Gas-Phase Dioxygen Activation by Binuclear Manganese Clusters

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Abstract: Binuclear manganese oxide cations, $Mn_2O_2^+$ (**1**) and Mn_2O^+ (**2**), have been prepared in the gas phase by a chemical route by using the reaction of O_2 with the ions formed from the ionization of $[Mn_2(CO)_{10}]$. Their reactivity towards selected neutrals has been probed by Fourier Transform Ion Cyclotron Resonance spectrometry (FT-ICR), and insights into the structure of the reagent ions and of ionic reaction intermediates have been obtained by collision-induced dissociation and by the outcome of ion–molecule reactions. Whereas dihydrogen proved to be unreactive, the hydrides H_2O, H_2S, and NH_3 react by exchange, addition, and oxidation pathways. Oxidative features are displayed also in the reactions of **1** and **2** with model organic molecules, such as methanol, acetaldehyde, and unsaturated hydrocarbons, which undergo dehydrogenation, O-atom transfer, and homolytic cleavage processes. Potentially catalytic cycles are indicated, based on the regeneration of **1** by ligand exchange of end product ions with O_2.

Keywords: cluster compounds • gas-phase reactions • manganese • mass spectrometry • oxidation

Introduction

There is growing interest in transition-metal oxides because of the manifold role played in a variety of important chemical and biochemical transformations.[1] In biology, metal sites have evolved as cofactors, which are active in highly specific oxidation/reduction processes. Among them, polynuclear manganese oxo centers perform the seemingly contrary tasks of producing dioxygen from the oxidation of water by the oxygen-evolving center (OEC) of photosystem II but also of rendering the dioxygen reduction products harmless. For example, hydrogen peroxide may be scavenged by manganese catalase.[2]

It is evidently desirable to develop simplified models for the complex systems in which polynuclear transition-metal oxo species are embedded at the active site of a biomolecule. However, one needs to be concerned with several factors contributing to their catalytic activity, such as the solvent, the ligands, the oxidation states of the metal atoms, and the features of the cavity hosting the metal core. In this respect, gas-phase studies present the advantage of naked metal core selection and allow one to unravel its reactivity behavior at a molecular level. Size-selected ionic clusters may be allowed to react with neutral molecules in a dielectric medium, namely, in the gas phase, which bears some similarity to the hydrophobic surroundings of the catalytic centers in many enzymes.[3]

Aiming to provide a reference model for the functions of Mn-based enzymes, we assayed the reactivity of $Mn_2O_y^+$ ($y=1,2$) ions by Fourier Transform ion cyclotron resonance (FT-ICR) mass spectrometry. The neutral reagents are either simple inorganic compounds, such as H_2 and the element hydrides XH_n (X = N, O, S), or exemplary organic molecules, such as methanol, acetaldehyde, and a few hydrocarbons. Structural information on the reagent ions was sought in their collision-induced dissociation (CID) mass spectra.

Results

$Mn_2O_2^+$: In the selected mode of the FT-ICR experiments, **1** is readily obtained as the single product ion from the displacement of all the carbonyls of $[Mn_2(CO)_4]^+$ by dioxygen, according to an already known reaction of $[Fe_2(CO)_4]^+$.[4] Probably due to the presence of strong oxide bonds, $Mn_2O_2^+$ appears to be endowed with a noticeable stability and is fairly resistant to dissociation. In fact, it undergoes only a very slow dissociation to Mn^+ ($k_{uni} = 0.005\ s^{-1}$), a process that is unaffected by the addition of unreactive gases. Several types of connectivities are conceivable in the ligation of a dioxygen molecule by a dinuclear manganese cluster. Some insight into the structural features of **1** may be derived from its fragmentation pattern. Upon CID, the prevailing loss of MnO_2, with concomitant generation of Mn^+ [Equation (1a)], is observed besides the fragmentation to Mn_2O^+ [Eq. (1b)] and Mn_2^+ [Eq. (1c)]. Considering the formal oxidation states

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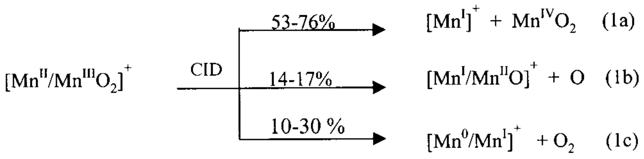
of manganese, we may envision channel (1 a) as a disproportionation process between the manganese atoms in the ionic and neutral products. This pathway is found to predominate over two- [Eq. (1b)] and four- [Eq. (1c)] electron reductions of the metal cluster, respectively.



Loss of neutral manganese atom(s) is not observed, which is at variance with the behavior of metal rich oxide clusters.[5]

The bimolecular reactivity of $Mn_2O_2^+$ has been probed towards selected neutrals (N). The measured rate constants along with the relative reaction efficiencies ϕ, defined as the ratio between the measured rate constant and the theoretical collision rate,[6] are listed in Table 1. The table shows also that the product ions are grouped according to the branching of the reagent ion, $Mn_2O_2^+$, into competitive pathways. Thus, in each set, ions are related to a primary product of $Mn_2O_2^+$ by consecutive reactions. The branching ratio of the primary product ions is given in parentheses. When **1** is left to react in the presence of ^{18}O-labeled water in the gas phase, a degenerate $^{16}O/^{18}O$ exchange (ϕ ca. 18%) is observed. The thermoneutral reactions leading to $Mn_2O^{18}O^+$ and $Mn_2{}^{18}O_2^+$ [Eqs. (2 a) and (2 b)] require the encounter of the reagents to form an ion-neutral complex, for which hydrogen shift processes take place from one O atom to the other, and this allows the loss of unlabeled H_2O.

$$Mn_2O_2^+ + H_2{}^{18}O \rightarrow Mn_2O^{18}O^+ + H_2O \qquad (2a)$$

$$Mn_2O^{18}O^+ + H_2{}^{18}O \rightarrow Mn_2{}^{18}O_2^+ + H_2O \qquad (2b)$$

Monitoring the time dependence of the ion abundances in the presence of $H_2{}^{16}O/H_2{}^{18}O$ (40:60 molar ratio), the $Mn_2O_2^+$/$Mn_2O^{18}O^+$/$Mn_2{}^{18}O_2^+$ ratios attain constant values, and these reflect statistically the relative pressures of the neutrals (Figure 1). The same equilibrium mixture of isotopomeric ions is obtained if the $Mn_2O^{18}O^+$ intermediate is isolated and left to exchange in the $H_2{}^{16}O/H_2{}^{18}O$ mixture. If the $Mn_2{}^{18}O_2^+$ ions that are formed as the end products of the exchange sequence with $H_2{}^{18}O$ are submitted to a pulse of unlabeled O_2, no reaction is observed, and this suggests the existence of a sizeable barrier to the displacement of an O_2 moiety. At longer reaction times, **1** undergoes the addition of water molecules leading to $Mn_2O_2(H_2O)^+$ and $Mn_2O_2(H_2O)_2^+$; moreover, a certain amount of $Mn_2O_2H_2^+$ is observed as well.

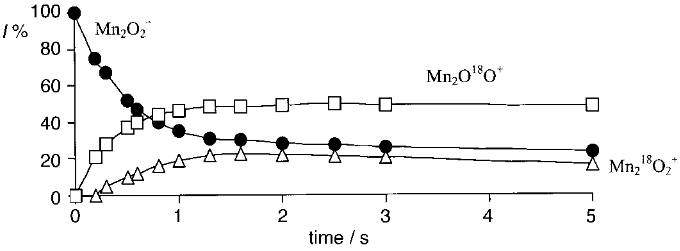


Figure 1. Time dependence of the $^{16}O/^{18}O$ exchange reaction of $Mn_2O_2^+$ ions at m/z 142 (●) in $H_2O/H_2{}^{18}O$ (45:55 molar ratio) at 2.6×10^{-8} mbar. Product ions are $Mn_2O^{18}O^+$ (□) at m/z 144 and $Mn_2{}^{18}O_2^+$ (△) at m/z 146.

The reaction of **1** with hydrogen sulfide yields Mn_2OS^+ in a process with a reaction efficiency of 55%, which is followed by a second exchange of O for a S atom, with concomitant loss of water, leading to $Mn_2S_2^+$. These processes, which parallel very closely the reactivity found with $H_2{}^{18}O$, are shown in Figure 2. Neither homolytic S–H bond cleavage nor O-atom transfer are ever observed, in spite of a small S–H bond dissociation energy and the relatively high oxophilicity of sulfur in H_2S.

Concerning the minor product $Mn_2S_2H_2^+$ (Figure 2; Table 1), it may originate from the reaction of H_2S with an intermediate complex, $Mn_2OS(H_2S)^+$ [Eqs. (3 a) and (3 b)], formed at a steady state with an undetectably low concentration, and the reaction leads to the product ion by addition of H_2S accompanied by loss of H_2SO. Involvement of $Mn_2S_2^+$ was excluded since no evidence was obtained for any reactivity of this ion towards H_2S.

$$Mn_2OS^+ + H_2S \rightarrow Mn_2OS(H_2S)^+ \qquad (3a)$$

$$Mn_2OS(H_2S)^+ + H_2S \rightarrow Mn_2S_2H_2^+ + H_2SO \qquad (3b)$$

Table 1. Rate constants (k_{exp}) and efficiences (ϕ) of the reactions of $Mn_2O_2^+$ ions with selected neutrals (N).

N	k_{exp}[a]	ϕ [%]	Product ions [%]
$H_2{}^{18}O$[b]	≥ 3.8	≥ 23	$Mn_2O^{18}O^+$, $Mn_2{}^{18}O_2^+$ (80); $Mn_2{}^*O_2H_2^+$, $Mn_2{}^*O_2(H_2{}^*O)_{1,2}^+$ (20)[c]
H_2O	≥ 0.7	≥ 4	$Mn_2O_2H_2^+$, $Mn_2O_2(H_2O)_{1,2}^+$
H_2S	7.3	58	Mn_2OS^+, $Mn_2S_2^+$ (95); $Mn_2S_2H_2^+$ (5)
NH_3	0.1	0.6	Mn^+, $Mn(NH_3)_{1,2}^+$ (74); $Mn_2O_2(NH_3)_{1,2}^+$ (26)
HCl	n.r.	n.r.	
H_2	n.r.	n.r.	
CH_3OH	3.1	21	Mn^+, $Mn(CH_3OH)_{1,2}^+$ (60); $Mn_2O_2H_2^+$, $Mn_2O_2CH_4^+$, $Mn_2O_2C_2H_6^+$ (40)
CH_3CHO	2.3	12	Mn^+, $Mn(C_2H_4O)_{1,2}^+$ (51); $Mn_2O_2C_2H_2^+$ (13); $Mn_2O_2H_2^+$ (22); $Mn_2O_2(C_2H_4O)^+$ (14)
i-C_4H_{10}	n.r.	n.r.	
C_2H_2	1.2	9.4	Mn^+ (52); Mn_2O^+ (36); Mn_2^+ (12)
C_2H_4	0.2	1.6	Mn^+ (60); Mn_2O^+ (5); $Mn_2OH_2^+$ (5); Mn_2^+ (30)
C_3H_4	3.1	24	Mn_2O^+ (15); Mn^+ (22); $Mn_2O_2H^+$, $Mn_2O_2H_2^+$ (7); $Mn_2OC_2H_2^+$ (7); $Mn_2OC_3H_2^+$, $Mn_2C_6H_4^+$ (49)
C_3H_6	0.9	6.9	$Mn_2O_2H^+$ (28); Mn^+ (44); Mn_2^+ (16); Mn_2O^+ (12)
C_6H_6	0.6	5.7	Mn^+, $Mn(C_6H_6)_{1,2}^+$ (61); Mn_2O^+ (12); $Mn_2O_2C_6H_6^+$ (27)

[a] Apparent bimolecular rate constants in 10^{-10} cm^3 molecules^{-1} s^{-1}; n.r. stands for no reactivity (Eff < 0.01 %). [b] H_2O (40 mol%); $H_2{}^{18}O$ (60 mol%). [c] *O stands for either ^{16}O or ^{18}O.

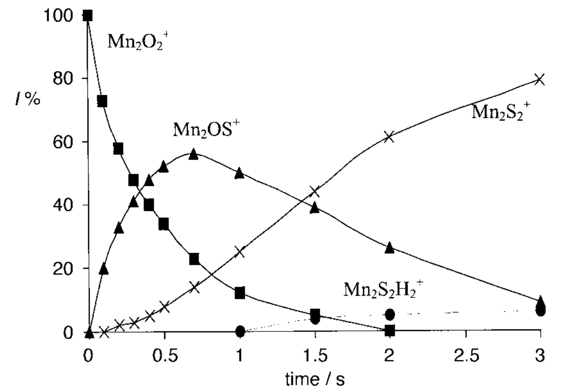


Figure 2. Relative intensities of major ions formed after selection of $Mn_2O_2^+$ ions (■) in H_2S at 3.0×10^{-8} mbar: Mn_2OS^+ ions at *m/z* 158 (▲); $Mn_2S_2^+$ ions at *m/z* 174 (×); $Mn_2S_2H_2^+$ ions at *m/z* 176 (●).

The $Mn_2O_2^+$ reaction with NH_3 does not lead to nitrogen-containing ions, other than addition products. Among the simple organic molecules that were left to react with **1**, methanol yields $Mn_2O_2H_2^+$, in addition to Mn^+. Whereas the formation of Mn^+ from this and other reactions gives very little information about the accompanying neutral species that may be formed, the formation of $Mn_2O_2H_2^+$ involves the abstraction of two hydrogen atoms with formal two-electron transfer from methanol to the metal cluster [Eq. (4)]. It is likely to be concomitant with the oxidation of methanol to formaldehyde, a process estimated to be endothermic by 84 kJ mol^{-1}.[7] In fact, the formation of $Mn_2O_2HD^+$ from the reaction of **1** with CD_3OH indicates that the abstraction of hydrogen atoms involves both the hydroxyl and the methyl groups of methanol. The observed kinetic isotope effect, $k(CH_3OH)/k(CD_3OH) = 1.24$, suggests the kinetic relevance of the C–H bond activation.

$$Mn_2O_2^+ + CH_3OH \rightarrow Mn_2O_2H_2^+ + CH_2O \qquad (4)$$

As evident from the kinetic plot of Figure 3, the primary product $Mn_2O_2H_2^+$ reacts further with the neutral to yield $Mn_2O_2CH_4^+$ and eventually $Mn_2O_2C_2H_6^+$ by the rapid ($\phi = 24\,\%$), consecutive exchange of an original OH moiety for an intact OCH_3 group, as evidenced by the use of the methanol isotopologue $CH_3{}^{18}OH$ [Eq. (5a) and (5b)].

$$Mn_2O_2H_2^+ + CH_3{}^{18}OH \rightarrow Mn_2OH(^{18}OCH_3)^+ + H_2O \qquad (5a)$$

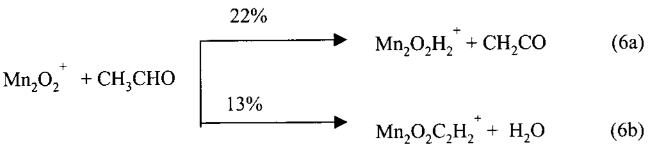
$$Mn_2OH(^{18}OCH_3)^+ + CH_3{}^{18}OH \rightarrow Mn_2(^{18}OCH_3)_2^+ + H_2O \qquad (5b)$$

This assignment is further supported by the formation of $Mn_2(OCD_3)_2^+$ as the end product from the reaction with CD_3OH. This reactivity behavior suggests a bis(hydroxy) structure for the reactant $Mn_2O_2H_2^+$.

In line with the expected decrease in oxidation properties, a changeover in reactivity is observed in passing from formal Mn^{II}/Mn^{III} oxide cluster **1**, which is able to undergo oxidative dehydrogenation, to the lower valent Mn^{I}/Mn^{II} species $Mn_2O_2H_2^+$, which promotes a formal ligand exchange involving elimination of water, with formation of secondary, $Mn_2OH(OCH_3)^+$, and tertiary products, $Mn_2(OCH_3)_2^+$, that keep the original formal metal oxidation states. The low-energy CID of $Mn_2(OCD_3)_2^+$ yields Mn_2O^+, $Mn_2OCD_3^+$, and $MnOCD_3^+$ in comparable amounts.

Both $Mn_2O_2H_2^+$ and $Mn_2(OCH_3)_2^+$ ions are efficiently reoxidized back to $Mn_2O_2^+$ when dioxygen is leaked into the FT-ICR cell at a partial pressure of approximately 8×10^{-8} mbar. When $Mn_2O_2^+$ is left to react with acetaldehyde, $Mn_2O_2C_2H_2^+$ (13 %) and $Mn_2O_2H_2^+$ (22 %) are formed as primary ionic products, besides Mn^+ (51 %) and the addition complex $Mn_2O_2(C_2H_4O)^+$ (14 %).

A feature of this reaction system is that, at variance with the above methanol sequence, the oxidative dehydrogenation of acetaldehyde, which presumably leads to ketene [Eq. (6a)], as well as the dehydration channel [Eq. (6b)] are competitive reactions.



$$Mn_2O_2^+ + CH_3CHO \xrightarrow{22\%} Mn_2O_2H_2^+ + CH_2CO \qquad (6a)$$

$$Mn_2O_2^+ + CH_3CHO \xrightarrow{13\%} Mn_2O_2C_2H_2^+ + H_2O \qquad (6b)$$

By analogy to Equation (4), in Equation (6a) **1** appears to activate the abstraction of two hydrogen atoms by promoting a process predicted to be endothermic by 84 kJ mol^{-1}, namely the oxidation of acetaldehyde to ketene.[7]

The possibility has been investigated that $Mn_2O_2H_2^+$ might perform the role of a hydrogenation reagent as well. To this end, its reactivity towards several neutrals has been checked with the result that only dioxygen is found to accomplish reoxidation to **1** [Eq. (7)], whereas the unsaturated species C_2H_4, C_3H_4, and CH_3CHO are all found to be unreactive.

$$Mn_2O_2H_2^+ + O_2 \rightarrow Mn_2O_2^+ + H_2O_2 \qquad (7)$$

Whereas dihydrogen and branched alkanes are not activated by **1**, small unsaturated hydrocarbons C_xH_y ($x,y = 2,2$; 2,4; 3,4; 3,6) and benzene react with sizeable efficiencies, and they yield oxidation products of

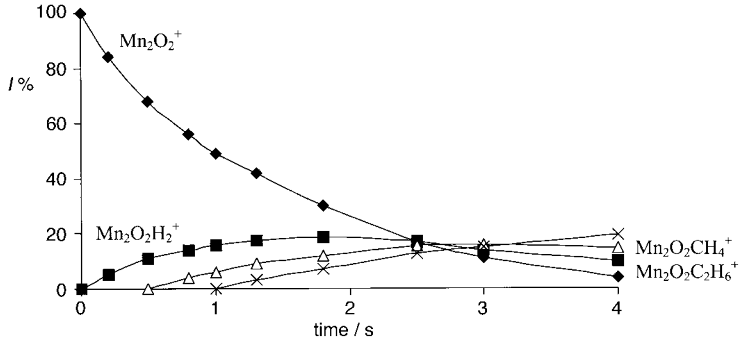


Figure 3. Relative intensities of major ions formed after selection of $Mn_2O_2^+$ ions (◆) in CH_3OH at 2.5×10^{-8} mbar: $Mn_2O_2H_2^+$ at *m/z* 144 (■); $Mn_2O_2CH_4^+$ ions at *m/z* 158 (△); $Mn_2O_2C_2H_6^+$ ions at *m/z* 172 (×).

the hydrocarbon together with Mn_2O^+, Mn^+, and Mn_2^+ that are frequently observed among the major ionic products. In addition to these processes, the $Mn_2O_2^+/C_3H_n$ ($n = 4,6$) systems exhibit one further reaction channel, leading to $Mn_2O_2H^+$, which is likely to arise from the homolytic fission of the methyl C–H bond, which forms the corresponding hydrocarbon radicals. In a subsequent H-atom abstraction process from propyne, $Mn_2O_2H^+$ yields small amounts of $Mn_2O_2H_2^+$.

Besides the reaction channels already considered, **1** reacts with C_3H_4 by a sequential facile reductive elimination of water, and this results in the formation of $Mn_2OC_3H_2^+$, an intermediate ion en route to formation of $Mn_2C_6H_4^+$ (Figure 4). The reaction of the tertiary product $Mn_2C_6H_4^+$ with dioxygen gives the parent ion **1** (20 %), in addition to Mn^+ (58 %) and Mn_2O^+ (22 %), in a 10 % efficient process. Finally, $Mn_2OC_2H_2^+$ is also formed as a primary product, which is not very abundant, according to a process formally corresponding to oxidation of the substrate coupled with C–C bond activation and loss of formaldehyde.

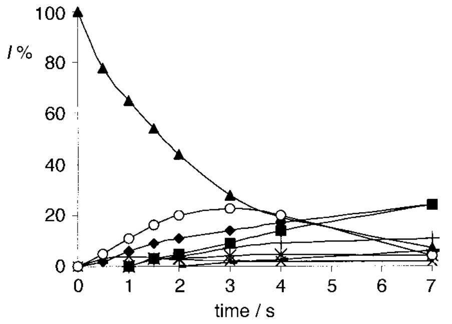


Figure 4. Relative intensities of major ions formed after selection of $Mn_2O_2^+$ ions (▲) in C_3H_4 at 2.1 x 10^{-8} mbar: Mn^+ at *m*/*z* 55 (◆); Mn_2O^+ at *m*/*z* 126 (■); $Mn_2O_2H^+$ at *m*/*z* 143 (×); $Mn_2O_2H_2^+$ at *m*/*z* 144 (–); $Mn_2OC_2H_2^+$ at *m*/*z* 152 (*); $Mn_2OC_3H_2^+$ at *m*/*z* 164 (○); $Mn_2C_6H_4^+$ at *m*/*z* 186 (+).

When benzene is the neutral substrate, an oxygen transfer process takes place that formally leads to C_6H_6O, besides fragmentation and addition processes.

Mn_2O^+: The reaction of $[Mn_2(CO)_4]^+$ with dioxygen affords a significant production of **2**. Mn_2O^+ is fairly stable and dissociates only slowly to Mn^+ ($k_{uni} = 0.06\ s^{-1}$).

As shown in Table 2, exemplary neutrals have been selected to probe the gas-phase reactivity of **2** with the aim of relating it to the corresponding ion chemistry of **1**. Apart from the prominent and unfortunately not very informative detachment of bare Mn^+, **2** exhibits somewhat similar reactivity properties with respect to **1**, though simple homolytic cleavages to release free radicals are not observed.

The reaction of **2** with H_2X (X = O, S) takes place by formal O-atom transfer to yield Mn_2^+ and neutral H_2XO. Similarly, an O-atom transfer process appears to be involved in the reaction of **2** with methanol, acetylene, and benzene. With regard to the possible occurrence of dehydration reactions, since they cannot proceed beyond one formal O-atom loss, $Mn_2{}^{18}O^+$ and Mn_2S^+ are the end products formed with $H_2{}^{18}O$ and H_2S, respectively.

It is noteworthy that methanol is almost the only one among the organic substrates in Table 2 that undergoes the abstraction of two hydrogen atoms leading to $Mn_2OH_2^+$, which may in turn undergo the formal exchange of an OH group with a methoxyl group to afford $Mn_2OCH_4^+$. Mn_2O^+ reacts with both H_2O and H_2S to yield $Mn_2OH_2^+$, the formation of which is still to be accounted for.

A completely different reactivity pattern is observed when the hetero analogue species Mn_2S^+, generated by reacting **2** with H_2S, reacts with the same substrate. A highly efficient dehydrogenation process ($\phi = 28\,\%$) leads to the formation of $Mn_2S_2^+$ [Eq. (8)], a species hardly reactive with any of the neutrals investigated, namely water, oxygen, and methanol.

$$Mn_2S^+ + H_2S \rightarrow Mn_2S_2^+ + H_2 \tag{8}$$

At variance with the multiple reaction pathways displayed by **1**, the reactivity of Mn_2O^+ towards acetaldehyde and propyne is rather low, and none of the oxidative features reported above for **1** have been observed.

Interestingly, $MnOH^+$ is formed from the reaction of **2** with acetylene, and this possibly involves the evolution of MnC_2H as a neutral.

Discussion

The reagent ions $Mn_2O_2^+$ and Mn_2O^+: However simple a tetra-atomic species such as $Mn_2O_2^+$ may appear at first glance, various electronic states and isomeric structures are conceivable. Discriminating between them is hardly possible, based on the available evidence. So the discussion on the observed reactivity pattern is related to the $Mn_2O_2^+$ and Mn_2O^+ ions specifically generated as previously described. However, **1** is formed by a ligand displacement process by O_2. The generation by this chemical route in conjunction with the relatively high pressure of the O_2 pulse, which also operates in removing any excess internal energy from unreactive collisions, are likely to concur with the formation of ground state species. Similar considerations apply to **2** though this species has been studied in lesser detail.

The equilibrium geometry of the neutral $(MnO)_2$ cluster is reported to be a rhombus by both theoretical and experimental studies.[8] The same structure may be tentatively assigned to the charged $Mn_2O_2^+$

Table 2. Rate constants (k_{exp}) and efficiences (ϕ) of the reactions of Mn_2O^+ ions with selected neutrals (N).

N	k_{exp}[a]	ϕ [%]	Product ions [%]
$H_2{}^{18}O$[b]	5.0	28	Mn^+ (60); Mn_2^+ (24); $Mn_2OH_2^+$ (14); $Mn_2{}^{18}O^+$ (2)
H_2S	1.3	11	Mn^+ (50); Mn_2^+ (15); $Mn_2OH_2^+$ (15); Mn_2S^+, $Mn_2S_2^+$ (20)
CH_3OH	6.9	46	Mn^+ (43); Mn_2^+ (38); $Mn_2OH_2^+$ (19)
CH_3CHO	2.6	13	Mn^+ (78); $MnOH^+$ (22)
C_6H_6	1.5	13	Mn^+ (88); Mn_2^+ (3); $Mn_2OC_6H_6^+$ (9)
C_3H_4	0.4	2.9	Mn^+ (85); $Mn_2OC_3H_4^+$ (15)
C_2H_2	0.8	6.1	Mn^+ (71); Mn_2^+ (11); $MnOH^+$ (18)

[a] See footnote [a], Table 1. [b] See footnote [b], Table 1.

species, as it is compatible with the low-energy CID fragmentation pattern. Also, the lack of isotope exchange between $Mn_2{}^{18}O_2{}^+$ and O_2 speaks against a possible side-on complex between $Mn_2{}^+$ and molecular oxygen. $(MnO)_2{}^+$ ions have also been obtained from the photoionization of $(MnO)_x$ clusters, though no information about their structure was given.[9] Indeed **1** may be structurally close to $Fe_2O_2{}^+$ ions as they are also reported to be unreactive with respect to O_2 displacement and to show a similar CID pattern.[10]

In the following paragraphs, the reactions of **1** and **2** with a few exemplary simple molecules are discussed. They are arranged into distinct groups in the attempt to provide a generalized reactivity pattern.

Dehydration processes: The loss of a water molecule may follow from the encounter of **1** with water, hydrogen sulfide, propyne, and acetaldehyde and ensuing bond rearrangement processes. Notably, the migration of two hydrogen atoms to form the departing water molecule is required. The fast, stepwise exchange reactions observed with $H_2{}^{18}O$ and H_2S demonstrate that no sizeable kinetic barriers are involved, and presumably efficiencies correlate with the driving force of the reaction. Indeed, the occurrence of ^{18}O incorporation from $H_2{}^{18}O$, which has been classified as an intermolecular dehydration,[11] has been frequently exploited as indirect evidence for the intermediacy of unstable, highly reactive high-valent metal oxo complexes in catalytic oxygenation reactions.[12] Within this framework, the exchange reactions of Equations (2a) and (2b) may be envisioned as a simple model for the involvement of oxygen-rich manganese oxide clusters in complex catalytic sites. The fast sequential reactions with H_2S that convert **1** into $Mn_2S_2{}^+$ find a counterpart in the same stepwise process displayed by $Fe_2O_2{}^+$.[13] The comparatively much lower efficiency for both the ^{18}O and S atom incorporation within **2** can be traced to the expected decrease in reactivity for the lower oxidized manganese species.[14]

Dehydrogenation: The reaction of **1** and **2** with methanol affords $Mn_2O_xH_2{}^+$, with $x = 2$ and 1, respectively, while only **1** gives the same product with acetaldehyde. The reactions of **1** with methanol and acetaldehyde can be envisioned as proceeding by activation of the C–H bond of the methyl group followed by hydrogen shift(s) and final elimination of CH_2O (unique pathway with methanol) or H_2O and CH_2CO (competitive routes with acetaldehyde). A formally similar process, leading to the incorporation of two H atoms into the reagent ion, has been described in the gas-phase reactions of $MnO_2{}^-$, $Mn_2O_3{}^-$, and $Mn_2O_4{}^-$ with methanol and primary alcohols.[15]

The reaction with water deserves special attention not only because of its biological relevance but also in view of the development of artificial photosynthetic systems. Indeed, among the large number of biomimetic Mn-enzyme models that have been designed and prepared, only a few of them have shown catalytic activity.[16] Due to the availability of multiple oxidation states, manganese oxides are commonly employed as oxidants in a variety of processes,[17] but oxidation of water to dioxygen is achieved by some colloidal Mn-oxo clusters only in the presence of strong oxidants.[18] Even if the detailed mechanism of water oxidation and the structure itself of the OEC remain matters of intense experimental investigation,[19] nonetheless the essential functions of the manganese clusters are recognized in binding and activating water, as well as in delocalizing oxidizing equivalents produced upon hydrogen atom stripping.[18, 20–22] In this context, it is noteworthy that **1** and **2** have accomplished the oxidation of methanol, a substrate closely related to the fundamentally important water molecule.

In a related, though distinct, context, a significant contribution towards the understanding of models for the OEC is due to a recent gas-phase reactivity study. Laser desorption/ionization mass spectrometry has shown that ionized complexes with a Mn_4O_4 cubane core decay by loss of O_2.[23] Dimeric Mn_2O_2 core complexes are reported not to conform to this reactivity behavior, which is confirmed by the relatively minor channel of O_2 loss upon CID of $Mn_2O_2{}^+$.

O-atom transfer: The release of an O atom from **1** yielding Mn_2O^+ appears to occur with the whole series of unsaturated hydrocarbons that have been assayed. Based on the way **1** is formed, this reaction ultimately represents an approach to stoichiometric oxidations by the abstraction of an oxygen atom from molecular oxygen. Manganese porphyrin complexes are efficient catalysts of olefin epoxidation with iodosylbenzene.[24] Among the numerous reagents devised as viable epoxidants of alkenes, metal-oxo, and related species are often used. In the gas phase, late-transition-metal oxides MnO^+, FeO^+, CoO^+, and NiO^+ rapidly oxidize ethene to most likely yield acetaldehyde rather than oxirane.[25] Due to the moderate reactivity shown by **1** as compared with that of MnO^+,[26] the former being, for example, unreactive towards alkanes and H_2, a gas-phase epoxidation as a result of O-atom transfer from **1** to the selected alkenes cannot be excluded a priori. Results have been reported for reactions in which suitably ligated metal oxides bring about selective epoxidation to avoid rearrangment to the more stable carbonyl compounds.[27]

The O-atom transfer process is displayed also in the reaction of **2** with selected substrates, and the corresponding product ion $Mn_2{}^+$ is obtained also by treating **2** with water, hydrogen sulfide, and methanol. The latter reactions, promoting oxidation to peroxide and sulfoxide species, show that **2** is a superior reagent in this respect if compared, for example, with FeO^+, which fails to activate X–O coupling for electronegative elements such as $X = O$ or S.[11]

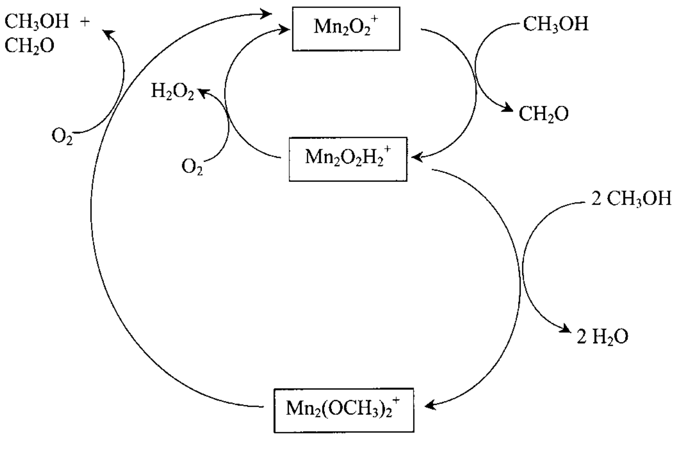
Homolytic cleavage: H-atom abstraction yielding $Mn_2O_2H^+$ is afforded only by the reaction of **1** with propene and propyne, for which the activation probably involves the allylic and propargylic C–H bonds (BDE, bond dissociation energy, of 355 and 372 kJ mol^{-1}, respectively).[28] Among the investigated substrates, only propyne is prone to undergo an oxidative C–C bond activation, and this activation formally leads to formaldehyde as the neutral product accompanying the formation of $Mn_2OC_2H_2{}^+$. The net cleavage of the H–OH bond (BDE = 497 kJ mol^{-1}) is not observed in the reaction of **1** with water. H-atom abstraction has been reported as a prominent reaction pathway in the gas-phase chemistry of

MnO^+ with H_2 and alkanes.[26] Clearly, the presence of an additional metal nucleus in **1** and **2** markedly reduces this type of reactivity.

Conclusion

The reported FT-ICR investigations of gaseous $Mn_2O_2^+$ ions point to their ability to activate catalytic processes with certain substrates. Catalytic gas-phase oxidation of methanol, acetaldehyde, and propyne by dioxygen can in fact be mediated by **1**.

As already outlined, **1** mediates the oxidation of methanol to yield formaldehyde and $Mn_2O_2H_2^+$, which is in turn able to react further with methanol to afford water and $Mn_2(OCH_3)_2^+$. If molecular oxygen is leaked into the FT-ICR cell, **1** is regenerated. This catalytic gas-phase oxidation converts methanol into a variety of controlled combustion products (Scheme 1). The overall sequence of steps, which can be seen as the $Mn_2O_2^+$-mediated conversion of methanol to CH_2O and H_2O ($\Delta H_r = -316.0\ kJ\,mol^{-1}$),[7] is thus comprised of two stages: in the first one, **1** catalyzes the convertion of CH_3OH and O_2 into CH_2O and H_2O_2 ($\Delta H_r = -52.4\ kJ\,mol^{-1}$),[7] and in the second one, $Mn_2O_2H_2^+$ serves as an intermediate for the dehydration of methanol.

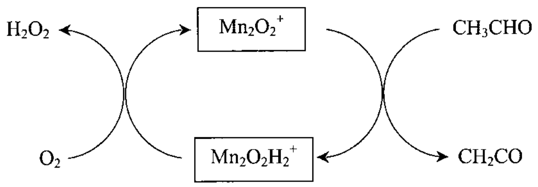


$$2\ CH_3OH + O_2 \longrightarrow 2\ CH_2O + 2\ H_2O \qquad \Delta H_r = -316.0\ kJ\ mol^{-1}$$

Scheme 1. Catalytic gas-phase oxidation of methanol.

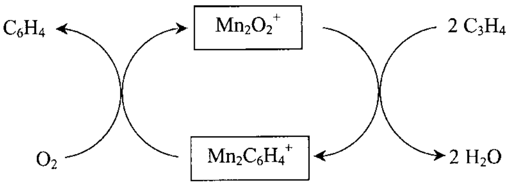
As depicted in Scheme 2, **1** also achieves the oxidation of acetaldehyde to ketene and hydrogen peroxide by oxygen ($\Delta H_r = -46.1\ kJ\,mol^{-1}$).[7] Whereas in this cycle $Mn_2O_2H_2^+$ is involved as an intermediate form of the catalyst, $Mn_2O_2^+$-mediated dehydration of propyne yields another active dimanganese species, namely $Mn_2C_6H_4^+$. The overall reaction in Scheme 3 describes the strongly exothermic oxidation of propyne by dioxygen to (*E*)-hexa-1,5-diyne-3-ene, a likely isomer for C_6H_4 ($\Delta H_r = -316.8\ kJ\,mol^{-1}$).[7]

The irreversible formation of sizeable amounts of the Mn^+ ion as the end product, that deters the catalytic efficiency of the reaction, suggests detachment processes activated by the excess energy liberated upon the interaction of the oxometal centers with the nucleophile.



$$CH_3CHO + O_2 \longrightarrow CH_2CO + H_2O_2 \qquad \Delta H_r = -49.0\ kJ\ mol^{-1}$$

Scheme 2. Oxidation of acetaldehyde.



$$2\ C_3H_4 + O_2 \longrightarrow C_6H_4 + 2\ H_2O_2 \qquad \Delta H_r = -316.8\ kJ\ mol^{-1}$$

Scheme 3. Oxidation of propyne by dioxygen.

Examples of gas-phase catalysis using O_2 as a reactant have been described.[25] In this context, $Mn_2O_2^+$-mediated processes have succeeded as well in the task of using molecular oxygen as a viable oxidant in the gas phase. Moreover, the mild experimental conditions result only in selective and clean oxidation reactions. The complete oxidation of methanol, acetaldehyde, or propyne to carbon dioxide and water would obviously be wasteful, whereas their partial oxidation to useful intermediates may suggest strategies for the synthesis of fine chemicals and biologically active compounds.

As a final remark, it may be noted that the reactivity features of both **1** and **2** lack the pronounced radical-like behavior displayed by MnO^+, namely the ability to perform H-atom abstraction from neutrals such as H_2, alkanes, and benzene.[25, 26]

Although the effect of a varying x/y ratio in oxo manganese cations, $Mn_xO_y^+$, cannot be predicted from the present results, it may conceivably be exploited for tuning chemical reactivity. The present results do in fact confirm the higher reactivity of oxide cations of the late first-row transition metals relative to the bare metal ions.[26]

Experimental Section

Materials: All chemicals were research grade products obtained from commercial sources and used as supplied. The gases used were purchased from Matheson Gas Products Inc. with a stated purity exceeding 99.95 mol%.

Procedure: The FT-ICR experiments were performed with a Bruker ApexTM47e spectrometer equipped with an external ion source, a cylindrical infinity cell (6 cm length, 6 cm diameter), and two pulsed valves. The cluster ions $Mn_2O_2^+$ (**1**) and Mn_2O^+ (**2**) were generated from the reaction of $[Mn_2(CO)_4]^+$, formed in the external ion source by chemical ionization of $[Mn_2(CO)_{10}]$ in Ar, with O_2, pulsed into the ICR cell up to the peak pressure of about 1×10^{-5} mbar, and this occurred plausibly by stepwise oxidation. After a suitable pumping time, the reactant ion was selected by a series of broad-band radiofrequency (rf) and single rf ejection pulses, to avoid unplanned excitation, and allowed to react with inorganic and organic substrates admitted into the ICR cell through leak valves at stationary pressures of 10^{-8} to 10^{-7} mbar. The pressure readings, obtained from the Bayard–Alpert ionization gauge, were calibrated by using the rate constant $k = 1.1 \times 10^{-9}\,cm^3\,s^{-1}$ for the reference reaction $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + CH_3^{\bullet}$ and corrected utilizing individual response factors.[29] In the reactions with $H_2{}^{18}O$ as the neutral reagent, one had to take into account the unavoidable presence of background traces of water, $H_2{}^{16}O$, in the analyzer cell. Therefore, the actual $H_2{}^{16}O/H_2{}^{18}O$ ratio was determined by the reaction with CH_5^+ ions to yield $H_3{}^{16}O^+$ and $H_3{}^{18}O^+$ in relative abundances that reflected the concentration of the neutrals.

The second-order rate constants (k_{exp}) were derived from the pseudo-first-order decay of the reactant ion intensity versus time and expressed as percentages (efficiencies) of the collision rate constant (k_{coll}) calculated by the parametrized trajectory theory.[6] In order to minimize interference by consecutive reactions, branching ratios for parallel reactions were obtained from the extrapolation of product ion intensities at initial times. The observed rate constants and the product distributions did not show any change by varying the number of thermalizing collisions of the reagent ion with the pulsed O_2 gas. The reproducibility of k_{exp} was always good, while the error of their absolute values, introduced mostly from the uncertainty in the concentration of the neutral, was estimated as ±30%. The elemental composition of the product ions was checked by accurate mass analysis by accumulating a series of 10–30 time domain signals to improve the S/N ratio. The reaction sequences were confirmed by selecting each reagent ion and checking its product ions.

CID experiments were performed on a desired ion by using kinetic excitation by a resonant radio-frequency pulse of variable duration at constant peak-to-peak voltage. During the following delay time, trapped excited ions underwent collisions with the target gas (Ar) at a static pressure of 3×10^{-8} mbar.

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