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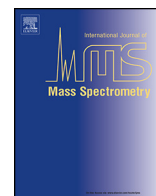


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# Gas-phase reactions of a novel chemical ionization reagent, $\text{ClMn}_2^+$ , with polar and nonpolar analytes in a linear quadrupole ion trap

Tiffany M. Jarrell, James S. Riedeman, Hilkka Kenttämäa\*

Department of Chemistry, Purdue University, Brown Building, 560 Oval Dr., West Lafayette, IN 47907, USA

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## ABSTRACT

A chemical ionization reagent ion,  $\text{ClMn}_2^+$ , has been identified for the analysis of mixtures of organic compounds since it allows ionization of both polar and nonpolar analytes so that only one product ion,  $\text{ClMn}^+$  adduct of the analyte, is generated without fragmentation. The reagent ion is formed upon ionization of  $\text{ClMn}(\text{CO})_5$  via corona discharge in an atmospheric pressure chemical ionization source of a linear quadrupole ion trap mass spectrometer. Volatile analytes were introduced into the ion trap via a reagent mixing manifold. Nonvolatile analytes were deposited on a titanium foil and desorbed using laser-induced acoustic desorption (LIAD). Formation of a  $\text{ClMn}^+$  adduct with no accompanying fragmentation was observed for all analytes, including branched saturated hydrocarbons. Calculations indicate that  $\text{ClMn}^+$  binds to saturated hydrocarbons via an agostic interaction involving the manganese center and a C—H bond of the analyte. The reagent ion  $\text{Mn}^+$  was also investigated. This ion forms a stable adduct with most analytes studied. It binds fairly strongly to saturated hydrocarbons via two agostic interactions with two C—H bonds instead of insertion into a C—H bond. However, it was found to cause fragmentation for alcohols.  $\text{ClMn}(\text{H}_2\text{O})^+$  has been previously shown to ionize most compounds by  $\text{ClMn}^+$  adduct formation but also to yield molecular ions for amines due to their low ionization energies ( $<8.3$  eV). However, electron transfer was not observed upon ionization of amines with the reagents reported here. The  $\text{CpCo}^+$  ion has been reported earlier to ionize most saturated hydrocarbons without fragmentation. However, it induces C—C bond cleavages for highly branched alkanes upon ionization. This was not observed for the reagent ions studied here.  $\text{ClMn}_2^+$  ion is a more universal ionization reagent than  $\text{Mn}^+$  and the previously reported reagent ions due to its ability to ionize analytes with low ionization energies without electron transfer and due to the complete lack of fragmentation for all analytes. Furthermore, based on the examination of six very different analytes, it has no significant bias toward specific types of analytes.

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## 1. Introduction

Mass spectrometry is well suited for analysis of complex mixtures without prior separation [1–3] if careful attention is paid to choosing a suitable ionization method. An ionization method well suited for mixture analysis should ionize different types of analytes by forming only one type of ion per analyte that contains the intact analyte molecule. This should take place without ionization bias or fragmentation to retain molecular weight and structural information and prevent convolution of the mass spectrum [4,5]. Electron ionization is one of the few ionization methods that is capable of ionizing all organic compounds.

Unfortunately, it induces fragmentation for most analytes, thus convoluting the mass spectra. Less fragmentation usually occurs upon traditional chemical ionization (CI) based on proton transfer reactions but the efficiency of ionization and extent of fragmentation both depend on the basicity of the analyte. Electrospray ionization (ESI) and traditional atmospheric pressure chemical ionization (APCI) ionize preferentially the most basic or most acidic analytes. In contrast, the aquachloromanganese(II) cation [ $\text{ClMn}(\text{H}_2\text{O})^+$ ] has been previously reported to enable efficient ionization of both polar and nonpolar analytes, including highly branched saturated hydrocarbons, via formation of a  $\text{ClMn}^+$  adduct without accompanying fragmentation [6–8]. Coupling the  $\text{ClMn}(\text{H}_2\text{O})^+$  reagent ion with laser-induced acoustic desorption (LIAD) enabled mass spectrometric analysis of analytes previously inaccessible to such analysis, such as saturated nonpolar hydrocarbons in base oil fractions [7]. However,  $\text{ClMn}(\text{H}_2\text{O})^+$  was

\* Corresponding author. Tel.: +765 494 0882; fax: +765 494 0239.

E-mail address: [hilkka@purdue.edu](mailto:hilkka@purdue.edu) (H. Kenttämäa).

found to ionize analytes with ionization energies less than 8 eV by electron transfer [8]. Therefore, this reagent is not suited for analysis of mixtures containing analytes with low ionization energies. In order to address this issue, gas-phase reactions of two new, less aggressive reagent ions,  $\text{ClMn}_2^+$  and  $\text{Mn}^+$ , were studied.

The previous studies on the reagent ion  $\text{ClMn}(\text{H}_2\text{O})^+$  were carried out using an obsolete Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR) [6–8]. In the study discussed here, a commercially available LQIT and a custom built dual linear quadrupole ion trap [9] (DLQIT) were used in order to take advantage of the faster duty cycles of the LQIT [10]. A variety of volatile analytes were studied to ensure unbiased ionization for both polar and non-polar analytes without fragmentation. In addition, LIAD was used to desorb large nonpolar hydrocarbons for ionization using  $\text{ClMn}_2^+$  and  $\text{Mn}^+$  in order to demonstrate the utility of this approach for analysis of petroleum samples.

## 2. Experimental

All reactions were examined in either a Thermo Scientific LTQ linear quadrupole ion trap (LQIT) equipped with a pulsed valve sample introduction interface [11] or a dual linear quadrupole ion trap mass spectrometer [9] (DLQIT) equipped with a reagent mixing manifold [12]. The same results were obtained for both instruments. Each instrument was operated using the LTQ Tune Plus interface and was equipped with an atmospheric pressure chemical ionization (APCI) source. Typical APCI parameters were as follows: discharge current, 3–4  $\mu\text{A}$ ; sheath gas ( $\text{N}_2$ ) flow, 0 (arbitrary units); auxiliary gas ( $\text{N}_2$ ) flow, 5 (arbitrary units); vaporizer temperature  $0^\circ\text{C}$ ; capillary temperature,  $275^\circ\text{C}$ .

$\text{ClMn}(\text{CO})_5$  was synthesized using a literature procedure [13] and used as a precursor for the generation of the reagent ions  $\text{ClMn}_2^+$  and  $\text{Mn}^+$ . All other reagents were purchased from Sigma–Aldrich and used without additional purification. The reagent ions were generated by allowing  $\text{ClMn}(\text{CO})_5$  (solid) to sublime from a glass slide inside the ion source at atmospheric pressure and by ionizing the vapors via corona discharge, which formed the ions  $\text{Mn}^+$  and  $\text{ClMn}_2^+$  in  $\sim 1:4$  abundance. The optimal tube lens voltage (115 V) was found to be higher than standard operating voltages (20–70 V). When using DLQIT equipped with two ion traps, reagent ions were accumulated in the front trap, isolated, and transferred into the back trap for reactions with analytes. In other words, in this experiment, the accumulation and isolation of the reagent ions and the reactions of the reagent ions with the analytes were separated in both time and space (front and back trap). In the LQIT, these events were only separated in time since they both occurred in the same ion trap.

For the DLQIT, all volatile analytes were introduced into the back ion trap of the instrument via the standard helium line by using a previously described reagent mixing manifold [14,15]. Analytes (neat) were introduced into the reagent mixing manifold via a syringe drive operating at a delivery rate of  $10\ \mu\text{L}/\text{h}$  and then diluted with helium at a flow rate of  $600\ \text{mL}/\text{min}$ . Nonvolatile analytes were introduced via laser-induced acoustic desorption (LIAD) with a fiber optic set-up [16] into the back ion trap of the DLQIT, as described previously for LQIT [16]. For the LQIT, volatile analytes were introduced into the ion trap by using a multi-ported pulsed valve sample introduction interface [11]. Analytes (5  $\mu\text{L}$  neat) were introduced into the pulsed valve sample introduction interface manually via a rubber septum by using a syringe. The reagent ions were isolated (2 Da window or  $\pm 1$  Da) by ejecting all unwanted ions from the ion trap. Each analyte was allowed to react for 30 ms with the isolated reagent ions (either  $\text{Mn}^+$  ( $m/z$  55) or

$\text{ClMn}_2^+$  ( $m/z$  145)). The nominal pressure of the ion traps in both instruments were maintained at  $0.5\text{--}0.7 \times 10^{-5}$  Torr. Helium was used as the buffer gas within the ion trap. Without isolation of the reagent ion, simple product distributions are not obtained. For mixtures containing analytes with very different concentrations, different ion accumulation times can be employed before examination of the ion-molecule reactions.

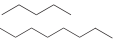
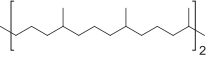



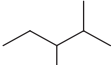
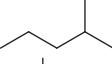
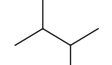





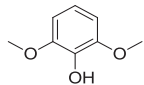
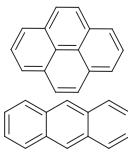



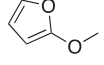
Density functional theory (DFT) combined with the hybrid generalized gradient approximation functional developed by Becke, Lee Yang, and Parr [17–19] (B3LYP) was used to compute optimized geometries of  $\text{ClMn}_2^+$ , ethane, the  $\text{ClMn}$ –ethane $^{++}$  adduct and the  $\text{Mn}$ –ethane $^{++}$  adduct. This method uses the Becke88 exchange functional combined with the Lee–Yang–Parr (LYP) correlation functional. Local minima predicted by this method were confirmed by computing the vibrational frequencies in order to verify the absence of imaginary frequencies. This also provided thermal and zero-point corrections to the calculated energies. The contracted double basis set 6–31 + G(d,p) [20] was used for the approximation of molecular orbitals. Enthalpies were calculated as the energy difference between products and reactants. All calculations were performed using the Gaussian 09 software suite (Revision C.01) [21].

## 3. Results and discussion

Several different types of analytes, including linear, branched and cyclic alkanes, thiophenes, furans, aromatic compounds, alcohols, ethers, ketones and amines, were used to test the utility of the manganese chemical ionization reagent ions  $\text{ClMn}_2^+$  and  $\text{Mn}^+$ . The ions were generated via corona discharge in an atmospheric pressure chemical ionization (APCI) source of a linear quadrupole ion trap. The isolated  $\text{ClMn}_2^+$  and  $\text{Mn}^+$  ions were allowed to react with each of the analytes for 30 ms. Every analyte yielded only one product ion for  $\text{ClMn}_2^+$  and most of them for  $\text{Mn}^+$  (Table 1). This was found to be true for analytes with a wide range of different ionization energies (Table 2). Reactions of  $\text{ClMn}_2^+$  with the analytes (X) yielded an adduct that had lost Mn ( $\text{ClMnX}^+$ ), while reactions of  $\text{Mn}^+$  yielded an adduct of  $\text{Mn}^+$  ( $\text{Mn(X)}^+$ ) for all analytes except for two alcohols that also showed loss of water (Table 2). This is true even for branched alkanes, such as 2,3-dimethylpentane (Table 1), which have been shown to fragment by C–C bond cleavages upon ionization with other fairly gentle reagent ions, such as  $\text{CpCo}^+$  [22]. Further, this also applies to analytes with low ionization energies [23] (IE; e.g., triethyl amine, IE = 7.5 eV; Table 2), which undergo [8] electron transfer with  $\text{ClMn}(\text{H}_2\text{O})^+$  to produce molecular ions in addition to the desired adducts with  $\text{ClMn}^+$ . Fig. 1 shows an example mass spectrum measured after reaction of a mixture of pentane, ethanol and triethylamine with  $\text{ClMn}_2^+$  for 30 ms. Only one product ion was formed for each of the analytes. Further, this experiment suggests that there is virtually no ionization bias for very different analytes. Examination of the reaction of an equimolar mixture of tetrahydrofuran and benzene yielded the same conclusions.

Since the  $\text{ClMn}(\text{H}_2\text{O})^+$  reactions reported previously [8] were performed in a different instrument (FT-ICR) from those used here, the reaction of triethylamine with  $\text{ClMn}(\text{H}_2\text{O})^+$  was repeated in the LQIT in order to test whether similar reactivity is observed. Fig. 2 compares reactions of  $\text{ClMn}(\text{H}_2\text{O})^+$  and  $\text{ClMn}_2^+$  with triethylamine (shown [8] previously to undergo electron transfer upon ionization with  $\text{ClMn}(\text{H}_2\text{O})^+$  in an FT-ICR) in the linear quadrupole ion trap. In agreement with literature, [8] electron transfer was observed for the reaction of  $\text{ClMn}(\text{H}_2\text{O})^+$  with triethylamine to form molecular ions (which react further to produce protonated triethylamine molecules). However, no electron transfer was observed when  $\text{ClMn}_2^+$  was allowed to react with triethylamine.

**Table 1**Product ions (with their  $m/z$ -values) formed in reactions of  $\text{ClMn}_2^+$  and  $\text{Mn}^+$  with a variety of polar and nonpolar analytes.

Analyte (MW)	Structure	$\text{ClMn}_2^+$ products, $m/z$	$\text{Mn}^+$ products, $m/z$
Linear alkanes			
Pentane (72)		Adduct–Mn, 162	Adduct, 127
Octane (114)		Adduct–Mn, 204	Adduct, 169
Squalane (422)		Adduct–Mn, 512	Adduct, 477
Tetracosane (338)		Adduct–Mn, 428	Adduct, 393
Cyclic alkane			
Cyclohexane (80)		Adduct–Mn, 170	Adduct, 135
Branched alkanes			
2,3-Dimethylpentane (100)		Adduct–Mn, 190	Adduct, 155
2-Methylpentane (86)		Adduct–Mn, 176	Adduct, 141
2,3-Dimethylbutane (86)		Adduct–Mn, 176	Adduct, 141
Thiophenes			
Tetrahydrothiophene (88)		Adduct–Mn, 178	Adduct, 143
3-Methylthiophene		Adduct–Mn, 188	Adduct, 153
Thiophene (84)		Adduct–Mn, 174	Adduct, 139
Aromatic			
Benzene (78)		Adduct–Mn, 172	Adduct, 133
Guaiacol (124)		Adduct–Mn, 214	Adduct, 179
Syringol (154)		Adduct–Mn, 244	Adduct, 209
Pyrene (202)		Adduct–Mn, 292	Adduct, 257
Anthracene (178)		Adduct–Mn, 268	Adduct, 233
Furan			
Tetrahydrofuran (72)		Adduct–Mn, 162	Adduct, 127
2-Methylfuran (82)		Adduct–Mn, 172	Adduct, 137
2-Methoxyfuran (98)		Adduct–Mn, 188	Adduct, 153

**Table 2**

Product ions (with their  $m/z$ -values) formed in the reactions of  $\text{ClMn}_2^+$  and  $\text{Mn}^+$  with small organic compounds with various functionalities and differing ionization energies. (IE; obtained from literature<sup>a</sup>).

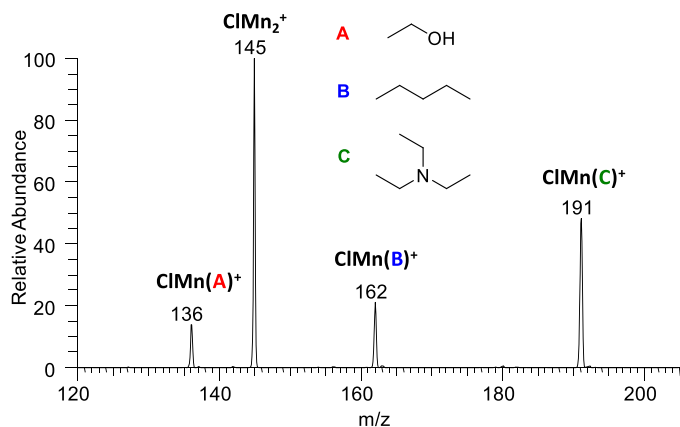
Analyte (MW)	IE in eV	$\text{ClMn}_2^+$ products, $m/z$	$\text{Mn}^+$ products, $m/z$
Triethylamine (101)	7.50	Adduct–Mn, 191	Adduct, 156
Diethylamine (73)	7.90	Adduct–Mn, 163	Adduct, 128
Dimethylamine (45)	8.24	Adduct–Mn, 135	Adduct, 100
Benzyl Alcohol (108)	8.26	Adduct–Mn, 198	Adduct, 163; Adduct–H <sub>2</sub> O, 145
Phenol (94)	8.49	Adduct–Mn, 184	Adduct, 149
Methyl <i>tert</i> -Butyl Ether (88)	9.24	Adduct–Mn, 178	Adduct, 143
Acetone (58)	9.7	Adduct–Mn, 148	Adduct, 113
Butanal (72)	9.8	Adduct–Mn, 162	Adduct, 127
<i>t</i> -Butanol (74)	9.9	Adduct–Mn, 164	Adduct, 129; Adduct–H <sub>2</sub> O, 111
<i>n</i> -Butanol (74)	9.99	Adduct–Mn, 164	Adduct, 129
<i>n</i> -Propanol (60)	10.22	Adduct–Mn, 150	Adduct, 115
Methanol (32)	10.85	Adduct–Mn, 122	Adduct, 87
Ethanol (46)	10.48	Adduct–Mn, 136	Adduct, 101

<sup>a</sup> [19].

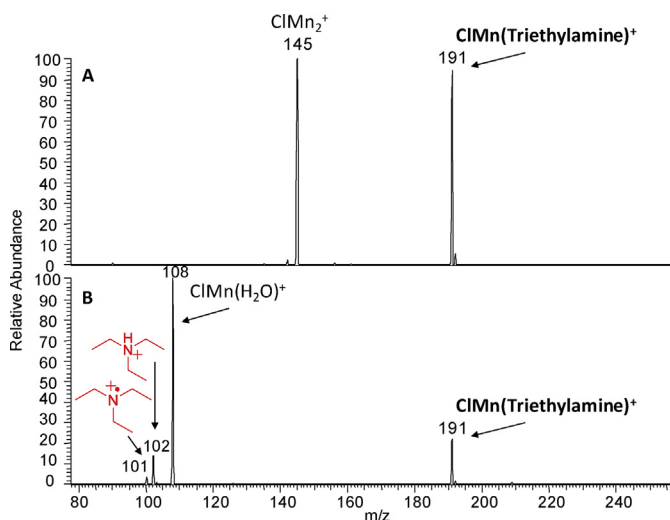
The reactions described above were also examined by quantum chemical calculations. The lowest-energy structures calculated for  $\text{ClMn}_2^+$  can be seen in Fig. 3B. The linear  $\text{Mn–Mn–Cl}$  structure is more stable by  $24.5 \text{ kcal mol}^{-1}$  than the bent  $\text{Mn–Cl–Mn}$  structure and hence it is likely to be the reagent ion involved in the experiments discussed here. Upon reaction of  $\text{ClMn}_2^+$  with analytes, Mn is eliminated and a  $\text{ClMn}^+$  adduct of the analyte molecule generated.  $\text{ClMn}^+$  contains a coordinatively unsaturated manganese atom with the  $d5$  [5] electron configuration. The  $d5$  [5] electron configuration is a stable high-spin configuration [24]. Thus, the interaction of  $\text{ClMn}^+$  with analytes may increase the coordination number of manganese but is unlikely to involve oxidative addition. The interaction of  $\text{ClMn}^+$  with a saturated alkane, ethane, was examined using the B3LYP/6–31G(d,p) level of theory. Based on the calculations, the bonding of  $\text{ClMn}^+$  with ethane is best described as an agostic interaction of the manganese center with a C–H bond in ethane. An agostic interaction is a three-centertwo-electron bond characterized by a metal (M) M–H bond with a length between 1.8 and 2.3 Å, and an M–H–C angle in the range  $90^\circ$ – $140^\circ$  [25]. The structure calculated for the  $\text{ClMn}^+$  adduct with ethane agrees very well with that description (Fig. 3A). Further, two different types of interactions of the reagent ion  $\text{Mn}^+$ , with the  $d$  [4] electron configuration, and ethane were examined. The formation of two agostic interactions of  $\text{Mn}^+$  with two C–H bonds in ethane was found to lower the Gibbs free

energy of the system by  $16.7 \text{ kcal mol}^{-1}$  more than formation of a C–H bond insertion product (Fig. 3C). Hence, C–H bond insertion is not likely to occur for this reagent ion, either.

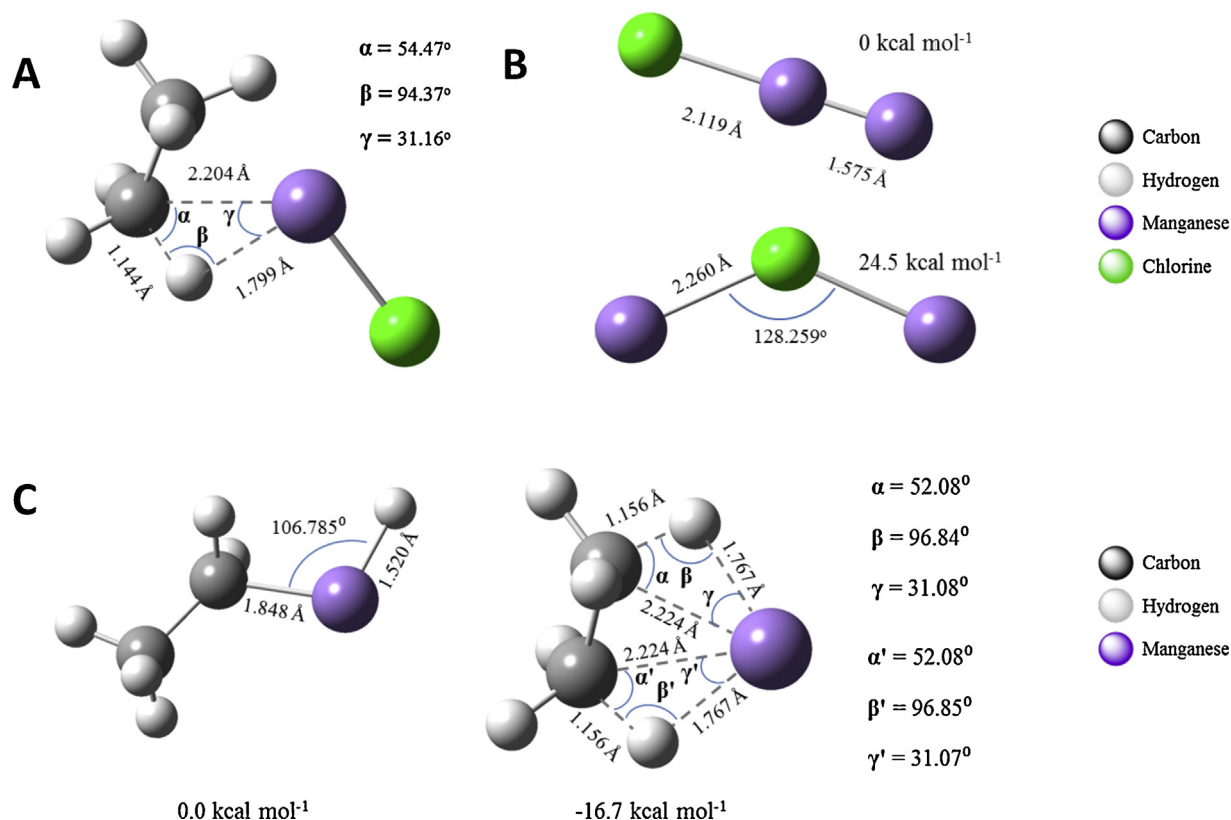
Finally, collision-activated dissociation (CAD) was used to examine the dissociation reactions of many of the  $\text{ClMn}^+$  adducts (Table 3). Six of the adducts, those of the saturated hydrocarbons and the smallest oxygen-containing analytes, exclusively or predominantly dissociate to form the neutral analyte and  $\text{ClMn}^+$  (for methanol, see Scheme 1A). This finding is in agreement with agnostic interactions between  $\text{ClMn}^+$  and the saturated hydrocarbons, as calculated, and dative bonding between oxygen-containing analytes and  $\text{ClMn}^+$  (a dative bond is a dipolar bond where both of the electrons in the bond are donated by the ligand and are typically formed between good Lewis acids and bases, such as a transition metal and a lone pair of electrons [26]). In sharp contrast, CAD of the  $\text{ClMn}^+$  adducts of ethanol and propanol involves cleavage of the C–O bond and predominant elimination of ethene and propene, respectively, to generate the  $\text{ClMn}(\text{H}_2\text{O})^+$  ion (possibly as shown in Scheme 1B for propanol). However, *t*-butanol adduct fragments by elimination of water. Apparently, at some point during CAD, water and isobutene are generated and they compete for binding with  $\text{ClMn}^+$ . Based on above results, isobutene forms the strongest bond with  $\text{ClMn}^+$ , followed by water,



**Fig. 1.** Mass spectrum measured after reaction of  $\text{ClMn}_2^+$  with an equimolar mixture of ethanol, pentane, and triethylamine introduced into the back ion trap of DLQIT via an external mixing manifold attached to the helium line. Nearly equal ionization efficiency is observed for these three very different analytes.



**Fig. 2.** Mass spectra measured after ion-molecule reactions of triethylamine with (A)  $\text{ClMn}_2^+$  and (B)  $\text{ClMn}(\text{H}_2\text{O})^+$ . Molecular ions of triethylamine generate protonated trimethylamine molecules upon secondary reactions.



**Fig. 3.** (A) Calculated geometry of the ClMn<sup>+</sup> adduct of ethane. (B) Isomers of ClMn<sub>2</sub><sup>+</sup> and their relative energies. (C) Calculated geometry and relative energy for Mn<sup>+</sup> after insertion into a C—H bond of ethane (left) and for Mn<sup>+</sup> bound to ethane via two agostic interactions (right).

propene and ethene. However, methanol binds even stronger than isobutene since the adduct of methyl *tert*-butyl ether undergoes elimination of isobutene to form ClMn(CH<sub>3</sub>OH)<sup>+</sup>. Cleavage of C—C bonds was observed for the adducts of butanal and tetrahydrofuran: the loss of propene occurred from each adduct to form ClMn(CH<sub>2</sub>O)<sup>+</sup> (for butanal, possibly as shown in Scheme 1C). Hence, formaldehyde binds stronger to ClMn<sup>+</sup> than propene. Interestingly,

the adducts of diethylamine and triethylamine were found to eliminate a hydrogen atom or form the ClMnH<sup>+</sup> ion, respectively.

The reasons for many of the above observations are currently unknown. A detailed study is in progress on the fragmentation patterns of ClMn<sup>+</sup> adducts of many more analytes in order to be able to make generalizations about the types of structural information available from these experiments.

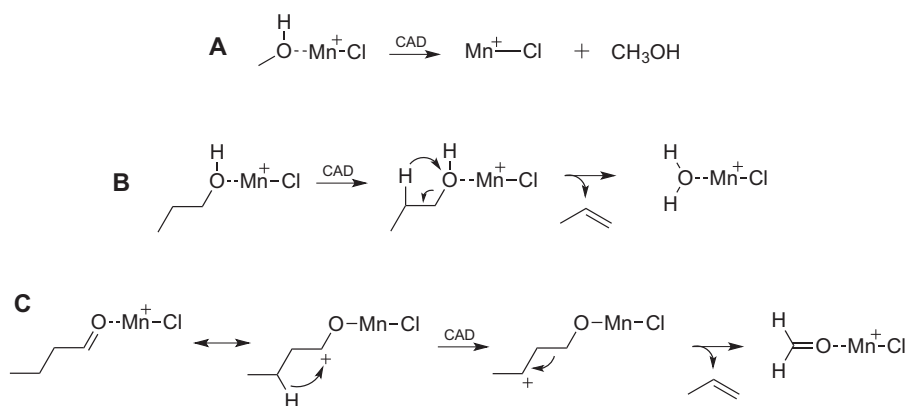
**Table 3**

Product ions (with their *m/z* ratios and relative abundances) formed upon collision-activated dissociation (CAD) of the ionic products of reactions of ClMn<sub>2</sub><sup>+</sup> with several analytes (X).

Analyte (X)	MS/MS fragment ions ( <i>m/z</i> ) of ClMnX <sup>+</sup> and their relative abundances	
Acetone	ClMn <sup>+</sup> (90)	100%
Methanol	ClMn <sup>+</sup> (90)	100%
2-Methylpentane	ClMn <sup>+</sup> (90)	100%
	ClMn(H <sub>2</sub> O) <sup>+</sup> (108) <sup>a</sup>	
	[(ClMnX)–H] <sup>+</sup> (175)	28%
Thiophene	ClMn <sup>+</sup> (90)	100%
Cyclohexane	ClMn <sup>+</sup> (90)	100%
Benzene	ClMn <sup>+</sup> (90)	100%
Diethylamine	[(ClMnX)–H] <sup>+</sup> (162)	100%
Triethylamine	ClMnH <sup>+</sup> (91)	100%
Ethanol	ClMn(H <sub>2</sub> O) <sup>+</sup> (108)	100%
<i>n</i> -Propanol	ClMn(H <sub>2</sub> O) <sup>+</sup> (108)	100%
	[(ClMnX)–H <sub>2</sub> O] <sup>+</sup> (132)	57%
<i>t</i> -Butanol	[(ClMnX)–H <sub>2</sub> O] <sup>+</sup> (146)	100%
Methyl <i>tert</i> -Butyl Ether	ClMn(CH <sub>3</sub> OH) <sup>+</sup> (122)	100%
Butanal	ClMn(CH <sub>2</sub> O) <sup>+</sup> (120)	100%
Tetrahydrofuran	ClMn(CH <sub>2</sub> O) <sup>+</sup> (120)	100%
	(X–H) <sup>+</sup> (71)	10%

<sup>a</sup> Secondary reaction product due to reaction with water always present in the ion trap.





**Scheme 1.** Proposed mechanisms for the fragmentation of the  $\text{ClMn}^+$  adducts of methanol, propanol and butanal.

#### 4. Conclusions

$\text{ClMn}_2^+$  chemical ionization reagent ion efficiently ionizes various types of analytes, both polar and nonpolar, to exclusively form  $\text{ClMn}^+$  adduct ions, which makes it a promising reagent for mixture analysis. Furthermore, no bias was found for any specific analytes. This reagent is better than the previously reported  $\text{ClMn}$  ( $\text{H}_2\text{O}^+$ ) and  $\text{CpCo}^+$  reagent ions due to its ability to ionize analytes with low ionization energies without the production of multiple product ions or fragment ions [1–3,27]. Calculations suggest that the adducts of  $\text{ClMn}^+$  with saturated hydrocarbons are bound via a relatively strong agostic interaction of the manganese center with a C–H bond while the adducts with oxygen-containing analytes involve dative bonding. Collision-activated dissociation of the  $\text{ClMn}^+$  adduct ions proceeds via several different pathways, depending on the structure of the analyte. Based on the observed fragmentation reactions, the strength of binding of  $\text{ClMn}^+$  gets weaker in the following order: methanol, isobutene, water, propene, ethane. The reactions of  $\text{Mn}^+$  were also explored with similar results. Based on calculations,  $\text{Mn}^+$  interacts with saturated hydrocarbons via two agostic interactions involving two C–H bonds. However,  $\text{Mn}^+$  is not suited for ionization of alcohols due to their fragmentation upon ionization.

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