CF_3^+ and CF_2H^+ : new reagents for n-alkane determination in chemical ionisation reaction mass spectrometry

Robert S. Blake^(a), Saleh A. Ouheda^(a), Corey J. Evans^(a) and Paul S. Monks^(a,b)

(a) Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, United Kingdom.

(b) Corresponding author

Summary

Alkanes provide a particular analytical challenge to commonly used chemical ionisation methods such as proton-transfer from water owing to their basicity. It is demonstrated that the fluorocarbon ions CF_3^+ and CF_2H^+ , generated from CF_4 , as reagents provide an effective means of detecting light n-alkanes in the range $\text{C}_2\text{-C}_6$ using direct chemical ionisation mass spectrometry. The present work assesses the applicability of the reagents in a Chemical Ionisation Mass Spectrometric (CI-TOF-MS) environments with factors such as high moisture content, operating pressures of 1–10 Torr, accelerating electric fields (E/N) and long-lived intermediate complex formation. Of the commonly used chemical ionisation reagents, H_3O^+ and NO^+ only react with hexane and higher while O_2^+ reacts with all the target samples, but creates significant fragmentation. By contrast, CF_3^+ and CF_2H^+ acting together were found to produce little or no fragmentation. In dry conditions with $E/N = 100$ Td or higher the relative intensity of CF_2H^+ to CF_3^+ was mostly less than 1% but always less than 3%, making CF_3^+ the main reagent ion. Using O_2^+ in a parallel series of experiments, a substantially greater degree of fragmentation was observed. The detection sensitivities of the alkanes with CF_3^+ and CF_2H^+ , while relatively low, were found to be better than those observed with O_2^+ . Experiments using alkane mixtures in the ppm range have shown the ionisation technique based on CF_3^+ and CF_2H^+ to be particularly useful for measurements of alkane/air mixtures found in polluted environments. As a demonstration of the technique's effectiveness in complex mixtures, the detection of n-alkanes in smoker's breath is demonstrated

Keywords

Chemical Ionisation, Mass Spectrometry, Time-of-Flight, n-Alkanes, Fluorocarbons

Introduction

Real-time measurement of volatile organic compounds (VOCs) using direct chemical ionisation (CI) mass-spectrometry has found widespread application in areas such as food science, plant studies, forensics, atmospheric science and medical applications.^{1,2} Alkanes are important target analytes in these application areas owing to their strong relationship to petroleum based fuels before and after combustion³ as well as being a product of a range of metabolic processes.⁴ Further, alkanes have been detected in the breath of cigarette smokers.⁵

CI is a blanket description for a collection of chemical processes, which produce low energy ionisation reagents. In many CI schemes detection and/or minimal fragmentation of the C₂-C₆ alkanes are difficult or impossible. Of the most commonly used CI reagents H₃O⁺ or NO⁺ show little or no reaction, while O₂⁺ reacts with all short-chain (<C₆) n-alkanes but tends to cause severe fragmentation.⁶ A suitable CI scheme should be able to produce measurably less fragmentation than O₂⁺ and react with all C₂-C₆ alkanes with similar sensitivity. The purpose of the present work was to demonstrate that the ion products produced from using CF₄ as a precursor, namely CF₃⁺ and CF₂H⁺ meet these requirements.

The three most prominent CI processes are proton transfer, charge transfer and hydride extraction. Proton transfer reaction mass spectrometry (PTR-MS) is a popular and versatile CI technique. PTR-MS relies on a reagent ion having a smaller proton affinity than a target VOC.^{1,7} The most commonly used reagents are H₃O⁺ and NH₄⁺, but there are many other suitable candidates for this role such as protonated acetone. For example, Inomata et al.⁸ used protonated acetone to differentiate between two isomeric VOCs ethyl acetate and 1,4-dioxane. Blake et al.⁹ also made use of the same technique of “bracketing” to distinguish between the isomers methyl vinyl ketone and methacrolein since protonated acetone has a proton affinity between those of the two isomers. Hydronium (H₃O⁺) does not protonate n-alkanes⁶ lower than C₆.

Another common CI method involves charge transfer where the ionisation potential of the target VOC is less than that of the reagent: common charge-transfer reagents include NO⁺ and O₂⁺. Španěl and Smith⁶ used selected ion flow tube mass spectrometry (SIFT), to investigate the reactions of H₃O⁺, NO⁺ and O₂⁺ with a large variety of VOCs including some common aromatic and aliphatic compounds. O₂⁺ with its ionisation energy (IE) of 12.07 eV reacts with all n-alkanes whose IEs range from 11.52 eV for ethane to 10.13 eV for hexane. The reactions become increasingly exothermic with an increasing number of carbon atoms in the chain. On the other hand, NO⁺ with an IE of 9.26 eV on its own cannot undergo charge transfer with the C₂-C₄ n-alkanes, but aided by the energy gained from the electric field in a drift tube, reactions with the C₅ and C₆ n-alkanes have been observed.

Chemical ionisation with NO⁺ has been used in selected situations to produce differentiation in the reaction products of structural isomers, as demonstrated by Wyche et al.¹⁰, Inomata et al.¹¹, Yamada et al.¹² and Amador-Munoz et al.¹³ have demonstrated the advantage of using a switchable ionisation mode (NO⁺/H₃O⁺/O₂⁺) in their investigations of some (>C₅) straight chain n-alkanes. Arnold et al.¹⁴ noted that while NO⁺ produced some product ions with C₄ and higher n-alkanes, the low yields observed counted against the use of NO⁺ as a precursor. More recently Koss et al.¹⁵ published the results of an extensive GC-MS/CI-TOF-MS survey of NO⁺ reactions with a large selection of OVOCs. Like Španěl and Smith⁶ they found NO⁺ showed no reaction with ethane, propane or n-butane, but they were able to derive a value for the sensitivity of its reaction with i-pentane by correlation with some GC-EIMS results. On the other hand, Wilson et al.¹⁶ did observe weak signs of product ions for n-alkanes with C₃ and greater, and reported approximate rate constants for them.

To date, there has been little effort to find CI reagents for use at pressures in the region of 1-10 Torr able to react with the entire set of C₂-C₆ n-alkanes with little or none of the fragmentation observed with O₂⁺. In order to address a requirement to determine the hydrocarbon composition of the components of oil shale,¹⁷ one of the avenues investigated was the use of the CF₃⁺ as a more suitable CI reagent than O₂⁺. Lias et al.¹⁸ and Tsuji et al.¹⁹ using ICR-MS found that two CF₄ ion products, CF₃⁺ and CF₂H⁺, reacted by hydride extraction to provide a promising CI means of detecting C₂-C₆ n-alkanes with less of the fragmentation produced by O₂⁺. The two relevant hydride reactions would be:

and

Further FT-ICR-MS information was provided by Dehon et al.²⁰ using CF₃⁺ ions with a selection of small n-alkanes and fluorocarbons. They found minimal fragmentation in the reaction products and demonstrated the potential of CF₃⁺ and CF₂H⁺ ions as CI reagents for alkane measurement. The observed rate constants with some common n-alkanes as reported by Lias et al.¹⁸ and Dehon et al.²⁰ showed good agreement with each other.

In this work, the reagent performance of the fluorocarbon ions CF₃⁺ and CF₂H⁺ is compared with that of O₂⁺ on the basis of yield, sensitivity and fragmentation behaviour when applied to the higher pressures common to CI Mass Spectrometry (1-10 Torr) with the presence of moisture and drift tube electric fields (E/N). As an example an application in the analysis of complex mixtures in smoker's breath is demonstrated.

Experimental

The CI-TOF-MS used in this work was a Kore P-4500-A time-of-flight mass spectrometer (Ennis et al.²¹). Positively charged CI reagent ions were reacted with the selected analyte, producing charged ion products which were then analysed by TOF-MS. The full principle and operation have been described in previous publications.^{10,22,23}

The experiments were performed at E/N values of 100 Td and 50 Td. E/N values in the region of 100 Td are typical running conditions in proton transfer work. The setting of E/N=50 Td was chosen to determine fragmentation at the lowest attainable value of E/N. The experiments were performed in conditions where the relative humidity was less than 0.01% in order to establish a baseline on which to gauge the effect of presence of moisture in the analyte. During subsequent experiments to establish the effects of moisture on yields, it was not always possible to maintain the same relative humidity values.

Reagent ions were generated by introducing pure CF₄ (BOC Special Gases, 99.999% purity) or O₂ gas (Zero Grade N2.6, BOC Special Gases), into a hollow cathode discharge ion source at a rate of 5-9 sccm. As CF₄ is a compound targeted for reduction in the Kyoto Protocol to the United Nations Framework Convention on Climate Change, care was taken to keep its usage as low as possible. Since CF₃⁺ and CF₂H⁺ both showed similar reaction rates with n-alkanes (for details see Table S-1) their combined yield was found to be a convenient metric for normalisation. The intensity of the unwanted NO⁺ and NO₂⁺, both of which could produce spurious reactions, was kept below 5% of CF₃⁺ by adjusting the discharge current and extraction voltage as described by Knighton et al.²⁴ Oxygen was used to create O₂⁺ ions at m/z=32. Since oxygen only produced one reagent ion of interest, it was only necessary to minimise intrusions from NO⁺ and NO₂⁺.²⁴

The ion source/drift tube assembly was heated and maintained at 343 K to avoid the effects caused by variation in ambient temperature. The sample pressure was maintained at 1.3 Torr while the pressure in the discharge region was also 1.3 Torr. Samples of the alkanes, ethane, propane and n-butane were supplied as 5 ppmV mixtures in nitrogen (NCP grade - BOC, Manchester). Nitrogen (also NCP grade) from the same batch used for the alkane samples was used for background measurements and the production of n-pentane and n-hexane bag samples. Mixtures of the alkane gas and N₂ produced sample concentrations, ranging from 0 to 5 ppmV. n-pentane and n-hexane samples (Sigma Aldrich) were prepared by two-stage dilution of nitrogen with 10 µl samples in 10 litre Tedlar bags to produce test concentrations in the range of 0 to 50.0 ppmV.

The effect of E/N on the production of CF₃⁺ and CF₂H⁺ using pure N₂ as the analyte was measured and the yield at 90% and close to 0% RH was measured for values of E/N ranging from 83 to 130 Td. In order to determine the effect of moisture on the experimental yield with the n-alkanes, test samples were split and passed through two mass flow controllers. One of the streams was humidified by passing through a bubbler and then recombined with the other stream. The resultant humidity was measured with a Hygrosens Hygro-Thermometer (Hygrosens Instruments GmbH, Loffingen, Germany). It was assumed that the concentration of the n-alkane was not affected by its passage through the bubbler and the combined output of the two streams was fixed at 500 sccm and a constant supply of 50 sccm was diverted for analysis in the CI-TOF-MS while the rest was vented to atmosphere. In order to exclude interference from moisture while performing the fragmentation measurements all traces of moisture were eliminated from the system. During the experiment to investigate the effects of moisture on ion yields it proved impractical to maintain the same degree of dryness for the wet/dry comparisons.

Results and Discussion

Introducing undiluted CF₄ into an electrical discharge source produced two predominant ions CF₃⁺ and CF₂H⁺ at m/z = 69 and 51, respectively. Discharging CF₄ produces CF₃⁺ and CF₂⁺ which rapidly interconverts in the presence of water to produce CF₂H⁺. The formation of CF₂H⁺ was strongly influenced by the value of E/N so that its relative abundance dropped from values ranging from 20% to 40% at 50 Td to 3% or often less than 1% at 100 Td at which stage it was possible to ignore its contribution to the reactions. It is worth noting that in Proton Transfer Reactions, H₃O⁺.H₂O water clusters have different Proton Affinities from the parent H₃O⁺ ions. Similarly the differing contributions of CF₃⁺ and CF₂H⁺ can also be a complicating factor and as in the case of H₃O⁺ and H₃O⁺.H₂O the mix of the two ions are sensitive to the value of E/N within the body of the drift tube reactor. The initial experiments were conducted in dry conditions (RH < 0.01%) to minimise the effect of water vapour in the sample mix. Using CF₄ as the CI precursor, ethane, propane and n-butane showed negligible signs of fragmentation at 50 Td and 100 Td (see Tables 1 and 2). The derived spectrum at 100 Td for each alkane was clear and unambiguous with minimal fragmentation. Figure 1 shows a composite spectrum of ethane, propane and n-butane. Pentane and hexane underwent some fragmentation, although this was less pronounced at 50 Td than at 100 Td. The present study found that the main fragments for pentane and hexane were the C_nH_{2n-1} ions following hydride extraction at 71 and 85 amu respectively and the propyl ion (C₃H₇⁺) at 43 amu, which seemed to be a favoured candidate for formation when energetically allowed.

Pentane exhibited some fragmentation in contrast to the results of Dehon *et al.*²⁰ who reported that while they observed complete fragmentation in pentane, there were weak signs of hydride transfer in hexane. Kinetic studies of the possible reaction mechanisms by the same group (Latappy *et al.*²⁵) showed that apart from direct hydride transfer which was not favoured, an alternative two-stage reaction scheme was possible in which a C₃H₇⁺ fragment rather than CF₃⁺ initiated the hydride transfer with the alkane molecule. While contributions

from such two-stage reaction processes would be small in low pressure working, at higher working pressures contributions from this route could become significant. Discussions with Mestdagh²⁶ confirmed from a re-examination of the original data²⁰ showed traces of hydride transfer were also observed in pentane and hexane. The secondary effect would be expected to be more prominent at higher working pressures and a characteristic would be the yield of the hydride transfer ion showing a positive deviation from linearity with increases in analyte concentration. At the higher pressures in use here, the molecular ion yields were found to be far more marked. For concentrations below 20ppm, the deviations from linearity for pentane and hexane were not significant so that it was not possible to decide whether a significant contribution from indirect hydride transfer present. For higher concentrations (> 20 ppm) the two stage reaction mode became increasingly prominent with the molecular ion yields deviating significantly.

There were no signs of electrophilic addition with HF elimination, prevalent in the reactions with unsaturated VOCs¹⁹ and carbonyl groups.²⁷ As the reactions become more exothermic, the tendency to expel secondary fragments (often in the form of the C₃H₅⁺ propyl ion) increases, and the contribution of the parent ion decreases correspondingly.

As O₂⁺ has an IE of 12.07 eV, it reacts with all the lighter n-alkanes except methane (which has an IE of 12.61 eV). In these experiments, all the n-alkanes tested underwent significant fragmentation at 100 Td as well as 50 Td. In the case of pentane and hexane, their molecular ions almost disappeared. CF₃⁺ performed far better, showing no significant signs of fragmentation of ethane, propane and n-butane, and only modest fragmentation with pentane and hexane (Figure 2). Calibration curves for all the n-alkanes, useful for data analysis, were easily obtained by partial dilution of the n-alkane with N₂ (Figure 3).

The detection sensitivity defined as the number of normalised counts per unit concentration over a given timescale for CF₃⁺ derived products at 100 Td (see Table 3) are slightly higher than those obtained with O₂⁺. The more “aggressive” action of O₂⁺ causes greater fragmentation throughout that shows up as lower peak intensities for the molecular ion and fragment ions. The LODs at 100 Td with CF₃⁺ were on average 0.014 ppm for a data acquisition run of 10 minutes not unexpected for reactions displaying low detection sensitivity, but acceptable when dealing with VOC concentrations of several ppmV. Detailed S:N and LOD and Signal to Noise figures for CF₃⁺ and O₂⁺ can be found as supplementary information in Tables S-4 and S-5. The LOD figures for O₂⁺ were worse than those for CF₃⁺. With the advent of newer high performance ion sources and further optimisation substantial performance improvements are likely. Extended versions of the Fragmentation Tables 1 and 2 can be found in the supplementary information section as Tables S-2 and S-3.

In order for the two fluorocarbon ions to qualify as useful CI reagents in the real world it is important to understand their origins and properties and the other factors affecting their production. For work at low E/N values such as 50 Td, less fragmentation occurs but the effect of larger quantities of CF₂H⁺ in the reagent mix will have to be taken into account.

CF₂H⁺ is believed to result from hydride transfer involving CF₂⁺ and background H₂O. At pressures of 10⁻⁶ Torr, Eyler et al.²⁸ observed that CF₂⁺ ions were only present in small traces that reacted swiftly with the CF₄ neutral species to form CF₃⁺ ions and so they were essentially absent from the ICR-MS work within 5 ms. At pressures of 0.1 Torr and higher Ehlerding et al.²⁹ produced CF₂⁺ ions in substantial quantities at 1 Torr in quantities sufficient to provide feed stock for CF₂H⁺ generation. At 50 Td the CF₂⁺ ions can react with H₂O by proton extraction to form CF₂H⁺. When E/N is raised to 100 Td an alternate reaction dominates and CF₂⁺ reacts with the reagent gas CF₄ to form CF₃⁺ ions as outlined by Eyler et al.²⁸. Thermodynamic calculations confirm that the reaction of H₂O with CF₂⁺ giving CF₂H⁺ is barely exothermic ($\Delta H = -13.2$ kJ mol⁻¹) but additional energy from the increased E/N could inhibit this exit

channel in favour of the competing reaction of CF_2^+ with its parent CF_4 to form CF_3^+ ($\Delta H = -92.18 \text{ kJ mol}^{-1}$) (see Table S-6 in the supplementary information).

In the initial exploratory experiments the relative humidity of the analytes did not exceed 0.01% to minimise interference from H_3O^+ . Dehon et al.²⁰ reported no signs of CF_3^+ ions reacting with H_2O present in ambient air at pressures of 10^{-4} Torr although when present as pure water vapour at the same pressure the presence of H_3O^+ was detected accompanied by a reduction in the yield of CF_3^+ . The presence of water could be considered as an additional component in the sample mix competing with the n-alkanes. Increases in relative humidity caused a significant reduction in yield of both the precursor and analyte products. The yield ratio decreased rapidly for $E/N < 100 \text{ Td}$ (see Figure 4). The n-alkanes also showed a drop in yield shown in more detail in Table S-7 in the supplementary information. The effects of significant moisture in the analyte would make it impossible to do useful work at 50 Td in any but the driest conditions.

Based on the calculations outlined in Table S-6, equation 1, it was found that that the reaction

is strongly endothermic ($\Delta H = +361.7 \text{ kJ mol}^{-1}$). As an alternative, Dehon et al.²⁰ proposed a two stage process in which firstly a thermodynamically allowed intermediate complex was formed, and then followed by a favoured proton transfer :

followed by

As the concentration of H_3O^+ rises as a result of lower E/N or higher moisture it will be necessary to account for contributions from this source. Where a multi-ion capability is available on the CI-TOF-MS, sample spectra using H_3O^+ can provide background estimation.

As the concentration H_3O^+ rose an encroaching group with a mass of 29.02 amu gained in prominence and partially obscured the C_2H_5^+ ethyl peak from ethane at 29.06 amu. The mass separation between the two groups is sufficient to resolve the two groups in modern instruments with mass resolutions of $m/\Delta m \sim 4000$ or better. While the same interfering group was observed when tested with pure N_2 as analyte, its origin has not been established satisfactorily. The phenomenon is not peculiar to the current work, as it has also been observed in conventional hydronium PTR work. The proton affinity of N_2 (493 kJ mol^{-1}) is well below that of H_2O (691 kJ mol^{-1}) and CF_2O (667 kJ mol^{-1}) so that forming N_2H^+ by proton transfer is not favoured, but cannot be excluded entirely. Another candidate with the same mass is CHO^+ but it is not clear by what mechanism it would be produced.

As a demonstration of the use of the fluorocarbon reagent in complex mixtures, samples of exhaled cigarette smoke were analysed using in a CI-TOF-MS using CF_4 as a CI reagent. Exhaled cigarette smoke is known to contain significant concentrations of n-alkanes.⁵ Figure 5 depicts the time evolution post-exposure of n-alkane decay in real-time, of a range of n-alkanes in a complex mixture. This would not be possible with a conventional GC-MS technique nor straight forward if using O_2^+ as the CI reagent.

CF_3^+ has been shown to be effective reagent ion for detecting the lighter n-alkanes. Unlike the reagents, H_3O^+ and NO^+ , both CF_3^+ and O_2^+ do react with all the C_2 - C_6 n-alkanes and with similar

detection sensitivity. The presence of moisture in the analyte complicates the analysis necessitating frequent calibration runs with known standards. However, CF_3^+ causes far less fragmentation than O_2^+ . The presence of the companion CF_2H^+ ions could complicate the analysis of the results, but interference from both these sources can be contained by adjusting the E/N. The main body of the experiments were carried out in conditions where the presence of complicating reactions such as water vapour and the effects of discontinuities in E/N such as those normally encountered in the CID (collision-induced dissociation) section of the drift tube were kept to a minimum. The important roles played by the presence of moisture and the ability of E/N to control the balance of the reactants have been studied, and some insight into the limits of applicability of the technique has been gained. Further studies of the behavior of CF_3^+ with other VOCs and OVOCs are required to test the advantages and limitations of CF_3^+ as an all-purpose reagent.

In the past, detecting the lighter n-alkanes using the conventional CI methods has presented a challenge. Either there was no reaction or when there was, it was accompanied by substantial fragmentation, CF_3^+ appears to be a worthy addition to the range of CI precursors and present new opportunities. When alkanes higher than C_4 are present, they will produce fragments that interfere with the lighter alkanes, so that their concentration can be estimated from the size of the $\text{C}_n\text{H}_{2n+1}$ groups. The yield change of these groups in moving from 100Td operation to 50Td, while substantial for a large change of E/N would be manageable when taking precautions to prevent variations in E/N during an experiment. Future work should include the effect on fragmentation of higher E/N values where greater fragmentation could be expected.

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Figures & Tables

Name	<i>m/z</i>	Fragments	% (CF ₄)	%ICR-MS*	%(O ₂)	% CF ₃ ⁺
ethane C ₂ H ₆	28	C ₂ H ₄ ⁺			14	80
	29	C ₂ H ₅ ⁺	99		83	
propane C ₃ H ₈	28	C ₂ H ₄ ⁺		-	28	77
	29	C ₂ H ₅ ⁺	1		4	
	43	C ₃ H ₇ ⁺	99		64	
n-butane C ₄ H ₁₀	43	C ₃ H ₇ ⁺	1	-	73	82
	57	C ₄ H ₉ ⁺	96		17	
n-pentane C ₅ H ₁₂	43	C ₃ H ₇ ⁺	6		45	60
	57	C ₄ H ₉ ⁺	1	93	11	
	71	C ₅ H ₁₁ ⁺	93	7	30	
n-hexane C ₆ H ₁₄	56	C ₄ H ₈ ⁺			28	64
	57	C ₄ H ₉ ⁺	5	47	42	
	85	C ₆ H ₁₃ ⁺	74	21	17	

*From Mestagh³¹

Table 1 - Relative abundance of the principal ion fragments observed at E/N=50 Td. An extended table of all the observed fragments can be found in Table S-2 in the supplementary information. The relative abundance of CF₂H⁺/(CF₂H⁺ + CF₃⁺) was higher for analytes prepared in Tedlar bags. This resulted in a reduced relative yield of CF₃⁺ (shown in the rightmost column).

Name	<i>m/z</i>	Fragments	% (CF ₄)	%(O ₂)	% CF ₃ ⁺
ethane C ₂ H ₆	28	C ₂ H ₄ ⁺		30	99.6
	29	C ₂ H ₅ ⁺	94	57	
propane C ₃ H ₈	28	C ₂ H ₄ ⁺		36	99.2
	29	C ₂ H ₅ ⁺	1	11	
	43	C ₃ H ₇ ⁺	97	45	
n-butane C ₄ H ₁₀	43	C ₃ H ₇ ⁺	1	74	99.6
	57	C ₄ H ₉ ⁺	96	4	
n-pentane C ₅ H ₁₂	43	C ₃ H ₇ ⁺	25	52	99.3
	57	C ₄ H ₉ ⁺		11	
	71	C ₅ H ₁₁ ⁺	75	3	
n-hexane C ₆ H ₁₄	56	C ₄ H ₈ ⁺		31	99.3
	57	C ₄ H ₉ ⁺	6	47	
	85	C ₆ H ₁₃ ⁺	44	1	

Table 2 - Relative abundance of observed ions at E/N=100 Td. An extended table of all the observed fragments can be found in Table S-3 in the supplementary information. The relative abundance of CF₂H⁺/(CF₂H⁺ + CF₃⁺) was higher for analytes prepared in Tedlar bags. This resulted in a reduced relative yield of CF₃⁺ (shown in the rightmost column).

Target alkane	ethane	propane	n-butane	n-pentane	n-hexane
m/z	29	43	57	71	85
Reagent					
CF ₃ ⁺	68.7	183.8	195.9	145.0	40.8
O ₂ ⁺	45.8	25.3	5.3	24.8	11.8

Table 3 – Comparative detection sensitivity at 100 Td of the C₂-C₆ alkanes with CF₃⁺ and O₂⁺. While the overall detection sensitivities rise with increasing length of the Carbon chain, more fragments occur, especially with O₂⁺. All sensitivities are in the units of counts min⁻¹ ppm⁻¹

Figure 1. Composite spectra for ethane, propane and butane at $E/N = 100$ Td using CF_3^+ as the reagent ion. For each component a background spectrum has been subtracted.

Figure 2 - Relative abundance of alkane molecular ions with O_2^+ and CF_3^+ at $E/N = 50$ Td and $E/N = 100$ Td.

Figure 3. Calibration plot for the $C_2 - C_6$ alkanes at $E/N=100Td$. The range of concentrations used with pentane and hexane extends beyond 5 ppm so that truncated versions of these are shown here. The vertical axis shows the accumulated counts per minute while the concentration of the analytes are shown as parts per million. For the calibration runs care was taken to minimise the presence of moisture so that CF_2H^+ ions contributed to less than 1% of the combined reactant population for all the n-alkanes tested. The deviation from a linear response for n-pentane and n-hexane for concentrations higher than 20ppm was noted and excluded from the estimates for the calibration *curves*. The causes are discussed in the text.

Figure 4. Dependence of reactant yields, ($\text{CF}_3^+ + \text{CF}_2\text{H}$) expressed as I_{90}/I_0 for moist (RH 90%) and dry (RH 0%) as a function of E/N . Neighbouring values of E/N in the region of 100 Td offer the best compromise between fragmentation and reactant reduction. In this area yields were most sensitive to small changes of E/N . The measurements used N_2 as the analyte to avoid interference from competing reactions.

Figure 5 - Decrease in the concentration of ethane (m29) and pentane (m71) in the breath of a volunteer cigarette smoker. The derived normalised count rate from 5 ppm ethane and pentane standards are shown in the group labelled B+S for comparison. Breath samples were then taken immediately after inhalation (t0) and then at 10 minutes (t1) and 30 minutes (t2) after inhalation. The influence of moisture and E/N on the ion yields are discussed in detail in the Results and Discussion section. This is early work and in the absence of detailed data it was assumed that since the breath sample had 90% RH at 298 K, the yields observed were 40% of the yield in the absence of moisture. Subsequent investigation into the effects of moisture on yields indicated that the initial assumptions of relative humidity were probably exaggerated. The observed CF_3^+ yields at time t0 was 65% and 78% at times t1 and t2 suggest that RH was considerably lower, possibly 40% to 50% resulting in alkane yields reduction of about 50%.

Supplementary information

		(a)CF ₂ H ⁺	(a)CF ₃ ⁺	(b)CF ₃ ⁺
methane	CH ₄			
ethane	C ₂ H ₆	5.5	3.7	3.2
propane	C ₃ H ₈	8.6	5.9	5.0
n-butane	C ₄ H ₁₀	11.8	7.5	6.2
n-pentane	C ₅ H ₁₂	13.1	8.9	8.9
n-hexane	C ₆ H ₁₄		10.5	8.6

Table S-1. Rate Coefficients of Hydride Transfer with linear n-alkanes ($k / 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

- a. Source: Lias et al.¹⁸
- b. Source: Dehon et al.²⁰

<u>Name</u>	<u>m/z</u>	<u>Fragments</u>	<u>% (CF₄)</u>	<u>% (O₂)</u>	<u>% CF₃[±]</u>
Ethane C ₂ H ₆	26	C ₂ H ₂ ⁺		1	80
	27	C ₂ H ₃ ⁺		2	
	28	C ₂ H ₄ ⁺		14	
	29	C ₂ H ₅ ⁺	99	83	
Propane C ₃ H ₈	26	C ₂ H ₂ ⁺		1	77
	27	C ₂ H ₃ ⁺		1	
	28	C ₂ H ₄ ⁺		28	
	29	C ₂ H ₅ ⁺	1	4	
	41	C ₃ H ₅ ⁺		2	
	43	C ₃ H ₇ ⁺	99	64	
n-Butane C ₄ H ₁₀	26	C ₂ H ₂ ⁺		<1	82
	27	C ₂ H ₃ ⁺		1	
	28	C ₂ H ₄ ⁺		3	
	29	C ₂ H ₅ ⁺	1	3	
	41	C ₃ H ₅ ⁺		2	
	43	C ₃ H ₇ ⁺	1	73	
	57	C ₄ H ₉ ⁺	96	17	
n-Pentane C ₅ H ₁₂	28	C ₂ H ₄ ⁺		1	60
	29	C ₂ H ₅ ⁺		3	
	41	C ₃ H ₅ ⁺		5	
	42	C ₃ H ₆ ⁺		2	
	43	C ₃ H ₇ ⁺	6	45	
	56	C ₄ H ₈ ⁺		3	
	57	C ₄ H ₉ ⁺	1	11	
	71	C ₅ H ₁₁ ⁺	93	30	
n-Hexane C ₆ H ₁₄	29	C ₂ H ₅ ⁺		<1	64
	41	C ₃ H ₅ ⁺		1	
	43	C ₃ H ₇ ⁺	20	5	
	56	C ₄ H ₈ ⁺		28	
	57	C ₄ H ₉ ⁺	5	42	
	58	C ₄ H ₁₀ ⁺		3	
	71	C ₅ H ₁₁ ⁺	1	3	
	85	C ₆ H ₁₃ ⁺	74	17	

Table S-2. Relative abundance of observed ions at E/N=50Td. The relative abundance of CF₂H⁺/*CF₂H⁺ + CF₃⁺) was higher for standards prepared in Tedlar bags. This resulted in a reduced relative yield of CF₃⁺(shown in the rightmost column).

<u>Name</u>	<u>m/z</u>	<u>Fragments</u>	<u>% (CF₄)</u>	<u>%(O₂)</u>	<u>% CF₂H⁺</u>
Ethane C ₂ H ₆	26	C ₂ H ₂ ⁺		2	99.6
	27	C ₂ H ₃ ⁺	4	10	
	28	C ₂ H ₄ ⁺		30	
	29	C ₂ H ₅ ⁺	94	57	
Propane C ₃ H ₈	26	C ₂ H ₂ ⁺		2	99.2
	27	C ₂ H ₃ ⁺		2	
	28	C ₂ H ₄ ⁺		36	
	29	C ₂ H ₅ ⁺	1	11	
	41	C ₃ H ₅ ⁺	2	4	
	43	C ₃ H ₇ ⁺	97	45	
n-Butane C ₄ H ₁₀	26	C ₂ H ₂ ⁺		<1	99.6
	27	C ₂ H ₃ ⁺		1	
	28	C ₂ H ₄ ⁺		3	
	29	C ₂ H ₅ ⁺	1	8	
	41	C ₃ H ₅ ⁺		7	
	42	C ₃ H ₆ ⁺		2	
	43	C ₃ H ₇ ⁺	1	74	
	57	C ₄ H ₉ ⁺	96	4	
n-Pentane C ₅ H ₁₂	27	C ₂ H ₃ ⁺		<1	99.3
	29	C ₂ H ₅ ⁺		2	
	41	C ₃ H ₅ ⁺		20	
	42	C ₃ H ₆ ⁺		8	
	43	C ₃ H ₇ ⁺	25	52	
	56	C ₄ H ₈ ⁺		4	
	57	C ₄ H ₉ ⁺		11	
	58	C ₄ H ₁₀ ⁺		<1	
	71	C ₅ H ₁₁ ⁺	75	3	
n-Hexane C ₆ H ₁₄	29	C ₂ H ₅ ⁺		1	99.3
	41	C ₃ H ₅ ⁺	2	7	
	42	C ₃ H ₆ ⁺		1	
	43	C ₃ H ₇ ⁺	48	8	
	56	C ₄ H ₈ ⁺		31	
	57	C ₄ H ₉ ⁺	6	47	
	58	C ₄ H ₁₀ ⁺		2	
	71	C ₅ H ₁₁ ⁺	<1	2	
	85	C ₆ H ₁₃ ⁺	44	1	

Table S-3. Relative abundance of observed ions at E/N=100Td. The relative abundance of CF₂H⁺/(CF₂H⁺ + CF₃⁺) was higher for analytes prepared in Tedlar bags. This resulted in a reduced relative yield of CF₃⁺(shown in the rightmost column).

Name	Fragment	100Td		50Td	
		S:N	LOD (ppm)	S:N	LOD (ppm)
Ethane	C ₂ H ₅ ⁺	2678	0.006	4755	0.003
Propane	C ₃ H ₇ ⁺	1046	0.014	1277	0.011
n-Butane	C ₄ H ₉ ⁺	24002	0.001	52560	0.001
n-Pentane	C ₅ H ₁₁ ⁺	2253	0.030	2678	0.030
n-Hexane	C ₆ H ₁₃ ⁺	1267	0.017	2249	0.003

Table S-4. Limits of detection (LOD) for the alkane/CF₃⁺ reactions for a run of 10 minutes. Operating at 50Td was degraded by increased background noise. Both the Signal to Noise (S:N) and the Limits of Detection (LOD) are calculated in accordance with the IUPAC recommendations ³⁰.

Name	Fragment	100Td		50Td	
		S:N	LOD (ppm)	S:N	LOD (ppm)
Ethane	C_2H_5^+	4475	0.003	8182	0.002
Propane	C_3H_7^+	4590	0.003	22145	0.001
n-Butane	C_4H_9^+	1172	0.013	18076	0.001
n-Pentane	$\text{C}_5\text{H}_{11}^+$	2363	0.006	10665	0.029
n-Hexane	$\text{C}_6\text{H}_{13}^+$	1942	0.008	5161	0.003

Table S-5. Limits of detection (LOD) for the alkane/ O_2^+ reactions for a run of 10 minutes. Both the Signal to Noise (S:N) and the Limits of Detection (LOD) are calculated in accordance with the IUPAC recommendations.³⁰

1. $\text{CF}_3^+ + \text{H}_2\text{O} \rightarrow \text{CF}_2\text{H}^+ + \text{HOF} \quad \Delta H = +361.7 \text{ kJ mol}^{-1}$
2. $\text{CF}_3^+ + \text{H}_2\text{O} \rightarrow \text{CF}_2\text{OH}^+ + \text{HF} \quad \Delta H = -142.8 \text{ kJ mol}^{-1}$
3. $\text{CF}_2^+ + \text{H}_2\text{O} \rightarrow \text{CF}_2\text{H}^+ + \text{OH} \quad \Delta H = -13.2 \text{ kJ mol}^{-1}$
4. $\text{CF}_2^{2+} + \text{H}_2\text{O} \rightarrow \text{CF}_2\text{OH}^+ + \text{H}^+ \quad \Delta H = -1725.5 \text{ kJ mol}^{-1}$
5. $\text{CF}_2^+ + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{CF}_3 \quad \Delta H = -92.185 \text{ kJ/mol}^{-1}$

Table S-6. Thermochemistry Calculations.

MP2/6-311G** calculations, ZPE was taken in to account. At E/N = 100Td, the centre of mass energy due to the electric field in the drift tube was 9.04 kJ mol^{-1} to which should be added the thermal energy of 4.19 kJ mol^{-1} for a total of $13.32 \text{ kJ mol}^{-1}$. A small presence of CF_2OH^+ at $m/z=67$ was noted in all the spectra. The value of ΔH obtained for reaction 2 above is in reasonable agreement the value of $\Delta H = -164.5 \text{ kJ mol}^{-1}$ reported by Grandinetti et al.³¹

n-Alkane	Mass (amu)	Percentage yield				Rel. CF ₃ ⁺ yield wet/dry %
		RH=0.1%	RH=20%	RH=45%	RH=90%	
Ethane	29	100	-	-	40	82/94
Propane	43	100	76	57	45.4	75/90
n-Butane	57	100	82	66	44.9	80/93
n-Pentane	71	100	82	65	44.9	73/82
	43	100	78	60	41.4	
n-Hexane	85	100	72	52	34.6	73/82
	57	100	77	58	44.4	
	43	100	78	58	41.2	

Table S-7. The effect of ambient moisture ranging from 0.1% to 90% RH on the yield of the principal fragments of the n-alkane reactions with CF₃⁺ and CF₂H⁺. In spite of the low relative humidity of the analytes, persistent residual moisture in the system had a significant effect on the results. The resolution of the equipment was not sufficient to distinguish between C₂H₅⁺ and an unidentified group possibly N₂H⁺ or COH⁺. The variation in the yield of the ion fragments are very similar. The value of E/N was ca. 100 Td, a region where the reactants' yield was most sensitive to small shifts in the value of E/N.