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Reduction of $[(FeTPP)_2O]^+SbF_6^-$ by Iodide Ion in Dichloromethane*

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Abstract

The oxidation in dichloromethane of the iodide ion of cetyltrimethyl ammonium iodide to iodine by the compound consisting of the hexafluoroantimonate anion and the dimeric iron tetraphenylporphyrin (bridged by oxygen) cation, $[Fe(TPP)_2O]^+SbF_6^-$, has been studied spectrophotometrically using the stopped-flow method. At 273 K, $d[Fe(TPP)_2O]/dt$ is equal to $8 \times 10^4[[Fe(TPP)_2O]^+][I^-]$ mol dm^{-3} s^{-1}; from this and other measurements E_a is estimated to be 13 kJ mol^{-1}. These results will be compared with other relevant kinetic data, and a possible reaction mechanism will be considered.

Introduction

Oxidised states of ferric porphyrins are considered to be of prime importance with respect to the action of oxygenases [1], catalase [2], and peroxidases [3]. Ferric porphyrins as model compounds have been oxidised using ferric salts [4], controlled potential electrolysis [5], salts of the nitric oxide cation (NO^+) [6], air and peroxyacids and hydrogen peroxide [7a, b]. Despite contrary conclusions in the first reports, most simple ferric porphyrins oxidize initially to ferric complexes of porphyrin π cation radicals [8, 9]. Evidence from recent Mössbauer spectroscopy studies [9] would indicate that ferric μ-carbido and oxidized μ-nitrido dimers contain iron(IV), as do oxidized iron–porphyrin carbene complexes and possibly the oxidized forms of catalase and peroxidase. Oxidized haem solutions, formed *in situ* from ferrihaems and hydrogen peroxide or peroxyacids [10], have been used in a kinetic study of their ability to oxidize iodide ion. It is possible that these solutions contain oxidised deuterohaem μ-oxo-dimers with both iron atoms formally in the iron(IV) state [7]. This paper describes the kinetics of reaction of a well characterized, stable cation radical [5, 11] dimer of the familiar FeTPP family $[(FeTPP)_2O]^+SbF_6^-$, with cetyltrimethylammonium iodide, (referred to as CTA^+I^-), an iodide freely soluble in dichloromethane.

Experimental

Materials

Aldrich A.C.S. reagent grade dichloromethane was used as solvent throughout. When dichloromethane which had been refluxed over calcium hydride was employed, no difference in results could be detected.

Cetyltrimethylammonium iodide was prepared from the corresponding bromide (Aldrich) and A.R. sodium iodide. In a typical preparation 7.3 g of CTA^+Br^- in 100 ml of 50/50 acetone/water was reacted with 1.5 g of sodium iodide in 30 ml of 50/50 acetone water. A further crop of fine white crystals could be obtained by adding 3 g of sodium iodide in 30 ml of 50/50 acetone/water to the filtrate. The precipitate was dried in an oven for 2 h at 80 °C and a portion recrystallized from dichloromethane/acetone (50/50) and dried.

Peroxylauric acid (60% per acid, 40% acid) was made by Swern's procedure [12]. 5 g of lauric acid was dissolved in 15 ml of 98% H_2SO_4, and 7.5 ml of 30% H_2O_2 was added dropwise with stirring, keeping the temperature below 10 °C. A white paste formed, which was stirred with ice, and then filtered and extracted with 40/60 petroleum spirit. The extract was washed with ice–water until a dichromate containing solution no longer showed the presence of hydrogen peroxide. Evaporation of solvent after drying the solution produced flaky

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*$[(FeTPP)_2O]^+SbF_6^-$ is the formula of the hexafluoro antimonate anion, in conjunction with the cation of dimeric iron tetraphenylporphyrin bridged by oxygen; it will be abbreviated as $D^+SbF_6^-$, in places in the text. Presented at the 186th American Chemical Society National Meeting, Washington, D.C., August 1983. Abstr. Inorg. 290.

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crystals of the peracid, which was analyzed iodometrically after Mair and Graupner [13].

$[(FeTPP)_2O]^+SbF_6^-$ was made by oxidation of $FeTPP^+SbF_6^-$ [14, 7b] with peroxylauric acid.*

In a typical preparation 0.377 g of $FeTPP^+SbF_6^-$ was dissolved in 100 ml of 50/50 dry benzene/dichloromethane and 0.075 g of peroxylauric acid in 20 ml of the benzene/dichloromethane mixture added to it. The brown solution became green–black, and addition of 40/60 petroleum spirit produced a fine blue–black precipitate with yellow supernatant fluid. The product was isolated by centrifugation and washed with benzene and 40/60 petroleum spirit until the washings were colorless, and dried at 80 °C. The product had a UV–Visible spectrum identical to that published for $[(Fe(TPP)_2O]^+ClO_4^-$ [5], and its infrared spectrum showed the strong band at 1270 cm^{-1} [8b] characteristic of the oxidized porphyrin ring and bands at 650 cm^{-1} and 265 cm^{-1} characteristic of the SbF_6^- ion, and also a band at 860 (880 shoulder) cm^{-1} characteristic of the Fe–O–Fe system, as well as the usual TPP bands. Voltammetry at a rotating platinum electrode in dichloromethane, 0.01 mol dm^{-3} $(n(CH_3)(CH_2)_5)_4N^+SbF_6^-$ gave half waves at 0.75 volt(1), 1.05 volts(11) (*vs.* SCE) of equal height, and one of double height at 1.55 volts(111), as described for the $(FeTPP)_2O$ family [5, 7b]. Current/voltage curves showed the first wave to represent oxidation with the second and third (double-height) waves representing reduction, confirming the μ-oxo-dimer monocation formulation. Atomic absorption measurements using $Fe(TPP)^+$-SbF_6^- as calibration also confirmed the 1:1 iron: antimony ratio in our product.

Kinetics

Preliminary experiments showed that the iodide reduced $[(FeTPP)_2O]^+SbF_6^-$ to $(FeTPP)_2O$ in dichloromethane. (Other workers have noticed similar reductions to iron(III) porphyrins by iodide ion). Figure 1 shows the difference spectrum in Soret and visible regions between starting solution of $D^+SbF_6^-$ diluted 1:1 with dichloromethane, and the same solution diluted 1:1 with a CTA^+I^- solution containing a ten-fold excess of iodide ion. The largest optical density increase is at 410 nm, and the largest decrease around 540 nm. The first kinetic work used a Nortech 'Canterbury' all-glass stopped-flow instrument with a 2×10^{-3} m observation path, at 291 K. Using a solution, 1.25×10^{-4} mol dm^{-3} in $D^+SbF_6^-$ a rapid ($k_{obs} > 100$ s^{-1}) first order decay at 540 nm was observed. The calculated absorbance change was small. The work presented here used the Nortech SF-3L stopped flow spectrometer (Hi-Tech Instruments, Salisbury, England), with a 1×10^{-2} m observation path, and with a liquid nitrogen controlled cooling system which with balancing heaters enabled temperatures from 288 to 257 K to be maintained easily to ±0.1 K. In a typical experiment using 4×10^{-5} mol dm^{-3} $D^+SbF_6^-$ the optical density, at 540 nm, at the end of the reaction was about 0.3 absorbance units, with a net change in absorbance of 0.4 volt corresponding to 0.0362 absorbance units. With more dilute solutions of cations changes of 0.08 volt were measured during the reaction, and for these small changes Δ(volt) $\propto$ Δ(% transmission) $\propto$ Δ(ab-

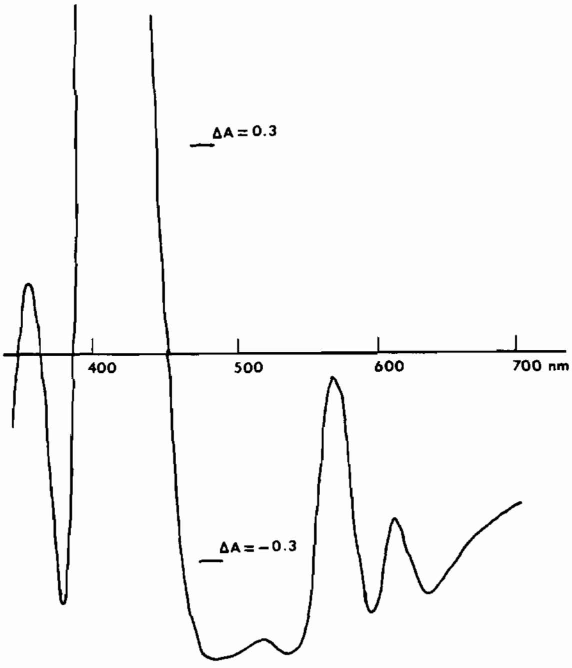

Fig. 1. Difference spectrum in the Soret and visible regions, between $D^+SbF_6^-$, and $D^+SbF_6^-$ mixed with CTA^+I^- in dichloromethane, at room temperature.

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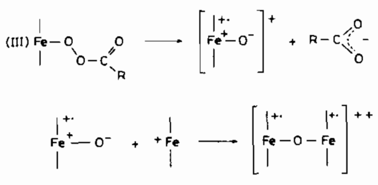
*If RCO•OOH attacks $Fe(TPP)^+$ and the O–O bond breaks heterolytically, the formally Fe(V) product can attack remaining $Fe(TPP)^+$ to produce the dication (μ-oxo-dimer less two electrons). This is the major product if all reagents are especially dry and reaction temperatures are kept around 10 °C. The mono-cation can be formed by reduction by adventitious impurities (perhaps water). An alternative could be attack on $Fe(TPP)^+$ by the intermediate formed by homolytic fission of **I**; but recent studies favor heterolytic fission [15].



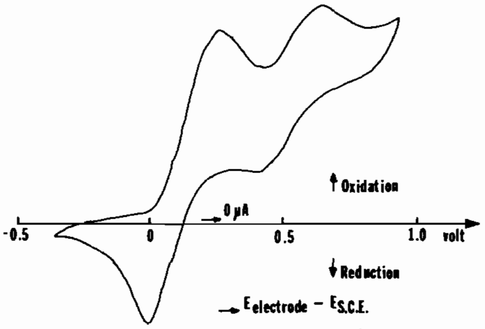


Fig. 2. Cyclic voltammogram of CTA^+I^-, $(nC_4H_9)_4N^+I^-$ and I_2, dissolved in dichloromethane.

sorbance). Data readout of Δ(volt) *versus* time was on a Tektronix oscilloscope, and data were traced directly from the screen and then hand-processed.

Voltammetry

Cyclic voltammetry at a scan rate of 2 volt min^{-1} was performed on CTA^+I^-, $(nC_4H_9)_4N^+I^-$, and on iodine, I_2, dissolved in dichloromethane wich was 0.1 mol dm^{-3} in $nC_4H_9(C_2H_5)_3N^+PF_6^-$. The last compound was made by reacting $n\text{-}C_4H_9Cl$ and $N(C_2H_5)_3$, and then isolated by double decomposition in water with $NH_4^+PF_6^-$ solution. Quasi-reversible waves with the iodide species were observed with anodic peaks at +0.25 volt and +0.65 volt with cathodic peaks at +0.425 volt and 0.075 volt *versus* SCE (*i.e.* $E_{1/2} = 0.16$ volt and 0.525 volt). Iodine itself produced two similar waves, with $E_{1/2} = 0.1$ volt and 0.5 volt. The peak to peak height (current axis) of the first wave is twice that of the second, more cathodic wave (Fig. 2). The iodide waves involve oxidation, the iodine waves reduction. This is similar to other work in nonprotic solvents and will be discussed below.

The cyclic voltammetry of CTA^+I^- was identical to that of the previously-reported NBu^+I^-, showing that the different cation, chosen for low-temperature solubility, introduced no further complications.

Results and Discussion

The voltammetric experiments on CTA^+I^- involve results very similar to those observed by others working with solvents such as acetonitrile, acetic anhydride, acetone, dimethoxyethane and nitromethane. In dichloromethane chronopotentiometry has confirmed the original proposal of Kolthoff and Coetzee [16] that the processes involved are:

$$\sim +0.16\ \text{V} \qquad 2I_3^- + 4e^- \rightleftharpoons 6I^-$$

$$\sim +0.53\ \text{V} \qquad 3I_2 + 2e^- \rightleftharpoons 2I_3^-$$

Measurements already performed in dichloromethane and confirmed with our materials, place the electrode potential of the first oxidation of $(FeTPP)_2O$ at 0.75 V, so the overall reaction in dichloromethane is:

$$2D^+SbF_6^- + 3CTA^+I^- \longrightarrow CTA^+I_3^- + 2CTA^+SbF_6^- + 2D \qquad (1)$$

On thermodynamic grounds, based on the measured $E_{1/2}$ values, a second reaction is possible once I_3^- has been generated by the first reaction.

$$2D^+SbF_6^- + 2CTA^+I_3^- \rightleftharpoons 3I_2 + 2CTA^+SbF_6^- + 2D \qquad (2)$$

As at all times in the kinetics experiments $[I^-] \gg 10[I_3^-]$, the second reaction would have to be considerably more favourable kinetically for it to be observed.

The difference in $E_{1/2}$ values measured means that ΔG° for the first reaction is -117 kJ (-58.5 kJ mol^{-1} for D^+) and for the second reaction -42 kJ (-21 kJ mol^{-1} for D^+), yielding equilibrium constants of 3.8×10^{20} and 1.7×10^3 respectively. In the first case oxidation would be complete under our conditions, and in the second it would proceed to the extent of 1% conversion at best.

Kinetics

At 258, 272.3 and 277.8 K the increase in photomultiplier voltage at 540 nm was consistent with first order kinetics, the iodide ion concentration always being at least ten times greater than that of the dimer cation. This indicates that the reaction is first order with respect to $[(FeTPP)_2O]^+SbF_6^-$. At all temperatures over the range of CTA^+I^- concentration of 10^{-4}–10^{-3} mol dm^{-3}, the observed rate constant is proportional to the iodide ion concentration, and indeed at 258 K this relationship pertains at iodide ion concentrations up to 5×10^{-3} mol dm^{-3}, though at that concentration the rate constant is subject to considerable error (Fig. 3). There is no

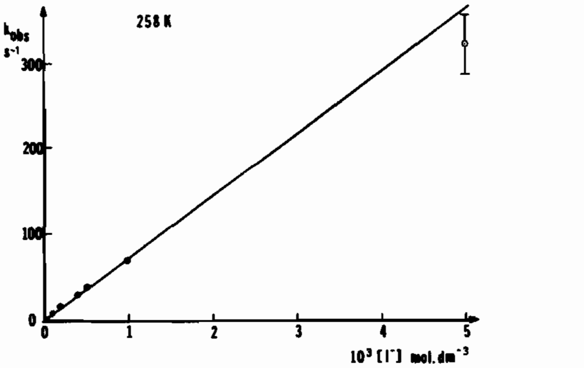


Fig. 3. Plot of first order rate constant (k_{obs}) *versus* $[CTA^+I^-]$ in dichloromethane at 258 K at constant $D^+SbF_6^-$ concentration.

TABLE I. Kinetic and Activation Parameters for Reaction of $(FeTPP)_2O^+SbF_6^-$ with CTA^+I^- in Dichloromethane

T (K)	k (mol dm^{-3})$^{-1}$ s^{-1}
258	6.87×10^4
272.3	9.20×10^4
277.8	1.04×10^5

k (298 K) = 1.46×10^5 (mol dm^{-3})$^{-1}$ s^{-1}
$\Delta H^{\neq} = 10.5$ kJ mol^{-1}
$\Delta S^{\neq} = -110$ J mol deg^{-1} (298 K)
$E_a = 13.0$ kJ mol^{-1}

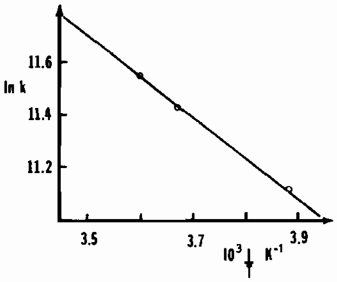


Fig. 4. Arrhenius plot: ln k (where k is the second order rate constant) *versus* reciprocal temperature (K) for reaction of $D^+SbF_6^-$ with CTA^+I^- in dichloromethane.

real evidence of a square term (second order) in iodide ion though extensive measurements might reveal a small contribution to the rate law. Thus the rate law is written as

$$\frac{d}{dt}[\text{dimer}] = k[CTA^+I^-][D^+SbF_6^-]$$

Table I shows the second order rate constants and the activation parameters obtained from them (Fig. 4).

Mechanism

In general outer-sphere reductions of metal complexes by solutions of aqueous iodide solution depend either on the first power of the iodide concentration or a combination of first and second powers. The first order term arises from electron transfer involving $I^- \rightarrow I^\bullet$, with the measured rate constant relating to $K_{IP}k_{et}$ (symbols defined below), and the degree of precursor ion-pair formation increasing linearly with $[I^-]$; K_{IP} being 10–100, ion-pair formation is not at saturation level*. The square term in iodide ion involves attack on the ion-pair (whose degree of formation depends on the iodide ion concentration) by a second iodide ion, and the electron transfer involves $I_2^{\dot{-}} \rightarrow I_2$, a thermodynamically easier process than $I^- \rightarrow I^\bullet$.

First term:

$$D^+ + I^- \overset{K_{IP}}{\rightleftharpoons} (D^+I^-)$$

$$(D^+I^-) \xrightarrow{k_{et}} (DI^\bullet)$$

$$(DI^\bullet) \xrightarrow{k_{dis}} (D + I^\bullet)$$

Second term:

$$(D^+I^-) + I^- \xrightarrow{k_{et(2)}} D + I_2^{\dot{-}}$$

Obviously the situation will be different when the solvent is dichloromethane, which has a dielectric constant of 9 at 298 K. Here the concentrations of iodide are such that substantial proportions of D^+I^- could be expected in solution, and indeed a value of $K_{IP} = 10^5$ would mean 90% of D^+ was present as the ion-pair. With virtual ion-pair saturation present the first power term in iodide ion could be due to attack of iodide ion on D^+I^-, virtually all D^+ being in that form

$$D^+ + I^- \overset{K_{IP}}{\rightleftharpoons} (D^+I^-)$$

$$(D^+I^-) + I^- \overset{K_{as}}{\rightleftharpoons} (D^+I^- \cdot I^-)$$

$$(D^+I^- \cdot I^-) \underset{k_{et}}{\overset{k_{et}}{\rightleftharpoons}} (D \cdot I_2^{\dot{-}})$$

$$(D \cdot I_2^{\dot{-}}) \xrightarrow{k_{dis}} D + I_2^{\dot{-}}$$

The third reaction is regarded as rate determining. If the equilibrium constant for the formation of the ion-pair K_{IP}, is $\geqslant 10^5$, the $[D^+] \rightarrow 0$ and $[D^+I^-] \rightarrow [D^+SbF_6^-]_{\text{initial}}$. The observed rate constant will then be a product of an association constant K_{as}, for association of the ion-pair with I^-, and k_{et} a rate constant for electron transfer, or if k_{dis} is slow, then $k_{obs} = K_{as}K_{et}k_{dis}$. As K_{as} is an ion-triplet formation constant, in a low dielectric constant solvent this would be expected to be low and thus saturation kinetics would not be expected to be observed, as is indeed the case.

The question as to whether the reaction is inner or outer sphere is interesting. Despite attempts to make it do so, $(FeTTP)_2O$ does not bind axial bases, neither does $(FeTPP)_2N$, in the same formal oxidation state as $((FeTPP)_2O)^+$. But there is evidence that $((FeTPP)_2N)^+$ can bind axial bases [5, 19]+.

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*An alternative view has been expressed recently by Wilmarth *et al.* [17] with $k_{obs} = K_{IP}K_{et}k_{dis}$; ($k_{dis}$ = rate constant for dissociation of successor complex. K_{et} = equilibrium constant for electron transfer, $(D^+I^- \cdot I^-)/(D \cdot I_2^{\dot{-}})$; k_{-1dis} is neglected).

+There is a weak binding of bases to (FeTPP)N at liquid nitrogen temperatures [18].

TABLE II. Free Energy Values[a]

	Reaction	$E°$ (V)	Reference	$\Delta G°$ (kJ mol^{-1})
I	$I^{\bullet} + e^- \rightarrow I^-$	~1.3	b	
	$D^+ + e^- \rightarrow D$	~1.0	c	
	$D^+ + I^- \rightarrow D + I^{\bullet}$			+28.8
II	$I_2^- + e^- \rightarrow 2I^-$	1.0	d	
	$D^+ + 2I^- \rightarrow D + I_2^{\dot{-}}$			+3.85
III	$I_2 + e^- \rightarrow I_2^{\dot{-}}$	0.16	e	
	$D^+ + I_2^- \rightarrow D + I_2$			−80.7

[a]Speculative free energy quantities for the three reactions based on the assumed values shown, as indicated in the text. [b]Ref. 13. [c]This work corrected for difference between SCE and NHE. [d]Ref. 22. [e]See p. 2237, ref. 23.

Goff wished to discover if ((FeTPP)$_2$O)$^{+\text{ or }2+}$ species bound axial bases, but found that the bases reduced the cations to μ-oxo dimer [20]. It would appear that the mechanism just discussed involves electron transfer from oxidized porphyrin to I^- via prior-bound I^-, and so is a type of inner-sphere electron transfer. It is I_2^- which leaves the successor complex, and so one does not know if the first-bound I^- was attached to Fe or to the porphyrin periphery. The only requirement of the kinetics is that binding of this first I^- must be complete, but precursor complex formation must not be so in the concentration range studied. The activation entropy in this low-dielectric solvent is negative enough to confirm that the transition state is at least bi-molecular.

The fate of the $I_2^{\dot{-}}$ generated as a result of I^- oxidation is worth some discussion. Two fates are envisaged for $I_2^{\dot{-}}$ in water:

(i) $2I_2^{\dot{-}} \longrightarrow I_3^- + I^-$

(ii) $I_2^{\dot{-}} + OX \longrightarrow Red + I_2$

In water reaction (i) proceeds rapidly ($k \sim 10^8$ s^{-1}), and Wilmarth calculates that for this system, the reaction in (ii) is even more rapid. A low dielectric constant solvent might well slow step (i) via mutual repulsion of similarly charged ions, whereas reaction (ii), between oppositely charged ions would be enhanced. If the potentials measured and estimated in water are assumed to hold in dichloromethane (which undoubtedly they do not) and are combined with E_0 for $D^+ + e^- \rightarrow D$, then Table II results. This shows the formation of $I_2^{\dot{-}}$ is probably much more favored than production of $I^{\bullet}$, and that the oxidation of $I_2^{\dot{-}}$ is a very favorable process indeed.

Unfortunately in dichloromethane $I_2^{\dot{-}}/I_2$ exchange rates and potentials for $I^{\bullet}/I^-$, I_2^-/I_2 half reactions are not available and so further speculation using Marcus theory is bound to be unfruitful. It should be mentioned though, that assuming there is an identity of potentials and electron exchange rate [21] in water and dichloromethane then the conclusion is that the D^+/D self exchange rate is 10^6 s^{-1}, which is fast on the NMR time scale, as found by Goff [8b].

Thus, in summary, this paper reports the first kinetic study of oxidised metalloporphyrin reduction, which is, under the conditions that could be used, a rapid second order reaction, requiring the cryostat mode of a stopped-flow spectrophotometer. The activated complex in the rate limiting step is most likely bimolecular, (suggested by the large negative value of the entropy of activation), but a complete mechanism description is not yet possible. Further studies, in progress, may allow greater certainty to accompany discussion of mechanism.

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