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# A Pulse Radiolysis Study of the $MnO_4^{2-}$ ion. The Stability of Mn(V) in 0.1 $M$ NaOH

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Although the hypomanganate ion, $MnO_4^{3-}$, can be stabilized only in extremely high base [1] reports of Mn(V) under more moderate conditions have been confined to its production as an uncharacterized reaction intermediate. For example, Mn(V) appears to be produced in the acid disproportionation of Mn(VI) [2] and as an intermediate in several permanganate redox reactions [1, 3–5]. However, there have been no direct studies of the spectral features or stability of the manganese (V) oxo-ion in the absence of very high concentrations of hydroxide ion.

In the present work, we have taken advantage of the relative stability of manganate ion, $MnO_4^{2-}$, in dilute base and have looked at the oxidation and reduction of Mn(VI) by the $O^-$ radical and the aquated electron respectively.

## Experimental

The optical pulse radiolysis experiments were carried out at the linear electron accelerator at the Hebrew University of Jerusalem. The experimental procedures have been described elsewhere [6]. All reactant solutions were 0.1 $M$ in hydroxyl ion concentration ($\mu = 0.1$ $M$) and the temperature was maintained at 22 ± 2 °C. Manganate was prepared as in ref. 2 and initial $MnO_4^{2-}$ concentrations varied from $2 \times 10^{-5}$ $M$ to $1 \times 10^{-4}$ $M$. Up to $2 \times 10^{-5}$ $M$ $MnO_4^-$ was added to some solutions.

Under the alkaline conditions of this study, the radiolysis of water in argon saturated solutions leads to essentially equal yields of the hydrated electron, $e_{aq}^-$, and $O^-$ ion. In $N_2O$ saturated solutions $e_{aq}^-$ is rapidly converted to $O^-$ [7]. Pulse intensity was such that the combined yield of $e_{aq}^- + O^-$, as measured by $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ dosimetry [6], was between about $8 \times 10^{-6}$ $M$ and $1.8 \times 10^{-5}$ $M$. In order to monitor spectral changes throughout the region from 300 nm to 740 nm, effective optical paths of both 12 cm and 2 cm were employed.

## Results and Discussion

In $N_2O$ saturated solutions of $MnO_4^{2-}$ the observed spectral changes can be attributed to the reaction

$$MnO_4^{2-} + O^- + H_2O \rightarrow MnO_4^- + 2OH^- \qquad (1)$$

with an observed second order rate constant $k_{MnO_4^{2-}+O^-} = 8 \times 10^8$ $M^{-1}$ $sec^{-1}$ (±25%). In argon saturated solutions, a much faster reaction was also observed giving rise to a rather long lived species with a spectral peak at 305 nm. We attribute this reaction to the reduction of $MnO_4^{2-}$ to Mn(V) by the aquated electron. The rate of this process is essentially diffusion controlled with a rate constant, $k_{MnO_4^{2-}+e_{aq}^-} = 2 \times 10^{10}$ $M^{-1}$ $sec^{-1}$, somewhat smaller than that reported for the reduction of permanganate by $e_{aq}^-$ ($k_{MnO_4^-+e_{aq}^-} = 3.7 \times 10^{10}$ $M^{-1}$ $sec^{-1}$) [8]. Throughout the region measured, comparison of optical density changes agree qualitatively with those expected for $MnO_4^{2-}$ loss accompanied by production of $MnO_4^{3-}$ and $MnO_4^-$, [1] except that the $MnO_4^{3-}$ absorbance near 700 nm was not persistent (*vide infra*). This is illustrated in Fig. 1 which gives absorbance changes after completion of the two formation reactions. The maxima at (a) and (b) are close to those reported for $MnO_4^{3-}$ and $MnO_4^-$, respectively. Two-step loss of $MnO_4^{2-}$ is observed at points (c) at which both $MnO_4^-$ and $MnO_4^{3-}$ have low absorbtivity. A $MnO_4^-$–$MnO_4^{2-}$ isosbestic point occurs near (d). Lack of quantitative agreement with expected changes in absorbtivities (observed changes were always somewhat less than expected) is probably due to the low concentration of $MnO_4^{2-}$ and large pulses employed which permit spontaneous loss of $e^-$ and $O^-$ on a time scale similar

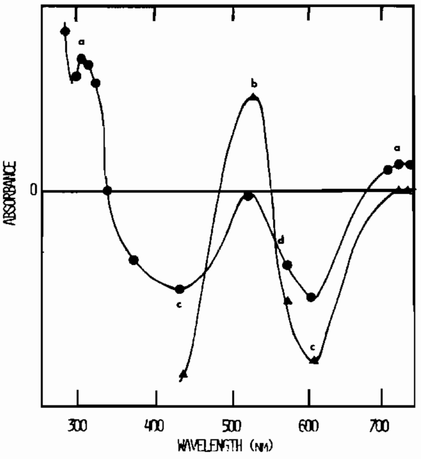

Fig. 1. Absorbance changes (arbitrary scale) for $3 \times 10^{-5}$ $M$ $MnO_4^{2-}$ solutions at 20 msec (●) and 2 μsec (▲) after the pulse.

to those of the desired reactions (*e.g.* $k_{e_{aq}^- + O^-} = 2 \times 10^{10}\ M^{-1}\ sec^{-1}$, $k_{e_{aq}^- + e_{aq}^-} = 5 \times 10^9\ M^{-1}\ sec^{-1}$ [9]).

In the absence of added $MnO_4^-$ the absorption increase at 305 nm is stable for at least 40 seconds (<15% change) in solutions with $MnO_4^{2-} \sim 2.5 \times 10^{-5}\ M$ and $Mn(V) \sim MnO_4^- \sim 3 \times 10^{-6}\ M$. Thus, it appears that in 0.1 $M$ $OH^-$ the hypomanganate ion should be stable towards reaction with the solvent for at least one minute. We may also estimate an upper limit for reaction between Mn(V) and $MnO_4^{2-}$ as for example in reaction (2).

$$Mn(V) + MnO_4^{2-} \xrightarrow{0.1\,M\ OH^-} Mn(IV) + MnO_4^-$$

$$k < 4 \times 10^4\ M^{-1}\ sec^{-1} \qquad (2)$$

At higher $[MnO_4^{2-}]$ and larger pulses a decomposition reaction involving both $MnO_4^-$ and Mn(V) is observed which is accompanied by apparent regeneration of $MnO_4^{2-}$. This behavior is consistent with the conproportionation reaction

$$MnO_4^- + Mn(V) \rightarrow 2MnO_4^{2-} \qquad (3)$$

A value of $k_{MnO_4^- + Mn(V)} \sim 10^4$ seems consistent for reaction (3). This value should be considered a rough estimate however, because of a variety of possible side reactions and the uncertainty over solute concentrations, especially in experiments with added $MnO_4^-$.

Our identification of metastable Mn(V) in 0.1 $M$ NaOH lends credence to the postulation of hypomanganate or complexed hypomanganate as an intermediate in a number of kinetic studies [1–5]. Although we did not observe a long-lived spectral absorbance at 700 nm and above, such an absorbance increase was observed in some experiments with a rate equal to that of Mn(V) formation but which decreased back to zero within about 2 msec (Fig. 1). It seems plausible that, since protonation is expected as basicity is decreased, the $MnO_4^{3-}$ ion produced in the initial reduction is converted during this time to $HMnO_4^{2-}$ which retains the 305 nm peak but does not absorb at higher wavelengths. While this interpretation is consistent with a recent electrochemical study [10], we cannot rule out instrumental artifacts at these higher wavelengths. The lack of long term stability for hypomanganate ion under these conditions is, indeed, indicative of a protonated species [1].

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