Short-Lived Manganate(VI) and Manganate(V) Intermediates in the Permanganate Oxidation of Sulfite Ion

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The nature of detectable short-lived intermediates is of extreme importance in studies on the mechanisms of permanganate oxidations of both inorganic and organic compounds.[2] In the oxidation of unsaturated carboxylic acids manganese(III)[3] and manganese(IV)[4] have been detected. Manganese(V) esters[2-5] are usually postulated as intermediates in these oxidations, but it is difficult to obtain direct evidence supporting this assumption because no stable reference compounds of this type have been characterized. The hypomanganate ion, MnO_4^{3-}, is often invoked as an intermediate in permanganate reactions with inorganic reductants[2,6] and in the disproportionation[7] of MnO_4^{2-}, but no direct detection has been reported.

We now report direct spectroscopic evidence for manganate(VI) and manganate(V) ions as short-lived intermediates in the permanganate oxidation of sulfite ion. The evidence is based on the known visible spectra of MnO_4^{2-} and MnO_4^{3-} ions.[2a,8] The experiments were carried out in a stopped-flow device[9] (mixing time 1 ms) combined with a Tracor Northern Diode Array Rapid Scan Spectrophotometer (DARSS, spectral range 200–800 nm).

The overall reaction between pH 8 and 12 (eq 1) consists of

$$2MnO_4^- + 3SO_3^{2-} + H_2O \rightarrow 2MnO_2 + 3SO_4^{2-} + 2OH^- \quad (1)$$

two distinct phases, viz., the accumulation and decay of MnO_4^{2-}. The four successive spectra shown in Figure 1 refer to the first, faster phase (55 ms). Scan 1 displays most of the spectral features of MnO_4^-, but superposition of another species is apparent. Scans 2–4 show the gradual disappearance of MnO_4^- and the formation of MnO_4^{2-}. The final spectrum is that of MnO_4^{2-} (bands at 436 and 610 nm), which persists for several hundred milliseconds. Significantly, the reduction of MnO_4^- to MnO_4^{2-} (eq 2) does not

$$2MnO_4^- + SO_3^{2-} + 2OH^- \rightarrow 2MnO_4^{2-} + SO_4^{2-} + H_2O \quad (2)$$

involve any detectable intermediate assignable as manganese(V). This is consistent with outer-sphere electron transfer steps 3 and 4, in line with earlier conclusions of Halperin and Taube.[10] Sulfite

$$MnO_4^- + SO_3^{2-} \rightarrow MnO_4^{2-} + SO_3^- \quad (3)$$

$$MnO_4^- + SO_3^- \rightarrow MnO_4^{2-} + SO_3 \quad (4)$$

$$SO_3 \rightarrow SO_4^{2-} \quad (5)$$

oxidation by copper(III) tetraglycine follows a similar mechanism, as demonstrated by Anast and Margerum.[11]

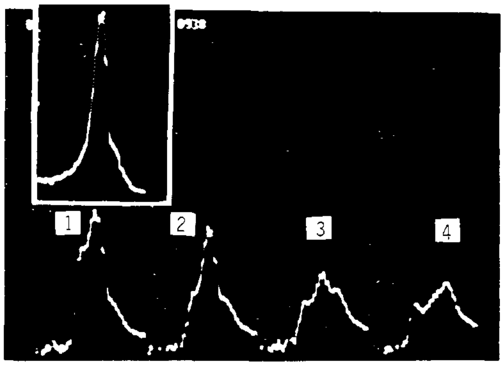

Figure 1. Four successive spectra (200–800 nm) in the first, faster phase of reaction 1. Duration of one scan: 5.15 ms. Time of triggering scan n is $t_n = 8.2 + 15.7(n - 1)$ ms after the flow stopped. Initial concentration: 2×10^{-4} M MnO_4^-, 5×10^{-4} M SO_3^{2-}, pH 9.10. Reactant solutions prepared and stored under N_2. Glass light pipes create an apparent zero absorbance below 400 nm. Insert: spectrum of MnO_4^- ion as recorded by the DARSS.

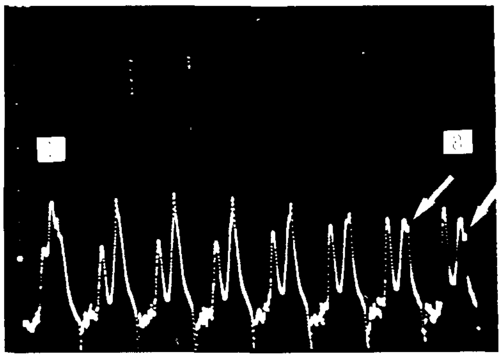

Figure 2. Eight successive spectra (200–800 nm) in the second, slower phase of reaction 1. Duration of one scan: 5.15 ms. Time of triggering scan n is $t_n = 49 + 123(n - 1)$ ms after the flow stopped. Conditions as in Figure 1. Arrows indicate the 660-nm band of MnO_4^{3-}.

The direct reduction of MnO_4^{2-} by sulfite is very slow, as revealed by experiments at pH 13.5, where it is stable against disproportionation. Thus MnO_4^{2-} is the product at pH >12.5, but below that pH it starts to decay via disproportionation in the second, slower phase, yielding MnO_4^- and manganese(IV). The slower phase is second order in MnO_4^{2-}, the rate constant increasing with decreasing pH. The MnO_4^- thus produced oxidizes SO_3^{2-} rapidly, as in steps 3 and 4. The manganese(IV) does not precipitate immediately as MnO_2, but forms a yellow solution stable for 20–40 min. These solutions may contain colloidal MnO_2.

The second phase of sulfite oxidation is accompanied by the spectral changes shown in Figure 2 (900 ms). MnO_4^- ion is present during scan 1, but it is absent from all the subsequent spectra. Afterward, the 430-nm band increases and the 610-nm band decreases in intensity. Remarkably, the latter band is asymmetric,

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the top intensity shifting gradually to higher wavelengths. Finally, a new band developes at about 660 nm. In the light of literature data,[2a,8] this can be assigned to the MnO_4^{3-} ion. To our knowledge this is the first clear-cut case where the transient appearance of a manganate(V) intermediate has been demonstrated in a permanganate oxidation.

The changes in relative intensity of the two bands in Figure 2 are due to the increasing concentration of the soluble manganese(IV) species, which does not absorb above ca. 540 nm but has a gradually increasing absorptivity below that wavelength.[4]

The slower phase can be rationalized in terms of the following reactions:

$$2MnO_4^{2-} \rightarrow MnO_4^{-} + MnO_4^{3-} \tag{6}$$

$$2MnO_4^{3-} \rightarrow MnO_4^{2-} + Mn^{IV}_{sol} \tag{7}$$

The MnO_4^- formed in (6) is rapidly reduced by sulfite to MnO_4^{2-}, eq 3-5; therefore, permanganate ion is not detectable during the slow phase. MnO_4^{2-} is consumed via disproportionation only, reaction 6.

Work is in progress on the kinetics of the title reaction.

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Registry No. SO_3^{2-}, 14265-45-3; MnO_4^-, 14333-13-2; MnO_4^{3-}, 14333-15-4; MnO_4^{2-}, 14333-14-3.

Evaluation of Reaction Free Energy Surfaces in Aqueous Solution: An Integral Equation Approach

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The effects of a solvent medium on chemical reactions can be very large. When a reaction occurs in a solution, one must consider not only the potential energy for the reaction species but also the free energy due to solvent rearrangement. As a result changes in the reaction rate of up to 20 orders of magnitude are well-known.[1] In this communication, we present a test of a computationally feasible method to calculate such solvent effects for polar systems. It is based on the use of our extended RISM integral equation approach[2] to calculate solvation structure and a charging approach[3] to obtain free energy differences. The integral equation approach used is based on the RISM integral equation generalized for continuous potentials, developed by Chandler and co-workers.[4,5] This element is in common with the further development by Kojima and Arakawa[6] and with the numerical studies by Johnson and Hazoume.[7] Our development for polar systems[2] is distinguished from these earlier studies in that the screening of the Coulomic interactions among charged sites in polar molecules is handled analytically at the outset in close analogy to the Debye–Huckel summation in ionic solutions. This provides substantial simplification from both the analytical and computational viewpoints. The test case is the free energy surface for the S_N2 exchange reaction of chloride with methyl chloride ($Cl^- + CH_3Cl$). Using the interaction site potentials calculated by Chandrasekhar et al.,[8] we are able to compare our results with their elegant Monte Carlo results along a reaction coordinate for collinear approach. The reaction coordinate here is defined as[8] $r_C = r_{CCl'} - r_{CCl}$ where Cl′ is the leaving group.

The reactant species for this calculation are conveniently viewed as a *single* polyatomic molecule with bond distances and interaction potentials with the solvent that are a function of the reaction coordinate. The S_N2 reaction free energy surface in solution is then equivalent to the calculation of the intramolecular potential of mean force or cavity distribution function[9,10] for the polyatomic at infinite dilution in a molecular solvent.

In order to calculate the (multipoint) potential of mean force or equivalent free energy, the pairwise additive site–site interaction potential of the solute–solvent system is expressed as a function of a coupling parameter λ.[3] That is, the total potential energy U is given by

$$U(\lambda) = \lambda \sum_{\mu\nu} u_{\mu\nu} + \sum_{\nu\nu'} u_{\nu\nu'} \tag{1}$$

where index μ refers to the atomic interaction sites on the "solute" molecule and ν to sites on the solvent molecules. The sums include all distinct intermolecular site–site pairs. The free energy of the system can be expressed as an integral over the coupling parameter as

$$A = A_0 + \int_0^1 d\lambda \; dA(\lambda)/d\lambda \tag{2}$$

where A_0 is a reference free energy (noninteracting solute).

With use of the relation of the free energy to the partition function, $-\beta A = \ln Q$, to take the free energy derivative (β is the inverse of the product of Boltzmann's constant and the temperature), the free energy can be expressed as

$$A - A_0 = \int_0^1 d\lambda \int dr \sum_{\mu\nu} u_{\mu\nu} \frac{e^{-\beta U(\lambda)}}{Q} \tag{3}$$

where $A - A_0$ is the free energy to add the solute molecule, and the spatial integration over r extends over all solvent coordinates. Equation 3 can be expressed exactly in terms of the solute–solvent radial site–site distribution functions[10] $g_{\mu\nu}(r)$ as

$$A - A_0 = 4\pi\rho \int_0^1 d\lambda \sum_{\mu\nu} \int_0^\infty dr \; r^2 u_{\mu\nu}(r) g^{\lambda}_{\mu\nu}(r) \tag{4}$$

where ρ is the solvent density and $g^{\lambda}(r)$ refers to the distribution functions for the system with the interaction potential $U(\lambda)$. The relevant potential of mean force is then given by the difference

$$W(r_C) = A\{r_C\} - A\{r_C = \infty\} + U_0(r_C) \tag{5}$$

where $A\{r_C\}$ is the charging free energy of the solute molecule with the intramolecular bond distances and solute–solvent interaction potentials defined by the reaction coordinate r_C[8] and $U_0(r_C)$ is the gas-phase intramolecular potential.

The solute–solvent correlation functions were calculated by using the extended RISM equation for infinitely dilute solutions.[2] The solvent was described here using the TIPS water potential;[11] the water pair distribution functions obtained by this procedure

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