A Self Exchange Rate Constant for Silver$^{II/III}$–Tetra(4-sulfonatophenyl)porphyrins

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The chemistry of water soluble silver porphyrins has been developed by Krishnamurthy and colleagues. This includes the synthesis of Ag(II) and Ag(III) porphyrins [1, 2], equilibrium studies of reversible Ag(I) complexations [3], and acid catalyzed disproportionation reactions of Ag(II) adducts [1]. The cation catalyzed kinetics of oxidation of silver(II)–tetra(4-sulfonatophenyl)porphyrin, Ag^{II}–TPPS, by IrCl$_6{}^{2-}$ have appeared [4], as has work by Neta and co-workers on the reductive demetallation [5] and oxidation of silver(II)–tetra(N-methyl-4-pyridyl)porphyrin Ag^{II}–TMPyP, by radiolysis techniques [6]. We wish to report the kinetics of reduction of Ag^{III}–TPPS into Ag^{II}–TPPS by the outer sphere reductants Fe(CN)$_6{}^{4-}$, Fe^{II}–EDTA^{2-} and Mo(CN)$_6{}^{4-}$.

Experimental

The Ag^{III}–TPPS complexes were synthesized by oxidation of Ag^{II}–TPPS with S$_2$O$_8{}^{2-}$ [1, 2]. Fe^{II}–EDTA^{2-} was prepared under argon by combination of equimolar amounts of prestandardized ferrous ammonium sulfate and EDTA. Mo(CN)$_8{}^{4-}$ concentrations were determined spectrophotometrically [7], and Fe(CN)$_6{}^{2-}$ was analyzed by titration with permanganate. The reactions were studied at 25 °C on a Durrum–Gibson stopped-flow apparatus under pseudo first order conditions, with at least a twenty fold excess of reductant to porphyrin concentration.

Results

The kinetics of the Ag^{III}–TPPS reduction by Fe(CN)$_6{}^{2-}$ at pH 7, (I = 0.1 NaCl) were first order in porphyrin and first order in ferrocyanide (1.0 × 10^{-4} M to 2.0 × 10^{-5} M), with a second order rate constant k of 5.6 (±0.8) × 10^5 M^{-1} s^{-1}. The reaction rate was independent of (H$^+$) between pH 5.8 to 7.5. At ionic strengths (I) of 0.01 and 0.1 in LiCl, NaCl or KCl, the specific rate constants were within 10% of one an-
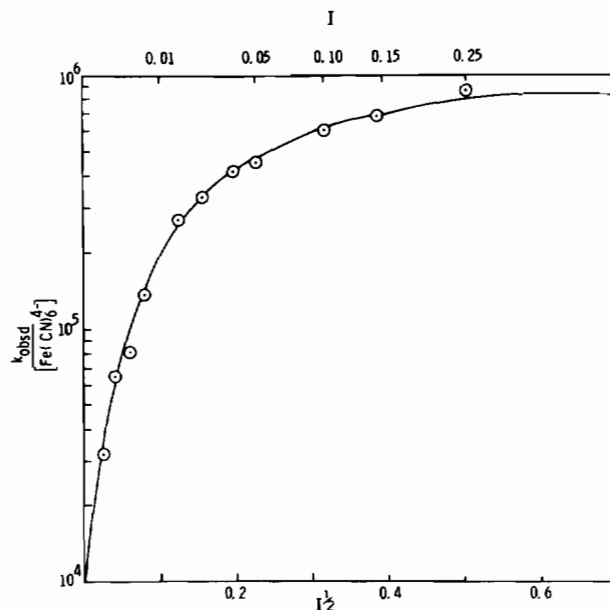
Fig. 1. Dependence of log k_{12} on $I^{1/2}$ for the Ag^{III}–TPPS/Fe(CN)$_6{}^{4-}$ reaction in NaCl, 25 °C, pH 7.0.

other. Figure 1 shows the relationship between log k and $I^{1/2}$. Between 15 °C and 39 °C, the activation parameters were $\Delta H^{\ddagger}$ = 14.5 kcal/mol and $\Delta S^{\ddagger}$ = 17 eu.

At pH 7 (I = 0.1, NaCl, 10^{-3} M Pipes buffer), the Mo(CN)$_8{}^{4-}$/Ag^{III}–TPPS reaction under pseudo first order conditions was first order in porphyrin and first order in Mo(CN)$_8{}^{4-}$ (1 × 10^{-3} M to 5 × 10^{-3} M). A second order forward rate constant of 2.5 (±0.5) × 10^3 M^{-1} s^{-1} was obtained.

The reaction between Fe^{II}–EDTA^{2-} and Ag^{III}–TPPS studied under argon at pH 5 was extremely fast, and only the last thirty percent was able to be followed on our apparatus. Under pseudo first order conditions, the reaction was first order in porphyrin and first order in Fe–EDTA (1.1 × 10^{-5} M to 7.8 × 10^{-5} M), with k = 3 (±1) × 10^7 M^{-1} s^{-1} at I = 0.1. The dependence of rate upon ionic strength was the same as shown in Fig. 1.

Discussion

Ag^{III}–TPPS is the strongest oxidant of the trivalent –TPPS complexes [8, 9] with reduction potentials in the order Ag$^{III/II}$–TPPS = +0.62 V, Co$^{III/II}$–TPPS = +0.21 V, Fe$^{III/II}$–TPPS = *ca.* –0.05 V and Mn$^{III/II}$–TPPS = –0.21 V (*vs.* NHE). The less basic M$^{III/II}$–TMPyP complexes are reduced at potentials 200–250 mv more positive than M^{III}–TPPS's, and Mn^{III}–TAP (tetra(4-N,N,N-trimethyl-

TABLE I. Rate Data for Ag^{III}–TPPS Reductions, 25 °C, $I = 0.1$.

Reductant	k_{12} (M^{-1} s^{-1})	k_{22} (M^{-1} s^{-1})[a]	K_{12}	k_{11} (M^{-1} s^{-1})[b]
Fe^{II}–EDTA^{2-}	3×10^7	3×10^4	3×10^8	2×10^3
$Fe(CN)_6{}^{2-}$	6×10^5	7.4×10^2	3.5×10^3	3×10^5
$Mo(CN)_8{}^{4-}$	3×10^3	3×10^4	6.2×10^{-4}	6×10^5

[a]The k_{22} values are from ref. [11], and the electrode potentials from ref. [13].   [b]k_{11} for $Ag^{III/II}$–TPPS.

TABLE II. Self Exchange Rate Constants for Metalloporphyrins.

	k_{11} (M^{-1} s^{-1})	I	Reductant	Reference
$Ag^{III/II}$–TPPS[a]	4×10^5	(0.1)	$Fe(CN)_6{}^{2-}$, $Mo(CN)_8{}^{4-}$	tp
$Mn^{III/II}$–TPPS	3×10^3	(0.1)	$Ru(NH_3)_6{}^{2+}$	14
$Mn^{III/II}$–TAP	3×10^3	(0.1)	$Ru(NH_3)_6{}^{2+}$	14
$Co^{III/II}$–TMPyP	20	(0.5)	$Ru(NH_3)_6{}^{2+}$	15
$Co^{III/II}$–TMPyP	6.0	(0.5)	$Fe(EDTA)^{2-}$	16
$Co^{III/II}$–TPPS	4.0	(0.5)	$Fe(EDTA)^{2-}$	16
$Co^{III/II}$–TAP	6.0	(0.5)	$Fe(EDTA)^{2-}$	16
$Co^{III/II}$–TMPyP	18	(0.25)	$V(H_2O)_6{}^{2+}$	17
$Co^{III/II}$–TPP(Py)$_2$[b]	9.7			18
$Fe^{III/II}$–TPPS	1×10^3	(0.24)	$V(H_2O)_6{}^{2+}$	18
$Fe^{III/II}$–TMPyP(H$_2$O)	1.2×10^6	(0.05)	$Ru(NH_3)_6{}^{2+}$	18
$Fe^{III/II}$–TMPyP(H$_2$O)(OH)	$>10^9$	(0.05)	$Ru(NH_3)_6{}^{2+}$	19
$Fe^{III/II}$–TMPyP(Im)$_2$	$>10^7$	(0.05)	$Ru(NH_3)_6{}^{2+}$	19
$Fe^{III/II}$–P(CN)$_2$[c]	10^6–10^8	(0.5)	$S_2O_4{}^{2-}$	16,20
$Fe^{III/II}$–P(CN)$_2$[d]	10^7–10^8			21

[a]Also from the Ag^{II}–TPPS/$IrCl_6{}^{4-}$ reaction, see ref. [4].   [b]TPP is tetraphenylporphyrin, k_{11} from PMR measurements in CHCl$_3$.   [c]P is everal 2,4-disubstituted deuterohemins.   [d]P is *para*-substituted tetraphenylporphyrins and several 2,4-disubstituted deuterohemindimethylesters in Me$_2$SO. k_{11} from PMR measurements.

anilinium)porphyrin) adducts have potentials [8] similar to those of M^{III}–TPPS, in line with their comparable basicities. Thus Ag^{III}–TPPS [1] and Ag^{III}–TAP [2] are stable in water, while Ag^{III}–TMPyP [E^o_{red} = +0.84 V] is unstable and rapidly forms [6] Ag^{II}–TMPyP under similar conditions. For example, we can form Ag^{III}–TMPyP by $S_2O_8{}^{2-}$ of $IrCl_6{}^{4-}$ oxidations in solution, but upon isolation, either by ion exchange chromatography to remove the negative reductants, or by precipitation by perchlorate, Ag^{II}–TMPyP is the observed product. Other workers using coulometry of $Br_2{}^-$ oxidations also noted the instability of Ag^{III}–TMPyP in aqueous solution [6].

The Ag^{III}–TPPS reductions are all presumable outer sphere in character, and the Marcus [10] relationship [$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$, ln $f = (\ln K_{12})^2/(4 \ln k_{11}k_{22}/10^{22})$] can be used to estimate the $Ag^{III/II}$–TPPS self exchange rate constant. Such self exchange values correlate a wide variety of kinetic data on classical Werner complexes [11], and have applications in the metalloprotein and metalloporphyrin fields [12]. For the reaction

$$Ag^{III}\text{–TPPS} + Fe(CN)_6{}^{2-} = Ag^{II}\text{–TPPS} + Fe(CN)_6{}^{3-} \quad (1)$$
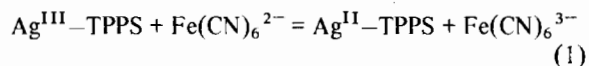
k_{12} is the Ag^{III}–TPPS/$Fe(CN)_6{}^{2-}$ cross reaction rate constant, k_{11} is the self exchange rate constant for the Ag^{III}–TPPS/Ag^{II}–TPPS reaction, k_{22} that for the $Fe(CN)_6{}^{2-/3-}$ exchange, and K_{12} the equilibrium constant [13] for the overall process. These parameters and the calculated k_{11} values for our reactions are listed in Table 1. The $Fe(CN)_6{}^{2-}$ and $Mo(CN)_8{}^{4-}$ reactions give similar k_{11}s for $Ag^{III/II}$–TPPS. The Fe-EDTA^{2-} reaction has the largest driving force, and such systems are well known [11] to deviate from the simple Marcus equation in the direction found.

Using an average k_{11} of 4×10^5 M^{-1} s^{-1}, the calculated k_{12} for the Ag^{III}–TPPS/$IrCl_6{}^{4-}$ reaction at I = 0.1 is 3×10^8 M^{-1} s^{-1}. This is within a factor of three of the observed (Na$^+$) value of 9×10^8 M^{-1} s^{-1} (k_{11} = 5.8×10^5 M^{-1} s^{-1}), where a dependence of rate upon cation type was found [3]. This silver (III/II) porphyrin self exchange rate constant, obtained from both oxidation and reduction reactions appears reasonable, and Table II is a list [14–21] of

such k_{11} values reported for other water soluble and water insoluble metalloporphyrins.

Figure 1 shows the marked dependence of the electron transfer rate constants on ionic strength for two negatively charge reactants, a result in accord with Bronsted—Bjerrum predictions. Similar rate behavior has been shown for porphyrin metal ion incorporation and acid solvolysis processes [22]. It should be noted that k_{12}s at different values of I will give different apparent self exchange rate constants k_{11}, and this should be considered when comparing metalloporphyrins of different charge types studied at various ionic strengths.

Acknowledgements

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