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The oxidation of bromide ion by $[(FeTPP)_2O]^+SbF_6^-$ in dichloromethane ‡

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The oxidation of cetyltrimethylammonium bromide (CTAB) by mono-oxidised iron(III) tetraphenylporphyrin μ-oxo-dimer, $[(FeTPP)_2O]^+SbF_6^-$, has been found to be much slower than the corresponding oxidation of iodide ion, but can still be studied by stopped-flow techniques. The stoichiometry of the reaction has been established as $2\,[Fe(TPP)_2O]^+ + 3Br^- \longrightarrow 2(FeTPP)_2O + Br_3^-$. The rate law for the reaction is $d\,[(FeTPP)_2O]/dt = [Fe(TPP)_2O^+]\cdot(k_f\,[CTAB] - k_r)$. The rate constant for the first term has been identified with the rate determining forward process, the formation of the unstable Br_2^-, and the second term with the attack of Br_2^- on the uncharged μ-oxo-dimer. A subsequent process involves what appears to be the rapid oxidation of Br_2^- in the presence of Br^- to give Br_3^-. At 298 K k_f is 737(±30) $M^{-1}\,s^{-1}$ and k_r is 0.80(±0.16) s^{-1}. For k_f, $\Delta H^‡ = 58.8(\pm1.6)$ kJ mol^{-1}, $\Delta S^‡ = 8.62(\pm0.45)$ J K^{-1} mol^{-1}; for k_r, $\Delta H^‡ = 43.6(\pm10.8)$ kJ mol^{-1}, $\Delta S^‡ = -97.8(\pm36.0)$ J K^{-1} mol^{-1}. The addition of cetyltrimethylammonium perchlorate (inert to reaction with the oxidised μ-oxo-dimer) slowed the reaction in a manner which indicated competition between perchlorate and bromide for the formation of ion pairs with the oxidised iron(III) dimer, the bromide ion pair being the reactive one.

Introduction

Models for and studies on oxidative enzymes which contain iron and porphyrin combined together in the prosthetic group have been legion since the pioneering studies of George[2] assigning formal oxidation states to compounds I and II, intermediates formed from the reaction of horseradish peroxidase (HRP) with hydrogen peroxide. The prosthetic group of HRP compound I has since been identified and modelled as a ferryl unit, $O{=}Fe^{IV}$, co-ordinated to a protoporphyrin IX cation radical,[3] and compound II as a ferryl unit co-ordinated to protoporphyrin IX (3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropanoic acid). Model compounds have been made and studied involving porphyrins and ferryl units,[4] porphyrins and iron(IV)[5] and porphyrin radical cations with iron(III)[6] to name but a few. The study of oxidised transition metal porphyrins both structurally and as catalysts is still expanding.[7]

Owing to our experience in the preparation of one class of oxidised porphyrin complex[8,9] we decided to commence a kinetic comparison of oxidised model compounds with this class. In a previous paper[1] we described the kinetics of reduction of iodide (cetyltrimethylammonium iodide, CTAI; cetyl = hexadecyl) by the singly oxidised form of iron(III) tetraphenylporphyrin μ-oxo-dimer, $[FeTPP–O–FeTPP]^+$ SbF_6^- (designated as D^+) which appeared stable in the solid state and reasonably long-lived in dry dichloromethane solution. Formally D^+ contains iron in both oxidation states III and IV, but further work[6b] has inclined investigators to the belief that the compound has two iron(III) centres, one of which is co-ordinated to a porphyrin radical cation. For the singly oxidised dimer the Mössbauer ^{57}Fe chemical shift, δ, is 0.295 mm s^{-1} at 300 K and the isotopic splitting, ΔE_Q, is 0.447 mm s^{-1},[6a] very close to iron(III) typical values rather than the values for Fe^{IV} (where δ typically is equal to zero[4c]). However, the ESR spectrum shows but one narrow peak at $g = 2$ with no fine structure, and no peak at $g = 6$ (characteristic of high spin iron(III) in a porphyrin environment); the overall magnetic moment for the singly oxidised dimer is $3.2 \pm 0.2\ \mu_B$ at 270 K,[6b] corresponding to two unpaired electrons on a spin-only basis. From this it has been inferred that, as in uncharged D, there is considerable antiferromagnetic coupling between the two iron centres; NMR results indicate that electron transfer between the porphyrin round one iron centre within the molecule and the radical cation round the other is extremely rapid.[6b] Coupling between unpaired spin on the Fe–O–Fe skeleton and on porphyrin is harder to assess. We shall refer to D^+ without specifying where the positive charge lies.

In our previous investigation[1] the simple rate law (1) applied.

$$d\,[(FeTPP)_2O]/dt = k[Fe(TPP)_2O^+][CTAI] \qquad (1)$$

We argued that in dichloromethane and with iodide present in excess, $[Fe(TPP)_2O]^+$ (D^+) was likely to be present almost exclusively as the ion pair, D^+I^-, ion pair saturation being the prevailing circumstance. Attack on this ion pair of free iodide was postulated as the rate-determining step, the precursor complex being $D^+I^-{\cdot}I^-$ and the successor complex $D{\cdot}I_2^-$ with electron transfer being inner sphere. The radical ion I_2^- could form I_3^- either by rapid disproportionation or by further attack of oxidised dimer ion pair on it, eqn. (2).

$$D^+I^- + I_2^- \longrightarrow D + I_3^- \qquad (2)$$

In this paper we describe the oxidation of bromide ion also in dichloromethane, by the same oxidised iron(III) porphyrin dimer, in the presence of the same cetyltrimethylammonium counter ion. The reaction is considerably slower than the oxidation of iodide, and we have been able to confirm both the

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‡ Oxidations by $[(FeTPP)_2O]^+SbF_6^-$. Part II.[1]

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stoichiometry and that ion pairing between bromide and positively charged dimer prior to reaction is crucial.

Experimental

Materials

BDH "Analar" dichloromethane was used after being refluxed for thirty minutes over calcium hydride and distilled into a predried flask. Cetyltrimethylammonium bromide (CTAB or QBr) from Aldrich was recrystallised from dry dichloromethane and stored *in vacuo* over phosphorus pentoxide. The perchlorate ($QClO_4$) was made by adding a saturated solution of sodium perchlorate in 2 : 1 ethanol–water to a similarly saturated solution of QBr in the same solvent. The white precipitate was collected, recrystallised from dichloromethane–acetone (1 : 1) solution and then dried and stored over phosphorus pentoxide at room temperature. **CAUTION:** no tendency to explode was noted, though perchlorate salts should always be handled with extreme caution. The tribromide (QBr_3) was prepared by taking 3.19 g (0.020 mol) of bromine in a sample bottle, dissolving it in the minimum amount of dry dichloromethane, adding 7.28 g (0.020 mol) of CTAB dissolved in the minimum of dry dichloromethane, and then shaking. The orange-yellow product was precipitated by adding dry pentane, collected, washed with pentane, and dried under vacuum.

The preparation of peroxolauric acid ($CH_3(CH_2)_{10}CO_3H$) and the hexafluoroantimonate of iron(III) tetraphenylporphyrin[10] have been described, as has the production of the oxidised μ-oxo-dimer $[(FeTPP)_2O]^+SbF_6^-$ from these reactants.[1,8,9] Experience showed that it was best to prepare $[(FeTPP)_2O]^+SbF_6^-$ freshly prior to use employing the following slightly modified procedure. In a typical preparation 0.020 g (3.5×10^{-5} mol) of 59% peroxouric acid, dissolved in the minimum amount of dry benzene, was added to 0.0912 g (1.0×10^{-4} mol) of $FeTPP^+SbF_6^-$ dissolved in the minimum amount of dried dichloromethane. The solution changed from brown to green-black. The addition of light petroleum (bp 40–60 °C) produced a fine blue-black precipitate with a yellow supernatant fluid. The product was isolated by centrifugation (4500 r.p.m. for approximately 15 minutes) and washed with benzene and light petroleum until the washings were colourless. The product was dried at 353 K for several hours: the UV-visible spectrum in dry dichloromethane was identical to that published for the monocation, $[(FeTPP)_2O]^+SbF_6^-$, by Baldwin and co-workers[8] and to that for $[(FeTPP)_2O]^+ClO_4^-$.[10] The infrared spectrum showed a strong band at 1275 cm^{-1}, a characteristic of the oxidised porphyrin ring[10] and bands at 650 and 280 cm^{-1}, characteristic of the SbF_6^- ion (seen previously in the $FeTPP^+SbF_6^-$ spectrum). As well as the usual bands due to the tetraphenylporphyrin unit there was a band at 865 cm^{-1} characteristic of the Fe–O–Fe system. The field desorption mass spectrum displayed a parent peak at m/z 1587 ($[DSbF_6]^+$) and one for D^+ at $m/z = 1352$. In these ways the product was identified as $[(FeTPP)_2O]^+SbF_6^-$.

All apparatus was cleaned and dried in an oven at 373 K before use.

Stoichiometry experiments

Making up the dilute solutions employed here involved the use of an "Oertling" microbalance and small aluminium foil weighing boats. The mass of a boat was determined and the appropriate mass of reactant added. The reactant was then added to the appropriate volumetric flask and the boat and residual reactant weighed again.

Spectra were obtained using a Hewlett Packard 8451A diode-array spectrophotometer. In a typical run a reference spectrum of the solvent, dry dichloromethane, between 340 and 760 nm was recorded as a baseline, prior to measuring the spectra of the reaction mixtures. Then a known concentration (*e.g.* 1.06×10^{-4} M) of $[(FeTPP)_2O]^+SbF_6^-$ solution was diluted 1 : 1 with dry dichloromethane in the sample cell, the spectrum was recorded (the concentration of $[(FeTPP)_2O]^+SbF_6^-$ was effectively 5.03×10^{-5} M and the spectrum could be compared directly with the spectra of each of the reaction sample mixtures). The spectra of a series of CTAB solutions (*e.g.* 1.50×10^{-5} to 4.77×10^{-4} M) were recorded in which equal volumes of 1.06×10^{-4} M $[(FeTPP)_2O]^+SbF_6^-$ and bromide solutions of known concentration were mixed. The wavelength chosen to monitor the reaction was 610 nm, at which substantial optical density changes were observed with consistency (Fig. 1).

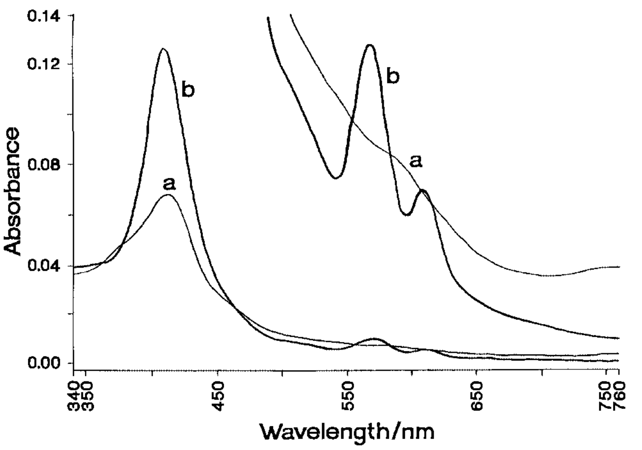

Fig. 1 Spectra of a $[(FeTPP)_2O]^+SbF_6^-$ in dichloromethane at 298 K, b "a" after reaction with excess of QBr. Main spectrum: absorbance from 0 to 1.4. Insert spectrum: absorbance from 0 to 0.14.

Kinetic experiments

Reaction kinetics was studied by the stopped-flow method and utilised a Hi Tech SF-3L unit suspended over a Gallenkamp refrigerated thermostat bath filled with 70 : 30 water–crude methanol: storage coils and the mixing/observation chamber were completely immersed in the bath. The bath capacity was ten litres and its insulation enabled it to retain a virtually constant temperature for the ten minute period of a series of stopped-flow runs using a particular concentration set. (This reduces all noise due to refrigeration or heating thermostat action.) A Bausch and Lomb grating monochromator with a tungsten–halogen lamp was used in conjunction with a Farnell stabilised power supply, and detection was *via* an IP28A photomultiplier and a Brookdeal or Farnell high-voltage power supply. The voltage developed to earth across a chosen high impedance was monitored as described in a recent paper;[11] the voltage/time curve was converted into an absorbance/time curve and analysed for first-order build up or decay using a BBC computer, as also described in that paper. The wavelength chosen was 410 nm.

Results and discussion

i Stoichiometry

The stoichiometry of the reaction between $[(FeTPP)_2O]^+SbF_6^-$ and CTAB was determined spectrophotometrically by the method of continuous varations.[12] The principle of the procedure is that when a solution of known concentration in $[(FeTPP)_2O]^+SbF_6^-$ is treated with a series of solutions of CTAB of equal volume containing bromide at a series of known and increasing concentrations the concentration of $[(FeTPP)_2O]^+SbF_6^-$ remaining in the reaction mixture will decrease and the proportion of μ-oxo-dimer product will increase. The concentration of the product, initially zero, will not continue to increase indefinitely as the bromide concentra-

Table 1 Absorbance data for the determination of the overall stoichiometry of the reaction of $[(FeTPP)_2O]^+SbF_6^-$ with cetyltrimethylammonium bromide, in dichloromethane at 25 °C

	Absorbance		
10^5[QBr]/M	460	570	610 nm
0	2.02	0.802	0.658
0.74	1.91	0.762	0.626
1.49	1.83	0.732	0.600
2.98	1.62	0.637	0.521
5.96	1.50	0.569	0.405
11.9	1.60	0.646	0.349
23.9	1.62	0.662	0.354

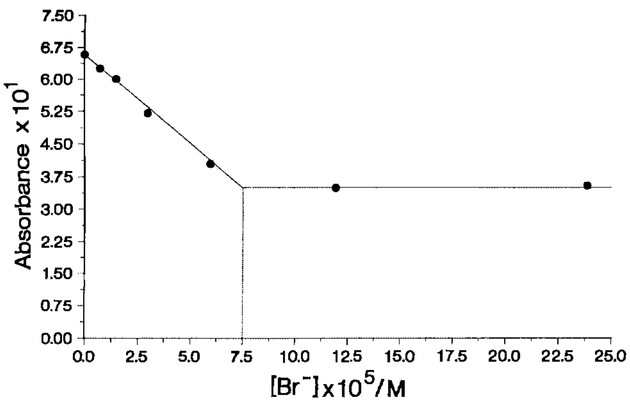

Fig. 2 Plot of absorbance at 610 nm *vs.* [Br$^-$] for the spectrophotometric titration of QBr (CTAB) and $[(FeTPP)_2O]^+SbF_6^-$ in dichloromethane at 298 K.

tion is increased because at a specific bromide ion concentration the reduction of $[(FeTPP)_2O]^+SbF_6^-$ to the μ-oxo-dimer will be complete, *i.e.* the concentration of $[(FeTPP)_2O]^+SbF_6^-$ will be zero and that of the μ-oxo-dimer will be equal to the initial concentration of $[(FeTPP)_2O]^+SbF_6^-$. If this concentration of bromide ion is exceeded there will be no additional increase in the concentration of the μ-oxo-dimer. The stoichiometry of the reaction will be discovered from the relationship between the CTAB concentration which represents the complete conversion of the reactants into products, and the initial concentration of $[(FeTPP)_2O]^+SbF_6^-$. In practical terms the bromide concentration at which the optical density change arrived at a limiting value was used to determine the reaction stoichiometry.

In a typical series of experiments (the results are listed in Table 1) the absorbance values of $[(FeTPP)_2O]^+SbF_6^-$ in the presence of CTAB decreased at 610 nm with increasing bromide ion concentration until a limiting absorbance value of 0.35 was reached, as illustrated in Fig. 2. The measured absorbance values of the reaction samples *vs.* the bromide concentration (Fig. 2) were extrapolated to determine the concentration of the bromide ion (7.5×10^{-5} M) at which the limiting absorbance was achieved. The ratio of $[(FeTPP)_2O]^+SbF_6^-$ to Br$^-$ was found to be 5.03×10^{-5} M : 7.5×10^{-5} M which simplifies to 1 : 1.5. Eqn. (3) is consistent with this ratio. It

$$2[Fe(TPP)_2O]^+ + 3Br^- \longrightarrow 2(FeTPP)_2O + Br_3^- \quad (3)$$

should be noted that this is of the same form as that proposed in our previous paper,[1] but there without confirmation.

ii Kinetics and mechanism

Preliminary experiments showed that in the presence of an excess of bromide the visible product was the μ-oxo-dimer, displaying characteristic absorbance maxima at 410, 570 and 610 nm. The wavelength 410 nm was chosen for monitoring the progress of reduction of D$^+$; a substantial increase in absorbance occurs here. Kinetic studies were performed at 273, 289, 298 and 303 K; at each temperature a series of CTAB concentrations from 10^{-4} to 10^{-2} M were employed, the initial concentration of D$^+$ being around 10^{-5} M for each run. Under these conditions of excess of bromide the change in optical density at 410 nm followed a first-order course, from which eqn. (4) can be deduced. At all temperatures the observed rate

$$d[D]/dt = k_{obs}\,[D^+] \quad (4)$$

constant was proportional to the sum of a constant term and a term proportional to the concentration of added CTAB, with no evidence of a second-order term in bromide concentration (Fig. 3). Thus eqn. (5) is obtained.[13] We have chosen to identify

$$k_{obs} = k[CTAB] + k' \quad (5)$$

the slope of the plot of k_{obs} *vs.* [CTAB] as the forward rate constant k, at 298 K equal to 738(±30) M^{-1} s^{-1}, and the constant k' as that for the reverse electron transfer, $D{\cdot}Br_2^- \longrightarrow D^+Br^-{\cdot}Br^-$. At 298 K this is equal to 0.8(±0.2) s^{-1}. An alternative identification of the k' term with a reduction process not dependent on bromide concentration is deemed unlikely, as D$^+$ is stable in pure dry dichloromethane, and also in the presence of a salt such as $Q^+ClO_4^-$. So $k = k_f$ and $k' = k_r$. The results are summarised in Tables 2 and 3.

Table 2 Rate constants at four temperatures and activation parameters for the reduction of $[(FeTPP)_2O]^+SbF_6^-$ by CTAB in dichloromethane

T/K	k_f/M^{-1} s^{-1}	Activation parameters, 298 K
273	92(±16)	E_a = 61.3(±3.2) kJ mol^{-1}
289	389(±16)	$A = 4.8(\pm0.2) \times 10^{13}$
298	737(±30)	$\Delta S^‡$ = 8.62(±0.45) J K^{-1} mol^{-1}
303	1400(±78)	$\Delta H^‡$ = 58.8(±1.6) kJ mol^{-1}
		$\Delta G^‡$ = 53.9(±2.2) kJ mol^{-1}

Table 3 Rate constants and activation parameters for the reverse of the reduction of $[(FeTPP)_2O]^+SbF_6^-$ by CTAB in dichloromethane

T/K	k_r/s^{-1}	Activation parameters, 298 K
273	0.23(±0.10)	E_a = 45.9(±10.7) kJ mol^{-1}
289	0.51(±0.09)	$A = 1.3(\pm0.3) \times 10^8$
298	0.80(±0.16)	$\Delta S^‡$ = −98(±36) J K^{-1} mol^{-1}
303	2.08(±0.20)	$\Delta H^‡$ = 43.6(±10.8) kJ mol^{-1}
		$\Delta G^‡$ = 70.2(±7.0) kJ mol^{-1}

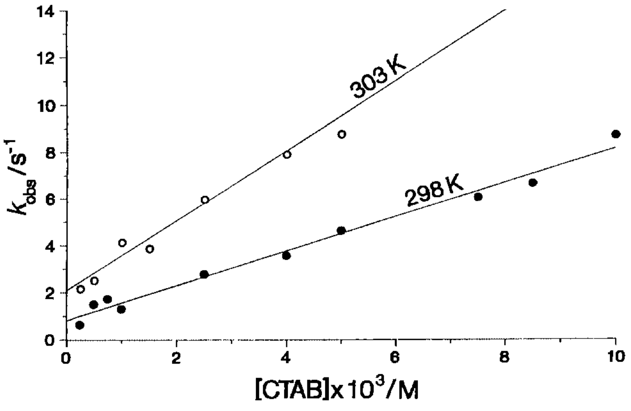

Fig. 3 Rate profiles for the reaction of CTAB with $[(FeTPP)_2O]^+SbF_6^-$ in dichloromethane.

Several approaches were tried to track down the most likely mechanism for the reaction. They are summarised in turn

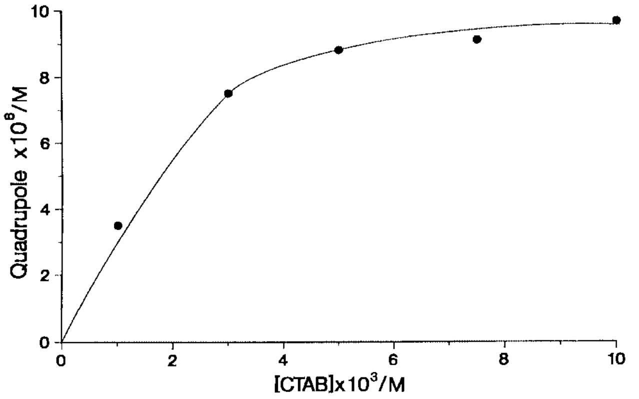

Fig. 4 Plot of the concentration of added CTAB *vs.* the calculated concentration of the quadrupole $\{[(FeTPP)_2O]^+Br^-,Q^+Br^-\}$.

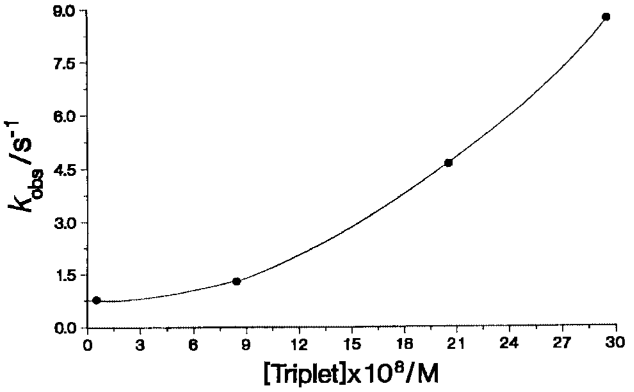

Fig. 5 Plot of the observed rate constant for the reaction of $[(FeTPP)_2O]^+SbF_6^-$ with CTAB *vs.* ion-triplet concentration for $[Br^-]$ up to 0.010 M.

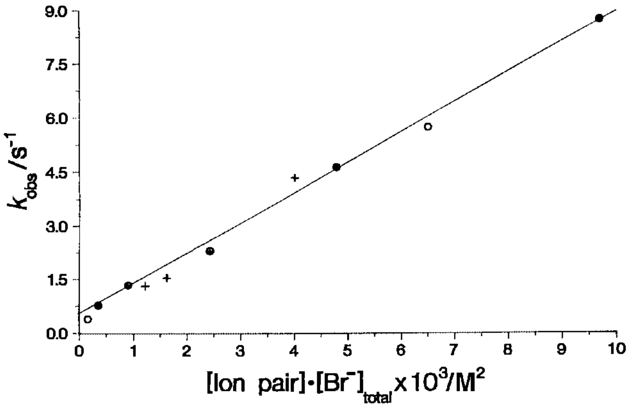

Fig. 6 Plot of k_{obs}, at 298 K, *vs.* the product of the ion pair concentration and the total bromide concentration $\{[Br^-]_{total}[(FeTPP)_2O^+\cdot Br^-]\}$: (●) in the absence of perchlorate, (○) in the presence of 0.0050 M perchlorate and (+) in the presence of varying perchlorate concentration and a constant bromide concentration of 0.0050 M.

below, the first sentence being the key assumption of each paragraph.

(i) Electron transfer is preceded by prior formation of a quadrupole $\{D^+Br^-,Q^+Br^-\}$, and the rate of reaction is that of rate determining electron transfer within the quadrupole to give D and the transient $Q^+Br_2^-$. As a first step the calculation of the ion-pair concentration for Q^+Br^- was performed using a value of K_{IP} of 10^5 M^{-1} (from Beard and Plesch[14]) for tetramethylammonium perchlorate in dichloromethane, relative permittivity $\varepsilon = 9$. Then the concentration of free bromide ion was calculated, and from this one was able to calculate the initial concentration of the ion pair, D^+Br^-. This concentration was then combined with the concentration of free bromide and the ion-triplet constant,[15] 10^2 M^{-2}, to give the concentration of the triplet $[\{Br^-D^+Br^-\}]$. This triplet concentration was combined with the concentration of free Q^+, using $K = 10^5$ M^{-1} to give the quadrupole concentration, treating the triplet as if it were just another negative ion. The quadrupole concentration was seen to saturate at total added bromide concentrations above 10^{-3} M, which does not reflect the observed rate behaviour (Fig. 4).

(ii) Rapid reversible formation of ion triplets, $\{Br^-D^+Br^-\}$, is the essential step before rate determining electron transfer to give D and the transitory species Br_2^-. This approach seemed promising, but a plot of rate constant *vs.* triplet concentration was not of the observed form, so it too was rejected (Fig. 5).

(iii) The rate determining step is attack of bromide in whatever form on the ion pair D^+Br^- to give D and the transient Br_2^-. When the ion-pair concentrations were calculated nearly all of the oxidised iron(III) dimer species was seen to be present as the ion pair. The assumptions used here give rise to agreement with the observed behaviour (Fig. 6, calculations as outlined later). It will be seen later that they also account for the observed kinetics in the presence of the inert electrolyte $Q^+ClO_4^-$. It should be noted that (iii) is in agreement with the stoichiometric findings: the reaction sequence is proposed to be as in Scheme 1.

a $$D^+ + Br^- \underset{\text{(very fast)}}{\overset{K_{IP}}{\rightleftharpoons}} \{D^+Br^-\}$$

b $$\{D^+Br^-\} + Br_T^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$(\{D^+Br\cdot{}^-Br^-\} \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} \{D\cdot Br_2^-\}) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D + Br_2^-$$

(Br_T^- is the sum of the free and ion-paired bromide ion)

c $$2Br_2^- \rightleftharpoons Br^- + Br_3^-$$

(very fast and equilibrium far to the right)

Scheme 1

It is postulated that the rate-determining steps here concern electron transfer. Step a involves the formation of an ion pair. To calculate this one needs to calculate the amount of free bromide provided by CTAB and then how much D^+ has been converted into $\{D^+Br^-\}$. These calculations indicate that though some 80% of the CTAB is present as ion pairs at the lowest concentration, 2.5×10^{-4} M CTAB, 80% of D^+ is present as ion pairs, and when [CTAB] is 1×10^{-2} M, 97% of D^+ is present as ion pairs. (The concentration of D^+ is assumed to be 1×10^{-5} M.) So these calculations say that $\{D^+Br^-\}$ formation can be considered complete before the reaction starts.

Step b concerns the formation of a precursor complex, $\{D^+Br\cdot{}^-Br^-\}$, its transition to the successor complex $\{D\cdot Br_2^-\}$ and the fission of this to D and Br_2^-. As far as the forward reaction is concerned we shall assume that the precursor complex is a transient intermediate and that the rate determining step is electron transfer described by k_{et}. The rationale for this is that, as described later, the differences in the heats of activation for bromide and iodide reduction are mirrored by the differences in electron affinities of Br_2 and I_2. It can be shown that if $k_{-1} \gg k_{et}$, $k_f = k_{et}k_1/k_{-1}$; if one says that the precursor complex is ion triplet-like, then as k_1/k_{-1} is like the association constant for ion triplet formation from an ion pair and a free ion and as this is approximately 1×10^2 M^{-1} one can calculate the probable value of k_{et} as around 7.37 ± 0.30 s^{-1} at 298 K.

With respect to the reverse reaction the arguments that transfer involves the production of transient Br_2^-, a radical anion, rather than the bromine atom, are very close to those already advanced in our first paper. Thus, in water Malone and Endicott[16] calculated that the reduction potential of $Br^{\bullet -}$–Br^- was 2.2 V and of Br_2^-–Br^- 1.9 V; Woodruff and Margerum[17] came to a similar conclusion, but reported a slightly larger difference in potentials. If the same holds true in dichloromethane one would expect the production of the radical anion to be favoured; a simple way of looking at it is to say that part of the energy needed to take an electron from the bromide ion is compensated for by the formation of a weak bond with another bromide to give Br_2^-. It is notable that Br_2^- is a stronger oxidising agent than I_2^-; the I_2^-–I^- potential has been given as around 1.0 V,[25] insufficient to be able to observe a back reaction, and indeed none was noted by us. It should also be noted that we have made attempts with bromine in dichloromethane and with $Q^+Br_3^-$ in dichloromethane to generate the oxidised dimer from the μ-oxo-dimer. Both attempts failed, in each case the product having the spectrum of FeTPP·Br. So it is reasonable to suppose that the simple back reaction can only be brought about by a species more oxidising than Br_2 or Br_3^-. This species is most probably the bromine molecule radical anion.[18] As well as being able to oxidise the μ-oxo-dimer, two of these radical anions can react extremely rapidly[19] to give Br^- and Br_3^-. In aqueous solution this has been reported to occur at near the collision frequency limit.[19] Even taking into account that repulsion between similarly charged ions will be greater in the low relative permittivity solvent dichloromethane, a rate constant of at least 10^6 M^{-1} s^{-1} still looks plausible.§

It should also be noted that this mechanism has close similarities to that proposed by Fudge and Sykes[20] for the reaction of iron(III) ions with iodide in aqueous solution, and by Nord *et al.*[21] in reactions where iodide or thiocyanate is oxidised by a series of metal(III) complexes. Dihalogen radical anions have featured as suggested intermediates in one electron reductions by halides in many cases, especially since their discovery as reactive transient species in Grossweiner's flash photolysis experiments.[18]

Referring to Scheme 1 once more, by analogy with the forward reaction the successor complex should lie in a shallow energy minimum, making it likely that $k_2 \gg k_{-et}$ and so giving $k_r = k_{-et}k_{-2}/k_2$. As the constant for association between D and Br_2^- is likely to be lower than an ion-triplet formation constant, k_r should be much closer to k_{-et} than k_f is to k_{et}.

There are interesting differences between the activation parameters here and in our previous paper. The forward rate constant at 298 K is over one hundred times less than with iodide as reducing agent, and the enthalpy of activation is five times greater. The actual difference in heats of activation is some 48 kJ mol^{-1}; a large part of that can be ascribed to the difference in electron affinities of Br_2 and I_2, some 34 kJ mol^{-1}.[22] Iodide reduction has a negative activation entropy whereas the bromide reduction displays a small positive activation entropy. The reverse reaction has a smaller heat of activation than the forward reaction; the overall reaction is endothermic to the extent of 15.2 kJ mol^{-1}. However, the reverse reaction has a negative entropy of activation, and the reaction overall has a negative free energy change of 16.5 kJ mol^{-1} or an equilibrium constant of 780 M^{-1} for the electron exchange at 298 K. The entropy change for the overall reaction is 106 J K^{-1} mol^{-1}, *i.e.* large and positive, hardly surprising if one starts off with what approximates to an ion triplet and finishes with what must be a much looser association between uncharged D and Br_2^-. The difference in the entropies of activation between the iodide and the bromide reaction is at first sight surprising, but if it is considered that the iodide transition state for reduction is early, *i.e.* like the tight ion-triplet precursor complex, and that the bromide transition state is late, like the loose successor complex between D and Br_2^-, then the values are more understandable. The negative entropy of the reverse reaction may concern separated D and Br_2^- coming together to form the more tightly bound transition state.

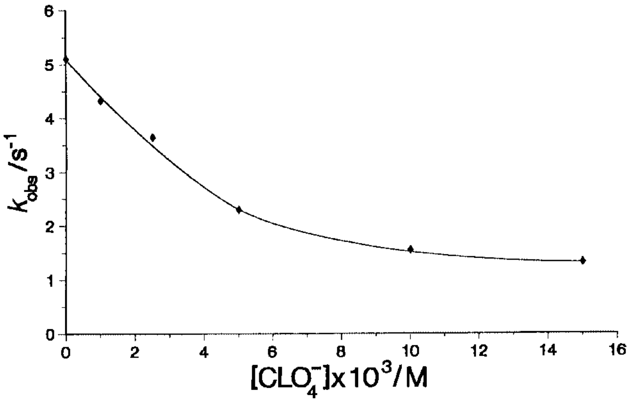

Fig. 7 Plot of k_{obs}, at 298 K, *vs.* varying perchlorate concentration, total bromide concentration being kept constant at 0.0050 M.

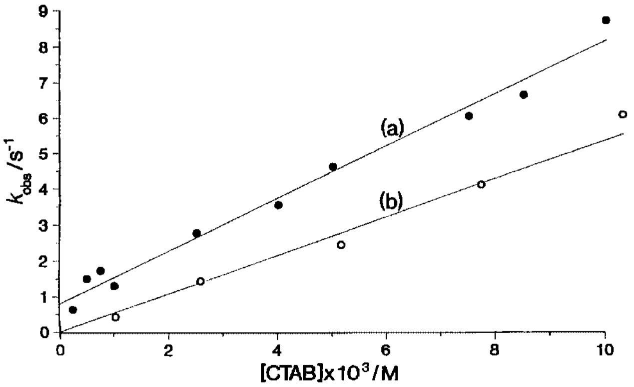

Fig. 8 Plot of k_{obs}, at 298 K, *vs.* varying bromide concentration: (a) in the absence of added perchlorate, (b) in the presence of 0.0050 M perchlorate.

iii Ion pairing

An important series of findings concerns the effect of added inert electrolyte $Q^+ClO_4^-$ on the rate of reaction. For a reaction series with a constant concentration of bromide and a varying concentration of perchlorate the observed rate constant declines in a non-linear fashion as the perchlorate concentration is increased (Fig. 7). For a series where there is a set amount of added perchlorate but a variable amount of bromide, a linear plot is obtained, but of a lesser slope from that without added perchlorate (Fig. 8), and with zero intercept.

The treatment used by one[23] of us on the solvolysis and anation of 1,10-phenanthrolineiron(II) in dmso in the presence of reactive (Cl^-) and non-reactive (ClO_4^-) ions can be applied to this case too. The concentration of free Q^+, $[Q]_{Free}$, was first calculated from the approximation that it is equal to the square root of ($[Q^+]_{Total}/10^5$), 1 × 10^5 being a suitable value for the ion-pair formation constant.[24] Then if $[QClO_4]_{Total}$ is *x*M and $[QBr]_{Total}$ is *y*M, the amounts of ion-paired ClO_4^- and Br^- are given by eqns. (6) and (7). Adding both of these quantities

$$[Q^+ClO_4^-]_{IP} = 10^5[Q]_{Free}\,x/(1 + 10^5[Q]_{Free}) \qquad (6)$$

$$[Q^+Br^-]_{IP} = 10^5[Q]_{Free}\,y/(1 + 10^5[Q]_{Free}) \qquad (7)$$

and subtracting them from $[Q^+]_{Total}$ gave a new value of $[Q]_{Free}$, and from this new values of $[Q^+ClO_4^-]_{IP}$ and $[Q^+Br^-]_{IP}$ were calculated, leading to a further new value of $[Q]_{Free}$. The values typically converged after four cycles.

The converged value of $[Q]_{Free}$ was then used to calculate free bromide and free perchlorate from eqns. (8) and (9). It should

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§ For example, let it be supposed that the reaction has a $\Delta G^\ddagger$ of activation of 4 kJ mol^{-1} in water. Then if $\Delta G^\ddagger$ varies as $1/\varepsilon$, in dichloromethane the value of $\Delta G^\ddagger$ will be 36 kJ mol^{-1} ($\varepsilon = 9$ rather than 81). Using a value of $kT/h = 6 \times 10^{12}$ M^{-1} s^{-1} at 300 K one can calculate $k = 2 \times 10^6$ M^{-1} s^{-1} from $k = kT/h\cdot e^{-(\Delta G^\ddagger/RT)}$.

$$[\mathrm{Br}^-]_{\mathrm{Free}} = [\mathrm{Q}^+\mathrm{Br}^-]_{\mathrm{IP}}/[\mathrm{Q}]_{\mathrm{Free}}10^5 \qquad (8)$$

$$[\mathrm{ClO_4}^-]_{\mathrm{Free}} = [\mathrm{Q}^+\mathrm{ClO_4}^-]_{\mathrm{IP}}/[\mathrm{Q}]_{\mathrm{Free}}10^5 \qquad (9)$$

be noted that although K_{IP} is given the value of 10^5 for both ions, one might more properly use values obtained from conductivity studies. The concentration of the ion pair $\mathrm{D}^+\mathrm{Br}^-$ was then given by eqn. (10).[23] This leads to a revised overall expression (11) for the forward rate constant.

$$[\mathrm{D}^+\mathrm{Br}^-]_{\mathrm{IP}} = 10^5[\mathrm{D}^+]_{\mathrm{Total}}[\mathrm{Br}^-]_{\mathrm{Free}}/\{1 + 10^5[\mathrm{Br}^-]_{\mathrm{Free}} + 10^5[\mathrm{ClO_4}^-]_{\mathrm{Free}}\} \qquad (10)$$

$$k_{\mathrm{obs}} = k_1[\mathrm{Br}^-]_{\mathrm{Total}}(10^5[\mathrm{D}^+]_{\mathrm{Total}}[\mathrm{Br}^-]_{\mathrm{Free}}/\{1 + 10^5[\mathrm{Br}^-]_{\mathrm{Free}} + 10^5[\mathrm{ClO_4}^-]_{\mathrm{Free}}\}) \qquad (11)$$

From this it can be seen that if our proposed mechanism holds the observed rate constant will vary approximately inversely as the added perchlorate concentration for a set concentration of added bromide (Fig. 7). The lessened slope of the plot of observed rate constant in the presence of a set concentration of perchlorate and a varying amount of added bromide (Fig. 8) is also accounted for. An interesting feature of the latter plot is the much smaller value of the reverse rate constant in the presence of perchlorate (it tends to zero). This is easy to account for in terms of competition between perchlorate and $\mathrm{Br_2}^-$ for the product dimer. Only encounters with the dibromide radical anion will be involved in the reverse reaction, and since the concentration of perchlorate is so much higher than that of the transient radical anion the number of active encounters will be negligible compared to those which do not lead to reaction.

In the literature of further-oxidised iron(III) species emphasis has been on oxygen atom transfer from the ferryl group, Fe=O, to the reducing agent. In this and our previous paper all the evidence points to the Fe–O–Fe grouping remaining intact in electron transfer. In the non-donor solvent dichloromethane it is to be expected that the sites *trans* to oxygen in D^+ are vacant, and bromide ion would be expected to co-ordinate transiently at one of these in forming the essential ion pair. In ferryl species there is generally a ligand (*e.g.* histidine) *trans* to the oxygen of the ferryl group blocking direct co-ordination to the iron, and electron transfer must go *via* the porphyrin ring (outer sphere) or by prior transient co-odination to the oxygen atom formally doubly bonded to the iron (inner sphere).

The formal oxidation state of iron in the oxidising agent D^+ is 3.5, and the conclusion from Goff's experiments[6b] is that each ring has a charge of +0.5. However, the blocking effect of perchlorate ions and the success of the ion-pairing treatment might suggest that iron is the site of bromide attack, as each ring provides such an area for attack on its circumference that effective blocking seems unlikely. On the other hand the effect of added perchlorate is to reduce the number of $\mathrm{D}^+\mathrm{Br}^-$ ion pairs wherever Br^- is situated adjacent to the D^+ species, so this apparently common-sense argument is not conclusive. It would be interesting to repeat these experiments for the doubly oxidised species[1,8] D^{2+}. This has a formal oxidation state of 4 for each iron atom, as in the ferryl grouping, and the UV-visible spectrum in the Soret region could be held to indicate a lot of porphyin radical cation character in the porphyrin rings, as do other parameters.[6b]

Conclusion

The reaction between a formally $\mathrm{Fe^{III}}$–O–$\mathrm{Fe^{IV}}$ porphyrin dimer (D^+) and a quaternary ammonium bromide in dichloromethane involves a dimer/bromide ion pair being attacked by bromide ion in both the form of a free ion and as an ion pair with the quaternary cation (an inner-sphere reaction). The products are $\mathrm{Br_3}^-$ and $\mathrm{(FeTPP)_2O}$. Adding quaternary ammonium perchlorate reduces the concentration of $\mathrm{D}^+\mathrm{Br}^-$ ion pairs, and the rate of reaction, in line with a model involving competitive ion pairing, with the perchlorate ion pair being inactive. There are good grounds for believing that the back reaction involves $\mathrm{Br_2}^-$. The reduction of D^+ by bromide is slower than by iodide, the difference being largely accounted for by the difference in the electron affinities of $\mathrm{Br_2}$ and $\mathrm{I_2}$. The activation parameters point to the bromide reaction having a later transition state than that of the iodide reaction.

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