Exploration of the utility of CF_3^+ as a reagent for chemical ionisation reaction mass spectrometry

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Abstract

The utility of CF_3^+ as a chemical-ionisation reagent for the identification of volatile organic compounds (VOCs) is explored. CF_3^+ and CF_2H^+ , produced from the discharge of CF_4 , have been used as chemical ionization (CI) precursor ions with a representative functional mixture of VOCs in Chemical Ionisation Reaction Mass Spectrometry (CIR-(TOF)-MS), a multi-reagent analogue of PTR-MS.

Reacting CF_3^+ with a functionally varied range of VOCs, under 100 Td and 120 Td accelerating electric fields (E/N), produced markedly different fragmentation patterns. Whereas hydride ion transfer was found to be the main reaction mechanism with n-alkanes. CF_3^+ acts as a Lewis acid, a strong electrophile with aromatics and nitriles. In VOCs with carbonyl groups, CF_3^+ forms an intermediate complex leading to the substitution of oxygen by fluorine. Target VOCs with longer alkyl chains in general show greater fragmentation, starting at C_5 and becoming progressively more significant by C_7 .

A brief comparison is made with the comparable H_3O^+ reactivity. From the comparison between CF_3^+ and H_3O^+ , it is clear that CF_3^+ is a “more aggressive” reagent ion but offers utility in terms of distinctive mass shifts with certain functional groups.

Introduction

Proton Transfer Reaction Mass Spectrometry (PTR-MS) has seen widespread uptake for the measurement of volatile organic compounds (VOCs) in a wide range of application areas.¹ Blake et al² demonstrated the application of a number of different CI reagents (NO^+ , NH_4^+ and O_2^+) in a more generalised technique they named Chemical Ionisation Reaction Mass Spectrometry (CIR-MS). The advantages of CIR-MS were demonstrated for isobaric compounds, in its ability to detect compounds not subject to proton transfer³ and the determination of proton affinities by bracketing.⁴ Latterly, Jordan et al, demonstrated the practical application of a PTR-MS with a switchable reagent ion capability (PTR + SRI-MS)⁵ which is now finding greater application.^{6,7} There is a strong analogy in the work in CIR-TOF-MS and PTR + SRI-MS to the capabilities of SIFT-MS⁸ which can switch between different reagent ions.

In recent work, we demonstrated the effectiveness of CF_3^+ and CF_2H^+ derived from CF_4 as chemical ionisation reagents for the quantification of n-alkanes in CIR-TOF-MS.⁹ The ion chemistry of CF_4 has been explored over a number of years. Early ion-cyclotron resonance mass spectrometry (ICR-MS) studies in the period 1973-1976 measured the reactions of halocarbon precursor ions with some common volatile organic compounds (VOC).¹⁰⁻¹² More recently, Dehon et al.¹³ returned to the field and extended the scope to include some common chloroalkanes.

The experimental environment of CIR-TOF-MS differs significantly from that of ICR-MS in terms of working pressure (1 Torr versus 1.0×10^{-5} Torr) and experiment cycle time (0.12 ms versus 100-1000 ms) which has the potential of affecting the dynamics and outcomes of the ion-molecule reactions. The main precursor ions produced from CF_4 are long-lived CF_3^+ ions and CF_2H^+ ions. The CF_2H^+ ions result from a reaction of CF_2^+ ions with background moisture. The role, if any, played by CF_3^+ and the effects of E/N in contributing to the production of CF_2H^+ needs further investigation as it is already known to be an important factor in the chain of reactions leading to the production of H_3O^+ . At pressures of 1.0×10^{-5} Torr any CF_2^+ formed is essentially absent after 5-10 ms in the ICR-MS work.¹¹ In the CIR-TOF-MS both CF_3^+ and CF_2H^+ are both normally present and have similar properties differing mainly in their reaction rates. In analysing experimental results, contributions from both precursor ions need to be considered, but it was still desirable to minimise the contribution of CF_2H^+ as much as possible with 3% or less being achievable.⁹

The observed strong electrophilic behaviour of CF_3^+ ions on aromatics and nitriles is supported by theoretical calculations showing that the electron withdrawing power of the three fluorine atoms in CF_3^+ should exceed its electron donating power, so that it acts as a strong Lewis acid.¹⁴

The present paper explores the utility of the ion products of tetrafluoromethane (CF_4) as a general chemical ionisation reagent particularly for application in a Chemical Ionization Reaction Time-of-Flight Mass Spectrometer (CIR-(TOF)-MS) with a wide range of functionally different VOCs. It demonstrates that the patterns of reactivity for some compound classes can be rationalised in terms of the Lewis acid/base formalism.

Experimental

The instruments used in this study were two identical CI-TOF-MS (Model 4500A, Kore Technologies, Ely) which have been described in detail elsewhere.^{3,15,16} One instrument used $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ and the second $\text{CF}_4/\text{CF}_3^+$. H_3O^+ ions were generated from saturated water vapour in high purity nitrogen (BOC, 99.998%). CF_3^+ was produced as previously described by Blake et al.⁹ Both machines have a collision induced decomposition (CID) section in the drift-tube assembly for controlling the formation of water clusters in PTR mode. For this work both drift tube reactors and the CID sections operated at the same values of E/N.

The analyte gas was delivered at a rate of 500 sccm of which 150 sccm fed into each of the two CI-TOF-MS and the remainder was vented to the atmosphere. When processing samples with unknown composition, an SPME fibre could be inserted into the vented stream for GC-MS analysis to help establish the identities of the unknowns.

The experimental work aimed to establish the viability of the use of CF_3^+ (and CF_2H^+) as a CI reagent that produces usable reaction yields with the target analytes. Since trace moisture is present in the experimental work, previous work has determined the effect of moisture and E/N on CF_3^+ and CF_2H^+ production.⁹ Those experiments⁹ explored the behaviour of CF_3^+ and CF_2H^+ production using dry and humidified N_2 as the carrier for a range of E/N values from 83 Td to 130 Td, from which the wet to dry yield ratio I_{90}/I_{100} (RH at 0% and 90%) of the CF_3^+ and CF_2H^+ yield was measured. The ratio ranged from a low of 5% for E/N < 83 Td to 60% for E/N > 130 Td. At 100Td the observed ratio was in the region of 30%, halfway between the two extremes, a good compromise setting for working. In order to simplify the analysis of the results, efforts concentrated on reducing the influence of ambient moisture as much as possible. For the sake of brevity when the term ' CF_3^+ ' is used, it should be understood to include the minor reagent CF_2H^+ as well.

The target VOC analytes (Sigma-Aldrich, Gillingham, Dorset, UK) are listed in Tables 2a-2c and 3a-3c. Analytes were prepared with initial concentrations of 10 – 50 ppmV by two stage dilution in 10 litre Tedlar bags (Thames-Restek UK, Ltd, Saunderton, Bucks., UK). In addition to producing spectra from reactions with CF_3^+ , the experimental procedure included simultaneous capture of H_3O^+ proton transfer spectra in a series of parallel experiments on the second CI-TOF-MS. The spectra based on CF_3^+ also contained a background of proton transfer reactions from traces of moisture in the analyte. Using the H_3O^+ -derived spectra from the second CI-TOF-MS as a template it was possible to separate the CF_3^+ and H_3O^+ background contributions.

In order to present the wide-range of results some formalisms have been created for presentation. While most of the expected minor alkyl chain fragments did not show any clear pattern, it was possible to show that it was possible to classify the results by the type of reaction. In the results sections and Tables 2a to 2c where E/N = 100 Td and Tables 3a -3c for E/N=120 Td a simplified presentation of the unclassifiable data was adopted by summarising fragment composition and relative intensity into a single column for the most prominent cases. The detailed fragmentation tables which include molecular structure diagrams for the most important cations are listed in the supplementary Information section as Tables S1 to S33.

The notation devised to classify the main types of reaction products observed in a compact form is shown in Table 1 where it is also compared with the more general form used in ion formulae.

- RH represents the neutral VOC
- R represents the ion (R^+) that remains after hydrogen loss (as shown in equ. 1)

- RH+3 represents the ion ((RH+F-O)⁺) in which fluorine has replaced oxygen in C=O carbonyl group (equ. 2)
- RCF₂ represents the ion (RCF₂⁺) where CF₃⁺ replaces H in RH with the formation of an HF molecule. This reaction is described by equ. 4a and 4b. Occasionally, a similar reaction will occur with a substituent of the analyte molecule.
- RHCF₃ ions are created as adducts (RHCF₃⁺) of electrophilic CF₃⁺ ions and electron rich VOCs such as aromatics. Most adducts are formed with parent ions, but occasionally adducts are formed with substituent ions.
- RH₂ represents the protonated version of RH from a proton transfer reaction with H₃O⁺.
- RHCF and RHCHF₂ cations are created from reactions with the secondary reagent CF₂H⁺ producing cations M+31 and M+51 respectively.

RCF₂ or RHCF₃ cations formed with a substituent of the parent VOC are shown with the proposed molecular structure of the fragment alongside.

Results and Discussion

The products of the reactions of H_3O^+ and CF_3^+ with the VOC analytes are shown in Tables 2a to 2c where $E/N = 100$ Td and Tables 3a -3c for $E/N = 120$ Td. Contributions from the ^{13}C isotopologues (1% relative abundance) have been removed as have peaks identified as originating from secondary PTR reactions (RH2) generated in environments of high relative humidity. Bromine-containing fragments of bromobenzene produce twin cations due to the 51:49 abundance of the main isotopes but combine when estimating fragmentation contributions. The initial VOC survey was carried out in dry laboratory conditions.

In a typical CF_3^+ CI spectrum such as figure 1, the main ion products following the introduction of undiluted CF_4 into the electrical discharge source are CF_3^+ with $M+69$ and CF_2H^+ at $M+51$. Any initial CF_2^+ ions formed appear to be short-lived or interact with CF_4 to form CF_3^+ , although CF_2^+ , if not present initially, does appear to exist in a transitory form to account for some observed reactions.⁹

From a survey of Tables 2 and 3, it can be seen that CF_3^+ reagent ions can react in several different ways depending on the VOC. With H_3O^+ , protonation is the principal form of reaction observed whereas with CF_3^+ the structure of the target VOC can lead to differing outcomes.

Alkanes - The simplest of reactions, observed most frequently in the lighter alkanes is by hydride transfer, where the difference in ionization energy is favourable, leading to hydride loss from the target molecule to form HF viz,^{9,13}

Hydride transfer is prevalent for $<\text{C}_7$ n-alkanes, but encountered less frequently with other VOCs. The two longer chain alkanes n-heptane and n-octane studied here were found to fragment strongly and provided little evidence of hydride transfer.

Similar fragmentation behaviour occurred with H_3O^+ so that longer alkyl chain VOCs are equally likely to break up no matter how gentle the ionisation process. In the case of n-heptane and n-octane, complete fragmentation of the alkyl chains occurred and no molecular ion peaks were observed (Tables 1a and 2a).

Alkenes - Hexene and α -pinene both exhibit hydride transfer (R^+) with CF_3^+ although substantive fragmentation also occurs. The proton transfer reactions produce mainly RH2 ions, characteristic of protonation, along with a similar large background of smaller intensity fragments (Tables 2a and 3a).

Alcohols - In contrast to H_3O^+ , the selected alcohols showed little reactivity with CF_3^+ . Methanol showed no discernible reaction, while ethanol (figure 2a) and propanol produced alkyl fragments such as R^+ , C_2H_3^+ , C_3H_5^+ , C_3H_3^+ and C_3H_7^+ . Hydronium reactions produce strong RH2 peaks with little fragmentation in methanol and ethanol. In ethanol, the main fragment at $M+29$ could be either C_2H_5^+ or HCO^+ . Similarly in propanol the major fragment at 43 amu raises the same question of whether it is CH_3CO^+ resulting from hydride extraction or C_3H_7^+ following the break-up of an intermediate $\text{C}_2\text{H}_5\text{O}^+\text{HCF}_3$. At $E/N = 120$ Td the strong appearance of C_2H_3^+ suggests that the latter alternative is most likely (Tables 2a and 3a). In the reaction with H_3O^+ the loss of OH to form water provides additional support for the readiness of alcohols to give up OH.

Ketones and aldehydes - Ketones and aldehydes with short alkyl chains show substitution of the carbonyl oxygen by fluorine (equ. 2). Ketones show some examples of RH+3, RCF2 or RHCF3 but these products are more common in aldehydes. Hexanal shows alkyl chain fragmentation. Generally, alkyl group

fragmentation is the characteristic in the longer chain members of these two VOC types (Tables 2b and 3b). While RH+3 end products were observed with acetone and butanone at E/N = 100 Td, they were present only with acetone at E/N = 120 Td. In hexanal and cyclohexanone, alkyl fragmentation dominates, while in the remaining aldehydes and ketones, RHCF3 formation is in evidence though again more at 100 Td than at 120 Td. In the accompanying proton transfer work, H₃O⁺ produced mostly protonated molecular ions (RH₂) with both ketones and aldehydes (Tables 2b and 3b).

It has long been known that with ketones and aldehydes CF₃⁺ preferentially targets the C=O carbonyl group¹⁰ viz

Infrared multiple photon dissociation (IRMPD) investigations on a range of ketones has provided evidence of the bond stretching action of CF₃⁺ ions on C=O bonds. A likely mechanism would involve an electrophilic attack by the CF₃⁺ ion on the carbonyl oxygen, initially forming an adduct. However, this adduct is short-lived and exothermic ($\Delta H < -200 \text{ kJ mol}^{-1}$) such that it easily overcomes any barrier to form a metathesis transition state (equ. 2) which then decays with the loss of CF₂O to produce a fluorine-stabilized carbocation.^{17,18} Acetone, acetaldehyde (figures 5a to 5d) and propanal (figure 2b) are good examples, where competition from long alkyl chains losing smaller chain fragments are absent.

The lifetime of the intermediate state envisaged is comparable to that of the CI-TOF-MS cycle time (ca. 40 μs) so that if significant traces of the remaining RHCF3 intermediate and RH+3 final state in acetone and acetaldehyde remain, it is possible to estimate the lifetime of the metathesis/intermediate states. Greater energy is added to the intermediate state as the E/N rises from 100 Td to 120 Td such that the decay rate of the RHCF3 group to the RH+3 group increases. Using ion mobility data¹⁹ estimates of the lifetimes of the RHCF3 groups (Table 4 and section S34) lie in the range of 50 to 350 μs . Increasing E/N shortens the observed lifetimes. In this context it is also worth noting that displacement reactions such as

have been observed in situations where there are weak bonds in carbonyl compounds.¹⁰

In hexanal and cyclohexanone alkyl fragment emission dominates, while in the remaining aldehydes and ketones, RHCF3 formation is in evidence, more strongly at 100 Td than at 120 Td. H₃O⁺ again produced mostly protonated molecular ions (RH₂) in both the ketones and aldehydes (Tables 2b and 3b).

Butanedione fragments extensively when reacting with CF₃⁺, and the RCF2 group at m/z 135 is one of the major fragments at 100 Td but somewhat reduced at 120 Td. While it contains two C=O bonds and lacks a long alkyl chain which would suggest a strong showing of the characteristic RH+3 products, these were not found. No RHCF3 group at m/z 155 was formed although there was evidence of a CF₃⁺ adduct with a substituent fragment at m/z 114. The most prominent fragment at m/z 43 corresponding to CH₃CO⁺ where the butanedione molecule had simply split in half. The disruptive effect of increased E/N caused the

appearance of a methyl fragment (15 amu) at 120 Td, something absent at 100 Td. On the other hand butanedione showed few signs of fragmentation in the proton transfer reactions at both 100 and 120 Td.

Acetates - The behaviour of the two acetate VOCs (Tables 2b and 3b) differed in that while methyl acetate formed an RHCF₃ complex (fig. 5e), with ethyl acetate, the ethyl substituent was stripped off leaving CH₃CO⁺ as the main reaction product (fig. 5f). Increasing E/N to 120 Td saw the appearance of a significant methyl group following further disintegration of the M-27 group at 61 amu. Of the two possible configurations for this group, C₂H₅O₂⁺ or CH₃CH₂CFH⁺ the former seems most likely.

Five and six-member rings – An interesting feature of the ion-molecule chemistry for this set of VOCs was the Lewis acid behaviour with electrophilic addition exhibited by CF₃⁺ in its reaction with cyclic hydrocarbons (Tables 2c and 3c). In benzene and toluene the major fragments were RCF₂ (figures 5g and 5h) whereas in styrene and o-xylene (figures 5i and 5j) RHCF₃ fragments were preferred, possibly due to geometric factors. Bromobenzene and ethylbenzene (figures 5k – 5l) have more complex decay schemes where CF₃⁺ appears to form adducts with fragments of the parent molecules. In addition to the five and six-membered heterocycles, the furans, pyridine and pyrrole, are rich in lone pair electrons (figure 3) and show the Lewis base behaviour. Similar behaviour was observed for DMS which while not having a ring structure, have lone pair electrons on the sulphur atom, showed similar behaviour to the cyclic VOCs.

Clearly, CF₃⁺ acts as a Lewis acid, an electrophile with the nucleophilic cyclic compounds,¹⁴ such that both RHCF₃ and RCF₂⁺ end products are formed. When CF₃⁺ reacts with an aromatic VOC, an intermediate is formed following an electrophilic substitution

followed by the subsequent elimination of HF to give

As seen with toluene (figures 2c and 5h). The electron-withdrawing power of CF₃⁺ on the lone pair electrons found in many 5- and 6-ringed VOCs (figure 3), is so strong that they out-compete most alternative reactions.

In styrene and xylene RHCF₃ cations feature strongly (figures 5i and 5j). The observed prominence of these cations from ethylbenzene demonstrates the α-cation increasing stabilising effects of fluorine²⁰ where it is assumed that the intensity of a cation to be related to its stability (figure 4).

Nitriles - The nitriles, also electron-rich donors, reacted strongly with CF₃⁺ to produce RHCF₃ products almost exclusively (figure 5m and tables 2c and 3c) with the CF₃⁺ group acting as a Lewis acid complexed with the Lewis base nitrile group. This well-known complexation is frequently used to activate nitriles. It is reasonable to assume that the cation (110 amu) in acetonitrile is the outcome of activation of nitrile by CF₃⁺ which facilitates the addition of hydride (figure 6). Similar behaviour is observed in acrylonitrile and propionitrile. Proton transfer reactions with H₃O⁺ led to the formation of the protonated RH₂ ion almost exclusively.

Exploration of the Effect of Moisture

Experiments in many “real-life” applications would encounter sample streams containing water that reacts with CF_3^+ to form H_3O^+ in a two-stage process,

and since the proton affinity of CF_2O (667 kJ mol^{-1}) is less than that of water (691 kJ mol^{-1}), CF_2OH^+ reacts with ambient water by proton transfer.²¹

Both CF_2OH^+ ($M+67$) and H_3O^+ feature prominently in most spectra obtained under “real-life” conditions. The yields from reaction (5) and possibly reaction (6) are affected by the value of E/N and moisture present in the analyte and reduce the amount of CF_3^+ available for reaction. When the relative humidity of the analyte is >95%, the CF_3^+ yield drops to 5% of the dry yield while $E/N < 83 \text{ Td}$. At 100 Td the yield is 25%, of the dry yield while at 120 Td and above the yield levels out at 60%.⁹ Most published CI-TOF-MS work is performed in the $100 - 130 \text{ Td}$ region where the ambient relative humidity is usually well below saturation. When selecting at which E/N to operate, its effect on analyte fragmentation may counteract the advantages of decreasing the loss of CF_3^+ .

In the proton transfer reaction series, protonation is observed in all instances where thermodynamically allowed and increased humidity leads to increased cluster formation of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$. Since these clusters do not have the same proton affinities as native H_3O^+ ions, significant cluster formation results in changed species-dependent protonation outcomes.

CF_3^+ and H_3O^+ performance compared

As a demonstration of the utility of CF_3^+ against the commonly used H_3O^+ , a series of experiments were conducted using the gaseous products from pervasively fracked shale. Previous work from Sommariva et al,²² has shown that a wide variety of hydrocarbons are released on fracture of shale and with the CF_3^+ work it was possible to extend the range of detection to some previously undetectable alkanes. Figure 1 shows the spectra obtained by crushing a sample of Bowland shale heated to 80°C and analysing the effluent using CF_3^+ and H_3O^+ as the principal reagents. It should be noted that pervasive fracking of shale also releases water vapour from the rock, making this a genuine “real-world” example. It was found that most of the assignments are unique to one or other of the reagents, with only a few instances of overlapping groups occurring. The instances of overlapping groups are shown as the horizontal bands in figure 7. The yields in the normalised spectra showed comparable reaction sensitivity for the two reagents.

Using more than one reagent ion made it possible to observe in real time, VOCs from the same sample reacting with one or the other of them, and this is clearly demonstrated in the shale gas VOC sample. By superimposing the normalised spectra from both reagents it is possible to identify and separate the contributions made by each of them. By applying a scaled version of the proton transfer spectrum to the CF_3^+ spectrum it was possible to quantify the contribution of the proton transfer groups in the CF_3^+ spectrum. A comparison of normalised spectra suggests the reaction sensitivities to both reagents were comparable.

Figure 7 is a pictorial version of the principal reaction products from the target VOCs with both CF_3^+ and H_3O^+ as can be found in tables 2a to 2c. The electrophilic action of CF_3^+ and its hydride capture reactions with $\text{C}_2\text{-C}_6$ n-alkanes define the two features that distinguish the value of CF_3^+ from other CI reagents. It is

clear that the gentler proton transfer reaction provided by H_3O^+ provides cleaner results over a wider range of analytes, so that CF_3^+ and CF_2H^+ induced reactions will mainly have a role in situations where proton transfer from H_3O^+ does not occur (e.g. $\text{C}_2\text{-C}_6$ n-alkanes) or produces ambiguous results. The electron extracting action of CF_3^+ is particularly suited for working with aromatics and nitriles and other electron-rich species as highlighted in figure 7. In the aldehydes and ketones tested, only the lighter members exhibited the oxygen/fluorine substitution in the carbonyl group and was observed more often with the aldehydes than the ketones tested. In strongly exothermic reactions longer alkyl chains fragment in preference to all other alternative reactions. This behaviour has been observed as well with other chemical ionisation reagents such as NO^+ and O_2^+ .^{3,4,6,23,24}

Conclusion

The utility of CF_3^+ as a chemical-ionisation reagent for the identification of volatile organic compounds (VOCs) has been explored and shown to have utility for the identification of volatiles in direct mass-spectrometry. CF_3^+ reacts with a wide range of VOCs showing characteristic reaction patterns. It seems to exhibit the widest variety of reactions with short chain molecules where alkyl chain fragmentation does not arise.

From this work, it suggests that if one were to arrange the most commonly used CI reagents in the order of “aggressive behaviour” it would be $\text{H}_3\text{O}^+ < \text{NO}^+ < \text{CF}_3^+ < \text{O}_2^+ < \text{X}^+$, where X represents a noble gas e.g. Kr. In addition, CF_3^+ and CF_2H^+ can initiate more complicated reaction alternatives than the other candidates when dealing with electron-rich multiple bonds in analytes, this may be considered as presenting interesting alternatives or challenges.

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Tables

Notation	RH	R	RH+3	RCF2	RHCF3	RH2
Ion formula	$(\text{RH})^{+\bullet}$	R^+	$(\text{RH}+\text{F}-\text{O})^+$	RCF_2^+	RHCF_3^+	RH_2^+
m/z	M	M-1	M+3	M+49	M+69	M+1

Table 1. Summary of the notation used for ion fragments. The notation for ion components in equations retain the conventional subscripts and superscripts, whereas the simpler forms are used in the body of the text and in table headers. The presence of the secondary reagent CF_2H^+ can give rise to RCHF and RHCHF2 groups with $m/z = M+31$ and $M+51$.

	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺		H ₃ O ⁺	H ₃ O ⁺	H ₃ O ⁺
Alkanes													
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
n-heptane	C7H16	100	C3H5 (5) C4H9 (90)	M-59 M-43	-	-	-	-	-		-		-
n-octane	C8H18	114	C4H9 (48) C5H11 (39)	M-57 M-44	-	-	-	-	-		-		-
Alkenes													
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
alpha-pinene	C10H16	136	C7H9 (35) C7H8 (6)	M-43 M-44	13	-	-	-	-		C6H9 (31)	M-55	56
hexene	C6H12	84	C3H7 (29) C4H7 (18)	M-41 M-29	33	-	-	-	-		C3H7 (26)	M-41	63
Alcohols													
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
methanol	CH4O	32	-		-	-	-	-	-		-		100
ethanol	C2H6O	46	C2H3 (11) C2H5 (78)	M-19 M-17	10	-	-	-	-		C2H5 (10)	M-17	88
propanol	C3H8O	60	C3H7 (95)	M-17	4	-	-	-	-		C3H7 (88)	M-17	-

[illegible]

Table 2a. Abridged table of the fragmentation yield (in %) of the alkanes, alkenes and alcohol at E/N=100 Td for both CF_3^+ and H_3O^+ . Detailed fragmentation tables are shown in the supplementary information.

	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺		H ₃ O ⁺	H ₃ O ⁺	H ₃ O ⁺
Ketones													
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
acetone	C ₃ H ₆ O	58	-		-	-	26		72		-		100
butanone	C ₄ H ₈ O	72	C ₂ H ₇ O (6) C ₄ H ₇ (44)	M-25 M-17	-	-	42	-	-		-		100
pentanone	C ₅ H ₁₀ O	86	C ₃ H ₅ (8) C ₃ H ₇ (17) C ₂ H ₄ OCF ₃ (72)	M-45 M-43 M+17	-	-	-	-			-		100
hexanone	C ₆ H ₁₂ O	100	C ₄ H ₇ (47) C ₆ H ₁₁ (16) C ₃ H ₄ OCF ₃ (15)	M-45 M-17 M+25	-	-	-	-			-		100
butanedione	C ₄ H ₆ O ₂	86	CH ₃ CO(48) C ₂ H ₅ OCF ₃ (13)	M-43 M+28	-	-	-	14			-		99
cyclohexanone	C ₆ H ₁₀ O	98	C ₄ H ₇ (4) C ₆ H ₉ (91)	M-43 M-17	-	-	-	-	-		-		100
Aldehydes													
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
acetaldehyde	C ₂ H ₄ O	44	C ₃ H ₄ OF (19)	M+31	-	-	47	-	34		-		100
acrolein	C ₃ H ₄ O	56	-		-	-	46	-	55		-		100

propanal	C3H6O	58	C3H5 (15)	M-17	-	-	63	-	-	-	100	
hexanal	C6H12O	100	C4H7 (45) C6H11 (39)	M-45 M-17	-	-	-	-	-	C6H11 (67)	M-17	25
Acetates												
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3	Fragment	m/z	RH2
methyl acetate	C3H6O2	74	C2H3O (13)	M-31	-	-	-	-	80	-		97
ethyl acetate	C4H8O2	88	C2H5O2 (21) C2H3O (71)	M-27 M-45	-	-	-	-	-	C2H5O2 (35)	M-27	61

Table 2b. Abridged table of the fragmentation yield (in %) of the ketone, aldehydes and acetates at E/N=100 Td for CF₃⁺ and H₃O⁺. Detailed fragmentation tables are shown in the supplementary information. RHCF3 fragments based on substituents are shown in red in the fragment column. RHCF2 fragments from CF₂H⁺ reactions are shown in blue in the same column.

	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺		H ₃ O ⁺	H ₃ O ⁺	H ₃ O ⁺
					+	+							
Aromatics													
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
benzene	C6H6	78	-	-	-	1	-	88	6		-		100
toluene	C7H8	92	-	-	4	-	-	89	2		-		100
ethylbenzene	C8H10	106	C6H7 (18) C6H5CFH (12) C6H5CF2 (43)	M-27 M+3 M+20	11	-	-	-	-		C3H7 (4)	M-63	90
styrene	C8H8	104	C6H5CFH (15) C8H7CF2 (12)	M+5 M+49	-	5	-	-	58		-		100
o-xylene	C8H10	106	-		10	4	-	17	64		-		100
bromobenzene	C6H5Br	157	C6H5 (10) C4H5 (13) C6H4CF3 (7)	M-80 M-10 M-21	6	-	-	47	7		-		100
100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
Nitriles													
acetonitrile	C2H3N	41	-	-	-	-	-	-	100		-		100

propionitrile	C3H5N	55	CNHCF3 (2)	M+22	-	-	-	-	98		-	100	
acrylonitrile	C3H3N	53	-	-	-	-	-	-	98		-	100	
100Td Other cyclic	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
furan	C4H4O	68	C4H4OHCF2 (11)	M+51	-	-	-	4	70		C3H5 (14.0) C3H3 (10.4)	M-27 M-29	73
methyl furan	C5H6O	82	C5H6OHCF2 (11)	M+51	7	18	-	-	44		-		95
pyrrole	C4H5N	67	-	-	-	-	-	22	61		-		95
pyridine	C5H5N	79	-	-	4	-	-	-	80		-		94
Non-cyclic 100Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
DMS	C2H6S	62	-	-	9	14	-	-	75		-		93

Table 2c. Abridged table of the fragmentation yield (in %) of cyclic VOCs and DMS tested at E/N=100 Td. Detailed fragmentation tables are shown in the supplementary information. Many of the target VOCs exhibit the Lewis Acid/Lewis Base behaviour (see text). Items in red are instances where .CF₂ or .CF₃ groups have reacted with substituents of the parent molecule. RHCF3 or RCF2 fragments based on substituents are shown in red in the fragment column. RHCF2 fragments from CF₂H⁺ reactions are shown in blue in the same column.

	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	m/z	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺		H ₃ O ⁺	H ₃ O ⁺	H ₃ O ⁺
Alkanes													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
n-heptane	C7H16	100	C3H5 (22) C4H9 (73)	M-59 M-43	-	-	-	-	-		-		-
n-octane	C8H18	114	C3H5 (25) C4H9 (40)	M-73 M-57	-	-	-	-	-		-		-
Alkenes													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
alpha-pinene	C10H16	136	C7H8 (21) C7H9 (23)	M-44 M-43	3	-	-	-	-		C6H9 (54)	M-55	39
hexene	C6H12	84	C2H5 (19) C4H7 (13)	M-5 M-29	-	-	-	-	-		C3H5 (49) C3H7 (39)	M-43 M-41	8
Alcohols													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
methanol	CH4O	32	-	-	-	-	-	-	-		-		100

ethanol	C ₂ H ₆ O	46	C ₂ H ₃ (21) C ₂ H ₅ (69)	M-19 M-17	11	-	-	-	-		C ₂ H ₃ (24) C ₂ H ₅ (26)	M-19 M-17	50
propanol	C ₃ H ₈ O	60	C ₃ H ₃ (20) C ₂ H ₃ (61)	M-21 M-33	-	-	-	-	-		C ₃ H ₅ (51) C ₃ H ₇ (37)	M-19 M-17	2

Table 3a - Abridged table of the fragmentation yield (in %) of the alkanes, alkenes and alcohol tested at E/N=120 Td. Detailed fragmentation tables are shown in the supplementary information.

	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺ z	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺		H ₃ O ⁺	m/z	H ₃ O ⁺
Ketones													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
acetone	C3H6O	58	C3H5 (26)	M-17	-	-	37	-	34		-	-	100
butanone	C4H8O	72	C2H3 (23) C2H5 (44) C2H4OCF3 (18)	M-45 M-43 M+21	-	-	1	-	-		C4H7 (2)	M-17	94
pentanone	C5H10O	86	C2H3 (17) C3H5 (46)	M-69 M-45	-	-	-	-	-		C3H9 (10)	M-41	88
hexanone	C6H12O	100	C2H5 (43) C4H7 (13) C3H4OCF3 (2)	M-71 M-45 M+6	-	-	-	-	-		C4H7 (3) C6H11 (4)	M-45 M-17	83
butanedione	C4H6O2	86	CH3(19) CH3CO (56)	M-71 M-43	-	-	-	2	-		C4H2O2 (4)	M-4	96
cyclohexanone	C6H10O	98	C3H5 (10) C6H9 (70)	M-57 M-17	-	-	-	-	-		-	-	100
Aldehydes													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
acetaldehyde	C2H4O	44	C2H3 (17) C2H3O (19)	M-17 M-1	-	-	54	-	10		-	-	100
acrolein	C3H4O	56	-	-	-	-	56	-	44		-	-	100
propanal	C3H6O	58	C3H5 (39) CH3CHF (26)	M-27 M-11	-	26	15	-	-		CH3O (20) C3H7 (10)	M-27 M-15	62

hexanal	C ₆ H ₁₂ O	100	C ₂ H ₅ (43) C ₄ H ₇ (19)	M-71 M-45	-	-	-	-	-	C ₄ H ₇ (34) C ₆ H ₁₁ (62)	M-45 M-17	2
Acetates												
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3	Fragment	m/z	RH2
methyl acetate	C ₃ H ₆ O ₂	74	C ₂ H ₃ O (28)	M-21	-	-	-	-	69	C ₂ H ₃ O (9)	M-21	88
ethyl acetate	C ₄ H ₈ O ₂	88	CH ₃ (22) C ₂ H ₃ O(65)	M-73 M-45	-	-	-	-	-	C ₂ H ₃ O (12)	M-45	82

Table 3b. Abridged table of the fragmentation yield (in %) of the ketone, aldehydes and acetates at E/N=120 Td. Detailed fragmentation tables are shown in the supplementary information. RHCF3 fragments based on substituents are shown in red in the fragment column.

	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺	CF ₃ ⁺		H ₃ O ⁺	H ₃ O ⁺	H ₃ O ⁺
Aromatics													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
benzene	C6H6	78	C3H7 (7)	M-35	-	7	-	85	1		-		100
toluene	C7H8	92	-		21	-	-	58	-		-		100
ethylbenzene	C8H10	106	C2H3 (3) C6H5CH2 (28)	M-79 M-15	9	2	-	54	-		C3H7 (36)	M-63	57
styrene	C8H8	104	C6H6CFH(28) C8H5OCF2 (17)	M+5 M+49	6	16	-	-	16		-		100
o-xylene	C8H10	106	C7H7 (30)	M-15	11	8	-	27	17		-		100
bromobenzene	C6H5Br	157	C6H5 (17) C6H6 (12) C6H4CF3 (7) C6H4BrCHF2(31)	M-80 M-79 M-2 M+51	7	-	-	-	5		-		100
Nitriles													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
acetonitrile	C2H3N	41	-		-	-	-	-	100		-		100

propionitrile	C3H5N	55	CNHCF3 (12)	M+31	-	-	-	-	87		-	100	
acrylonitrile	C3H3N	53	C2H3 (5) C2H7 (18)	M-26 M-22	-	-	-	-	47		-	100	
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
Other cyclic													
furan	C4H4O	68	-		-	-	-	12	43		-	96	
methyl furan	C5H6O	82	C5H6OHCF2 (1)	M+51	9	20	-	-	25		-	95	
pyrrole	C4H5N	67	-		-	-	-	49	40		-	96	
pyridine	C5H5N	79	-		5	-	-	-	80		-	94	
Non-cyclic													
120Td	M	m/z	Fragment	m/z	R	RH	RH+3	RCF2	RHCF3		Fragment	m/z	RH2
DMS	C2H6S	62	-		10	25	-	-	49		-	93	

Table 3c. Abridged table of the fragmentation yield (in %) of cyclic VOCs and DMS at E/N=120 Td. Detailed fragmentation tables are shown in the supplementary information. RHCF3 fragments based on substituents are shown in red in the fragment column. RHCF2 fragments from CF₂H⁺ reactions are shown in blue in the same column.

VOC	RHCF3	RH+3	T _{100Td} μs	T _{120Td} μs
Acetone	127	61	366.2	128.9
Acetaldehyde	113	47	132.2	50.8

Table 4. - Estimates for the lifetimes of intermediate/metathesis transition states in the decay of CF_3^+ reactions with acetone and acetaldehyde. These calculations assume that all the dissociation takes place in the drift tube (see experimental). The possibility of further dissociation occurring within the flight path of the mass spectrometer is discussed in the main text.

Figures

Figure 1 - Observed mass spectrum from the superimposed normalised H₃O⁺ (red) and CF₃⁺ (blue) results (10⁶ ncps) at E/N = 100 Td obtained from a sample of fractured Bowland Shale. The H₃O⁺ spectrum is coloured red while the CF₃⁺ product ions are coloured blue. The inset diagram shows the superimposed proton transfer spectrum scaled to fit the observed intensity of H₃O⁺ in the CF₃⁺ spectrum in which it plays a smaller part.

Figure 2 – Examples of the main reaction pathways for CF_3^+ chemical ionisation at $E/N = 100$ Td. Hydride transfer was generally found to be more strongly favoured in reactions with C_2 – C_5 n-alkanes. Hydride transfer (equ. 1) in ethanol is depicted in figure 2a, along with emission of the C_2H_5^+ group (29 amu) which is the preferred route. Oxygen substitution by fluorine in the carbonyl group of propanal resulted in a strong type $\text{RH}+3$ appearance at 61 amu. CF_2OH^+ , at 67 amu (an intermediate in equ. 5 and equ. 6) is present in all four examples. Toluene in Fig 2c is one of several VOCs that show a strong tendency to form a complex RCF_2 , and acetonitrile (figure 2d) and the other nitriles tested, show a strong preference for the formation of RHCF_3 compounds (equ. 4a and 4b).

Figure 3 – Five or six-member ring VOCs such as the aromatics, furans, pyrrole and pyridine act as Lewis bases donating electrons to the Lewis acid CF_3^+ ions.

Figure 4 - The presence of additional fluorine atoms in a substituent of the reaction products of 5- or 6- members ring VOCs, such as styrene, contribute to its stability. It is assumed that the stability of each configuration is related to its observed yield.

Source	Fragment	Mass	%(100Td)	%(120Td)
Acetone (a)	$(\text{CH}_3)_2\text{C}^+\text{F}$	61	25.9	36.8
(b)	$\text{CH}_3\text{COCH}_3\text{CF}_3^+$	127	71.6	34.3
Acetaldehyde (c)	CH_3CFH^+	47	46.6	54.0
(d)	$\text{CH}_3\text{CHOCF}_3^+$	113	34.0	9.8
Methyl Acetate (e)	$\text{CH}_3\text{OCOCH}_3\text{CF}_3^+$	143	80.2	68.6
Ethyl Acetate (f)	$\text{C}_2\text{H}_3\text{O}^+$	43	70.5	65.0
Benzene (g)	$\text{C}_6\text{H}_5\text{CF}_2^+$	127	88.2	84.5
Toluene (h)	$\text{C}_7\text{H}_7\text{CF}_2^+$	141	88.9	57.6
Styrene (i)	$\text{C}_8\text{H}_8\text{CF}_3^+$	173	57.5	16.3

o-Xylene (j)	$C_8H_{10}.CF_3^+$	175	63.4	17.2
Bromobenzene (k)	$C_6H_4.CF_3^+$	145	6.2	7.3
Ethylbenzene (l)	$C_6H_5.CF_2^+$	127	42.5	53.9
Acetonitrile (m)	$CH_3CN.CF_3$	127	100	100

Figure 5 - This figure contains an extract of some ions of interest taken from the detailed fragmentation tables S1 to S35 in the supplementary data section. All the items are example of R.CH₂ and R.CH₃ fragments for 5- and 6-member ring VOCs and nitriles. They depict the structure of the fragments produced as well as the likely location of the charge.

Figure 6 - Nitriles with lone pairs of electrons react with Lewis acid CF_3^+ .