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Regioselectivity in the gas-phase reactions of the $O^{\cdot-}$ radical anion with (η^5 -cyclopentadienyl)tricarbonylmanganese(I) and (η^5 -methylcyclopentadienyl)tricarbonylmanganese(I): formation and structure of $C_5H_5MnO_n^-$ and $C_6H_7MnO_n^-$ ($n = 1, 2$) ions

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Abstract

The gas-phase reactions of the $O^{\cdot-}$ ion with (η^5 -cyclopentadienyl)tricarbonylmanganese(I), $CpMn(CO)_3$, and (η^5 -methylcyclopentadienyl)tricarbonylmanganese(I), $CH_3CpMn(CO)_3$, have been studied with Fourier transform ion cyclotron resonance. The main reactions are (i) proton abstraction, (ii) loss of CO_2 , and (iii) expulsion of two or three CO molecules from the collision complex. Initial attack on a CO ligand is the main process as indicated by experiments with $^{18}O^{\cdot-}$ and the ion/molecule reactions of the product ions resulting from the loss of three CO molecules with water, aliphatic alcohols, methanethiol and SO_2 . The attack on a CO ligand followed by loss of three CO molecules is suggested to yield $C_5H_5MnO^-$ ions with a (cyclopentadienone) MnH^- structure in the reaction with $CpMn(CO)_3$ and (methylcyclopentadienone) MnH^- ions if $CH_3CpMn(CO)_3$ is the substrate. A possible mechanism for the process leading to the indicated transformation of the Cp and CH_3Cp ligands into C_5H_4O and $CH_3C_5H_3O$ ligands, respectively, is discussed together with the formation of (fulvene) $Mn(OH)^-$ ions following attack of $O^{\cdot-}$ on $CH_3CpMn(CO)_3$. The (cyclopentadienone) MnH^- and (methylcyclopentadienone) MnH^- ions react with N_2O by oxygen atom abstraction to form $C_5H_5MnO_2^-$ and $C_6H_7MnO_2^-$ ions, respectively.

Key words: FT-ICR; Organomanganese compounds; Nucleophilic additions; Atomic oxygen radical anion; Ion/molecule reactions

1. Introduction

Nucleophilic addition reactions are studied extensively in organometallic chemistry and are often applied for synthetic purposes [1]. A central topic in the studies of these processes concerns the regioselectivity in the

attack of nucleophiles on species containing unsaturated ligands, such as CO, cyclopentadienyl, ethene or benzene [1,2]. In general terms, the site of attack of a nucleophile on an organometallic compound can depend on the coordinative saturation of the metal centre, the nature of the metal atom and ligands as well as on the properties of the medium in which the reactions occur. The presence of

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indirect reactants such as solvent molecules and counter ions can obscure, however, studies aimed at obtaining fundamental mechanistic insight into nucleophilic addition reactions. In this respect, several reports have demonstrated that these reactions can be studied in the gas phase thus avoiding the influence of the indirect reactants, which are inevitably present in the condensed phase [3–5]. The main part of the reported studies concerned with gas-phase nucleophilic additions describes reactions of anions with transition metal carbonyl compounds, e.g. $\text{Fe}(\text{CO})_5$ [6–8]. These reactions proceed by loss of one or more CO molecules from the collision complex and are viewed as involving initial attack on a CO ligand followed by migration of the nucleophile to the metal atom succeeded to some extent by the loss of a second CO molecule. Nucleophilic attack on an organic ligand has been described for the gas-phase reaction of H^- with $(\eta^6\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, which is reported to proceed in part by initial attack on the benzene ring and subsequent migration of a hydrogen atom to the metal centre followed by loss of C_6H_6 [9]. Recently, we reported that anions such as alkoxide ions react with $\text{CpCo}(\text{CO})_2$ in the gas phase at a carbonyl ligand and/or directly at the metal centre, whereas the reaction with the $\text{O}^{\cdot-}$ radical anion involves competing attack on the Cp ligand and one of the CO ligands prior to the loss of two CO molecules [10]. Attack on the Cp ligand was proposed to yield mainly a (cyclopentadienone) CoH^- ion, whereas initial attack on a CO ligand was suggested to generate a metallacyclopentadiene species with a CO as well as a hydride ligand and/or a (cyclobutadiene) $\text{Co}(\text{CO})\text{H}^-$ species. These structural assignments were based on a study of the reactions between the product ions generated by attack of $\text{O}^{\cdot-}$ on $\text{CpCo}(\text{CO})_2$ and a series of substrates including NO, SO_2 , water, aliphatic alcohols and carboxylic

acids. For example, the competing losses of CO and $\text{C}_5\text{H}_4\text{O}$ from the collision complex in the reaction with SO_2 was taken as an indication of the presence of these ligands in the reactant cobalt containing ions.

The possibility for attack of a negative ion on an organic ligand with the formation of new metal containing species motivated us to extend the study of the gas-phase reactions between the $\text{O}^{\cdot-}$ ion and organometallic compounds with a Cp ligand. In the present paper we are concerned with the regioselectivity of the reactions of the $\text{O}^{\cdot-}$ radical anion with the two manganese compounds, $\text{CpMn}(\text{CO})_3$ and $\text{CH}_3\text{CpMn}(\text{CO})_3$. These compounds were chosen for a closer study in order to investigate whether competing attack of the $\text{O}^{\cdot-}$ ion on a Cp ligand and a CO ligand is a general phenomenon. Moreover, we wanted to examine whether ions comparable to those derived from $\text{CpCo}(\text{CO})_2$ [10] are generated in the reaction with the manganese compounds. To gain this insight, we applied the Fourier transform ion cyclotron resonance (FT-ICR) [11,12] method in combination with stable isotopic labelling and probed the structures of the initial product ions by investigating their ion/molecule chemistry.

2. Experimental

The experiments were performed with an FT-ICR instrument constructed and designed at the University of Amsterdam [13–15]. In a typical experiment the primary negative ions were formed by a pulsed electron beam with a duration of 0.1 s and trapped in a magnetic field of 1.24 T by applying a negative voltage of ≈ -1 V to the trapping plates of the cubic inch cell. The $\text{O}^{\cdot-}$ ions were formed by dissociative capture of electrons with an energy of about 1.2 eV by N_2O [16], whereas the $^{18}\text{O}^{\cdot-}$ ions were generated by reacting $\text{O}^{\cdot-}$ with H_2^{18}O [17]. The ions of interest were isolated

by removing all other ions from the cell by a series of r.f. pulses, which were adjusted such that unwanted translational excitation of the remaining ions was minimized [18]. In the experiments with $^{18}\text{O}^{\cdot-}$, minor amounts of $\text{O}^{\cdot-}$ ions were formed by the reaction of the $^{18}\text{O}^{\cdot-}$ ions with the N_2O molecules present in the cell [19,20]. These $\text{O}^{\cdot-}$ ions were ejected continuously from the cell during the entire reaction period. Continuous ejection of a product ion during the reaction period proved necessary also in other experiments and was achieved normally by applying an r.f. pulse of low amplitude to the excitation plates of the cell during the reaction time. The reactions of the ions of interest with a given substrate were followed as a function of time by varying the delay between the selection of the reactant ions and the detection of the ions present in the cell. Dissociative capture of electrons with a kinetic energy of ≤ 1 eV by $\text{CpMn}(\text{CO})_3$ and $\text{CH}_3\text{CpMn}(\text{CO})_3$ gave rise to abundant $\text{CpMn}(\text{CO})_2^-$ and $\text{CH}_3\text{CpMn}(\text{CO})_2^-$ ions, whereas $\text{CpMn}(\text{CO})^-$ and $\text{CH}_3\text{CpMn}(\text{CO})^-$ ions were generated in a relatively low abundance. The formation of these ions by dissociative capture of low kinetic energy electrons present in the cell during the reaction time was prevented by ejecting the electrons as described in a previous paper [21].

The partial pressure of a neutral compound in the instrument was normally $\approx 2 \times 10^{-5}$ Pa. The partial pressure of nitrous oxide was $\approx 4 \times 10^{-5}$ Pa in the experiments concerned with the chemistry of the $\text{C}_5\text{H}_5\text{MnO}_2^-$ and $\text{C}_6\text{H}_7\text{MnO}_2^-$ ions generated in the reactions of the respective $\text{C}_5\text{H}_5\text{MnO}^-$ and $\text{C}_6\text{H}_7\text{MnO}^-$ ions with N_2O (vide infra). The pressures were measured on an uncalibrated ionization gauge placed in a side arm of the main pumping line. The inlet lines and the main vacuum vessel of the instrument were at room temperature, while the temperature of the trapping plate opposite the filament side was measured to be 300–340 K in a typical experiment.

3. Materials

Most of the chemicals were commercially available and used without further purification. The $\text{CH}_3\text{CpMn}(\text{CO})_3$ compound contained $\leq 10\%$ $\text{CpMn}(\text{CO})_3$. The presence of $\text{CpMn}(\text{CO})_3$ in the sample of the methyl substituted compound had no apparent effect on the results of the experiments described in the present paper. The $\text{CH}_3\text{CH}_2\text{CD}_2\text{OH}$ ($> 95\%$ d_2) compound was prepared by a LiAlD_4 reduction of propionic acid and purified by distillation [22].

4. Results

4.1. Reactions of $\text{O}^{\cdot-}$ with $\text{CpMn}(\text{CO})_3$ and $\text{CH}_3\text{CpMn}(\text{CO})_3$

The $\text{O}^{\cdot-}$ radical anion reacts with $\text{CpMn}(\text{CO})_3$ and $\text{CH}_3\text{CpMn}(\text{CO})_3$ in the gas phase by a number of competing processes including proton abstraction, loss of CO_2 and the expulsion of two or three CO molecules from the collision complex (Table 1). In addition, hydrogen atom abstraction and formal abstraction of H_2^+ occur to a minor extent. The latter processes are observed commonly in the reactions of $\text{O}^{\cdot-}$ with organic compounds such as alkenes, aromatic compounds and halogen substituted methanes [23,24].

The overall reactivity of the $\text{O}^{\cdot-}$ ion towards the two manganese compounds is similar although proton abstraction is somewhat more important in the reaction with $\text{CH}_3\text{CpMn}(\text{CO})_3$ than with $\text{CpMn}(\text{CO})_3$ suggesting that the methyl substituted compound is more acidic than $\text{CpMn}(\text{CO})_3$ ($\Delta H_{\text{acid}}^\circ \approx 1556 \text{ kJ mol}^{-1}$) [5] in the gas phase. In addition, loss of two CO molecules from the collision complex is less important in the reaction with $\text{CH}_3\text{CpMn}(\text{CO})_3$ than with $\text{CpMn}(\text{CO})_3$. The present results for the reactions of the $\text{O}^{\cdot-}$ ions

Table 1

Relative abundances of the product ions formed in the reaction of the $O^{\cdot-}$ ion with $CpMn(CO)_3$ and $CH_3CpMn(CO)_3$ (reaction time 0.2 s)^a

$CpMn(CO)_3$			$CH_3CpMn(CO)_3$ ^b		
Product ion ^c	Neutral products ^c	Yield (%)	Product ion ^c	Neutral products ^c	Yield (%)
HO^-	$C_5H_4Mn(CO)_3$	2	HO^-	$C_6H_6Mn(CO)_3$	5
$CpMn^-$	$CO_2 + 2CO$	< 1	CH_3CpMn^-	$CO_2 + 2CO$	1
$C_5H_5MnO^-$ ^d	3CO	28 ^e	$C_6H_7MnO^-$ ^d	3CO	24 ^e
$CpMn(CO)^-$	$CO_2 + CO$	5	$CH_3CpMn(CO)^-$	$CO_2 + CO$	5
$C_6H_5MnO_2^-$ ^f	2CO	27	$C_7H_7MnO_2^-$ ^f	2CO	12
$CpMn(CO)_2^-$	CO_2	11	$CH_3CpMn(CO)_2^-$	CO_2	13
$C_7H_5MnO_3^-$ ^f	CO	3	$C_8H_7MnO_3^-$ ^f	CO	2
$(C_5H_3)Mn(CO)_3^-$	H_2O	3	$(C_6H_5)Mn(CO)_3^-$	H_2O	7
$(C_5H_4)Mn(CO)_3^-$	$OH^{\cdot}$	16	$(C_6H_6)Mn(CO)_3^-$	$OH^{\cdot}$	29
$(C_5H_4O)Mn(CO)_3^-$	$H^{\cdot}$	4	$(C_6H_6O)Mn(CO)_3^-$	$H^{\cdot}$	2

^aIons with an elemental composition of $C_5H_5^-$ and $C_6H_7^-$ are also observed. The yields of these ions vary from experiment to experiment indicating that they arise by proton abstraction from cyclopentadiene and methyl substituted cyclopentadiene generated by thermal decomposition of the respective metal compounds.

^bThe sample of $CH_3CpMn(CO)_3$ contained $\approx 10\%$ $CpMn(CO)_3$ (see Experimental).

^cAssumed structure or assigned elemental composition.

^dSee text for possible structures of these ions.

^eThe $C_5H_5MnO^-$ and $C_6H_7MnO^-$ ions react with N_2O to form $C_5H_5MnO_2^-$ and $C_6H_7MnO_2^-$ ions, respectively (see text). The relative yields given of the $C_5H_5MnO^-$ and $C_6H_7MnO^-$ ions have been obtained by adding the relative abundance of a given dioxide ion to that of the related monoxide ion.

^fThe structures of these ions have not been ascertained, see text.

with the two manganese compounds are in contradiction to a recent study of VanOrden and Buckner [25]. According to their FT-ICR experiments, the $O^{\cdot-}$ ion reacts with $CH_3CpMn(CO)_3$ in the gas phase only by the loss of CO_2 from the collision complex as observed for the reactions with transition metal carbonyl compounds such as $Cr(CO)_6$ and $Fe(CO)_5$ [25,26]. The present experiments as well as our previously reported findings for $CpCo(CO)_2$ demonstrate [10], however, that the $O^{\cdot-}$ ion can react in a complex manner with organometallic species containing a Cp or a CH_3Cp ligand.

Loss of CO_2 from the collision complex yields $CpMn(CO)_2^-$ and $CH_3CpMn(CO)_2^-$ ions (Table 1). These species can be formed also by capture of low energy electrons by the neutral manganese compounds (see Experimental Section) and in order to ascertain the origin of the $CpMn(CO)_2^-$ and $CH_3CpMn(CO)_2^-$ ions generated in the experiments with $O^{\cdot-}$, we ejected the latter ion from

the cell prior to the reaction period. Under these conditions, the $CpMn(CO)_2^-$ and $CH_3CpMn(CO)_2^-$ ions are not observed revealing that the ejection of low energy electrons from the cell is sufficiently efficient for an unambiguous study of the reactions of $O^{\cdot-}$ with the neutral manganese species. The $CpMn(CO)_2^-$ and $CH_3CpMn(CO)_2^-$ ions may be formed also in the reaction between the manganese compounds and the NO^- ions, which are generated by attack of $O^{\cdot-}$ on the N_2O molecules present in the cell. However, continuous ejection of NO^- during the reaction period discloses that only a very minor part of the manganese containing ions are formed by this pathway. In other words, the $CpMn(CO)_2^-$ and $CH_3CpMn(CO)_2^-$ ions are generated predominantly by the reaction of the $O^{\cdot-}$ ion with $CpMn(CO)_3$ and $CH_3CpMn(CO)_3$, respectively.

The loss of two carbon monoxide molecules from the collision complex following attack of $O^{\cdot-}$ leads to $C_6H_5MnO_2^-$ and $C_7H_7MnO_2^-$

ions, whereas ions with the elemental composition of $C_5H_5MnO^-$ and $C_6H_7MnO^-$ are generated by the loss of three CO molecules (Table 1). The occurrence of these processes raises the questions as to (i) whether the attacking $O^{\cdot-}$ ion is incorporated in the product ions, and (ii) whether attack occurs initially at a CO ligand, the organic ligand or the metal centre. In order to answer these questions, we studied the reactions of the $^{18}O^{\cdot-}$ ion with the two manganese compounds.

The ions generated by loss of carbon dioxide from the collision complex in the reaction of $^{18}O^{\cdot-}$ with either of the two manganese compounds do not incorporate the label as illustrated by the exclusive loss of $CO^{18}O$ in the reaction with $CH_3CpMn(CO)_3$ (Eq. (1)):

In the reaction of $^{18}O^{\cdot-}$ with $CpMn(CO)_3$, $\approx 85\%$ of the ions formed by loss of two carbon monoxide molecules incorporates the label as indicated in Eq. (2):

In the reaction of $^{18}O^{\cdot-}$ with $CH_3CpMn(CO)_3$, more than 95% of the product ions generated by loss of two carbon monoxide molecules retains the ^{18}O atom (Eq. (3)):

The extent of incorporation of the ^{18}O atom in the product ions resulting from the loss of

three carbon monoxide molecules is lower than for the product ions due to the loss of two carbon monoxide molecules as can be seen by comparing the results in Eqs. (4) and (5) with those given in Eqs. (2) and (3).

The relative abundances of the $C_5H_5Mn^{18}O^-$ and $C_5H_5MnO^-$ ions (Eq. (4)) and of the $C_6H_7Mn^{18}O^-$ and $C_6H_7MnO^-$ ions (Eq. (5)) are significantly different from the abundance ratio of 25:75, which is predicted for a statistical process in which all four oxygen atoms have become equivalent prior to loss of three carbon monoxide molecules. This implies that the four oxygen atoms do not become structurally identical prior to product formation as indicated also by the exclusive loss of carbon dioxide molecules containing the ^{18}O atom (Eq. (1)).

4.2. Reactions of the $C_5H_5MnO^-$ ions

The $O^{\cdot-}$ ion reacts relatively readily with $CpMn(CO)_3$ and a sufficient yield of the $C_5H_5MnO^-$ ions is obtained after 0.2 s for the study of the reactions between these ions and various substrates. In the reaction of the $C_5H_5MnO^-$ ions with the parent compound, a CO molecule is expelled from the collision complex (Eq. (6)). This reaction is very slow indicating that its occurrence does not hamper the study of the reactions

Table 2

Relative abundances of the product ions formed in the reactions of the $C_5H_5MnO^-$ and $C_6H_7MnO^-$ ions with SO_2 .^a

$C_5H_5MnO^-$			$C_6H_7MnO^-$		
Product ion ^b	Neutral product(s) ^c	Yield (%)	Product ion ^b	Neutral product(s) ^c	Yield (%)
$HMnSO_2^-$	C_5H_4O	70	$HMnSO_2^-$	C_6H_6O	55
$C_3H_4MnO^-$	C_2HO_2S	15	$HMnSO_3^-$	C_6H_6	25
$HMnSO^-$ ^d	$C_5H_4O_2$	10	$C_4H_6MnO^-$	C_2HO_2S	5
[Adduct] ^e		4	$HMnSO^-$ ^d	$C_6H_6O_2$	10
[Adduct–H ₂ O] ^e	H_2O	1	[Adduct–H ₂ O] ^e	H_2O	5

^aAfter a reaction time of 0.2 s, see text.^bAssumed structure or assigned elemental composition.^cPossible elemental composition of the neutral species expelled from the collision complex.^dThe $HMnSO^-$ ions are isobaric with $HMnO_3^-$ ions. Based on the present experiments it is not possible to exclude whether the latter ions are also generated.^eSee text and Appendix A.

with other substrates.

With N_2O , the main part ($\approx 85\%$) of the $C_5H_5MnO^-$ ions reacts by oxygen atom transfer to generate $C_5H_5MnO_2^-$ ions (Eq. (7)) [27,28]. This process is relatively facile although it is not capable of competing effectively with the reactions between the $C_5H_5MnO^-$ ions and the selected substrates. In most of the experiments concerned with the ion/molecule chemistry of the $C_5H_5MnO^-$ ions, the $C_5H_5MnO_2^-$ ions were ejected continuously from the cell during the entire reaction period (see Experimental Section).

Dioxide ions are formed also by the loss of H_2 from the collision complex in the reaction with H_2O . If D_2O is the substrate, only HD is expelled as shown in Eq. (8):

Loss of a hydrogen molecule from the collision complex is also the only reaction observed

with unlabelled aliphatic alcohols. In the reaction with the deuterium labelled alcohols, CD_3OH and $CH_3CH_2CD_2OH$, only H_2 is eliminated, whereas with CD_3OD , CH_3OD and CH_3CH_2OD , HD is expelled from the collision complex (Eq. (9)). These findings reveal that the generated hydrogen molecule consists of one of the hydrogen atoms of the reactant ion and the hydrogen atom of the hydroxy group of the alcohol:

Notwithstanding the low pressures commonly applied in FT-ICR experiments, the primary product ions formed by loss of a hydrogen molecule in the reaction with the aliphatic alcohols and water react further with these substrates to form stable adduct ions (Eq. (10); see also Appendix A):

A minor fraction of the $C_5H_5MnO^-$ ions is observed to be unreactive towards the

aliphatic alcohols. This is disclosed by the results of experiments in which the ions react with an alcohol for 1–1.5 s after which the remaining $C_5H_5MnO^-$ ions are isolated by ejecting all other ions from the cell. In the subsequent collisions between the remaining ions and the neutral species present in the FT-ICR cell, no products from a reaction with the alcohol are generated. Based on such experiments we estimate that roughly 20% of the $C_5H_5MnO^-$ ions are unreactive towards aliphatic alcohols and water.

Expulsion of a hydrogen molecule from the collision complex is the only reaction occurring with methanethiol. With acetic acid as the substrate, proton abstraction with formation of acetate ions occurs in addition to the loss of a H_2 molecule. With NO no reaction is observed, whereas the $C_5H_5MnO^-$ ions react readily and completely with SO_2 by a number of competing processes (Table 2). The most important of these reactions involves the loss of a neutral species with the elemental composition of C_5H_4O as shown in Eq. (11):

4.3. Reactions of the $C_6H_7MnO^-$ ions

The O^- ion reacts readily with $CH_3Cp-Mn(CO)_3$ and in most experiments the $C_6H_7MnO^-$ ions are isolated after a reaction time of 0.25 s. Subsequently, the ions are allowed to react with a selected substrate in the presence of the neutral organometallic compound and N_2O . With the parent compound, the $C_6H_7MnO^-$ ions react slowly by loss of a CO molecule from the collision complex, whereas the reaction with N_2O proceeds by oxygen atom transfer (Eq. (12)). As observed also for the $C_5H_5MnO^-$ ions, some of the $C_6H_7MnO^-$ ions (30%) appear not to react with N_2O . In most experiments, the $C_6H_7MnO_2^-$ ions formed in the reaction with

N_2O are ejected continuously from the cell during the entire reaction period, thus allowing the reactions of the $C_6H_7MnO^-$ ions with the substrates to be studied selectively.

Ions with the elemental composition of $C_6H_7MnO_2^-$ are formed also in the reaction with H_2O , which involves only the loss of H_2 from the collision complex (Eq. (13)):

In the reaction with D_2O , some of the $C_6H_7MnO^-$ ions react to expel HD from the collision complex with the formation of $C_6H_6DMnO_2^-$ ions (Eq. (14)):

The product ions formed by loss of a hydrogen molecule react further with D_2O by exchange of three hydrogen atoms for deuterium atoms (Eq. (15)) and to afford stable adduct ions (see Fig. 1 and Appendix A). The occurrence of this exchange prevents a determination of the extent to which H_2 is expelled in the primary reaction between $C_6H_7MnO^-$ and D_2O , whereas the loss of a D_2 molecule is not occurring as revealed by the absence of formation of $C_6H_7MnO_2^-$ ions (see Fig. 1).

A minor part of the $C_6H_7MnO^-$ ions react readily with D_2O by exchange of hydrogen atoms for deuterium atoms as shown in Fig. 1. Only three of the seven hydrogen atoms are exchanged for deuterium atoms in the presence of D_2O (Eq. (16)):

The distribution of the ions containing deuterium atoms is: 40% ($C_6H_6DMnO^-$), 40%

Table 3

Relative importance of H₂ and H₂O loss in the reactions of the C₆H₇MnO[−] ions with methanol as a function of the time delay prior to their isolation^a

Delay before isolation of the reactant ion ^a (s)	Reaction time (s)	Conversion into products (%)	Loss (%)	
			H ₂	H ₂ O
0.25	0.6	60	90	10
0.65	0.6	30	70	30
1.65	0.6	10	0	100

^aDelay between the start of the electron beam and the isolation of the C₆H₇MnO[−] ions. The duration of the electron beam pulse was 0.1 s; see text.

Fig. 1. Hydrogen–deuterium exchange in the C₆H₇MnO[−] / CH₃CpMn(CO)₃/D₂O system followed as a function of reaction time. The group of peaks indicated by I in the figure represents the C₆H₇MnO[−] ions (d₀) and the fraction of these ions which exchanges up to three hydrogen atoms for deuterium atoms. The group of peaks indicated by II represents the ions formed by loss of HD in the reaction with D₂O and in the subsequent exchange with D₂O. The group of signals indicated by III corresponds to stable adduct ions formed in the reactions of the latter ions with D₂O (see text).

($C_6H_5D_2MnO^-$) and 20% ($C_6H_4D_3MnO^-$) after a reaction time of 0.3 s, whereas this distribution is displaced in favour of the ions containing three deuterium atoms at prolonged reaction times (see Fig. 1). The ions with three deuterium atoms remain in the cell even after reaction times of 2 s indicating that the $C_6H_7MnO^-$ ions which undergo hydrogen/deuterium exchange with D_2O do not react to expel HD or H_2 from the collision complex. As can be seen in Fig. 1, some of the $C_6H_7MnO^-$ ions do not react with D_2O either by exchange or to expel HD/ H_2 . In conclusion, the results of the experiments with D_2O indicate that at least three isomeric $C_6H_7MnO^-$ ions are formed in the reaction of O^- with $CH_3CpMn(CO)_3$.

Loss of a hydrogen molecule is observed also in the reactions with aliphatic alcohols and yields product ions which react further with an alcohol molecule to form stable adduct ions (Eq. (17); see also Appendix A):

In addition to the loss of a hydrogen molecule, a water molecule is expelled from the collision complex (Eq. (18)):

The ratio between the abundances of the product ions resulting from H_2 and H_2O loss is 90:10 after the ions have reacted with methanol for 0.6 s as indicated in Table 3. This ratio is obtained if the $C_6H_7MnO^-$ ions are isolated 0.25 s after the start of the electron beam pulse (the duration of this pulse was 0.1 s; see Experimental Section). A ratio of 70:30 is obtained, however, if the reactant $C_6H_7MnO^-$ ions are isolated after a delay of 0.65 s and subsequently allowed to react with

methanol for 0.6 s. Concurrent with this change in the product ratio in favour of the ions arising by H_2O loss, the overall reaction becomes slower as indicated by the conversions into products given in Table 3. With a delay of 1.65 s prior to the isolation of the $C_6H_7MnO^-$ ions, loss of H_2 is no longer observed and in the subsequent reaction with methanol only H_2O elimination occurs. After still longer delay times, roughly 15% of the initially generated $C_6H_7MnO^-$ ions remains in the FT-ICR cell. These residual $C_6H_7MnO^-$ ions display no reactivity towards methanol. Combining these observations, the results of the experiments with methanol suggest that the main fraction of the $C_6H_7MnO^-$ ions react relatively fast by loss of H_2 from the collision complex, whereas a minor part of the ions reacts relatively slowly to expel an H_2O molecule. In addition, a minor fraction of the ions appears unreactive towards methanol.

Elimination of a hydrogen molecule is likewise the main reaction with methanethiol, which also proceeds by loss of a water molecule from the collision complex (Eqs. (19) and (20)):

No reaction was observed with NO as the substrate, whereas the $C_6H_7MnO^-$ ions react completely with SO_2 by a number of processes including the competing losses of C_6H_6O and C_6H_6 (Table 2).

4.4. Reactions of the $C_5H_5MnO_2^-$ and $C_6H_7MnO_2^-$ ions

The $C_5H_5MnO^-$ and $C_6H_7MnO^-$ ions react with N_2O and H_2O to incorporate an

oxygen atom thus forming $\text{C}_5\text{H}_5\text{MnO}_2^-$ and $\text{C}_6\text{H}_7\text{MnO}_2^-$ ions (see Eqs. (7), (8), (12) and (13)). Both of the latter two ions react with water to generate stable adduct ions (see Appendix A). Significantly, the $\text{C}_5\text{H}_5\text{MnO}_2^-$ ions formed in the reaction with N_2O exchange one oxygen atom for an ^{18}O atom in the presence of H_2^{18}O (Eq. (21)) indicating that the two oxygen atoms in the dioxide ions are structurally distinguishable. Moreover, the $\text{C}_5\text{H}_5\text{MnO}^{18}\text{O}^-$ ions formed in the reaction of $\text{C}_5\text{H}_5\text{MnO}^-$ with H_2^{18}O do not exchange the ^{16}O atom for an ^{18}O atom in the presence of H_2^{18}O .

The two dioxide ions react with aliphatic alcohols (ROH , $\text{R} = \text{CH}_3$, C_2H_5 and $n\text{-C}_3\text{H}_7$) and methanethiol mainly by simple adduct formation and the loss of a water molecule from the collision complex as exemplified for methanol in Eqs. (22) and (23):

Adduct formation and loss of a water molecule occur also in the reactions of both of the $\text{C}_5\text{H}_5\text{MnO}_2^-$ and $\text{C}_6\text{H}_7\text{MnO}_2^-$ ions with SO_2 . In addition to these reactions, loss of a neutral species with the elemental composition of $\text{C}_6\text{H}_6\text{O}$ from the collision complex is observed in the reaction of the $\text{C}_6\text{H}_7\text{MnO}_2^-$ ions with SO_2 in line with the results for the related monoxide ions (see Table 2). The reactivity of the dioxide ions appears to be independent of whether they are formed in the reactions of the corresponding monoxide ions with N_2O or H_2O . The pronounced formation of adduct ions restricts, however, the insight into the structures of the $\text{C}_5\text{H}_5\text{MnO}_2^-$ and

$\text{C}_6\text{H}_7\text{MnO}_2^-$ species, which could be derived from their bimolecular chemistry.

5. Discussion

5.1. Site of attack by the $\text{O}^{\cdot-}$ ion

The main concern in the present study is an experimental determination of the regioselectivity in the gas phase reactions of the atomic oxygen radical anion with $\text{CpMn}(\text{CO})_3$ and $\text{CH}_3\text{CpMn}(\text{CO})_3$. In principle, the $\text{O}^{\cdot-}$ ion can react at either site of the manganese containing molecules, that is, competing attack on a CO ligand, the organic ligand and the metal centre cannot be excluded a priori. If initial attack on a CO ligand occurs in the reaction of the $^{18}\text{O}^{\cdot-}$ ion with $\text{CpMn}(\text{CO})_3$ this may be expected to yield intermediate 1 in Scheme 1. This species can expel CO^{18}O in agreement with the result in Eq. (1) or eliminate two CO molecules with formation of ion 2 in Scheme 1. Initial attack of the $^{18}\text{O}^{\cdot-}$ ion on the organic ligand or at the

Scheme 1. Possible mechanism for initial attack of the $^{18}\text{O}^{\cdot-}$ ion on a carbonyl ligand and the predicted extent of incorporation of the ^{18}O atom in the ions formed by loss of two and three carbon monoxide molecules, respectively.

metal centre could proceed as illustrated in Scheme 2 for the reaction with $\text{CpMn}(\text{CO})_3$. In this hypothetical scheme, the reaction at the metal centre is assumed to involve a η^5 to η^3 change in the bonding of the C_5H_5 ligand prior to attack at the manganese atom [29], whereas the reaction at the Cp ligand is presumed to occur from the exo-side of the ring as suggested for the comparable reaction of $\text{O}^{\cdot-}$ with the $\text{CpCo}(\text{CO})_2$ compound [10]. The mechanistic proposals in Schemes 1 and 2 lead to the prediction that the ^{18}O atom is retained in the product ions generated by the loss of two carbon monoxide molecules irrespective of the initial site of attack (vide infra). In other words, the insight into the regioselectivity may be obtained more readily

by considering the extent to which the label is incorporated in the product ions resulting from the loss of three carbon monoxide molecules.

As indicated in Scheme 1, initial attack on a CO ligand and the loss of two CO molecules can lead to ion 2, which may expel CO and C^{18}O with equal probability. In contrast, initial attack on the metal or the organic ligand is anticipated to lead to complete incorporation of the label in the ions formed by loss of three carbon monoxide molecules as shown in Scheme 2. In the reactions of $^{18}\text{O}^{\cdot-}$ with the $\text{CpMn}(\text{CO})_3$ compound, the $\text{C}_5\text{H}_5\text{Mn}^{18}\text{O}^-$ and $\text{C}_5\text{H}_5\text{MnO}^-$ ions are generated in an abundance ratio of 55:45 (Eq. (4)). Based on the proposal in Scheme 1, initial CO attack can account for the generation of 45% $\text{C}_5\text{H}_5\text{Mn}^{18}\text{O}^-$ and 45% $\text{C}_5\text{H}_5\text{MnO}^-$ ions, whereas the remaining 10% $\text{C}_5\text{H}_5\text{Mn}^{18}\text{O}^-$ ions are liable to be formed as a result of attack on the Cp ligand and/or the metal centre in $\text{CpMn}(\text{CO})_3$. Similar considerations apply to the results of the reactions between the $^{18}\text{O}^{\cdot-}$ ion and $\text{CH}_3\text{CpMn}(\text{CO})_3$. Loss of three carbon monoxide molecules from the collision complex yields for this substrate $\approx 70\%$ $\text{C}_6\text{H}_7\text{Mn}^{18}\text{O}^-$ and $\approx 30\%$ $\text{C}_6\text{H}_7\text{MnO}^-$ ions (Eq. (5)). This leads to the suggestion that initial attack on a CO ligand by $^{18}\text{O}^{\cdot-}$ is responsible for the formation of 30% $\text{C}_6\text{H}_7\text{MnO}^-$ and 30% $\text{C}_6\text{H}_7\text{Mn}^{18}\text{O}^-$ ions, whereas the remaining 40% $\text{C}_6\text{H}_7\text{Mn}^{18}\text{O}^-$ ions are likely to be generated by other routes (vide infra).

5.2. Structures and formation of the $\text{C}_5\text{H}_5\text{MnO}^-$ and $\text{C}_6\text{H}_7\text{MnO}^-$ ions

A detailed and unambiguous analysis of the structure(s) of the ions generated by attack of $\text{O}^{\cdot-}$ on the manganese compounds is restricted owing to the presently limited knowledge of the gas-phase ion chemistry of organometallic negative ions. On the basis of the results of the bimolecular chemistry of the $\text{C}_5\text{H}_5\text{MnO}^-$

Scheme 2. Possible mechanism for the initial attack of the $^{18}\text{O}^{\cdot-}$ ion on either the metal centre or the Cp ligand together with the predicted extent to which the ^{18}O atom is incorporated in the product ions resulting from the loss of two and three carbon monoxide molecules, respectively.

and $C_6H_7MnO^-$ ions some insight into the possible structures of these species can be obtained. In particular, the predominant reaction of the $C_5H_5MnO^-$ ions with SO_2 involves the loss of a neutral species with the elemental composition of C_5H_4O (Eq. (11) and Table 2). This elemental composition may represent a single neutral species or, for example, a CO and a C_4H_4 molecule. However, loss of CO from the collision complex in the reaction with SO_2 is not observed and, in addition, no reaction occurs with NO even though this neutral species is known to be able to displace a CO ligand in organometallic negative ions [10,30,31]. The loss of C_5H_4O leads, therefore, to the suggestion that $C_5H_5MnO^-$ ions with a cyclopentadienone and a hydride ligand are formed; that is, ion **8** is generated in the reaction of $O^{\cdot-}$ with $CpMn(CO)_3$ [32].

The formation of ion **8** is also supported by the observation that one of the hydrogen atoms of the reactant ions is incorporated in the hydrogen molecule expelled in the reactions with water (Eq. (8)) and aliphatic alcohols (Eq. (9)). The reaction with the aliphatic alcohols can be formulated as insertion into the O–H bond followed by reductive elimination of a hydrogen molecule as shown in Scheme 3 [1].

The main fraction of the $C_5H_5MnO^-$ ions ($\approx 80\%$) reacts with the alcohols by reductive elimination of a hydrogen molecule, whereas the remaining ions are unreactive. Moreover, in the reactions with SO_2 , $\approx 70\%$ of the product ions arises by loss of C_5H_4O from the collision complex. These results indicate that **8** is the main species formed in the reac-

Scheme 3. Proposed mechanism for the loss of H_2 in the reactions of the (cyclopentadienone) MnH^- ions with aliphatic alcohols.

tion with the $O^{\cdot-}$ ion. In combination with the results of the experiments with $^{18}O^{\cdot-}$, which indicates that nearly all of the ions ($\leq 90\%$) are generated following attack on a CO ligand, we are forced to conclude that **8** is formed by initial reaction at a CO ligand in contrast to what could be anticipated on the basis of Scheme 2 (*vide supra*). In Scheme 4 attack on a CO ligand is suggested to be followed by loss of two CO molecules and intramolecular attack of either of the two oxygen atoms of the $-C(O^-)O^{\cdot}$ group in **1'** on the Cp ligand. This yields intermediate **11** in which one of the carbon atoms of the ring carries an oxygen atom at the endo-side and a hydrogen atom at the exo-side. Subsequently, a CO molecule may be expelled concurrent with structural reorganization leading to **8**. Based on the present results it is not possible to reach a conclusion as to the precise nature and sequence of the chemical events leading to

Scheme 4. Proposed mechanism for the formation of (cyclopentadienone)MnH⁻ ions following initial attack of the O⁻ ion on a CO ligand in CpMn(CO)₃.

8 from **11**. It is evident, however, that one of the hydrogen atoms of the original Cp ligand migrates to the metal centre at some stage during the process yielding **8**.

A further uncertainty relates to whether two CO molecules are expelled prior to the migration of an oxygen atom to the organic ligand. The proposal shown in Scheme 1 is based upon the expectation that two CO molecules are expelled before an oxygen atom migrates to the remaining part of the ion. Based on this suggestion, initial attack of the ¹⁸O⁻ ion on a CO ligand is predicted to lead to complete retention of the label in the product ions generated by the loss of two CO molecules. In the performed experiments with the ¹⁸O⁻ ion, $\approx 85\%$ of the ions generated by loss of two carbon monoxide molecules retains the label in the reaction with CpMn(CO)₃ (Eq. (2)), whereas $\approx 95\%$ of the product ions of this process incorporates the label if CH₃CpMn(CO)₃ is the substrate (Eq. (3)). These findings indicate that an oxygen atom in intermediates **1** (Scheme 1) and **1'** (Scheme 4)—or the comparable species formed in the reaction with CH₃CpMn(CO)₃—can migrate before two carbon monoxide molecules are expelled. Insight into the relative importance of this migration prior to the loss of two carbon monoxide molecules is not readily

achieved, however, from the extent of the incorporation of the label in the product ions of this process. Nevertheless, the probability for migration of the ¹⁸O atom will be the same for **1** and **2** in Scheme 1. This means that the predicted extent of incorporation of the label in the product ions formed by loss of three carbon monoxide molecules is the same regardless of whether an oxygen atom migrates prior to or following the expulsion of two carbon monoxide molecules.

In the reaction of O⁻ with CpCo(CO)₂, ions with a (cyclopentadienone)CoH⁻ structure were concluded to arise as a result of initial attack on the Cp ligand [10]. In the present study of the reaction with the related manganese compounds, it is clear that agreement between the different observations can be achieved by postulating the formation of ion **8** following initial attack on a CO ligand. The mechanistic details of the process leading to the formation of these ions are unknown and at present we are unable to explain the different behaviour observed for the cobalt and the manganese compounds. Another uncertainty relates to the non-reactive C₅H₅MnO⁻ ions. In the experiments with ¹⁸O⁻, it is observed that the C₅H₅MnO⁻ ions react completely with N₂O and the parent organometallic compound (see Eqs. (6) and (7), respectively), whereas some of the C₅H₅Mn¹⁸O⁻ ions appear unreactive towards these substrates. In other words, the non-reactive ions contain the ¹⁸O atom suggesting that these species are formed by initial attack on the metal and/or the Cp ligand (see also Scheme 2). From the present results it is not possible to conclude whether, for example, CpMnO⁻ ions are formed as a result of attack on the metal centre as suggested in Scheme 2. However, the CpMnO⁻ ion is a 15-electron species and one may expect such an ion to be able to react with aliphatic alcohols on the basis of the reported occurrence of dehydrogenation in the reaction

between the comparable 17-electron ion, CpCoO^- , and methanol in the gas phase [33]. Irrespective of the structure(s) of the unreactive ions, we notice that they represent a minor fraction of all the $\text{C}_5\text{H}_5\text{MnO}^-$ ions generated by loss of three carbon monoxide molecules from the collision complex in the reaction with $\text{CpMn}(\text{CO})_3$.

The main part of the $\text{C}_6\text{H}_7\text{MnO}^-$ ions react with water and aliphatic alcohols by loss of a hydrogen molecule from the collision complex (Eqs. (13), (14) and (17)) and in the reaction with SO_2 , about 55% of the ions expels a neutral species with the elemental composition of $\text{C}_6\text{H}_6\text{O}$ (Table 2). These results suggest that the main part of the $\text{C}_6\text{H}_7\text{MnO}^-$ has a structure, which is similar to the one proposed for the ions generated in the reaction with $\text{CpMn}(\text{CO})_3$, that is, ion **12** arises following attack of O^- on $\text{CH}_3\text{CpMn}(\text{CO})_3$. In view of the conclusion that initial attack on a CO ligand is responsible for 60% of all the ions formed by the loss of three carbon monoxide molecules, we suggest that **12** is formed as shown for **8** in Scheme 4:

The formation of **12** following attack on a CO ligand implies that all the 30% $\text{C}_6\text{H}_7\text{MnO}^-$ ions generated in the reaction with $^{18}\text{O}^-$ has this structure. A different situation arises for part of the 70% $\text{C}_6\text{H}_7\text{Mn}^{18}\text{O}^-$ ions, which are liable to have a distinct structure. This is supported by the occurrence of water loss in the reaction of the $\text{C}_6\text{H}_7\text{MnO}^-$ ions with alcohols and methanethiol (Eqs. (18) and (20)). Furthermore, 25–30% of the $\text{C}_6\text{H}_7\text{MnO}^-$ ions reacts with SO_2 to expel C_6H_6 (Table 2) and a minor

fraction of the ions react with D_2O by hydrogen–deuterium exchange (Eq. (16) and Fig. 1). The loss of a water molecule in the reaction with methanethiol indicates that a hydroxy ligand is present, whereas the loss of C_6H_6 in the reaction with SO_2 points toward the formation of $\text{C}_6\text{H}_7\text{MnO}^-$ ions containing a ligand with this elemental composition. These findings suggest the formation of a (fulvene)- $\text{Mn}(\text{OH})^-$ ion [34]; that is, ion **13** may be formed in addition to **12**.

A possible mechanism for the formation of **13** involves initial hydrogen atom abstraction by the oxygen radical anion from the methyl group of the substrate molecule to give species **14** in Scheme 5. The hydroxide ion in **14** can attack a CO ligand to generate **15** prior to migration of the hydroxy group to the metal centre and the loss of three carbon monoxide molecules. A similar mechanism has been proposed for the reaction of the hydroxide ion with $\text{CpCo}(\text{CO})_2$, which yields a $\text{CpCo}(\text{OH})^-$ ion after the loss of two carbon monoxide molecules [10]. In the reaction of the H^{18}O^- ion with $\text{CpCo}(\text{CO})_2$, the label was incorporated almost completely in the product ions resulting from the loss of two carbon monoxide molecules. In the present context, it may be expected, therefore, that 1,3-H shifts between the oxygen atoms in **15** are not occurring. This leads to the prediction that all the product ions of the pathway involved retain the label if $^{18}\text{O}^-$ is the reactant ion. Formation of **13** by a pathway involving intermediate **14** is thus in agreement with the conclusion that all the $\text{C}_6\text{H}_7\text{MnO}^-$ ions formed in the reactions with the $^{18}\text{O}^-$ ion have structure **12** (vide supra). An alternative mechanism

Scheme 5. Proposed mechanism for the formation of the (fulvene)Mn(OH)⁻ ions in the reaction of the O⁻ ion with CH₃CpMn(CO)₃.

for the generation of **13** could involve initial attack on a CO ligand to give **16** which then rearranges to **15** by an intramolecular H-shift (Scheme 5). However, if ¹⁸O⁻ is the reactant ion, such a mechanism would lead to incorporation of the label in 50% of the product ions of the process in conflict with the proposal that none of the C₆H₇MnO⁻ ions formed in the reaction with ¹⁸O⁻ (Eq. (5)) has structure **13**.

Ion **13** may be responsible for the exchange of three hydrogen atoms for deuterium atoms in the presence of D₂O (Eq. (16) and Fig. 1). The exchange of only three hydrogen atoms could imply that this process involves the hydrogen atom of the hydroxy ligand and the two hydrogen atoms of the methylene group of the fulvene ligand. A possible mechanism for the exchange involves insertion into an O–D bond with formation of

Scheme 6. Possible mechanism for the hydrogen–deuterium exchange in the reactions of the (fulvene)Mn(OH)⁻ ions with D₂O.

17a in Scheme 6. This step may be followed by reductive elimination of HDO or a shift of the deuterium atom bonded to the manganese atom to the methylene group can occur thus forming **18**. Transfer of a hydrogen atom from the generated CH₂D group in **18** leads to **17b**, which then expels H₂O to give an ion containing two deuterium atoms (see Scheme 6). The process can be repeated until three of the hydrogen atoms have been exchanged for deuterium atoms as observed experimentally (Fig. 1).

Based largely upon the reactions with SO₂ (Table 2), we conclude that 25–30% of the ions are formed with structure **13**, whereas 55–60% of the ions have structure **12**. The remaining 10–20% of the ions

represent the unreactive fraction of the $C_6H_7MnO^-$ ions and from the present results we are unable to reach a conclusion as to the structure(s) of these $C_6H_7MnO^-$ ions.

5.3. Formation and structure of the $C_5H_5MnO_2^-$ and $C_6H_7MnO_2^-$ ions

In the reactions of the $C_5H_5MnO^-$ ions with N_2O , roughly 85% of the ions reacts by oxygen atom abstraction to form $C_5H_5MnO_2^-$ ions [27] in line with the relative yield of the ion **8**. Similarly, the percentage ($\approx 70\%$) of the $C_6H_7MnO^-$ ions which reacts with N_2O by oxygen atom transfer is close to the relative yield of **12** ($\approx 60\%$). The reaction with N_2O is likely, therefore, to involve **8** and **12**, respectively, indicating that the $C_5H_5MnO_2^-$ ions may contain a cyclopentadienone ligand and the $C_6H_7MnO_2^-$ ions a methylcyclopentadienone ligand. In addition, the loss of a water molecule in the reactions of either dioxide ion with aliphatic alcohols, methanethiol and SO_2 indicates the presence of a hydroxy ligand. This implies that oxygen atom transfer leads to **19** and **20**:

The presence of structurally distinguishable oxygen atoms in the $C_5H_5MnO_2^-$ ions is indicated also by the result that only one oxygen atom is exchanged for an ^{18}O atom in the presence of $H_2^{18}O$ (Eq. (21)). For the $C_6H_7MnO_2^-$ ions, the presence of the methylcyclopentadienone ligand is supported by the occurrence of loss of C_6H_6O in the reactions with SO_2 .

Scheme 7. Formation of the (cyclopentadienone) $Mn(OH)^-$ ions in the reactions of the (cyclopentadienone) MnH^- ions with N_2O or H_2O .

The reactivity of the $C_5H_5MnO_2^-$ and $C_6H_7MnO_2^-$ ions generated in the reactions with water is similar to the reactivity of the ions formed with N_2O as the substrate. The ions **19** and **20** are suggested, therefore, to arise in the reactions with water as well as with N_2O (Scheme 7). With N_2O as the substrate [27], bond formation between the manganese atom and the oxygen atom of the substrate molecule is suggested to precede the expulsion of N_2 with formation of **22** in Scheme 7. Subsequently, ion **22** can rearrange to **19**. In the reaction with water, insertion into an O–H bond is proposed to be followed by reductive elimination of H_2 , thus forming **19** directly.

6. Conclusions

The present results for the reactions of the atomic oxygen radical anion with $CpMn(CO)_3$ and $CH_3CpMn(CO)_3$ indicate

that initial attack occurs mainly on a CO ligand and only to minor extent on the Cp/CH₃Cp ligand and/or the metal centre. Reaction at a CO ligand and the loss of three carbon monoxide molecules in the reaction with CpMn(CO)₃ is proposed to yield a (cyclopentadienone)MnH[−] ion. Similarly, initial attack on a CO ligand in CH₃CpMn(CO)₃ is suggested to yield a (methylcyclopentadienone)MnH[−] ion. The conversion of the Cp and CH₃Cp ligands into cyclopentadienone and methylcyclopentadienone ligands, respectively, is formulated as an intramolecular oxygen atom transfer accompanied by a shift of a hydrogen atom from the original organic ligand to the metal centre. In addition to a (methylcyclopentadienone)MnH[−] ion, the reaction of O[−] with CH₃CpMn(CO)₃ leads to a (fulvene)-Mn(OH)[−] species by a process, which is suggested to involve initial hydrogen atom abstraction from the methyl group in the substrate molecule followed by attack of the HO[−] ion on a CO ligand in the generated (fulvene)Mn(CO)₃ species.

The relatively limited insight into the chemistry of organometallic negative ions in the gas phase prevents firm conclusions with regard to the precise structures of the product ions and the mechanisms of the processes leading to their formation. The results of the experiments with the ¹⁸O[−] ion in combination with the observed bimolecular chemistry of the C₅H₅MnO[−] and C₆H₇MnO[−] product ions illustrate, however, that the O[−] ion can react with organometallic species in the gas phase with formation of new organometallic negative ions, whose chemistry may be of general interest.

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8. References

- [1] J.P. Collman, L.S. Hegedus, R.S. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
- [2] L.P. Pauson, *J. Organometal. Chem.*, 200 (1980) 207.
- [3] I.K. Gregor and M. Guilhaus, *Mass Spectrom. Rev.*, 3 (1984) 39.
- [4] R.R. Squires, *Chem. Rev.*, 87 (1987) 623.
- [5] R.R. Squires and K.R. Lane, in D.H. Russell (Ed.), *Gas Phase Inorganic Chemistry*, Plenum Press, New York, 1989, Chapter 2, p. 43.
- [6] K.R. Lane, R.E. Lee, L. Sallans and R.R. Squires, *J. Am. Chem. Soc.*, 106 (1984) 5767.
- [7] K.R. Lane, L. Sallans and R.R. Squires, *J. Am. Chem. Soc.*, 107 (1985) 5369.
- [8] K.R. Lane, L. Sallans and R.R. Squires, *J. Am. Chem. Soc.*, 108 (1986) 4368.
- [9] K.R. Lane and R.R. Squires, *J. Am. Chem. Soc.*, 107 (1985) 6403.
- [10] K.J. van den Berg, S. Ingemann and N.M.M. Nibbering, *Organometallics*, 11 (1992) 2389.
- [11] K.-P. Wanczek, *Int. J. Mass Spectrom. Ion Processes*, 95 (1989) 1.
- [12] A.G. Marshall and F.R. Verdun, *Fourier Transforms in NMR, Optical, and Mass Spectrometry*, Elsevier, Amsterdam, 1990.
- [13] L.J. de Koning, C.W.F. Kort, F.A. Pinkse and N.M.M. Nibbering, *Int. J. Mass Spectrom. Ion Processes*, 95 (1989) 71 (and references cited therein).
- [14] R.A.L. Peerboom, S. Ingemann, N.M.M. Nibbering and J.F. Liebman, *J. Chem. Soc., Perkin Trans. 2*, (1990) 1825 (and references cited therein).
- [15] N.M.M. Nibbering, *Rapid Commun. Mass Spectrom.*, 7 (1993) 747.
- [16] P.J. Chantry, *J. Chem. Phys.*, 51 (1969) 3369.
- [17] J.H. Futrell and T.O. Tiernan, in J.L. Franklin (Ed.), *Ion-Molecule Reactions*, Vol. 2, Plenum Press, New York, 1972, p. 485.
- [18] A.J.R. Heck, L.J. de Koning, F.A. Pinkse and N.M.M. Nibbering, *Rapid Commun. Mass Spectrom.*, 5 (1991) 406.
- [19] S.E. Barlow and V.M. Bierbaum, *J. Chem. Phys.*, 92 (1990) 3442.
- [20] R.A. Morris, A.A. Viggiano and J.F. Paulson, *J. Chem. Phys.*, 92 (1990) 3448.
- [21] J.C. Kleingeld and N.M.M. Nibbering, *Lect. Notes Chem.*, 31 (1982) 209.

- [22] Vogel's Textbook of Practical Organic Chemistry, 5th edn., Longman, Harlow, 1989.
- [23] N.M.M. Nibbering, Adv. Phys. Org. Chem., 24 (1988) 1.
- [24] J. Lee and J.J. Grabowski, Chem. Rev., 92 (1992) 1611.
- [25] S.L. VanOrden and S.W. Buckner, Polyhedron, 10 (1991) 2487.
- [26] K.J. van den Berg, S. Ingemann and N.M.M. Nibbering, Org. Mass Spectrom., 28 (1993) 527.
- [27] Oxygen atom transfer in the reactions of metal containing negative ions with N_2O in the gas phase will be discussed in a forthcoming paper, K.J. van den Berg, I.K. Gregor, S. Ingemann and N.M.M. Nibbering, in preparation.
- [28] Oxygen abstraction from N_2O in the gas phase has been reported in a number of instances for metal containing positive ions or bare metal cations; see for example: K. Eller and H. Schwarz, Chem. Rev., 91 (1991) 1121.
- [29] J.M. O'Connor and C.P. Casey, Chem. Rev., 87 (1987) 307.
- [30] R.N. McDonald and P.L. Schell, Organometallics, 7 (1988) 1806.
- [31] R.R. Corderman and J.L. Beauchamp, Inorg. Chem., 16 (1977) 3135.
- [32] The precise bonding between the cyclopentadienone or methylcyclopentadienone ligand and the metal centre in the present ions is not known, but may be considered to be η^4 as indicated by results in:
- (a) J.H. Bieri, A.S. Dreiding, T.C.C. Gartenmann, E.R.F. Gesing, R.W. Kunz and R. Prewé, J. Organometal. Chem., 306 (1986) 241.
- (b) R.L. Beddoes, E.S. Cook and M.J. Morris, Polyhedron, 8 (1989) 1810.
- [33] D. Wang and R.R. Squires, J. Am. Chem. Soc., 109 (1987) 7557.
- [34] The bonding between a fulvene ligand and a metal centre is normally η^6 ; see U. Kölle, B.-S. Kang and U. Thewalt, J. Organomet. Chem., 386 (1990) 267. For an example of η^4 coordination of a tetramethylfulvene ligand, see D.S. Glueck and R.G. Bergman, Organometallics, 9 (1990) 2862.
- [35] R.H. Fokkens, I.K. Gregor and N.M.M. Nibbering, Rapid Commun. Mass Spectrom., 5 (1991) 368.
- [36] S.T. Graul and R.R. Squires, Mass Spectrom. Rev., 7 (1988) 263.
- [37] M.K. Murphy and J.L. Beauchamp, J. Am. Chem. Soc., 98 (1976) 5781.
- [38] R.L. Woodin and J.L. Beauchamp, Chem. Phys., 41 (1979) 1.
- [39] G. Caldwell and J.E. Bartmess, J. Phys. Chem., 85 (1981) 3571.
- [40] M.J. McEwan, V.G. Anicich, W.T. Huntress, P.E. Kemper and M.T. Bowers, Chem. Phys. Lett., 75 (1980) 278.
- [41] P. Kofel and T.B. McMahon, J. Phys. Chem., 92 (1988) 6174.
- [42] M.J. McEwan, A.B. Denison, W.T. Huntress, Jr., V.H. Anicich, J. Snodgrass and M.T. Bowers, J. Phys. Chem., 93 (1989) 4064.
- [43] S. Ingemann, R.H. Fokkens and N.M.M. Nibbering, J. Org. Chem., 56 (1991) 607.

9. Appendix A

Several of the ions examined in the present study react predominantly with a substrate molecule to form stable adduct ions with an unknown structure. This holds for the $\text{C}_5\text{H}_4\text{MnO}_2\text{R}^-$ ions generated by the loss of H_2 from the collision complex in the primary reaction of the $\text{C}_5\text{H}_5\text{MnO}^-$ ions with an aliphatic alcohol (Eq. (10)). These $\text{C}_5\text{H}_4\text{MnO}_2\text{R}^-$ ions react further quite readily with an alcohol molecule to generate adduct ions and a similar situation applies to the $\text{C}_6\text{H}_6\text{MnO}_2\text{R}^-$ ions derived from the $\text{C}_6\text{H}_7\text{MnO}^-$ ions as indicated in Eq. (17). Adduct formation is observed also for the reactions of the $\text{C}_5\text{H}_5\text{MnO}_2^-$ and $\text{C}_6\text{H}_7\text{MnO}_2^-$ ions with water, alcohols, methanethiol and SO_2 (see Eq. (23)). In addition, stable adducts have been reported to be formed as terminal ionic products in the reactions of the MnO_3^- ion with aliphatic alcohols [35].

Prevalent formation of adduct ions is often reported for reactions occurring in flowing afterglow (FA) or selected ion flow tube instruments (SIFT) [36]. For example, adduct ions are reported to be formed in the reactions of carbanions and alkoxide ions with CpMn(CO)_3 in a FA instrument [5]. The formation of adducts in these instruments is ascribed normally to the occurrence of third body collisions between the reactant species and the helium carrier gas present at a pressure of ≈ 70 Pa [36]. These collisions can remove part of the excess energy with the result that the internal energy is decreased and dissociation either to the reactant species

or the formation of separated product ions of a reaction is no longer possible. In a typical FT-ICR experiment the pressure is too low ($\leq 10^{-4}$ Pa) for the occurrence of third body collisions. Nevertheless, the formation of stable adduct ions under FT-ICR conditions has been reported in some instances [35,37–43]. The reported examples include the formation of proton bound adducts by association of an alkoxide ion to an alcohol molecule [39] or a carboxylate anion to a molecule of the conjugate acid [43]. The formation of stable adducts at low pressures is commonly ascribed to the emission of IR photons, thus lowering the internal energy below the threshold for dissociation. In the present cases, radiative stabilization may be held responsible for the formation of adducts in the reactions of the $\text{C}_5\text{H}_4\text{MnO}_2\text{R}^-$, $\text{C}_6\text{H}_6\text{MnO}_2\text{R}^-$, $\text{C}_5\text{H}_5\text{MnO}_2^-$ and $\text{C}_6\text{H}_7\text{MnO}_2^-$ ions. We note that these ions are relatively large implying that the number of degrees of freedom over which the energy may be distributed is relatively large for the adducts formed with an aliphatic alcohol molecule. This may decrease the rate of a possible reaction with the result that the lifetime of

the excited adduct is enhanced. An increased lifetime enhances also the probability for photon emission and the formation of an adduct with an internal energy below the threshold for dissociation. The structures of the present adducts are not known and it is uncertain whether insertion of the metal centre into a bond of the substrate has occurred. In this respect we note that adduct formation competes with loss of water in the reactions of the $\text{C}_5\text{H}_5\text{MnO}_2^-$ and $\text{C}_6\text{H}_7\text{MnO}_2^-$ ions with aliphatic alcohols, methanethiol and SO_2 . The loss of water is observed to become more important if the kinetic energy of the reactant $\text{C}_5\text{H}_5\text{MnO}_2^-$ or $\text{C}_6\text{H}_7\text{MnO}_2^-$ ion is increased by applying a suitable r.f. pulse to the excitation plates of the FT-ICR cell [12]. This is in keeping with the formation of adducts with a relatively high internal energy and an associated increase in the rate of the reaction leading to water loss. Furthermore, the average lifetime of the adducts generated in the reactions of ions with excess kinetic energy may be relatively short with the result that photon emission competes less effectively with product ion formation.