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KINETICS AND MECHANISM IN THE OXIDATION OF METAL VAPORS

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The results of laboratory experiments designed to gain an understanding of the
kinetics and mechanism of gas-phase metal oxidation reactions of thorium and
uranium are presented. The experiments were conducted in an apparatus which
utilizes RF heating and laser radiation for the production of the metal vapor
and time-of-flight mass spectrometry for product identification and
quantitative measurements of reactants and products. Measurements were made

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on the oxidation of thorium and uranium by molecular and atomic oxygen, as well as N_2O, and values of the rate constants are given.

KINETICS & MECHANISM IN THE OXIDATION OF METAL VAPORS

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Joseph A. Golden

This report has been reviewed by the RADC Information Office (OI),
and is releasable to the National Technical Information Service (NTIS).

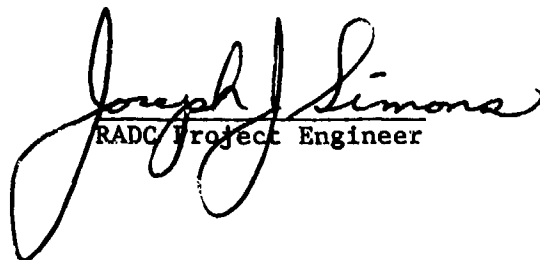This technical report has been reviewed and is approved.

RADC Project Engineer

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ABSTRACT

In an effort to understand the kinetics and mechanisms of gas-phase metal oxidation reactions, experiments were continued in an apparatus which utilizes RF heating and laser radiation for the production of the metal vapor and time-of-flight mass spectrometry for product identification and quantitative measurements of reactants and products.

Measurements were continued on the oxidation of thorium and uranium by molecular and atomic oxygen, as well as N_2O and rate constants were measured for following reactions:

$$Th + O \longrightarrow ThO^+ + e \qquad (1)$$

$$Th + N_2O \longrightarrow ThO^+ + N_2 + e \qquad (2)$$

$$U + O_2 \longrightarrow UO^+ + O + e \qquad (3)$$

$$U + N_2O \longrightarrow UO^+ + N_2 + e \qquad (4)$$
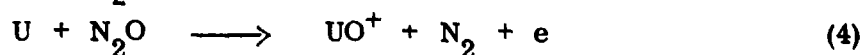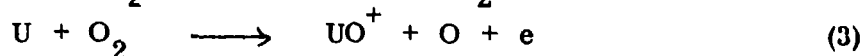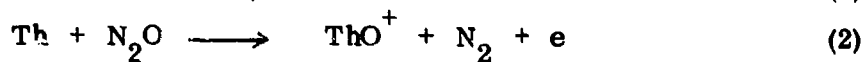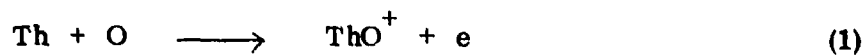
where
$$k_1 = 3.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_2 = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_3 = 8.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_4 = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

I. INTRODUCTION·

The oxidation of refractory metals in the gas phase is a relatively new area of research. Fite, et al[1] have recently published results on the oxidation of uranium vapor by molecular and atomic oxygen. The oxidation of gaseous thorium by molecular oxygen undertaken by Zavitsanos and Golden and some of the results were reported previously[2,3]. Using experimental techniques developed and documented in previous reports[3] the scope of the work was extended and rates were measured for other reactions involving thorium and uranium.

II. EXPERIMENTAL

A. MATERIALS

High purity samples of thorium "crystal bar" and uranium powder were obtained from Ventrol Metal Hydride Division, Beverly, Mass.

When Knudsen crucibles were used as containers, the structural material was tungsten. Best results, in terms of reducing background ThO and UO were obtained with single crystal tungsten liners.

B. APPARATUS

The heating methods considered for this study are induction RF heating and laser radiation.

1. Induction Heating

The use of RF heating in high-temperature mass spectrometric work has been previously demonstrated[4] and utilized in obtaining temperatures as high as $3000^{\circ}K$.

The experimental arrangement is shown in Figure 1. Figure 1 shows the in-ductively heated Knudsen cell in-place in the Bendix Model 12 time-of-flight mass spectrometer. The water-cooled induction coil enters the furnace chamber from the bottom flange. The crucible and its holder are supported on three tantalum rods on the inlet assembly.

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The Knudsen crucible dimensions are 0.25 in. I.D. x 0.45 in. deep with a 0.05 in. wall with a crucible cover, 0.125 in. thick x 0.35 in. dia., 60° conical orifice whose minor diameter is 0.03 in.

The temperature of the crucible is measured with a Leeds and Northrup manual optical pyrometer by sighting into the orifice (as shown in Figure 1). Corrections due to prism and window were made in all the reported temperature values.

The vapor generated in the crucible in Chamber II, after traveling 2 cm through a vacuum of $P_{II} 10^{-6}$ torr, enters Chamber I (through a slit 0.5 cm x .05 cm) and reacts with oxygen whose pressure P_I can be as high as 2×10^{-3} torr. The vapor travels 6 cm in Chamber I before it reaches point G where an electron beam of controlled energy is directed perpendicular to the metal vapor beam and its reaction products with oxygen. At this point, the ratio of unreacted metal oxide can be determined mass spectro-metrically as a function of oxygen pressure and metal vapor density.

2. Laser Heating

Another heating arrangement involves use of pulsed laser, ruby or CO_2. The beam enters a chamber through a window (glass for ruby, NaCl for CO_2) and strikes a metal target as shown in Figure 3. The generated vapor plume moves away from the metal surface and reacts with the surrounding oxygen. The ratio of metal vapor to oxidation products is measured with the time-of-flight mass spectrometer.

Special measurements on reactants and products are also made.

III. EXPERIMENTAL RESULTS

1. Oxidation of Uranium by Molecular Oxygen

A rate was reported by Fite[1] for the reaction

$$U + O_2 \xrightarrow{\ k_1\ } UO_2^+ + e \tag{1}$$
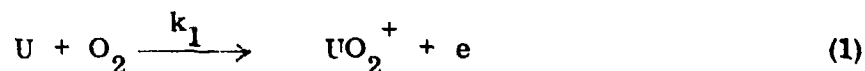
When the oxygen pressure was increased 10^{-4} torr in addition to the above process another ion producing reaction was identified in the process of our work; that being

A - INDUCTION COIL
B - TANTALUM HEAT SHIELD
C - KNUDSEN CRUCIBLE AND LID
D - WATER COOLED PORTION OF
    CHAMBER
E - MOVABLE SHUTTER
F - TOF SOURCE ENTRANCE SLIT

G - IONIZING ELECTRON BEAM
H - ION GRID
I - VIEWING WINDOW ON MULTIWINDOW
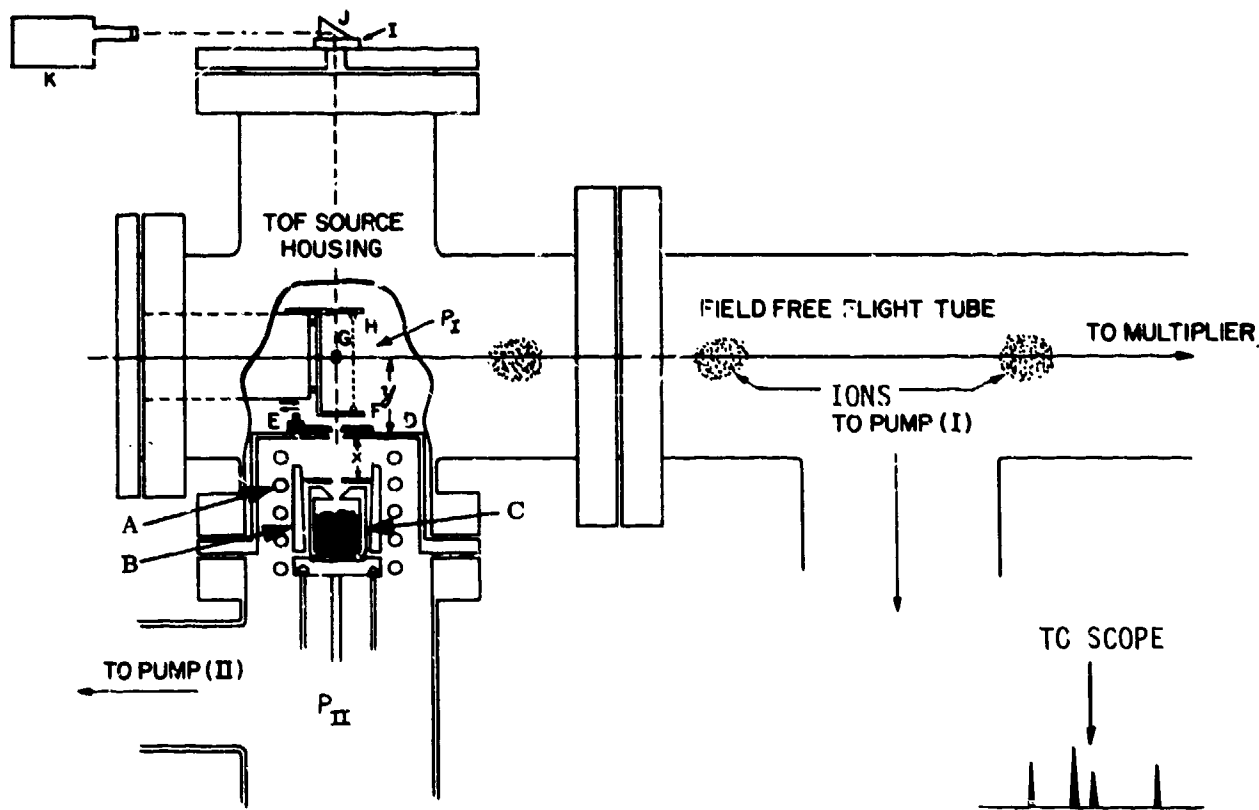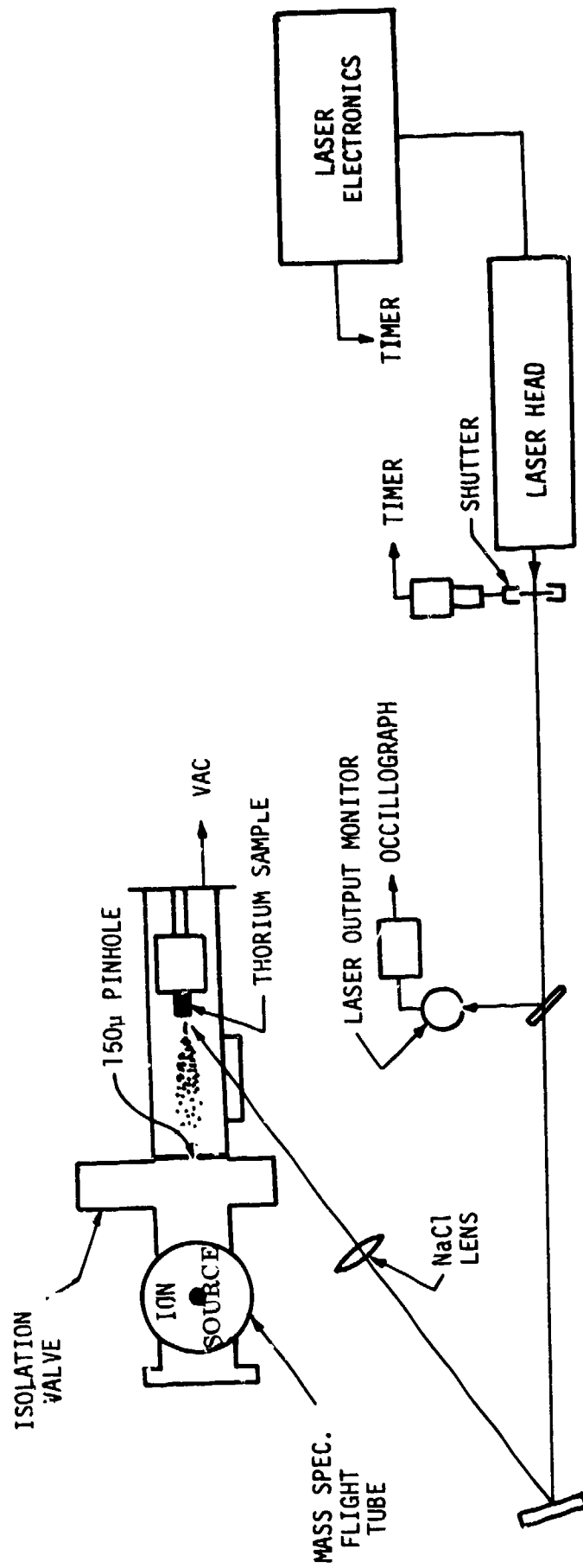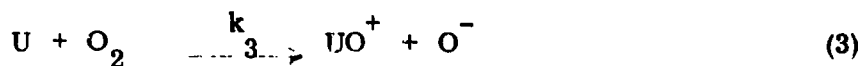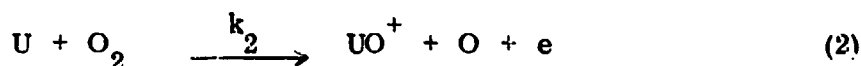   ASSEMBLY
J - PRISM
K - OPTICAL PYROMETER

Figure 1 - KNUDSEN CRUCIBLE MASS SPECTROMETER APPARATUS

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Figure 2 - LASER HEATING EXPERIMENT

tne formation of UO^+ via one of the following two possible processes:

$$U + O_2 \xrightarrow{k_2} UO^+ + O + e \qquad (2)$$

$$U + O_2 \xrightarrow{k_3} UO^+ + O^- \qquad (3)$$

In order to identify the step accounting for the formation of UO^+ the polarity of the mass spectrometer was reversed in order to search for the negative ion O^-. In view of the fact that (under condition of equivalent sensitivity) no negative ion O^- was observed it was concluded that most the observed UO^+ was formed mainly via step (2). Unless of course the life of O^- is less than the flight time in the mass spectrometer which is of the order of 25 μsec. That is to say . at negative ions which loose their charge during flight time are not focussed properly and thus escape detection. The expressions describing ion formation in the U/O_2 system are :

$$\frac{d\,(UO_2^+)}{dt} = k_1\,(U)\,(O_2) \qquad \text{and}$$

$$\frac{d\,(UO^+)}{dt} = (k2 + k3)\,(U)\,(O_2) \simeq k_2\,(U)\,(O_2)$$

or

$$\frac{k2}{k1} = \frac{d\,(UO^+)}{d\,(UO_2^+)}$$

Since the product species UO^+ and UO_2^+ are expected to have nearly equal multiplier efficiencies it is expected that the ratio of ion intensities $I\,(UO^+)$, $I\,(UO_2^+)$ is equal to the ratio of rate constants $k2/k1$ under conditions of equal $(U)/(O_2)$ ratios

i.e.

$$\frac{k2}{k1} = \frac{I\,(UO^+)}{I\,(UO_2^+)}$$

or

$$k2 = k1\,\frac{I\,(UO^+)}{I\,(UO_2^+)}$$

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It is therefore possible to determine k2 (if k1 is known) by measuring the intensity ratio of UO^+ and UO_2^+ formed simultaneously in the same run from reaction between U(g) and O_2.

Several runs were made under conditions where the oxygen pressure was in the range $(1.1 - 4.4) \times 10^{-4}$ torr at two different temperatures $2273^\circ K$ and $2323^\circ K$. (Under these conditions the number density of U(g) in the reaction chamber was several orders of magnitude lower than that of O_2). Data obtained from this series of experiments are shown in Table I along with the determination of k2 = $(8.2 \pm 3) \times 10^{-14} cm^3$ molecule^{-1} sec^{-1}.

In view of the fact that reaction (2) is endothermic by 2 eV while reaction (3) is endothermic by only 0.5 eV a case can be made for the existence of O^-, in which case the value of k2 represents the rate of UO^+ formation by reactions (2) or (3) or both. As far as it pertains to the intended application, however, it does not matter.

2. The Oxidation of Thorium by Atomic Oxygen.

The relative abundance of atomic oxygen in the upper atmosphere is high and reactions involving atomic oxygen are obviously important.

As part of this research several methods were examined in conjunction with atomic oxygen production; the method which proved successful in our case involved thermal decomposition of O_2 in an indium furnace, heated by the same induction field as the crucible containing the thorium.

When thorium was allowed to react with partially decomposed oxygen it became apparent that in addition to the formation of ThO_2^+ (which was reported before[2]) ThO^+ was observed as well, due to the following reactions

$$Th + O_2 \xrightarrow{k4} ThO_2^+ + e \qquad (4)$$
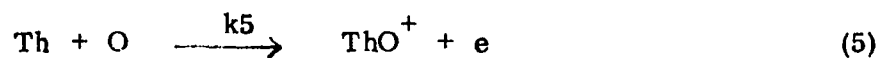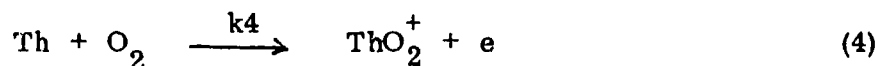
$$Th + O \xrightarrow{k5} ThO^+ + e \qquad (5)$$

Figure 3 shows a typical mass spectrum of these two ions recorded in the absence of an ionizing electron beam. The intensity ratio of the observed ions $\dfrac{I (ThO^+)}{I (ThO_2^+)}$ is related to the ratio of rate constants k4 and k5 and the degree of O_2 dissociation as follows:

TABLE I

RATE CONSTANT FOR THE FORMATION OF UO^+ FROM $U + O_2$

CHEMI-ION INTENSITY		$\dfrac{I\,(UO^+)}{I\,(UO^+_2)}$	P_{O_2} X 10^{-4}	$T\,^{\circ}K$	k_2
$I\,(UO^+)$	$I\,(UO^+_2)$		(torr)		(cm^3 molecule^{-1} sec^{-1})
800	46,800	1.71×10^{-2}	4.4	2323	6.8×10^{-14}
600	23,000	2.61×10^{-2}	2.6	2323	10×10^{-14}
170	5,720	2.97×10^{-2}	1.1	2323	12×10^{-14}
300	30,055	1.02×10^{-2}	3.6	2273	4.1×10^{-14}

Average $(8.2 \pm 3) \times 10^{-14}$
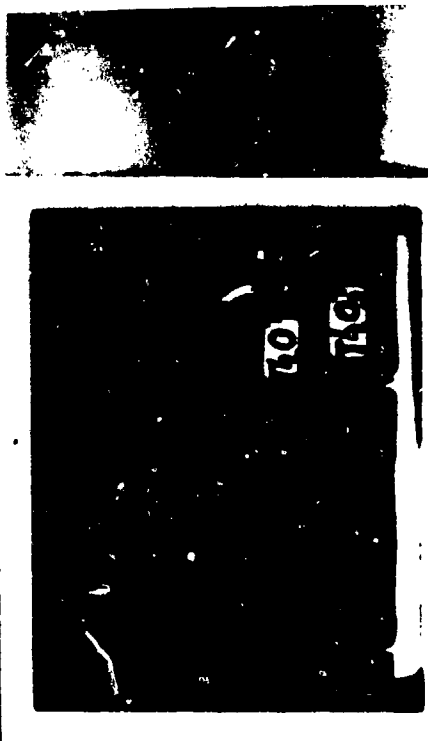
FIGURE 3. FORMATION OF CHEMI-IONS ThO$^+$ AND ThO$_2^+$

$$\frac{I\,(ThO^+)}{I\,(ThO_2^+)} = \frac{k5}{k4} \quad X \quad \frac{PO}{PO_2}$$

or
$$k5 = k4 \quad X \quad \frac{I\,(ThO^+)}{I\,(ThO_2^+)} \quad X \quad \frac{PO_2}{PO}$$

Based on the equilibrium predictions at 2248^oK at a total oxygen pressure of 10^{-3} torr the ratio of PO/PO_2 is 0.111. The observed ratio of chemi-ion intensities at the same temperature was:
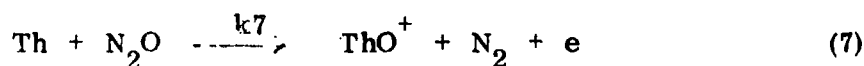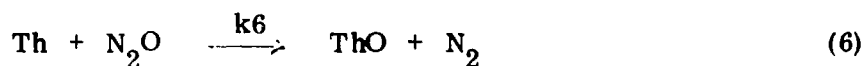
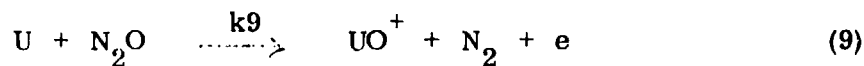$$\frac{I\,(ThO^+)}{I\,(ThO_2^+)} = 7$$

therefore $k5 = 63 \; X \; k4$

or*
$$= 63 \; X \; 4.9 \; X \; 10^{-12} = 3.1 \; X \; 10^{-10} \; cm^3 \; molecule^{-1} \; sec^{-1}$$

3. Oxidation of Thorium and Uranium by N_2O

The first step in the oxidation of gaseous thorium and uranium by N_2O can proceed as follows:

$$Th + N_2O \quad \xrightarrow{\;k6\;} \quad ThO + N_2 \tag{6}$$

$$Th + N_2O \quad \xrightarrow{\;k7\;} \quad ThO^+ + N_2 + e \tag{7}$$

and with uranium respectively

$$U + N_2O \quad \xrightarrow{\;k8\;} \quad UO + N_2 \tag{8}$$

$$U + N_2O \quad \xrightarrow{\;k9\;} \quad UO^+ + N_2 + e \tag{9}$$
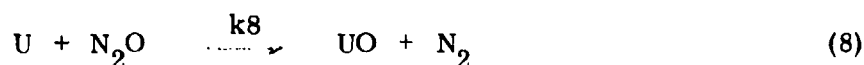
The formation of the neutral monoxides ThO and UO are highly exothermic by about 6 eV while the formation of UO^+ and ThO^+ are exothermic by 0.5 to 1 eV and are all thermodynamically favorable.

*k4 was determined and reported in a previous report[2].

Data has been obtained thus far which allows determination of k7 and k9 via the ratio method (applied previously) which allows determination of one rate constant relative to another: In this case rates for reactions (7) and (9) were compared to corresponding rates of reactions (4) and (1). The corresponding relationships are:

$$k7 = k4 \times \frac{I(ThO^+)}{I(ThO_2^+)} \times \frac{PO_2}{PN_2O} \times \frac{I(Th^+)_{O_2}}{I(Th^+)_{N_2O}} \quad (10)$$

$$k9 = k1 \times \frac{I(UO^+)}{I(UO_2^+)} \times \frac{PO_2}{PN_2O} \times \frac{I(U^+)_{O_2}}{I(U^+)_{N_2O}} \quad (11)$$

The intensities of the metal ions were obtained with an ionizing electron beam set at 11 eV, and are proportional to the metal number density.

Two separate experiments were obviously required. One using O_2 as the oxidant the second N_2O.

$$I(Th^+)_{O_2}, \; I(U^+)_{O_2} \; \text{and} \; I(Th^+)_{N_2O}$$

$$I(U^+)_{N_2O} \qquad \qquad \text{represent metal atom intensities as observed in the two}$$

different experiments prior to the introduction of reactants O_2 and N_2O respectively. Thorium oxidation at $2273^{0}K$ under conditions where P_{O_2} = 2.5 X 10^{-4} torr, P_{N_2O} =

4.2 X 10^{-4} torr and $\dfrac{I(Th^+)_{O_2}}{I(Th^+)_{N_2O}}$ = 2.5 resulted a ratio $\dfrac{I(ThO^+)}{I(ThO_2^+)}$ = 0.29

and a value for

$$k7 = 2.2 \times 10^{-12} \; cm^3 \; molecule^{-1} \; sec^{-1}$$

Similar treatment of uranium data resulted in a value of k9 = 1.2×10^{-12} cm^3 $molecule^{-1}sec^{-1}$

IV. CONCLUDING REMARKS

Based on results obtained to date the following conclusions can be made:

1. The oxidation of thorium in gas phase by molecular and atomic oxygen produces chemi-ions such as ThO_2^+ and ThO^+ respectively with corresponding rate constants 4.9×10^{-12} cm^3 molecule^{-1} sec^{-1} and 3.1×10^{-10} cm^3 molecule^{-1}sec^{-1}

   The molecular oxygen reaction produces ThO at a (gas kinetic) rate of $(5.1 \pm 1.1) \times 10^{-10}$.

2. The oxidation of uranium by O_2 produces UO at gas kinetic rate, UO_2^+ with a rate constant $(4.9 \pm 2.4) \times 10^{-10}$ and UO^+ with rate constant 8.4×10^{-14}.

3. Reactions of both thorium and uranium with N_2O produce the monoxide ions ThO^+ and UO^+ with corresponding rate constants 2.2×10^{-12} and 1.2×10^{-12}.

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