by (2) and $k_2 = [10.7\pm0.3]\times10^{-2}$ mol^{-1} dm^3 s^{-1}. No attempts were made to characterize the intermediate, [HAg^Itapp]. But in an equilibrium study [8] published earlier such species were shown to be intermediates in the Ag^+ ion reaction with porphyrins. At the low concentrations of porphyrin used in the study [$\approx 10^{-7}$ mol^{-1} dm^3] any elemental silver formed could not be detected visually in the form of a mirror.

Experimental observation and kinetic data rule out a mechanistic scheme such as

$$HAg(tapp) + Ag^+ \rightleftharpoons Ag_2(tapp) + H^+$$

$$Ag_2(tapp) \longrightarrow Ag(tapp) + Ag^0$$

because such a scheme leads to a reduced rate expression, whereby the rate becomes independent of the $[Ag^+]$ concentration which is contrary to experimental observation. That aquated Ag^+ is able to oxidize silver(I) in the porphyrin complex is not unusual since evidence abounds in the literature [9] about changes in reduction potentials between the same metal ion in a complex and the free aquated species. This is exemplified by values of $E°$ (versus NHE) for cobalt at 298 K:

$$Co^{3+}(aq) + e = Co^{2+}(aq) \qquad E° = +1.808\ V$$

$$[Co(NH_3)_6]^{3+}(aq) + e = [Co(NH_3)_6]^{2+}(aq) \qquad E° = +0.108\ V$$

Demetallation of Ag(tapp)

Analyses of the spectrum of the solution employed in the kinetic runs indicated the presence of silver porphyrin species in solution in addition to the dication form of the porphyrin $[H_4tapp^{2+}]$ in equimolar amounts as noted in the case of Ag(tpps) [2]. Such an observation is consistent with the following reaction stoichiometry:

$$2Ag(tapp) + 4H^+ \longrightarrow H_4tapp^{2+} + Ag(tapp) + Ag^+$$

The presence of Ag^+ was verified by turbidity on addition of $Cl^-(aq)$.

The kinetics of the demetallation reaction were monitored under pseudo-first-order conditions in the Ag(tapp) dimer. The observed pseudo-first-order rate constants, k_o are listed in Table 1. The plot of k_o as a function of $[H^+]^2$, Fig. 2, was linear with zero intercept. The slope of the plot, $k = 1.28 \pm 0.02$ mol^{-2} dm^6 s^{-1}.

TABLE 1. Dependence of k_o on $[H^+]$ for demetallation reaction of Ag(tapp)

$10^3 \times [H^+]$ (mol dm^{-3})	$10^4 \times k_o$ (s^{-1})	$10^3 \times [H^+]$ (mol dm^{-3})	$10^4 \times k_o$ (s^{-1})
7.50	1.59	57.4	45.5
12.5	3.58	64.8	54.9
18.8	6.31	74.8	74.3
25.0	10.7	82.0	86.1
42.4	27.8	87.7	96.8
50.0	35.7	92.7	117.0

$\mu = 0.10$ mol dm^{-3} [Na NO_3]. 25.0 ± 0.1 °C.

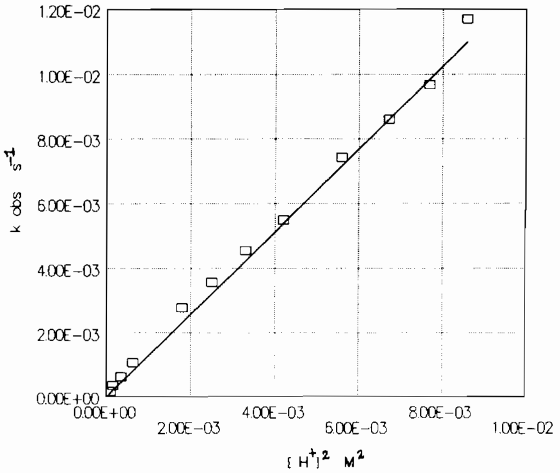

Fig. 2. Plot of pseudo-first-order rate constants, k_o vs. $[H^+]^2$ for the demetallation reaction of Ag(tapp). (Points are experimental and the line calculated by regression analysis).

In the case of demetallation of Ag(tpps), the mechanism proposed consisted of two successive pre-equilibrium steps of aggregation and intramolecular redox reaction leading to a mixed valent dimer. Based on the results presented here, the following mechanism is proposed for the demetallation reaction of Ag(tapp):

$$2Ag(tapp) \rightleftharpoons [Ag(tapp)]_2 \qquad K_d$$

$$H^+ + [Ag(tapp)]_2 \rightleftharpoons [Ag^{III}(tapp)\text{--}HAg^{I}(tapp)]^+ \qquad k_3, k_{-3}, K_3 \qquad (3)$$

$$[Ag^{III}(tapp)\text{--}HAg^{I}(tapp)]^+ + H^+ \longrightarrow Ag(tapp)^+ + H_2tapp + Ag^+ \qquad k_4 \qquad (4)$$

$$H_2tapp + 2H^+ \longrightarrow H_4tapp^{2+} \qquad \text{fast}$$

For this mechanism, the derived rate law is: $-d\{[Ag(tapp)]_2\}/dt = k_4K_3[H^+]^2[Ag(tapp)]_2/[1 + (k_4/k_{-3})(H^+)]$. The product $[(k_4/k_{-3})[H^+]] \ll 1$. Therefore the rate expression becomes $-d\{[Ag(tapp)]_2\}/dt = k_4K_3[H^+]^2[Ag(tapp)]_2$ with $k_4K_3 = 1.28 \pm 0.02$ mol^{-2} dm^6 s^{-1}. Both this abbreviated version as well as the unabbreviated version of rate expressions resemble the general forms of rate law observed for many water soluble metalloporphyrin demetallations [10]. But part of the metalloporphyrin getting oxidized in the process as noted here, is an unusual occurrence. Evidence for the existence of a mixed valent dimer results from the oxidation reaction of Ag(tapp) employing aquated silver(I) ions. If indeed such a mixed valent dimer exists in solution, then the addition of Ag^+ could oxidize the univalent silver porphyrin part of the dimer, as observed above. The reaction of Ag(tapp) with aquated silver(I) was investigated over a five-fold variation in $[Ag^+]$ concentration [1.0×10^{-2} mol dm^{-3} to 5.33×10^{-2} mol dm^{-3}] with pH = 7.00, $\mu = 0.1$ mol dm^{-3} ($NaNO_3$). This reaction was also found to be first order in the Ag(tapp) dimer. But the pseudo-first-order rate constants, k_o were constant (1.795×10^{-3} s^{-1}) for the whole range. This indicated that the reaction was zero order with respect to Ag(I). This observation could be accommodated in the following mechanism, which is totally consistent with the demetallation:

$$2\mathrm{Ag(tapp)} \rightleftharpoons [\mathrm{Ag(tapp)}]_2 \qquad K_\mathrm{d}$$

$$\mathrm{H}^+ + [\mathrm{Ag(tapp)}]_2 \rightleftharpoons [\mathrm{Ag^{III}(tapp)\text{–}HAg^{I}(tapp)}]^+ \qquad k_3, k_{-3}, K_3 \qquad (3)$$

$$[\mathrm{Ag^{III}(tapp)\text{– –}HAg^{I}(tapp)}]^+ \longrightarrow \mathrm{Ag(tapp)}^+ + \mathrm{HAg^{I}(tapp)} \qquad (5)$$

$$\mathrm{HAg^{I}(tapp)} + \mathrm{Ag}^+ \longrightarrow \mathrm{Ag(tapp)} + \mathrm{H}^+ + \mathrm{Ag}^0 \qquad \text{(fast)}$$

An alternate to step (5) would be:

$$[\mathrm{Ag^{III}(tapp)\text{–}HAg^{I}(tapp)}]^+ + \mathrm{Ag}^+ \longrightarrow \mathrm{Ag(tapp)}^+ + \mathrm{Ag(tapp)} + \mathrm{H}^+ + \mathrm{Ag}$$

But this would lead to a rate dependent on $[\mathrm{Ag}^+]$. Qualitative runs indicated that this reaction proceeds faster with decreasing pH.

In summary, Ag(tapp) demetallates through disproportionation analogous to Ag(tpps). On dimerization, Ag(tpps) Soret shifts towards longer wavelengths while that of Ag(tapp) shifts toward shorter wavelengths. Demetallation of Ag(tpps) was first order in $[\mathrm{H}^+]$ while for Ag(tapp) it is found to be second order in $[\mathrm{H}^+]$. Aquasilver(I) oxidizes a transient monosilver(I) porphyrin to silver(I) porphyrin.

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