X-ray Absorption Spectra of MnO_4^- and MnO_4^{2-} with Synchrotron Radiation: A Study of Structure and Bonding Properties of Transition-Metal Complexes in Solution

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We wish to report differences in the structures of the K X-ray absorption edges of solid $KMnO_4$ and aqueous solutions of permanganate and manganate. The applicability of synchrotron radiation to the determination of solution structures[1] is further demonstrated by these results.

An X-ray absorption spectrum may be divided into the near-edge and the EXAFS regions.[2-15] Below the ionization threshold (E_0), discrete absorption peaks are often observed. These absorptions arise from transitions of the core electrons (e.g., K electrons) to unoccupied bound states.[12-14] Absorption features in the near-edge region above the threshold are often broad and exhibit shake resonances.[16,17] In the EXAFS region (from ~40 to ~1000 eV above E_0) the absorption coefficient oscillates. $\chi(k)$, the conventional EXAFS function,[6] is usually written as

$$\chi(k) = \sum_i A_i(k) \sin [2kr_i + \phi_i(k)] \tag{1a}$$

$$A_i = [N_i/(kr_i^2)]f_i(\pi,k) \exp(-2\sigma_i^2k^2) \exp(-2r_i/\lambda) \tag{1b}$$

$$k = [2m(E - E_0)]^{1/2}/\hbar \tag{1c}$$

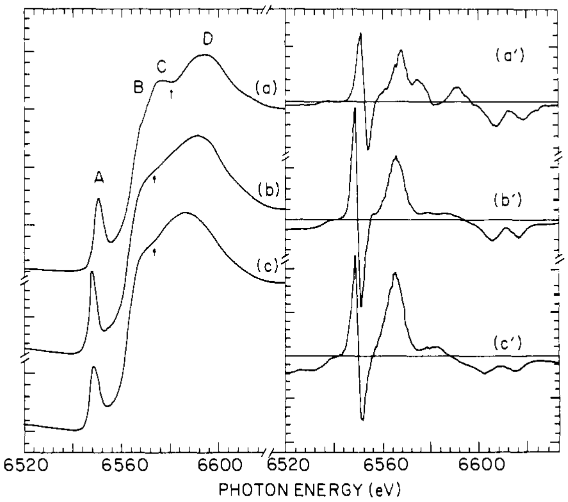

Figure 1. Edge structure of (a) $KMnO_4$ (solid), (b) $KMnO_4$ (aqueous), and (c) K_2MnO_4 (aqueous) and their corresponding first derivatives; the arrows indicate the tentative position of E_0 obtained from EXAFS analysis.

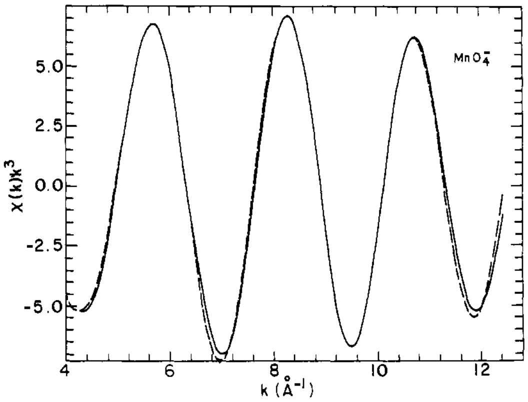

Figure 2. Best fit for the filtered $KMnO_4$ (aqueous) EXAFS (dotted curve) $\chi(k)k^3$ with theoretical functions (ref 11). The original data were Fourier filtered with a window (~0.4–2.0 Å in the r space) and then truncated to this data length in k space.

Table I. EXAFS Parameter[a] of MnO_4^-, MnO_4^{2-}, and $Mn(H_2O)_6^{2+}$

sample	r, Å	σ, Å[e]
$KMnO_4$ (solid)	1.631 (1.629 ± 0.008)[b]	0.048
$KMnO_4$ (aqueous)	1.624	0.054
K_2MnO_4 (aqueous)	1.666 (1.660 ± 0.009)[c]	0.056
$Mn(H_2O)_6^{2+}$ (aqueous)	2.177[d]	0.081

[a] These are $\chi(k)k^3$ fits from $k = 4$ to $k = 12.5$ Å^{-1}. Fitting one set of data as a model compound onto another gives nearly the same r values; errors are ≤0.01 Å for r; these are room temperature measurements. The r values in parentheses are from X-ray crystal structures. EXAFS results for MnO_4^- ($r = 1.649$ Å) from ref 19(b) are slightly different from ours; a detailed comparison will be given elsewhere. [b] From X-ray structure of $KMnO_4$ crystal. This is an average value of 1.622, 1.625, and 1.634 (2) Å; see ref 22. [c] From X-ray structure of K_2MnO_4 crystal. This is an average of 1.647, 1.669, and 1.661 (2) Å; see ref 22. [d] The X-ray crystal structure has not been well determined. [e] σ is the root mean square deviation of r used in eq 1b; estimated uncertainty is ±0.005 Å.

where k is the wave vector, E is the photon energy, N_i the coordination number of the ith shell, r_i is the radial distance to the ith atom, $f_i(\pi,k)$ is the back-scattering amplitude function (which depends only upon the nature of the scattering atom), σ_i^2 is the mean square deviation of r_i, ϕ_i is the phase-shift function for both the absorber and scatterer, and λ is the mean free path of the photoelectrons ($\exp(-2r_i/\lambda)$ is close to unity for the nearest neighbors in a molecular complex).

X-ray absorption spectra were recorded in a transmission mode at the Stanford Synchrotron Radiation Laboratory. The permanganate solutions were prepared as saturated solutions (~0.5 M) in triple distilled water. The manganate ion was obtained by

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reducing strongly basic permanganate solutions with Na_2SO_3. The EXAFS spectra were analyzed by using eq 1 with a filtered Fourier transform and fitting procedure in which theoretical phase shift and amplitude functions described by Teo and Lee[11] are used. The absorption edge regions were recorded at small energy steps[18] at room temperature.

Differences in the Mn K near-edge spectrum between polycrystalline $KMnO_4$ and aqueous solutions of MnO_4^- and MnO_4^{2-} are observed. The near-edge regions are displayed in Figure 1 together with their first derivatives. It can be noted that peaks B and C in Figure 1 are considerably broader for the MnO_4^- solution than for solid $KMnO_4$ while peak A, the 1s → t_2(3d) transition, is narrower. Further, a small shift to lower binding energy upon solvation is observed. At the present time, most of this shift is attributed to the instrumentation.[18]

Peaks B and C are consistent with those reported previously[14,19] and can be assigned tentatively to 1s → a_1(4s) and 1s → t_2(4p) transitions.[17,20] The broadening of these features in solution, particularly peak C (Figure 1), cannot be due to vibrational or collisional broadening. If these mechanisms were pertinent, one would expect a similar, if smaller, effect on the 1s → t_2(3d) transition peak A. We propose that the broadening of peaks B and C is due to the formation of virtual resonance (hybridized) states in the dielectric medium. Since the 4p orbitals extend radially from the MnO_4^- framework, they can form dynamic "band"-like states with the solvent. This mechanism would broaden the Mn 4p levels of the solid into a resonance state in solution.

Peak D is located 42 and 38 eV above the 1s → t_2(3d) transition in MnO_4^- and MnO_4^{2-}, respectively. These are the resonance states discussed by Kutzler et al.[17] We are presently carrying out calculations[21] for the MnO_4^- and MnO_4^{2-} ions in order to assign the near-edge spectra quantitatively.

Our EXAFS results for these systems, perhaps the most important information in the present study, are given in Table I together with X-ray crystal data.[22] A typical fit of our data is shown in Figure 2. We can see from Table I that MnO_4^- acts as a unit in both solid and solution. The values for the metal-oxygen distances determined by EXAFS and X-ray crystal structure are in close agreement. The difference in the Mn–O bond distance Δr between MnO_4^- and MnO_4^{2-} in solution[23] is 0.042 Å.

The values for the manganese-oxygen bond distances determined in this study allow one to calculate the activation parameters for the $MnO_4^{2-/1-}$, electron-exchange reaction.[24-26] When formulas based upon a harmonic oscillator model are used,[26] the Mn–O distance in the transition state is calculated to be 1.644 Å. This corresponds to an inner-sphere reorganization energy of only 1.6 ± 0.2 kcal mol^{-1}. The amount of stretching (and compression) of the Mn–O bonds required to reach the transition state are 0.020 and 0.022 Å for MnO_4^- and MnO_4^{2-}, respectively. These can be compared to the amplitude of the totally symmetric vibration σ_{vib}. Using 839 and 812 cm^{-1} for the symmetric breathing frequency ($\bar{\nu}$) of MnO_4^- and MnO_4^{2-}[27] and $\sigma_{vib}^2 = (h/32\pi^2\mu c\bar{\nu}) \coth (hc\bar{\nu}/2kT)$,[28] we obtain $\sigma_{vib} = 0.018$ Å for both Mn–O bonds. Thus the symmetric breathing motion at room temperature encompasses almost all of the reorganization necessary. These results can be contrasted with those found for the relatively slow $Fe(H_2O)_6^{2+/3+}$ exchange reaction.[29] For the iron system the difference in Fe–O bond lengths between the two oxidation states is 0.11 Å[1] which results in an inner-sphere reorganization energy of 5 kcal mol^{-1}. For this reaction the Fe–O reorganizations are 0.065 and 0.040 Å, and the totally symmetric vibrational amplitude (σ_{vib}) are 0.023 and 0.019 Å for $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, respectively.[1]

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(18) (a) The resolution of the focused EXAFS beam line with Si $\langle 111 \rangle$ crystals is ~3 eV at the Mn K edge (~6.5 keV) (this work). Caution must be used in measuring binding-energy shifts, because of beam instability and monochromator tuning effects. $KMnO_4$ has been used as a standard for the calibration of photon energy and resolution of the spectrometer. A width of ~1.5 eV has been obtained for the 1s → 3d transition with the SSRL wiggler beam line, compared to ~4 eV reported here. (b) We have observed shifts varying from ~1 eV to a few tenths of an electron volt by running solid and solution samples alternately; more quantitative results which can only be obtained with spectrometers of high resolution are needed to establish the correlation between binding-energy shift and solvation.

(19) The gross feature of the near edge spectrum of MnO_4^- has been reported earlier by: (a) Jaklevic, J.; Kirby, J. A.; Klein, M. P.; Robertson, A. S.; Brown, G. S.; and Eisenberger, P. *Solid State Commun.* **1977**, *23*, 679. (b) Rabe, P.; Tolkiehn, G.; Werner, A. *J. Phys. C* **1979**, *12*, 1173. No discussion or comparison of the $KMnO_4$ solid and solution results are given in these studies, however.

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Photodissociation Spectra of Pyridinyl Radical Dimers Detected by Reverse Pulse Polarography. Revised View of the Electrochemistry of Nicotinamide Adenine Dinucleotide

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In our studies of 1-alkyl-2-carbomethoxypyridinyl radicals (**2·**),[1] we concluded that the absorption spectrum of the major form present in solution (the radical dimer) could be best explained by interpreting the longest wavelength absorption as a $\pi\sigma \rightarrow \pi\sigma^*$ transition.[1] Although photodissociation of the dimer [(**2·**)$_2$] to the pyridinyl radical (**2·**) can be produced readily by irradiation in thin films at low temperatures or by nanosecond laser pulse irradiation of acetonitrile solutions at 337 nm, it was not possible to obtain excitation spectra for dissociation from these experiments.[1]

Examination of the spectra of 1-alkyl-3-carbomethoxy- and 1-alkyl-3-carbamidopyridinyl radical dimers (3–3) indicated that the longest wavelength absorption bands had (a) a peculiarly low absorption coefficient (in comparison to related 1,4-dihydro-

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