Solution Chemistry of Silver Porphyrins. Oxidation of 5,10,15,20-Tetra(3'-*N*-methylpyridinio)porphyrinatodisilver(I)

Joseph M. Okoh and Manickam Krishnamurthy *
Department of Chemistry, Howard University, Washington, D.C. 20059, U.S.A.

Peroxodisulphate oxidation of a silver(I) complex of 5,10,15,20-tetra(3'-*N*-methylpyridinio)-porphyrin, believed to be 2:1 (metal:ligand), to the silver(II) complex has been investigated at 25 °C and $I = 0.1$ mol dm^{-3}. This reaction was found to be first order each in silver(I) and peroxodisulphate ions and zero order in porphyrin. The second-order rate constant for the oxidation is computed to be 3.45×10^{-2} dm^3 mol^{-1} s^{-1}, which is in agreement with independently determined rate constants for the reaction of Ag^+ with $S_2O_8^{2-}$.

Dorough *et al.*[1] synthesized the 5,10,15,20-tetraphenylporphyrinate complex of silver(I) and characterized it as having a metal:ligand ratio of 2:1. Recently we[2] found with water-soluble porphyrins that this 2:1 complex is in labile equilibrium with aquasilver(I) ions and free-base porphyrin. The rate of formation of these complexes is very fast and with some porphyrins, a fast disproportionation of the complex follows, resulting in a silver(II) porphyrin product. Such disproportionation in the case of 5,10,15,20-tetra(3'-*N*-methylpyridinio)-porphyrinatodisilver(I), Ag_2(tmpyp) (charges omitted throughout), is very slow, usually taking several hours at room temperature.

Though there have been several studies[3,4] of silver(I)-catalyzed peroxodisulphate oxidation of various organic substrates, there is only one report[5] in the literature of peroxodisulphate oxidation of a silver(I) complex. We have investigated the peroxodisulphate oxidation of the labile silver(I) complex Ag_2(tmpyp) and the results are reported herein.

Experimental

5,10,15,20-Tetra(3'-*N*-methylpyridinio)porphyrin tetraiodide, $[H_2tmpyp]I_4$, was synthesized as described in the literature[6,7] and converted to the more soluble acetate form by ion exchange. Chemicals such as $K_2S_2O_8$ (Baker Analyzed), $AgNO_3$ (Mallinckrodt) and hepes [*N*-(2-hydroxyethyl)piperazine-*N*'-ethane-2-sulphonic acid, Sigma] were used as received. Silver nitrate solution was standardized by Mohr titration[8] and peroxodisulphate by iodometry at 525 nm.[8]

A Beckman model CIII Acta u.v.–visible spectrophotometer was used for spectral studies. A Radiometer model PHM 64 research pH meter was used for pH measurements. Kinetic studies were performed on a Durrum stopped-flow spectrophotometer, thermostatted to 25.0 ± 0.1 °C at 473 nm [$\lambda_{max.}$ of Ag_2(tmpyp)]. All peroxodisulphate and silver–porphyrin solutions were freshly made and used the same day. Ionic strength was maintained at 0.1 mol dm^{-3} with $NaNO_3$ and pH was maintained at 7.0 with buffer (hepes; 0.01 mol dm^{-3}) for all studies.

A plot of absorbance *versus* time was found to be linear for over 90% of the reaction, indicating the reaction to be zero order in porphyrin. The rates of the reaction were obtained from the slopes of such plots. The difference in absorption coefficients of the reactant and product porphyrins is 1.18×10^5 dm^3 mol^{-1} cm^{-1} at 473 nm.

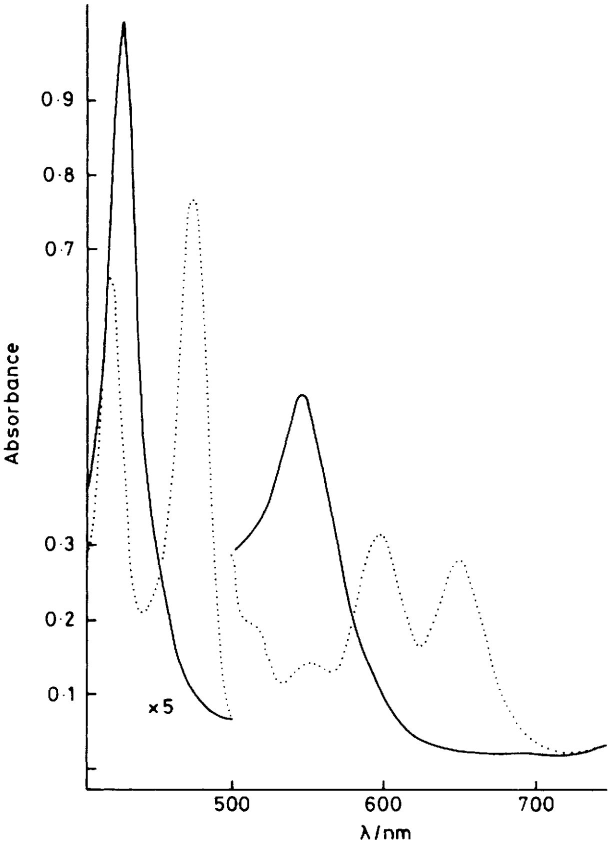

Figure 1. Spectra of the reactants (. . . .), recorded before the addition of $S_2O_8^{2-}$, and the products (——). The reactant solution was 1.0×10^{-5} mol dm^{-3} in H_2tmpyp, 2.0×10^{-4} mol dm^{-3} in Ag^+, pH 7.0 ([hepes] = 0.01 mol dm^{-3}), and $I = 0.1$ mol dm^{-3} ($NaNO_3$). The product solution contained 4.0×10^{-3} mol dm^{-3} peroxodisulphate in addition. Path length = 5.0 cm

Results and Discussion

The spectra of reactants and products of this study are presented in Figure 1. Since Ag^{III}(tmpyp), synthesized chemically by a different method, absorbs at 424, 532, and 560.5 nm in the region 450—600 nm and since the product spectrum

(425, 542 nm) is identical to that of Ag^{II}(tmpyp), obtained by disproportionation, the product of peroxodisulphate reaction is clearly identified as Ag^{II}(tmpyp). The stoicheiometry for the peroxodisulphate oxidation could not be determined due to the intense colour of the porphyrin complex and due to the instability towards disproportionation of the silver(I) complex over the long periods necessary to establish the stoicheiometry. However, since it is generally known that peroxodisulphate is a two-electron oxidant, the same was assumed for this study: equations (1) and (2).

$$2\,Ag^+ + H_2tmpyp \rightleftharpoons Ag_2(tmpyp) + 2\,H^+ \quad (1)$$

$$S_2O_8^{2-} + 2\,Ag_2(tmpyp) \longrightarrow 2\,Ag^{II}(tmpyp) + 2\,SO_4^{2-} + 2\,Ag^+ \quad (2)$$

In order to determine the effect of oxidant concentration on the rate, the reaction was investigated over a ten-fold range, (1.0—10.0) × 10^{-3} mol dm^{-3}, of $S_2O_8^{2-}$ concentration. Plots of the rates against $[S_2O_8^{2-}]$ and $[Ag^+]$ are shown in Figure 2. The linearity of these plots establishes that the reaction is first order each in silver(I) and peroxodisulphate ions. Thus the observed rate law for this reaction is given by equation (3).

$$-\tfrac{1}{2}\,d[S_2O_8^{2-}]/dt = -d[Ag_2(tmpyp)]/dt = k[S_2O_8^{2-}][Ag^+] \quad (3)$$

The second-order rate constant, *k*, for this peroxodisulphate oxidation is computed to be 6.92 × 10^{-2} dm^3 mol^{-1} s^{-1}. The fact that the reaction is zero order in porphyrin eliminates a mechanism whereby $S_2O_8^{2-}$ oxidizes a porphyrin-bound silver(I). This rate law is of the same form as observed in many other silver(I)-catalyzed reactions of peroxodisulphate with a diverse variety of other reducing agents, including oxovanadium(IV), peroxovanadium(V), oxalate, thiosulphate, and cerium(III). The initial process in the generally accepted mechanism[9] for these reactions is equation (4) (slow), followed by equation (5) (very fast).

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\cdot -} \quad (4)$$

$$SO_4^{\cdot -} + Ag^+ \longrightarrow Ag^{2+} + SO_4^{2-} \quad (5)$$

It is the silver(II) species thus formed which oxidizes the substrate in a fast step. From such a proposal, the first initial oxidation of silver(I) to silver(II), equation (4), is the rate-determining step. The step in which Ag^{2+} reacts with Ag_2(tmpyp), equation (6), could either be oxidation or

$$Ag^{2+} + Ag_2(tmpyp) \longrightarrow Ag^{II}(tmpyp) + 2\,Ag^+ \quad (6)$$

displacement of bound silver(I). Neither of these two possibilities can be distinguished kinetically for this system. The silver(I) complex is kinetically very labile,[2] existing in solution in dynamic equilibrium with H^+ and Ag^+ ions. By comparing the Ag^{2+}-displacement path with the direct reaction of Cu^{2+} with H_2tmpyp (the rate constant being 12.4 dm^3 mol^{-1} s^{-1} at 39 °C),[10] one can safely place a lower limit, $k \geqslant 12$ dm^3 mol^{-1} s^{-1}, for the displacement path since (*i*) such displacements with labile complexes are very fast indeed[11,12] and (*ii*) the rate constants for complexation of Ag^{2+} with various amino acids have been found in the range 10^6—10^8 dm^3 mol^{-1} s^{-1}.[13]

Another fast step, equation (7), could also result from the initial process. Our kinetic data would not rule out this possibility either. As there was no bleaching (decolorization)

$$SO_4^{\cdot -} + Ag_2(tmpyp) \longrightarrow Ag^{II}(tmpyp) + Ag^+ + SO_4^{2-} \quad (7)$$

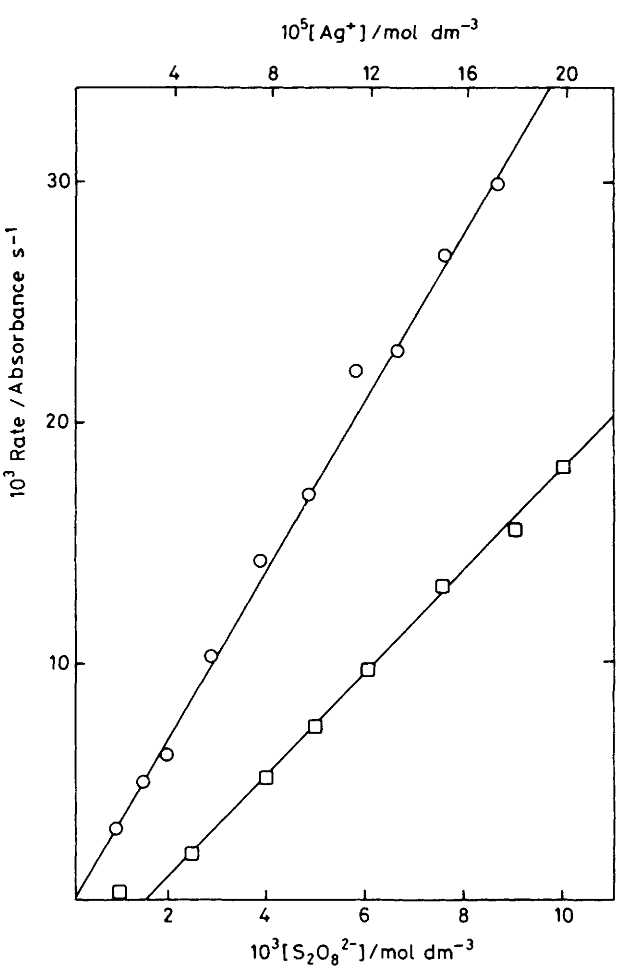

Figure 2. Dependence of pseudo-zero-order rates on $[S_2O_8^{2-}]$ (○) and $[Ag^+]$ (□). [The units for the vertical axis can be converted to mol dm^{-3} s^{-1} by dividing by the product of path length (2.1 cm) and absorption coefficient (1.18 × 10^5 dm^3 mol^{-1} cm^{-1})]

observed, reaction of the free-radical ion with the porphyrin skeleton can be ruled out.

As mentioned earlier, there is only one report of a peroxodisulphate oxidation of a silver(I) complex in the chemical literature. Miller[5] investigated the peroxodisulphate oxidation of 2,2′-bipyridyl and ethylenebis(biguanide) complexes of silver(I) in 50% acetone–water solutions. He found the reaction to be first order each in the complex and in peroxodisulphate. For the reaction of $S_2O_8^{2-}$ with 2,2′-bipyridylsilver(I) one can compute a second-order rate constant of 4.79 dm^3 mol^{-1} s^{-1} at I = 0.065 mol dm^{-3} and 25 °C from his data. Our data could not be compared with the previous data[5] for several reasons such as the difference in solvents, mechanism, *etc.* But for the silver(I)-catalysed peroxodisulphate oxidations, a variety of values ranging from 5.04 × 10^{-3} dm^3 mol^{-1} s^{-1} (I = 0.65 mol dm^{-3})[14] to 1.7 × 10^{-2} dm^3 mol^{-1} s^{-1} (pH 5.5, I = 0.5 mol dm^{-3})[15] including 6.92 × 10^{-3} dm^3 mol^{-1} s^{-1} (I = 0.1 mol dm^{-3}),[16] all at 25 °C, have been reported recently. Our value of 3.45 × 10^{-2} dm^3 mol^{-1} s^{-1} (I = 0.1 mol dm^{-3}, pH 7.0, and 25 °C) falls slightly outside this range. Most of the peroxodisulphate oxidations have been carried out in strongly acidic solutions and consequently dependence on acidity has not been noted. But Ohashi and Yamamoto[15] found a strong dependence of this second-order rate constant on pH, varying from 9 × 10^{-3} dm^3 mol^{-1} s^{-1} at pH 3.0 to 1.7 × 10^{-2} dm^3 mol^{-1}

s^{-1} at pH 5.5. Our data were obtained at pH 7.0. Thus it appears that our data would conform to the well established mechanism for such peroxodisulphate oxidations.

In conclusion, the oxidation of Ag_2(tmpyp) by peroxodisulphate occurs through aquasilver(I) ions with which the metal porphyrin is in labile equilibrium.

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