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Temperature dependence of the kinetics of the reaction $Al+O_2 \rightarrow AlO+O$

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The temperature and pressure dependence of the rate constant for the reaction $Al+O_2$ has been measured by observing both Al disappearance and AlO appearance. No pressure dependence is observed from 10 to 100 Torr total pressure of Ar at room temperature. Over the range 298–1083 K, a fit to the measured data yields the expression $k(T) = (1.62 \pm 0.13) \times 10^{-10}$ cm^3 s^{-1} exp[(-0.16 ± 0.08) kcal mol$^{-1}/RT$].

1. Introduction

Aluminum is a standard component in many solid propellants and explosives [1]; a typical composition is 70–90% ammonium perchlorate and 10–30% aluminum. The detailed combustion chemistry of practical systems such as these is poorly understood; in part, because there is a limited amount of kinetic data on the reactions of species such as Al, AlO and AlCl [2–9].

The reaction of atomic aluminum with molecular oxygen,

$$Al+O_2 \rightarrow AlO+O , \qquad (1)$$

is obviously a key reaction in the oxidation of aluminum and is exothermic by 3.6 kcal/mol at room temperature. There has been one previous investigation of the temperature dependent rate constant for this reaction. Fontijn, Felder and Houghton [2,3] report a rate constant over the range 300–1700 K of $k(T) = 3.0 \times 10^{-11}$ cm^3 s^{-1} exp$(-18/T)$. The lack of a temperature dependence observed for this reaction over the wide temperature range investigated has been attributed to formation of an intermediate complex with subsequent decomposition into $AlO+O$.

There have been several studies of the dynamics of this reaction since the pioneering work of Dagdigian, Cruse and Zare [10] who observed a non-Boltzmann product vibrational distribution after reaction in a beam-gas arrangement. Pasternack and Dagdigian [11] studied this reaction using a velocity selected Al atom beam and found that as the kinetic energy of the collision is increased ≈ 80% of the additional energy is disposed of as product translation and rotation. Both of these papers conclude that the reaction occurs on an attractive surface but that no long-lived intermediate is involved. They speculate that the stable O–Al–O structure is not accessible in a thermal experiment and that the reaction proceeds by end-on attack. Costes et al. [12] have recently reexamined this reaction using a crossed beam system. They find that at the lowest translational energy studied, 0.083 eV, the available energy is randomized among the product degrees of freedom, which suggests a well on the potential energy surface. They attribute the minor deviations from statistical behavior observed at higher energies to a decrease in the lifetime of the adduct with increasing energy.

Serebrennikov, Osin and Maltsev [13] have used the matrix isolation technique to obtain the infrared spectrum of the products of reaction (1). By analogy with the groups I and II metal oxides, they assign the intermediate trapped in an Ar matrix as cyclic, C_{2v} AlO_2. Sonchik, Andrews and Carlson [14] have also obtained the infrared spectrum of the products trapped in N_2 and Ar matrices. They identify a species in the N_2 matrix that they assign as a bent, C_s AlOO species. Little of this species is present in the Ar matrix, a fact they attribute to the more efficient removal of excess reaction energy in an N_2 matrix. Rozhanskii et al. [15] find evidence for both cyclic and linear forms of OAlO in N_2 matrices and Rozhanskii, Serebrennikov and Shevel'kov [16] report the fluorescence spectrum of the linear form in both Ar and N_2 matrices.

The available theoretical studies support the sideways attack argument. Zyubina [17] reports no minimum for AlOO at his highest level of theory. Rubio, Ricart and Illas [18] performed CASSCF calculations on AlO_2 and found no minima corresponding to $C_{\infty v}$ or C_s AlOO structures. They found minima corresponding to ground and excited state C_{2v} structures. More recently, Marshall et al. [19] have examined the $Al+O_2$ system with a UMP2 calculation. They find evidence for a stable AlOO species at the unrestricted Hartree–Fock level but were unable to locate it using UMP2. They find stable C_{2v} and linear OAlO structures with the linear being lowest with "no evidence for a barrier to insertion".

As a part of our program to investigate the important reactions of Al and AlO over wide temperature and pressure ranges, we have examined the kinetics of reaction (1). We report here the temperature and pressure dependence of the rate constant for reaction (1) over the range 298–1083 K and 10–100 Torr total pressure obtained from measurements of Al atom disappearance and AlO appearance.

2. Experimental

The kinetic measurements were carried out using a pump–probe experimental arrangement in our high temperature reactor. The apparatus and experimental details have been described in detail recently [20]. Briefly, Al atoms are generated by the 248 nm photolysis of trimethyl aluminum (TMA) [21] and probed by resonance fluorescence o the $^2S_{1/2}$–$^2P_{1/2}$ transition near 394.4 nm. The product AlO is probed by exciting fluorescence using the $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ (1,0) band near 466 nm and detecting the (1,1) band around 490 nm. The photolysis laser is a Lambda Physics EMG 201 MSC excimer laser and the probe laser is a Lambda Physics excimer-pumped dye laser (EMG102/FL2002). The pump and probe laser beams collinearly counterpropagate through the reactor and fluorescence is collected at 90° to the laser paths with a two-lens telescope and imaged through an iris onto a filtered photomultiplier tube (RCA C31000M). A narrow-band interference filter (Corion SS-4000-2 or P10-490-S) and an acetone filter are used to decrease scattered laser light. The PMT output is captured by a gated integrator and digitized by a microcomputer.

Temporal profiles are obtained by varying the delay time between the photolysis and probe lasers under computer control. A minimum delay of 1–5 μs is used to insure thermalization of the system. Direct determination of the gas temperature in the reaction zone is achieved by measuring the rotational temperature of the product AlO. Excitation spectra are recorded at various probe delays (10 to 100 μs) and probe laser pulse energies (2 to 45 μJ). The rotational temperatures obtained under all conditions are the same within experimental error. All experiments are carried out under pseudo first-order conditions. In the absence of added O_2, the observed Al disappearance is due to diffusion from the viewing region and reaction with precursor molecules and gas impurities. When O_2 is added, the temporal profile is well approximated by a single exponential decay over 4–5 lifetimes.

All gases flow through calibrated mass flow meters or controllers before mixing and admission to the cell. Typical flow conditions are 30–70 SCCM or 0.05% TMA/Ar mixture, 0–10 SCCM O_2, 10–60 SCCM Ar over the windows of the cell and 2000–6000 SCCM Ar. TMA (Texas Alkyls) is subjected to several freeze–pump–thaw cycles before use. Ar (Air Products, 99.995%) and O_2 (Matheson, 99.98%) are used as received.

3. Results and discussion

We measured the pressure dependence of the reaction $Al+O_2$ at room temperature by monitoring the disappearance of Al. These data are listed in table 1 and plotted in fig. 1. As can be seen, there is no observable pressure dependence of the rate constant over this pressure range. The average of the room temperature measurements is (1.62 ± 0.13)

Table 1
Measured pressure dependence of the room temperature rate constant for the reaction $Al+O_2$

Total pressure (Torr)	$k_{measured}\pm 1\sigma$ (10^{-10} cm^3 s^{-1})
10	1.62±0.12
20	1.55±0.12
20	1.62±0.12
50	1.72±0.13
100	1.71±0.13

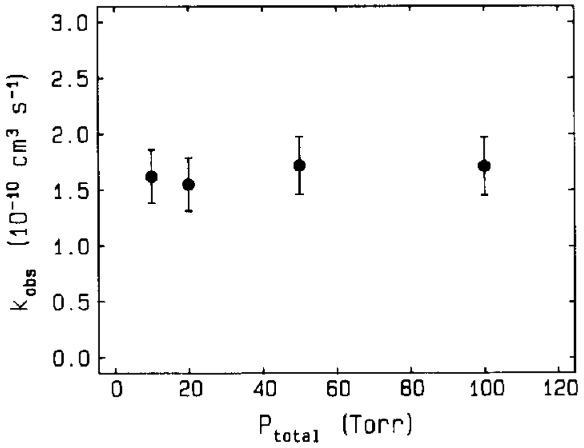

Fig. 1. Pressure dependence of the measured bimolecular rate constants for the reaction $Al+O_2$ at room temperature in Ar buffer gas.

$\times 10^{-10}$ cm^3 s^{-1}. The temperature dependence of the rate constant for this reaction was determined from a series of measurements at a total pressure of ≈20 Torr. Data corresponding to measurement of both Al disappearance and AlO appearance are listed in table 2 and the Al disappearance data are displayed as an Arrhenius plot in fig. 2. The precision of the product appearance measurements is lower due to interference from the secondary reaction $AlO+O_2$. At two of the temperatures, we obtained appearance rate constants for AlO in both $v''=0$ and 1. Within the precision of the measurements we observe no preferential population of either vibrational level of AlO. This agrees with the results of the earlier dynamics experiments [10–12] that showed near statistical or only slightly hotter vibrational distributions in the product. A fit to the Al disappearance data, which is shown in fig. 2 as a solid line, results in the Arrhen-

Table 2
Temperature dependence of the rate constant for the reaction $Al+O_2$

$T\pm 1\sigma$ (K)	$k_{measured}\pm 1\sigma$ (10^{-10} cm^3 s^{-1})
298	1.62±0.13
422±23	1.58±0.14 1.22±0.12 [a]
518±12	1.64±0.14 1.32±0.12 [a]
578±8	1.51±0.14
640±25	1.42±0.13 1.24±0.11 [a] 1.83±0.17 [b]
668±15	1.56±0.14 1.26±0.11 [a] 1.66±0.16 [b]
834±12	1.37±0.13
1083±48	1.29±0.12

[a] Monitor AlO ($v=0$) appearance.

[b] Monitor AlO ($v=1$) appearance.

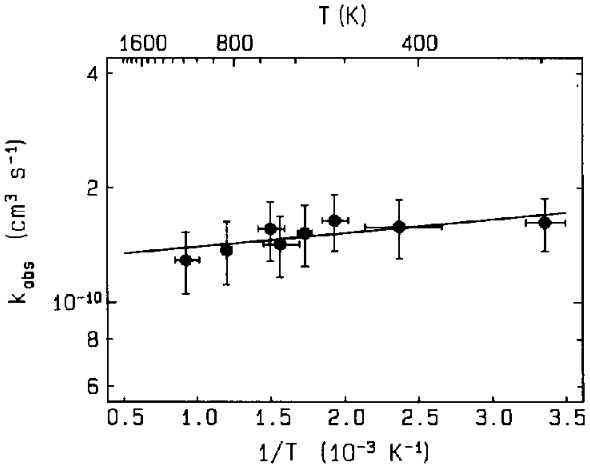

Fig. 2. Arrhenius plot for the bimolecular rate constants for the reaction $Al+O_2$ as measured by observing Al atom disappearance. The vertical and horizontal error bars represent 2σ error bars in the rate constants and temperatures, respectively. The solid line is the result of a weighted, linear least squares fit to the Al atom decay data as discussed in the text.

ius parameters $A=(1.30\pm0.11)\times10^{-10}$ cm^3 s^{-1} and $E_a=-0.16\pm0.08$ kcal mol^{-1}.

Our measured near-zero activation energy agrees well with the earlier series of measurements by Fontijn et al. [2,3]; -160 ± 80 cal mol^{-1} versus -36 cal mol^{-1}. The individual rate constants we measure however, are approximately five time larger than the earlier results. Fontijn [22] has recently selectively remeasured the rate constant for the reaction of $Al+O_2$ and reports results in good agreement with those reported here.

Our kinetic results can be understood in terms of a mechanism involving complex formation with rapid dissociation to products. At the total energies we sample, the complex lifetime is obviously quite short as we are unable to see any effect of complex stabilization. It is tempting to propose a mechanism involving a short-lived AlOO intermediate which decomposes after energy randomization into AlO+O in accord with the results of the dynamics experiments [10–12]. Marshall et al. [19], however, have performed QRRK calculations on their ab initio surface that involves Al insertion with no barrier and predict a rate constant 1.4 times that measured here and essentially no stabilization of the complex at pressures appropriate to this study. This should not be taken as confirmation of the mechanism however, equivalent results can be obtained assuming end-on approach. Definitive answers as to the mechanism and geometry of the intermediate complex will have to wait on refinement of the theoretical calculations on this system.

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