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Product ion distributions for the reactions of NO^+ with some N-containing and O-containing heterocyclic compounds obtained using SRI-TOF-MS

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ABSTRACT

Product ion distributions for the reactions of NO^+ with nine O-containing and six N-containing heterocyclic compounds present in human volatilome have been determined under the conditions of a Selective Reagent Ionization Time of Flight Mass Spectrometer (SRI-TOF-MS) at E/N values in the drift tube reactor ranging from 90 to 130 Td. This study was undertaken to provide the kinetics data by which these heterocyclic compounds could be analyzed in biogenic media using SRI-TOF-MS. The specific heterocyclic compounds are furan, 2-methylfuran, 3-methylfuran, 2,5-dimethylfuran, 2-pentylfuran, 2,3-dihydrofuran, 1,3-dioxolane, 2-methyl-1,3-dioxolane, γ-butyrolactone, pyrrole, 1-methylpyrrole, pyridine, 2,6-dimethylpyridine, pyrimidine, and 4-methylpyrimidine. Charge transfer was the dominant mechanism in the majority of these NO^+ reactions generating the respective M^+ parent cation, but in the pyridine, pyrimidine, and 4-methylpyrimidine reactions, stable NO^+M adduct ions were the major products with M^+ ions as minor products. The reactions of dioxolanes with NO^+ proceeded by hydride ion transfer only producing $(M-H)^+$ ions. Fragmentation of the excited nascent product ions $(M^+)^*$ did not occur for the majority of these reactions under the particular chosen conditions of the SRI-TOF-MS reactor, but partial fragmentation did occur in the 2,3-dihydrofuran and 2-pentylfuran reactions. However, lowering of the E/N in the drift tube suppresses fragmentation of $(M^+)^*$ ions and promotes the formation of NO^+M adduct ions, whereas increasing E/N has the opposite effect, as expected. The product ion distributions were seen to be independent of the humidity of the sample gas.

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1. Introduction

Volatile heterocyclic compounds are commonly reported constituents of the human volatilome. Members of this chemical family have been detected in human breath [1–3], urine [3–6], blood [2] and skin emanations [7–9]. In vitro studies evidenced the production of heterocyclic compounds by pathogenic organisms responsible for several diseases and thereby revealed the potential of these volatile organic compounds (VOCs) for non-invasive diagnosis and therapy monitoring [10–12]. For instance, 2-pentylfuran was shown to be a biomarker for lung colonization/infection by fungal pathogens [12,13], whereas pyrrole and 3-methylpyrrole were suggested to be chemical indicators of *Pseudomonas aeruginosa* infections [11]. Several heterocyclics in urine were also suggested as potential indicators of prostate cancer [14]. Thus, the analysis of volatile heterocyclic compounds in exhaled breath and the headspace of other biogenic fluids could be a valuable diagnostic tool.

The human volatilome consists of hundreds of VOCs representing different chemical families [15]. Reliable identification and quantification of compounds/biomarkers in such a complex matrix can pose a number of analytical challenges and problems. Real-time mass spectrometric analytical techniques [16], such as proton-transfer reaction mass spectrometry (PTR-MS) and selected ion

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[1] It is with deep sadness that we record the untimely passing of our dear friend and co-author Anton Amann who contributed very much to the research described in this paper and indeed initiated the project. In addition to being a great friend to all of us and an exceptional human being, Anton was variously a mentor and highly respected colleague and excellent scientist who will be greatly missed.

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flow tube mass spectrometry (SIFT-MS) [17,18], are particularly attractive analytical methods for detecting and quantifying VOCs in biological, medical and environmental matrices. This is due to their versatility, excellent sensitivity and real-time response. In particular, the last feature opens up a new fascinating opportunity of tracking rapid short-time changes in the human volatilome, which can provide invaluable information on normal and abnormal processes occurring in the body [19–22]. Moreover, real-time analysis improves the quality and reliability of the results, since sample collection, storage and pre-concentration that can result in loses of trace compounds and contamination are avoided. Recently, the analytical power of the classic PTR-MS instruments has been notably improved by the exploiting time-of-flight (TOF) mass spectrometry and by allowing precursor (reagent) ions such as NO^+, O_2^+, and Kr^+ to be used as alternatives to the usual H_3O^+ ions, thus creating a Selective Reagent Ionization Time of Flight Mass Spectrometry (SRI-TOF-MS) [23,24]. In particular, the TOF mass filter provides higher mass (m/z) resolving power (up to 5000 $m/\Delta m$), which facilitates the separation of isobaric analyte ions that are sometimes formed during the analysis of the human volatilome.

The main goal of the present study was to determine the product ion distributions for the reactions of NO^+ ions with some selected N-containing and O-containing heterocyclic compounds using an SRI-TOF-MS instrument. The reactions of NO^+ with several S-containing heterocyclic compounds were the subject of our recent articles [25,26], where the true value of NO^+ reagent ions was demonstrated. A valuable characteristic of NO^+ reactions with VOCs is the diversity of reaction mechanisms that occur under thermal energy conditions, as revealed by numerous SIFT-MS studies [17]. These include charge (electron) transfer, hydride ion (H^-) transfer, hydroxide ion (OH^-) transfer, alkoxide ion (OR^-) transfer and NO^+ ion-molecule association. Interestingly, different chemical classes of VOCs undergo characteristic reaction processes with NO^+, which is analytically very useful and in some cases helps to identify structural isomers of compounds [16–18]. The product ion distributions of the reactions of NO^+ with most VOCs under the suprathermal energy conditions of SRI-TOF-MS reactors [24] are poorly known. This situation limits the applicability of SRI-TOF-MS instruments for trace gas analysis. The present study and our previous studies of NO^+ reactions with aldehydes and organosulphur compounds [24,25] are intended to partially fill this literature data gap and thus to facilitate analyses of these classes of VOCs in biogenic media.

2. Experimental

2.1. Materials and standard mixtures

Single-compound calibration mixtures were prepared from the pure liquid heterocyclic compounds, which were purchased from Sigma–Aldrich (Austria), SAFC (USA), and Alfa Aesar (USA). The purity of each liquid compound is given in Table 1 to assist interpretation of the observed product ion distributions of the reactions. All purities are seen to be better than 97% with the majority at 99%.

Gaseous standard mixtures were prepared using the procedure described in our recent article [26]. It should be stressed that the product ion distributions were investigated using 3 distinct concentrations of each analyte in high purity air at partial pressures ranging from approximately 20 to 230 ppbv and at two different absolute humidity levels of <0.1% and 4.9%, the latter approximately corresponding to that of exhaled breath.

2.2. SRI-TOF-MS analysis

The NO^+ reactions were studied using an Ionicon Analytik (Innsbruck, Austria) type 8000 SRI-TOF-MS instrument and the analytical procedure outlined in Mochalski et al. [26]. The settings of the ion source were chosen as follows: ion source current 5 mA, source voltage (Us) 20 V, source-out voltage (Uso) 70 V, and source valve opening 40%. The levels of the major "impurity ions" relative to that of the NO^+ precursor ion for these conditions were H_3O^+ (0.2–0.3%), O_2^+ (0.3–0.4%) and NO_2^+ (1.3–1.5%). The NO^+/heterocyclic compound reactions occurred in the drift tube at a total pressure of 2.3 mbar and at a gas temperature of 60 °C. The product ion distributions were investigated for five distinct E/N ratios in the reaction tube ranging from 90 to 130 Td with incremental changes of 10 Td, as adjusted by changing the voltage difference along the drift section over the range of 400–600 V. The ion mass (m/z) calibration was regularly checked using the presence of the impurity ions of known m/z values: H_3O^+ (19.0178), $^{15}NO^+$ (30.9945), and NO_2^+ (45.9924).

The instrument-specific ion mass-dependent discrimination functions ("transmission") was determined using a standard gas mixture containing 14 compounds having molecular masses ranging from 21 to 180 (Restek TO-14A Aromatics Mix), in accordance with the procedure recommended by the instrument manufacturer (Ionicon Analytik) [27]. The transmission factors for the observed ions were calculated using an algorithm implemented in the software provided by the manufacturer (PTR-MS Viewer 3.1.0).

The standard mixtures of heterocyclic compounds, which act as both the sample and carrier gas, were introduced into the drift tube of the SRI-TOF-MS instrument at a steady flow rate of 20 mL/min via a 2-m long, heated (40 °C) Teflon transfer line, which minimizes the surface adsorption of water vapour and the heterocyclic compounds under study.

The spectral scans of the TOF analyzer ranged from approximately m/z 2.7 to 500 and were acquired in a time of 30 s by co-adding 750 000 single 40-μs long TOF-MS extractions recorded at a sampling frequency of $1/\Delta t = 10$ GHz. The actual mass resolution obtained from the detected peaks was ≈4000 at m/z 100. The total duration of a single measurement was 5 min, which corresponds to 10 mass spectra acquired per reactant gas concentration level. The average of the ion signal levels at each m/z value from these 10 spectra was used to calculate the percentages of the product ions for each of the NO^+/heterocyclic reactions.

3. Results and discussion

Table 1 shows the percentage product ion distributions for the reactions of NO^+ with the 15 heterocyclic compounds. These percentages refer to the ion signal intensities corrected for the transmission factors referred to above and are the averages of intensities obtained for 3 distinct mean concentrations (of 10 spectra) for each heterocyclic compound. Only product ions with abundance exceeding 2% of the total signal were included in Table 1, recognizing that signals at this low level might originate from reactions of the injected "impurity ions" with the heterocyclic compound and/or reactions of the NO^+ ions with any impurities that are present in the liquid heterocyclic compounds and appear in the sample mixture.

Scrutiny of Table 1 reveals that charge (electron) transfer producing stable M^+ parent ions is the dominant mechanism in most of the reactions; it is the single product ion channel in most of the furan reactions and in both pyrroles reactions. The small fractions of other product ions in the 2-pentylfuran reaction is probably related to the lower purity of this compound (see Table 1) and the possibility that the liquid impurities are more volatile than the majority 2-pentylfuran. The dominance of charge transfer in these heterocyclic compound reactions is surely due to their ionization energies (IE) being lower than the IE of the NO molecule (9.26 eV), equivalent to the recombination energy of ground vibronic state NO^+ [28], which energetically allows charge transfer to occur [17].

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