International Journal of Mass Spectrometry 194 (2000) L1–L5

Letter

A novel inductively coupled plasma/selected-ion flow tube mass spectrometer for the study of reactions of atomic and atomic oxide ions

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Received 27 September 1999; accepted 5 October 1999

Abstract

A novel inductively coupled plasma/selected-ion flow tube (ICP/SIFT) mass spectrometer has been constructed for the study of the kinetics and product distributions of reactions of atomic and atomic oxide ions with neutral molecules. The ICP essentially provides a universal source for atomic ions. The operation of the instrument is demonstrated with prototype reactivity and kinetic measurements. (Int J Mass Spectrom 194 (2000) L1–L5) © 2000 Elsevier Science B.V.

Keywords: SIFT; ICP; Gas-phase ion chemistry; Kinetics

1. Introduction

The extraordinary utility of the selected ion flow tube (SIFT) technique as an instrument for the measurement of the reactivity of thermalized ions at room temperature is limited only by the versatility of the ion source used to generate the ions upstream of the flow tube. In order to maximize the utility of flow-tube techniques, users have adopted a variety of modes of ion production. These include microwave and dc discharges, conventional low- and high-pressure electron-impact sources, and flowing-afterglow sources [1]. Ionization techniques for the production of metal ions that have been employed with flow reactors include electron-impact ionization of metal vapour generated with a resistive furnace, thermionic emission from a tungsten surface, and laser vapourization [1]. These techniques tend to be specific and restrictive. More recently, glow discharge plasmas have been used and these can provide a larger variety of metal ions [2,3]. In our own laboratory, for the production of the atomic metal ions Mg^+ and Fe^+, we routinely have used electron impact ionization of vapours of organometallic compounds containing the

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PII S1387-3806(99)00233-X

metal of interest. Although effective, this method relies on the availability of the volatile organometallic parent compound and is somewhat awkward and time consuming in operation as it requires frequent cleaning of the source and sample replenishment. In sharp contrast, the generation of metal ions in an inductively coupled plasma (ICP), operating at plasma temperature of ~7500 K, requires only the injection of a dilute solution of any compound containing the metal of interest and can be continuous, even for months at a time [4]. However, as the conventional ICP operates at atmospheric pressure, a differentially pumped interface is required to allow plasma-ion sampling. We describe here a novel ICP/SIFT mass spectrometer that has been constructed and operated in our laboratory for the study of the kinetics and product distributions of reactions of atomic and atomic oxide ions with neutral molecules. ICP-MS was originally developed for elemental and isotopic analysis [4], but in the application described here the ICP is intended to provide essentially a universal source for atomic ions for injection into a flow tube, although selected doubly charged atomic ions and atomic oxide ions can be produced as well. We shall demonstrate here that the ICP/SIFT configuration allows the routine measurement of fundamental aspects of reactions of atomic and atomic oxide ions with neutral molecules proceeding at room temperature.

2. Experimental

The SIFT mass spectrometer in the Ion-Chemistry Laboratory at York University, described in detail elsewhere [5,6], has been modified to accept ions generated in an ICP torch through an atmosphere/vacuum interface. A rf power supply and ICP torch assembly from a commercial instrument (ELAN series, PE/SCIEX) was modified for stand-alone operation. The ICP ion source and interface are shown schematically in Fig. 1. The interface was used as supplied with skimmer and sampling cones, each with a 1.0 mm orifice, and a 5.0 mm shadow stop to block out UV photons. The region between the sampling cone and skimmer was pumped by a 1000 L min^{-1} rotary vane pump (Alcatel 2060, Paris, France) and that after the skimmer was pumped by a 200 L s^{-1} turbomolecular pump (Leybold Hy.Cone 200, Cologne, Germany). The existing reagent-ion selection quadrupole was fitted with an rf-only quadrupole prefilter 116 mm in length. This prefilter was capacitively coupled to the resolving quadrupole with a matched set of high-voltage 100 pf capacitors. The prefilters were floated at −36 V with respect to the instrument ground coupled through 20 MΩ resistors.

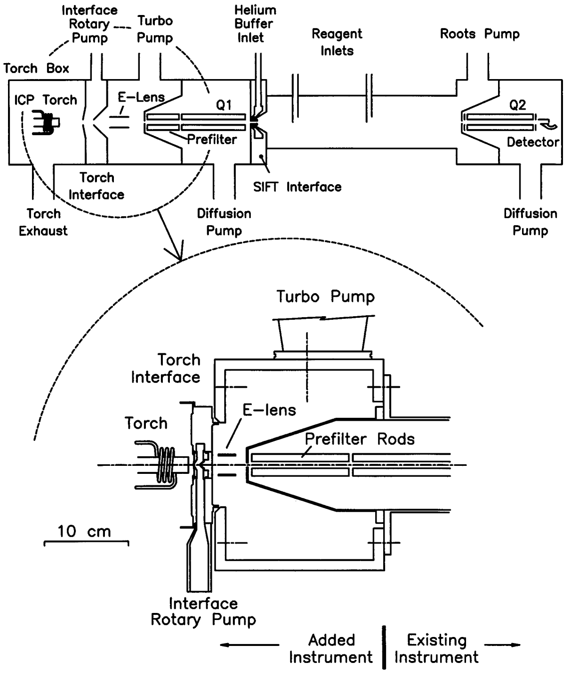

Fig. 1. Schematic view of the working ICP/SIFT instrument together with a scaled close-up of the ICP/SIFT interface.

Metal-salt solutions were peristatically pumped (Gilson Minipuls 3, two channel) to a nebulizer at rates between 0.25 and 0.40 mL min^{-1}. The nebulizer is of crossed-flow gem-tip design, spraying into a Scott-type double-pass chamber. The nebulized solution was carried to the plasma region by a ceramic (alumina) injector. The metal-salt solutions were generally 5 ppm wt/vol in water generated by a Millipore MilliQplus water purification system. Solutions were stabilized with 2 to 2.5% acid, either nitric or hydrochloric as the situation required.

The rf power supply was typically set to transmit 1050 W of power (free-running frequency, 40 MHz).

Table 1
A comparison of results obtained with the ICP/SIFT with previous SIFT measurements. Rate coefficients are in units of cm^3 $molecule^{-1}$ s^{-1}

Reaction		B.R.[a]		k_{ICP}	k_{other}	Reference
$Fe^+ + CO$	$\rightarrow$ products			$<2 \times 10^{-13}$	$<1 \times 10^{-14}$	[7]
$Fe^+ + N_2O$	$\rightarrow FeO^+ + N_2$			3.4×10^{-11}	3.1×10^{-11}	[7]
$Ar^+ + N_2O$	$\rightarrow N_2O^+ + Ar$			3.5×10^{-10}	3.3×10^{-10}	[8]
$Ar_2^+ + CO$	$\rightarrow CO^+ + 2Ar$	0.95	1.0	7.3×10^{-10}	8.5×10^{-10}	[9]
	$\rightarrow ArCO^+ + Ar$	0.05				
$Ar_2^+ + H_2$	$\rightarrow ArH^+ + H + Ar$	0.6	0.7	6.3×10^{-10}	5.0×10^{-10}	[10]
	$\rightarrow ArH_2^+ + Ar$	0.4	0.3			
$Fe^+ + C_2H_4 + He$	$\rightarrow Fe^+ \cdot C_2H_4 + He$			7.2×10^{-11}	6.1×10^{-11}	[11]

[a] B.R. is the measured branching ratio. The ICP/SIFT results are given first.

The plasma torch was a standard Fassel-type design. The flows of argon into the three torch inputs were 14–15 L min^{-1}, outer; 2 L min^{-1}, intermediate or plasma gas; and 1.0–1.2 L min^{-1}, inner or nebulizer gas. The nebulizer gas flow was adjusted to maximize the ion signal detected downstream of the SIFT.

Helium was used as the SIFT buffer gas at 0.350 Torr. The tube temperature was 296 ± 2 K. The sampled plasma ions were allowed to thermalize by collisions with He ($\sim 4 \times 10^5$ collisions) prior to entering the reaction region further downstream. Reagent gases had purities better than 99.5%. Trans-2-hexene was 99% pure (Aldrich).

3. Results

A large number of diverse atomic ions and a few atomic oxide ions were successfully generated in the ICP and detected downstream of the flow region of the SIFT. High intensities (>1000 counts s^{-1}) were observed for Ag^+, Cu^+, Fe^+, Nb^+, Sc^+, Y^+, and La^+. Medium intensities (100 to 1000 counts s^{-1}) were observed for Au^+, Nd^+, Al^+, As^+, and Na^+. Only low intensities (<100 counts s^{-1}) were achieved for Zn^+, Os^+, Se^+, B^+, and Li^+. High intensities also were observed for the "background" ions Ar^+, Ar_2^+, and ArO^+ arising from the argon plasma gas. High signals of ClO^+ could be produced by pumping a 35% HCl solution into the nebulizer.

All indications so far are that the thermalization of the ICP ions entering the flow tube is effective prior to their entry into the reaction region. Several reactions of ICP ions were investigated that had previously been measured with the SIFT or related techniques in which the ions were generated using conventional electron-impact ionization. Both fast and slow reactions were investigated and, in each case, agreement was found within experimental error in the measured rate coefficients (±30%) and product distributions (±10%). Results are displayed in Table 1.

Several reactivity measurements also were made with ions derived from the ICP that we have not previously generated in the SIFT by conventional methods. Fig. 2 shows a composite of reaction-rate profile measurements made with Ag^+, Nb^+, ArO^+, and ClO^+. Ag^+ was found to react with *trans*-2-hexene sequentially to produce the double adduct ion $Ag^+ (C_6H_{12})_2$ according to reactions (1) and (2). Reaction (1) proceeds with an effective bimolecular rate coefficient of 1.4×10^{-9} cm^3 $molecule^{-1}$ s^{-1}.

$$Ag^+ + trans\text{-}2\text{-}C_6H_{12} + He \rightarrow Ag^+ \cdot C_6H_{12} + He \quad (1)$$

$$Ag^+C_6H_{12} + trans\text{-}2\text{-}C_6H_{12} + He \rightarrow Ag^+ \cdot (C_6H_{12})_2 + He \quad (2)$$

Fig. 2 shows that the chemistry of Nb^+ with acetylene proceeds according to reaction (3) apparently by ion-induced polymerization (3).

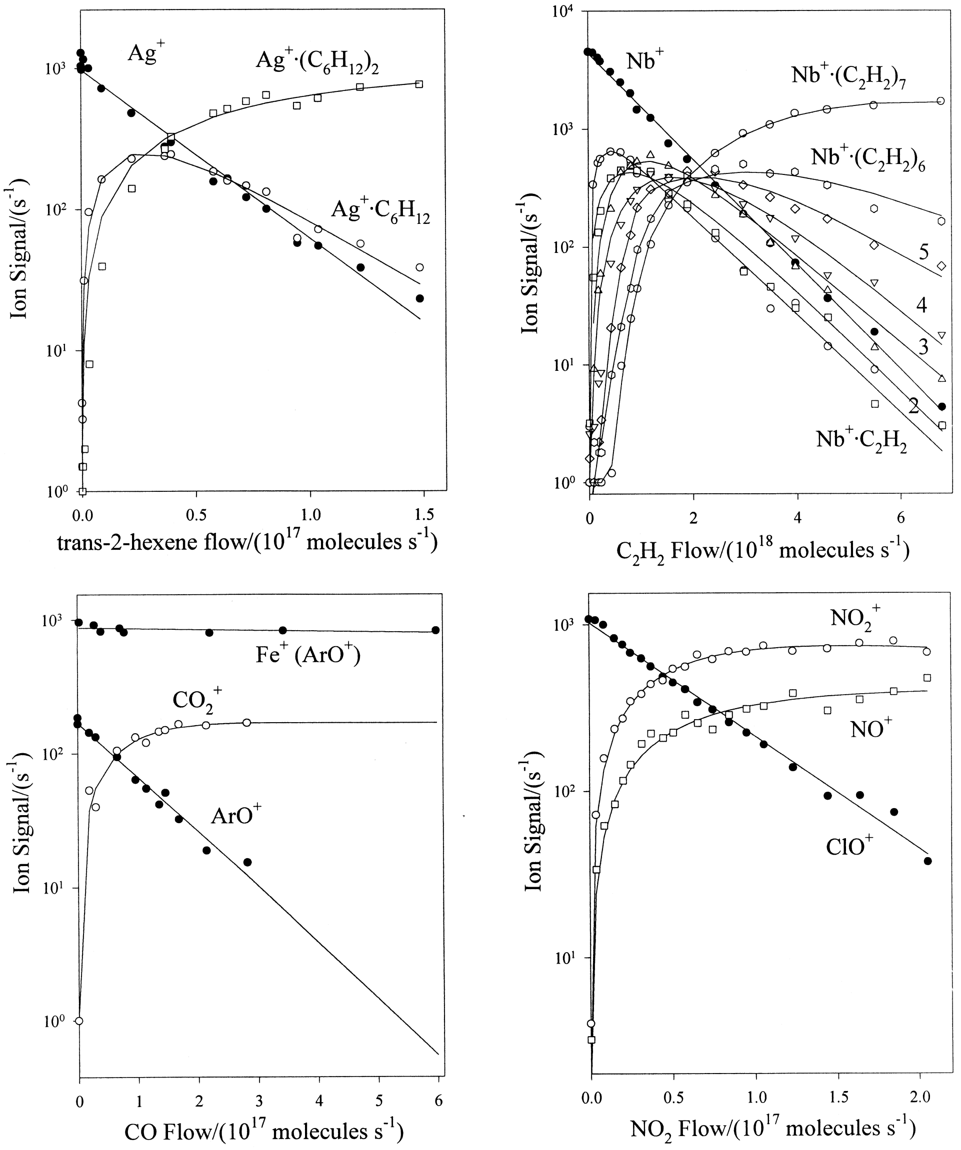

Fig. 2. Composite of reaction profiles measured for reactions of selected atomic and atomic oxide ions.

$$\mathrm{Nb^+ \cdot (C_2H_2)_{\mathit{n}} + C_2H_2 + He \rightarrow Nb^+ \cdot (C_2H_2)_{\mathit{n}+1}} \tag{3}$$

The addition is rapid and up to 16 molecules of C_2H_2 were observed to add sequentially. The initiation step has a measured rate coefficient $k = 2.5 \times 10^{-10}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. ArO^+ was observed to react with CO by O^+ transfer according to reaction (4) with $k = 5.0 \times 10^{-10}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

$$\mathrm{ArO^+ + CO \rightarrow CO_2^+ + Ar} \tag{4}$$

In contrast, the isobaric ion Fe^+ is unreactive with CO, $k < 2 \times 10^{-13}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. ClO^+

reacts with NO_2 by electron transfer [reaction (5a)] and O^- transfer [reaction (5b)] in a proportion of 7 to 3 with $k_5 = 9.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$$ClO^+ + NO_2 \rightarrow NO_2^+ + ClO \tag{5a}$$

$$\rightarrow NO^+ + ClO_2 \tag{5b}$$

The semilogarithmic decays of the reacting ions show good linearity in each case over more than one order of magnitude (see Fig. 2). This is indicative of well-defined internal energies of the ions entering the reaction region of the SIFT apparatus: the reacting ions appear to be in a single, presumably ground, electronic state. A mixture of states would result in curved semilogarithmic decays in the likely event that different states have different reactivities.

Clearly the ICP/SIFT apparatus is well-suited for the generation of atomic and atomic oxide ions, including a large range of metal ions, and the measurement of their reactivities at room temperature in helium bath gas at 0.35 Torr.

Acknowledgements

D.K.B. thanks the Natural Sciences and Engineering Research Council, the National Research Council of Canada, and MDS SCIEX for the financial support of this research. We are also grateful to MDS SCIEX for providing the ICP source and rf power supply and for the construction of the ICP/SIFT interface.

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