Ion mobility studies on the negative ion-molecule chemistry of pentachloroethane

González-Méndez, R, Watts, P, Howse, DC, Procino, I, McIntyre, H & Mayhew, CA

Original citation & hyperlink:
González-Méndez, R, Watts, P, Howse, DC, Procino, I, McIntyre, H & Mayhew, CA 2017, 'Ion mobility studies on the negative ion-molecule chemistry of pentachloroethane' *International Journal of Mass Spectrometry*, vol 417, pp. 16-21
https://dx.doi.org/10.1016/j.ijms.2017.04.011

DOI 10.1016/j.ijms.2017.04.011
ISSN 1387-3806

Publisher: Elsevier

ION MOBILITY STUDIES ON THE NEGATIVE ION-MOLECULE CHEMISTRY OF PENTACHLOROETHANE

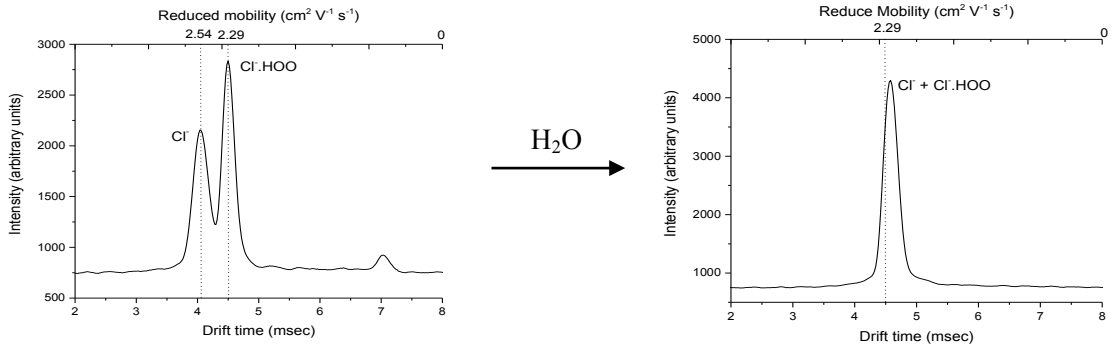
Ramón González-Méndez,[1*] Peter Watts,[1] David C. Howse,[1] Immacolata Procino,[2] Henry McIntyre,[2] and Chris A. Mayhew[1,3]

1. School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
2. Smiths Detection, Century House, Maylands Avenue, Hemel Hempstead, Hertfordshire, HP2 7DE, UK
3. Institut für Atemgasanalytik, Leopold-Franzens-Universität Innsbruck, Rathausplatz 4, A-6850 Dornbirn, Austria

* Corresponding Author Tel.:+44 121 414 4668. E-mail: R.GonzalezMendez@bham.ac.uk

Key words: Ion Mobility Spectrometry; IMS-MS; Pentachloroethane; Chlorinated Ethane; Ion-Molecule Chemistry

GRAPHICAL ABSTRACT



Abstract

In this study we present an investigation of the negative ion-molecule chemistry of pentachloroethane (PCE) in air based Ion Mobility Spectrometry and Ion Mobility Spectrometry-Mass Spectrometry systems. The observed product ions are Cl^-, produced by dissociative electron attachment, and Cl^-.HOO resulting from a reaction with O_2^-. Based upon the moisture content of the system, these ions can be observed as a doublet in a 'dry' system or as a singlet in a 'wet' system. The nature of the Cl^-.HOO product ion was investigated by using isoflurane (ISOF) as a probe to monitor the changing ratios of $Cl^-$and Cl^-.HOO as the PCE concentration decreased. This confirmed the origins of the two product anions. Electronic structure calculations are provided. These have aided the understanding of the reaction processes observed.

1. Introduction

The ability to quickly and accurately identify hazardous compounds, and particularly within a complex chemical environment, is vital to homeland security. Ion Mobility Spectrometry (IMS) has found worldwide deployment in security areas such as airports. However, it has limitations in terms of selectivity, and false positives do occur. To limit these, the ion chemistry in the reaction of the region of the IMS can be manipulated. This is achieved by doping the carrier gas. Chlorine containing compounds are used in ion mobility spectrometers operating in negative ion mode to enhance specificity and sensitivity.[1-12] Unfortunately the most suitable, in terms of its facile dissociative electron attachment (DEA) with thermal electrons and its volatility, is carbon tetrachloride, CCl_4, which is now banned by the Montreal Protocol.[13] Hexachloroethane, HCE, is commonly used in laboratory investigations, and has been described in a recent paper on the ion-molecule chemistry of the anaesthetics isoflurane (ISOF, $CF_3CHClOCHF_2$) and enflurane (ENF, CHF_2OCF_2CHFCl).[14] However, its vapour pressure at low temperatures makes it unsuitable for use in practical systems for use in the field. The volatility of pentachloroethane, PCE (CCl_3CHCl_2), makes it more suitable for use in such practical devices as the Smiths Detection Lightweight Chemical Detector used in this study.[15]

The investigation presented in this paper continues our work on the negative ion-molecule chemistry of chlorinated compounds in IMS systems.[14] Two systems have been used for this work, a Smiths Detection IMS - henceforth referred to as the Smiths system,[15] and a home-made IMS/MS located in the Molecular Physics Group at the University of Birmingham - referred to as the Birmingham system. An additional motivation for this study comes from preliminary experiments with PCE, which in the Birmingham IMS/MS system showed only one ion mobility peak, whilst the Smiths IMS system showed a doublet peak structure. The results of the present study, which used ISOF as a probe compound, allowed these apparently conflicting observations to be rationalised.

The experimental work presented in this paper is supported by electronic structure calculations at the B3LYP level, which provide useful energetic calculations for the DEA processes and various chemical reactions.

2. Experimental Details

2.1. Ion Mobility Spectrometry (IMS) and Ion Mobility Spectrometry-Mass Spectrometry (IMS/MS)

The Birmingham IMS/MS system used in this study has been described elsewhere,[16-20] and hence only a brief description is provided here. This instrument consists of two glass drift tube regions each of 10 cm in length. The first, the reaction region containing a cylindrical radioactive ion source (nominal 10 mCi ^{63}Ni foil), is physically separated from the second region, the drift region, by a Bradbury-Nielson (B-N) gate. A forward flow of the buffer gas flows through the radioactive source and into the glass jacket towards the B-N grid. A contraflow of the same buffer gas is introduced through apertures near to a Faraday plate (FP). The analyte of interest is introduced in the forward flow with the help of syringes. Forward and contraflows are set at 0.4 L min^{-1} and 0.8 L min^{-1} (at slightly above the ambient atmospheric pressure and room temperature), respectively, and controlled by mass flow controllers (Alicat Scientific, Arizona, USA, $\pm$1% accuracy). The two flows are vented out of the drift tube through holes in the B-N ring. The drift tube's pressure is measured with a strain gauge absolute pressure sensor (Edwards, West Sussex, UK, model ASG 2000). A thermocouple is used to monitor the temperature of the buffer gas near to the exhaust region and the temperature of the drift tube is electronically controlled at a constant temperature of 30 ± 1ºC. An electric field along the axis of the drift tube is set at 200 V cm^{-1}.

The FP is protected by a screen grid to shield it from the electric field produced by the oncoming ion swarm. At the centre of the FP there is a 0.07 mm pinhole, separating the IMS from the lower pressure quadrupole mass spectrometer region. The product ions are separated according to their m/z values using quadrupole mass filter and detected using a secondary electron multiplier. For this identification of the m/z values the B-N grid in the drift tube is kept open in order to maximise ion signal intensity.

To obtain ion mobility spectra, the B-N gate is used to pulse reactant and product ions generated in the reaction region into the drift region tube at a frequency of 25 Hz and a pulse width of 600 µs (600 µs was necessary, because at shorter pulse widths the ion signals associated with isoflurane and enflurane were significantly weaker, presumably owing to the transit times of the product ions through the B-N grid). Mobility spectra were acquired by means of purposely written software using Labview.[20] Total ion mobility spectra were acquired using the FP. Tuned ion mobility spectra were obtained by sampling ions through the FP and then allowing a specific m/z through the mass filter. The tuned ion mobility spectra were used to verify contributions of product ions to the individual peaks in the total ion mobility spectra.[20]

The Smiths system used is a modified Lightweight Chemical Detector (LCD).[15,21] Two IMS cells, one for positive ions and one for negative ions, are housed in the same

instrument. The data presented in this paper were acquired in the negative mode cell. Each cell consists of two regions: reaction and drift regions. The reaction region, containing a dual-point corona discharge ionization source,[22] is open to ambient air via a pinhole through which air is pulled into the system for sampling. Connected to the reaction region are On-demand Vapour Generators (OVGs) for injecting PCE and isoflurane in the system.[23] The ions generated in the reaction region migrate under the influence of an electric field towards a B-N gate. Once transferred through the B-N gate in the drift region, the ions drift towards a FP for detection. The electric field, generated by applying a voltage gradient across the electrodes placed along the whole drift tube length (reaction and drift regions), was set to be about 200 V cm^{-1}. The drift gas has a flow of 150 mL min^{-1} and consists of air at atmospheric pressure. It is generated by a fan which recirculates air through the IMS cells and a molecular sieve. The molecular sieve traps water in order to keep a low level of moisture in the system. In order to increase the moisture level in the IMS cell, a fraction of the drift gas was pumped from the body of molecular sieve, circulated in the headspace above a saturated solution of lithium chloride (headspace air with relative humidity of 11.30%), and mixed back into the drift air flow close to the FP.

2.2 Procedures and chemicals

Isoflurane (with stated purity of 99%) was purchased from Sigma Aldrich (Dorset, UK). Pentachloroethane (96% pure) was purchased from Alfa Aesar (Lancashire, UK). All the samples were used without further purification. At room temperature they are both liquids.

In the Birmingham system, typically 50 µL were spotted onto cotton and placed inside a glass syringe (Weber Scientific, New Jersey, USA) which was inserted through a septum into the forward flow at a constant rate using a syringe driver (Cole Palmer 74900 series, Illinois, USA). In the Smiths system, OVGs were used as the sampling method.

Zero air grade and pure nitrogen (oxygen free and 99.998% purity) carrier gases used for this experiment were purchased from BOC Gases (Manchester, UK). Prior to entering the reaction region all carrier gases were passed through moisture and hydrocarbon traps (Supelco 23991 and Agilent BHT-4 respectively).

2.3. Density Functional Theory (DFT) Calculations

These were conducted using Gaussian09W and GaussView05 for Windows.[24] Unless otherwise stated all calculations used the B3LYP functional and the 6-31+G(d,p) basis set, a combination which has been found to be satisfactory.[14] Stable species were characterised by

the absence of an imaginary frequency. Vertical Attachment Energies (VAEs) were determined by doing a frequency job after placing a negative charge on the ground state geometry of the neutral.

3. Results and Discussion

3.1 Pentachloroethane

3.1.1 Electron attachment

DEA in nitrogen to give both Cl^- and Cl_2^- is thermodynamically favourable (Table 1) although only the former is observed.

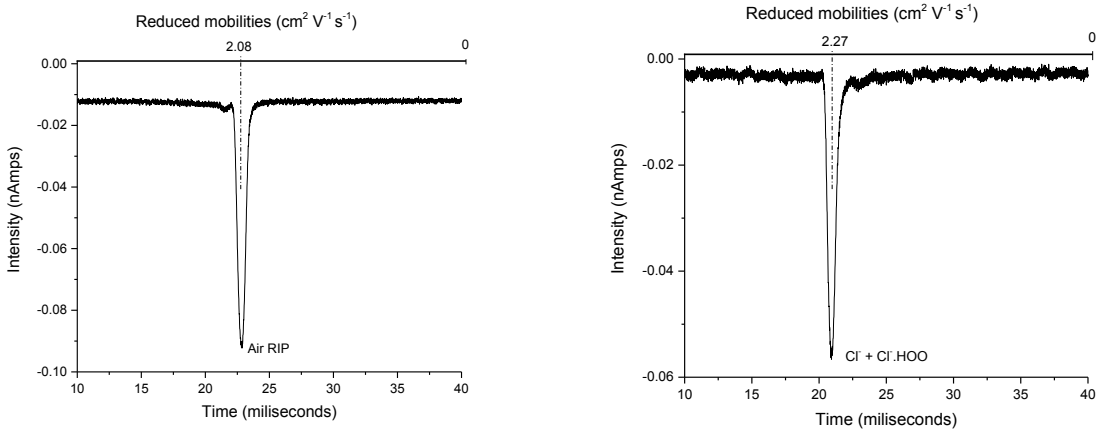
Table 1. Calculated ΔHs and ΔGs for the DEA of PCE leading to Cl^- and Cl_2^-. DFT calculations were performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reactants	Ionic products	ΔH_{298} kJ mol^{-1}	ΔG_{298} kJ mol^{-1}
PCE + e	Cl^-	-119	-161
	Cl_2^-	-190	-244

The calculated VAE is negative (-7.0 kJ mol^{-1}) as expected from the observed resonance with electrons at 0 eV. No Cl_2^- was observed, although it is reported to occur at 0 eV by Matias *et al* in a study involving DEA at low pressures.[25]

3.1.2 Reactions in air

In the Birmingham system only a single IMS peak was observed. Tuned *m/z* experiments showed it to be a mixture of $Cl^-.(H_2O)_n$ (n=0,1) and *m/z* 68. Figure 1 shows the Reactant Ion Peak (RIP) for (a) air (b) for PCE (obtained in the system sufficiently doped with PCE for the air RIP to be fully depleted).



a b

Figure 1. IMS spectra showing the RIP for (a) an air system and (b) for a heavily doped PCE system. In all figures only the core ions are given in the annotations, water clusters have been omitted.

As the concentration of PCE reduced, but with the air RIP still completely depleted, a peak on the low mobility side of the PCE RIP appeared (figure 2). Tuned ion mobility showed that this results from an anion at *m/z* 68. This is ascribed to be Cl^-.HOO (see later).

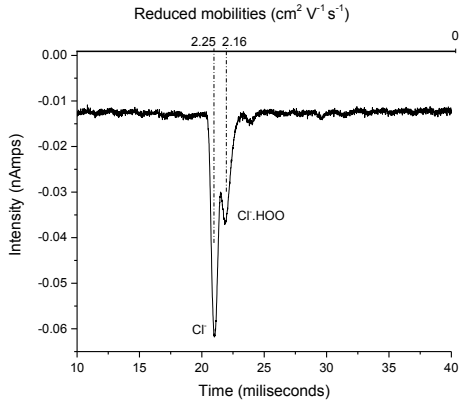
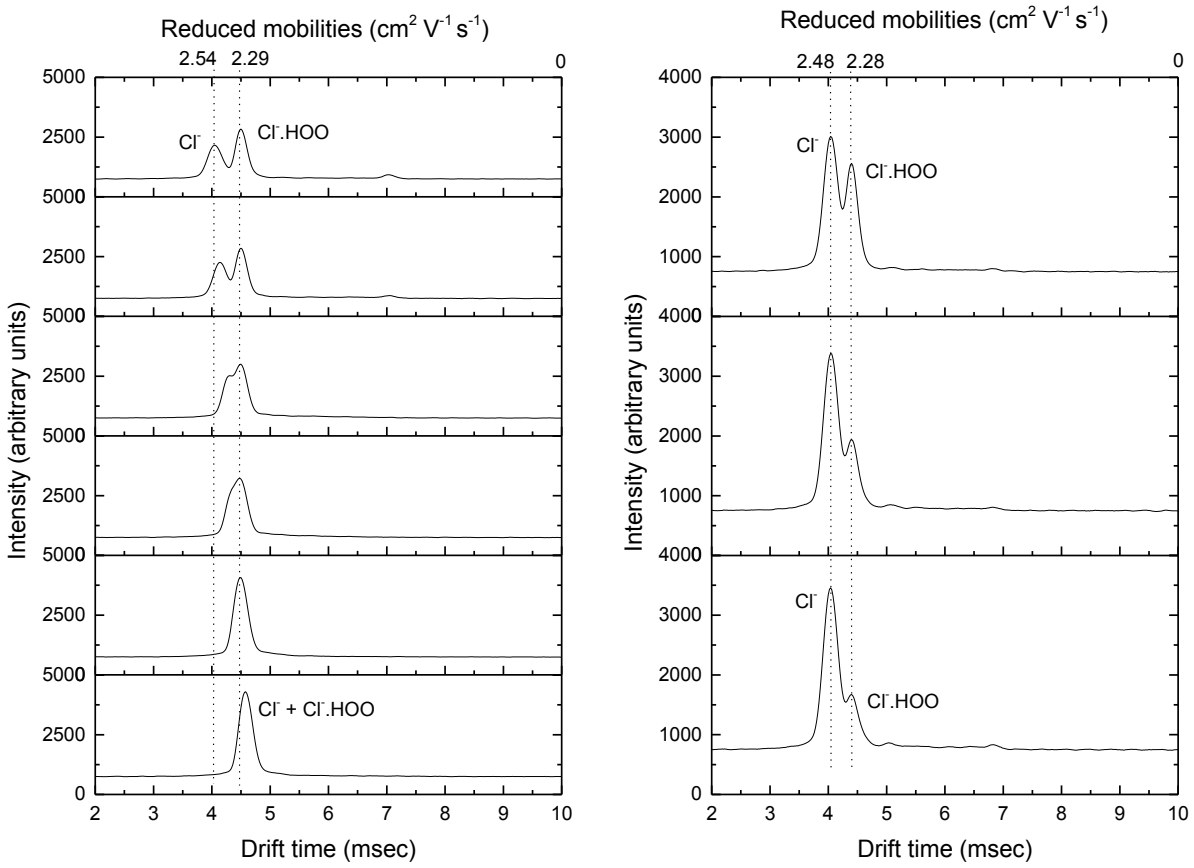


Figure 2. IMS spectrum in an air system doped with PCE at a lower concentration of PCE than in figure 1 (b), but still sufficiently high to completely deplete the air RIP.

In the Smiths system (see Figures 3a and 3b), under very dry conditions (it is not possible to be quantitative at such low water concentrations in such a small IMS device) either a singlet or a doublet or various intermediate mobility peaks could be observed dependent upon the PCE and water concentrations. In Figures 3a and 3b the more mobile peaks are ascribed to Cl^- and the less mobile peaks to Cl^-.HOO. Figure 3a shows that as the humidity increases the Cl^- peak decreases in mobility due to hydration subsequently merging

with the $Cl^-.HOO$. As will be seen later, Cl^- readily complexes with one H_2O molecule, whereas $Cl^-.HOO$ does not. Figure 3b shows that as the PCE concentration increases the ratio $Cl^-.HOO$ to Cl^- decreases.



a b

Figure 3. (a) IMS spectra of PCE showing the effect of the internal moisture and how, as the humidity increases, the Cl^- peak decreases in mobility due to hydration subsequently merging with the $Cl^-.HOO$ peak. The level of moisture gradually increases from the top to the bottom plot. (b) IMS spectra of PCE acquired at different PCE concentrations showing the effect of the PCE concentration on the relative intensities of Cl^- and $Cl^-.HOO$. The PCE concentration gradually increases from the top to the bottom plot.

A detailed inspection of the results showed that, dependent upon the PCE and water concentrations, either a singlet or a doublet or various intermediate mobility peaks could be observed both in the Smiths and Birmingham systems.

The ion with *m/z* 68 is assigned as Cl^-.HOO as DFT calculations showed that it is essentially Cl^- hydrogen bonded to HOO (figure 4).

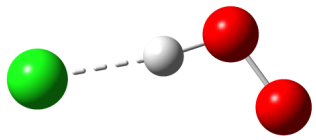


Figure 4. Structure of Cl^-.HOO obtained from DFT calculations.

The same result is obtained starting from Cl^- associating with OOH as from HCl associating with O_2^-. As electron attachment to PCE in the IMS system gives only Cl^-, it can be safely assumed that the formation of Cl^-.HOO arises from the reaction of PCE with O_2^-. The overall energetics for this reaction are ΔH_{298} -180 kJ mol^{-1} and ΔG_{298} -196 kJ mol^{-1}, assuming that the neutral product is CCl_2CCl_2. This is supported by the observation that as the concentration of PCE increased so did the proportion of Cl^- as would be expected if O_2 and PCE are in competition for the electrons. The initial (albeit transient) product of the reaction of O_2^- with PCE is a complex with the oxygen close to the hydrogen of the PCE, as shown in Figure 5, and Table 2 for the energetics. An alternative conformation with the oxygen orientated away from the CCl_3 group is slightly less stable.

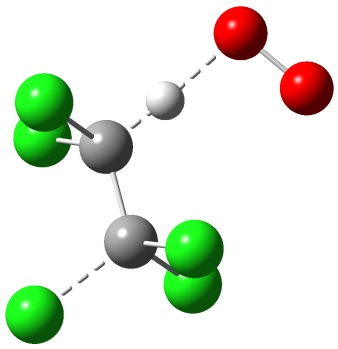


Figure 5. Structure of PCE.O_2^- complex obtained from DFT calculations.

Table 2. Energetics for the formation of various species relative to PCE + O_2^-. DFT calculations were performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reaction	Species	ΔH_{298} kJ mol^{-1}	ΔG_{298} kJ mol^{-1}
1	Complex PCE.O_2^- (Fig 4)	-104	-73
2	$C_2Cl_5^-$ + HOO	-82	-107
3	C_2Cl_4 + Cl^- + HOO	-70	-113
4	C_2Cl_4 + Cl^-.HOO	-180	-196
5	$CHCl_2CCl_2$ + Cl^- + O_2	-59	-102
6	Barrier for rotation around the C-C bond of PCE	+38	+43
7	Barrier for rotation around the C-C bond of PCE.O_2^-	+33	+22

Of primary interest is the formation of Cl^-.HOO. Reactions 3 and 5 may contribute to the production of Cl^- but are probably of little importance compared to the DEA with free electrons. It is not proposed that reactions 2 and 3 occur (except as precursors to reaction 4) but are included to illustrate that sufficient energy is available in the transient PCE.O_2^- complex to allow complex conformational changes to occur. This is necessary as formation of Cl^-.HOO from the complex (reaction 4) requires a concerted lengthening on the C-H bond and a rotation of the C-Cl bonds around the C-C bond. Despite many attempts no transition state has yet been found, and this difficulty is attributed to the proposed concerted nature of the transition state.

3.1.3 Reactions of H_2O with Cl^- and Cl^-.HOO

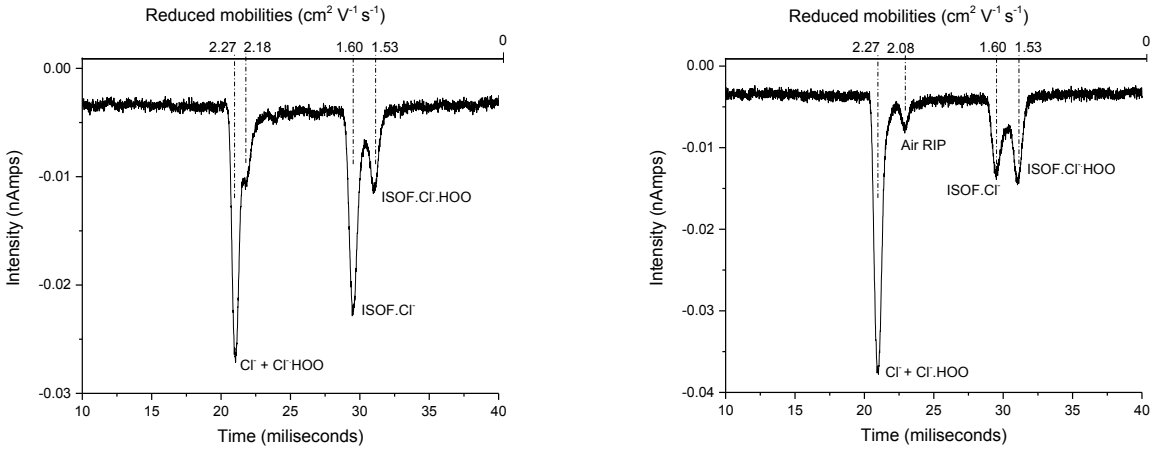
It can be seen from Table 3 that Cl^- will readily complex with one water, but that Cl^-.HOO will not as the HOO is effectively solvating Cl^-, i.e. taking the place of H_2O in the $Cl^-.H_2O$ complex. The strength of the Cl^-.HOO complex can be seen in the last row of Table 3. Thus in a 'dry' system the doublet of Cl^- and Cl^-.HOO is observed and as the water concentration increases the Cl^- complexes with water thus decreasing its mobility and eventually merging with the Cl^-.HOO to give a singlet (see Figure 1b).

Table 3.Calculated ΔHs and ΔGs for the reactions of $Cl^-.(H_2O)_n$ (n = 0, 1 and 2) with H_2O, Cl- with HOO, and $Cl^-.HOO.(H_2O)_n$ (n = 0 and 1) with H_2O. DFT calculations performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reactants	Products	ΔH_{298} kJ mol^{-1}	ΔG_{298} kJ mol^{-1}
$Cl^- + H_2O$	$Cl^-.H_2O$	-60	-37
$Cl^-.H_2O + H_2O$	$Cl^-.2H_2O$	-54	-18
$Cl^-.2H_2O + H_2O$	$Cl^-.3H_2O$	-47	-10
$Cl^-.HOO + H_2O$	$Cl^-.HOO.H_2O$	-52	-16
$Cl^-.HOO.H_2O + H_2O$	$Cl^-.HOO.2H_2O$	-44	-7
$Cl^- + HOO$	$Cl^-.HOO$	-111	-83

3.2 Reaction of ISOF in a PCE doped system

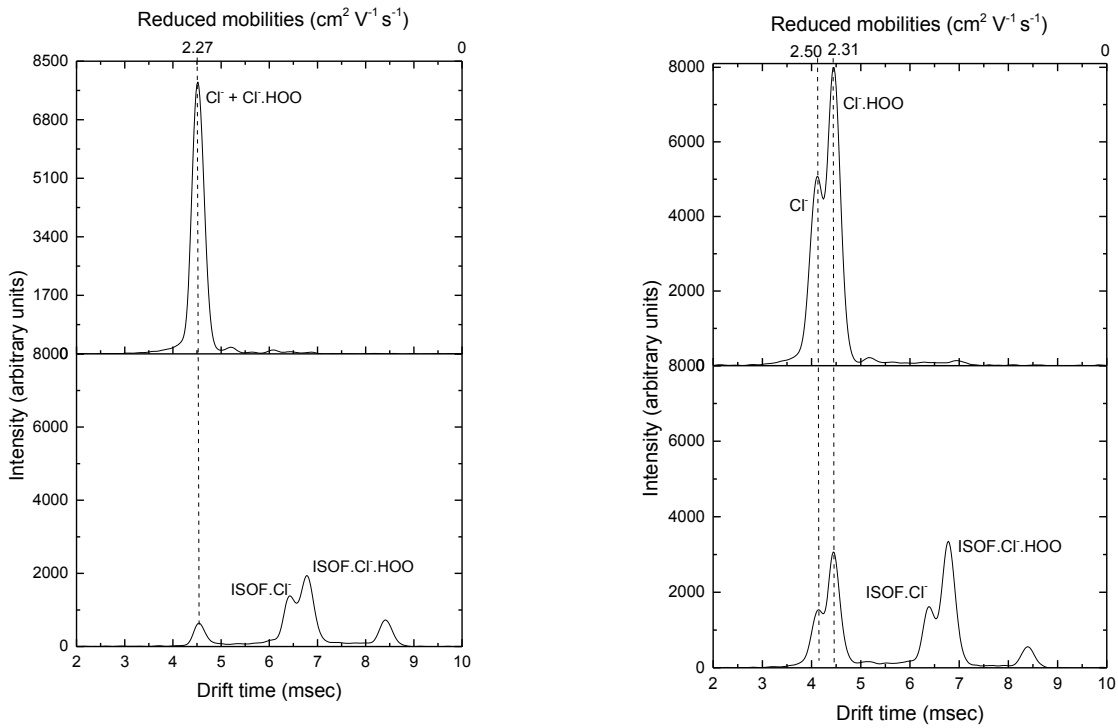
As a way to fully understand the occurring chemistry, the properties of the $Cl^-.HOO$ ion were investigated by using ISOF as a probe in both instruments. For such a purpose sufficient PCE was introduced to replace the air RIP (figure 1a) with a PCE RIP of Cl^- and $Cl^-.HOO$ (figure 1b). In the Birmingham system, addition of ISOF (shown in Figure 6a) results in the formation of two product ions *m/z* analysed as ISOF.Cl^- and ISOF.Cl^-.HOO the latter being the less mobile peak. The IMS spectrum in Figure 6b (when compared with that shown in figure 6a) demonstrates the variability in relative proportions of product ions. For figure 6b the PCE concentration had been allowed to decay as can be seen by the appearance of the air RIP at reduced mobility K_o= 2.08 cm^2 V^{-1} s^{-1}. In Section 3.1.2 it was suggested that as the PCE concentration decreased the ratio of $Cl^-.HOO/Cl^-$ would increase, and this is well demonstrated by the changing ratios of ISOF.$Cl^-$and ISOF.Cl^-.HOO in Figures 6a and 6b.



a b

Figure 6. (a) IMS spectrum for an air system doped with PCE with ISOF added. (b) IMS spectrum for an air system doped with PCE (in lower concentration when compared with 6a) following addition of ISOF. The small peak at $K_o = 2.08$ cm^2 V^{-1} s^{-1} is the remnant of the air RIP.

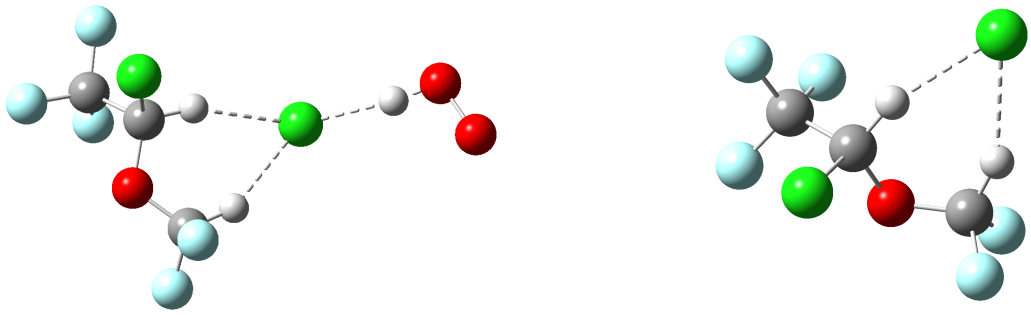
For the Smiths system results of similar experiments are shown in figure 7 under wet and dry conditions.



a b

Figure 7. Smiths IMS spectra of PCE (top line plots) and ISOF (bottom line plots) acquired in a PCE doped system in a) “wet” conditions; b) “dry” conditions.

DFT calculations provided stable structures for the ISOF.Cl^-.HOO and ISOF.Cl^- product ions, as shown in Figure 8.



ISOF.Cl^-.HOO ISOF.Cl^-

Figure 8. Structure of ISOF monomer product ions ISOF.Cl^-.HOO and ISOF.Cl^- obtained from DFT calculations.

The energetics for the reactions of ISOF with Cl^- and Cl^-.HOO are summarised in Table 4.

Table 4. ΔHs and ΔGs for the reaction of ISOF with various anions. DFT calculations performed using the B3LYP functional and the 6-31+G(d,p) basis set.

Reactants	Ionic Products	ΔH_{298} kJ mol^{-1}	ΔG_{298} kJ mol^{-1}
ISOF + Cl^-.HOO	ISOF.Cl^-.HOO	-76	-50
ISOF.Cl^-.HOO + ISOF	$ISOF_2$.Cl^-.HOO	-58	-2
ISOF + Cl^-	ISOF.Cl^-	-108	-79
ISOF.Cl^- + ISOF	$ISOF_2$.Cl^-	-74	-40

Calculations showed that the dimer complex of ISOF and Cl^-.HOO is thermo neutral and even if formed it will be unstable in the drift region and hence is unlikely to be observed in accord with experiment.

4. Conclusions

After introduction of PCE into an air based IMS system, two product ions were observed, Cl^- by DEA and Cl^-.HOO by reaction with O_2^-. These anions can be observed as a doublet in a 'dry' system or as a singlet in a 'wet' system. In the wet system Cl^- clusters with water thus reducing its mobility whereas Cl^-HOO does not. Because DEA and reaction with O_2^- are in competition the ratio of the two product ions is dependent upon PCE concentration. An

additional factor leading to this dependence is that PCE and O_2 are competing for electrons, the PCE leading to Cl^- through DEA and the O_2 leading to O_2^-. Cl^-.HOO complexes with ISOF as does Cl^-. This is nicely demonstrated by two ISOF product peaks being observed even in a wet system when only a singlet PCE based RIP is observed.

The results presented here illustrate the care that must be taken in interpreting even apparently simple chemical systems in an IMS instrument. Electronic structure calculations have provided valuable insight into the processes observed.

Acknowledgements

The Early Stage Researcher (RGM) acknowledges the support of the PIMMS Initial Training Network which in turn is supported by the European Commission's 7th Framework Programme under Grant Agreement Number 287382.

References

1. Puton, J.; Nousiainen, M.; Sillanpää, M., Ion mobility spectrometers with doped gases. *Talanta* **2008,** *76* (5), 978-987.
2. Ewing, R. G.; Atkinson, D. A.; Eiceman, G. A.; Ewing, G. J., A critical review of ion mobility spectrometry for the detection of explosives and explosive related compounds. *Talanta* **2001,** *54* (3), 515-529.
3. Spangler, G. E.; Carrico, J. P.; Campbell, D. N., Recent advances in ion mobility spectrometry for explosives vapor detection. *Journal of Testing and Evaluation* **1985,** *13* (3), 234-240.
4. Daum, K. A.; Atkinson, D. A.; Ewing, R. G., Formation of halide reactant ions and effects of excess reagent chemical on the ionization of TNT in ion mobility spectrometry. *Talanta* **2001,** *55* (3), 491-500.
5. Proctor, C. J.; Todd, J. F. J., Alternative reagent ions for plasma chromatography. *Analytical Chemistry* **1984,** *56* (11), 1794-1797.
6. Rajapakse, M. Y.; Stone, J. A.; Eiceman, G. A., Decomposition Kinetics of Nitroglycerine·Cl–(g) in Air at Ambient Pressure with a Tandem Ion Mobility Spectrometer. *The Journal of Physical Chemistry A* **2014,** *118* (15), 2683-2692.
7. Rajapakse, R. M. M. Y.; Stone, J. A.; Eiceman, G. A., An ion mobility and theoretical study of the thermal decomposition of the adduct formed between ethylene glycol dinitrate and chloride. *International Journal of Mass Spectrometry* **2014,** *371* (0), 28-35.

8. Kozole, J.; Levine, L. A.; Tomlinson-Phillips, J.; Stairs, J. R., Gas phase ion chemistry of an ion mobility spectrometry based explosive trace detector elucidated by tandem mass spectrometry. *Talanta* **2015,** *140* (0), 10-19.

9. Li, G.; Zhang, Z.; Huang, Q.; Guo, T.; Zhang, X., A Novel Pulsed Doping Method for Enhancing the Sensitivity of Ion Mobility Spectrum (IMS) for Detecting Explosives and a Mechanism Study. *Sensor Letters* **2015,** *13* (9), 778-784.

10. Lawrence, A. H.; Neudorfl, P., Detection of ethylene glycol dinitrate vapors by ion mobility spectrometry using chloride reagent ions. *Analytical Chemistry* **1988,** *60* (2), 104-109.

11. Matz, L. M.; Tornatore, P. S.; Hill, H. H., Evaluation of suspected interferents for TNT detection by ion mobility spectrometry. *Talanta* **2001,** *54* (1), 171-179.

12. Ewing, R.; Atkinson, D.; Benson, M., Atmospheric pressure ionization of chlorinated ethanes in ion mobility spectrometry and mass spectrometry. *Int. J. Ion Mobil. Spec.* **2015,** *18* (1-2), 51-58.

13. Montreal Protocol on Substances that Deplete the Ozone Layer. 1522 UNTS 3; 26 ILM 1550 (1987). http://www.unep.org/OZONE/pdfs/Montreal-Protocol2000.pdf (accessed 29-03-2017)

14. González-Méndez, R.; Watts, P.; Howse, D.C.; Procino, I.; McIntyre, H.; Mayhew C. A, Ion mobility studies on the negative ion-molecule chemistry of isoflurane and enflurane. *Journal of the American Society for Mass Spectrometry.* **2017,** Feb 21 (DOI:10.1007/s13361-017-1616-0 . [Epub ahead of print]).

15. Detection, S. High Performance CWA Identifier And TIC Detector. http://www.smithsdetection.com/index.php?option=com_k2&view=item&id=86&Itemid=600#.WAi4JHoVqzs (accessed 29-03-2017).

16. Liu, Y., Mayhew, C.A. and Peverall, R., A new experimental approach to investigate the kinetics of low energy electron attachment reactions. *International journal of mass spectrometry and ion processes* **1996***, 152(2)*, 225-242.

17. Jarvis, G. K., Peverall, R. and Mayhew, C. A., A novel use of an ion-mobility mass spectrometer for the investigation of electron attachment to molecules. *Journal of Physics B: Atomic, Molecular and Optical Physics* **1996**, *29(19)* L713.

18. Jarvis, G. K., Mayhew, C. A., Singleton, L., and Spyrou, S. M. An investigation of electron attachment to $CHCl_2F$, CHClF2 and CHF_3 using an electron-swarm mass spectrometric technique. *International journal of mass spectrometry and ion processes* **1997***, 164 (3),* 207-223.

19. Bell, A.; Giles, K.; Moody, S.; Watts, P., Studies on gas-phase positive ion—molecule reactions of relevance to ion mobility spectrometry The reactions of 2-methyl-2-propanol (t-butyl alcohol) with protonated water clusters in an ion mobility system. *International journal of mass spectrometry and ion processes* **1998,** *173* (1), 65-70.

20. Howse, D. C. Development and application of an ion mobility spectometer-quadrupole mass spectometer instrument. PhD, University of Birmingham, 2015.

21. St J, T.; Piper, L.; Connor, J.; FitzGerald, J.; Adams, J.; Harden, C. S.; Shoff, D.; Davis, D.; Ewing, R., Design aspects and operation characteristics of the lightweight chemical detector. *Int. J. Ion Mobil. Spectrom.* **1998,** *1*, 58-63.

22. Turner, R. B.; Taylor, S. J.; Clark, A.; Arnold, P. D. Corona discharge ion source for analytical instruments. US Pat. 6 225 623, May 1 2001.

23. Atkinson, J. R.; FitzGerald, J. P.; Taylor, S. J., Vapour Generators. US 20090133469 A1, May 28 2009.

24. Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., Gaussian 09, revision A. 1. *Gaussian Inc., Wallingford, CT* **2009**.

25. Matias, C.; Mauracher, A.; Huber, S. E.; Denifl, S.; Limão-Vieira, P.; Scheier, P.; Märk, T. D.; González-Méndez, R.; Mayhew, C. A., Dissociative electron attachment to the volatile anaesthetics enflurane and isoflurane and the chlorinated ethanes pentachloroethane and hexachloroethane. *International Journal of Mass Spectrometry* **2015,** *379* (0), 179-186.