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Kinetic study of the reaction of $Mn(a^6S_{5/2})$ with N₂O from 448 to 620 K

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The gas phase reactivity of $Mn(a^6S_{5/2})$ with N₂O in the temperature range 448–620 K is reported. Manganese atoms were produced by the photodissociation of 2-methylcyclopentadienyl manganese tricarbonyl and detected by laser-induced fluorescence. The reaction rate of the $a^6S_{5/2}$ state is very slow and temperature dependent. The rate constants are independent of total pressure indicating a bimolecular reaction. The rate constants are described in Arrhenius form by $(2.05\pm0.45)\times10^{-10} \exp(-44.7\pm1.0 \text{ kJ/mol/}RT) \text{ cm}^3 \text{ s}^{-1}$. © 1996 American Institute of Physics. [S0021-9606(96)02919-5]

INTRODUCTION

The gas-phase chemistry of transition metal (TM) atoms in oxidation reactions has recently received considerable attention.¹ In this paper we report a kinetic study of the ground state of Mn with nitrous oxide,

$$\operatorname{Mn}(a^{6}S_{5/2}) + \operatorname{N}_{2}\operatorname{O}(X^{-1}\Sigma^{+}) \to \operatorname{MnO} + \operatorname{N}_{2}.$$
(1)

The only other previously reported study of Reaction (1) involved high velocity Mn atoms produced by laser vaporization in a beam/gas arrangement in which the time resolved MnO chemiluminescence was observed.² The production of excited MnO in reaction (1) was found to have a large translational threshold energy. Arguments were presented which predicted significant barriers should also be present for the production of ground state MnO, although no quantitative results were presented.

Recently, Fontijn and co-workers have advanced a resonance interaction model³⁻⁶ to predict Arrhenius parameters and rate constants for metal atoms reacting with N₂O. In this model, the activation barriers are calculated by taking into account the ionization potential and *sp* promotion energy of the metal, the electron affinity of N₂O, and the bond energy of the metal oxide product. Many main group metals have been studied in reactions with N₂O and this model appears to describe these reactions reasonably well. In contrast, relatively few experimental studies have been performed on TM atoms; consequently, this model is essentially untested for TM atoms. Therefore, it is desirable to obtain temperature dependent studies for the reaction of nitrous oxide with several transition metals to determine the applicability of the resonance interaction model to TM's.

EXPERIMENT

Pseudo-first order kinetic experiments ([Mn] \leq [N₂O]) 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.¹ Briefly, the reaction chamber is a fourway cross with attached side arms and a sapphire window for optical viewing. The reaction chamber is enclosed within a convection oven for temperature dependence experiments. Manganese atoms were produced by the

248 nm photodissociation of 2-methylcyclopentadienyl manganese tricarbonyl, (MMT). Mn atoms were detected via LIF using an excimer-pumped dye laser tuned to the $z^6 P_{7/2}^{0} \leftarrow a^6 S_{5/2}$ transition at 403.076 nm.⁷ The fluorescence was detected at 90° to the counterpropagated laser beams with a three-lens telescope imaged through an iris. The LIF signal from the photomultiplier tube was sent to a gated boxcar sampling module, and the digitized output was stored and analyzed by a computer. The MMT precursor was entrained in a flow of N2 gas. The diluted precursor, N2 buffer gas, and N₂O flowed through calibrated mass flow meters and flow controllers prior to admission to the reaction chamber. Total flows were between 400 and 1500 sccm. Typical precursor pressures inside the reaction chamber ranged from 0.5 to 4.8 mTorr assuming saturated conditions⁸ in the MMT saturator. The delay time between the photolysis and dye-laser pulses was varied by a digital delay generator controlled by a computer. LIF decay traces consisted of 200 points; each point is an average of 3 laser shots.

DATA ANALYSIS AND RESULTS

The decay rates of the ground state $(a^6S_{5/2})$ of Mn as a function of N₂O pressure were investigated as a function of



FIG. 1. Typical plots for determination of k_{2nd} . The pressure in parentheses is the total pressure at which the experiments were performed. The inset is a $Mn(a^6S_{5/2})$ first-order decay curve corresponding to the point at 130 Torr N₂O pressure for the 523 K data $(1/\tau=0.020 \ \mu s^{-1})$.

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TABLE I. Bimolecular rate constants (/10⁻¹⁵) for $Mn(a^6S_{5/2}) + N_2O$ in N_2 buffer gas.

Temperature (K)	Total pressure (Torr)	Total flow (sccm)	MMT pressure (mTorr)	Bimolecular rate constant $(\text{cm}^3 \text{ s}^{-1}, /10^{-15})$
448	250	650	3.8	1.6
448	250	650	4.8	1.6
473	200	600	4.0	2.9
498	125	1500	1.3	4.6
498	200	1400	2.2	4.9
523	150	450	1.0	8.1
548	100	450	1.0	13.
573	50	800	0.5	20.
573	100	800	1.0	20.
598	100	750	1.4	29.
620	100	850	1.2	41.
620	100	400	1.5	40.

temperature and total pressure. First-order exponential decays of Mn in the presence of N₂O were observed from which the first-order rate constant, $1/\tau$, is determined using least-squares linear regression. The observed second-order rate constant is determined from a plot of $1/\tau$ vs N₂O pressure (Fig. 1). Measured rate constants for the $a^6S_{5/2}$ state at various temperatures and pressures are listed in Table I. Attempts were made to measure the rate constant at lower temperatures than 448 K; however, at lower temperatures, the rate constant was smaller than the lower limit of our apparatus under these conditions. Rate constants were found to be independent of total pressure, total flow rate, and precursor partial pressure to within experimental uncertainty. The pressure independence indicates bimolecular kinetics. The relative uncertainty (i.e., the reproducibility) of our the rate constants is estimated at $\pm 10\%$. The absolute uncertainties are estimated to be $\pm 20\%$ and are based on the sum of the statistical scatter in the data and uncertainty in the flowmeter readings (5%) and the pressure reading (1%).

An Arrhenius plot (Fig. 2) of the rate constants is linear and yields Arrhenius parameters of 44.7 ± 1.0 kJ/mol and $(2.05\pm0.45)\times10^{-10}$ cm³ s⁻¹ for the activation energy and frequency factor, *A*, respectively. The experimental uncer-



FIG. 2. Arrhenius plot for the reaction of $Mn(a^6S_{5/2})$ with N₂O. The solid line is a weighted exponential fit to the equation $k(T) = A \exp(-E_a/RT)$. Error bars represent $\pm 10\%$ uncertainty.

TABLE II. Experimental E_a 's, calculated resonance interaction model E_a 's, ionization potentials, sp and sd promotion energies, enthalpy changes for M+N₂O→MO+N₂ and transition metal oxide bond energies, all in kJ/mol.

ТМ	E_a (expt) ^a	$E_a (\text{calc})^{\text{b}}$	IP ^c	$\frac{\text{PE}}{(sp)^{d}}$	PE (sd) ^e	$\Delta H^{ m f}$	Oxide BE ^g
$Ti(^{3}F)$	12.5 ^h	8.0	659	190	78	-501	$663(^{3}\Delta)$
$Cr(^7S)$	21.7 ⁱ	20.8	653	279	0	-291	425(⁵ Π)
$Mn(^{6}S)$	42.3	18.4	717	220	204	-190	$357(^{6}\Sigma^{+})$
$Fe(^5D)$	42.2 ^j	23.9	762	231	83	-246	$405(^{5}\Delta)$
$Cu(^2S)$	39.6 ^k	39.6 ¹	745	365	0	-118	$269(^{2}\Pi)$
$Mo(^7S)$	39 ^m	28.1	685	306	0	-430	482(⁵ Π)
$W(^5D)$	23.8 ⁿ	22.6	770	232	35	-508	656(⁵ Π)

^aExperimental E_a 's were determined from a fit of the rate constants to the equation $k=AT^{1/2}\exp(-E_a/RT)$ for comparison to the activation barrier calculated from the resonance interaction model.

^bReference 3.

^cReference 11.

^dEnergy difference (determined from Ref. 11) of the $s^{x}d^{n-x}$ ground state and the lowest energy $s^{x-1}d^{n-x}p^{1}$ state.

^eEnergy difference (Ref. 11) of the ground state and the lowest energy $s^{1}d^{n-1}$ state.

 $^{\mathrm{f}}\mathrm{At}$ 298 K, calculated from Ref. 9 except for the Mn reaction (Refs. 9 and 10).

^gReference 10.

^hReference 12.

ⁱReference 13.

^jReference 14.

^kReference 15.

^lThe resonance interaction model uses parameters based on this reaction; therefore, the calculated E_a matches the experimental value exactly.

^mReference 16.

ⁿReference 17.

tainties represent $\pm 2\sigma$. A fit to the equation $k = AT^{1/2} \exp(-E_a/RT)$ yields $E_a = 42.3 \pm 1.0$ kJ/mol and $A = (5.9 \pm 1.1) \times 10^{-12}$ cm³ K^{-1/2} s⁻¹.

DISCUSSION

The production of MnO from $Mn(a^6S_{5/2})$ reacting with N₂O has a significant barrier ($E_a = 44.7 \text{ kJ/mol}$) despite the reaction's exothermicity of 190 kJ/mol at 298 K.9,10 This activation energy is over twice the value predicted by the resonance interaction model [E_a =18.4 kJ/mol for an equation of the form $k = AT^{1/2} \exp(-E_q/RT)$].³ Clearly, the resonance interaction model does not accurately predict the barrier for this reaction. It is not surprising that this model does not accurately predict the kinetic behavior of transition metals due to the neglect of both the TM's d electrons and the product metal oxide's electronic structure. Previous studies of TM's indicate the TM's electron configuration plays a significant role in the dynamics of the reactions.¹ Table II presents a compilation of the presently known experimental values of activation energies for TM's along with the calculated values from the resonance interaction model. Obviously, this theory does not predict E_a 's accurately for transition metal atoms. Furthermore, it does not appear there is a correlation between the activation energy and other parameters such as ionization potential, sp or sd promotion energy, the metal oxide bond energy or the exothermicity of the reaction. A systematic study of the reactions of the remainder of the transition metals with N_2O is currently underway to gain a better understanding of the dynamics of these reactions.

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