Cation Radicals of Phenothiazines. Part 4.[1] Electron Transfer Between Aquamanganese(III) and *N*-Alkylphenothiazines

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The kinetics of electron transfer between aquamanganese(III) and *N*-alkylphenothiazines, giving rise to the corresponding cation radicals, has been investigated in the range 0.20—1.50 mol dm^{-3} $HClO_4$ at different temperatures. The main reaction path has been assigned to the unhydrolysed species Mn^{3+}(aq), and there is a dependence of the rate constants on the corresponding reduction potentials.

THE role of manganese as an essential cofactor in photosynthetic water oxidation [2] has prompted several investigations on the chemical properties of various manganese complexes.[3] Manganese(III) is one of the possible oxidation states, which is often postulated as an intermediate in the cyclic redox processes.[2,4]

The kinetics of oxidation of organic substrates by means of aquamanganese(III) have therefore attracted attention [5] and different reaction mechanisms have been proposed for the species Mn^{3+}(aq) and $[Mn(OH)]^{2+}$(aq).[6]

In our previous studies, the kinetics and mechanism of electron transfer between Fe^{III},[1a] Co^{III},[1b] Np^{VI},[1c] in aqueous perchlorate media, as well as $[Fe(CN)_6]^{3-}$,[1a] with a series of *N*-alkylphenothiazines (later referred to as ptz) were investigated.

The present paper deals with the kinetics and mechanism of electron transfer between ptz and aquamanganese(III).

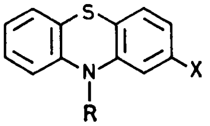
EXPERIMENTAL

Reagents.—Manganese(III) solutions were prepared by anodic oxidation of manganese(II) perchlorate solutions, as previously described.[5] Manganese(II) perchlorate was prepared by dissolution of $Mn[CO_3]$ in aqueous perchloric acid, the product being twice recrystallized from water. The phenothiazines (collected in Table 1) were supplied by Rhône-Poulenc. Perchloric acid and sodium perchlorate were used to adjust the acidity and the ionic strength. Doubly distilled water was used.

Procedure.—Manganese-(III) and -(II) solutions were standardized as previously described.[5] The kinetic runs were performed with a Durrum–Gibson stopped-flow spectrophotometer, in the spectral range 510—560 nm, by operating with ptz in excess. The concentration of Mn^{III} was 2.0×10^{-5}—2.5×10^{-5} mol dm^{-3}, while that of ptz ranged from 5.0×10^{-5} to 2.0×10^{-4} mol dm^{-3}. The acidity ($HClO_4$) range investigated was 0.20—1.50 mol dm^{-3}, the ionic strength being kept constant at 2.0 mol dm^{-3}. Kinetic runs were carried out at 7.0, 25.0, and 35.0 °C. Second-order plots were linear for at least three half-lives; the method proposed by Corbett [7] was also used and gave consistent values.

TABLE 1

Reduction potentials of investigated phenothiazines and spectral characteristics of the corresponding cation radicals

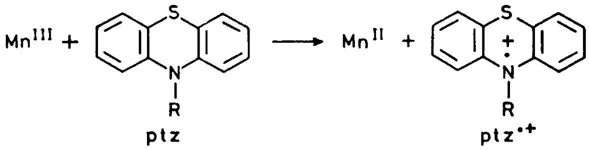


Compound	X	R	$E^{\ominus}$/V *	λ/nm	$10^{-3}\varepsilon$/ dm^3 mol^{-1} cm^{-1}
(1)	OH	$CH_2CH_2CH_2N(CH_3)_2$	0.62_5	562	9.5
(2)	OCH_3	$CH_2CH_2CH_2N(CH_3)_2$	0.71	566	9.0
(3)	H	$CH_2CH_2CH_2N(CH_3)_2$	0.71_5	513	9.2
(4)	H	$CH_2CH_2CH_2\overline{NCH_2CH_2N(CH_3)CH_2CH_2}$	0.72	514	9.4
(5)	Cl	$CH_2CH_2CH_2N(CH_3)_2$	0.78	525	10.2
(6)	H	$CH_2CH_2N(CH_3)_2$	0.82	511	10.5
(7)	H	$CH_2CH(CH_3)N(CH_3)_2$	0.86_5	515	9.3
(8)	H	$CH(CH_3)CH_2N(CH_3)_2$	0.89	524	8.8

* Derived from equilibrium measurements with Fe^{III};[1a] 25.0 °C, $[HClO_4]$ = 1.00 mol dm^{-3}, I = 1.0 mol dm^{-3}.

RESULTS AND DISCUSSION

Stoicheiometry.—By operating with Mn^{III} as limiting reagent, in order to avoid further oxidation of the cation radicals,[8] and by evaluating spectrophotometrically the cation radical formed, a 1 : 1 stoicheiometry was established, according to equation (1).



(1)

Kinetics.—The linearity of the second-order plots and the consistency of the second-order rate constants at different reagent concentrations suggest a first-order dependence on each reagent, according to the rate law (2). The acidity has a large effect on the reaction rates,

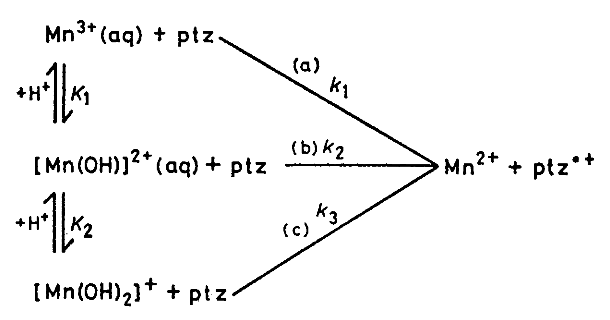
$$-\mathrm{d}[\mathrm{Mn^{III}}]/\mathrm{d}t = k_{\mathrm{obs.}}[\mathrm{Mn^{III}}][\mathrm{ptz}] \qquad (2)$$

as reported in Table 2, which collects the second-order rate constants at different acidities and temperatures.

TABLE 2

Second-order rate constants ($10^{-4}k_{\mathrm{obs.}}$/dm^3 mol^{-1} s^{-1}) for reactions of $\mathrm{Mn^{III}}$ with phenothiazines (I = 2.0 mol dm^{-3})

		[HClO$_4$]/mol dm^{-3}				
Compound	θ_c/°C	0.20	0.40	0.70	1.00	1.50
(1)	7.0	3.9	6.5	8.8	12.2	13.4
	25.0	7.1	11.2	16	23	25
(2)	7.0	1.0_5	1.5	2.2_5	2.8	3.2
	25.0	1.7_5	2.7	3.8	5.2	5.8
(3)	7.0	1.2_0	2.0_5	2.8	3.8	4.0
	25.0	2.3_5	3.6	5.3	7.0	7.6
	35.0	3.7		10.0		14.5
(4)	7.0	1.12	2.0	2.7	3.3	4.1
	25.0	2.2	3.5	4.8	6.5	7.2
(5)	7.0	0.71	1.1_5	1.6_5	2.2	2.3_5
	25.0	1.3_5	2.3	2.8_5	4.2_5	4.6
	35.0	1.7		4.1		6.6
(6)	7.0	0.21	0.35	0.47	0.65	0.71
	25.0	0.44	0.73	1.0_0	1.4_5	1.6
	35.0	0.72		1.7		2.4
(7)	7.0	0.23	0.35	0.43	0.64	0.68
	25.0	0.43	0.67	0.90	1.2_0	1.3_5
	35.0	0.70		1.5		2.3
(8)	7.0	0.24	0.35	0.46	0.68	0.71
	25.0	0.42	0.68	0.99	1.3_0	1.4_5



SCHEME

The treatment of the data can be based on the assumption that fast protolytic equilibria are established, according to the Scheme. A rate equation of the form (3) can then be derived and rearranged into (4). The protolytic equilibria of $\mathrm{Mn^{3+}(aq)}$ have attracted the interest of several investigators. Essentially, the conclusion was reached that K_1 *ca.* 1 mol dm^{-3} from spectrophotometric as well as potentiometric measurements.[9,10]

$$k_{\mathrm{obs.}} = \frac{k_1 + k_2K_1[\mathrm{H^+}]^{-1} + k_3K_1K_2[\mathrm{H^+}]^{-2}}{1 + K_1[\mathrm{H^+}]^{-1} + K_1K_2[\mathrm{H^+}]^{-2}} \qquad (3)$$

$$k_{\mathrm{obs.}}([\mathrm{H^+}] + K_1 + K_1K_2[\mathrm{H^+}]^{-1}) = k_1[\mathrm{H^+}] + k_2K_1 + k_3K_1K_2[\mathrm{H^+}]^{-1} \qquad (4)$$

If K_1 is assumed to be 0.93 mol dm^{-3} as in previous studies concerning $\mathrm{Mn^{III}}$,[5] with the related $\Delta H^{\ominus}$ = 4.8 kcal mol^{-1},[9,*] the plots in Figure 1 are obtained (K_2 is assumed to be negligible); the absence of a significant intercept indicates that the contribution from a reaction involving $[\mathrm{Mn(OH)}]^{2+}$(aq) may be neglected under the present conditions. Table 3 collected the rate constants and corresponding activation parameters.

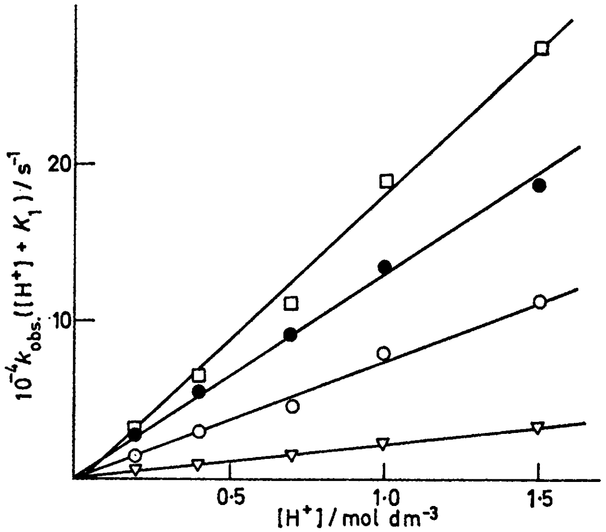


FIGURE 1 Plot of $k_{\mathrm{obs.}}([\mathrm{H^+}] + K_1)$ as a function of [H$^+$] for reaction of $\mathrm{Mn^{III}}$ with different phenothiazines: (□) (1), 7.0; (●) (3), 25.0; (○) (5), 25.0; (▽) (7), 25.0 °C

Similar (negligible) contributions of hydrolysed species to reactions were previously found with $\mathrm{Fe^{III}}$,[1a] $\mathrm{Co^{III}}$,[1b] and $\mathrm{Np^{VI}}$:[1c] in the present case, it is suggested that the reactivity of the hydrolysed species is approximately one to two orders of magnitude less than that of the unhydrolysed species. However, it is noteworthy that the reduction of $\mathrm{Mn^{III}}$ with several species has been shown to proceed largely through a path involving $[\mathrm{Mn(OH)}]^{2+}$(aq):[5,11] only in the case of tetramethylhydrazine[12] was this path found to be negligible. These results, together with the present data, suggest that, when transferable hydrogen atoms are present, $[\mathrm{Mn(OH)}]^{2+}$(aq) is the preferred reactant species, but in other cases a simple electron transfer to $\mathrm{Mn^{3+}(aq)}$ is operative.

TABLE 3

Rate constants ($10^{-4}k_1$/dm^3 mol^{-1} s^{-1})[a] and activation parameters for reactions of $\mathrm{Mn^{3+}(aq)}$ with phenothiazines[b]

	θ_c/°C				
Compound	7.0	25.0	35.0	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
(1)	19	41		6.5 ± 0.8	−11.0 ± 2.5
(2)	4.5	$9._5$		6.3 ± 0.9	−14.6 ± 3.0
(3)	5.5	$13._0$	26	8.7 ± 0.7	−5.7 ± 2.3
(4)	5.5	$12._0$		6.6 ± 1.0	−13.1 ± 3.3
(5)	3.3	7.5	$12._0$	7.3 ± 0.5	−11.8 ± 1.7
(6)	1.0_0	2.6	4.2	8.2 ± 0.5	−10.8 ± 1.7
(7)	0.9_5	2.2_5	3.9	8.0 ± 0.6	−11.8 ± 2.0
(8)	0.9_5	2.3		7.5 ± 1.0	−13.5 ± 3.3

[a] The standard deviation of the rate constants is 4—6%.
[b] Derived by assuming K_1 = 0.93 mol dm^{-3} and $\Delta H^{\ominus}$ = 4.8 kcal mol^{-1}.[9]

A recent work by Biedermann and Palombari[13] reported a higher value for K_1 (2.5 mol dm^{-3}) and an

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[*] Throughout this paper: 1 cal = 4.184 J.

estimate of K_2 (0.5 mol dm^{-3}). If these values are used, plots of the left-hand side of equation (4) as a function of $[H^+]$ were still linear, although with less satisfactory correlation coefficients, showing that path (b) is significant, while (c) can probably be neglected. The values of the rate constant k_1 are very close to those listed in Table 3, while those of k_2 are about half the corresponding constants for path (a). It is not the purpose of the present paper to draw any conclusion on the protolytic equilibria concerning Mn^{3+}(aq). However, it is noteworthy that, in the present reactions, path (b) becomes kinetically relevant only when such high values of the hydrolysis constants are considered.

It is evident from the data of Table 3, as is expected for an outer-sphere mechanism, that the free energy of activation is a function of the overall free energy of reaction.[14] Figure 2 shows a plot of the logarithm of the rate constant k_1 against the reduction potentials of the investigated phenothiazines.

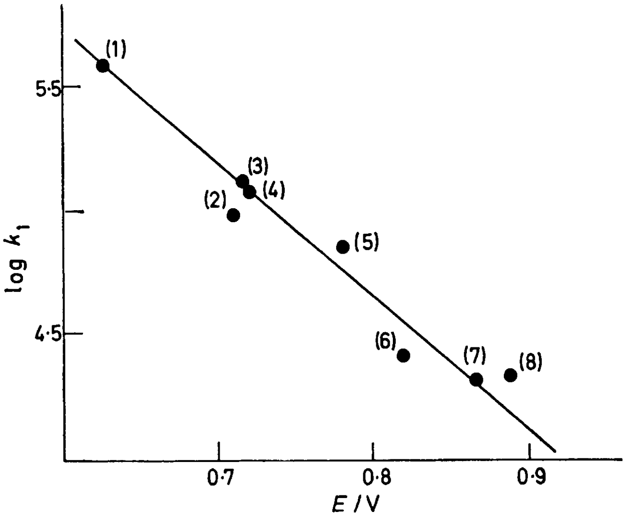

FIGURE 2 Plot of log k_1 against $E^{\ominus}$ for reaction of Mn^{3+}(aq) with phenothiazines (numbered as in Table 1)

Few cases of outer-sphere electron transfer involving Mn^{3+}(aq) are known without ambiguity: Diebler and Sutin[15] attempted to obtain some information on the $Mn^{3+/2+}$ couple from the reaction with phenanthroline complexes of iron(II) ($[FeL_3]^{2+}$). The Marcus theory[16] expresses the relation between the free energy of activation and the overall free energy of reaction in terms of equations (5)—(8), where Z is the collision

$$\Delta G^*_{12} = w_{12} + [\lambda_{12}(1 + \Delta G^{\ominus\prime}/\lambda_{12})^2/4] \qquad (5)$$

$$\lambda_{12} = 2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22}) \qquad (6)$$

$$\Delta G^{\ominus\prime} = \Delta G^{\ominus} - w_{12} + w_{21} \qquad (7)$$

$$k = Z \exp(-\Delta G^*_{12}/RT) \qquad (8)$$

frequency in solution, assumed to be 10^{11} dm^3 mol^{-1} s^{-1}, w_{12} and w_{21} are the work terms required to bring the reactants and products together, respectively, and w_{11} and w_{22} the work terms related to the self-exchange rates. By neglecting first the work terms, the value of λ_{12} which optimizes the present experimental data is 64 kcal mol^{-1}. From the known self-exchange rate for $ptz^{\cdot+}$–ptz systems ($\Delta G^* = 3.3$ kcal mol^{-1})[1a] and taking into account that Marcus theory predicts, particularly for aqua-ions, higher reaction rates,[17] a lower limit for the rate constant for $Mn^{3+/2+}$(aq) self exchange can be derived as 1×10^{-10} dm^3 mol^{-1} s^{-1}. A similar value can be derived from data for $[FeL_3]^{2+}$,[15] by adopting an appropriate self-exchange rate for $[FeL_3]^{3+/2+}$ couples.[18]

It is of interest that if the hydrolysis constants of Biedermann and Palombari[13] are assumed, then for path (b), involving $[Mn(OH)]^{2+}$(aq), the reaction rates should also depend on the nature of the compound; this conclusion is not in accord with the results obtained with substrates having transferable hydrogen atoms, for which a limiting mechanism has been advanced.[11] In the outer-sphere oxidations of $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ (en = ethylenediamine) by iron(III), the species $[Fe(OH)]^{2+}$(aq) was found to be a reactant, although the corresponding rate constants were about one sixth those for Fe^{3+}(aq).[19]

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