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# Kinetics of oxidation of thiosulfate ion by mixed-valence bis($\mu$-oxo) dimanganese complexes

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**Abstract**—The mixed-valence $Mn^{III,IV}$ complexes, $[Mn_2O_2(bipy)_4]^{3+}$ (**1**) and $[Mn_2O_2(phen)_4]^{3+}$ (**2**) aquates rapidly but partially to $[Mn_2O_2(bipy)_3(H_2O)_2]^{3+}$ (**1a**) and $[Mn_2O_2(phen)_3(H_2O)_2]^{3+}$ (**2a**) in aqueous solutions containing excess bipy-$Hbipy^+$ (for **1**) and phen-$Hphen^+$ (for **2**) buffer in the range pH 4–5. In such media, the complexes suffer little auto-decomposition, core rearrangement and polynucleation, but are reduced by an extraneous reducing agent. For example, excess $S_2O_3^{2-}$ reduces these complexes to $Mn^{II}$, and $S_4O_6^{2-}$ is produced quantitatively. The aqua complexes **1a** and **2a** are kinetically more active than the corresponding parent complexes **1** and **2**. Comparison with kinetic data for reactions of the complexes with $NO_2^-$, $HSO_3^-$, hydroquinone and ascorbic acid indicates a one-electron, outer-sphere rate determining step. Structural flexibility and ease of elongation of the metal–ligand bonds play important roles in controlling the kinetic lability. © 1997 Elsevier Science Ltd

*Keywords*: kinetics, thiosulfate, manganese.

Bis($\mu$-oxo)dimanganese(III,IV) complexes are of current interest as photosystem II models [1,2], as redox catalysts [3], and as mixed-valence species exhibiting intervalence charge transfer [4]. The complexes $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ (**1**, bipy = 2,2′-bipyridine) and its analogue, $[(phen)_2Mn^{III}(O)_2Mn^{IV}(phen)_2]^{3+}$ (**2**, phen = 1,10-phenanthroline) are the two earlier-known members of this class [5–7]. Detailed investigations have been carried out on their molecular structures [6,7], electrochemical behaviour [6–8], water-splitting properties [3] and aqueous solution chemistry [6,9–13]. It has been found that **1** and **2** are reasonably stable against redox decomposition in aqueous buffer made of their respective ligands. Since stable complexes of manganese(IV) are hardly known in aqueous solution [14–18], **1** and **2** offer the opportunity to examine in aqueous media the influence of thermodynamic driving force on reduction rates of $Mn^{IV}$ centers within a $N_4O_2$ dinuclear environment. We report kinetic investigations of $S_2O_3^{2-}$ oxidation by **1** and **2**, including reactivity comparisons for sulfite, nitrite and ascorbate anions and the hyroquinone molecule, studied earlier [10,19, 20].

## EXPERIMENTAL

The bipyridine complex, **1**$(ClO_4)_3\cdot 2H_2O$ was prepared as reported [6]. Its analogue, **2**$(ClO_4)_3$ was prepared by a literature method [6], slightly modified for the recrystallization procedure [20]. Purity of both the complexes was found to be excellent from their known molar extinction coefficients and the positions of UV–vis spectral peaks.

Sodium thiosulfate (A.R., B.D.H.) was recrystallized from hot water. Solutions of $S_2O_3^{2-}$ were prepared in water and standardized by iodometry [21]. The solution was always freshly prepared each day. All other solutions were prepared and standardized as described earlier [10].

Kinetics for **1** and **2** were measured at 370 and 410 nm, respectively, in the thermostatted ($\pm 0.1^\circ C$) cell housing (CPS 240A) of a Shimadzu spectrophotometer (UV-1601PC). At these wavelengths, changes in absorbance are high and the products are weakly absorbing at most. The ionic strength was generally maintained at 2.0 mol $dm^{-3}$ for **1** and at 1.0 mol $dm^{-3}$ for **2** by adding $NaNO_3$. The reaction mixtures for **1** were buffered using $c_{bipy}$ ($=[bipy]+[Hbipy^+]$) in the range 5–25 mmol $dm^{-3}$, while $c_{phen}$ ($=[phen]+[Hphen^+]$) in the range 3–12 mmol $dm^{-3}$ were used for **2**. Solution pH were mea-

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sured with an Orion (710A) pH meter and $[H^+]$ evaluated as described earlier [22]. The pH ranges for the reaction mixtures were selected to avoid autodecomposition of the complexes during kinetic measurements. All kinetics were carried out under first-order conditions with the reductant in excess. The first-order rate constants $k_0$ were evaluated by least squares analysis of the $\ln(A_t - A_\infty)$ *vs* time ($t$) data as usual.

Reaction stoichiometries were measured under the kinetic conditions by iodimetric estimation of unspent thiosulfate. It was verified that under the experimental conditions the ligands do not interfere with the measurements.

Formation of a polythionate was proved according to a method of Kolthoff and Belcher [23]. The polythionate formed in the reactions of **1** and **2** were reduced to $S_2O_3^{2-}$ by using excess KCN. $S_2O_3^{2-}$ thus formed was estimated iodimetrically.

## RESULTS AND DISCUSSION

Measurement of unreacted thiosulphate indicated a 1 : 3 stoichiometry [eq. (1)]. Addition of excess KCN to the product solution generated extra $S_2O_3^{2-}$, equal to half the amount of $S_2O_3^{2-}$ consumed in reaction (1). This supports correctness of the stoichiometric equation (1) and production of $S_4O_6^{2-}$, which reacts with excess KCN according to eq. (2).

$$2[Mn^{III}O_2Mn^{IV}]^{3+} + 6\,S_2O_3^{2-} + 8H^+ \rightarrow 4Mn^{II} + 3\,S_4O_6^{2-} + 4H_2O \quad (1)$$

$$S_4O_6^{2-} + 3CN^- + H_2O \rightarrow S_2O_3^{2-} + SCN^- + SO_4^{2-} + 2HCN \quad (2)$$

Stoichiometries other than (1) can occur in oxidations of thiosulfate. However, formation of tetrathionate is probably the most common [24].

In aqueous acidic media both complexes **1** and **2** undergo extensive acid-catalysed aquation and protonation of a bridging oxo-ligand. Both the processes lead to complex redox chemistry [9–13], e.g. dimer cleavage, disproportionation and core-rearrangement. However, only simple aquation equilibria (3a) and (3b) are established in the range pH 4.0–6.0, maintained with an excess L-HL$^+$ buffer (for **1**, L = bipy; for **2**, L = phen) [2,10,19].

$$\underset{\textbf{(1)}}{[Mn_2O_2(bipy)_4]^{3+}} + H^+ + 2H_2O \xrightleftharpoons{K_{1H}} \underset{\textbf{(1a)}}{[Mn_2O_2(bipy)_3(H_2O)_2]^{3+}} + Hbipy^+ \quad (3a)$$

$$\underset{\textbf{(2)}}{[Mn_2O_2(phen)_4]^{3+}} + H^+ + 2H_2O \xrightleftharpoons{K_{2H}} \underset{\textbf{(2a)}}{[Mn_2O_2(phen)_3(H_2O)_2]^{3+}} + Hphen^+ \quad (3b)$$

$K_{1H}$ and $K_{2H}$ could not be measured spectrophotometrically because very small spectral changes result due to reactions (3a) and (3b) under the experimental conditions. Spectral changes increase largely if $[H^+]$ is increased and [L] is decreased, but with such changes set in other complicated equilibria, mentioned above.

The reactions exhibit excellent first-order kinetics at least up to 90% completion. Variation in the monitoring wavelength (370, 640, 820 nm for **1**, and 410, 640, 820 nm for **2**) changes neither the first-order nature nor the $k_0$ values. The observed first-order kinetics and invariance of $k_0$ with change in $\lambda$, together with the absence of any absorbance change immediately after mixing, testify that the first act of electron transfer is rate determining and that, all subsequent steps are rapid.

$k_0$ for both **1** and **2** increases with increasing $[S_2O_3^{2-}]$ with no indication for rate saturation even when $[S_2O_3^{2-}] = 220$[complex] and plots of $k_0$ *vs* $[S_2O_3^{2-}]$ are straight lines ($r \geqslant 0.98$) passing through the origin (Fig. 1). $k_0$ increases linearly with increasing $[H^+]$ (Fig. 2), but remains unchanged when [complex] is varied. $k_0$ decreases with increasing $c_L (= [HL^+] + [L])$ (Fig. 3); it also decreases with increasing ionic strength, as expected for reactions between oppositely charged species. Reactions of the bipy complex **1** at $I = 1.0$ mol dm$^{-3}$ are fast and rates are marginal for accurate measurement by conventional spectrophotometry and a higher ionic strength ($I = 2.0$ mol dm$^{-3}$) had to be used. However, in such a media, solubility of **2** and the ligand phen is too low. Nevertheless, reactions of **2** are slower than those of **1** and kinetic measurements on **2** at $I = 1.0$ mol dm$^{-3}$ appeared convenient both from the point of solubility and rate of reaction.

Variation of $k_0$ with [L], the molar concentration

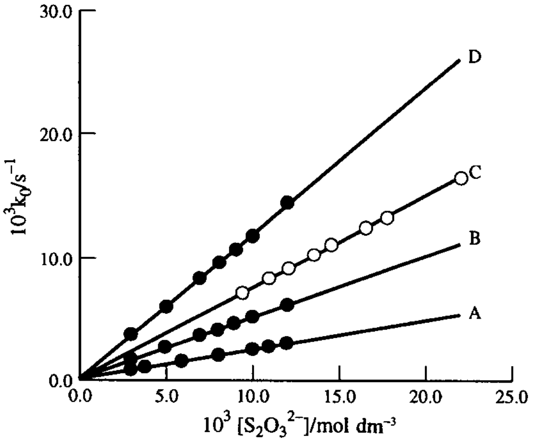

Fig. 1. Variation of $k_0$ with $[S_2O_3^{2-}]$ for complexes **1**(○) and **2**(●). (A) 20.0°C; pH, 4.8; $c_{phen}$, 8.0 mmol dm$^{-3}$. (B) 30.0°C; pH, 4.8; $c_{phen}$, 11.0 mmol dm$^{-3}$. (C) 30.0°C; pH, 4.5; $c_{bipy}$, 10.0 mmol dm$^{-3}$. (D) 30.0°C; pH, 4.8; $c_{phen}$, 11.0 mmol dm$^{-3}$. $I = 1.0$ (A, B, D) and 2.0 (C) mol dm$^{-3}$.

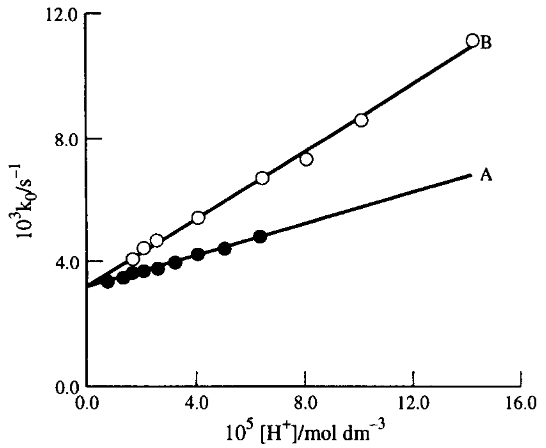

Fig. 2. Dependence of $k_0$ on [H$^+$] for complexes **1**(○) and **2**(●). (A) $c_{\text{phen}}$, 12.0 mmol dm$^{-3}$; [$S_2O_3^{2-}$], 7.0 mmol dm$^{-3}$; *I*, 1.0 mol dm$^{-3}$. (B) $c_{\text{bipy}}$, 10.0 mmol dm$^{-3}$; [$S_2O_3^{2-}$], 6.5 mmol dm$^{-3}$; *I*, 2.0 mmol dm$^{-3}$. [complex], 0.1 mmol dm$^{-3}$ (A, B).

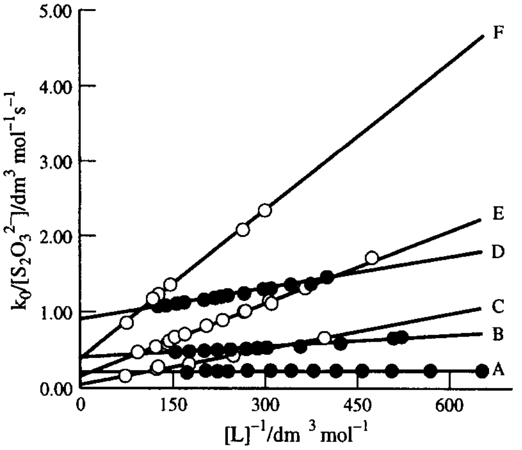

Fig. 4. Graphical evaluation of kinetic parameters for complexes **1**(○) and **2**(●). Temperature: 20.0°C (A, C); 30.0°C (B, E); 40.0°C (D, F). [complex], 0.1 mmol dm$^{-3}$. *I*, 1.0 (A, B, D) and 2.0 mol dm$^{-3}$ (C, E, F). pH range, 3.85–5.05. $c_L$, 5–25 mmol dm$^{-3}$.

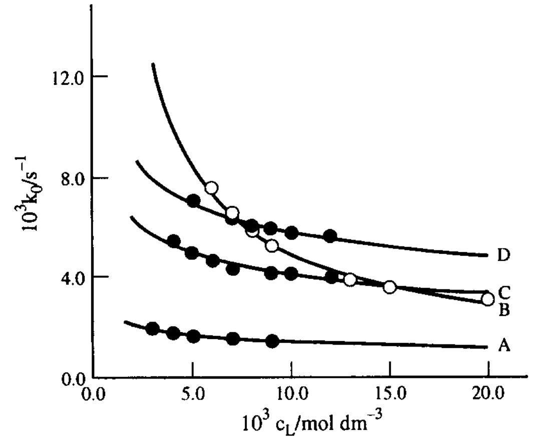

Fig. 3. Variation of $k_0$ with $c_L$ for complexes **1**(○) and **2**(●). (A) pH, 5.20; [$S_2O_3^{2-}$] = 7.0 mmol dm$^{-3}$; 20.0°C. (B) pH, 4.50; [$S_2O_3^{2-}$], 6.5 mmol dm$^{-3}$; 30.0°C. (C) pH, 4.90; [$S_2O_3^{2-}$], 8.0 mmol dm$^{-3}$; 30.0°C. (D) pH, 5.0; [$S_2O_3^{2-}$], 5.0 mmol dm$^{-3}$; 40.0°C. $I$ = 1.0 (A, C, D), and 2.0 (B) mol dm$^{-3}$. [complex], 0.1 mmol dm$^{-3}$ for all.

of the free ligand base, nicely fits ($r \geqslant 0.98$) eq. (4) (Fig. 4).

$$k_0 = (a+b/[\mathrm{L}])[S_2O_3^{2-}] \qquad (4)$$

For a given $c_L$, [L] was calculated from eq. (7), where $n = 1$ for L = bipy and $n = 2$ for L = phen; $K_1 = 10^{-4.42}$ and $K_2 = 10^{-4.95}$ are literature values [25, 26].

$$\mathrm{Hbipy}^+ \xrightleftharpoons{K_1} \mathrm{H}^+ + \mathrm{bipy} \qquad (5)$$

$$\mathrm{Hphen}^+ \xrightleftharpoons{K_2} \mathrm{H}^+ + \mathrm{phen} \qquad (6)$$

$$[\mathrm{L}] = K_n c_L/(K_n + [\mathrm{H}^+]) \qquad (7)$$

The nature of dependence of $k_0$ on [L] suggests ligand dissociation pre-equilibria [eq. (8)] followed by rate-determining concurrent reactions of $S_2O_3^{2-}$ with the parent complex [eq. (9)] and the aqua complex [eq. (10)]. Further, $H_2S_2O_3$ is a strong acid, its reported [27] p$K_{a1}$ = 0.35 and p$K_{a2}$ = 1.01 at 25°C. Hence, $S_2O_3^{2-}$ is considered as the only effective reducing agent in the experimental pH range 4–5.

$$\underset{\mathbf{n}}{[Mn_2O_2(L)_4]^{3+}} + 2H_2O \xrightleftharpoons{K_{dn}} \underset{\mathbf{na}}{[Mn_2O_2(L)_3(H_2O)_2]^{3+}} + L \qquad (8)$$

$$\underset{\mathbf{n}}{[Mn_2O_2(L)_4]^{3+}} + S_2O_3^{2-} \xrightarrow{k_n} \text{Products} \qquad (9)$$

$$\underset{\mathbf{na}}{[Mn_2O_2(L)_3(H_2O)_2]^{3+}} + S_2O_3^{2-} \xrightarrow{k_{nA}} \text{Products} \qquad (10)$$

For the bipy complex **1**, L = bipy and $n = 1$, while for the phen complex **2**, $n = 2$ and L = phen. Provided that total complex, $c_M$ = [**n**] + [**na**], total thiosulphate = [$S_2O_3^{2-}$] and [L] ≫ $K_{dn}$, the scheme leads to eq. (11), which is equivalent to eq. (4).

$$k_0 = \{3k_n + 3k_{nA}K_{dn}/[L]\}[S_2O_3^{2-}] \qquad (11)$$

$k_n$ and $k_{nA}$ $K_{dn}$ values at different temperatures were evaluated from $k_0/[S_2O_3^{2-}]$ *vs* 1/[L] plots, (Fig. 4) at different temperatures. These kinetic parameters along with their corresponding activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been presented in Table 1.

The $k_n$ and $k_{nA}$ paths definitely represent multistep processes in which only the first act of electron transfer controls the measured $k_0$. All subsequent steps are rapid and likely to be 1e changes. We presume

Table 1. Kinetic parameters for oxidation of $S_2O_3^{2-}$ with $[Mn^{III}Mn^{IV}]$ complexes[a]

| | Rate constants ($dm^3\ mol^{-1}\ s^{-1}$) at | | | | |
|---|---|---|---|---|---|
| | 20.0°C | 30.0°C | 40.0°C | ΔH# ($kJ\ mol^{-1}$) | ΔS# ($J\ K^{-1}\ mol^{-1}$) |
| $10^2k_1$: | 2.00 ± 0.2 | 5.13 ± 0.2 | 12.7 ± 1.2 | 68 ± 5.0 | −44 ± 12 |
| $10^4k_{1a}K_{d1}$: | 5.17 ± 0.15 | 10.80 ± 0.23 | 22.1 ± 0.8 | 53 ± 3.0 | −126 ± 8 |
| $10^2k_2$: | 6.43 ± 0.4 | 13.5 ± 0.9 | 30 ± 2 | 56 ± 4.0 | −78 ± 10 |
| $10^5k_{2a}K_{d2}$: | 5.05 ± 0.4 | 16.8 ± 0.8 | 46 ± 3 | 81 ± 4.0 | −51 ± 9 |

[a] $I = 2.0$ mol $dm^{-3}$ for $k_1$ and $k_{1a}K_{d1}$; $I = 1.0$ mol $dm^{-3}$ for $k_2$ and $k_{2a}K_{d2}$.

that the $\{Mn_2O_2\}^{n+}$ cores are retained except for the $\{Mn^{II}Mn^{III}O_2\}^+$ species, which is unstable in the presence of water [28]. Previous kinetic studies [10,19] support the presumed 1e changes and retention of nuclearity. Both the presumptions are further supported by (a) known [6–8] stepwise 1e redox processes of dinuclear Mn complexes at the electrodes, (b) the fact that nuclearity is preserved among the several oxidation levels of dinuclear catalase enzyme models [28,29], (c) the fact that bond connectivities are retained [30,31] among the various "S-states" [32] involved in the photosystem II and (d) the fact that higher-valent manganese has a propensity to form and retain bis($\mu$-oxo) complexes in faintly acidic media [33–35]. The established involvement [24,36,37] of $S_2O_3^-$ radical in the oxidation reactions of $S_2O_3^{2-}$ producing $S_4O_6^{2-}$ also supports the presumed 1e changes.

The best value available for $E_f$ of the $S_2O_3^{2-/-}$ couple is −1.30 V. [24] Compared to this, $E^0$ for the $S_2O_3^{2-}/S_4O_6^{2-}$ couple has a much more favourable value, +0.08 V [38]. However, EPR measurements and M.O. calculations imply [39–43] that the molecular structure of $S_2O_3^{2-}$ is very similar to that of $S_2O_3^-$. It is, therefore, expected that the internal Frank–Condon barrier for 1e oxidation of $S_2O_3^{2-}$ should be lower than that for 2e oxidations, in spite of the higher thermodynamic price for 1e oxidations. The low kinetic barrier for 1e changes is manifested in self-exchange rate for the $S_2O_3^{2-/-}$ couple. The value ($2.3 \times 10^5$ $dm^3\ mol^{-1}\ s^{-1}$) is among the largest for a main group system [44–49]. The $S_2O_3^-$ produced in the 1e oxidation by the $Mn^{III,IV}$ complexes, ultimately produces $S_4O_6^{2-}$, plausibly through the very rapid reactions depicted in eq. (12), which provides a much more efficient pathway [50–52] than eq. (13) for the decay of the radical intermediates [53,54].

$$S_2O_3^- + S_2O_3^{2-} \longrightarrow S_4O_6^{3-} \xrightarrow{-1e} S_4O_6^{2-} \qquad (12)$$

$$2S_2O_3^- \longrightarrow S_4O_6^{2-} \qquad (13)$$

The reaction between $S_2O_3^-$ and $S_2O_3^{2-}$ producing $S_4O_6^{3-}$ is well-known and $E^0$ for the $S_4O_6^{3-/2-}$ couple is 1.08 V [36, 55]. Thus, $S_4O_6^{3-}$ is a strong reducing agent and largely compensates for the unfavourable thermodynamics for 1e oxidation of $S_2O_3^{2-}$ to $S_2O_3^-$.

Acid decomposition of thiosulfate ion poses a potential complication in the study of its redox reactions. The decomposition [56] is a second-order process in $[S_2O_3^{2-}]$ [eq. (14)],

$$\text{Rate} = 2k[HS_2O_3^-][S_2O_3^{2-}] \qquad (14)$$

where $k = 0.5$ $dm^6\ mol^{-2}\ s^{-1}$. Such decomposition appears sometimes as a concurrent second-order path in redox kinetics involving $S_2O_3^{2-}$. In our kinetic measurements no significant deviation from first-order kinetics could be seen and there was no indication for a $[S_2O_3^{2-}]^2$ term. It appears, therefore, that under our experimental conditions, acid decomposition of $S_2O_3^{2-}$ is very much slower compared with its redox reactions with **1** and **2**. The slow decomposition rate is no doubt a consequence of the low $[H^+]$ and low $[S_2O_3^{2-}]$ used by us.

Another potential complication in the study of redox kinetics using $S_2O_3^{2-}$ arises from the catalysis by trace metal ions of the first transition series. For example, $Cu^{II}$ is an excellent catalyst [36, 57] for the oxidation of $S_2O_3^{2-}$ by $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, $[Co(ox)_3]^{3-}$, $[Fe(bipy)_3]^{3+}$ and $[Os(phen)_3]^{3+}$. Similar catalytic reactions could be anticipated in the reactions of **1** and **2** with $S_2O_3^{2-}$. However, we faced no such complications and observed reproducible kinetics. Probably, the use of excess bipyridine and phenanthroline as buffering materials in our experiments has masked any trace catalyst metal ions, present as impurities.

Provided that $\log f_{12} \sim 0$, the Marcus cross relation [58–61] may be written as eq. (15), where the terms have their usual significances.

$$\log k_{12} - 0.5 \log k_{22} = 0.5(\log k_{11} + \log w_{12}) + 8.47(E_1 - E_2) \qquad (15)$$

Reduction potentials for **1** and **2** in acetonitrile are known to be very close, 0.29 and 0.30 V (*vs* SCE), respectively. It is expected that reduction potentials of the corresponding aqua complexes **1a** and **2a** in aqueous media be also close to each other. Assuming further that $\log k_{11}$ is closely similar for the two aqua complexes and that $\log w_{12}$ remains fairly constant for the series of reactions, one expects a linear relation between $\log k_{12}$ and $E_2$, the formal reduction potential

Table 2. An approximate Marcus correlation for oxidation with dinuclear [$Mn^{III}Mn^{IV}$] complexes.: 30.0°C, rate constants in $dm^3 mol^{-1} s^{-1}$

| SL. no. | Reductant | $k_{12}$ | $k_{22}$ | $E_f$(N.H.E.) | $\log k_{12}$–0.5 $\log k_{22}$ |
|---|---|---|---|---|---|
| 1 | $S_2O_3^{2-}$ | 28.5 (bipy)[a] | $2.3 \times 10^5$ [24] | 1.30 [24] | −1.22 |
| | | 15.0 (phen)[b] | | | −1.50 |
| 2 | Hydroquinone | 160 (bipy) [14] | $7.0 \times 10^5$ [66] | 1.08 [67] | 0.72 |
| 3 | $NO_2^-$ | 34.9 (bipy) [14] | 0.30 [24] | 0.87 [68] | 1.80 |
| | | 58.8 (phen) [20] | | | 2.29 |
| 4 | $HSO_3^-$ | 200 (bipy) [14] | 4.0 [69] | 0.72 [69] | 2.0 |
| 5 | Ascorbate | $1.2 \times 10^5$ (bipy) [14] | $3.5 \times 10^5$ [70] | 0.71 [70] | 2.31 |

[a] This work, $k_{12} = k_{1a}K_{d1}/K_1$.

[b] This work, $k_{12} = k_{2a}K_{d2}/K_2$.

for different reductants [62–64] (Table 2). The solid line in the Fig. 5 has been drawn with a theoretical slope = 8.47, expected for an outer-sphere, one-electron transfer reaction and the data in Table 2 agree well with this theoretical line.

Equation (11) was derived under the assumption that $[L] \gg K_{dn}$. Validity of eq. (11) under our conditions, therefore, sets upper limits for the dissociation constants as: $K_{d1} < 1.4 \times 10^{-3}$ mol dm$^{-3}$ and $K_{d2} < 8 \times 10^{-4}$ mol dm$^{-3}$. The lower limits for the rate constants are, therefore, set at 0.77 dm$^3$ mol$^{-1}$ s$^{-1}$ for $k_{1a}$ and 0.21 dm$^3$ mol$^{-1}$ s$^{-1}$ for $k_{2a}$ at 30°C. It is thus found that the aqua complexes **1a** and **2a** are kinetically more active than their respective parent complexes **1** and **2**. Similar trends of reactivity have been observed earlier [10,20] for **1** and **2** reacting with $NO_2^-$ and it is a well-known trend for the redox reactions of mononuclear complexes of higher-valent manganese [22,65] in aqueous solution. There may be three possible reasons for higher reactivity of the aqua complexes **1a** and **2a** than their respective parents **1** and **2**: (1) Replacement of a chelating ligand by the weaker donor $H_2O$ makes the metal centre more open and more electron defficient. (2) The Ox.Red precursor complexes for **1a** and **2a** may be stabilized by hydrogen bonds, not possible for **1** and **2**, [20] and (3) the metal–ligand bonds are more flexible in the aquated complexes, which therefore have a lower Frank–Condon barrier.

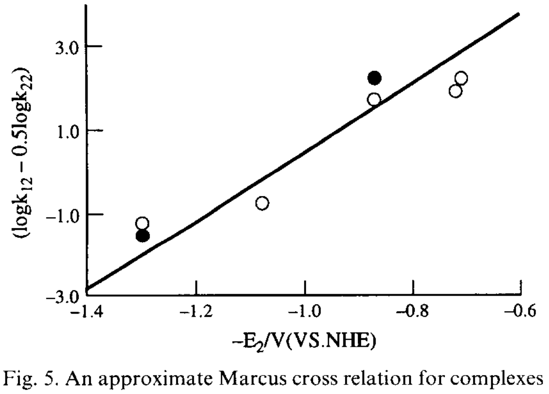

Fig. 5. An approximate Marcus cross relation for complexes **1**(○) and **2**(●). [$S_2O_3^{2-}$] (1), hydroquinone (2), $NO_2^-$ (3), $HSO_3^-$ (4), Hasc$^-$ (5).

The phen complexes are more rigid than the bipy complexes. One can expect that the Frank–Condon barrier for **1a** should be lower than that for **2a**. Accordingly, $k_{1a}$ is higher than $k_{2a}$.

A comparison of $k_1$ and $k_2$ is not warranted at this stage, since the modest difference in their values may be an effect of different ionic strengths at which $k_1$ and $k_2$ have been evaluated.

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