A pilot study of ion - molecule reactions at temperatures relevant to the atmosphere of Titan

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Abstract Reliable theoretical models of the chemical kinetics of the ionosphere of Saturn's moon, Titan, is highly dependent on the precision of the rates of the reactions of ambient ions with hydrocarbon molecules at relevant temperatures. A Variable Temperature Selected Ions Flow Tube technique, which has been developed primarily to study these reactions at temperatures within the range of 200 – 330 K, is briefly described. The flow tube temperature regulation system and the thermalisation of ions are also discussed. Preliminary studies of two reactions have been carried out to check the reliability and efficacy of kinetics measurements: (i) Rate constants of the reaction of CH_3^+ ions with molecular oxygen were measured at different temperatures, which indicate values in agreement with previous ion cyclotron resonance measurements ostensibly made at 300K. (ii) Formation of CH_3^+ ions in the reaction of N_2^+ ions with CH_4 molecules were studied at temperatures within the range 240 – 310 K which showed a small but statistically significant decrease of the ratio of product CH_3^+ ions to reactant N_2^+ ions with reaction temperature.

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Keywords Titan ionosphere, Variable Temperature Selected Ions Flow Tube, VT-SIFT, CH_3^+ ions, ion-molecule reactions

Introduction

The atmosphere of Saturn's moon, Titan, consists principally of nitrogen gas with 2 - 3 % of methane and trace amounts of hydrocarbons and nitriles (Anicich et al. 2004; Vuitton et al. 2009a; Wahlund et al. 2009). Large hydrocarbon ions ($C_xH_y^+$) and nitrogen-containing ions ($C_xH_yN_z^+$) were identified by the ion-neutral mass spectrometer (INMS) during the Cassini-Huygens mission (Waite 2005; Waite 2007). However, interpretation of the observed data is uncertain and the nature of the physical and chemical processes leading to formation of large organic molecules in the Titan atmosphere is in doubt. Theoretical models of Titan's ionosphere do not agree with observations, especially in the abundances of the observed large negative ions. This is largely due to lack of knowledge of the rate constants of relevant ion-molecule reactions. The overall precision of theoretical models of planetary atmospheres has unambiguously been shown to be highly sensitive to the rates of the ionic reactions involved. The published kinetics data, mostly obtained at room temperature and extrapolated to the temperature of the Titan ionosphere (~ 80K) based on the Arrhenius equation (Dutuit et al. 2009b; Vuitton et al. 2009b), are likely to be inaccurate and there are few relevant kinetics data for the important ionic reactions.

To begin to provide kinetics data closer to the required temperature, a selected ions flow tube SIFT-MS apparatus, previously has been used for study of gas - phase ion - molecule reactions at 300K for biomedical applications (Španěl et al. 1996; Španěl et al. 2006), has been modified in our laboratory to allow ion-molecule reaction studies at temperatures in the range 200 – 330 K, thus creating a Variable Temperature Selected Ions Flow Tube (VT-SIFT) apparatus. This will soon provide kinetics data necessary for the better modelling of Titan´s atmosphere.

Experimental

The newly built VT-SIFT instrument includes a novel temperature variable flow tube (see fig. 1) and a temperature regulation system that was used to study temperature dependence of $CH_3^+ + O_2$ and $N_2^+ + CH_4$ reactions (see fig. 2). In the present configuration, reactant ions are produced in an electron impact ion source operating at typically 70 ± 15 eV. The ions are extracted from the source, mass selected with an RF quadrupole mass filter and injected into the flow tube at laboratory energy of typically 5 eV, where they are captured by a neutral flowing carrier gas and convected along the flow tube. The carrier gas (helium in these experiments) is introduced into the flow tube via multiple nozzles surrounding the ion beam forming a Venturi-type inlet (Smith and Španěl 2005). The oxygen or methane reactant gas is added 10 cm downstream directly into the carrier gas using an on-axis inlet port. All ions and neutrals are rapidly thermalized in multiple collisions with helium carrier gas atoms. In the present experiments, the carrier gas pressure was typically 0.7 mbar (helium atoms number density $2x10^{16}$ cm^{-3}) and rapidly reaches thermal equilibrium with the internal surface of the cooled flow tube. The convected ions are sampled downstream by a pinhole orifice and pass into the quadrupole mass spectrometer/detection system and analysed using a PC data acquisition system. For typical conditions, the mean free path of ions in helium atom collisions ($<10^{-6}$ m) is for several orders-of-magnitude shorter than the distance between the injected ion entrance orifice to the reactant gas inlet port ($\sim 10^{-2}$ m). Thus, the number of collisions of injected ions with helium atoms is judged to be sufficient for translation and internal energy thermalization of the ions. The reaction time and the number densities of reactant neutrals are defined by the carrier gas and sample gas flow rates and the total pressure and gas temperature. The fractional number density of the reactant gas molecules in the helium carrier gas can be found from the ratio of its flow rate and that of the helium (see Španěl et al. 2011). Trace water vapour is removed from the helium carrier gas using a liquid nitrogen-cooled zeolite trap (fig. 1).

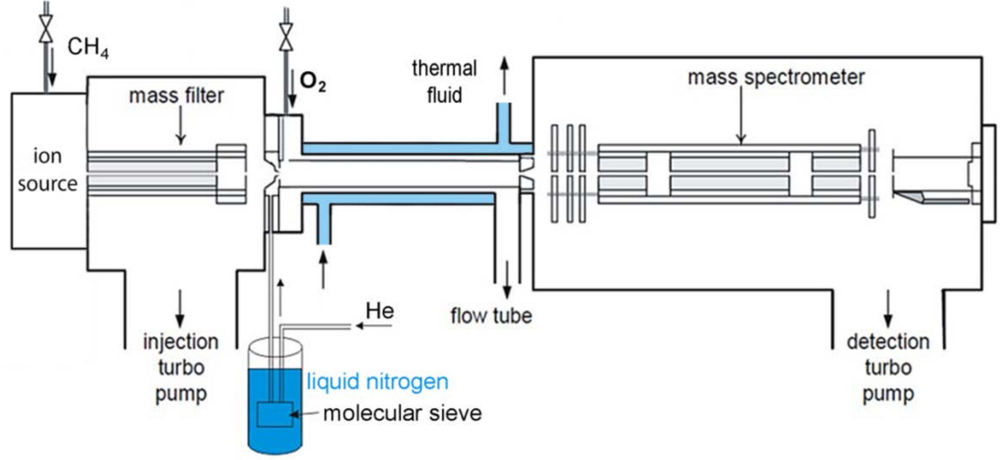

Fig. 1 Scheme of the Variable Temperature Selected Ions Flow Tube apparatus, VT-SIFT

The flow tube walls, and hence the helium carrier gas, is cooled by pumping refrigerated liquid ethanol through the hollow walls of the flow tube (double pipe heat exchanger system) in a closed cycle. The temperature of the helium can be varied over the range 200 – 330 K by adjusting the temperature and pumping speed of the ethanol. The small temperature gradient along the flow tube is measured by five K - type thermocouple sensors; the temperature difference across the flow tube (length 40 cm) does not exceed 5 K at all temperatures within the explored range.

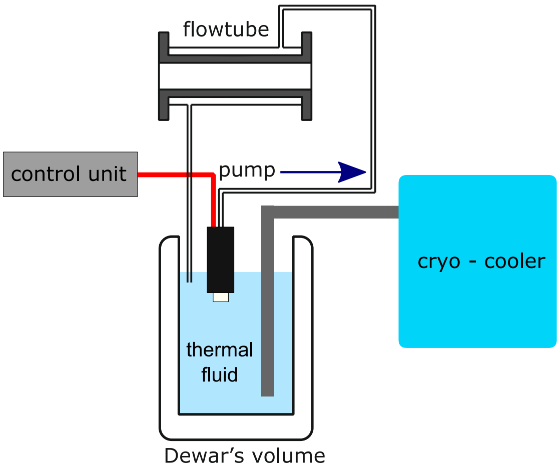

Fig. 2 Flow tube temperature control system.

The partial rate coefficients for specific binary channels of the above two ion molecule reactions were determined from the ratio of the product ion count rate to the reagent ion count rate. For more details of measurements of rate coefficients in fast flow tube instruments see Španěl et al. (1996) and Španěl et al. (2006).

Results

In this VT-SIFT apparatus, CH_3^+ ions were produced by the electron ionization of CH_4 molecules and their reaction with molecular oxygen introduced via the inlet port (see fig. 1) was studied over the temperature range 245 – 305 K. The reaction proceeds thus:

$$CH_3^+ + O_2 + He \rightarrow CH_3O_2^+ + He \quad (1a)$$

$$CH_3^+ + O_2 \rightarrow HCO^+ + H_2O \quad (1b)$$

The association channel (1a) is considered to be the most relevant channel for interstellar chemistry and was studied previously using the original SIFT instrument (Adams and Smith 1981). The exothermic binary channel (1b) was observed in the present study as a small count rate of HCO^+ product ions, which becomes dominant at low number densities of neutrals, for example, at high altitudes in Titan's ionosphere. The measured rate constant for this channel $k_{1b} = (4.7 \pm 0.9) \cdot 10^{-11}$ $cm^3 s^{-1}$ at 302 ± 1 K, see fig. 3, in agreement with a previous ion cyclotron resonance (ICR) measurement (Huntress 1977). These results are used to estimate the absolute error of rate coefficient measurements using this new VT-SIFT instrument by comparison with published data (Huntress 1977). However, experimental data over a significant carrier gas pressure range are required to totally exclude internal excitation of ions or the (unlikely) influence of impurities that can disproportionally affect studies of such slow reactions. The apparent small decrease of k at the lower temperature to of 248 ± 5 K (fig. 3) is not statistically significant and so the rate coefficient of the reaction is essentially constant over the explored temperature range.

The reaction of the N_2^+ ions with methane has two exothermic bimolecular channels:

$$N_2^+ + CH_4 \rightarrow CH_3^+ + N_2 + H, \qquad (2a)$$

$$N_2^+ + CH_4 \rightarrow CH_2^+ + N_2 + H_2, \qquad (2b)$$

Channel (2a) is very dominant (>90% of the total products; Tichý et. al. 1979). The rate of reaction (2) is known to be independent of collision energy in the range of 0.1 – 3 eV (Nicolas et al. 2003b). The temperature dependence of the formation of the CH_3^+ ions was explored (the minor CH_2^+ channel neglected) and the results are shown in fig. 4.

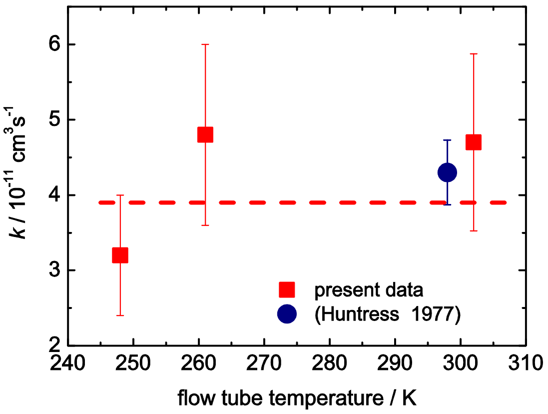

Fig. 3 Preliminary measurements of the $CH_3^+ + O_2$ reaction rate coefficient in the temperature range 245 – 305 K (red squares) compared to a previous ICR measurement ostensibly at 297 K (blue circle)

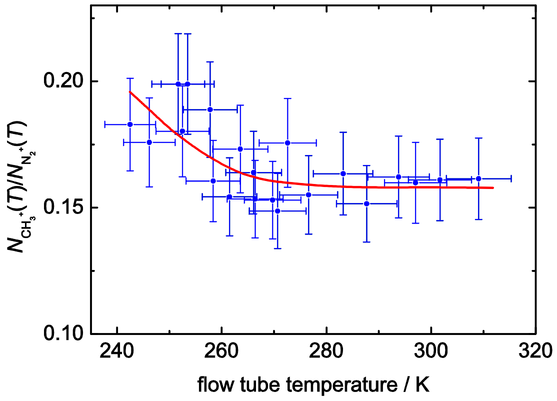

Fig. 4 Measurements of the signal ratio of CH_3^+ ions, N_{CH3+}, to N_{N2+}, in the N_2^+ reaction with CH_4 over the temperature range 240 – 310 K at a constant CH_4 flow rate.

Concluding remarks

These exploratory studies of the reactions (1) of CH_3^+ ions with O_2 molecules have revealed that the rate coefficient of the binary channel (1b) measured at 300 K that produces HCO^+ is in a reasonable agreement with previous measurements. Significant temperature dependence was not observed in the range of 245 – 305 K. The exothermicity of the reaction (1b), evaluated from the heat of formation of reactants and products, is 4.3 eV, yet the reaction is inefficient which implies a large potential barrier to reaction presumably associated with the significance rearrangement required to access the HCO^+ product. The parallel ternary association reaction (1a) is very slow under the conditions of present experiment (effective binary rate constant for a typical helium number density is less than 10^{-}

^{12} cm^3s^{-1}) (Adams and Smith 1981), but is expected to increase at lower temperatures pertaining to planetary atmospheres and dense interstellar gas clouds.

The small but significant inverse temperature dependence of the production of CH_3^+ions in the N_2^+ reaction (2) implies an increasing rate of the reaction at the lower temperature of the Titan atmosphere. The negative temperature trend appears to conform to previous measurements at 8 – 15 K (Randeniya and Smith 1991) and at 70 K (Rowe et al. 1989), but a temperature dependence was not explored in these previous studies. Negative temperature dependence is not in accordance with Arrhenius ideas, but rather with the more efficient formation of intermediate ion-molecule complexes at low temperatures that can increase the rate of the reaction (Fernandez-Ramos et al. 2006). This emphasises the need for more measurement of the temperature dependencies of reaction rates of ion-molecules that are used in modelling Titan atmosphere ion chemistry that of other planetary atmosphere. Such is the major objective of the planned experiments using the new VT-SIFT constructed in our Prague laboratory.

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