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Temperature dependent study of the kinetics of Sc($a^2D_{3/2}$) with O_2 , N_2O , CO_2 , NO and SO₂

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Abstract

The gas phase reactivity of $Sc(a^2D_{3/2})$ with O_2 , N_2O , CO_2 , NO and SO_2 in the temperature range 298–523 K is reported. The bimolecular rate constants are described in Arrhenius form by $k(O_2) = (1.7 \pm 0.4) \times 10^{-10} \exp(-7.9 \pm 0.7 \text{ kJ/mol}/RT)$ cm³s⁻¹, $k(N_2O) = (1.7 \pm 0.3) \times 10^{-10} \exp(-12.0 \pm 0.6 \text{ kJ/mol}/RT)$ cm³s⁻¹, $k(CO_2) = (7.3 \pm 1.3) \times 10^{-11} \exp(-12.3 \pm 0.6 \text{ kJ/mol}/RT)$ cm³s⁻¹ where the uncertainties are $\pm 2\sigma$. The rate constants with NO and SO₂ were temperature insensitive with room temperature rate constants of 1.5×10^{-11} and 2.0×10^{-10} cm³s⁻¹, respectively. The disappearance rates for all the reactants are independent of total pressure indicating a bimolecular abstraction mechanism. \mathbb{C} 1997 Elsevier Science B.V.

1. Introduction

Recently considerable attention has been focused on the oxidation reactions of gas-phase transition metal atoms [1-20]. Transition metal chemistry is an intriguing field of study due to the high multiplicities of many of the atomic ground states and the large number of low-lying metastable states. The cumulative data thus far reported indicate the different electronic states in these atoms have a dramatic effect on the dynamics of transition metal reactions [5].

In this Letter we report a temperature-dependent kinetic study of the $a^2D_{3/2}$ state of scandium with

 O_2 , N_2O , CO_2 , NO and SO_2 . All five abstraction reactions to produce ScO are exothermic:

 $Sc + O_2 \rightarrow ScO + O \quad \Delta H^\circ = -183 \text{ kJ},$ (1)

$$Sc + N_2O \rightarrow ScO + N_2 \quad \Delta H^\circ = -514 \text{ kJ},$$
 (2)

$$Sc + CO_2 \rightarrow ScO + CO \quad \Delta H^\circ = -149 \text{ kJ}, \quad (3)$$

$$Sc + NO \rightarrow ScO + N \quad \Delta H^{\circ} = -50 \text{ kJ},$$
 (4)

$$Sc + SO_2 \rightarrow ScO + SO \quad \Delta H^\circ = -130 \text{ kJ}, \quad (5)$$

so there are no thermodynamic barriers to reaction [21,22]. By obtaining Arrhenius parameters for these reactions, we distinguish between steric factors and energy barrier effects. The only previously reported rate constants for the reactions of scandium under multiple collision conditions was a room temperature study involving O_2 , N_2O and NO using a fast flow tube [17]. A bimolecular abstraction mechanism was established based on detection of the ScO product. A

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mechanism involving electron transfer from a neutral M + OX reactant surface to an ion pair $M^+O^- + X$ product surface was proposed for these reactions.

Products of scandium oxidation reactions have also been directly observed in single-collision beamgas experiments. Parson and co-workers used LIF detection to observe the ScO product for a beam of scandium atoms reacting with O₂, NO and SO₂ [23]. Reaction cross sections were reported for these reactions although the absolute accuracies were estimated to be inaccurate by as much as 300%. Gole and co-workers [24,25] have carried out an analogous beam-gas experiment in which the visible chemilumescence of excited ScO was characterized for scandium with O₂ and N₂O. In this study, activation energies were reported for the production of excited state ScO based on the temperature dependence of the chemiluminescence signal. Activation energies for the production of ground state products, however, have yet to be reported.

This study continues our efforts to further understand the dynamics of gas phase transition metal reactions. Although primarily phenomenological, the increase in the data base of these reactions should yield greater insight into the important factors affecting transition metal chemistry.

2. Experimental

Experiments were performed under pseudo-first order conditions ([Sc] \ll [oxidant]) using a laser photolysis/laser induced fluorescence (LIF) technique. The technique has been described in detail elsewhere [2]. Briefly, the reaction chamber is a stainless steel four-way cross with attached sidearms and a sapphire window for optical viewing. The reaction chamber is enclosed in a convection oven to allow for determination of temperature dependent rate constants.

Scandium atoms were produced by the 248 nm photodissociation of either hexafluoroacetylacetonate scandium, [Sc(hfa)₃], or tris(2,2,6,6-tetramethyl-3,5-heptanedionato) scandium, [Sc(TMHD)₃] using the focused output of an excimer laser. Scandium atoms were detected via LIF using an excimer pumped dye laser tuned to the $y^2 D_{3/2}^{\circ} \leftarrow a^2 D_{3/2}$ transition at 402.04 nm [26]. The LIF was detected at 90° to the

counterpropagated laser beams with a three-lens telescope imaged through an iris. The LIF was sent to a gated boxcar sampling module, and the digitized output was stored and analyzed by a computer. The delay time between the photolysis pulse and the dye-laser pulse was varied by a digital delay generator controlled by a computer. LIF decay traces consisted of 200 points, each point averaged for at least 4 laser shots and represented a decay of approximately three reaction lifetimes.

Vapor from the solid precursor was entrained in a flow of N_2 buffer gas. The buffer, reactant and precursor carrier gases flowed through calibrated mass flow meters and flow controllers prior to admission to the reaction chamber. Pressures were measured with capacitance manometers, and chamber temperatures were measured with a thermocouple.

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%), NO (Liquid Carbonic, 99.0%), SO_2 (MG Industries, 99.9%), CH_4 (Linde Specialty Gas, 99.999%), N_2 (Potomac Airgas, Inc., 99.998%), $Sc(hfa)_3$ (Strem, 99.9%) and $Sc(TMHD)_3$ (Strem, 99%).

3. Data analysis and results

The characteristics of the two precursors used in this study require a brief description. Sc(hfa)₃ could be used from room temperature up to 473 K inasmuch as Sc(hfa)₃ decomposes above 473 K. Sc(hfa)₃ required high UV laser photolysis fluences (approximately 1 J/cm^2 or higher) to photodissociate to scandium atoms; i.e., at low laser fluences no scandium signal was observed. Sc(TMHD)₃ could only be used at temperatures higher than 100°C due to its low vapor pressure at room temperature. Sc(TMHD)₃ required heating to approximately 100°C in order to get enough precursor molecules into the gas phase. The maximum temperature attainable in these studies was limited to 523 K since Sc(TMHD)₃ decomposes above this temperature. Sc(TMHD)₃ required much smaller UV laser fluences than Sc(hfa)₃ to produce scandium atoms.

Initially, different rate constants were obtained for



Fig. 1. Typical Sc($a^2 D_{3/2}$) decay curves with added N₂O. Temperature = 423 K, $P_{\text{total}} = 20.0$ Torr. (a) $P(N_2O) = 0.087$ Torr, Sc(TMHD)₃ precursor, $P(CH_4) = 12$ Torr, $\tau = 32$ µs and (b) $P(N_2O) = 0.034$ Torr, Sc(hfa)₃ precursor, $\tau = 72$ µs. The lines through the data are exponential fits. The inset is a logarithm plot of the data.

the two precursors at a given temperature; the rate constants measured using Sc(TMHD)₃ as the precursor were systematically smaller than those rate constants measured using Sc(hfa)₃. This disparity was attributed to the production of excited states of scandium in the photodissociation of $Sc(TMHD)_3$. The cascading of excited states to the ground state caused an apparent increase in the measured time constants determined using Sc(TMHD)₃. Thus, a quencher gas was required in experiments involving Sc(TMHD)₃ where the quencher needed to efficiently relax the excited states without reacting with the ground state. Methane was found to meet these two requirements. A methane partial pressure of up to 12 Torr was used for the experiments involving Sc(TMHD)₃. In the presence of sufficient methane, at a given temperature the rate constants determined using $Sc(TMHD)_3$ as the precursor were within the experimental uncertainty of those determined using $Sc(hfa)_3$.

The loss of ground state scandium in the presence of oxidant is described by the first-order decay constant, k_1 ,

$$k_1 = 1/\tau = k_0 + k_2 [\text{oxidant}],$$
 (6)



Fig. 2. Typical plots for determining k_{2nd} . Data shown is for $Sc(a^2D_{3/2})+N_2O$. The solid line for each set of data is a linear regression fit from which k_{2nd} is obtained.

where τ is the first-order time constant for the removal of scandium under the given experimental conditions, k_o (= 1/ τ_o) is 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. Fig. 1 shows the typical decrease in the Sc LIF signal as a function of laser delay for the reaction with N₂O. In this figure, the lines through the data are exponential fits from which the pseudo-first order rate constant, $1/\tau$, is obtained.

The second-order rate constant is determined from

Second-order rate constants ^a $(/10^{-12} \text{ cm}^3 \text{ s}^{-1})$ for the $a^2 D_{3/2}$ state of scandium with O₂, N₂O, CO₂, NO and SO₂

					-	
T (K)	02	N ₂ O	CO ₂	NO	SO ₂	
298 ^b	6.7	1.4	0.53	15.0	200.0	
348	11.0	2.7	0.99			
373	14.0	3.6	1.4	14.0	210.0	
398	16.0	4.3	1.8			
423	17.0	5.8	2.1			
448	19.0	6.8	2.7	18.0		
473	24.0	8.0	3.0			
498	25.0	9.0	3.8			
523	27.0	11.0	4.3			

^a Uncertainties for the rate constants are $\pm 30\%$.

Table 1

^b The rate constants at 298 K represent room temperature rate constants; room temperature varied between 296 K and 299 K.

a plot of $1/\tau$ vs. reactant number density. The second-order rate constants are presented in Table 1. Typical plots for obtaining second-order rate constants are presented in Fig. 2; the slope yields the observed rate constant. The rate constants in Table 1 were measured at 20 Torr total pressure. Room temperature rate constants were measured from 10 to 50 Torr; the rate constants are independent of total pressure within experimental uncertainty indicating termolecular processes are unimportant. The relative uncertainty (i.e., the reproducibility) of the secondorder rate constants is estimated at $\pm 10\%$. The absolute uncertainties are conservatively estimated to be $\pm 30\%$ and are based on the sum of the statistical scatter in the data, uncertainty in the flow meter (5%), flow controller (5%), and pressure readings (1%), and errors associated with incomplete mixing.

Arrhenius plots (ln k vs. 1/T) for O₂, N₂O and CO₂ are shown in Fig. 3. The rate constants are described by $k(O_2) = (1.7 \pm 0.4) \times 10^{-10} \exp(-7.9 \pm 0.7 \text{ kJ/mol/RT}) \text{ cm}^3 \text{ s}^{-1} k(N_2\text{O}) = (1.7 \pm 0.3) \times 10^{-10} \exp(-12.0 \pm 0.6 \text{ kJ/mol/RT}) \text{ cm}^3 \text{ s}^{-1}$ and $k(CO_2) = (7.3 \pm 1.3) \times 10^{-10} \exp(-12.3 \pm 0.6 \text{ kJ/mol/RT}) \text{ cm}^3 \text{ s}^{-1}$, where the uncertainties are $\pm 2\sigma$.



Fig. 3. Arrhenius plots for the collisional disappearance of $Sc(a^2D_{3/2})$ with O_2 , N_2O and CO_2 . The solid line is a weighted exponential fit to the equation $k(T) = A \exp(-E_a / RT)$. Error bars are $\pm 30\%$.

4. Discussion

In these experiments only the $a^2D_{3/2}$ ground state was studied inasmuch as a previous room temperature study reported the spin-orbit excited state, $a^2 D_{5/2}$ ($E = 168 \text{ cm}^{-1}$), has removal rate constants equal to the ground state in the presence of O_2 , N_2O and NO [17]. Thus, either the reaction rate constants for the two states are equal or the intramultiplet mixing rate is fast relative to chemical reaction. Here we assumed the removal rate constants for the two spin-orbit states do not have different temperature dependences and that the two states exhibit the same reactivities with CO₂ and SO₂. Other transition metal atoms with small spin-orbit splittings have exhibited no spin-orbit dependence for their removal rate constants under multiple collision conditions [1,4,7,9,15-18].

The room temperature rate constants reported by Ritter and Weishaar for O_2 , N_2O and NO are approximately 25% lower than the values reported here. [17] Their method relied on an indirect measurement of the scandium atom velocity down their flow tube; thus, a systematic error of 25% in their data is not surprising. Our results are consistent with their data within the absolute accuracy of the two experimental methods.

Our results for the reaction of ground state scandium with all five oxidants are consistent with a bimolecular abstraction reaction as reported previously [17,23–25]. Unfortunately, little is known about the potential energy surfaces for the interaction of transition metal atoms with even the simplest of molecules. A complete understanding of these reactions awaits advances in theoretical dynamics calculations for these systems. Nevertheless, it is still useful to assess the experimental data reported thus far to look for general trends and correlations between the reaction rates and the physical properties of the transition metal.

Table 2 lists the activation energies of the reported bimolecular abstraction reactions of transition metals with O_2 , N_2O and CO_2 . A comparison of the activation energies of the exothermic reactions of other transition metals with O_2 indicates the activation energy of scandium is similar to other s²d^{*n*-2} atoms occurring by a bimolecular abstraction mechanism. While modest barriers are encountered for

Transition metal	TMO bor	ıd	<u> </u>	· · · · · · · · · · · · · · · · · · ·		Ref.
	IP ^a (eV)	energy ^b (kJ/mol)	$\frac{E_{a}(O_{2})}{(kJ/mol)}$	$\frac{E_{\rm a}(\rm N_2O)}{\rm (kJ/mol)}$	$\frac{E_{\rm a}(\rm CO_2)}{\rm (kJ/mol)}$	
$Sc(s^2d^1 2D_{3/2})$	6.56	677	7.9	12.0	12.3	this work
$Ti(s^2 d^2 {}^3F_2)$	6.83	668	11.6	14.3	14.9	[15]
$V(s^2 d^{3/4} F_{3/2})$	6.74	621	9.0	10.7	12.1	[16,28]
$Cr(s^{1}d^{5} {}^{7}S_{3})$	6.76	425	$\geq 40^{\circ}$	22	\geq 74 °	[19]
$Mn(s^2d^{5} {}^6S_{5/2})$	7.43	399	≥ 141 °	45	≥ 175 °	[3]
$Fe(s^2d^{6} {}^5D_4)$	7.90	386	≥ 85 °	44	≥ 119 °	[7]
$Cu(s^1d^{10} S_{1/2})$	7.72	266	≥ 213 °	40	≥ 247 °	[20]
$Nb(s^{1}d^{4} {}^{6}D_{1/2})$	6.77	765	≈ 0	≈ 0	≈ 0	[9]
$Mo(s^{1}d^{5} {}^{7}S_{3})$	7.10	556	≈ 0	39	d	[1,4]
$Ta(s^2 d^{3/4} F_{3/2})$	7.88	795	7.8	13.6	26.8	[10]
$W(s^2 d^{4/5} D_0)^{5/2}$	7.98	668	12.7	25.6	d	[2,8]
$Os(s^2d^{6} {}^5D_4)$	8.7	575	9.0	38.1	d	[5]

Ionization potentials, transition metal oxide bond energies and activation energies for the reactions $TM(g) + OX(g) \rightarrow TMO(g) + X(g)$

^a Ref. [27]. ^b Ref. [21].

^c Thermodynamic barrier calculated from Refs. [21,22].

^d Not measured.

Table 2

 $s^2 d^{n-2}$ transition metal atoms, the two transition metals with $s^1 d^{n-1}$ ground state configurations (Nb and Mo) exhibit no barrier to reaction. Thus, the O₂ reactions of transition metals with $s^1 d^{n-1}$ ground state configurations react more efficiently than transition metals with $s^2 d^{n-2}$ configurations. Apparently, the closed shell nature and the more diffuse spatial extent of the s electrons in $s^2 d^{n-2}$ atoms introduces a barrier in the reactions of these atoms.

Trends in the removal rates of excited states of some of the transition metals have shown the same relationship with respect to electron configuration. Molybdenum and tungsten have excited states with s²d⁴ configurations which react at a slower rate than the lower energy s^1d^5 states with O_2 [1,2]. The 5s¹4d⁴ ground state of niobium reacts near the gas kinetic collision rate with O2, while the excited $5s^24d^3 {}^4F_{9/2}$ state reacts about fifty times slower at room temperature. [9] Studies of the excited states of vanadium [16] and titanium [18] indicate the excited $s^{1}d^{n-1}$ states in the presence of O₂ have removal rate constants over an order of magnitude greater than the ground $s^2 d^{n-2}$ states. These studies did not distinguish between physical quenching and chemical reaction; therefore, the larger rate constants for the excited states may have a significant physical quenching component.

The reactions involving transition metal atoms

with CO₂ and N₂O are not as straightforward as those involving O_2 . For reactions with CO_2 , the majority of transition metal abstraction reactions have large endothermicities such that bimolecular abstraction reaction rates near room temperature are too slow to measure. For those cases with exothermic reactions, diverse behavior is observed (Table 2). The abstraction reactions of all the transition metal atoms with N₂O are exothermic due to the formation of the stable N_2 and metal monoxide molecules. Despite this exothermicity, metal atom reactions with N₂O have been observed to have significant energy barriers. In order to conserve electron spin, the ${}^{1}\Sigma^{+}$ ground state of N₂O correlates diabatically to $O(^{1}D_{2}) + N_{2}(^{1}\Sigma^{+})$, 15868 cm⁻¹ above the $O(^{3}P_{2})$ $+ N_2(^{1}\Sigma^{+})$ asymptote [27]. Thus, for all transition metal reactions with N₂O, the lowest energy reaction pathway requires a transition from reactant surfaces of $O(^{1}D_{2})$ character to surfaces of $O(^{3}P)$ character in order to access the low-energy product states [17]. A similar argument applies to the reactions of CO₂. Thus, to understand the reactions of CO_2 and N_2O_2 , attention must be given to multidimensional intersections among diabatic potential energy surfaces arising from both ground and low-lying excited states of the reactants. The large number of low-lying states for many transition metals means numerous potential energy surfaces are accessible in the entrance channel. Consequently, the activation barrier is a complex interplay of how a transition metal's reactant surfaces evolve into the accessible product channels. A complete explanation of this behavior awaits accurate theoretical calculations.

All of the transition metal atoms with exothermic abstraction reaction channels with NO and SO₂ reported thus far have small barriers ($E_a < 5 \text{ kJ/mol}$) [4,8–10,15,16]. Apparently, strong attractive interactions occur with NO and SO₂ regardless of the electron configuration of the transition metal. NO reacts with transition metals at an even faster rate than O_2 despite NO's smaller electron affinity. Honma and coworkers [13] have explained this trend as arising from the singly occupied π orbital on NO which is localized on the nitrogen atom. The interaction between this 1π orbital and the valence s electron can form an attractive interaction. Such an interaction is not possible in O₂ since the singly occupied π^* orbital has a counterpart with opposite phase at the second oxygen atom, which would cause additional repulsion.

5. Summary

We have measured bimolecular reaction rate constants and Arrhenius parameters for the reactions of the $a^2D_{3/2}$ state of scandium with O_2 , N_2O , CO_2 , NO and SO_2 over the temperature range 298–523 K. In each case abstraction of an oxygen atom to produce the transition metal oxide is the reaction channel. The activation energies for all the reactions are small. Reaction barriers are attributed to the closed shell nature and long range repulsion of the filled 4s subshell. The simple electron transfer mechanism [17] previously used to explain transition metal oxidation reactions is clearly inadequate to explain the accumulated data reported thus far.

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