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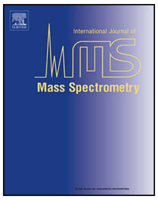

Full Length Article

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-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.

1. 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 al. [2] 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 transfer [3] 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-MS [8] 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

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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.

2. 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 H_2O/H_3O^+ and the second CF_4/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 experiments [9] 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_{00} (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 100 Td the observed ratio was in the region of 25%, 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 l 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 CIR-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 CIR-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–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–S33.

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.

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

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 VOC and its associated ion
- R represents the ion (R^+) that remains after hydrogen loss (as shown in Eq. (1))
- RH + 3 represents the ion ($(RH + F - O)^+$) in which fluorine has replaced oxygen in C═O carbonyl group (Eq. (2))
- RCF2 represents the ion (RCF_2^+) where CF_3^+ replaces H in RH with the formation of an HF molecule. This reaction is described by Eqs. (4a) and (4b). Occasionally, a similar reaction will occur with a substituent of the analyte molecule.
- RHCF3 ions are created as adducts ($RHCF_3^+$) of electrophilic CF_3^+ 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 H_3O^+.
- RHCF and RHCHF2 cations are created from reactions with the secondary reagent CF_2H^+ 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.

3. Results and discussion

The products of the reactions of H_3O^+ and CF_3^+ with the VOC analytes are shown in Tables 2a–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 Fig. 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 2a–2c and Table 3a–3c3a–3c, it can be seen that CF_3^+ reagent ions can react in several different ways

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