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Quantification of the gas phase methyl iodide using O_2^+ as the reagent ion in the PTR-ToF-MS technique

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ABSTRACT

The charge-transfer-reaction between molecular oxygen ions (O_2^+) and methyl iodide (CH_3I) is studied to investigate if consistent environmental quantification of the gas phase CH_3I is possible without prior calibration. The neutral CH_3I molecule was chosen because this compound is of atmospheric chemistry and environmental importance in the field of nuclear power plant safety and nuclear energy. Molecular oxygen was used as a reagent ion source in a commercial Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) to produce molecular oxygen ions (O_2^+). The use of O_2^+ ions allows for fast, sensitive and specific detection of gas phase CH_3I via an electron exchange reaction $O_2^+ + CH_3I \rightarrow CH_3I^+ + O_2$. The instrument response was linear in the 0.23–150 ppbv range and its sensitivity was humidity independent. The detection sensitivity of CH_3I normalized by the O_2^+ count rate of 10^6 cps was found to be $S = 22.6 \pm 0.3$ ncps/ppbv, independent of relative humidity. A typical O_2^+ primary ion signal was $(2.0 \pm 0.2) \times 10^6$ cps. The lowest measured CH_3I concentration was 0.23 ± 0.10 ppb. Error is $\pm\sigma$. The theoretical collision rate based on the dipole moment and molecular polarizability values is calculated using the Langevin collision rate (k_L) approximation, the average-dipole-orientation (ADO) theory and the capture rate coefficient (k_{CAP}) based on trajectory calculations. The experimental rate constant, k_{exp}, for the electron transfer reaction between O_2^+ ions and CH_3I is calculated to be $(1.72 \pm 0.22) \times 10^{-9}$ cm^{3}s^{-1}. Listed errors are $\pm\sigma$ and represent precision only. The experimentally determined value agrees very well with the theoretical collision rate values, $k_L = 1.24 \times 10^{-9}$ cm^{3}s^{-1}, $k_{ADO} = 1.73 \times 10^{-9}$ cm^{3}s^{-1} and $k_{CAP} = 1.48 \times 10^{-9}$ cm^{3}s^{-1}. The obtained results indicate that the PTR-MS technique is an excellent analytical method to quantify gas phase CH_3I.

1. Introduction

First observed by Lovelock et al. [1], methyl iodide is a natural photochemical source of iodine in the atmosphere [2]. As first suggested by Chameides and Davis et al. [2], iodine and its oxides play an important role in the oxidizing capacity of the troposphere [3], aerosol formation and in the ozone depleting cycles in the troposphere [4,5] and stratosphere [6]. The atmospheric photochemistry of methyl iodide is also of interest in the nuclear industry safety field to better understand chemical processes responsible for the formation of different fission products if a major nuclear power plant accident type Three Mile Island (U.S.A.) [7], Chernobyl (Ukraine) [8] and Fukushima (Japan) [9] were to occur, again. It is known that iodine and methyl iodide are two of the more important fission products that are released from UO_2 fuel during a major nuclear power plant accident in pressurized water reactors due to their volatility and radiological health impact [10]. Furthermore, methyl iodide is a fission product that is difficult to retain by post-accident filtration systems [11] and is currently used in the nuclear industry field to test the organic iodine capture ability, ageing and performance of emergency charcoal filters [12,13]. Other important methyl iodide applications include agrarian control of insects, plant parasitic metabolites, soil-borne pathogens and weed seeds [14].

To date, most gas phase environmental methyl iodide measurements are based on gas chromatographic (GC) separation equipped with a mass spectrometer (MS) or an electron capture detector (ECD). A more recent atmospheric gas phase methyl iodide measurement method is based on resonant fluorescence spectroscopy [15]. While GC-ECD (LD~10 ppt) and GC–MS (LD~100 ppt) methods are two very sensitive analytical techniques used to detect gas phase methyl iodide in various environment settings, they do not offer the time resolution and response needed to measure rapid flux or concentration changes in the gas phase. The newer resonant fluorescence technique used to detect gas phase methyl iodide in the

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atmosphere is fast, sensitive and selective but remains a research-grade instrument that requires advanced technical expertise and skills and may be difficult to apply in routine analyses. The chemical ionization mass spectrometric (CIMS) technique has the potential for fast, sensitive, specific and real time methyl iodide measurements when rapid changes in the gas phase mixing ratios need to be known or monitored continuously.

The proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) is a type of CIMS instrument. The PTR-ToF-MS combines the concept of chemical ionization [16] with the flow-drift-tube technique [17]. This technique is often used for sensitive detection of volatile organic compounds (VOCs) in the atmosphere. The two more common CI reagents used in CIMS to detect atmospheric VOCs include hydronium ions (H_3O^+) and molecular oxygens ions ($O_2{}^+$). While H_3O^+ are good proton sources, these CI reagent ions can be applied only to gas-phase compounds with proton affinities (PA) higher than that of water, PA(H_2O) = 691.0 kJ.mol^{-1} [18,19]. Since, the proton affinity of CH_3I, PA(CH_3I) = 691.7 kJ.mol^{-1} [18,19], is only slightly higher than that of water, H_3O^+ ions may not be the ideal reagent to use to detect gas phase methyl iodide. In theory, H_3O^+ ions may be used to ionize CH_3I, whilst this reaction is only slightly exothermic (ΔPA~0.7 kJ.mol^{-1}). A recent study showed that H_3O^+ ions may still be successfully used to quantify methyl iodide in the atmosphere [20]. On the other hand, $O_2{}^+$ ions are often used as an alternative chemical ionization reagent in PTR-ToF-MS. Contrary to H_3O^+, which is a soft ionizer, the $O_2{}^+$ ion is observed to be a more aggressive chemical ionization reagent. That is, the $O_2{}^+$ reagent ion ionization results in a mass spectrum not dissimilar to electron impact albeit less fragmented. That is, the more energetic $O_2{}^+$ ions produce characteristic mass spectral ̈fingerprint ̈that is less fragmented compared to electron impact and the mother ion is clearly identifiable and can be easily quantified. Contrary to the proton transfer reaction between the H_3O^+ ion and CH_3I molecule, the electron transfer reaction between $O_2{}^+$ ion (IE = 12.0697 ± 0.0002 eV) [19] and methyl iodide molecule (IE = 9.54 ± 0.02 eV) [19] is highly exothermic. As a result, the use of molecular oxygen as a CI reagent the PTR-ToF-MS instruments to detect CH_3I is proposed. It is shown that the proposed PTR-ToF-MS technique is an ideal tool for online analyses of relatively fast changing concentrations of methyl iodide

2. Experimental

The charge transfer reaction between the $O_2{}^+$ reagent ion and CH_3I was studied using a commercial PTR-ToF 8000 mass analyzer (Ionicon Analytik GmbH, Innsbruck, Austria). The experimental details that are particularly relevant to this work are given below.

Generation of gas phase CH_3I. The gas phase CH_3I concentration was generated using the gas saturation method, one of the oldest and most versatile ways of studying heterogeneous equilibria involving low vapor pressure compounds, first developed by Regnault [21]. The gas saturation method used in this work is similar to the one described originally by Markham [22]. Briefly, nitrogen carrier gas was allowed to flow though the volume containing the CH_3I sample that itself was mixed with glass beads and supported on a fritted glass surface. The saturator volume itself was immersed in a temperature-controlled fluid and kept at a constant temperature using a temperature-controlled circulating bath with an accuracy of ± 0.1 K. The temperature inside the saturator volume was measured using a Type-*J* thermocouple (Omega) with an accuracy of ±0.1 K. The carrier gas was allowed to enter the saturator volume, equilibrate with the sample and was then allowed to exit through a capillary exit and allow to flow through a glass tube. The geometry of the exiting glass tube was such that the diameter of the glass tube increased with increasing length. This was done to avoid any sample condensation as the sample and the carrier gas were allowed to leave the saturator system. Concentration of CH_3I at the exit of the saturation system was calculated from the given vapor pressure, mass flow rates, pressure within the saturator and the total pressure. Concentration of CH_3I at the exit of the saturation system was calculated using the Dalton's law of partial pressures. Assuming that the gas within the saturation system is a mixture of dry nitrogen and CH_3I, the volume mixing ratio of the latter can be defined as the following:

$$[CH_3I] = \frac{p_{CH_3I}}{p_S}$$

where P_{CH_3I} is the vapor pressure of CH_3I and P_s, the total pressure within the saturation system, was P_s = 957 Torr. The Antoine type equation used to calculate the vapor pressure of CH_3I is the following [23]:

$$\log_{10}(p) = 4.1554 - \frac{1177.78}{\mathrm{T(K)} - 32.058}$$

where the pressure p is in units of bar and the temperature T is in Kelvin and in the range from 218 K to 315.6 [23]. Under normal operating conditions, the saturator was kept at T = 274 K. At this temperature, the vapor pressure of CH_3I within the saturator was calculated to be 146.37 ± 3.40 Torr. Under typical experimental conditions, the gas phase CH_3I mixing ratio within the saturation system was about 15%. This vapor pressure was then further diluted using dry nitrogen carrier gas and a system of mass flow controllers to obtain the desired mixing ratio in the range 0.23–150 ppbv. Further, the carrier gas was allowed to pass through a bubbler filled with deionizer water at room temperature to evaluate the impact of relative humidity (%RH) on the signal sensitivity. The relative humidity was varied between 0.3 ± 0.2 and 76 ± 0.5%.

PTR-ToF-MS instrument. A commercial PTR-ToF 8000 mass analyzer (Ionicon Analytik GmbH, Innsbruck, Austria) was used to study the $O_2{}^+$ reagent ion ionization process with CH_3I. The reaction chamber pressure (pdrift) was 2.10 mbar, drift tube voltage was 544 V and the drift tube temperature was held constant at T=333.15K. The corresponding *E/N* ratio was 127 Td. (1Td=10^{-17} Vcm^2) where *E* is the electric field strength applied to the drift tube and *N* is the buffer gas density.

Materials. The nitrogen carrier gases used in this study was generated using the N2LCMS 1 Nitrogen Generator (Claind S.r.l., Italy). Iodomethane was purchased at Acros Organics (Belgium) and the stated minimum purity was 99%. To limit any photo-catalytic or thermal decomposition during storage, CH_3I original container bottles were stored under dark conditions at T = 6 °C. Oxygen gas was purchased at Linde Gas (Linde France S.A.) and had the stated minimum purity of 99.9995%. Deionized water with a resistivity greater than 18 MΩ was prepared by allowing tap water to pass first through a reverse osmosis demineralization filter (ATS Groupe Osmose) and then through a commercial deionizer (Milli-pore, Milli-Q).

3. Results

3.1. Chemical ionization scheme for CH_3I

The electron transfer reaction between the $O_2{}^+$ ion (IE = 12.0697 ± 0.0002 eV) [19] and methyl iodide molecule (IE = 9.54 ± 0.02 eV) [19] is highly exothermic. As a result, molecular oxygen appears to be an ideal reagent source to be used in the PTR-ToF-MS technique to quantify gas phase methyl iodide. Based on other works [24–26] where molecular oxygen was used as a chemical ionization reagent to detect gas phase compounds of