Metal-Ion Oxidations in Solution. Part XV.[1] Rate-determining Dimerisations in Redox Reactions of Iron(III) with some α-Mercaptocarboxylic Acids

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The kinetics of decomposition of iron(III)–sulphur-bonded complexes with α-mercaptocarboxylic acids (HORSH) have been investigated. A rate-determining dimerisation is considered to take place with a two-electron transfer

$$\mathrm{Fe^{III} + HORSH \xrightleftharpoons{K_1} [Fe^{III}(ORS)]^+ + 2H^+} \qquad \text{(i)}$$

$$\mathrm{2[Fe^{III}(ORS)]^+ \xrightarrow{k_0} 2Fe^{II} + HORS{\cdot}SROH} \qquad \text{(ii)}$$

leading directly to the disulphide product. The effect of methyl substituents on the ligands suggests an associative mechanism. At 25 °C, for mercaptoacetic acid, $k_0 = 167 \pm 18$ l mol^{-1} s^{-1} ($\Delta H^\ddagger = 5 \pm 1.5$ kcal mol^{-1}, $\Delta S^\ddagger = -31 \pm 5.5$ cal K^{-1} mol^{-1}); 2-mercaptopropionic acid, $k_0 = 130 \pm 10$ l mol^{-1} s^{-1} ($\Delta H^\ddagger = 9 \pm 2$ kcal mol^{-1}, $\Delta S^\ddagger = -18 \pm 3$ cal K^{-1} mol^{-1}); 2-mercapto-2-methylpropanoic acid, $k_0 = 47 \pm 8$ l mol^{-1} s^{-1} ($\Delta H^\ddagger = 14 \pm 4$ kcal mol^{-1}, $\Delta S^\ddagger = -5 \pm 1.5$ cal K^{-1} mol^{-1}); and 2-mercaptosuccinic acid, $k_0 = 68 \pm 7$ l mol^{-1} s^{-1} ($\Delta H^\ddagger = 10 \pm 1.5$ kcal mol^{-1}, $\Delta S^\ddagger = -16 \pm 2$ cal K^{-1} mol^{-1}). Apparent differences in the overall rates of the redox reaction with methylation are explicable in terms of variation in the equilibrium constant K_1.

BLUE-VIOLET complexes have long been known as precursors to electron transfer in the iron(III) oxidation of sulphur-containing ligands.[2] These intermediates have been identified under both acidic and basic conditions and in the latter, where the life-times are somewhat longer, kinetic investigations [3-8] of the redox processes have resulted in the postulation of a mechanism involving a further complex in which there are two $\mathrm{Fe^{III}}$ ions.[5-7] Use of an excess of reducing substrate has, however, led to some confusion as to the exact nature of the intermediates. In the reaction with thiosulphate in acidic media, Holluta and Martini [9] postulated a similar mechanism involving a dimeric species derived from the interaction of $\mathrm{[Fe(S_2O_3)_2]^-}$ with a second mol of $\mathrm{Fe^{3+}}$. In contrast, Schmidt [10] and later Page [11] showed the thiosulphate complex to be a 1 : 1 species and in order to explain the kinetics of the electron-transfer reaction Page invoked several reaction paths with half-order concentration dependences. Two previous papers [1,12] in this series have dealt with the formation and characterisation of bidentate chelate complexes of $\mathrm{Fe^{III}}$ with α-mercaptocarboxylic acids, and we here report a study of the corresponding redox reactions.

EXPERIMENTAL

Stock solutions of iron(III) perchlorate, perchloric acid, sodium perchlorate, and the thiol acids, mercaptoacetic ($\mathrm{H_2ma}$), 2-mercaptopropionic ($\mathrm{H_2mp}$), 2-mercapto-2-methylpropanoic ($\mathrm{H_2mmp}$), and 2-mercaptosuccinic ($\mathrm{H_3ms}$), were prepared and used as described previously.[1,12] A solution of iron(II) perchlorate was obtained by electrolytic reduction of iron(III) perchlorate (0.5M) in perchloric acid (1.5M) under a nitrogen atmosphere.‡ Standardisation against potassium dichromate showed virtually quantitative conversion to $\mathrm{Fe^{II}}$. The acid content was determined by titration to pH 4 using standard sodium hydroxide solution.

Kinetic measurements were made on a stopped-flow apparatus of the type described by Sturtevant.[13] Since the intermediate complexes absorb more strongly than either the reactants or products over the wavelength range studied, the reactions were monitored by the decrease in optical density at the wavelength maxima of the particular complex (*ca.* 600 nm). Use of a Nova 2000 computer enabled all points on the oscilloscope trace to be converted into optical density by comparison with a point ($t = \infty$) of known optical density. Solutions were not in general outgassed before use in the apparatus although the dependence of the reaction on dissolved oxygen was tested by thoroughly outgassing several solutions as previously described [1,12] and carrying out the kinetic experiments under an atmosphere of nitrogen.

The stoicheiometry of the reaction (Table 1) was measured by the decrease in $\mathrm{Fe^{III}}$ immediately after the blue colour due to the intermediate complex had been discharged.

TABLE 1

Stoicheiometric ratios of the reactants [a] [equation (1)]

Ligand	$\mathrm{Fe^{III}}$: HORSH
$\mathrm{H_2ma}$	1.12 ± 0.17
$\mathrm{H_2mp}$	0.88 ± 0.10
$\mathrm{H_2mmp}$	0.91 ± 0.10
$\mathrm{H_3ms}$	0.93 ± 0.05 [b]

[a] Based on determination of residual $\mathrm{Fe^{III}}$ after reaction. [b] Ref. 12.

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‡ 1M = 1 mol dm^{-3}, 1 cal = 4.184 J.

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Under conditions of excess of metal ion, this indicated conversion of all the mercaptocarboxylic acid (HORSH) to the corresponding disulphide, the remaining Fe^{III} being

$$2Fe^{II} + 2HORSH \longrightarrow 2Fe^{II} + HORS{\cdot}SROH + 2H^+ \quad (1)$$

determined spectrophotometrically by adding excess of thiocyanate to the solution. Oxidation of the disulphide product by excess of Fe^{III} is probable but this reaction is slow enough to be neglected in the present study. Iron(II) was detected as a product of the reaction by the appearance of a red colour on addition of 1,10-phenanthroline. The other major product isolated was identified as the corresponding disulphide [ν(S–S) at 515 and 534 cm^{-1} in the Raman spectrum].

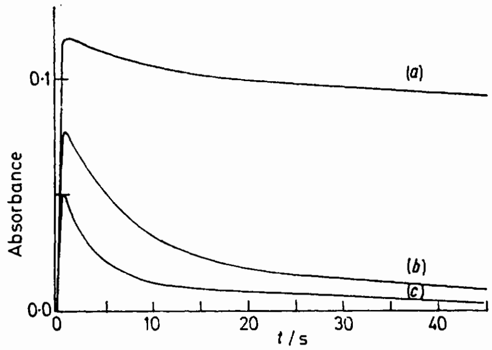

FIGURE 1 Oscilloscope traces of absorbance against time at $[Fe^{3+}] = 0.05$M, $[H^+] = 0.3$M, $I = 1.00$M, and 25 °C: (*a*), $[H_2mmp] = 0.00248$; (*b*), $[H_2mp] = 0.00294$; (*c*), $[H_2ma] = 0.00258$M

RESULTS AND DISCUSSION

(a) *Kinetics of Reaction.*—The complex-formation reaction may be expressed as in (2) [1,12] and ε and K_1 values relating to the complex $[(H_2O)_4Fe(ORS)]^+$ were identified. In the electron-transfer reaction the instantaneous rate was independent of $[H^+]_0$, $[Fe^{III}]_0$, $[HORSH]_0$, and $[Fe^{II}]_0$, suggesting a reaction of the complex $[(H_2O)_4Fe(ORS)]^+$ alone. A plot of $\log_{10}$ (instantaneous rate) against $\log_{10}$ (D) was linear with a gradient between 2 and 3, the exact value depending on the ligand involved. Whilst a mechanism might be postulated involving a bimolecular reaction of the complex, a termolecular process is considered unlikely and the observation of an order greater than two is explicable by the nature of equilibrium (2). Under the conditions used in this study, $[Fe(OH_2)_6]^{3+}$, HORSH, and $[(H_2O)_4Fe(ORS)]^+$ are all present in solution with the metal ion in excess, thus enabling an investigation of the decomposition of only the mono complexes of Fe^{III}.

A mechanism consistent with all the observed facts may be derived as follows (water molecules are excluded for clarity). The initial reactant concentrations may be expressed in the forms (5) and (6) (assuming no added Fe^{2+} and that hydrolysed species may be regarded as having negligible concentration under the conditions used [1,12,14]). Hence we obtain equation (7).

$$Fe^{3+} + HORSH \overset{K_1}{\rightleftharpoons} [Fe(ORS)]^+ + 2H^+ \quad (2)$$

$$2[Fe(ORS)]^+ \xrightarrow{k_0} 2Fe^{2+} + HORS{\cdot}SROH \quad (3)$$

$$K_1 = \frac{[Fe(ORS)^+][H^+]^2}{[Fe^{3+}][HORSH]} \quad (4)$$

$$[Fe^{3+}]_0 = [Fe^{3+}] + [Fe(ORS)^+] + [Fe^{2+}] \quad (5)$$

$$[HORSH]_0 = [HORSH] + [Fe(ORS)^+] + [Fe^{2+}] \quad (6)$$

$$[Fe^{3+}]_0 - [HORSH]_0 = [Fe^{3+}] - [HORSH] \quad (7)$$

After the initial induction period (formation of complex), since equilibrium (2) is adjusted more rapidly than the rate at which the redox reaction proceeds (Figure 1), from (4) and (7) equations (8) and (9) may be derived. From equation (5) we obtain (10), and from (9) the expression (11) may be derived. The rate of the electron-transfer reaction (3) may be written as (12) and by differentiating (11) and substituting into (12) it may be shown that (13) holds.

$$K_1[Fe^{3+}]([Fe^{3+}] - [Fe^{3+}]_0 + [HORSH]_0) = [Fe(ORS)^+][H^+]^2 \quad (8)$$

Plots of instantaneous rate immediately after the induction period for complex formation (2) against the function on the right-hand side of equation (13) using values of K_1 and ε found previously yielded constant values of k_0. Integrating equation (13) gives (14). The complex concentration at $t = 0$ may be approximated by the equilibrium concentration (15). Plots of the left-hand side of equation (14) against time (Figure 2) showed good linearity in all cases and where the errors involved in the parameters ε and K_1 were small this extended to greater than 80% completion of reaction. Excellent agreement was observed between the values of k_0 obtained by this method and those using the method of

$$[Fe^{3+}] = \tfrac{1}{2}\left([Fe^{3+}]_0 - [HORSH]_0 + \left\{([Fe^{3+}]_0 - [HORSH]_0)^2 + \frac{4[Fe(ORS)^+][H^+]^2}{K_1}\right\}^{\frac{1}{2}}\right) \quad (9)$$

$$[Fe^{2+}] = [Fe^{3+}]_0 - [Fe^{3+}] - [Fe(ORS)^+] \quad (10)$$

$$[Fe^{2+}] = [Fe^{3+}]_0 - \tfrac{1}{2}([Fe^{3+}]_0 - [HORSH]_0) - \left(\left\{([Fe^{3+}]_0 - [HORSH]_0)^2 + \frac{4[Fe(ORS)^+][H^+]^2}{K_1}\right\}^{\frac{1}{2}}\right) - [Fe(ORS)^+] \quad (11)$$

$$d[Fe^{2+}]/dt = 2k_0[Fe(ORS)^+]^2 \quad (12)$$

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instantaneous rates [equation (13)] and representative data under various conditions are presented in Table 2. In view of the uncertainties involved, the substantial constancy of the value of k_0 on variation of $[\mathrm{Fe}^{3+}]_0$, $[\mathrm{HORSH}]_0$, and $[\mathrm{Fe}^{2+}]_0$ confirms rate equation (12). Mean values of k_0 for each ligand at various temperatures are presented together with the corresponding thermodynamic parameters in Table 3. Values of twice the root-mean-square errors are quoted to take account of any uncertainty in k_0 introduced by the inaccuracies in the parameters K_1 and ε.[1,12] Despite these fairly large error limits, significant trends in the values of k_0 with ligand are observed.

$$-\mathrm{d}[\mathrm{Fe(ORS)}^+]/\mathrm{d}t = \frac{2k_0\left\{\dfrac{K_1{}^2([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}{[\mathrm{H}^+]^4} + \dfrac{4K_1[\mathrm{Fe(ORS)}^+]}{[\mathrm{H}^+]^2}\right\}^{\frac{1}{2}}[\mathrm{Fe(ORS)}^+]^2}{1 + \left\{\dfrac{K_1{}^2([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}{[\mathrm{H}^+]^4} + \dfrac{4K_1[\mathrm{Fe(ORS)}^+]}{[\mathrm{H}^+]^2}\right\}^{\frac{1}{2}}} \quad (13)$$

$$\left(\frac{[\mathrm{H}^+]^3\left\{\dfrac{1 + 4[\mathrm{H}^+]^2[\mathrm{Fe(ORS)}^+]}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}\right\}^{\frac{1}{2}}}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)} + 1\right)\frac{1}{[\mathrm{Fe(ORS)}^+]} + \frac{2[\mathrm{H}^+]^4}{K_1{}^2([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^3}\log_e\left(\frac{\left\{\dfrac{1 + 4[\mathrm{H}^+]^2[\mathrm{Fe(ORS)}^+]}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}\right\}^{\frac{1}{2}} - 1}{\left\{\dfrac{1 + 4[\mathrm{H}^+]^2[\mathrm{Fe(ORS)}^+]}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}\right\}^{\frac{1}{2}} + 1}\right) + Q = 2k_0t \quad (14)$$

where $Q =$

$$-\left(\frac{[\mathrm{H}^+]^2\left\{\dfrac{1 + 4[\mathrm{H}^+]^2[\mathrm{Fe(ORS)}^+]_0}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}\right\}^{\frac{1}{2}}}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)} + 1\right)\frac{1}{[\mathrm{Fe(ORS)}^+]_0} - \frac{2[\mathrm{H}^+]^4}{K_1{}^2([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^3}\log_e\left(\frac{\left\{\dfrac{1 + 4[\mathrm{H}^+]^2[\mathrm{Fe(ORS)}^+]_0}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}\right\}^{\frac{1}{2}} - 1}{\left\{\dfrac{1 + 4[\mathrm{H}^+]^2[\mathrm{Fe(ORS)}^+]_0}{K_1([\mathrm{Fe}^{3+}]_0 - [\mathrm{HORSH}]_0)^2}\right\}^{\frac{1}{2}} + 1}\right)$$

$$[\mathrm{Fe(ORS)}^+]_0 = \tfrac{1}{2}\left\{[\mathrm{Fe}^{3+}]_0 + [\mathrm{HORSH}]_0 + \frac{[\mathrm{H}^+]^2}{K_1}\right\} - \left\{\left([\mathrm{Fe}^{3+}]_0 + [\mathrm{HORSH}]_0 + \frac{[\mathrm{H}^+]^2}{K_1}\right)^2 - 4[\mathrm{Fe}^{3+}]_0[\mathrm{HORSH}]_0\right\}^{\frac{1}{2}} \quad (15)$$

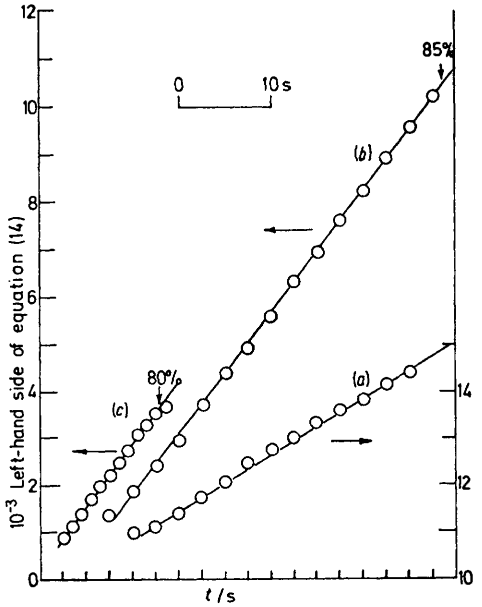


FIGURE 2 Plots of the left-hand side of equation (14) against time for the traces in Figure 1. The data are displaced on the time axis for the sake of clarity

(b) *Mechanism of Reaction*.—The extreme simplicity of the observed rate law (12) suggests that a bimolecular reaction mechanism is operative in these systems. Such rate-determining steps are not unknown for reactions of $\mathrm{Fe^{III}}$ and for the corresponding complexes in more basic media Leussing and his co-workers postulated a dimerisation process yielding a binuclear $\mathrm{Fe^{III}}$ intermediate in which two sulphydryl groups are attached to the same $\mathrm{Fe^{III}}$ ion and two-electron transfer *via* a hydroxyl bridge gives direct formation of the disulphide product. We consider a modification of this mechanism to be operative in the reactions examined above where both monomeric species are 1 : 1 complexes.

The expected lability of these mono complexes suggests that an inner-sphere electron transfer involving a transition state of the type (A) is possible. Since the reaction rates are one to two orders of magnitude greater than the overall anation rates[1,12] of the complexes, no metal–ligand cleavage is expected to take place and the rates may be governed either by rate-determining substitution of co-ordinated sulphur or by an increased rate of solvent exchange in the complexes. The effects of substituents X and Y on the thermodynamic parameters are consistent with an associative mechanism of this type where increasing the bulk of the group next to the sulphur intro-

TABLE 2

Rate constants, k_0, for various ligands at differing hydrogen-ion concentrations and $I = 1.0$M

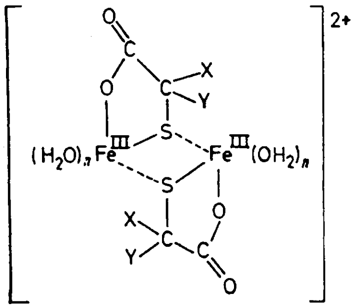
Ligand	θ_c/°C	$[H^+]$/M	$10^3[HORSH]_0$ / M	$10^2[Fe^{III}]_0$ / M	k_0 / l mol^{-1} s^{-1}
H_2ma	10	0.3	2.58	2.5	99
				5.0	104
		0.4	2.56	2.5	89
				5.0	100
	15	0.3	3.97	2.5	122
				5.0	117
		0.4	2.56	2.5	132
				5.0	134
	20	0.3	2.58	0.23	138
				1.75	147
				2.33	138
				2.92	149
				3.50	138
				5.83	141
		0.4	2.10	5.0	153
	25	0.3	2.58	2.5	164
				5.0	161
		0.4	2.56	2.5	168
				5.0	171
H_2mp	10	0.3	2.94	2.5	53
				5.0	54
		0.4	2.56	2.5	48 [a]
				5.0	62
	15	0.3	3.03	2.5	76
				5.0	83
		0.4	2.56	2.5	82
				5.0	88
	20	0.3	2.62	1.17	103 [a]
				1.75	98
				2.33	104 [a]
				2.92	98 [a]
				3.50	96
				4.67	101
				5.83	100
			2.64	2.5	102 [b]
				5.0	97 [b]
				2.5	96 [c]
				5.0	100 [c]
			2.54	1.46	97
				2.92	102 [d]
				4.38	100 [d]
				5.83	119 [d]
				2.92	102
				4.38	102 [a]
				5.83	101
		0.4	2.10	5.0	98
		0.25	2.48	2.5	100 [a]
		0.3			103
		0.4			101
		0.45			115
		0.50			99
		0.60			110
	25	0.3	2.94	2.5	124
				5.0	128
		0.4	2.56	2.5	136
				5.0	129
H_2mmp	10	0.3	2.48	2.5	33 [a]
				5.0	18 [a]
	15	0.3	2.58	2.5	25 [a]
				5.0	17 [a]
	20	0.3	2.77	1.75	45 [a]
				2.92	41 [a]
				3.50	28 [a]
				4.67	31
				5.84	28 [a]
		0.4	1.95	5.0	36
	25	0.3	2.48	2.5	44 [a]
				5.0	47
H_3ms [d]	10	0.3	2.57	2.5	27
				5.0	28
		0.4	2.51	2.5	27
				5.0	28
	15	0.3	2.71	2.5	38
				5.0	41

TABLE 2 (*Continued*)

θ_c/°C	$[H^+]$/M	$10^3[HORSH]_0$ / M	$10^2[Fe^{III}]_0$ / M	k_0 / l mol^{-1} s^{-1}
	0.4	2.51	2.5	40
			5.0	41
20	0.3	4.0	4.22	56
			3.17	61
			2.64	57
			2.11	53
			1.58	54
			1.06	54
			0.53	56
	0.4	4.0	5.3	59
			4.2	58
			3.7	60
			3.6	54
			3.2	57
			2.6	55
			2.1	52
			1.1	60
			0.5	60
	0.5		4.0	55
			3.5	61
			3.0	56
			2.5	56
			2.0	56
			1.5	55
			1.0	65
			0.5	56
	0.6		3.7	55
			3.17	57
			2.64	56
			2.11	55
			1.58	59
			1.06	62
25	0.3	2.57	2.5	68
			5.0	66
	0.4	2.51	2.5	72
			5.0	67

[a] From instantaneous rates [equation (13)]. [b] $[Fe^{II}]_0 = 0.00321$M. [c] $[Fe^{II}]_0 = 0.00642$M. [d] With rigorous oxygen exclusion.

duces steric hindrance which reduces the rate of dimerisation. If the effect were electronic in origin, acceleration



(A)

of the rate by methyl substituents would be envisaged contrary to the observed trend in rates. The negative activation entropies are also in accord with an associative mechanism.

While the exact nature of the interaction between two mono complexes remains uncertain, clearly the driving force must allow the two Fe^{III} centres to act as a concerted two-electron oxidant in the proximity of two sulphydryl groups with resulting disulphide formation thus eliminating the need to invoke high-energy radical species. Bimolecular redox reactions involving Fe^{III}

have also been reported for the oxidation of hydroxylamine [15] to give dinitrogen oxide (N_2O) where two hydroxylamine bridges are postulated in the intermediate. Further mechanisms of this type might be expected in the oxidation of species such as sulphurous acid,[16] iodide,[17] thiosulphate,[11] and thiocyanate [18] where the products are dimeric, though other mechanisms have been postulated in these cases. It is of interest to note that in the corresponding reaction of the Cr^{VI} mono complex with both thiourea [19] and cysteine [20] the major reaction path in the redox step involves incorporation of a second mol of reductant with subsequent reaction to a Cr^{IV} intermediate. Again the thermodynamic aspect of disulphide-bond formation is a feature of the kinetic path.

TABLE 3

Rate constants and thermodynamic parameters

Ligand	θ_c/°C	k_0 l mol^{-1} s^{-1}	$\Delta H^{\ddagger\,a}$ kcal mol^{-1}	$\Delta S^{\ddagger\,a}$ cal K^{-1} mol^{-1}
H_2ma	10	96.1 ± 6.1	5.3 ± 1.4	−30.7 ± 5.4
	15	126.4 ± 5.5		
	20	139.0 ± 5.9		
	25	166.9 ± 8.8		
H_2mp	10	53.3 ± 5.3	9.1 ± 2.2	−18.4 ± 3.4
	15	82.2 ± 4.1		
	20	101.1 ± 2.9		
	25	130.2 ± 5.1		
H_2mmp	10	24.0 ± 13.1 [b]	13.6 ± 3.9	−5.2 ± 1.3
	15	20.5 ± 10.2		
	20	33.9 ± 6.5		
	25	47.2 ± 4.0		
H_3ms	10	27.3 ± 2.2	10.1 ± 1.6	−16.0 ± 2.1
	15	40.1 ± 1.9		
	20	57.0 ± 0.8		
	25	67.7 ± 3.7		

[a] Error limits quoted are two standard deviations derived from an unweighted least-squares procedure. [b] Excluded in calculation of the thermodynamic parameters, since the data were derived solely from instantaneous rates.

Increasing methylation of these thiol ligands has previously been considered to retard the rate of electron transfer.[21,22] The evidence for such findings has been the persistence of coloured intermediates with H_2mmp or pencillamine compared with H_2ma or cysteine (Figure 1). It appears from our present data, where the rate of the redox reactions varies by only a factor of three, that such conclusions must be revised. It is apparent that these effects are attributable not solely to the electron transfer but more to the thermodynamic equilibrium constant for formation of the complexes which in the case of H_2mmp and H_2ma [1] vary by a factor of ten thus markedly affecting the concentration of the complexes available for reaction.

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