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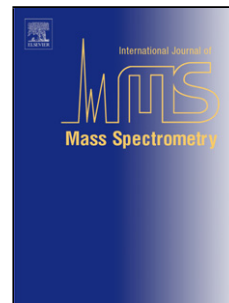
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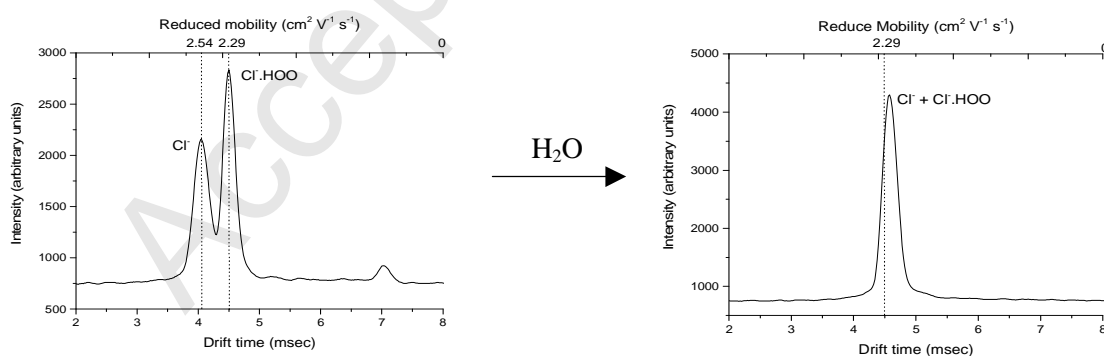
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Ion mobility studies on the negative ion-molecule chemistry of pentachloroethane**HIGHLIGHTS**

- Investigation of the negative ion-molecule chemistry of pentachloroethane, PCE, in both nitrogen and air for both Ion Mobility Spectrometry (IMS) and Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS) systems.
- Based upon the moisture content of the system, product ions can be observed as a doublet in a 'dry' system or as a singlet in a 'wet' system.
- Extra care that must be taken in interpreting even apparently simple chemical systems in an IMS instrument.

GRAPHICAL ABSTRACT

26 **ION MOBILITY STUDIES ON THE NEGATIVE ION-MOLECULE**
 27 **CHEMISTRY OF PENTACHLOROETHANE**

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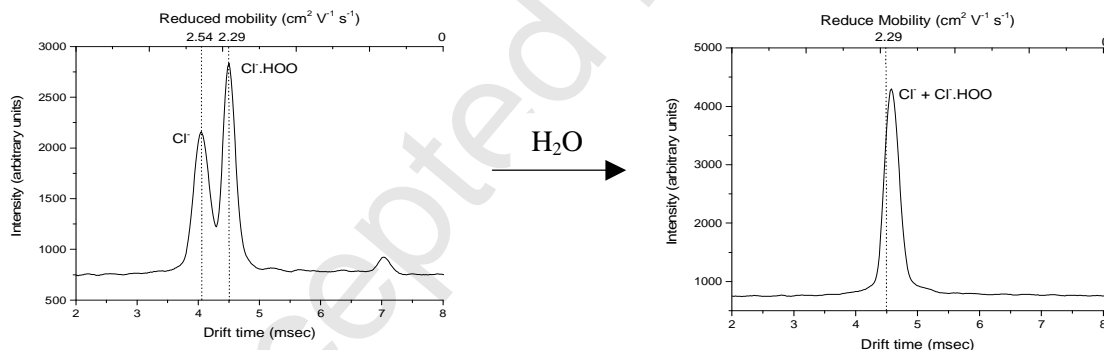
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39 Key words: Ion Mobility Spectrometry; IMS-MS; Pentachloroethane; Chlorinated Ethane;
 40 Ion-Molecule Chemistry

41

42 **GRAPHICAL ABSTRACT**

43



44

44

45 **Abstract**

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

56

57

57 **1. Introduction**

58 The ability to quickly and accurately identify hazardous compounds, and particularly within a
59 complex chemical environment, is vital to homeland security. Ion Mobility Spectrometry
60 (IMS) has found worldwide deployment in security areas such as airports. However, it has
61 limitations in terms of selectivity, and false positives do occur. To limit these, the ion
62 chemistry in the reaction of the region of the IMS can be manipulated. This is achieved by
63 doping the carrier gas. Chlorine containing compounds are used in ion mobility spectrometers
64 operating in negative ion mode to enhance specificity and sensitivity.¹⁻¹² Unfortunately the
65 most suitable, in terms of its facile dissociative electron attachment (DEA) with thermal
66 electrons and its volatility, is carbon tetrachloride, CCl₄, which is now banned by the
67 Montreal Protocol.¹³ Hexachloroethane, HCE, is commonly used in laboratory investigations,
68 and has been described in a recent paper on the ion-molecule chemistry of the anaesthetics
69 isoflurane (ISOF, CF₃CHClOCHF₂) and enflurane (ENF, CHF₂OCF₂CHFCl).¹⁴ However, its
70 vapour pressure at low temperatures makes it unsuitable for use in practical systems for use
71 in the field. The volatility of pentachloroethane, PCE (CCl₃CHCl₂), makes it more suitable
72 for use in such practical devices as the Smiths Detection Lightweight Chemical Detector used
73 in this study.¹⁵

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

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

86

87 **2. Experimental Details**

88 **2.1. Ion Mobility Spectrometry (IMS) and Ion Mobility Spectrometry-Mass** 89 **Spectrometry (IMS/MS)**

90 The Birmingham IMS/MS system used in this study has been described elsewhere,¹⁶⁻
91 ²⁰ and hence only a brief description is provided here. This instrument consists of two glass
92 drift tube regions each of 10 cm in length. The first, the reaction region containing a
93 cylindrical radioactive ion source (nominal 10 mCi ⁶³Ni foil), is physically separated from the
94 second region, the drift region, by a Bradbury-Nielson (B-N) gate. A forward flow of the
95 buffer gas flows through the radioactive source and into the glass jacket towards the B-N
96 grid. A contraflow of the same buffer gas is introduced through apertures near to a Faraday
97 plate (FP). The analyte of interest is introduced in the forward flow with the help of syringes.
98 Forward and contraflows are set at 0.4 L min⁻¹ and 0.8 L min⁻¹ (at slightly above the ambient
99 atmospheric pressure and room temperature), respectively, and controlled by mass flow
100 controllers (Alicat Scientific, Arizona, USA, ± 1% accuracy). The two flows are vented out
101 of the drift tube through holes in the B-N ring. The drift tube's pressure is measured with a
102 strain gauge absolute pressure sensor (Edwards, West Sussex, UK, model ASG 2000). A
103 thermocouple is used to monitor the temperature of the buffer gas near to the exhaust region
104 and the temperature of the drift tube is electronically controlled at a constant temperature of
105 30 ± 1°C. An electric field along the axis of the drift tube is set at 200 V cm⁻¹.

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

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

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

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

140

141 **2.2 Procedures and chemicals**

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

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

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

153

154 **2.3. Density Functional Theory (DFT) Calculations**

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

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

161

162 3. Results and Discussion

163 3.1 Pentachloroethane

164

165 3.1.1 Electron attachment

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

168

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

Reactants	Ionic products	$\Delta\text{H}_{298} \text{ kJ mol}^{-1}$	$\Delta\text{G}_{298} \text{ kJ mol}^{-1}$
PCE + e	Cl^-	-119	-161
	Cl_2^-	-190	-244

171

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

175

176 3.1.2 Reactions in air

177 In the Birmingham system only a single IMS peak was observed. Tuned m/z experiments
 178 showed it to be a mixture of $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n=0,1$) and m/z 68. Figure 1 shows the Reactant Ion
 179 Peak (RIP) for (a) air (b) for PCE (obtained in the system sufficiently doped with PCE for the
 180 air RIP to be fully depleted).

181

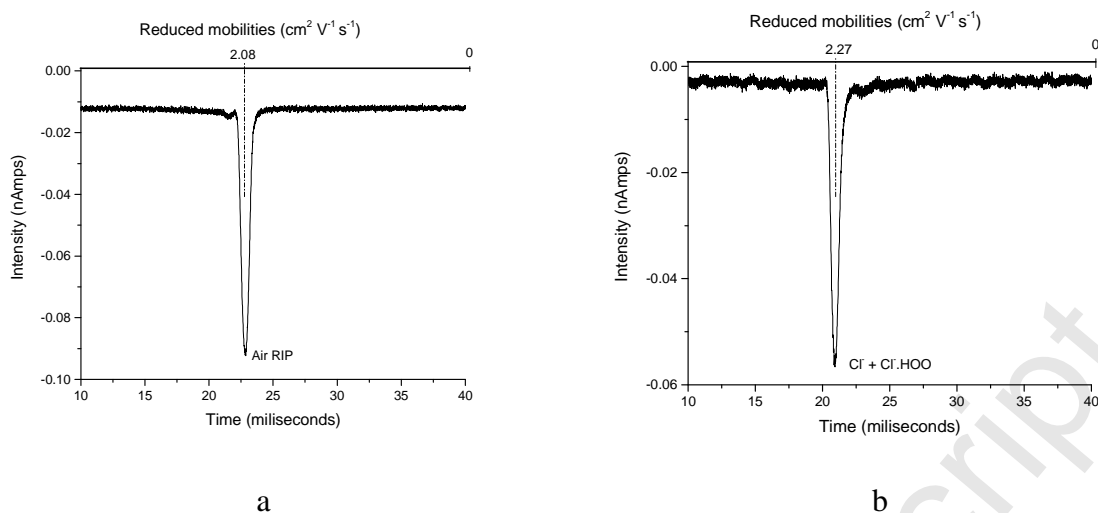


Figure 1. IMS spectra showing the RIP for (a) an air system and (b) for a heavily doped PCE system. In all figures only the core ions are given in the annotations, water clusters have been omitted.

182

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

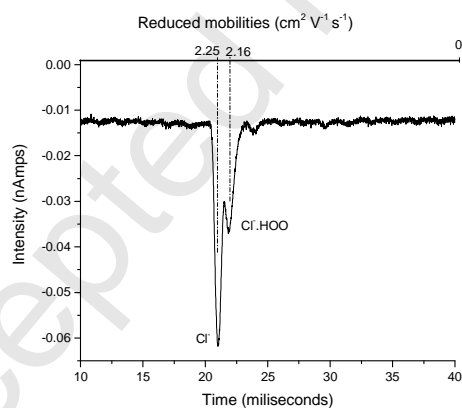


Figure 2. IMS spectrum in an air system doped with PCE at a lower concentration of PCE than in figure 1 (b), but still sufficiently high to completely deplete the air RIP.

186

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

193 with the $\text{Cl}^{\cdot}\text{HOO}$. As will be seen later, Cl^{\cdot} readily complexes with one H_2O molecule,
 194 whereas $\text{Cl}^{\cdot}\text{HOO}$ does not. Figure 3b shows that as the PCE concentration increases the ratio
 195 $\text{Cl}^{\cdot}\text{HOO}$ to Cl^{\cdot} decreases.

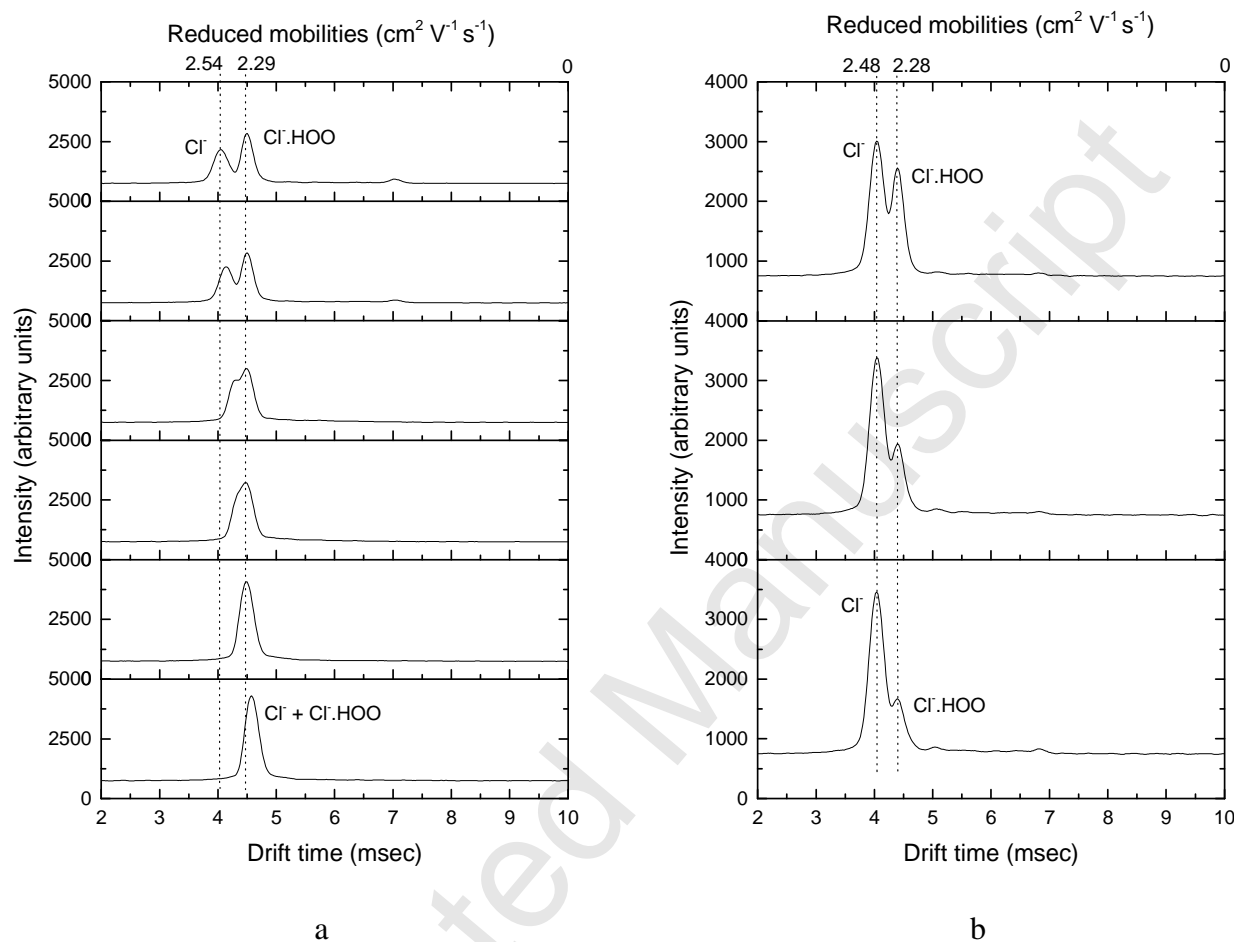


Figure 3. (a) IMS spectra of PCE showing the effect of the internal moisture and how, as the humidity increases, the Cl^{\cdot} peak decreases in mobility due to hydration subsequently merging with the $\text{Cl}^{\cdot}\text{HOO}$ peak. The level of moisture gradually increases from the top to the bottom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

196

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

200

201 The ion with m/z 68 is assigned as $\text{Cl}^{\cdot}\text{HOO}$ as DFT calculations showed that it is
 202 essentially Cl^{\cdot} hydrogen bonded to HOO (figure 4).

203

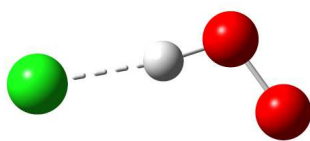


Figure 4. Structure of $\text{Cl}^{\cdot}\text{HOO}$ obtained from DFT calculations.

204

205 The same result is obtained starting from Cl^{\cdot} associating with OOH as from HCl
 206 associating with $\text{O}_2^{\cdot-}$. As electron attachment to PCE in the IMS system gives only Cl^{\cdot} , it can
 207 be safely assumed that the formation of $\text{Cl}^{\cdot}\text{HOO}$ arises from the reaction of PCE with $\text{O}_2^{\cdot-}$.
 208 The overall energetics for this reaction are $\Delta H_{298} -180 \text{ kJ mol}^{-1}$ and $\Delta G_{298} -196 \text{ kJ mol}^{-1}$,
 209 assuming that the neutral product is CCl_2CCl_2 . This is supported by the observation that as
 210 the concentration of PCE increased so did the proportion of Cl^{\cdot} as would be expected if O_2
 211 and PCE are in competition for the electrons. The initial (albeit transient) product of the
 212 reaction of $\text{O}_2^{\cdot-}$ with PCE is a complex with the oxygen close to the hydrogen of the PCE, as
 213 shown in Figure 5, and Table 2 for the energetics. An alternative conformation with the
 214 oxygen orientated away from the CCl_3 group is slightly less stable.

215

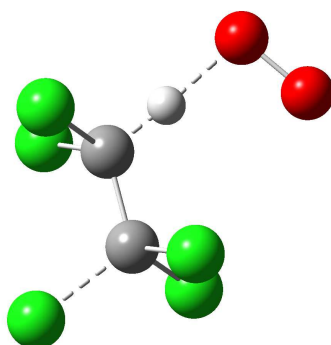


Figure 5. Structure of $\text{PCE}\cdot\text{O}_2^{\cdot-}$ complex obtained from DFT calculations.

216

217

218

219

220

221 Table 2. Energetics for the formation of various species relative to $\text{PCE} + \text{O}_2^{\cdot-}$. DFT
 222 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 ₂ Cl ₅ ⁻ + HOO	-82	-107
3	C ₂ Cl ₄ + Cl ⁻ + HOO	-70	-113
4	C ₂ Cl ₄ + Cl ⁻ .HOO	-180	-196
5	CHCl ₂ CCl 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

223

224 Of primary interest is the formation of Cl⁻.HOO. Reactions 3 and 5 may contribute to
 225 the production of Cl⁻ but are probably of little importance compared to the DEA with free
 226 electrons. It is not proposed that reactions 2 and 3 occur (except as precursors to reaction 4)
 227 but are included to illustrate that sufficient energy is available in the transient PCE.O₂⁻
 228 complex to allow complex conformational changes to occur. This is necessary as formation
 229 of Cl⁻.HOO from the complex (reaction 4) requires a concerted lengthening on the C-H bond
 230 and a rotation of the C-Cl bonds around the C-C bond. Despite many attempts no transition
 231 state has yet been found, and this difficulty is attributed to the proposed concerted nature of
 232 the transition state.

233

234 3.1.3 Reactions of H₂O with Cl⁻ and Cl⁻.HOO

235 It can be seen from Table 3 that Cl⁻ will readily complex with one water, but that Cl⁻.HOO
 236 will not as the HOO is effectively solvating Cl⁻, i.e. taking the place of H₂O in the Cl⁻.H₂O
 237 complex. The strength of the Cl⁻.HOO complex can be seen in the last row of Table 3. Thus
 238 in a 'dry' system the doublet of Cl⁻ and Cl⁻.HOO is observed and as the water concentration
 239 increases the Cl⁻ complexes with water thus decreasing its mobility and eventually merging
 240 with the Cl⁻.HOO to give a singlet (see Figure 1b).

241

242 Table 3. Calculated ΔH s and ΔG s for the reactions of Cl⁻.(H₂O)_n (n = 0, 1 and 2) with H₂O,
 243 Cl⁻ with HOO, and Cl⁻.HOO.(H₂O)_n (n = 0 and 1) with H₂O. DFT calculations performed
 244 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 ₂ O	Cl ⁻ .H ₂ O	-60	-37
Cl ⁻ .H ₂ O + H ₂ O	Cl ⁻ .2H ₂ O	-54	-18
Cl ⁻ .2H ₂ O + H ₂ O	Cl ⁻ .3H ₂ O	-47	-10
Cl ⁻ .HOO + H ₂ O	Cl ⁻ .HOO.H ₂ O	-52	-16
Cl ⁻ .HOO.H ₂ O + H ₂ O	Cl ⁻ .HOO.2H ₂ O	-44	-7
Cl ⁻ + HOO	Cl ⁻ .HOO	-111	-83

245

246 **3.2 Reaction of ISOF in a PCE doped system**

247 As a way to fully understand the occurring chemistry, the properties of the Cl⁻.HOO ion were
 248 investigated by using ISOF as a probe in both instruments. For such a purpose sufficient PCE
 249 was introduced to replace the air RIP (figure 1a) with a PCE RIP of Cl⁻ and Cl⁻.HOO (figure
 250 1b). In the Birmingham system, addition of ISOF (shown in Figure 6a) results in the
 251 formation of two product ions m/z analysed as ISOF.Cl⁻ and ISOF.Cl⁻.HOO the latter being
 252 the less mobile peak. The IMS spectrum in Figure 6b (when compared with that shown in
 253 figure 6a) demonstrates the variability in relative proportions of product ions. For figure 6b
 254 the PCE concentration had been allowed to decay as can be seen by the appearance of the air
 255 RIP at reduced mobility $K_0 = 2.08$ cm² V⁻¹ s⁻¹. In Section 3.1.2 it was suggested that as the
 256 PCE concentration decreased the ratio of Cl⁻.HOO/Cl⁻ would increase, and this is well
 257 demonstrated by the changing ratios of ISOF.Cl⁻ and ISOF.Cl⁻.HOO in Figures 6a and 6b.

258

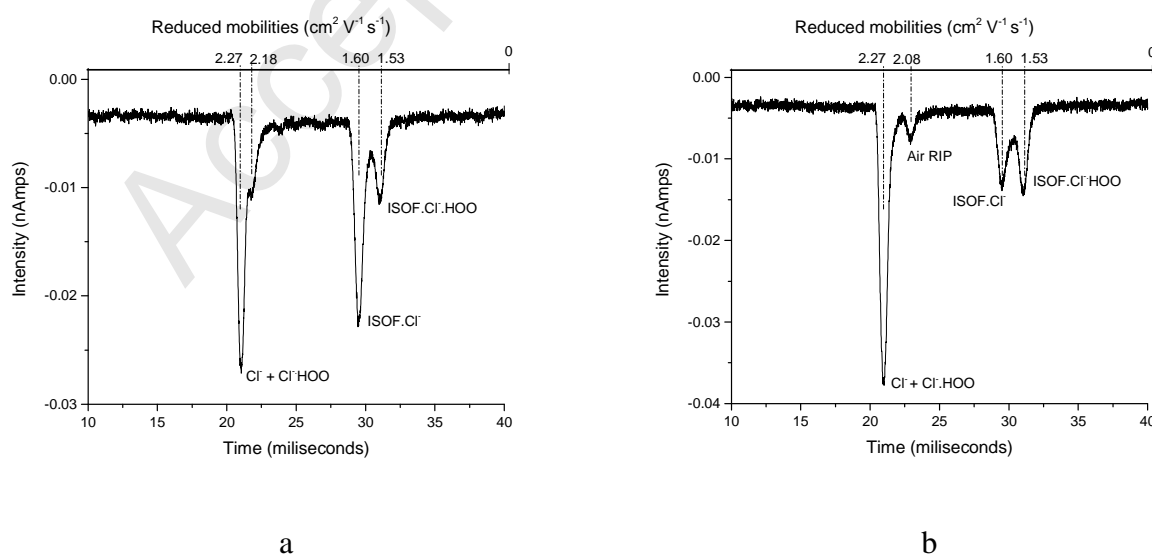


Figure 6. (a) IMS spectrum for an air system doped with PCE with ISOF added. (b) IMS

spectrum for an air system doped with PCE (in lower concentration when compared with 6a) following addition of ISOF. The small peak at $K_0 = 2.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is the remnant of the air RIP.

259

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

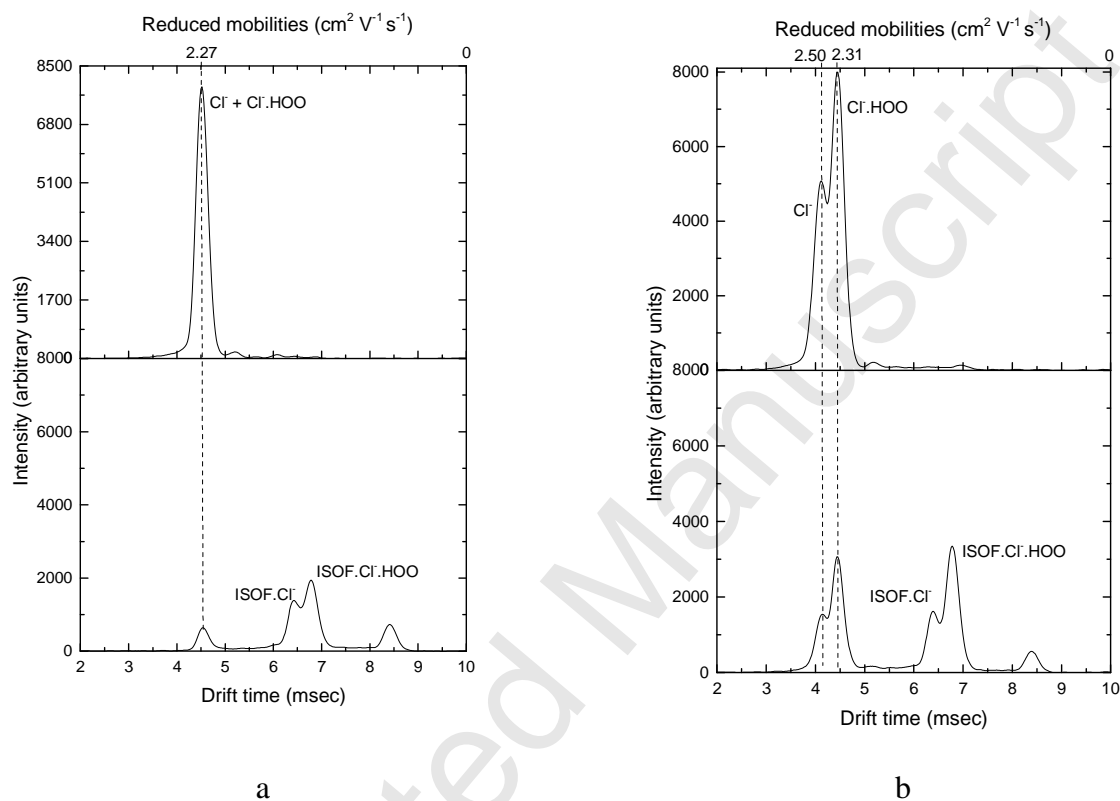


Figure 7. Smiths IMS spectra of PCE (top line plots) and ISOF (bottom line plots) acquired in a PCE doped system in a) “wet” conditions; b) “dry” conditions.

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

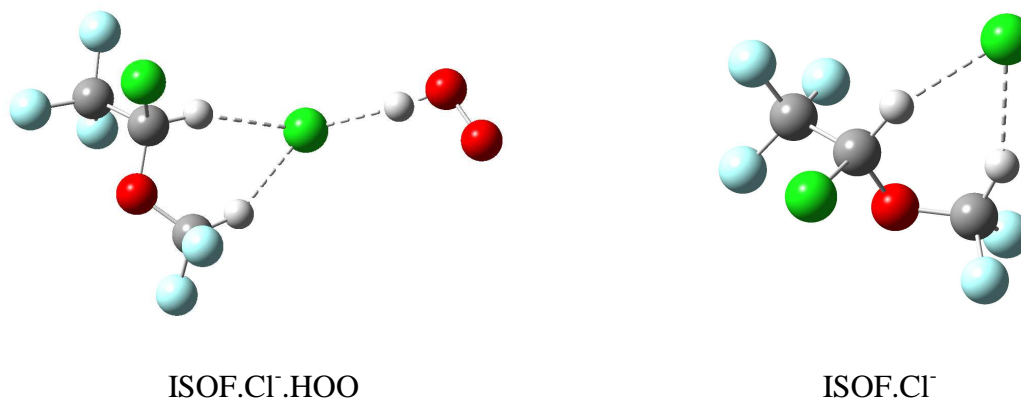


Figure 8. Structure of ISOF monomer product ions ISOF.Cl⁻.HOO and ISOF.Cl⁻ obtained

from DFT calculations.

264

265 The energetics for the reactions of ISOF with Cl^- and $\text{Cl}^-\cdot\text{HOO}$ are summarised in
266 Table 4.

267

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

Reactants	Ionic Products	$\Delta\text{H}_{298} \text{ kJ mol}^{-1}$	$\Delta\text{G}_{298} \text{ kJ mol}^{-1}$
ISOF + $\text{Cl}^-\cdot\text{HOO}$	ISOF. $\text{Cl}^-\cdot\text{HOO}$	-76	-50
ISOF. $\text{Cl}^-\cdot\text{HOO}$ + ISOF	ISOF ₂ . $\text{Cl}^-\cdot\text{HOO}$	-58	-2
ISOF + Cl^-	ISOF. Cl^-	-108	-79
ISOF. Cl^- + ISOF	ISOF ₂ . Cl^-	-74	-40

270

271 Calculations showed that the dimer complex of ISOF and $\text{Cl}^-\cdot\text{HOO}$ is thermo neutral
272 and even if formed it will be unstable in the drift region and hence is unlikely to be observed
273 in accord with experiment.

274

275 4. Conclusions

276 After introduction of PCE into an air based IMS system, two product ions were observed, Cl^-
277 by DEA and $\text{Cl}^-\cdot\text{HOO}$ by reaction with O_2^- . These anions can be observed as a doublet in a
278 'dry' system or as a singlet in a 'wet' system. In the wet system Cl^- clusters with water thus
279 reducing its mobility whereas $\text{Cl}^-\cdot\text{HOO}$ does not. Because DEA and reaction with O_2^- are in
280 competition the ratio of the two product ions is dependent upon PCE concentration. An
281 additional factor leading to this dependence is that PCE and O_2 are competing for electrons,
282 the PCE leading to Cl^- through DEA and the O_2 leading to O_2^- . $\text{Cl}^-\cdot\text{HOO}$ complexes with
283 ISOF as does Cl^- . This is nicely demonstrated by two ISOF product peaks being observed
284 even in a wet system when only a singlet PCE based RIP is observed.

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

288

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