Gas-phase ion–molecule reaction in an RF ion trap. Reactivity of the 5d transition series of metal ions (Lu+, Hf+, Ta+, and W+) with O_2

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Ions in an externally generated laser plasma of heavy metals have been directly confined in an RF ion trap and subjected to ion–molecule reactions. Trapped metal ions as well as their chemical reaction products have been detected with a quadrupole mass spectrometer. The first four ions of 5d transition series (Lu+, Hf+, Ta+, W+) are found to be highly reactive with O_2: Lu+ and Hf+ form monoxide ions whereas Ta+ and W+ first become monoxides and are stabilized as dioxides, being consistent with the reaction processes observed by a recent FTICR measurement. The determined reaction rate increases with the number of 5d electrons, contrary to the FTICR data for Hf+ and W+. The influence of insufficient thermalization of ions on the reaction rates is discussed as a possible origin of this discrepancy.

1. Introduction

Gas-phase reactions of transition metals with molecules have become a subject of much interest in recent years. In particular, metal ion–molecule reactions have been investigated intensively in the past decade as a result of the development of ion-beam mass spectrometry [1–8], Fourier transform ion cyclotron resonance (FTICR) [9–13], and the improved flow tube reactor method [14,15]. A number of works have been carried out for the oxidation reaction [2,3,10,13], and the reaction of ions with hydrocarbons [1,4–12,14,15] for the study of C–C and C–H bond cleavage by gas-phase metal ions. However, chemical reactions of the third row transitional metal ions have been studied less frequently than those of the first and the second rows. This is partly because free atoms of heavy refractory metals are not easy to make. Thus laser ablation is nearly the only way to produce gas-phase atomic ions of these metals. Recently Irikura and Beauchamp have investigated the reaction properties of third row transition metal ions by FTICR combined with laser ablation [10].

The combination of an RF ion trap and laser ablation is one of the promising methods for studying the

chemical properties of refractory metal ions. We have been able to confine ions in an RF ion trap directly from externally generated laser plasma using laser ablation [16]. This method is found to be useful for trapping the ions of heavy refractory metals. Difficulties were originally anticipated for the direct capture of externally generated ions into the trap due to the excess kinetic energy of injected ions. However, under the presence of light buffer gas such as He, we have obtained ion confining times in the range of a few minutes to a few hours depending on the ionic species. This long confinement time provides an opportunity to study slow chemical reactions with an RF ion trap. The reaction time which is realized in our RF ion trap is approximately three orders of magnitude longer than that in FTICR. Although laser ablation is intrinsically a violent process, the long confinement time and the introduction of light buffer gas in an RF ion trap ensure complete thermalization of the ions involved in the chemical reactions. In this Letter, we report chemical reactions of the first four metal ions of the 5d transition series with O_2 in an RF ion trap.

2. Experimental

The principal part of the RF ion trap with the laser ablation method has been reported previously [16]. Here we briefly describe the RF ion trap system for mass-selective detection of trapped ions and refer to some improvements made since then.

A simplified scheme of the experimental apparatus is depicted in fig. 1. The apparatus consists of an RF ion trap (made of copper electrodes), a vacuum chamber, a metal sample, and a pulsed Nd:YAG laser (LUMONICS MINI-Q) as a metal vaporization source. The RF ion trap has a cylindrical shape ($r_0 = 22.6$ mm, $z_0 = 16$ mm), which consists of a cylinder (a ring electrode) with 4 holes of 6 mm diameter and two round mesh plates (end-cap electrodes) at both ends. These holes are used for the injection of ions as well as for guiding the laser beam for metal vaporization. Radio frequency of typically 0.5–1 MHz is applied between the end-cap and ring electrodes at the voltage of 800 V p–p. A dc voltage in the range of several volts is also applied in series with the RF voltage. The vacuum chamber is evacuated with a turbomolecular pump. A liquid N_2 trap
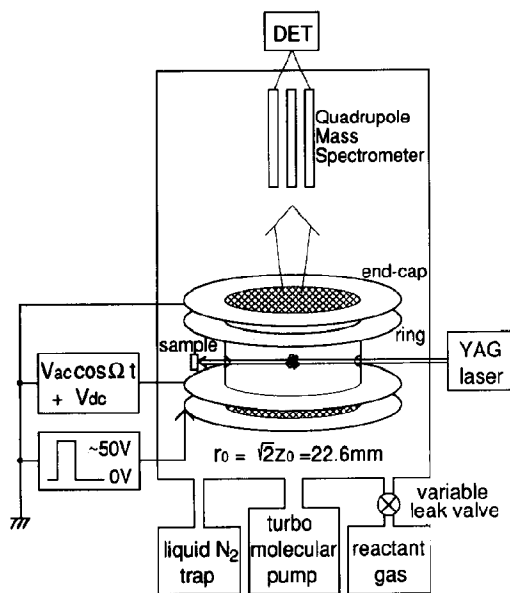

Fig. 1. A block diagram of the RF ion trap system. The ions in laser plasmas generated externally by YAG laser ablation are introduced into the trap. Trapped ions are evacuated by applying an electric pulse to the trap electrodes and detected with a quadrupole mass spectrometer.

is found effective to lengthen the ion storage time by removing H_2O in the residual gas. The pressure attained in this system is better than 2×10^{-9} Torr. The He buffer gas up to 10^{-5} Torr is introduced to the chamber for thermalizing the trapped ions. Output of the YAG laser, typically several mJ with 10 ns pulse width, is focused onto a metal sample placed near one of the holes on the ring electrode. Typically 10^{10} ions are produced at each shot of the YAG laser pulse. Approximately 10^6 ions are eventually confined in the trap. Within the first 20–30 s after the laser ablation, the number of trapped ions decreases rather rapidly. After this period trapped ions become nearly stable so that it is possible to observe the chemical reaction slowly occurring in the RF ion trap. A small amount of O_2 (10^{-8}–10^{-9} Torr) is introduced to the vacuum chamber through a variable leak valve. The pressure is measured with a nude ionization gauge and the relative sensitivity to O_2 is taken into account.

The ions are trapped and driven out by a pulsed voltage applied between the two end-cap electrodes after a certain delay time, and are detected with a quadrupole mass spectrometer (ANELVA AQA-360). This method provides mass-selective detection of any kinds of ions within the mass range up to 360 amu, which is limited by the quadrupole mass spectrometer used.

3. Results and discussion

The reaction of heavy metal ions (Lu^+, Hf^+, Ta^+, W^+) with O_2 was studied under various experimental conditions. These ions are all highly reactive with the O_2 gas and undergo the following exothermic reaction:

$$M^+ + O_2 \rightarrow MO^+ + O . \tag{1}$$

The TaO^+ and WO^+ ions go through a further oxidation reaction,

$$MO^+ + O_2 \rightarrow MO_2^+ + O . \tag{2}$$

Typical time evolutions of the amount of heavy metal ions and their chemical reaction products are shown in fig. 2 for Lu^+ and Ta^+. The observed reaction processes agree with the previous results on Hf^+, W^+ [10], and Ta^+ [13]. The data, which are taken after the first 30 s from the ion production, are used for
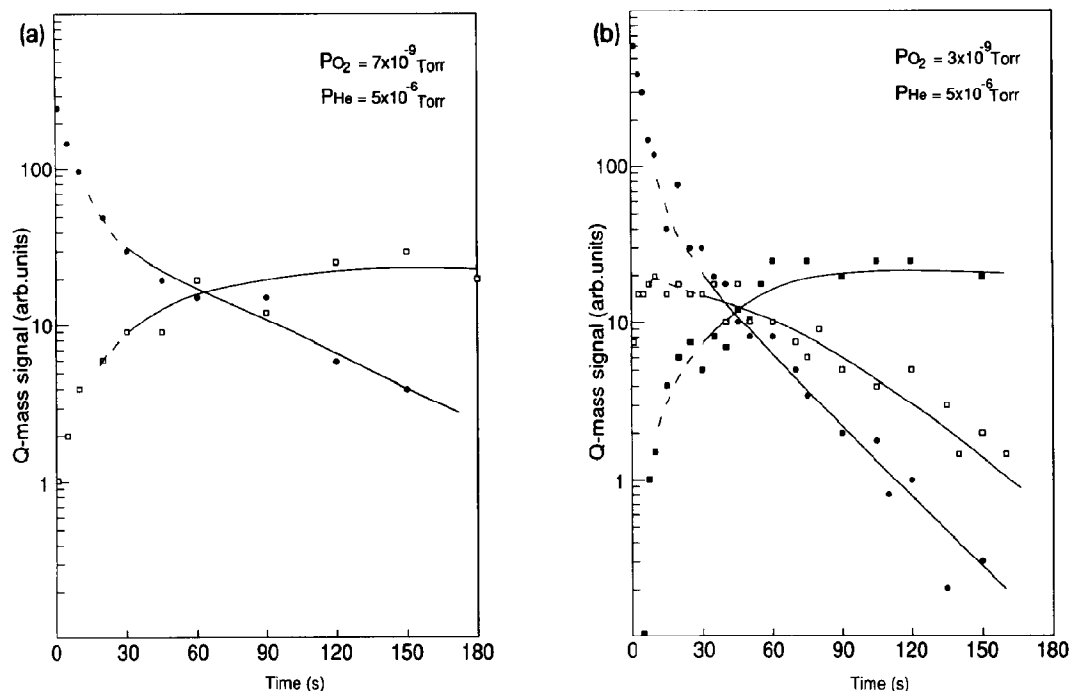
Fig. 2. Time evolution of trapped heavy metal ions and their chemical reaction products with O_2. (a) Reaction of Lu^+ with O_2. ($\bullet$) $M=175$ (Lu^+); ($\square$) $M=191$ (LuO^+). (b) Reaction of Ta^+ with O_2. ($\bullet$) $M=181$ (Ta^+); ($\square$) $M=197$ (TaO^+); ($\blacksquare$) $M=213$ (TaO_2^+).

determination of the rate constants in eq. (1) at 300 K. The rate constants are determined by fitting the experimental data to the ordinary coupled differential equations with four adjustable parameters for Lu^+ and Hf^+ (a reaction rate, an escape rate, and two initial concentrations of M^+ and MO^+), and six for Ta^+ and W^+ (two reaction rates, an escape rate, and three initial concentrations of M^+, MO^+, and MO_2^+). A typical escape rate of the ions from the trap is $1/500$ s^{-1}, irrespective of the presence of the O_2 gas. The maximum error in the reaction rates is 10% when the escape rate is neglected. The rate constants are summarized in table 1 together with the corresponding rate constants for Hf^+ and W^+ measured by FTICR. The data are taken at more than three different oxygen pressures and averaged. Quoted errors are estimated from the standard deviations of the measured values. Although the time scales used in the present work are approximately three orders of magnitude longer than those used in the FTICR measurements, the rate constants determined in the two different experiments show a rea-

sonable agreement. In our measurement, the error limit in absolute values is estimated to be a factor of two due to the uncertainty in the pressure measurement. However, the relative error of approximately 20% allows us to discuss the relative reactivity of the metal ions of the 5d transition series. The measured reaction rate constant increases monotonically from Lu^+ to W^+ as the number of 5d electrons increases.

Table 1
Chemical reaction rates for $M^+ + O_2 \rightarrow MO^+ + O$

M	This work [a]	Previous work [b]
Lu	0.64(11) [c]	
Hf	1.8(2)	4.5
Ta	3.0(6)	
W	3.2(8)	1.5
TaO	3.5(11)	
WO	3.7(19)	1.0

[a] In units of 10^{-10} s^{-1} molecule^{-1} cm^3 at 300 K.
[b] Ref. [10].
[c] Numbers in parentheses are two standard deviations in units of the last significant digits.

The rate constants for TaO^+ and WO^+ show nearly identical figures with those for Ta^+ and W^+ though larger errors are estimated.

In order to discuss the difference of reactivity among different ionic species, electron spin and electron configuration are the two important factors to be considered [17]. Preference of the spin states of reactants is not clear for the reaction of heavy transition metal ions with oxygen molecules since O_2 has a triplet ground state and many of the heavy transition metal ions and their oxide ions have high-spin ground states [2]. Thus the electron configuration is more likely to the influential in metal–oxygen reaction rates. Lu^+ and Hf^+ have filled 6s orbitals in their ground states ($6s^2$ for Lu^+ and $6s^2 5d^1$ for Hf^+). On the other hand, Ta^+ and W^+ have the $6s^1 5d^{n-1}$ ($n=4$ and 5 for Ta^+ and W^+, respectively) configuration. The first row transition metal ions often show high reactivity when the ions have vacant 4s orbitals for accepting electrons and extra 3d orbital electrons for electron donation [17]. The reactivity is further enhanced when the $3d^n$ levels are in the ground or low-lying excited states [14]. If this is also the case for the third row transition metal ions, the unfilled 6s electrons and the more 5d electrons are likely to contribute to the reactivity as far as the reaction is exothermic. Moreover, the energies required for promoting ions from the ground state to either the $6s^1 5d^{n-1}$ or the $5d^n$ metastable state decrease from Lu^+ to W^+. The energies of these configurations show strong correlation with the present reactivity. Although the difference in size of the 6s and 5d orbitals for the third row transition metal ions is smaller than the corresponding difference for the first row ions, the increase in the reaction rate from Lu^+ to W^+ suggests that the influence of electron configuration on the reactivity is similar to that for the first row transitional metal ions.

Our result on the relative reactivities of Hf^+ and W^+ differs from that of FTICR [10]. One possibility is the different efficiency of thermalization in these two experiments. The Hf^+, Ta^+, and W^+ ionic species have a large number of metastable states in the low-energy region. Since laser ablation is a violent process, it is highly probable that it changes the population distributions among these metastable states and affects the reaction rates, causing an apparent difference in the reaction rates for the ions

that are not well thermalized. Unfortunately, the present measurement does not allow us to study the influence of metastable ions on the reactions because metastable ions are all quenched during the waiting time of 20–30 s, which is necessary for the stabilization of the ions. For confirmation of this effect, it will be worth studying changes in the reaction rates by exciting the trapped ions into one of the metastable states with lasers. This will give direct information on state-selected reaction processes.

The present experiment also implies that a chemical reaction as well as charge transfer process is in fact an important factor to limit the ion storage time in an ion trap. Since some ions react rapidly with a small amount of residual gas, it indicates the reason why high vacuum is essential for an ion trap to obtain a long confinement time.

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