Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 241 (2005) 63–73

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

An experimental study of ligand exchange and bond insertion in the reactions of dimanganese carbonyl ions with alcohols in the gas phase

Eric S.E. van Beelen, Steen Ingemann*

Swammerdam Institute for Life Sciences, Faculty of Science, University of Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands

Received 13 September 2004; accepted 1 November 2004
Available online 8 December 2004

Abstract

The gas-phase reactions of dimanganese carbonyl ions ($Mn_2(CO)_n^+$; $n = 1–5$) with methanol have been studied with the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The predominant reaction of the $Mn_2(CO)_n^+$ ions with up to four CO ligands involves the incorporation of methanol and the loss of one or more CO ligands, whereas the $Mn_2(CO)_5^+$ ion reacts by the successive addition of two alcohol molecules. The efficiency of the overall reaction with methanol decreases with the number of CO ligands present in the manganese containing ion. In addition, the reactions of the $Mn_2(CO)_4^+$ ion with ethanol and *n*-propanol have been examined and observed to be less efficient than the reaction with methanol. The efficiency of the reaction of the $Mn_2(CO)_4^+$ ion with CD_3OH, C_2D_5OH or n-C_3D_7OH is significantly lower than of the reaction with the related unlabelled species revealing the occurrence of a significant isotope effect on the overall process. The primary product ions of the reactions of $Mn_2(CO)_4^+$ with an alcohol react further with the formation of $Mn_2(CO)_n(ROH)_2^+$ ($n = 0–2$) ions. These latter ions react with an alcohol molecule with the formation of collision complexes that expel a hydrogen or alkane molecule together with the CO ligands. Based upon experiments with CD_3OH, C_2D_5OH and n-C_3D_7OH, respectively, the loss of a hydrogen molecule is concluded to involve insertion into the O—H bond, whereas alkane elimination is a result of insertion into the C—O bond of the alcohol.

Keywords: Fourier transform ion cyclotron resonance; Dimanganese carbonyl ions; Aliphatic alcohols; Ligand exchange; Bond insertion

1. Introduction

The study of transition metal containing ions in the gas phase offers the opportunity to probe their intrinsic chemical and physical properties in the absence of complicating factors such as interactions with solvent molecules and counter ions [1,2]. The gas-phase chemistry of electronically and coordinatively unsaturated transition metal ions [3] is not only inherently interesting, but can also provide insight into the mechanisms of reactions in solution and on surfaces and thus lead to a better description of the properties of intermediates species [4,5]. The extensive literature on transition metal ions in the gas phase reveal a rich chemistry involving fundamental processes that are well-known for condensed phase systems, such as ligand exchange and insertion into a C–H, C–O or C–C bond [6,7]. Most of the reported studies concerned with the gas-phase ion–molecule chemistry are focused on bare transition metal ions or metal ions bonded to ligands such as CO and a cyclopentadienyl group [1–5]. The ion–molecule chemistry of small transition metal clusters [8,9] have been examined less extensively even though the results of such studies may assist in understanding catalytic reactions under heterogeneous conditions.

Transition metal complexes are also of crucial importance in biological systems in which they often act as an essential part of the reactive centers of enzymes. In this context, manganese is an important element that is part of the active site

---

* Corresponding author. Tel.: +31 205 256 967; fax: +31 205 256 971.
E-mail address: ingemann@science.uva.nl (S. Ingemann).

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.11.003

of the photosystem II [10] and a number of catalases [11,12]. The studies of the biological systems – in particular dinuclear manganese containing catalases [13] – have inspired the development of complexes that are capable of catalyzing the oxidation of simple organic molecules [14,15]. Notwithstanding the interest in manganese containing complexes in biological and chemical systems, relatively little is know about the intrinsic ion–molecule reactions of such species in the gas phase. The bare Mn^+ ion has been studied and is reported to be relatively unreactive towards simple molecules in the electronic ground state [16,17], whereas the excited states of Mn^+ react with alkanes by C–H and C–C bond insertion [18]. Insertion into a C–C bond is reported to occur also in the unimolecular dissociations of metastable complexes of Mn^+ and 4-octyne [19] and selective activation of the C–O bond is known to be involved in the loss of water from metastable complexes of Mn^+ and 2-butanol [20]. Ligand substitution has been examined for a variety of RMn^+ ions with crown ethers and reported to involve the replacement of the smaller crown ether by the higher homologue [21]. The dimanganese ion, $Mn_2{}^+$, has not been studied in great detail but is reported to react predominantly with aliphatic alcohols by cleavage of the Mn–Mn bond with the formation of $Mn(ROH)^+$ ions that may attain a $Mn(R)(OH)^+$ structure [22]. Other studies of binuclear manganese containing species have addressed the clustering reactions of ions derived from $Mn_2(CO)_{10}$ [23] and the ion–molecule chemistry of the $Mn_2O_2{}^+$ and Mn_2O^+ ions formed in the reactions of $Mn_2(CO)_4{}^+$ with O_2 [24]. A systematic study of the reaction of dimanganese carbonyl ions with simple molecules has not been undertaken even though these are formed in relatively high yields by electron ionization of $Mn_2(CO)_{10}$ [25,26]. In order to obtain more insight into the gas-phase ion–molecule chemistry of dimanganese containing species we allowed a series of $Mn_2(CO)_n{}^+$ ions to react with aliphatic alcohols in a Fourier transform ion cyclotron resonance (FT-ICR) instrument [27]. Specifically, the present study was undertaken in order to determine the reactivity of the $Mn_2(CO)_n{}^+$ ions as a function of the number of CO ligands, to examine the extent of ligand exchange and to study the propensity for cleavage of Mn–Mn bond. The aliphatic alcohols were selected as substrates with the purpose of examining the possible occurrence of insertion into a covalent bond in the substrate by one of the manganese atoms of the reactant ions. In addition, the alcohols were chosen for a closer study, because such species can emerge as important intermediates in the synthesis of hydrocarbons by the Fischer-Tropsch process over catalyst that may contain manganese [28,29].

2. Experimental section

2.1. Instrumental method

The experiments were performed with the use of a Bruker Daltonics APEX II FT-ICR mass spectrometer which has been described previously [30]. The dimanganese carbonyl ions were formed by electron ionization of $Mn_2(CO)_{10}$ as introduced into the external ion source with a direct insertion probe at a temperature of 25–30 °C. The ion-source temperature was maintained at 100 °C and the electron energy was between 30 and 70 eV. The $Mn_2(CO)_n{}^+$ ions with $n = 2, 3, 4, 5$ and 10 were the most abundant in the series, whereas the remaining ions were formed in a relatively low yield (Fig. 1).

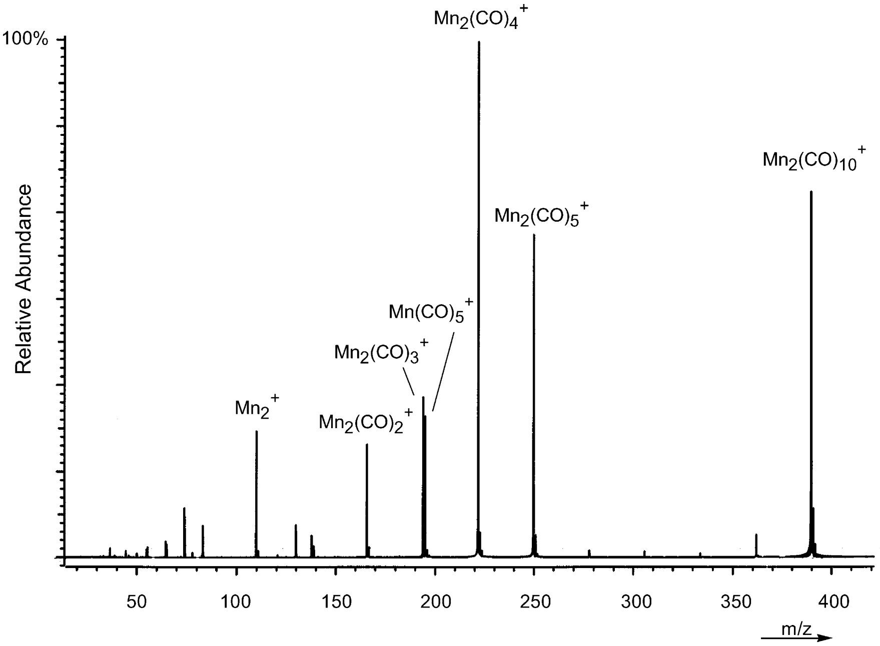


Fig. 1. Electron ionization (70 eV) mass spectrum of $Mn_2(CO)_{10}$ as recorded with the Bruker Daltonics APEX II FT-ICR mass spectrometer.

The ions were extracted from the ion source and accelerated into a 3 keV beam that was focused with a series of electric lenses and deflection plates while entering the magnetic field of 4.7 T. Subsequently, the ions were decelerated to a kinetic energy that was sufficiently low to allow trapping of the ions in the infinity cell of the instrument. The aliphatic alcohols were introduced into the FT-ICR main vacuum system through a leak valve until the indicated pressure was about 2.5×10^{-8} mbar. The indicated pressures were corrected for the sensitivity of the ionization gauge for the neutral species according to a reported procedure (see also ref. [31]). In brief, the measured partial pressures were corrected with the use of $R = 0.36\alpha + 0.30$ in which R is the sensitivity relative to N_2 ($R(N_2)$ is arbitrarily set to 1 and α is the molecular polarizability) [32].

Collisional lowering of the kinetic energy of the ions trapped in the FT-ICR was achieved by admitting Ar gas to the cell through a pulsed-valve. The valve was open for a period of 60–120 ms; the exact time depended on the pressure of Ar gas (0.5–1 bar) in the reservoir connected to the valve itself. The indicated peak pressure of Ar in the vacuum system of the instrument was 10^{-5} mbar. After a period of 1.5 to 2 s the pressure in the FT-ICR cell was sufficiently low to allow a given $Mn_2(CO)_n{}^+$ ion to be selected by ejection of all other ionic species from the FT-ICR cell. The isolation of the ions of interest was achieved in such manner that the off-resonance excitation of their kinetic energy was avoided [33]. After the isolation procedure, the reactions of the selected ions with a given substrate were followed as a function of time.

2.2. Materials

All chemicals were obtained commercially and used without purification. The (un)labelled aliphatic alcohols used were dried on molecular sieves (4 Å) for at least two days prior to use.

3. Results

3.1. Reaction rates

In the present experiments, the $Mn_2(CO)_n{}^+$ ions were isolated in such a way that the excess kinetic energy was brought to a minimum prior to the reactions with a given alcohol in line with previous studies [30,34]. The precise distribution of the internal and kinetic energy of the ions is unknown but a linear dependence (correlation coefficient ≥ 0.990) of the natural logarithm of the normalized abundance of the reactant $Mn_2(CO)_n{}^+$ ions with time was observed in all experiments (see Fig. 2). This is in agreement with the fact that the kinetics of ion–molecule reactions in an FT-ICR instrument are pseudo-first-order since the number of ions are normally a factor of 10^4 lower than of the neutral reactants.

The experimental pseudo-first-order rate constants were converted subsequently into the second order constants with the use of the corrected pressure of a given alcohol and an assumed temperature of 298 K. Even though the corrected pressure of the alcohol was used to estimate the rate constants, the values given in Table 1 may be associated with a relatively large systematic error (30–50%). Relative to each other, the rate constants are considered to be sufficiently precise to allow a determination of the trend in the reactivity of the ions towards the (un)labelled alcohols. The reactivity order of the ions is indicated by the efficiency of the overall reactions obtained as the ratio between the experimental rate constant and the collision rate constant obtained from the average dipole orientation (ADO) theory [35,36]. The efficiencies obtained

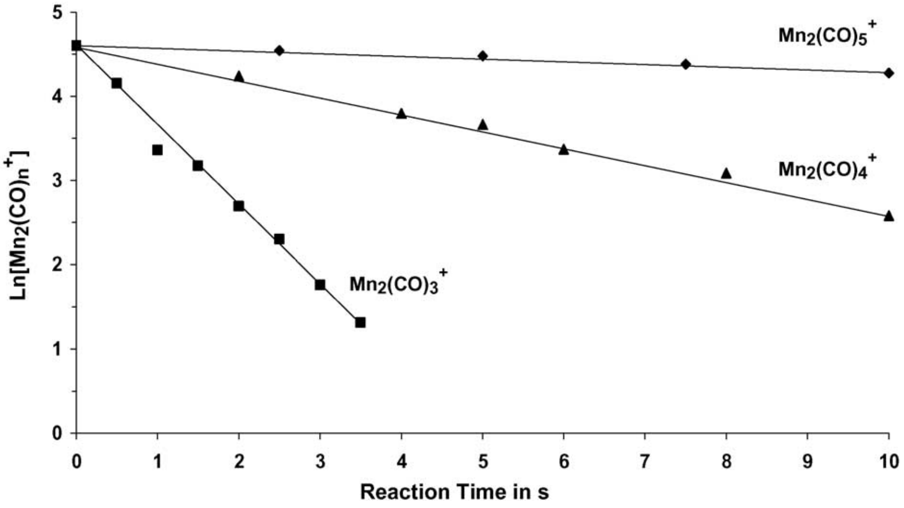


Fig. 2. Time dependence of the natural logarithm of the normalized abundance of the $Mn_2(CO)_n{}^+$ ions in the presence of CH_3OH in the FT-ICR cell. The pressure of methanol was in the different experiments: $P(CH_3OH) = 2.5 \times 10^{-8}$ mbar (reactant ion: $Mn_2(CO)_3{}^+$); $P(CH_3OH) = 1.4 \times 10^{-8}$ mbar (reactant ion: $Mn_2(CO)_4{}^+$); $P(CH_3OH) = 0.95 \times 10^{-8}$ mbar (reactant ion: $Mn_2(CO)_5{}^+$).

Table 1
Rate constants (in cm^3 $molecule^{-1}$ s^{-1}) and efficiencies of the reactions of the $Mn_2(CO)_n^+$ ions (n = 2–5) with (un)labelled methanol, ethanol and *n*-propanol, respectively[a]

Reactant ion	Alcohol	Rate constant k_{exp}	k_{ADO}[b]	Efficiencies	Relative efficiencies
$Mn_2(CO)_2^+$	CH_3OH	8.22×10^{-10}	1.55×10^{-9}	0.53	1
$Mn_2(CO)_3^+$	CH_3OH	7.48×10^{-10}	1.54×10^{-9}	0.49	0.92
$Mn_2(CO)_4^+$	CH_3OH	5.58×10^{-10}	1.52×10^{-9}	0.37	0.70
$Mn_2(CO)_4^+$	CD_3OH	1.96×10^{-10}	1.48×10^{-9}	0.13	0.25
$Mn_2(CO)_5^+$	CH_3OH	1.69×10^{-10}	1.51×10^{-9}	0.11	0.21
$Mn_2(CO)_4^+$	CH_3CH_2OH	4.73×10^{-10}	1.51×10^{-9}	0.31	0.58
$Mn_2(CO)_4^+$	CD_3CD_2OH	1.96×10^{-10}	1.45×10^{-9}	0.13	0.25
$Mn_2(CO)_4^+$	$CH_3CH_2CH_2OH$	2.51×10^{-10}	1.47×10^{-9}	0.17	0.32
$Mn_2(CO)_4^+$	$CD_3CD_2CD_2OH$	1.17×10^{-10}	1.40×10^{-9}	0.08	0.15

[a] The rate constants may be associated with an absolute error of 30–50%. Relative to each other the rate constants are considered to be more precise (see text).

[b] The efficiencies have been obtained as the ratio between the experimentally obtained rate constant and the collision rate constant as estimated with the use of the average dipole orientation (ADO) theory (see refs. [35,36]).

by this procedure are given in Table 1 together with the values relative to the reaction with the highest efficiency.

3.2. Reactions with methanol

The ionic products of the reactions between the $Mn_2(CO)_n^+$ ions ($n = 1$–5) and methanol are summarized in Table 2. The results for the ions with $n = 2$–5 are obtained from experiments in which a given dimanganese carbonyl ion is isolated and then allowed to react with methanol for 10–15 s. The distinction between the initial product ions and the ions formed by consecutive ion–molecule reactions is achieved from the plots of the normalized abundances of the various ions as function of time (see, for example

Table 2
Relative yield (in %) of the product ions formed in the reaction of the $Mn_2(CO)_n^+$ ions ($n = 1$–5) with methanol

Reactant ion	Product ion[a]	Relative abundance			
		Initial CH_3OH	Initial CD_3OH	75% conversion[b] CH_3OH	75% conversion[b] CD_3OH
$Mn_2(CO)^+$	$Mn_2(ROH)^+$	100[c]		–[c]	
$Mn_2(CO)_2^+$	$Mn_2(ROH)^+$	100		91	
	$Mn(ROH)_2^+$			9	
$Mn_2(CO)_3^+$	$Mn_2(CO)_2(ROH)^+$	27		21	
	$Mn_2(CO)(ROH)^+$	73		27	
	$Mn_2(ROH)_2^+$			39	
	$Mn(ROH)_2^+$			13	
$Mn_2(CO)_4^+$	$Mn_2(CO)_3(ROH)^+$	100	100	23	28
	$Mn_2(CO)_2(ROH)_2^+$			12	14
	$Mn_2(CO)(ROH)_3^+$			11	11
	$Mn_2(CO)_4(ROH)^+$	–[d]	–[d]	3[d]	6[d]
	$Mn_2(CO)_2(ROH)^+$	–[e]	–[e]	–	–
	$Mn_2(CO)(ROH)^+$	–[e]	–[e]	–	–
	$Mn_2(CO)(ROH)_2^+$			10	8
	$Mn_2(ROH)^+$	–[f]	–[f]	4[f]	8[f]
	$Mn_2(ROH)_2^+$			9	6
	$Mn_2(ROH)_3^+$			4	3
	$Mn_2(RO)_2^+$			2	2
	$Mn_2(RO)_2(ROH)^+$			12	11
	$Mn_2(O)(ROH)_2^{+}$[g]			3	2
	$Mn(CO)(ROH)_3^+$			3	1
	$Mn(ROH)_2^+$			4	–
$Mn_2(CO)_5^+$	$Mn_2(CO)_5(ROH)^+$	100		20	
	$Mn_2(CO)_5(ROH)_2^+$			80	

[a] The structures of the product ions are assumed.

[b] 75% conversion into products; the pressure of CH_3OH or CD_3OH was 1.4×10^{-8} mbar.

[c] Mn_2^+ ions are also formed (see text); the Mn_2^+ ions were the most abundant ionic species present at reaction times of more than 1 s.

[d] These product ions are formed in the beginning in a yield below or close to 1% (see also Table 3).

[e] Low yields (≤1%) are observed initially; these ions are likely to react further with methanol and – as a result – are not observed at longer reaction times.

[f] Small amounts (≤1%) are observed at short reaction times; these ions can react slowly with methanol to afford $Mn(ROH)_2^+$ ions (see text).

[g] These ions may also attain a $Mn_2(OH)(RO)(ROH)^+$ structure.

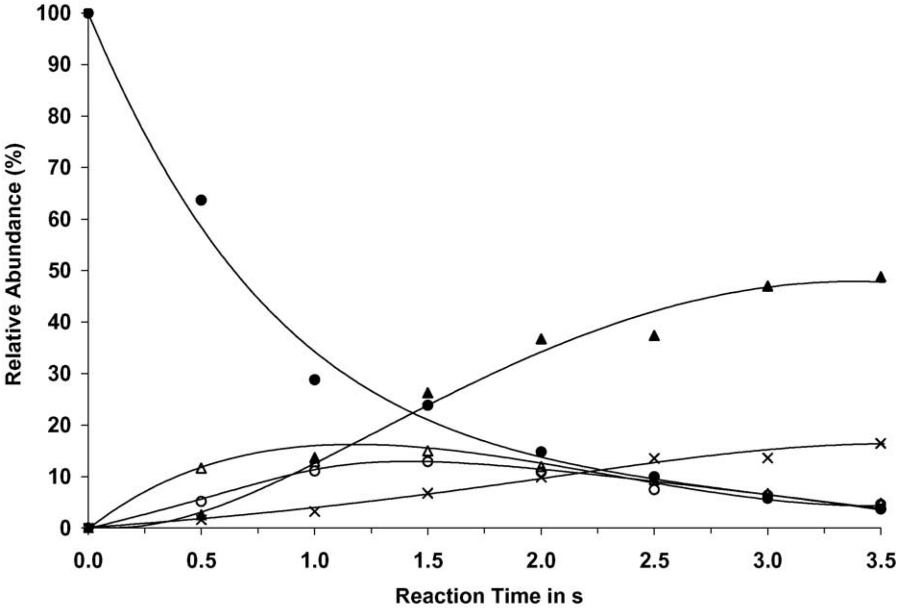


Fig. 3. The reaction of the $Mn_2(CO)_3^+$ ion with methanol followed as a function of reaction time: (●) ($Mn_2(CO)_3^+$); (○) ($Mn_2(CO)_2(CH_3OH)^+$); (△) ($Mn_2(CO)(CH_3OH)^+$); (▲) ($Mn_2(CH_3OH)_2^+$); (×) ($Mn(CH_3OH)_2^+$); $P(CH_3OH) = 2.5 \times 10^{-8}$ mbar.

Figs. 3 and 4). The initial abundances of the primary product ions given in Table 2 are derived from the normalized product ion abundances for reaction times up to a few seconds [37].

Only minor amounts of $Mn_2(CO)^+$ ions are generated by electron ionization of $Mn_2(CO)_{10}$ (Fig. 1). The low abundance of the $Mn_2(CO)^+$ ions hampered the experiments concerned with the rate of the reaction with methanol. Nevertheless, it could be observed that $Mn_2(CO)^+$ reacts readily with methanol by loss of CO from the collision complex. Also, abundant Mn_2^+ ions are formed possibly as a result of a facile dissociation of the $Mn_2(CO)^+$ ions (see Section 4).

The $Mn_2(CO)_2^+$ ion reacts readily with methanol by the loss of two CO ligands and the formation of ions which are formulated as $Mn_2(CH_3OH)^+$ (Eq. (1) and Table 2). The precise structure of the latter ions is unknown and the presence of an intact alcohol molecule in the various product ions is assumed for simplicity throughout Section 3 and in the Tables (vide infra). Irrespective of the precise structure of the $Mn_2(CH_3OH)^+$ ions, these are observed to react relatively

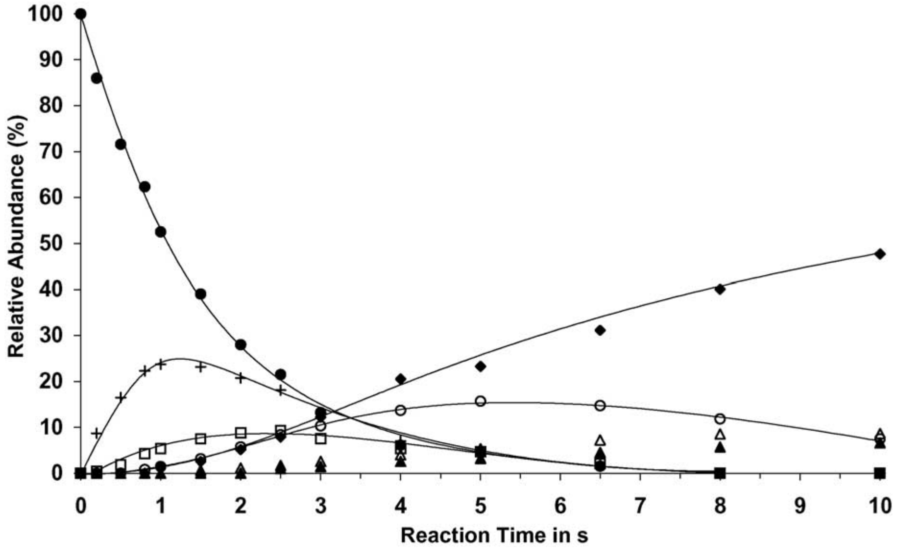


Fig. 4. The main reaction products of the reaction of the $Mn_2(CO)_4^+$ ion with CH_3OH followed as a function of reaction time: (●) ($Mn_2(CO)_4^+$); (+) ($Mn_2(CO)_3(CH_3OH)^+$); (□) ($Mn_2(CO)_2(CH_3OH)_2^+$); (○) ($Mn_2(CO)(CH_3OH)_3^+$); (△) ($Mn_2(O)(CH_3OH)_2^+$); (♦) ($Mn_2(CH_3O)_2(CH_3OH)^+$); (▲) ($Mn_2(CH_3O)_2^+$); $P(CH_3OH) = 1.4 \times 10^{-8}$ mbar. Lines are drawn only for the five most abundant ions for reasons of clarity.

slowly with methanol by cleavage of the Mn–Mn bond thus leading to $Mn(CH_3OH)_2^+$ ions (Eq. (2)).

$$Mn_2(CO)_2^+ + CH_3OH \rightarrow Mn_2(CH_3OH)^+ + 2CO \quad (1)$$

$$Mn_2(CH_3OH)^+ + CH_3OH \rightarrow Mn(CH_3OH)_2^+ + Mn \quad (2)$$

Comparable results are obtained for $Mn_2(CO)_3^+$; that is, in the reaction with methanol one or two CO ligands are expelled from the collision complex with formation of $Mn_2(CO)_2(CH_3OH)^+$ and $Mn_2(CO)(CH_3OH)^+$ ions, respectively (see Fig. 3 and Table 2). These ions react further with methanol with the expulsion of the CO ligand(s) from the collision complex and the formation of $Mn_2(CH_3OH)_2^+$ ions. In addition, cleavage of the Mn–Mn bond occurs to a minor extent in the consecutive reactions and leads to the $Mn(CH_3OH)_2^+$ ions that are observed also in this reactant system.

The $Mn_2(CO)_4^+$ ion reacts predominantly by incorporation of methanol concomitant with the loss of a CO ligand (Eq. (3)) and only to a minor extent by formation of an adduct ion (Eq. (4)). In addition, small amounts of a series of $Mn_2(CO)_n(CH_3OH)^+$ ($n = 0$–2) ions are formed initially as the result of the loss of more than one CO ligand from the collision complex (Table 2).

$$Mn_4(CO)_2^+ + CH_3OH \rightarrow Mn_2(CO)_3(CH_3OH)^+ + CO \quad (3)$$

$$Mn_4(CO)_2^+ + CH_3OH \rightarrow Mn_2(CO)_4(CH_3OH)^+ \quad (4)$$

Cleavage of the Mn–Mn bond occurs also during the consecutive ion–molecule reactions in the $Mn_2(CO)_4^+$/methanol system as revealed by the generation of minor amounts of $Mn(CO)(CH_3OH)_3^+$ and $Mn(CH_3OH)_2^+$ ions (Table 2).

The incorporation of methanol is consecutive for the $Mn_2(CO)_4^+$ ion and results in $Mn_2(CO)_2(CH_3OH)_2^+$ and $Mn_2(CO)(CH_3OH)_3^+$ ions (see Fig. 4). Some $Mn_2(CO)(CH_3OH)_2^+$ ions are also formed together with $Mn_2(CH_3OH)_2^+$ ions indicating that the incorporation of the second methanol molecule is associated with the loss of more than one CO ligand. This is corroborated by experiments in which the $Mn_2(CO)_3(CH_3OH)^+$ ions are isolated and allowed to react selectively with methanol. In these experiments, about 90% $Mn_2(CO)_2(CH_3OH)_2^+$ ions are formed together with 5% $Mn_2(CO)(CH_3OH)_2^+$ and 5% $Mn_2(CH_3OH)_2^+$ ions.

Ions with an assigned structure of $Mn_2(CH_3O)_2^+$ and $Mn_2(CH_3O)_2(CH_3OH)^+$ are also formed in the reactions of $Mn_2(CO)_4^+$ with methanol (Table 2). These product ions are likely to arise during the reactions of the $Mn_2(CO)_n(CH_3OH)^+$ species ($n = 0$–2) in keeping with the results of experiments in which the $Mn_2(CO)_2(CH_3OH)_2^+$ ions react selectively with methanol to afford 35% $Mn_2(CH_3O)_2(CH_3OH)^+$ ions and 65% $Mn_2(CO)(CH_3OH)_3^+$ ions (Eqs. (5) and (6)).

$$Mn_2(CO)_2(CH_3OH)_2^+ + CH_3OH \rightarrow Mn_2(CH_3O)_2(CH_3OH)^+ + H_2 + 2CO \quad (5)$$

$$Mn_2(CO)_2(CH_3OH)_2^+ + CH_3OH \rightarrow Mn_2(CO)(CH_3OH)_3^+ + CO \quad (6)$$

Small amounts of ions with a composition of $Mn_2(O)(CH_3OH)_2^+$ are observed also at longer reaction times. The origin of these ions is somewhat uncertain but they are suggested to be formed in the consecutive reactions of the $Mn_2(CO)_n(CH_3OH)_2^+$ ($n = 0$–2) ions.

With CD_3OH as the substrate, ions with an assigned structure of $Mn_2(CD_3O)_2(CD_3OH)^+$ and $Mn_2(O)(CD_3OH)_2^+$ are generated during the successive reactions of the $Mn_2(CO)_4^+$ ions. The formation of the $Mn_2(CD_3O)_2(CD_3OH)^+$ ions reveals that the loss of a hydrogen molecule involves only the hydroxylic hydrogen atoms of the alcohol as exemplified in Eq. (7). Also, the formation of $Mn_2(O)(CD_3OH)_2^+$ reveals that the methane molecule expelled consists of the intact methyl group and a hydroxylic hydrogen atom (Eq. (8)). This is further supported by experiments with $^{13}CH_3OH$ as the substrate; that is, a $^{13}CH_4$ molecule is expelled in the consecutive reactions of $Mn_2(CO)_4^+$ with 13-C labelled methanol.

$$Mn_2(CO)_2(CD_3OH)_2^+ + CD_3OH \rightarrow Mn_2(CD_3O)_2(CD_3OH)^+ + H_2 + 2CO \quad (7)$$

$$Mn_2(CO)_2(CD_3OH)_2^+ + CD_3OH \rightarrow Mn_2(O)(CD_3OH)_2^+ + CD_3H + 2CO \quad (8)$$

The $Mn_2(CO)_5^+$ ion appears unable to undergo ligand exchange with methanol and reacts simply by the consecutive addition two CH_3OH molecules (Eq. (9) and Table 2)

$$Mn_2(CO)_5^+ \quad \rightarrow \xrightarrow{2CH_3OH} \quad Mn_2(CO)_5(CH_3OH)_2^+ \quad (9)$$

3.3. *Reaction of $Mn_2(CO)_4^+$ with ethanol and n-propanol*

The $Mn_2(CO)_4^+$ ion reacts similarly with ethanol as with methanol; that is, the initial reaction leads to incorporation of an ethanol molecule and the loss of one and two CO ligands with the formation of $Mn_2(CO)_3(ROH)^+$ and $Mn_2(CO)_2(ROH)^+$ ions, respectively (Table 3). The former ions can react further to incorporate ethanol and expel one to three CO ligands thus leading to a series of $Mn_2(CO)_n(ROH)_2^+$ ($n = 0$–2) ions. Likewise, the $Mn_2(CO)_2(ROH)^+$ ion can react with ethanol under the expulsion of one or two CO ligands from the collision complex to afford $Mn_2(CO)(ROH)_2^+$ and $Mn_2(ROH)_2^+$ ions, respectively (Table 3).

Ions with a composition of $Mn_2(RO)_2(ROH)^+$ and $Mn_2(RO)_2^+$ are formed also in the consecutive ion–molecule

Table 3
Relative yield (in %) of the product ions formed in the reaction of $Mn_2(CO)_4^+$ with ethanol and *n*-propanol[a]

Product ion	Relative abundance							
	Initial CH_3CH_2OH	Initial CD_3CD_2OH	75% conversion[b] CH_3CH_2OH	75% conversion[b] CD_3CD_2OH	Initial *n*-C_3H_7OH	Initial *n*-C_3D_7OH	75% conversion[b] *n*-C_3H_7OH	75% conversion[b] *n*-C_3D_7OH
$Mn_2(CO)_3(ROH)^+$	85	80	34	36	26	50	13	20
$Mn_2(CO)_2(ROH)_2^+$			2	6			1	–
$Mn_2(CO)(ROH)_3^+$			2	3				–
$Mn_2(CO)_4(ROH)^+$			2	4			3	10
$Mn_2(CO)_2(ROH)^+$	15	20	3	–	21	15	2	–
$Mn_2(CO)(ROH)^+$	–[c]	–[c]	–[c]	–[c]	53	35	19	11
$Mn_2(CO)(ROH)_2^+$			16	17			–	3
$Mn_2(ROH)^+$			3	2			8	3
$Mn_2(ROH)_2^+$			11	8			10	1
$Mn_2(RO)_2(ROH)^+$			8	9			6	11
$Mn_2(RO)_2^+$			4	3			13	7
$Mn_2(O)(ROH)_2^+$[d]			5	4			11	17
$Mn_2(O)(ROH)^+$[e]			–	–			11	13
$Mn(CO)(ROH)_3^+$			9	8			–	–
$Mn(ROH)_2^+$			1	–			3	4

[a] The structures of the product ions are assumed.

[b] 75% conversion into products, $P(C_2H_5OH) = 1.2 \times 10^{-8}$ mbar; $P(C_2D_5OH) = 1.1 \times 10^{-8}$ mbar; $P(C_3H_7OH) = 1.0 \times 10^{-8}$ mbar; $P(C_3D_7OH) = 0.9 \times 10^{-8}$ mbar.

[c] These product ions are formed initially in a relative yield close to 1%.

[d] These ions may also have a $Mn_2(OH)(RO)(ROH)^+$ structure.

[e] Alternatively, these ions can be formulated as $Mn_2(OH)(RO)^+$ species.

reactions of $Mn_2(CO)_4^+$ with ethanol. The formation of these ions are ascribed to the loss of H_2 from the collision complexes that are formed during the reactions of the series of $Mn_2(CO)_n(ROH)_2^+$ ($n = 1$–2) ions. In addition, this latter ion series can be held responsible for the formation of ions of $Mn_2(O)(ROH)_2^+$ ions by the expulsion of an ethane molecule from the collision complexes.

In keeping with the results for the deuterium labelled methanol, the $Mn_2(CO)_4^+$ ion reacts with CD_3CD_2OH to afford $Mn_2(CO)_n(CD_3CD_2OH)_2^+$ ($n = 0$–2) ions that react further with ethanol under the expulsion of H_2 or C_2D_5H from the collision complexes as illustrated in Eqs. (10) and (11).

$$Mn_2(CO)_2(C_2D_5OH)_2^+ + C_2D_5OH \rightarrow Mn_2(C_2D_5O)_2(C_2D_5OH)^+ + H_2 + 2CO \qquad (10)$$

$$Mn_2(CO)_2(C_2D_5OH)_2^+ + C_2D_5OH \rightarrow Mn_2(O)(C_2D_5OH)_2^+ + C_2D_5H + 2CO \qquad (11)$$

The overall results for the reactions of $Mn_2(CO)_4^+$ ion with *n*-proponal are comparable to those obtained with ethanol as the substrate. A main difference is that up to three CO ligands are eliminated in the primary reaction with *n*-propanol, whereas only two CO ligands are expelled in the reaction with ethanol (Table 3). With *n*-propanol the $Mn_2(RO)_2(ROH)^+$ and $Mn_2(RO)_2^+$ ions are formed in a somewhat higher yield than during the reactions with ethanol. This holds in particular for the $Mn_2(O)(ROH)_2^+$ and $Mn_2(O)(ROH)^+$ ions indicating that the loss of C_3H_8 is a more facile process in the reactions of the $Mn_2(CO)_n(ROH)_2^+$ ions for *n*-propanol than for ethanol. With the labelled *n*-propanol, $CD_3CD_2CD_2OH$, H_2 or C_3D_7H are expelled in the consecutive ion–molecule reactions in keeping with the results for deuterium labelled ethanol and methanol.

4. Discussion

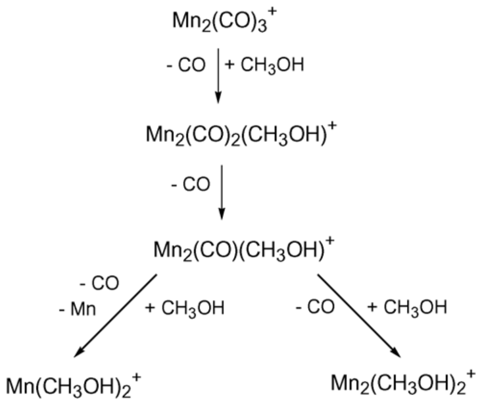
The results in Tables 1 and 2 reveal that the dimanganese carbonyl ions react readily with methanol and that the nature of the primary and consecutive reactions is strongly dependent on the number of CO ligands present in the reactant ion. In terms of reaction rates, we observe a smooth decrease in the efficiency of the reaction as the number of CO ligands is increased from 2 to 5; that is, the $Mn_2(CO)_2^+$ reacts about a factor of 5 faster than the $Mn_2(CO)_5^+$ ion under our experimental conditions (Table 1). The monotonous decrease in reaction efficiency with an increase in the number of CO ligands is distinct from the trend in reactivity reported for transition metal carbonyl anions; for example, the $Mn(CO)^-$ and $Mn(CO)_2^-$ ions are unreactive towards methanol in the gas phase, whereas the $Mn(CO)_3^-$ ion reacts readily by a formal ligand substitution process and bond activiation leading to the loss of one or two H_2 molecules [34].

The present results reveal also that the reaction rate of the $Mn_2(CO)_4^+$ ions with aliphatic alcohols decreases in the series methanol, ethanol and *n*-propanol. A significant change in reaction efficiency is also observed if the alkyl group of the alcohol is fully labelled with deuterium atoms. For methanol, the efficiency of the reaction of $Mn_2(CO)_4^+$ decreases from 0.37 (CH_3OH) to 0.13 (CD_3OH) and for *n*-propanol the efficiency decreases from 0.32 (n-C_3H_7OH) to 0.15 (n-C_3D_7OH; see Table 1). Irrespective of the fact that the experimental rate constants and efficiencies may be associated with a relatively large systematic error (see Section 2), the results reveal the occurrence of an isotope effect on the overall reaction rates of 2.8 for methanol, 2.3 for ethanol and 2.1 for n-propanol as the substrate. The presence of such isotope effects argues against the suggestion that the reaction of the $Mn_2(CO)_4{}^+$ ion with the aliphatic alcohols is a simple ligand exchange process associated to some extent with the loss of additional CO ligands. A simple view on the occurrence of isotope effects could be that the rate-determining step involves insertion by one of the manganese centers into a H(D)–C bond of the aliphatic alcohols. However, the manganese ion is known to be relative unreactive in its electronic ground state [16,17] and not particularly prone to undergo H–C insertion reactions. In other words, it is considered unlikely that insertion into a H–C of one of the alcohol molecules occurs in the reactions of the $Mn_2(CO)_4{}^+$ ion. This view is supported by the fact that none of the other results obtained in this study supports the occurrence of such a reaction step (vide infra). The lower rate of the reactions with the aliphatic alcohols may be thought, therefore, to arise by rate determining insertion into the O–H and/or the C–O bond of the alcohol molecule that is incorporated into the reactant $Mn_2(CO)_4{}^+$ ion. The occurrence of such a secondary isotope effect requires that a significant change occurs in the vibrational modes of the H(D)–C bonds remote to the bond-insertion site. In general terms, it may be expected that insertion into the O–H bond would effect the vibrational modes of the methyl or methylene group of the evolving alkoxy group to a smaller extent than an insertion into the C–O bond. If the isotope effect is caused by insertion into the C–O bond, this implies that insertion into the C–O bond of one of the manganese center of the reactant $Mn_2(CO)_4{}^+$ ions is associated with a kinetic barrier and that H(D)-C vibrational modes of the evolving methyl or methylene group are altered significantly upon reaching the transition state for this step in the overall reaction sequence. It could also be mentioned that sizable normal secondary deuterium isotope effects can be observed for unimolecular reactions of gaseous ions [38,39] and that the size of the effect is strongly dependent on the distance to the cleavage site [40]. Irrespective of the precise origin of the present isotope effect, it is suggested that the incorporation of an alcohol molecule into the dimanganese containing ions is unlikely to be a simple ligand substitution type process.

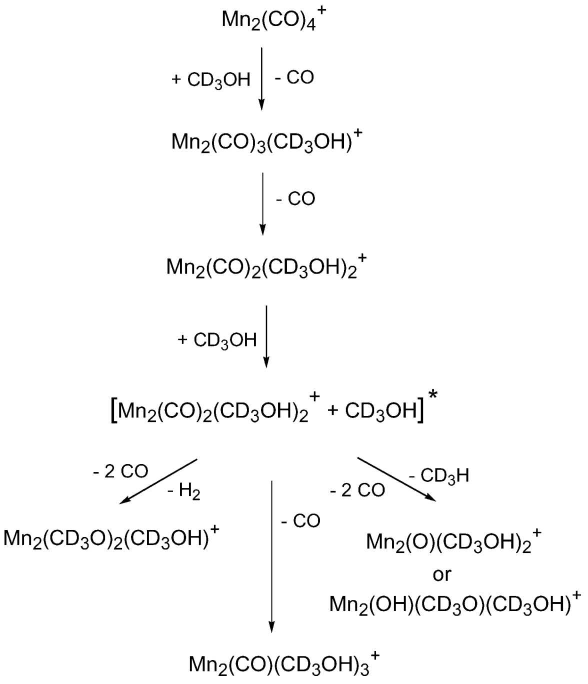
The incorporation of an alcohol molecule in the reactant ions is to some extent associated with the loss of CO (Table 2). The extent to which CO ligands are expelled in the initial reaction depends on the reactant $Mn_2(CO)_n{}^+$ ion as well as on the size of the aliphatic alcohol. For the $Mn_2(CO)_2{}^+$ ion, both CO ligands are expelled in the reaction with methanol, whereas the $Mn_2(CO)_3{}^+$ ion reacts with the loss of one and two CO molecules. For $Mn_2(CO)_4{}^+$ only one CO ligand is expelled and for the $Mn_2(CO)_5{}^+$ ion adduct formation occurs (Table 2). In terms of bond dissociation energies, the average value for the Mn–CO bonds in the $Mn_2(CO)_{10}{}^+$ ion has been given as 70–75 kJ mol^{-1} on the basis of appearance energy measurements [41] and determinations of threshold value for collision-induced CO loss from a limited series of $Mn_2(CO)_n{}^+$ ions [42] in line with photo dissociation experiments that indicate an upper limit of 105 kJ mol^{-1} [43,44]. However, the value for the $Mn_2(CO)^+$ ion can be estimated to be only about 25 kJ mol^{-1} from the reported appearance energy measurements. Such a low value for the Mn-CO BDE is in line with the facile loss of CO from the $Mn_2(CO)^+$ ion and the ready reaction of this particular ion with methanol (see Section 3). For the other ions included in this study, the reported appearance energies [41] give rise to approximate BDE values of 123 kJ mol^{-1} ($Mn_2(CO)_2{}^+$), 100 kJ mol^{-1} ($Mn_2(CO)_3{}^+$), 81 kJ mol^{-1} ($Mn_2(CO)_4{}^+$) and 141 kJ mol^{-1} ($Mn_2(CO)_5{}^+$). Even though these values are slightly larger than the average value suggested in the literature, the estimates indicate a non-systematic trend in Mn-CO BDE with an increase in the number of CO ligands. Upon the assumption that the BDE is nearly constant, the decrease in the tendency to expel CO could imply that the incorporation of a methanol molecule becomes energetically less favorable as the number of ligands is increased in the $Mn_2(CO)_n{}^+$ ions. This would then mean that the reaction of the $Mn_2(CO)_2{}^+$ ion with methanol is more exothermic than the reaction of the $Mn_2(CO)_5{}^+$ with this substrate.

For the ethanol as the substrate, the initial reaction of the $Mn_2(CO)_4{}^+$ ion leads to a pronounced loss of two CO ligands, whereas the reaction with methanol results in a negligible amount of product ions formed by the loss of two CO ligands. This may indicate that the reaction with ethanol is more exothermic than with methanol and a similar thought could explain the pronounced loss of up to three CO ligands in the initial reaction of the $Mn_2(CO)_4{}^+$ ion with n-propanol (Table 3).

In the initial reactions of the $Mn_2(CO)_n{}^+$ ions with the alcohols, cleavage of the Mn–Mn bond is not observed. This is in contrast to the reactions of the $Mn_2{}^+$ ion with methanol which involves predominant Mn–Mn bond rupture and the formation of $Mn(CH_3OH)^+$ ions [22]. Clearly, the absence of this process even in the reaction of the $Mn_2(CO)^+$ ion indicates that the formal exchange of a CO ligand for a methanol molecule releases insufficient energy for cleavage of the Mn–Mn bond. A more detailed analysis of the energetics of these reactions is hindered, however, by the absence of consistent thermodynamic data for the dimanganese carbonyl ions. Even the BDE of the $Mn_2{}^+$ ion is uncertain; that is, the BDE of the $Mn_2{}^+$ ions is indicated to be about 80 kJ mol^{-1} on the basis of collision-induced dissociation (CID) experiments [45], whereas photo dissociation experiments suggests that the value should exceed 134 kJ mol^{-1} [46] but be lower than 184 kJ mol^{-1} [43]. With respect to the $Mn_2(CO)_n{}^+$ ions (n = 2–5), CID experiments with the $Mn_2(CO)_2{}^+$ ions indicate that the loss of a Mn atom from this ion has a threshold energy of more than 202 kJ mol^{-1}



Scheme 1. Overall view of the initial and consecutive reactions of the $Mn_2(CO)_3^+$ ion with methanol.

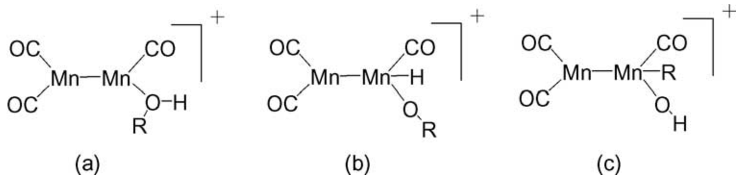


Scheme 3. Overview of the most important initial and consecutive reactions of the $Mn_2(CO)_4^+$ ion with CD_3OH.

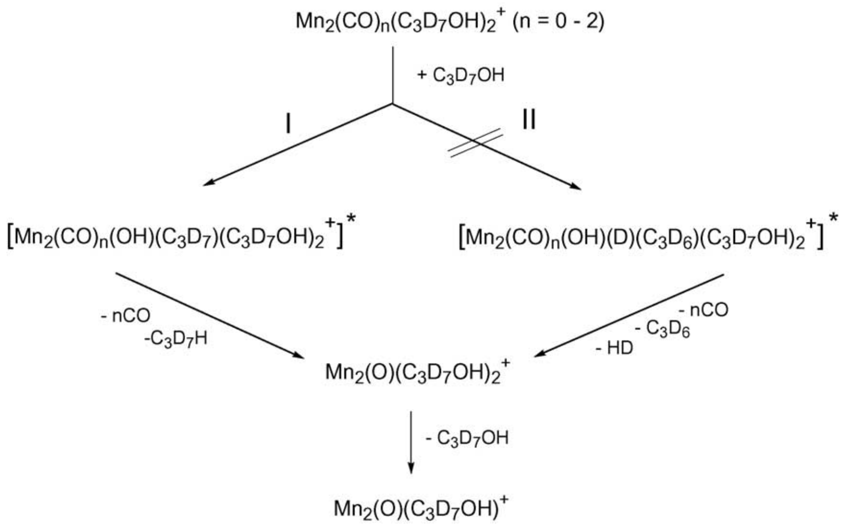
[42]. For the $Mn_2(CO)_{10}^+$ ion, the strength of the Mn–Mn bond has been given as 80 kJ mol^{-1} [25] and 92 kJ mol^{-1} [47], whereas a value of about 46 kJ mol^{-1} is obtained on the basis of reported thermodynamic data [41]. In other words, it could be expected that the Mn–Mn bond is particular weak in the Mn_2^+ ion and the ionized $Mn_2(CO)_{10}$ system, whereas the $Mn_2(CO)_n^+$ ($n = 1$–4) may have stronger Mn–Mn bonds in agreement with the conclusion reached on the basis of photo dissociation experiments [44]. As a result the rupture of the Mn–Mn bond may be unable to compete with the formal exchange of a CO ligand for methanol or the slow addition of methanol as observed for $Mn_2(CO)_5^+$ (Table 2).

Cleavage of the Mn–Mn bond is occurring, however, in the consecutive reactions, for example, of the $Mn_2(CO)_3^+$ ion with methanol (Table 2). The reaction sequence shown in Scheme 1 involves an initial formal ligand substitution with concomitant loss of one or two CO ligands. This is followed by a second exchange reaction leading to the $Mn_2(CH_3OH)_2^+$ ion that competes with cleavage of the Mn–Mn bond to afford $Mn(CH_3OH)_2^+$ ions. In this scheme, the formal substitution reaction is shown as leading to ions with an intact alcohol molecule. Other ion structures may be attained, however, as shown in Scheme 2 for the main product ion of the reaction between $Mn_2(CO)_4^+$ and one of the alcohols. In Scheme 2, ion **a** represents the product of a ligand exchange reaction whereas the ions **b** and **c** arise by O–H and C–O bond insertion, respectively. Bridging of the CO ligands between the metal centers may also be possible as well as multiple bonding between the manganese atoms as reported for homoleptic $Mn_2(CO)_n$ ($n = 7$–9) neutral species on the basis of DFT calculations [48].

The formation of ions such as **b** and **c** is not only supported by the isotope effect on the reaction rates but also by the findings for the consecutive ion–molecule reactions observed for the $Mn_2(CO)_4^+$ ion. The overall main reactions of this particular ion with CD_3OH are shown in Scheme 3. The first reaction is shown as a formal substitution process followed by a secondary reaction with CD_3OH leading to $Mn_2(CO)_2(CD_3OH)_2^+$ ions that can react further to expel CO together with H_2 or CD_3H (see also Table 2). Clearly, the occurrence of H_2 loss is consistent with insertion into the O–H bond either in the initial step and/or during the consecutive incorporation of methanol. The absence of loss of HD or D_2 also supports the anticipation that insertion by a manganese center into a D–C (or H–C bond) of methanol is not occurring (vide supra). The loss of CD_3H is indicative of C–O bond insertion and may be thought to lead to oxo-dimanganese species even though other structures such as a $Mn_2(OH)(CD_3O)(CD_3OH)^+$ species can also be formed (see Scheme 3).



Scheme 2. Possible structures of the ions formed by the formal ligand exchange reaction of the $Mn_2(CO)_3^+$ ion with an aliphatic alcohol.



Scheme 4. Possible reactions of the $Mn_2(CO)_n(n\text{-}C_3D_7OH)_2^+$ ions with *n*-C_3D_7OH. Reaction I involves an insertion into the C—O bond followed by the elimination of C_3D_7H and the CO ligands. Reaction II represent a hypothetical insertion into the C—O bond and a C—D bond followed by the expulsion of C_3D_6 and HD together with the CO ligands (see text).

In mechanistic terms the reactions of the $Mn_2(CO)_4^+$ ions with ethanol and *n*-propanol can be formulated as for methanol in Scheme 3. In particular, the results of the labelling experiments with ethanol and *n*-propanol reveal the hydrogen molecule expelled in the consecutive reactions originate entirely from the hydroxylic groups. This process leads to $Mn_2(RO)_2^+$ as well as $Mn_2(RO)_2(ROH)^+$ possibly as a result of a somewhat pronounced formation of $Mn_2(CO)_2(ROH)^+$ ions in the primary reactions and of $Mn_2(CO)(ROH)_2^+$ ions in the secondary reactions with ethanol or *n*-propanol (Tables 2 and 3). In comparison with methanol, the formation of $Mn_2(O)(ROH)_2^+$ ions occurs to almost the same extent with ethanol but is significantly enhanced if *n*-propanol is the substrate. For this alcohol, the process leads also to $Mn_2(O)(ROH)^+$ ions indicating that the loss of propane may be energetically more favorable for *n*-propanol than for methanol or ethanol (see also Scheme 4). In terms of a possible reaction pathway, the neutral product of this channel could be an alkene and a hydrogen molecule if ethanol or *n*-propanol is the substrate. For the labelled *n*-propanol this implies that D–C bond cleavage is involved at some stage of the reaction and that an intermediate containing an alkene ligand, an OH group and a deuteride could be formed during the overall process leading to the observed $Mn_2(O)(C_3D_7OH)_2^+$ ions as indicated in Scheme 4. However, the formation of an alkene and molecular hydrogen is estimated to be less favorable than formation of an alkane with $136\,kJ\,mol^{-1}$ for ethanol and with $125\,kJ\,mol^{-1}$ if *n*-propanol is the substrate [49]. The unfavorable energetics of this pathway may in part be responsible for the fact that only ions corresponding to the loss of H_2 are formed in the reactions with the labelled ethanol and *n*-propanol and thus argue against the occurrence of an insertion into a H–C (or D–C) bond of the manganese centers during the consecutive reactions of the $Mn_2(CO)_4^+$ ions with the aliphatic alcohols.

5. Conclusions

The $Mn_2(CO)_n^+$ ions ($n = 1$–4) react with methanol by a formal ligand substitution process that is associated with the loss of CO ligands, whereas addition of methanol occurs in the reactions of the $Mn_2(CO)_5^+$ ion. The efficiency of the reaction with methanol decreases as the number of CO ligands in the reactant increases; that is, in the series $Mn_2(CO)_2^+$, $Mn_2(CO)_3^+$, $Mn_2(CO)_4^+$ and $Mn_2(CO)_5^+$. Also, the efficiency of the reactions of the $Mn_2(CO)_4^+$ decreases in the series methanol, ethanol and *n*-propanol. Notably, the efficiency of the reaction of $Mn_2(CO)_4^+$ with CD_3OH is significantly lower than with CH_3OH and a similar finding is obtained for ethanol and *n*-propanol. The origin of this isotope effect is uncertain but its occurrence suggests that the initial incorporation of an alcohol molecule is not a simple substitution process.

Cleavage of the Mn–Mn bond is not observed in the primary reactions of the dimanganese carbonyl ions but occurs to some extent in the subsequent reactions of some of the product ions of the formal substitution process. In the consecutive reactions of the $Mn_2(CO)_4^+$ ion with the alcohols, an $Mn_2(CO)_2(ROH)_2^+$ ion is formed. This ion is indicated to react further by competing insertion into the O–H bond and C–O bond of the substrate. The occurrence of O–H bond insertion is revealed by the loss of a hydrogen molecule consisting of hydroxyl hydrogen atoms, whereas C–O bond insertion is held responsible for the loss of an alkane during the consecutive reactions.

Acknowledgements

The authors thank the Netherlands Organization of Scientific Research (CW/NWO) for support.

References

[1] K. Eller, H. Schwarz, Chem. Rev. 91 (1991) 1121.
[2] B.S. Freiser (Ed.), Organometallic Ion Chemistry, Kluwer Academic Publishers, Dordrecht, 1996.
[3] H. Schwarz, Int. J. Mass Spectrom. 237 (2004) 75.
[4] D.A. Plattner, Int. J. Mass Spectrom. 207 (2001) 125.
[5] M.T. Rodgers, P.B. Armentrout, Mass Spectrom. Rev. 19 (2000) 215.
[6] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, third edition, Wiley, New York, 2001.
[7] J.P. Collman, L.S. Hegedus, J.R. Norton, F.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, 1987.
[8] See for example K. Koszinowski, D. Schröder, H. Schwarz, Organometallics 23 (2004) 1132.
[9] V.E. Brondybey, M.K. Beyer, J. Phys. Chem. A 105 (2001) 951.
[10] K.N. Ferreira, T.M. Iverson, K. Maghlaoui, J. Barber, S. Iwata, Science 303 (2004) 1831.
[11] K. Wieghardt, Angew. Chem. Int. Ed. Engl. 28 (1989) 1153.
[12] V.L. Pecaro (Ed.), Manganese Redox Enzymes, VCH Publishers, New York, 1992.
[13] A.J. Wu, J.E. Penner-Hahn, V.L. Pecoraro, Chem. Rev. 104 (2004) 903.
[14] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457.
[15] See for example J. Brinksma, M.T. Rispens, R. Hage, B.L. Feringa, Inorg. Chim. Acta 337 (2002) 75.
[16] P.B. Armentrout, L.F. Halle, J.L. Beauchamp, J. Am. Chem. Soc. 103 (1981) 6501.
[17] F. Strobel, D.P. Ridge, J. Phys. Chem. 93 (1989) 3635.
[18] L.S. Sunderlin, P.B. Armentrout, J. Phys. Chem. 94 (1990) 3589.
[19] C. Schulze, H. Schwarz, J. Am. Chem. Soc. 110 (1988) 67.
[20] D. Schröder, H. Schwarz, Int. J. Mass Spectrom. 231 (2004) 139.
[21] D.V. Zagorevskii, J.L. Holmes, C.H. Watson, J.R. Eyler, Eur. J. Mass Spectrom. 3 (1997) 27.
[22] B.S. Larsen, R.B. Freas III, D.P. Ridge, J. Phys. Chem. 88 (1984) 6014.
[23] W.K. Meckstroth, R.B. Freas, W.D. Reents Jr., D.P. Ridge, Inorg. Chem. 25 (1985) 3139.
[24] B. Chiavarino, M.E. Crestoni, S. Fornarini, Chem. Eur. J. 8 (2002) 2740.
[25] H.J. Svec, G.A. Junk, J. Am. Chem. Soc. 89 (1967) 2836.
[26] J. Opitz, D. Bruch, Int. J. Mass Spectrom. 124 (1993) 157.
[27] See for example A.G. Marshall, C.L. Hendrickson, Int. J. Mass Spectrom. 215 (2002) 59.
[28] M.J. Overett, R.O. Hill, J.R. Moss, Coord. Chem. Rev. 206/207 (2000) 581.
[29] See for example J. Wang, Y. Liu, J. Chang, Y.-N. Wang, L. Bai, Y.-Y. Xu, H.-W. Ziang, Y.-W. Li, B. Zhong, Ind. Eng. Chem. Res. 42 (2003) 5066.
[30] M. Born, S. Ingemann, N.M.M. Nibbering, J. Phys. Chem. 100 (1996) 17662.
[31] E.S.E. van Beelen, T.A. Koblenz, S. Ingemann, S. Hammerum, J. Phys. Chem. A 108 (2004) 2787.
[32] J.E. Bartmess, R.M. Georgiadis, Vacuum 33 (1983) 149.
[33] A.J.R. Heck, L.J. de Koning, F.A. Pinkse, N.M.M. Nibbering, Rapid. Commun. Mass Spectrom. 5 (1991) 406.
[34] K.J. van den Berg, S. Ingemann, N.M.M. Nibbering, Org. Mass Spectrom. 28 (1993) 527.
[35] T. Su, M.T. Bowers, in: M.T. Bowers (Ed.), Gas Phase Ion Chemistry, vol. 1, Academic Press, New York, 1979, p. 83 (Chapter 3).
[36] T. Su, M.T. Bowers, Int. J. Mass Spectrom. Ion Phys. 12 (1973) 347.
[37] See also K.J. van den Berg, S. Ingemann, N.M.M. Nibbering, Organometallics 11 (1992) 2389.
[38] P.J. Derrick, Mass Spectrom. Rev. 2 (1983) 285.
[39] K. Norrman, T.B. McMahon, Int. J. Mass Spectrom. 182/183 (1999) 381.
[40] S. Ingemann, S. Hammerum, P.J. Derrick, J. Am. Chem. Soc. 110 (1988) 3869.
[41] J. Opitz, Eur. J. Mass Spectrom. 7 (2001) 55.
[42] W. Yu, X. Liang, R.B. Freas, J. Phys. Chem. 95 (1991) 3600.
[43] R.E. Tecklenburg, D.H. Russell, J. Am. Chem. Soc. 109 (1987) 7654.
[44] F.H. Strobel, D.H. Russell, J. Cluster Sci. 2 (1991) 57.
[45] K. Ervin, S.K. Loth, N. Aristov, P.B. Armentrout, J. Phys. Chem. 87 (1983) 3593.
[46] M.F. Jarrold, A.J. Illies, M.T. Bowers, J. Am. Chem. Soc. 107 (1985) 7339.
[47] J.A. Connor, M.T. Zafarani-Moattar, J. Bickerton, N.I. El Saied, S. Suradi, R. Carson, G.A. Takhin, H.A. Skinner, Organometallics 1 (1982) 1166.
[48] Y. Xie, J.H. Jang, R.B. King, H.F. Schaefer III, Inorg. Chem. 42 (2003) 5219.
[49] P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry Webbook, NIST Standard Reference Database Number 69, March 2003. National Institute of Standards and Technology, Gaithersburg (http://webbook.nist.gov/).