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A selected ion flow tube study of the reactions of H_3O^+, NO^+ and $O_2^{\bullet+}$ with methyl vinyl ketone and some atmospherically important aldehydes

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Abstract

The rate constant and product ion distribution of the reactions of H_3O^+, NO^+ and $O_2^{\bullet+}$ with methyl vinyl ketone (MVK), methacrolein (MaCR), pivaldehyde, 2-methyl-butanal, glyoxal, *o*-, *m*- and *p*-tolualdehyde have been investigated at 150 Pa and 297 K using a selected ion flow tube (SIFT). All reactions, except the NO^+/glyoxal reaction, proceed at a rate close to the collisional rate, calculated with the Su and Chesnavich model, using the polarizability and electric dipole moment of the compounds derived from quantum chemical calculations.

All H_3O^+ reactions proceed by proton transfer, non-dissociative for all compounds, except for 2-methyl-butanal, where two minor channels resulting from fragmentation after protonation are observed.

Association is the only pathway in the NO^+/MVK and NO^+/glyoxal reaction. Hydride ion transfer is the major process occurring in all the other NO^+ reactions. Elimination of CHO for pivaldehyde and association for MaCR are also non-negligible channels in their reaction with NO^+.

All $O_2^{\bullet+}$ reactions result in the parent cation by charge transfer and in at least one fragment ion.

Hydration of the product ions has been investigated by adding water vapor in the reaction zone. A method is proposed to derive the three-body association rate constants of the product ions with water and to estimate the rate constants of the reactions of the hydrated precursor ions $H_3O^+\cdot H_2O$ and $NO^+\cdot H_2O$ with the reactants.

Keywords: SIFT; Ion/molecule reactions; Aldehydes; Methyl vinyl ketone; Proton transfer; Charge transfer; Hydride ion transfer

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1. Introduction

Aldehydes and other carbonyl compounds are widespread chemicals, which play an important role in the chemistry of the polluted troposphere. They can contribute to the formation of tropospheric ozone through their photo-chemistry in the gas phase [1] and take part in the generation of secondary aerosols through heterogeneous processes [2]. On local scale, aldehydes are toxic pollutants for human health [3,4].

Carbonyl compounds and aldehydes are introduced in the atmosphere by several antropogenic and natural sources. They are emitted from combustion processes of fossil fuels, industrial processes, waste disposal and biomass burning [5–7]. In addition, they arise as secondary pollutants from the photo-oxidation of volatile organic hydrocarbons, emitted in the atmosphere by industrial and biologic processes [8–10]. They can also be produced directly by various vegetation forms [11,12].

Aldehydes have been detected in the environment by a variety of techniques, based upon Fourier transform infrared spectroscopy, differential absorption in the near UV and GC–MS [8].

A very successful technique, which has recently been used for their measurement, is proton transfer reaction-mass spectrometry (PTR-MS) [13], which is based upon the mass spec-

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trometric detection of the product ions generated from the reaction of the trace gas to be detected with H_3O^+ ions. A similar technique, which may be somewhat less sensitive, but which may allow a better identification of the chemicals to be measured, is the selected ion flow tube-mass spectrometry (SIFT-MS) method, developed and applied by Smith and co-workers for the measurement of a number of organic compounds [14–18]. In the latter method, not only the products of the reaction of the H_3O^+ ion with the compound to be detected are measured, but also the products of the reactions of NO^+ and $O_2^{\bullet+}$ ions.

The application of PTR-MS and SIFT-MS techniques, however, requires the knowledge of the kinetic and mechanistic data (reaction rate constants and product ion distribution) of the ion/molecule reactions involved.

Such data have been measured for several chemicals in the laboratory [19] and have recently been extended systematically by Španěl and co-workers to set-up a database of kinetic and mechanistic data for the detection of several organic compounds, including some aldehydes and ketones [20–22]. Although the existing database is quite extensive, some data are still missing, especially for some important atmospheric volatile compounds.

In this work, we have performed a study to extend the database to glyoxal, methacrolein (MaCR), methyl vinyl ketone (MVK), *o*-, *m*- and *p*-tolualdehyde.

The dicarbonyl compound glyoxal is formed in the atmosphere as a result of the photo-oxidation (reaction with OH) of toluene [23], which is an aromatic compound emitted in the atmosphere by automobile exhaust. Glyoxal is also a product of the photo-oxidation of other aromatic compounds [24–26] and of some biogenic species such as isoprene [27] and α-pinene [28]. Glyoxal is also believed to contribute significantly to the yield of secondary aerosols [2].

Methyl vinyl ketone and methacrolein are two major products, formed by the oxidation of isoprene (one of the major biogenic volatile organic compounds) by hydroxyl radicals and ozone, and minor products of the reaction of isoprene with NO_3 radicals [9].

The aromatic aldehydes *o*-, *m*- and *p*-tolualdehyde are emitted into the atmosphere as pollutants from motor vehicles [29,30] and are also produced in the atmosphere from the oxidation of xylenes [24,26,31]. Xylenes are released to the atmosphere from industrial sources, such as chemical plants, and from automobile exhaust.

In addition to these six compounds, reviewed above, we have added to our study the ion/molecule reactions of H_3O^+, NO^+ and $O_2^{\bullet+}$ with pivaldehyde and 2-methyl-butanal, two other atmospherically important aldehydes.

Apart from giving the information required for in situ detection of these compounds through SIFT-MS, our present data also give information for PTR-MS applications.

When SIFT-MS is used to identify and to quantify trace gases in various applications (such as environmental or breath analysis) the samples are generally "humid". Therefore, it is essential to know if the ionic products of the H_3O^+, NO^+ and $O_2^{\bullet+}$ reactions associate with water and if the hydrates of the precursor ions also react with the trace gases under consideration. The formation of hydrates of the ionic products has thus also been studied here by introducing water vapor into the flow tube. Three-body association rate constants for the protonated products (see Section 3.2.1) and reaction rate constants for $H_3O^+{\cdot}H_2O$ and $NO^+{\cdot}H_2O$ with the reactants (see Section 3.1) have been derived, using a method described in Appendix A.

2. Experimental

Measurements are performed with a selected ion flow tube similar to the original design by Smith and Adams [32]. Since a detailed description of the equipment has been given in a previous publication [33], only a brief review of the instrument is given here.

The precursor ions H_3O^+, NO^+ and $O_2^{\bullet+}$ are generated in a microwave discharge in a mixture of air and water vapor at a total pressure of 20 Pa. By a set of electrostatic lenses ions are extracted from the discharge into a differentially pumped quadrupole mass spectrometer, which selects the appropriate ion. The mass selected ions are then injected into a 51 cm long flow tube with inner diameter of 4 cm, where they are convectively transported by a helium buffer gas flow. The reactant gas is introduced through a ring-shaped inlet, located 23.7 cm downstream from the injection point of the ions. At the downstream end of the flow tube ions are sampled through a 0.4 mm hole and introduced into the quadrupole analyzer, where they are filtered according to their mass to charge ratio. Ions are detected by an electron multiplier and the resulting signal is treated by pulse counting techniques.

All measurements were performed at 150 Pa and 297 K.

Ion/molecule reaction rate constants k were derived from the logarithmic decay $\ln(I/I_0) = -kt[X]$ of the source ion current I versus the concentration of the reactant neutral $[X]$ in the flow tube and from the residence time t of the ions in the flow tube, which can be measured separately.

The reactant neutral is diluted in helium in a volume calibrated glass container. The concentration of this reactant in the flow tube was varied by regulation of the flow rate from this glass container into the flow tube by means of a heated (315 K) needle valve. The reactant gas flow was inferred from the pressure decay versus time in the glass container. The concentration $[X]$ of the reactant was derived from the simultaneous measurement of the main carrier gas flow and of the pressure in the flow tube. In this way, the absolute reaction rate constants k of H_3O^+ could be determined. For each k measurement, at least four different mixing ratios of the volumetric mixtures were used. The rate constants for the reactions with NO^+ and $O_2^{\bullet+}$ were then determined in a relative way, as described in a previous paper [33] and as used in previous studies by Španěl et al. [20].