Inorganica Chimica Acta, 31 (1978) L421–L422
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The Kinetics and Mechanism of Oxidation of Octaethylporphinatosilver(II) by Iron(III) Perchlorate in Chloroform–Methanol Solution

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Received September 12, 1978

The synthesis and characterization of silver(II) porphyrin complexes have received some attention recently [1]. The method of synthesis for these complexes generally follows a disproportionation of silver(II) ions in the presence of porphyrin. Magnetic susceptibility measurements show that the silver(II) porphyrins are paramagnetic with one unpaired electron due to the silver(II) $4d^9$ electronic structure. Electron paramagnetic resonance studies on several silver(II) porphyrins also gave isotropic g values which are consistent with a planar structure for silver(II) porphyrin complexes. The uv–visible electronic absorption spectra of the silver(II) porphyrins are characterized by the usual two peaks at 500–600 nm and the intense Soret band below 450 nm of metallopoprhyrin complexes.

Of particular interest to us is the possibility of oxidizing octaethylporphinatosilver(II) ($Ag^{II}OEP$) to its corresponding Ag(III) complex electrolytically and chemically [2–5]. The kinetics and mechanism for the oxidation of silver(II) porphyrin have never been investigated. Using the stopped-flow method, we have investigated the kinetics and mechanism of the fast oxidation of $Ag^{II}OEP$ by Fe^{+3} in chloroform/methanol solution.

Experimental

Silver(II) octaethylporphyrin and the corresponding $Ag^{III}OEP(ClO_4)$ were prepared according to procedures described in literature [2, 3]. The Ag^{II}-OEP is normally extracted with benzene, dried and dissolved in chloroform. An appropriate volume of methanol was added to achieve the desired chloroform/methanol solvent system. Care was exercised to exclude light in the preparative process and fresh solutions were made for each kinetic run. The uv–visible spectra of the prepared solutions were routinely checked with a Cary 14 recording spectrophotometer. Eastman tetrabutylammonium perchlorate was recrystallized twice from ethanol–water solutions, vacuum dried at 60 °C and used in cyclic voltammetry experiments. All other reagents were reagent grade and all solutions were made in redistilled–deionized distilled water.

TABLE I. The Effect of Aged $Ag^{II}OEP$ Solution on Rate of Reaction.[a]

Time, hr	k_{obs}, sec^{-1}
0	2.79
1	5.10
2	8.62
3	9.27
4	11.95
5	14.2
13	13.6

[a] 25 °C, $[Ag^{II}OEP] = 1.70 \times 10^{-5}$ *M*, $[Fe^{(III)}] = 8.30 \times 10^{-4}$ *M*, in 1:1 (volume ratio) $CHCl_3/CH_3CN$ solvent system.

All the kinetic runs were conducted under pseudo-first-order conditions with at least a ten-fold excess of oxidant. A typical run consisted of rapid mixing of the freshly prepared $Ag^{II}OEP$ (use within half hour) and $Fe(ClO_4)_3$ solutions in a stopped-flow apparatus and following the reaction by monitoring the appearance of $Ag^{III}OEP^+$ at 552 nm. Plots of $\log(A - A_\infty)$ *versus* time were linear over several half-lives and the observed rate constants were obtained from the slopes of these plots. Three kinetic traces were taken for each run to obtain consistency in results.

Cyclic voltammetry measurements were conducted with a three-electrode potentiostat circuit and an MPI MP-1042 Voltammetry Controller. The working electrode was a Pt bead electrode, a Beckman SCE served as the reference electrode while the counter electrode consisted of a small Pt gauze (5 mm X 3 mm). The current *versus* potential scans were recorded with an x–y recorder.

Results and Discussion

Preliminary studies have shown that when Ag^{II}-OEP solutions were allowed to stand for a period of time in the presence of light the observed rate constants for the reactions were higher and irreproducible. To establish the effect of standing of $Ag^{II}OEP$ solution on the rate of reaction, $Ag^{II}OEP$ solutions were prepared in the dark and kinetic runs were performed allowing one hour interval for each successive kinetic measurement. The time dependent study was conducted at 25 °C under pseudo-first-order conditions in a 1:1 volume ratio of $CHCl_3/CH_3OH$ (12.4 *M* CH_3OH) solvent system. The observed rate constants for the time dependent study are listed in Table I. The rate increases up to a maximum of five folds

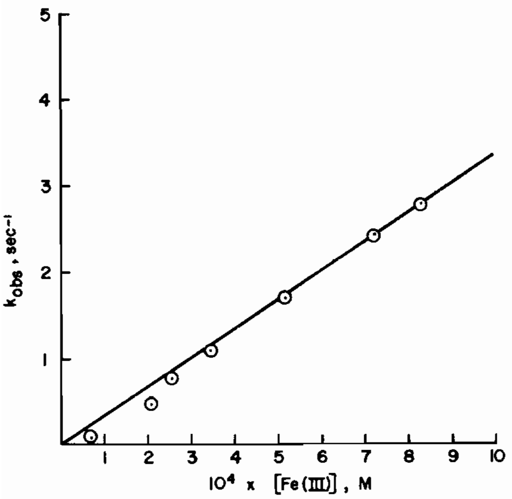

Figure 1. [Fe(III)] *versus* k_{obs}. Reaction conditions: [Ag^{II}-OEP] = 1.70 X 10^{-5} to 2.15 X 10^{-5} *M*, [Fe(III)] = 0.72 X 10^{-4} to 8.30 X 10^{-4} *M*, and in 1:1 volume ratio $CHCl_3/CH_3OH$ solution.

after a standing period of approximately five hours and appears to stay unchanged thereafter. This enhancement in rate of reaction by allowing Ag^{II} OEP to age is probably due to the formation of Ag(II) ions from the dissociation of Ag^{II}OEP. Apparently Ag(II) catalyses the oxidation of Ag^{II} OEP by Fe(III), eqs. (1) and (2):

$$Ag^{II}OEP \rightleftharpoons Ag(II) + OEP^{-2} \qquad (1)$$

$$Ag^{II}OEP + Fe(III) \xrightarrow{Ag(III)} Ag^{III}OEP^{+} + Fe(II) \qquad (2)$$

Experimental evidence supporting the role of Ag(II) has been examined. When a small amount of $HClO_4$ is introduced to Ag^{II}OEP solution, there is an initial reduction of absorbance at 552 nm but a subsequent increase in absorbance is observed. The final solution visible absorption spectrum is that of $Ag^{III}OEP^{+}$. This is consistent with the postulation that the Ag(II) produced upon the acidification would oxidize the Ag^{II}OEP to $Ag^{III}OEP^{+}$. Furthermore, a preliminary stopped-flow study shows that $Ag^{II}(bipy)_2^{2+}$ oxidizes Ag^{II}OEP very rapidly.

The rate law for the oxidation of Ag^{II}OEP by Fe(III) at 25 °C was therefore studied in the dark with Ag^{II}OEP-solution freshly prepared and used within half an hour. With [Ag^{II}OEP] varied from 1.70 X 10^{-5} *M* to 2.15 X 10^{-5} *M* and [Fe(III)] in excess and ranged from 0.72 X 10^{-4} to 8.30 X 10^{-4} *M*, a linear relationship betweeen k_{obs} and [Fe(III)], Figure 1, is obtained for the reaction in 1:1 volume ratio of $CHCl_3/CH_3OH$. The observed rate law is therefore

$$-d[Ag^{II}OEP]/dt = k_2[Ag^{II}OEP][Fe(III)] \qquad (3)$$

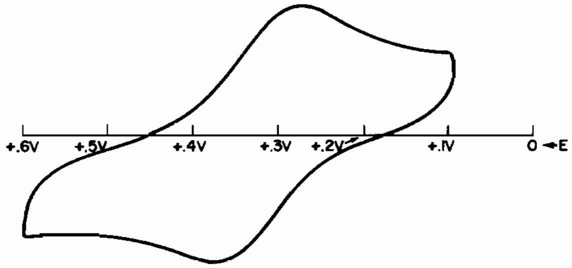

Figure 2. Cyclic Voltammogram recorded for Ag^{II}OEP in 70(v)% $CHCl_3$: 30(v)% CH_3OH solution containing 0.1 *M* TBAP. Scan rate 160 mv/sec.

where k_2 is the slope of the k_{obs} *versus* [Fe(III)] plot in Figure 1. The value of k_2 determined for the oxidation of Ag^{II}OEP by Fe(III) at 25 °C is 3.35 X 10^3 M^{-1} sec^{-1}.

Cyclic voltammetry study on Ag^{II}OEP = Ag^{III}-OEP^{+} + e in solutions of different volume ratios of $CHCl_3/CH_3OH$ (20% to 50% CH_3OH) gave a constant $E_{1/2}$ value of +0.33 v (*versus* SCE), Figure 2. However, a value of +.44 v in DMSO for $E_{1/2}$ has been reported which is +0.11 v higher than the present $CHCl_3/CH_3OH$ system [2–4]. Further CV results obtained for Ag^{II}OEP in $CHCl_3/CH_3CN$ yielded $E_{1/2}$ = +0.46 v. The change in values of $E_{1/2}$ in different solvent systems is more likely due to the dielectric nature of the solvent systems rather than a change in the structure of the square planar Ag^{II} OEP. The constancy of $E_{1/2}$ of Ag^{II}OEP in different concentration ratios of $CHCl_3/CH_3OH$ solvent system as well as the appearance of a single one electron transfer reaction confirms the absence of other chemical reactions coupled to the electron transfer. Thus, within the solvent systems investigated, the kinetics and mechanism for the oxidation of Ag^{II}-OEP by Fe(III) can be expected to be the same.

Acknowledgment

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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