Further Evidence for Substitution Controlled Mechanisms in Redox Reactions of $MnOH_{aq}^{2+}$

G. DAVIES

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

Criteria for distinguishing inner-sphere, substitution-controlled mechanisms for redox reactions of transition metal aquocomplexes were summarized in a recent Review[1]. In particular, it was suggested there that variations in activation parameters for a series of reactions of $CoOH_{aq}^{2+}$ with a common mechanism of this type might be attributed to the effect of the formal charge product of the reactants in determining the enthalpy ΔH_0, and entropy, ΔS_0, of ion-association as part of the establishment of reaction precursors. Thus, for a dissociative interchange mechanism[2]

$$M + B^n \xrightarrow{\text{fast}} M, B^n \quad K_0 \tag{1}$$

$$M, B^n \xrightarrow{k_2} [MB^n] \tag{2}$$

we have $\Delta H_{obsd}^{\ddagger} = \Delta H_0 + \Delta H_2^{\ddagger}$ and $\Delta S_{obsd}^{\ddagger} = \Delta S_0 + \Delta S_2^{\ddagger}$; the observed activation parameters will be functions of the formal charge, n, on reactant B^n if $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are characteristic of the metal center M^1.

Although the detailed electronic and other requirements for substitution-controlled phenomena are still not fully understood, it would seem that some of the distinguishing mechanistic features[1] are recognizable even at quite labile metal centers, in particular at $MnOH_{aq}^{2+}$.[3] Briefly, the rate constants of redox reactions of $MnOH_{aq}^{2+}$ with a range of structurally distinct, but formally neutral, species fall in the narrow range $(2.3 - 8.3) \times 10^4 \ M^{-1} \ sec^{-1}$ at 25 °C and are of the same order of magnitude as that for complex formation with HF;[4] however, there is a dearth of potentially useful[1] experimental activation parameter data for aquomanganese(III) redox reactions, although data are available for the oxidation of thioureas[5] and, very recently, *o*-dihydroxybenzene[6].

The thiourea data[5] were originally interpreted in terms of attack of monoprotonated thiourea species TH^+ at the manganese(III) center over the majority of the experimental[5] acidity range, based on an assumed equilibrium constant[7] of $10^2 \ M^{-1}$ for reaction (3), where T is the unprotonated thiourea molecule.

$$T + H^+ \rightleftharpoons TH^+ \tag{3}$$

However, the rate constants derived on this basis[5] were larger than expected[3] for protonated reactants (*e.g.*, NH_3OH^+ and $NH_3NH_2^+$) and agreed better with typical values for formally neutral reductant species[5] (see above). Comparison of the available kinetic data for oxidation of thioureas[5] and *o*-dihydroxybenzene[6] by Mn_{aq}^{3+} and $MnOH_{aq}^{2+}$ which is now possible (Table) strongly suggests, at least for $MnOH_{aq}^{2+}$, that a substitution-controlled mechanism is operable for neutral reactants on the basis of both rate constants *and* activation parameters[8]; the equilibrium constant for reaction (3) is evidently much smaller than previously assumed[5] in aqueous acidic perchlorate media, as supported by independent spectrophoto-

TABLE. Kinetic Data for Redox Reactions of Aquomanganese(III) Species.

Reductant	$10^{-4} k_{Mn^{3+}}$[a]	$10^{-4} k_{MnOH^{2+}}$[a]	$\Delta H^{\ddagger}_{Mn^{3+}}$[b]	$\Delta S^{\ddagger}_{Mn^{3+}}$[c]	$\Delta H^{\ddagger}_{MnOH^{2+}}$[b]	$\Delta S^{\ddagger}_{MnOH^{2+}}$[c]
$(NH_2)_2CS$[d]	2.6	3.6	9 ± 1	−6 ± 2	11 ± 1	0 ± 2
$(MeNH)_2CS$[d]	≲ 0.16	3.2_5			10 ± 1	−1 ± 2
$(EtNH)_2CS$[d]	≲ 0.06	2.3			7 ± 1	−11 ± 2
$(CH_2NH)_2CS$[d]	≲ 0.2	8.3			10 ± 1	2 ± 2
H_2Cat[e]	0.65	2.9	10 ± 1	−12 ± 3	10 ± 1	−6 ± 3

[a] Units are $M^{-1} \ sec^{-1}$ at 25.0 °C.   [b] Units are kcal mol⁻¹.   [c] Units are cal deg⁻¹ mol⁻¹.   [d] Reassigned data from ref. 5 (see text).   [e] Data from Table IV of ref. 6: H_2Cat = *o*-dihydroxybenzene. The reported activation parameters for $MnOH_{aq}^{2+}$ have been corrected for the enthalpy and entropy of acid-dissociation of Mn_{aq}^{3+} (ref. 3).

metric data in concentrated aqueous sulfuric acid[9].

Perhaps the most encouraging aspect of the above considerations is an indication that variations in activation parameters *do* have potential as criteria for distinguishing the phenomenon of substitution-control in labile redox systems[1]. The enthalpy and entropy of activation for $CoOH_{aq}^{2+}$ reactions increase by *ca.* 2.5 kcal mol^{-1} and 10 caldeg^{-1} mol, respectively when the formal charge, n, decreases from 0 to -1 in B^n.[1] If these trends are maintained for the analogous substitution-controlled reactions of $MnOH_{aq}^{2+}$, then from the Table we have $\Delta H_{MnOH^{2+}}^{\ddagger}$ ~ 12 kcal mol^{-1} and $\Delta S_{MnOH^{2+}}^{\ddagger} \approx 5$ cal deg^{-1} mol^{-1} for negatively charged reductants, corresponding to $k_{MnOH^{2+}} \approx 1 \times 10^5 M^{-1}$ sec^{-1} at 25 °C. The only available estimate for the rate of oxidation of a negatively charged reductant by aquomanganese(III) is $k_{obsd} \geqslant 3 \times 10^5 M^{-1}$ sec^{-1} in the reaction with SCN$^-$ in 1.0 *M* HClO$_4$ at ionic strength 4*M* and 25 °C.[5,11]

References

1 I. Bodek and G. Davies, *Coord. Chem. Rev., 14*, 269 (1974).

2 T. W. Swaddle, *Coord. Chem. Rev., 14*, 217 (1974).

3 G. Davies, *Coord. Chem. Rev., 4*, 199 (1969).

4 H. Diebler, *Z. Phys. Chem., 68*, 64 (1969).

5 G. Davies, *Inorg. Chem., 11*, 2488 (1972).

6 E. Mentasti, E. Pelizzetti, E. Pramauro and G. Giraudi, *Inorg. Chim. Acta, 12*, 61 (1975).

7 T. J. Lane, J. A. Ryan and L. J. Walter, *J. Am. Chem. Soc., 78*, 5560 (1956). The equilibrium constant was calculated from data obtained in 50% aqueous dioxan.

8 The rate data for N,N'-diethylthiourea are anomalous for both Mn^{3+}$_{aq}$ and MnOH^{2+}$_{aq}$ and suggest the existence of special steric requirements for the oxidation of this particular ligand.

9 M. J. Janssen, *Rec. Trav. Chim. Pays Bas, 81*, 650 (1962); R. Zahradník, *Coll. Czech. Chem. Comm., 24*, 3678 (1959). We are grateful to Dr. M. R. Hoffmann for bringing these references to our attention. The kinetic data reported in ref. 5 now suggest that protonation of thiourea and its N,N'-dialkyl derivatives is only significant at [HClO$_4$] $\geqslant$ 3.0*M* (temperature dependent). However, the available kinetic data[5] are insufficient to allow realistic separation of kinetic and thermodynamic components and the oxidative instability of the thioureas in concentrated perchloric acid precludes independent determination of the equilibrium constants for reactions 3.[5,10]

10 I. Bodek and G. Davies, unpublished observations.

11 The rate constants for dissociatively-controlled substitution of NCS$^-$ at Fe(III)$_{aq}$ and Co(III)$_{aq}$ centers are anomalously greater than those for Cl$^-$ and Br$^-$, so the estimate for halide ions made here may, in fact, be fairly accurate.