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# Kinetic study of gas-phase $Lu(^{2}D_{3/2})$ with $O_{2}$ , $N_{2}O$ and $CO_{2}$

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#### Abstract

The second-order rate constants of gas-phase Lu( ${}^{2}D_{3/2}$ ) with O<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> from 348 to 573 K are reported. In all cases, the reactions are relatively fast with small barriers. The disappearance rates are independent of total pressure indicating bimolecular abstraction processes. The bimolecular rate constants (in molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>) are described in Arrhenius form by  $k(O_2) = (2.3 \pm 0.4) \times 10^{-10} \exp(-3.1 \pm 0.7 \text{ kJ mol}^{-1}/RT)$ ,  $k(N_2O) = (2.2 \pm 0.4) \times 10^{-10} \exp(-7.1 \pm 0.8 \text{ kJ mol}^{-1}/RT)$ ,  $k(CO_2) = (2.0 \pm 0.6) \times 10^{-10} \exp(-7.6 \pm 1.3 \text{ kJ mol}^{-1}/RT)$ , where the uncertainties are  $\pm 2\sigma$ . © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The kinetics of gas-phase reactions involving metal atoms with oxygen-containing oxidants has recently received considerable attention [1–4]. Metal atom chemistry is an intriguing field of study due to the high multiplicities of the atomic ground states and the large number of low-lying metastable states.

In this Letter, we report a gas-phase kinetic study of the ground  ${}^{2}D_{3/2}$  state of lutetium with O<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>. Lutetium is the rarest of the lanthanides and is unique among the lanthanides due to its f subshell being completely filled. Because of its filled f subshell, the condensed phase reactivity and spectroscopy of lutetium is similar to that of the Group 3 metals.

We are unaware of any rate constant measurements involving lutetium in the gas-phase with oxygen-containing oxidants. This study continues our efforts to further understand the dynamics of gas-phase metal reactions. Although primarily phenomenological, the increase in the database of these reactions should yield greater insight into the important factors affecting gas-phase metal atom reactions.

# 2. Experimental

Pseudo-first-order kinetic experiments  $([Lu] \ll [oxidant])$  were carried out in an apparatus with slowly flowing gas using a laser photolysis/ laser-induced fluorescence (LIF) technique. The experimental apparatus and technique have been described in detail elsewhere [5]. Briefly, the reaction chamber is a stainless steel reducing 4-way cross with attached side arms and a sapphire window for optical viewing. The reaction chamber is enclosed within a convection oven (Blue M, model 206F) for temperature dependence experiments.

Lutetium atoms were produced by the 248 nm photodissociation of tris(2,2,6,6-tetramethyl-3,5-

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heptanedionato) lutetium (III) [Lu(TMHD)<sub>3</sub>] using the focused output of an excimer laser (Lambda Physics Lextra 200). The photolysis laser output was focused using a lens (f = 564 mm)positioned approximately one focal length from the detection zone. Lutetium atoms were detected via LIF using an excimer-pumped dye laser (Lambda Physics Lextra 50/ScanMate 2E) tuned to the  ${}^{2}D_{5/2}^{0} \leftarrow {}^{2}D_{3/2}$  transition at 465.802 nm and the  ${}^{2}D^{0}_{5/2} \rightarrow {}^{2}D_{5/2}$  fluorescence at 513.509 nm was isolated with an interference filter [6]. The fluorescence was detected at 90° to the counterpropagated laser beams with a three-lens telescope imaged through an iris. A photomultiplier tube (Hamamatsu R375) was used in collecting the LIF which was subsequently sent to a gated boxcar sampling module (Stanford Research Systems SR250), and the digitized output was stored and analyzed by a computer.

Because of the low vapor pressure of the precursor at room temperature, the precursor required heating to get enough molecules into the gas phase. Thus, the lowest temperature at which kinetic experiments could be performed corresponded to 348 K. Below these temperatures the LIF signal was too weak to measure reliable values of the rate constant.

The heated precursor was entrained in a flow of nitrogen buffer gas. The precursor carrier gas, buffer gas and reactant gases flowed through calibrated mass flow meters and flow controllers prior to admission to the reaction chamber. Each sidearm window was purged with a slow flow of nitrogen buffer gas to prevent deposition of the transition metal and other photoproducts. Pressures were measured with MKS Baratron manometers, and chamber temperatures were measured with a thermocouple.

The delay time between the photolysis pulse and the dye-laser pulse was varied by a digital delay generator (Stanford Research Systems DG535) controlled by a computer. The trigger source for these experiments was scattered pump laser light incident upon a fast photodiode. LIF decay traces consisted of 200 points, each point averaged for four laser shots.

The Lu(TMHD)<sub>3</sub> precursor was synthesized from  $Lu(NO_3)_3$  and Li(TMHD) similar to that

reported previously [7]. The following reagents were used as received:  $O_2$  (MG Industries, 99.8%),  $N_2O$  (MG Industries, electronic grade, 99.999%),  $CO_2$  (MG Industries, anaerobic grade, 99.9%) and  $N_2$  (Potomac Airgas, Inc., 99.998%).

#### 3. Data analysis and results

The decay rates of the  ${}^{2}D_{3/2}$  state of lutetium as a function of reactant pressure were investigated at various temperatures and total pressures. The loss of ground state atoms is described by the first-order decay constant,  $k_{1}$ 

$$k_1 = 1/\tau = k_0 + k_2[\text{oxid}],\tag{1}$$

where  $\tau$  is the first-order time constant for the removal of the transition metal under the given experimental conditions,  $k_0 (= 1/\tau_0)$  the loss term due to diffusion out of the detection zone and reaction with the precursor and precursor fragments, and  $k_2$  is the second-order rate constant. Typical decay profiles are shown in Fig. 1. A time constant,  $\tau$ , for each decay profile was determined using a linear least-squares procedure. The second-order rate constant is determined from a plot of  $1/\tau$  vs. reactant number density. Typical plots for obtaining second-order rate constants are presented in Fig. 2; the slope yields the observed rate constant. The relative uncertainty (i.e., the reproducibility) of the secondorder rate constants is estimated at  $\pm 20\%$  based on repeated measurements of rate constants under identical temperature and total pressure conditions. The absolute uncertainties are estimated to be  $\pm 30\%$  and are based on the sum of the statistical scatter in the data, uncertainty in the flowmeter and flow controller readings (5%)and the total pressure reading (1%), and uncertainties due to incomplete gas mixing and incomplete relaxation of excited states produced in the photolysis event.

Second-order rate constants for the  ${}^{2}D_{3/2}$  state reacting with O<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> at 5 Torr from 373 to 573 K are listed in Table 1. Rate constants could not be measured above 573 K due to thermal decomposition of the precursor. The rate constants at 398 K for these reactions were also



Fig. 1. Typical Lu( ${}^{2}D_{3/2}$ ) decay curves in the presence of oxidant at 473 K,  $P_{\text{total}} = 5.0$  Torr. (a)  $P(O_2) = 97$  mTorr,  $\tau = 36.1 \text{ } \mu\text{s}$ ; (b)  $P(N_2O) = 194$  mTorr,  $\tau = 50.5 \text{ } \mu\text{s}$ ; (c)  $P(CO_2) = 89$  mTorr,  $\tau = 78.6 \text{ } \mu\text{s}$ . The solid lines through the data are exponential fits. The inset is a ln plot of the data.



Fig. 2. Typical plots for determining  $k_{2nd}$  for  $Lu({}^{2}D_{3/2})$  at 448 K. The solid line for each set of data is a linear regression fit from which  $k_{2nd}$  is obtained.

measured at 20 Torr and are independent of total pressure within experimental uncertainty.

The rate constants (in molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>) are described in Arrhenius form (see Fig. 3) by:



Fig. 3. Arrhenius plots for the collisional disappearance of  $Lu(^{2}D_{3/2})$ . Each solid line is a linear regression fit of the rate constants to the equation  $k(T) = Ae^{-Ea/RT}$ .

$$k(O_2) = (2.3 \pm 0.4) \times 10^{-10}$$
  
  $\times \exp(-3.1 \pm 0.7 \text{ kJ mol}^{-1}/RT),$  (2)

$$k(N_2O) = (2.2 \pm 0.4) \times 10^{-10}$$
  
  $\times \exp(-7.1 \pm 0.8 \text{ kJ mol}^{-1}/RT),$  (3)

$$k(\text{CO}_2) = (2.0 \pm 0.6) \times 10^{-10}$$
  
  $\times \exp(-7.6 \pm 1.3 \text{ kJ mol}^{-1}/RT),$  (4)

where the uncertainties are  $\pm 2\sigma$ .

# 4. Discussion

The pressure independence observed for these reactions indicates termolecular processes are unimportant; therefore, bimolecular abstraction reactions are indicated. The production of LuO on the ground state surface is exothermic for all the oxygen-containing reactants reported here. The exothermicities for the reactions with  $O_2$ ,  $N_2O$ and  $CO_2$  are 193, 524, and 159 kJ/mol, respectively; [8] thus, no thermodynamic barriers exist for these reactions. The experimentally measured

Table 1 Second-order rate constants<sup>a</sup>( $/10^{-11} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$ ) for the  ${}^2D_{3/2}$  state of lutetium with O<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>

2, 2 2				
T (K)	$O_2$	$N_2O$	CO <sub>2</sub>	
348	7.8	1.9	1.4	
373	8.3	2.3	1.8	
398	9.1	2.6	1.8	
423	9.2	2.9	2.4	
448	8.9	3.3	2.4	
473	10	4.0	3.2	
498	11	4.2	3.1	
523	11	4.0	3.4	
548	11	4.8	3.6	
573	12	5.0	4.1	

<sup>a</sup> Uncertainties are estimated at  $\pm 30\%$ .

barriers for all these reactants are small (<8 kJ/ mol), and in every case reaction occurs on average in fewer than about 20 hard-sphere collisions.

Previous studies of the other lanthanides reacting with O2, N2O and CO2 indicated the activation energies for these reactions are correlated to the energy required to promote an electron out of the filled 6s subshell [2-4]. The lowest excited state of lutetium with an s<sup>1</sup> configuration is the  $5d^{1}6s^{1}6p^{14}F^{0}_{3/2}$  state 17,427 cm<sup>-1</sup> above the ground state [9]. This relatively large excitation energy should result in higher activation energies compared to those measured in this study; i.e., the activation energies for O<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> reactions are predicted to be 11, 20 and 38 kJ/mol, respectively. These calculated activation energies are based on extrapolating the data from the other lanthanide studies assuming a linear correlation between the measured activation energy and the excitation energy [2–4]. Thus, the activation energy for lutetium does not appear to show the same dependence on the s<sup>2</sup> to s<sup>1</sup> excitation energy as observed for the other lanthanides.

The dynamics of the gas-phase reactions of lutetium do not exhibit the same pattern as observed for the other lanthanides. In common practice, scandium, yttrium and lanthanum are arranged together in Group 3 with the lanthanide series following lanthanum. Yttrium is closer in size and properties to lutetium so that an argument has been made that lutetium should be placed in Group 3 preceded by the La–Yb elements [10]. This argument is also supported by the gas-phase reactivities of these elements. The rate constants reported here for lutetium reacting with  $O_2$ ,  $N_2O$  and  $CO_2$  are very similar to the rate constants reported for yttrium and scandium with these oxidants while the rate constants for lanthanum are about an order of magnitude higher [11,12].

## 5. Summary

We have measured bimolecular reaction rate constants and Arrhenius parameters for the reactions of the  ${}^{2}D_{3/2}$  state of lutetium with O<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>. In each case, abstraction of an oxygen atom to produce the metal oxide is the reaction channel. The activation barriers for these reactions are small ( $E_{a} < 8$  kJ/mol).

## Acknowledgements

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