

Permanganate formation in the reactions of ozone with Mn(II): a mechanistic study

Erika Reisz, Achim Leitzke, Alexandra Jarocki, Rudolf Irmischer and Clemens von Sonntag

ABSTRACT

Ozone treatment of Mn^{2+} -containing waters is reported to lead to MnO_4^- formation. This complex reaction is investigated on the model level. In neutral solution, the main product is MnO_2 and only 10% MnO_4^- are formed even at high ozone excess. In acid solution, however, or in neutral solution when Mn^{2+} is complexed by polyphosphate, oxalate, sulfate, bicarbonate or phosphate, the reaction proceeds to MnO_4^- in an up to 100% yield. In this reaction, three-times more O_3 is consumed than stoichiometrically required indicating that higher manganese oxidation states can also be reduced by O_3 (e.g., $MnO^{2+} + O_3 \rightarrow Mn^{2+} + 2O_2$). In acid solution or in the presence of a complexing agent and with Mn(II) in excess, Mn(III) is formed by comproportionation of Mn(II) with Mn(IV). Mn^{2+} -containing waters are accompanied by Fe^{2+} that also induces MnO_4^- formation. Fe^{2+} reacts 650-times faster with O_3 than Mn^{2+} , and the oxidation of Mn^{2+} by Fe(IV) to Mn(III) can circumvent MnO_2 formation. Mn(III) can then be oxidized to MnO_4^- . The thermodynamics of the suggested reactions is discussed. The MnO_4^- formation in drinking water and wastewater is most likely due to the presence of Fe^{2+} in these waters rather than due to complexation of Mn^{2+} by NOM or inorganics.

Key words | iron, manganese, oxalate, ozone, permanganate, polyphosphate

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INTRODUCTION

Ozonation is widely used in drinking water treatment for disinfection (Ellis 1991; von Gunten 2003b) as well as for the removal of unwanted contaminants (von Gunten 2003a). In the effluents of municipal wastewater treatment plants, there are still a large number of micropollutants (pharmaceuticals, human care products, technical products with endocrine properties) present after the biological treatment (Richardson & Bowron 1985; Halling-Sørensen *et al.* 1998; Hirsch *et al.* 1999; Ternes 2001; Heberer 2002; Soulet *et al.* 2002; Huggett *et al.* 2003; Lee *et al.* 2003; McArdell *et al.* 2003; Ternes *et al.* 2003; Fahlenkamp *et al.* 2004; Miao *et al.* 2004; Quintana & Reemtsma 2004; Halden & Paull 2005; Jones

et al. 2005; Quintana *et al.* 2005). Even at these very low concentrations, they are harmful to aquatic life. With this in mind, an improvement of the water quality of our surface waters requires some action, and the elimination of these micropollutants from wastewater effluents is now widely studied. Adsorption on activated carbon (Nowotny *et al.* 2007) and ozonation of the effluents (Ternes *et al.* 2003; Huber *et al.* 2005) are the most promising approaches.

There is an increasing concern as to the formation of unwanted by-products, and our mechanistically-oriented studies on the reactions of ozone in aqueous solution were mainly undertaken to be able to predict such potential

oxidation by-products (Schuchmann & von Sonntag 1989; Akhlaq *et al.* 1990; Dowideit & von Sonntag 1998; Muñoz & von Sonntag 2000a,b; Flyunt *et al.* 2001; Leitzke *et al.* 2001, 2003; Muñoz *et al.* 2001; Mvula & von Sonntag 2003; Reisz *et al.* 2003; Lange *et al.* 2006; Nöthe *et al.* 2007) but also to get some insight into the mechanism of the ozone-induced degradation of the nucleic acid (Theruvathu *et al.* 2001; Flyunt *et al.* 2002, 2003) that must contribute to the inactivation of viruses and possibly also of bacteria. Here, we address another mechanistically most interesting aspect of the chemistry of ozone in aqueous solution. It has been noticed that ozone treatment of manganese-containing waters leads to the formation of permanganate, MnO_4^- (Gregory & Carlson 2001). In this reaction, manganese has to be oxidized from the Mn(II) to the Mn(VII) state. Ozone can provide at the most two oxidation equivalents, and five oxidation equivalents are required here. Thus, this reaction is a multi-step process. A two-electron oxidation of Mn^{2+} gives rise to MnO_2 (a brownish colloid), and in distilled water MnO_2 is the main product even though at a high excess of O_3 some MnO_4^- is formed as well (see below). It will be shown, that the MnO_4^- formation is strongly influenced by various parameters such as pH, presence of complexing agents or Fe^{2+} ions. It is the aim of this paper to elucidate the conditions that favour MnO_4^- formation by studying this interesting phenomenon under well-defined artificial conditions (for short communications of some aspects see Reisz *et al.* (2004a,b)). These data will provide the basis of a discussion of the processes that may be involved in the formation of MnO_4^- in the O_3 treatment of drinking water and wastewater for which some examples will also be given. To our knowledge, no mechanistic study has been carried out as yet, although ozone reactions with Mn^{2+} have found quite some attention in the context of drinking water treatment (Reckhow *et al.* 1991; Andreozzi *et al.* 1992, 1995, 1997; Gregory & Carlson 2001).

METHODS

Manganese sulfate monohydrate (Merck), potassium permanganate (Merck), perchloric acid (70%, Merck), oxalic acid dihydrate (Merck), polyphosphoric acid (Acros) and potassium indigotrisulfonate (Riedel de Haën)

were used as received. Ozone was generated with an O_2 -fed ozonator (BMT 802X, BMT Messtechnik, Berlin). In the ozonation experiments at Timișoara, an air-fed ozonator (Fischer 500 M) was used. Ozone stock solutions were prepared using Milli-Q-filtered (Millipore) water. Their O_3 concentration was determined spectrophotometrically taking $\epsilon(260 \text{ nm}) = 3,300 \text{ M}^{-1} \text{ cm}^{-1}$ (Forni *et al.* 1982; Hart *et al.* 1983). MnO_2 and MnO_4^- were also determined spectrophotometrically (Figure 1). Colloidal MnO_2 has a characteristic UV/Vis spectrum with a maximum near 350 nm (Baral *et al.* 1985; Mulvaney *et al.* 1990). With $[\text{O}_3]_0 \geq [\text{Mn}^{2+}]_0$, the absorbance at 350 nm increased linearly with $[\text{Mn}^{2+}]_0$. Assuming an MnO_2 yield of 100%, we obtain $\epsilon(350 \text{ nm}) = 8,930 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure 1). This colloid is sufficiently stable for using its UV/Vis absorption for the quantification of MnO_2 as long as the measurement is done within several minutes after ozonation.

When both had to be measured, the MnO_2 concentration was determined at 420 nm, where the MnO_4^- absorption is negligible. When the MnO_4^- concentration was low as compared to MnO_2 , the spectrum of MnO_2 was subtracted electronically to an extent that only the MnO_4^- spectrum remained. The resulting error may rise to $\sim 15\%$ at very low $\text{MnO}_4^-/\text{MnO}_2$ ratios. For the determination of Mn^{3+} and MnO_4^- in acid solution (cf. Figure 4), absorption (A) measurements were done at two wavelengths (λ_1 , λ_2 , 480 nm & 525 nm) using appropriate absorption coefficients, ϵ , according to $\epsilon(\text{Mn}^{3+})_{\lambda_1} \times [\text{Mn}^{3+}] \times l + \epsilon(\text{MnO}_4^-)_{\lambda_1} \times [\text{MnO}_4^-] \times$

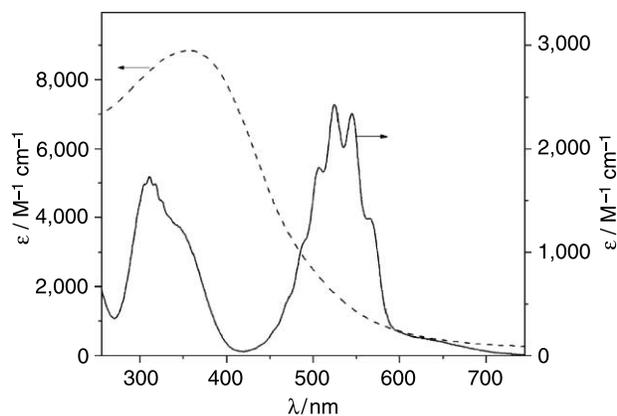


Figure 1 | UV/Vis spectra of colloidal MnO_2 (dashed line, left axis) and MnO_4^- (full line, right axis). The spectrum of MnO_2 has been obtained by ozonation of Mn^{2+} at pH 7.

$l = A_{\lambda 1}$ and $\varepsilon(\text{Mn}^{3+})_{\lambda 2} \times [\text{Mn}^{3+}] \times l + \varepsilon(\text{MnO}_4^-)_{\lambda 2} \times [\text{MnO}_4^-] \times l = A_{\lambda 2}$, typically with path length $l = 1$ cm. When the total absorption was very low, 5 cm cells were used to obtain a better reading. UV/Vis spectra were recorded on either a Perkin Elmer Lambda 16 or a Tidas 16 (J&M, Aalen) instrument.

An excess of O_3 , when intended, was confirmed by UV spectroscopy (pronounced peak at 260 nm). The alternative, the bleaching of indigotrisulfonate (Hoigné 1998; Muñoz & von Sonntag 2000a), is not feasible in our system, since all our products react very rapidly with this dye (cf. Table 1; see also Séby *et al.* (1995)).

Stopped-flow experiments were carried out with the help of a Biologic SFM3 instrument. UV/Vis spectra were recorded with a Tidas 16 instrument, and the kinetics was evaluated with the Kinspec software. For following conductometric changes, a home-made set-up (Dowideit & von Sonntag 1998; Leitzke *et al.* 2003) was used. In the competition kinetics with *trans*-1,2-dichloroethene, the *trans*-1,2-dichloroethene and O_3 concentrations were kept constant and the Mn^{2+} concentration was varied. The MnO_2 absorbance was the measured entity.

RESULTS AND DISCUSSION

Rate constants

The rate of reaction of non-complexed Mn^{2+} (aqua- Mn^{2+}) with O_3 was measured by following the kinetics of the build-up of the MnO_2 absorption at 350 nm or changes in the conductance (Figure 2).

The aggregation of MnO_2 is much faster (Pick-Kaplan & Rabani 1976) than the kinetics of the ozone reaction, and thus no lag phase in the buildup of the MnO_2 absorption was observed. Based on these two sets of data, ozone reacts with aqua- Mn^{2+} at $1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. A somewhat lower value of $1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ has been obtained by competition with *trans*-1,2-dichloroethene for which a rate constant with O_3 of $6.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ has been reported (Dowideit & von Sonntag 1998). A value of $1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ is given for HClO_4 solutions (Table 1). Complexation of Mn^{2+} by oxalate lowers the reactivity of Mn(II), while complexation by polyphosphosphate considerably enhances it (Figure 2 and Table 1). These rate constants were measured at 470 nm (oxalate) and 511 nm (polyphosphate), as under such conditions Mn(III) is formed (see below). Complexation by

Table 1 | Rate constants of reactions relevant to the present study (unit: $\text{M}^{-1} \text{ s}^{-1}$)

| Reaction | Rate constant | Reference |
|---|----------------------|--------------------------------|
| $\text{Mn}^{2+} + \text{O}_3 \rightarrow \text{MnO}_2 + \text{O}_2$ (HClO_4 , pH 0–2) | 1.5×10^3 | (Jacobsen <i>et al.</i> 1998a) |
| $\text{Mn}^{2+} + \text{O}_3 \rightarrow \text{MnO}_2 + \text{O}_2$ (H_2SO_4 , pH 0–2) | 1.8×10^3 | (Jacobsen <i>et al.</i> 1998a) |
| $\text{Mn}^{2+} + \text{O}_3 \rightarrow \text{MnO}_2 + \text{O}_2$ (11.5 M H_2SO_4) | 3.9×10^3 | (Tyupalo & Yakobi 1980) |
| $\text{Mn}^{2+} + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+ + \text{O}_2$ (stopped-flow, pH 7) | 1.3×10^3 | This work |
| $\text{Mn}^{2+} + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+ + \text{O}_2$ (competition, pH 7) | 1.0×10^3 | This work |
| Mn(II) oxalate + $\text{O}_3 \rightarrow$ Mn(IV) oxalate + O_2 (pH 0) | 760 | This work |
| Mn(II) polyphosphate + $\text{O}_3 \rightarrow$ Mn(IV) polyphosphate + O_2 (pH 7) | 1.4×10^4 | This work |
| $\text{MnO}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+$ (pH 7) | $> 5 \text{ s}^{-1}$ | This work |
| $\text{Fe}^{2+} + \text{O}_3 \rightarrow \text{FeO}^{2+} + \text{O}_2$ (HClO_4 , pH 0–3) | 8.5×10^5 | (Jacobsen <i>et al.</i> 1997) |
| $\text{Fe}^{2+} + \text{O}_3 \rightarrow \text{FeO}^{2+} + \text{O}_2$ (HClO_4 , pH 0–2) | 8.2×10^5 | (Lögager <i>et al.</i> 1992) |
| $\text{FeO}^{2+} + \text{Fe}^{2+} \rightarrow$ products (HClO_4 , pH 0–2) | 1.4×10^5 | (Lögager <i>et al.</i> 1992) |
| $\text{FeO}^{2+} + \text{Fe}^{2+} + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}$ (HClO_4 , pH 0–2) | 7.2×10^4 | (Jacobsen <i>et al.</i> 1997) |
| $\text{FeO}^{2+} + \text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2\text{Fe}^{4+}$ (HClO_4 , pH 0) | 1.8×10^4 | (Jacobsen <i>et al.</i> 1997) |
| $\text{FeO}^{2+} + \text{Mn}^{2+} + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{Mn}^{3+} + \text{H}_2\text{O}$ (HClO_4 , pH 0) | 1×10^4 | (Jacobsen <i>et al.</i> 1998b) |
| $\text{Mn}^{3+} +$ indigotrisulfonate \rightarrow bleaching (0.25 M HClO_4) | 2×10^4 | This work |
| $\text{MnO}_2 +$ indigotrisulfonate \rightarrow bleaching (pH 7) | $> 10^7$ | This work |
| $\text{MnO}_4^- +$ indigotrisulfonate \rightarrow bleaching (pH 7) | 1.3×10^3 | This work |

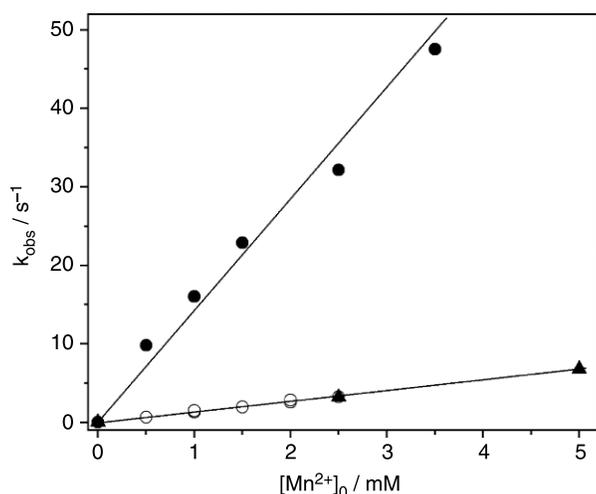


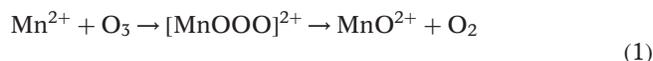
Figure 2 | Rate of reaction of O_3 with aqua- Mn^{2+} (open circles: optical detection of MnO_2 at 350 nm; closed triangles: conductometric detection) and Mn(II) complexed by polyphosphate ([polyphosphoric acid] $_0$ /[Mn^{2+}] $_0$ = 5) (closed circles; optical detection of Mn(III) at 511 nm). pH 7, $[\text{O}_3] \ll [\text{Mn}^{2+}]$.

sulfate in acid solution also seems to enhance the reactivity (Table 1; for the effect of sulfate in enhancing the MnO_4^- yield see below).

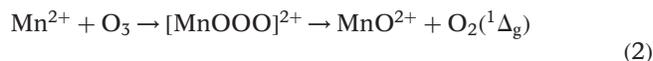
Formation of MnO_2 and MnO_4^- in neutral solution

In neutral solution, aqua- Mn^{2+} is mainly oxidized to colloidal MnO_2 . Originally it has been thought that the reaction of O_3 with Mn^{2+} is a one-electron transfer reaction (Tyupalo & Yakobi 1980), but later it has been convincingly shown that it must be an O-transfer (or two-electron oxidation) process (Jacobsen *et al.* 1998a). This type of reaction is also observed with many other inorganic and organic compounds, for example, Br^- , I^- (Liu *et al.* 2001; Muñoz *et al.* 2001), Fe^{2+} (Lögager *et al.* 1992; Jacobsen *et al.* 1997), sulfides and disulfides (Muñoz *et al.* 2001), methanesulfonic acid (Flyunt *et al.* 2001) and amines (Muñoz & von Sonntag 2000b). For Br^- which reacts only slowly with O_3 , there is kinetic evidence for the formation of an adduct as an intermediate as the reaction is reversible (Liu *et al.* 2001). A short-lived adduct has also to be assumed for all the other cases where an O-transfer is observed. With the sulfur compounds, singlet dioxygen, $\text{O}_2(^1\Delta_g)$, is released in 100% yield as required by the spin conservation rule. This rule is weakened by the heavy-atom effect due to spin-orbit coupling, and triplet (ground-state) dioxygen which is lower in energy by 94 kJ mol^{-1} than $\text{O}_2(^1\Delta_g)$ is formed in competition. For example in the case of Br^- , the $\text{O}_2(^1\Delta_g)$ yield is only

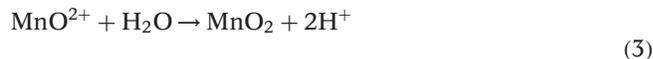
54%, and with I^- this value drops even to 14% (Muñoz *et al.* 2001). It is expected that O_3 will also form first an adduct with Mn^{2+} by replacing one of the water molecules of the solvation shell. In this adduct, a Mn(III) ozonide, $[\text{Mn}^{3+}\text{OOO}^-]^{2+}$, manganese must exert a heavy-atom effect, and, depending on its lifetime, the O_2 that is released may be at least partly in its ground state [Reactions (1) and (2)]. The Gibbs energies of the reactions were based upon available thermodynamic data (Rosseinsky & Nicol 1965; Dobos 1975) ($\Delta_r G'_{298}$ refers to conditions where all activities are 1 M except for H^+ which is at 10^{-7} M).



$$\Delta_r G'_{298} = -106 \text{ kJ mol}^{-1}$$



$$\Delta_r G'_{298} = -12 \text{ kJ mol}^{-1}$$

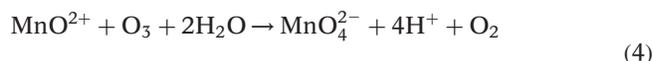


$$\Delta_r G'_{298} = -133 \text{ kJ mol}^{-1}$$

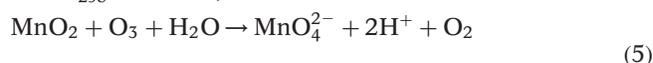
In Reaction (3), two mol H^+ are released. As measured by stopped flow with optical and conductometric detection, the kinetics of MnO_2 build-up and H^+ formation practically coincide (Figure 2). This shows that in neutral solution MnO^{2+} is very short-lived indeed, and from the above data we conclude that k_3 must be $\geq 5 \text{ s}^{-1}$.

At pH 7 and with a large excess of O_3 , only very small amounts of MnO_4^- are formed. For example, at $42 \mu\text{M Mn}^{2+}$ and $350 \mu\text{M O}_3$, MnO_2 is the main product and only $3.8 \mu\text{M MnO}_4^-$ are formed (9% with respect to Mn^{2+}). A marked catalytic destruction of the residual excess ozone by MnO_2 was not observed.

Thermodynamical data indicate that MnO^{2+} [Reaction (4)] and MnO_2 [Reaction (5)] may be further oxidized by O_3 to Mn(VI) , although Reaction (5) is exoenergetic only as long as ground state (triplet) O_2 is released.



$$\Delta_r G'_{298} = -178 \text{ kJ mol}^{-1}$$

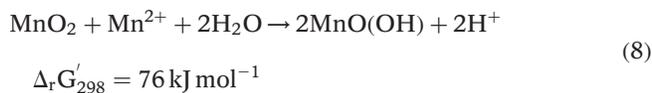
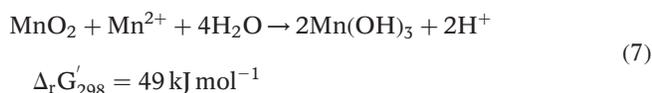
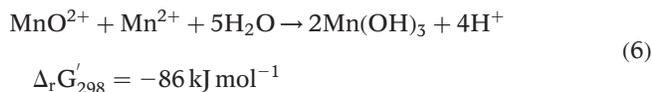


$$\Delta_r G'_{298} = -44 \text{ kJ mol}^{-1}$$

Experimentally, however, it is found that an oxidation of MnO_2 by O_3 does not occur, not even upon bubbling a freshly prepared MnO_2 colloid with O_3 for 10 min. For

Reaction (5) to proceed, O_3 has first to add to the manganese in the MnO_2 . Aggregation of MnO_2 , colloid formation, will compete with this reaction. Solid MnO_2 has a rutile structure, where each manganese atom is surrounded by six oxygens. In case the MnO_2 colloid has essentially the same structure and this structure is tight, it will prevent an easy access of O_3 to the manganese in the colloid. Moreover, colloid formation reduces the number of MnO_2 particles, and this is an additional kinetic disadvantage. From this, it follows that the oxidation to MnO_4^- observed at low Mn^{2+} concentrations and a large excess of O_3 must be attributed to Reaction (4) as the first step. This reaction is in competition with the hydrolysis of MnO^{2+} [Reaction (3)].

A conproportionation of Mn^{2+} with MnO^{2+} to Mn(III) is thermodynamically favourable [Reaction (6)], whereas with MnO_2 it is not [Reactions (7) and (8)].



Although Reaction (6) is thermodynamically favoured, at low Mn^{2+} concentrations such as $5 \times 10^{-4} \text{ M}$ ($[O_3] = 1.7 \times 10^{-4} \text{ M}$), no Mn(III) is formed as the hydrolysis of MnO^{2+} is fast. The MnO_2 colloid that is formed under such conditions [Reaction (3)], does not dissolve upon acidification [cf. Reactions (9) and (10)]. At higher Mn^{2+} concentrations, there is a mixture of MnO_2 and Mn(III) colloids. At $5 \times 10^{-2} \text{ M}$ Mn^{2+} , only an Mn(III) colloid is formed that dissolves upon acidification. The spectrum of the resulting species, probably a mixture of Mn^{3+} and $Mn(OH)^{2+}$, is shown in Figure 3.

It will be shown next that in acid solutions and also in neutral solutions in the presence of complexing agents Mn(III) is formed, when Mn^{2+} is in excess. However with O_3 in excess, the oxidation proceeds to MnO_4^- in high yields.

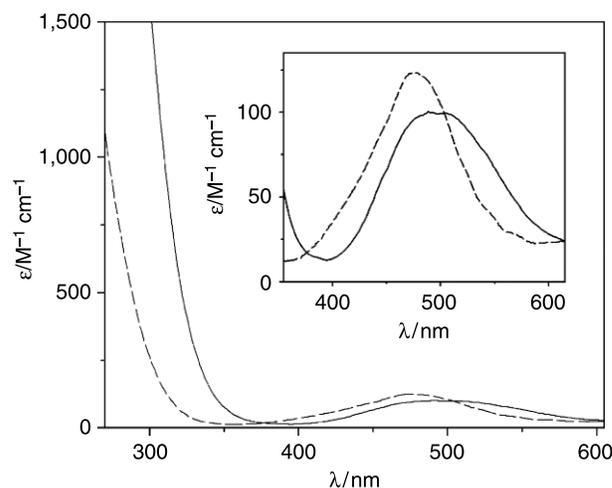
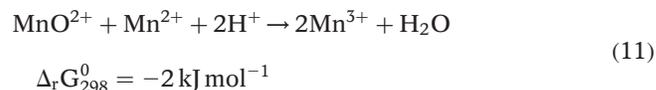
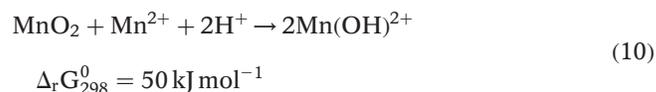
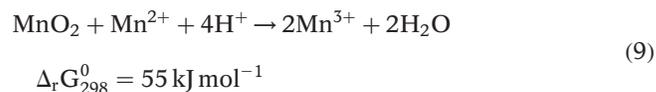


Figure 3 | UV/Vis spectra of Mn(III) formed in the reaction of O_3 ($160 \mu\text{M}$) with Mn^{2+} (1 mM) at pH 0 (1 M HClO_4), dashed line, and complexed by polyphosphate ($1 \times 10^{-2} \text{ M}$) in neutral solution, solid line. Inset: enlargement of the long-wavelength bands.

Formation of Mn(III) and MnO_4^- in acid solution

At pH 0 and with an excess of Mn^{2+} that prevents the reaction of O_3 with ozonation products, Mn(III) is formed. This follows from the agreement of the spectrum shown in Figure 3 with that of Mn(III) reported in the literature (Diebler & Sutin 1964; Davies 1969).

Even at the low pH of our experiments, not all of the Mn(III) is present as Mn^{3+} , and some of it should be present as $Mn(OH)^{2+}$ (the most recent value for the pK of the hydrolysis of Mn^{3+} is given as -0.4 (Biedermann & Palombari 1978)). The thermodynamics show that MnO_2 and Mn^{2+} do not conproportionate [Reactions (9) and (10)], not even in acid solution. In contrast, MnO^{2+} can conproportionate with Mn^{2+} at high H^+ and Mn^{2+} concentrations [Reaction (11)].



It has been briefly mentioned that at low Mn^{2+} concentration and with ozone in large excess MnO_4^- is

formed in strongly acid solution (Jacobsen *et al.* 1998a), and this aspect is now studied in more detail.

At a constant O_3 concentration of $150 \mu\text{M}$, the Mn^{2+} concentration has been varied, and the yields of Mn(III) and MnO_4^- were calculated. At high Mn^{2+} concentrations, Mn(III) is the only product (see above), but upon lowering the Mn^{2+} concentration, MnO_4^- is increasingly formed (Figure 4).

In Figure 5, the MnO_4^- yield is plotted as a function of the O_3 concentration. In these experiments, the Mn^{2+} concentration was $50 \mu\text{M}$, and it is seen from these data that MnO_4^- formation does not set in before the O_3 concentration has reached about twice this value.

Up to an $[O_3]_0/[Mn^{2+}]_0$ ratio of 2, higher oxidation states of manganese are formed, but not yet MnO_4^- . After the onset of the MnO_4^- formation, at an O_3 concentration near $100 \mu\text{M}$, the MnO_4^- yield increases close to linearly with the O_3 concentration. The observed stoichiometry of the oxidation of the intermediate(s) formed after the lag phase is 7.5 mol O_3 per mol MnO_4^- (at $400 \mu\text{M}$ O_3 , the overall stoichiometry is 10 mol O_3 per mol MnO_4^-). If only O-transfer reactions to Mn^{2+} and higher manganese oxidation states would occur the stoichiometric value would be 2.5. This not being the case indicates that MnO_4^- formation is a more complex reaction. Notably, manganese at higher oxidation states that are intermediates en route to MnO_4^- must react with O_3 to manganese at lower oxidation states and two molecules of O_2 . In these

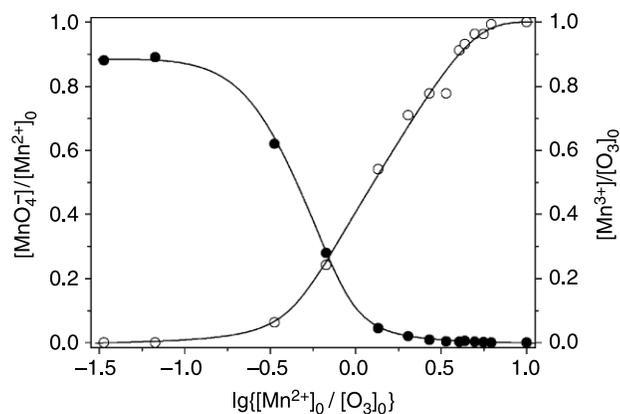


Figure 4 | Reaction of ozone ($150 \mu\text{M}$) with varying amounts of Mn^{2+} at pH 0 (1M HClO_4). Formation of Mn(III) and MnO_4^- as a function of the decadic logarithm (\lg) of the $[Mn^{2+}]_0/[O_3]_0$ ratio. Right scale (open circles): $[Mn^{3+}]/[O_3]_0$; left scale (closed circles): $[MnO_4^-]/[Mn^{2+}]_0$. Lines are drawn to guide the eye.

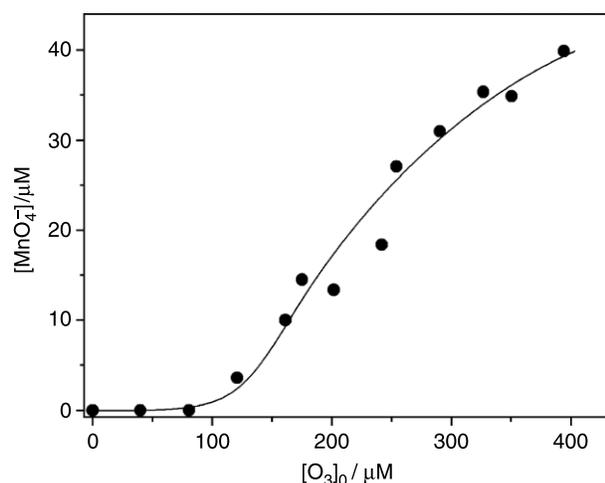
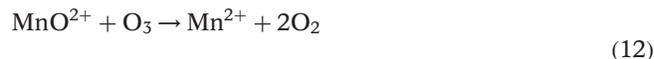
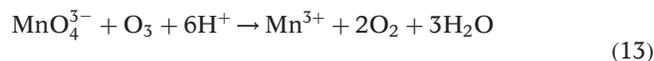


Figure 5 | Formation of MnO_4^- in the ozonolysis of Mn^{2+} ($50 \mu\text{M}$) at pH 0 (1M HClO_4). The line is drawn to guide the eye.

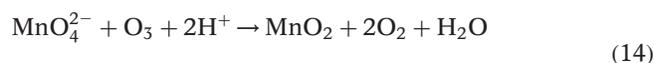
reactions, O_3 acts as a *reductant*. That this is thermodynamically feasible is shown in Reactions (12)–(14).



$$\Delta_r G_{298}^0 = -220 \text{ kJ mol}^{-1}$$

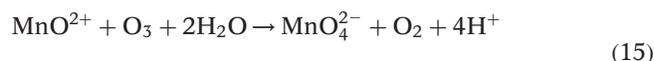


$$\Delta_r G_{298}^0 = -428 \text{ kJ mol}^{-1}$$

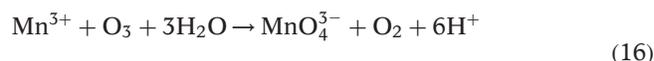


$$\Delta_r G_{298}^0 = -362 \text{ kJ mol}^{-1}$$

For the oxidation of MnO^{2+} to MnO_4^- one may consider the direct pathway [Reaction (15)], or an oxidation of Mn^{3+} [Reaction (16)] which has been formed upon conproportionation of MnO^{2+} with Mn^{2+} [Reaction (11)]. The oxidation of Mn^{3+} by O_3 is thermodynamically not favoured, at least when the product of this reaction is not protonated (no thermodynamic data are available to calculate Gibbs energies for the reaction of Mn^{3+} with O_3 when the products are protonated species such as HMnO_4^{2-} , H_2MnO_4^- and H_3MnO_4).

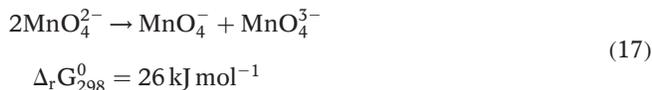


$$\Delta_r G_{298}^0 = -18 \text{ kJ mol}^{-1}$$

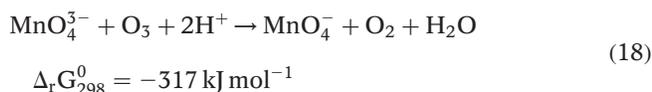


$$\Delta_r G_{298}^0 = 102 \text{ kJ mol}^{-1}$$

The same situation prevails for the subsequent disproportionation of Mn(VI) [Reaction (17)].



Yet, the oxidation of MnO_4^{3-} to MnO_4^- by O_3 is thermodynamically strongly favoured [Reaction (18)].



Hence, Reaction (17) becomes possible, because the MnO_4^{3-} concentration in the system remains low due to its ready oxidation by O_3 [Reaction (18)].

As there is a dramatic difference between the MnO_4^- yield in neutral and acid solutions, an H^+ concentration dependence has been studied. In these experiments, H_2SO_4 has been used for acidification. As is seen from Figure 6, a MnO_4^- yield of 100% is reached at an H^+ concentration of 10^{-2} M.

With 1 M HClO_4 , a maximum MnO_4^- yield of 90% has been obtained under the same conditions (Figure 4, very large excess of O_3). In the case of H_2SO_4 , the formation of a maximum at an H^+ concentration of 10^{-2} M can be explained by a contribution of two effects. The effect of the H^+ concentration that favours MnO_4^- formation

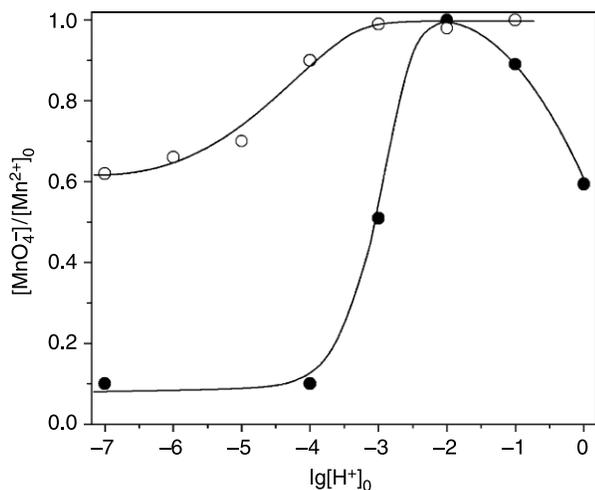


Figure 6 | Formation of MnO_4^- yields in the reaction of $10 \mu\text{M Mn}^{2+}$ with O_3 ($150 \mu\text{M}$) acidified with H_2SO_4 in the absence (solid circles) and in the presence of $0.5 \text{ M Na}_2\text{SO}_4$ (open circles). Lines are drawn to guide the eye.

(see above), is overlain by a complexation of Mn^{2+} by SO_4^{2-} that results in an SO_4^{2-} -complexed MnO^{2+} intermediate. Evidence for an SO_4^{2-} effect is shown by the addition of Na_2SO_4 . Even at pH 4, where in the absence of Na_2SO_4 the MnO_4^- yield is as low as in neutral solution, addition of $0.5 \text{ M Na}_2\text{SO}_4$ raises the MnO_4^- yield to 90%. Interestingly, in the absence of Na_2SO_4 the MnO_4^- yield falls again below an H^+ concentration of 10^{-2} M. The reason for this may be attributed to the fact that in this pH range the SO_4^{2-} is partially protonated ($\text{p}K_a(\text{HSO}_4^-) = 1.9$), and HSO_4^- has to be considered as a complexing agent aside SO_4^{2-} . There is not yet a clear answer to the question as to what determines the maximum MnO_4^- yield at an excess of O_3 . It is suggested that there must be a competition between hydrolysis and oxidation of Mn(IV) species (aqua- MnO^{2+} or complexed- MnO^{2+}). Both reactions are characterized by rate constants that depend on the nature of the complexing agent. The MnO_4^- yield will be high, when the rate of oxidation ($k_{\text{oxidation}} \times [\text{O}_3]$) is much higher than the rate of hydrolysis to non-reactive MnO_2 ($k_{\text{hydrolysis}}$). It will be low, when the ratio $k_{\text{oxidation}} \times [\text{O}_3]/k_{\text{hydrolysis}}$ is low. The increase in the MnO_4^- yield upon complexation of $\text{Mn}^{2+}/\text{MnO}^{2+}$ by SO_4^{2-} finds some analogy in the effects of polyphosphate, phosphate, bicarbonate and oxalate. The strongest complexing agent investigated here is polyphosphate, and its effect on modifying the ozone chemistry of Mn^{2+} is reported next. Some data that have already been reported (Reisz et al. 2004a; Reisz 2005) will find a new interpretation now.

Formation of Mn(III), Mn(IV) and MnO_4^- in the presence of polyphosphate

When Mn^{2+} is complexed by polyphosphate in neutral solution, the O_3 reaction is considerably faster than that of aqua- Mn^{2+} (Table 1). The species that is observed in the presence of a large excess of Mn^{2+} ($[\text{Mn(II)}]_0 \geq 10^{-3} \text{ M}$, $[\text{polyphosphate}]_0 = 10^{-2} \text{ M}$ and $[\text{O}_3]_0 = 2 \times 10^{-4} \text{ M}$) is Mn(III) polyphosphate. The UV/Vis spectrum (Figure 3; $\lambda_{\text{max}} = 490 \text{ nm}$, $\epsilon \approx 100 \text{ M}^{-1} \text{ cm}^{-1}$) is similar to that of aqua- Mn^{3+} ($\lambda_{\text{max}} = 480 \text{ nm}$, $\epsilon \approx 120 \text{ M}^{-1} \text{ cm}^{-1}$; Figure 3 and Diebler & Sutin (1964)) and of Mn(III) pyrophosphate ($\lambda_{\text{max}} = 515 \text{ nm}$, $\epsilon \approx 80 \text{ M}^{-1} \text{ cm}^{-1}$ (Diebler & Sutin 1964)). The 490 nm absorption is noticeably broader than that

of aqua-Mn³⁺/Mn(OH)²⁺ (Figure 3). This could be accounted for if there were more than one Mn(III) polyphosphate species present under this condition. This aspect has not been investigated any further.

It is very remarkable that this 490 nm absorption is stable over night, and we conclude that the Mn(III) polyphosphate complex(es) must be very strong. Aqua-Mn(III), however, hydrolyzes and aggregates quite rapidly in neutral solution and fades away even in acid solution. The formation of MnO₄⁻ as a function of O₃ concentration is shown in Figure 7.

At equal concentrations of Mn²⁺ and polyphosphate (30 μM) and a large excess of O₃, the maximum MnO₄⁻ yield is 75% (Figure 7, main graph). When the [polyphosphate]₀/[Mn²⁺]₀ ratio is raised, the MnO₄⁻ yield drops considerably (Figure 8).

Two aspects are remarkable, the relatively low (as compared to sulfate) MnO₄⁻ yield at low Mn²⁺ concentrations and O₃ in excess and the marked drop of the MnO₄⁻ yield as the polyphosphate concentration is increased. On the basis of the above discussion, this implies that the $k_{\text{oxidation}} \times [\text{O}_3]/k_{\text{hydrolysis}}$ ratio is not very high at the lowest polyphosphate concentration and drops further as the polyphosphate concentration is increased. There has been some indication that there was more than one Mn(III)

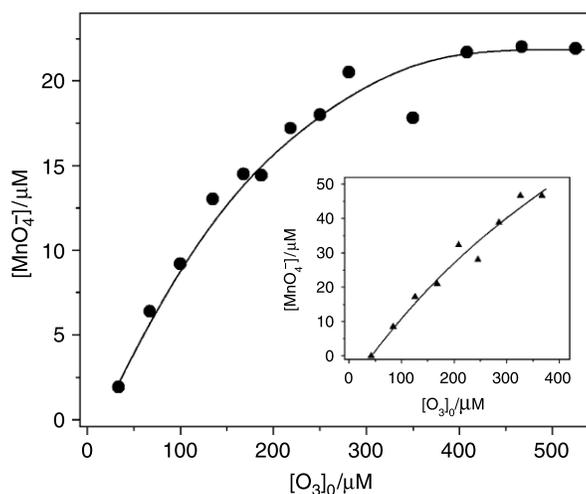


Figure 7 | Formation of MnO₄⁻ in the ozonolysis of Mn²⁺ (30 μM) in the presence of equal amounts of polyphosphate as a function of the O₃ concentration. Inset: ditto, but [Mn²⁺]₀ = [polyphosphate]₀ = 100 μM. Lines are drawn to guide the eye.

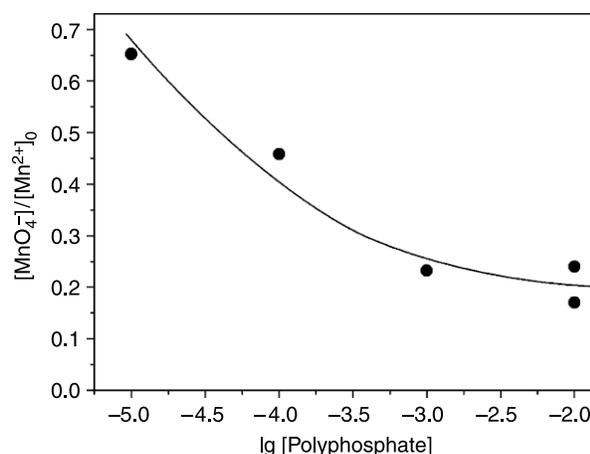


Figure 8 | Permanganate yield in the reaction of Mn²⁺ (10 μM) with a large excess of O₃ (200 μM) as a function of the polyphosphate concentration (logarithmic scale). The line is drawn to guide the eye.

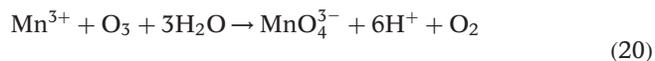
polyphosphate species in the experiment on which Figure 3 is based, and a similar situation may prevail for Mn(IV) as the polyphosphate concentration is changed. Although for this key question it is not yet possible to provide kinetic data, we may address some thermodynamic aspects, pertinent to this system.

Complexation of Mn²⁺ and MnO²⁺ may not affect the thermodynamics of MnO²⁺ formation much [Reactions (1) and (2)]. Yet, it has a marked effect on the reaction of Mn(II) with Mn(IV) [Reaction (19)] (note the formation of a very stable Mn(III) polyphosphate complex at a large excess of Mn²⁺).



$$\Delta_r G'_{298} = 78 \text{ kJ mol}^{-1}$$

In contrast to acid solutions where the oxidation of Mn³⁺ by ozone is not thermodynamically favoured, it may well proceed in neutral solution [Reaction (20)] even when complexation of Mn³⁺ would reduce the Gibbs energy markedly.



$$\Delta_r G'_{298} = -137 \text{ kJ mol}^{-1}$$

An oxidation of MnO₄³⁻ by O₃ to MnO₄⁻ is also thermodynamically feasible in neutral solution ($\Delta_r G'_{298} = -237 \text{ kJ mol}^{-1}$). This also holds for an oxidation

of MnO^{2+} to MnO_4^{2-} ($\Delta_r G'_{298} = -178 \text{ kJ mol}^{-1}$) and for the disproportionation of MnO_4^{2-} into MnO_4^- and MnO_4^{3-} ($\Delta_r G'_{298} = 26 \text{ kJ mol}^{-1}$). This shows that in neutral solution and in the presence of polyphosphate two routes to MnO_4^- are available in contrast to acid solutions, where there is only one.

Formation of MnO_2 and MnO_4^- in the presence of oxalate

Oxalate complexes Mn^{2+} ($\lg K = 3.75$) (Sillen & Martell 1964), and it must also complex Mn^{3+} and MnO^{2+} . Under nearly stoichiometric conditions ($50 \mu\text{M Mn}^{2+}$ and $150 \mu\text{M O}_3$), the MnO_4^- yield is close to 100% at high oxalate concentrations (Figure 9).

At low oxalate concentrations, the main product is MnO_2 . There is an intermediate range, where both products are formed, but there is a major material balance deficit (cf. open triangles in Figure 9). Supported by a more extended study (Reisz 2005), this deficit can be explained as follows. MnO^{2+} can be complexed not only by one oxalate (dominating at low oxalate concentrations) but also by a second one (dominating at high oxalate concentrations). Similar to Mn(III) oxalate, Mn(IV) oxalate may decarboxylate in competition to a further oxidation by O_3 . The monooxalato complex has a lower electron density at manganese than the dioxalato complex and hence a stronger

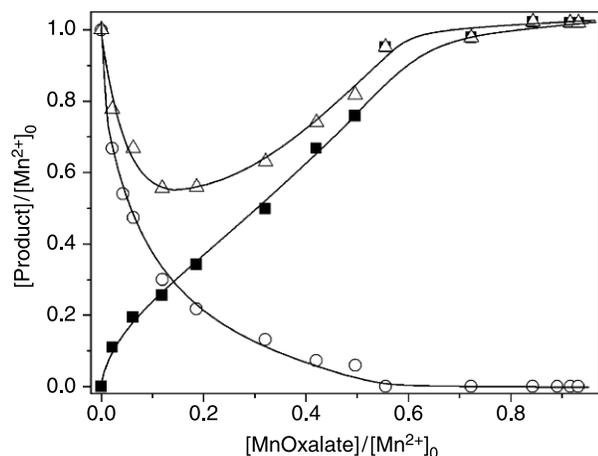
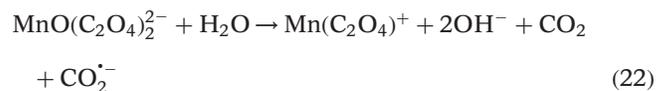


Figure 9 | MnO_2 yields (open circles), MnO_4^- yields (closed squares) and their combined yields (open triangles) in the reaction of Mn^{2+} ($50 \mu\text{M}$) with O_3 ($150 \mu\text{M}$) as a function of the fraction of oxalate complexed Mn^{2+} at pH 7. Lines are drawn to guide the eye.

oxidative power. Thus, it will decompose much faster [Reaction (21)] than the dioxalato complex [Reaction (22)].



The deficit in the material balance (reformation of Mn^{2+}) shown in Figure 9 as a function of $[\text{Mn oxalate}]/[\text{Mn}^{2+}]_0$ is suggested to result from two competing processes. First, there is the formation of short-lived $\text{MnO}(\text{C}_2\text{O}_4)$ that decays into Mn(III) and $\text{CO}_2^{\cdot-}$ [Reaction (21); note that $\text{CO}_2^{\cdot-}$ is a strong reducing agent that will provide another reduction equivalent]. As the $[\text{Mn oxalate}]/[\text{Mn}^{2+}]_0$ ratio is increased, the longer-lived $\text{MnO}(\text{C}_2\text{O}_4)_2^{2-}$ will increasingly become of importance with the effect that the material balance is regained and MnO_4^- formation dominates eventually.

Using the stopped-flow technique and working with a large excess of Mn^{2+} in strongly acid solution, evidence for the formation and subsequent decay of Mn(III) oxalato complexes has been obtained (Reisz 2005). Supporting the above suggestion, the Mn(III) monooxalato complex decomposes faster than the Mn(III) dioxalato complex.

Formation of permanganate in the presence of bicarbonate and phosphate

Bicarbonate and phosphate buffers (pH 7) also enhance MnO_4^- formation (Figure 10).

Compared to polyphosphate, phosphate buffer is much less effective in complexing $\text{Mn}^{2+}/\text{MnO}^{2+}$, and a decrease of MnO_4^- yield at high concentrations as in the case of polyphosphate (Figure 8) is not apparent here (Figure 10). Yet both systems show relatively low maximum MnO_4^- yields. In contrast, bicarbonate is a poor complexing agent, but at high concentration, the maximum MnO_4^- yield approaches 100%.

Formation of permanganate in the presence of Fe^{2+}

An O_3 treatment of Mn^{2+} -containing raw waters gives rise to MnO_4^- , but the pH is not low enough and the concentrations of complexing agents are most likely not sufficiently high to

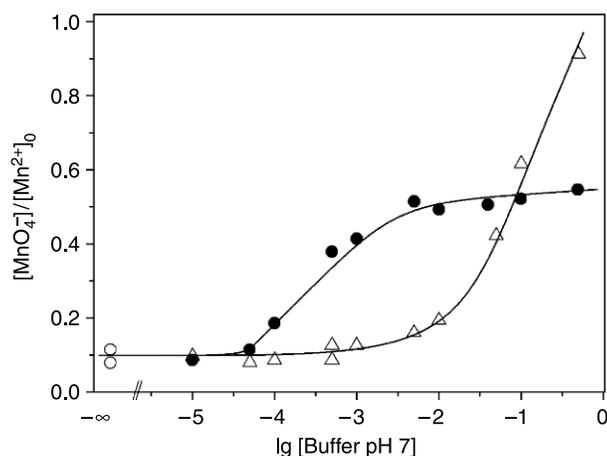


Figure 10 | Permanganate yield in the reaction of $10\ \mu\text{M}$ Mn^{2+} in the presence of an O_3 excess ($160\ \mu\text{M}$) as a function of the logarithm of phosphate (closed circles) and bicarbonate (triangles) buffer concentrations at pH 7. The open circles are data in the absence of any buffer. Lines are drawn to guide the eye.

explain the high MnO_4^- yields according to phenomena described above (for some data see below). Thus, another mechanism must operate here.

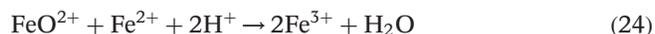
Mn^{2+} is only found in the raw water, when reducing conditions prevail. Thus, Mn^{2+} and Fe^{2+} are always present side by side, and the Fe^{2+} concentration typically exceeds the Mn^{2+} concentration. For example in Temesvar (Timișoara, Romania), the average Mn^{2+} concentration is $10\ \mu\text{M}$, while the accompanying Fe^{2+} concentration is $70\ \mu\text{M}$ in some of the ground waters used for drinking water treatment. The biologically treated wastewater effluents of the Emschergenossenschaft (Bottrop, Germany) also contain some Fe^{2+} and Mn^{2+} . This led us to investigate, whether the presence of Fe^{2+} may induce MnO_4^- formation. The reactions of O_3 with Fe^{2+} and Mn^{2+} , respectively, under conditions similar to drinking water treatment (that is, in the presence of DOC) have already been studied (Reckhow *et al.* 1991), but the more realistic situation, namely, when Fe^{2+} and Mn^{2+} are both present, has not yet been investigated.

Fe^{2+} reacts 650-times faster with O_3 than Mn^{2+} (Table 1). Thus even at about equal concentrations, Fe^{2+} is predominantly oxidized to the ferryl ion [Reaction (23); rate constants in Table 1].

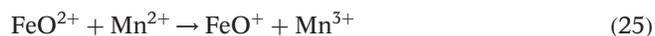


Subsequent oxidations will be governed by the reactions of the ferryl ion. The oxidation of Fe^{2+} by the ferryl ion

(in acid solution) is quite fast [Reaction (24); rate constant in Table 1].



The ferryl ion also oxidizes Mn^{2+} under such conditions [Reaction (25); rate constant in Table 1].



It is reasonable to assume that the same type of reactions also occur in neutral solutions albeit at somewhat different rates and, of course, with different intermediates. For example, Reaction (25) may result in a binuclear complex such as $\text{Fe(III)OMn(III)O}^{2+}$. In contrast to MnO_2 , such Mn(III) species may stand a chance of being further oxidized by O_3 . In Figure 11, the formation of MnO_4^- is shown for a progressive ozonation of two solutions that contain $25\ \mu\text{M}$ Mn^{2+} and either $25\ \mu\text{M}$ or $90\ \mu\text{M}$ Fe^{2+} .

First, all the Fe^{2+} is converted to Fe(IV) [Reaction (23); note the 650-fold higher reactivity of Fe^{2+} towards O_3 as compared to Mn^{2+}] and MnO_4^- formation sets in, when Mn^{2+} has been oxidized to Mn(III)/Mn(V). Although at the highest O_3 concentrations used in these experiments some O_3 remained, the MnO_4^- yield reached only one quarter of the Mn^{2+} originally present.

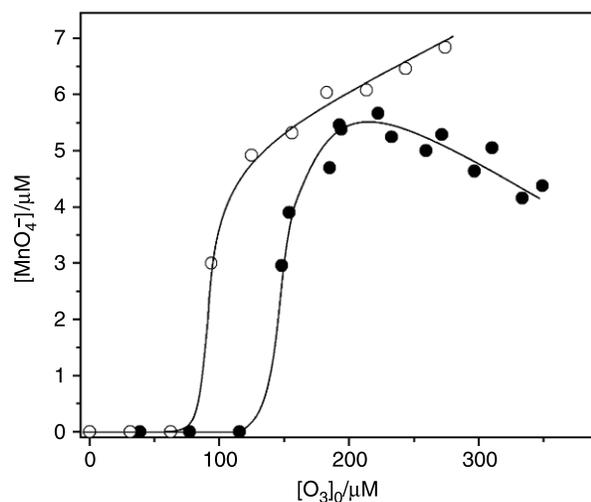


Figure 11 | Formation of MnO_4^- in the ozonolysis of Mn^{2+} in the presence of Fe^{2+} as a function of the O_3 concentration (closed circles: $[\text{Mn}^{2+}]_0 = 25\ \mu\text{M}$ and $[\text{Fe}^{2+}]_0 = 90\ \mu\text{M}$; open circles: $[\text{Mn}^{2+}]_0 = [\text{Fe}^{2+}]_0 = 25\ \mu\text{M}$). Lines are drawn to guide the eye.

From Figure 12, it can be seen that the MnO_4^- formation strongly depends on the $[\text{Fe}^{2+}]_0/[\text{Mn}^{2+}]_0$ ratio. The highest MnO_4^- yield is obtained at a 1:1 ratio, where it increases nearly linearly with the total Fe^{2+} plus Mn^{2+} concentration (Figure 12, inset).

From these data, it is evident that a substantial part of the Mn^{2+} can be converted into MnO_4^- (one quarter at the maximum, cf. Figure 12, main graph) and that the majority (three quarters) ends up as O_3 -inert products, most likely MnO_2 or a mixed oxide of Fe_2O_3 and MnO_2 .

Formation of permanganate in manganese-containing drinking water and wastewater

One of the Timișoara raw waters used for drinking water contains substantial amounts of Mn^{2+} ($10\ \mu\text{M}$) and Fe^{2+} ($70\ \mu\text{M}$). This does not pose a problem in the processing of this raw water to drinking water as an oxidation with air is sufficient to eliminate these contaminants. Yet, we used this Mn^{2+} and Fe^{2+} content to measure the efficiency of MnO_4^- formation upon ozonation. In batch experiments carried out at Duisburg with distilled water containing the above Mn^{2+} and Fe^{2+} concentrations (mixing 1 vol. of this water with 1 vol. O_3 solution), MnO_4^-

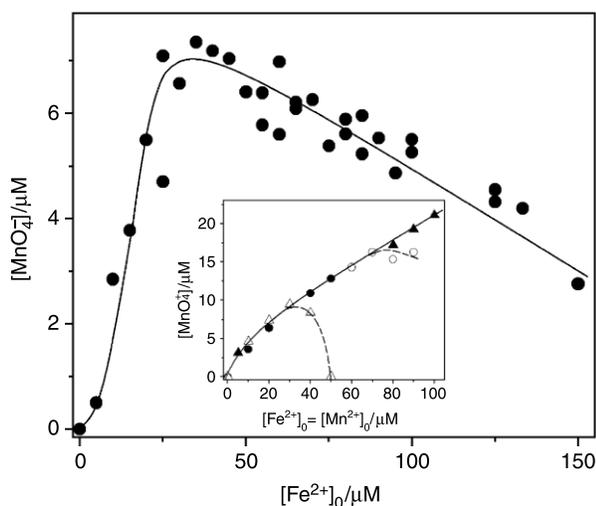


Figure 12 | Formation of MnO_4^- in the ozonolysis of Mn^{2+} ($25\ \mu\text{M}$) as a function of the Fe^{2+} concentration with O_3 in excess. Inset: MnO_4^- yield in the ozonolysis of Mn^{2+} in the presence of equal amounts of Fe^{2+} as a function of the Fe^{2+} (as well as Mn^{2+}) concentration with O_3 in excess (closed triangles: $[\text{O}_3] = 480\ \mu\text{M}$; closed circles: $[\text{O}_3] = 310\ \mu\text{M}$; open circles: $[\text{O}_3] = 280\ \mu\text{M}$; open triangles: $[\text{O}_3] = 120\ \mu\text{M}$). Lines are drawn to guide the eye.

formation set in at an O_3 concentration 1.5 times that of the Fe^{2+} concentration and approached final yields near 25% of $[\text{Mn}^{2+}]_0$ once the O_3 concentration was 4 times that of the Fe^{2+} concentration (data not shown). In a field experiment at Timișoara with a slow O_3 input, no MnO_4^- was formed even upon prolonged bubbling. This interesting effect must have a kinetic reason. At the slow rate at which O_3 was delivered, any Mn(III) formed in Reaction (25) may have disproportionated into Mn^{2+} and MnO_2 (the reverse of Reaction (9) is thermodynamically favoured), and the Mn^{2+} reformed would then be oxidized to MnO_2 .

The wastewater from the Emschergerossenschaft at Bottrop also contains some Mn^{2+} ($4.4\ \mu\text{M}$) and Fe^{2+} ($11\ \mu\text{M}$ Fe^{2+}) in its biologically treated effluent. In the course of a study on the elimination of micropollutants by ozone, it has been observed that the water turns pink upon ozonation and that this colour fades away after some time (N. Mora Naranjo and N. Große, private communication). An analysis as above showed that this pink colour is due to the presence of $0.6\ \mu\text{M}$ MnO_4^- . At $4.4\ \mu\text{M}$ Mn^{2+} present, the MnO_4^- yield is 14%. This high yield cannot be attributed to a reaction of Mn^{2+} with O_3 , since wastewater consumes O_3 rather quickly (about $180\ \mu\text{M}$ O_3 out of $230\ \mu\text{M}$ O_3 added react with the wastewater matrix within 20 s (Nöthe 2008)). As a consequence of this rapid O_3 decay, only those micropollutants are eliminated effectively whose O_3 rate constant exceeds $10^3\ \text{M}^{-1}\ \text{s}^{-1}$ considerably (Nöthe 2008). As can be seen from Table 1, it is not expected that NOM at the prevailing concentration (DOC near $10\ \text{mg}\ \text{L}^{-1}$) can raise by complexation of Mn^{2+} the rate constant considerably (note that complexation by oxalate causes a drop in the rate constant, cf. Table 1) to a level that makes an effective oxidation of Mn^{2+} feasible under these conditions. On the other hand, Fe^{2+} reacts with ozone with a rate constant of $8.5 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$, that is, this reaction is sufficiently fast for a complete conversion of Fe^{2+} into Fe(IV) even in the presence of the wastewater matrix. Fe(IV) does not react at an appreciable rate with the DOC (Hug & Leupin 2003), and this allows the oxidation of Mn^{2+} by Fe(IV) . From this, we conclude that the co-contaminant Fe^{2+} is essential for the oxidation of Mn^{2+} by O_3 in the above wastewater and also most likely the cause of MnO_4^- formation in drinking water, whenever substantial ($>10\%$) MnO_4^- formation is observed.

CONCLUSION

Upon O_3 treatment of Mn^{2+} -containing drinking water and wastewater, MnO_4^- formation may occur. A maximum yield of 10% can be accounted for by a direct oxidation of Mn^{2+} , as indicated by experiments in distilled water. For enhancing the MnO_4^- yield beyond this value, co-solutes such as complexing agents or Fe^{2+} are required. The NOM concentration in such waters is typically too low for complexing Mn^{2+} effectively. This also holds for a contamination by inorganic Mn^{2+} -complexing agents. On the other hand, Fe^{2+} and Mn^{2+} are usually present side by side, and it is suggested that MnO_4^- formation is then a Fe^{2+} -mediated process.

The observation that O_3 may also act as a *reducing* agent is not without precedence. En route from Br^- to BrO_3^- , there is also a reduction step ($BrO^- + O_3 \rightarrow Br^- + 2O_2$) that competes with the oxidation step ($BrO^- + O_3 \rightarrow BrO_2^- + O_2$) thereby enhancing the O_3 demand beyond stoichiometry (Haag et al. 1982; Haag & Hoigné 1983; von Gunten & Hoigné 1992; von Gunten & Hoigné 1994, 1996; von Gunten et al. 1995; Naumov & von Sonntag 2008).

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