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ALUMINUM OXIDE KINETICS

Arthur Fontijn, et al

AeroChem Research Laboratories

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Reaction (1) is then studied by the addition of larger quantities of O₂. Rate coefficients are obtained from the observed variations in the relative AlO concentration, $[\text{AlO}]_{\text{rel}}$, as a function of reaction time, $[\text{O}_2]$ and total pressure (or $[M]$) at each of several temperatures.

The measurements thus far have shown that it is indeed possible to study AlO kinetics using these techniques. The first quantitative result, under a single flow condition at 1200 K indicates that $k_1 \approx 10^{-13}$ ml molecule⁻¹ sec⁻¹ for AlO ($v = 1$), i.e., $k_1 \approx 10^{-2} k_2$ at 1200 K. Because of this difference in k_1 and k_2 it is possible to distinguish the range of $[\text{O}_2]$ at which each reaction dominates and thus to obtain values for both k_1 and k_2 in the same experiment. The value of k_2 thus obtained in the initial experiments is consistent with that previously measured from our Al-consumption experiments. Using the collision frequency rate factor as an upper limit for k_1 , the measurement of k_1 suggests an activation energy for (1) of < 0.9 eV, a value midway between the two previously suggested extremes for the ΔH .

A comparison of the present value of k_1 with limiting values of k_{-2} shows that, at 1200 K, Reaction (-2) dominates (1) for $[\text{O}_2]/[\text{O}] < 30$ or for $[\text{O}_2]/[\text{O}] < 12$ if the endothermicity of (-2) is taken as 0.1 or 0.2 eV respectively.

ALUMINUM OXIDE KINETICS

Arthur Fontijn
William Felder

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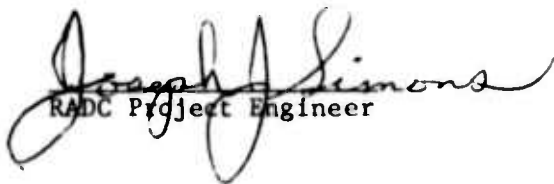
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REPORT SUMMARY

For several problems related to disturbed atmospheres, the identity and atmospheric lifetimes of metal oxides (particularly those of Al) need to be established. Using the AeroChem high-temperature fast-flow reactor¹ we have previously determined, by observing metal atom disappearance, the rate coefficients for the formation of AlO^2 and FeO^3 via the reactions of the free metal atoms with O_2 . In the present work we are providing kinetic information on Al oxide reactions. To measure such kinetics we have modified the reactor to allow direct observation of AlO by laser induced resonance fluorescence. We report here on the experimental methods and on our first observations on the reaction



To produce AlO, Al is vaporized, entrained in Ar, and O_2 added to this stream to form AlO via the rapid² reaction



Reaction (1) is then studied by the addition of larger quantities of O_2 . Rate coefficients are obtained from the observed variations in the relative AlO concentration, $[\text{AlO}]_{\text{rel}}$, as a function of reaction time, $[\text{O}_2]$ and total pressure (or $[M]$) at each of several temperatures.

The measurements thus far have shown that it is indeed possible to study AlO kinetics using these techniques. The first quantitative result, under a single flow condition at 1200 K indicates that $k_1 \approx 10^{-13}$ ml molecule⁻¹ sec⁻¹ for AlO ($v = 1$), i.e., $k_1 \approx 10^{-2} k_2$ at 1200 K. Because of this difference in k_1 and k_2 it is possible to distinguish the range of $[\text{O}_2]$ at which each reaction dominates and thus to obtain values for both k_1 and k_2 in the same experiment. The value of k_2 thus obtained in the initial experiments is consistent with that previously measured from our Al-consumption experiments.² Using

¹ Fontijn, A., Kurzius, S.C., Houghton, J.J., and Emerson, J.A., "Tubular Fast-Flow Reactor for High Temperature Gas Kinetic Studies," Rev. Sci. Instr. 43, 726 (1972).

² Fontijn, A., Felder, W., and Houghton, J.J., "Kinetics of Al Atom Oxidation," Final Report, DNA 3242F, AeroChem TP-299, September 1973.

³ Fontijn, A., Kurzius, S.C., and Houghton, J.J., "High-Temperature Fast-Flow Reactor Studies of Metal-Atom Oxidation Kinetics," Fourteenth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1973) p. 167.

the collision frequency rate factor as an upper limit for k_1 , the measurement of k_1 suggests an activation energy for (1) of < 0.9 eV, a value midway between the two previously suggested extremes ^{4,5} for the ΔH .

A comparison of the present value of k_1 with limiting values of k_{-2} shows that, at 1200 K, Reaction (-2) dominates (1) for $[O_2]/[O] < 30$ or for $[O_2]/[O] < 12$ if the endothermicity of (-2) is taken as 0.1 or 0.2 eV respectively.⁶

Further work toward accurately determining k_1 and its temperature dependence, for both AlO $v = 1$ and $v = 0$, and obtaining additional kinetic data on Reaction (2) using the present technique is under way.

-
- ⁴ Linevsky, M.J. and Alyea, F., "Spectroscopy of Metal Oxides," RADC-TR 73-391, November 1973.
 - ⁵ Farber, M., Srivastava, R.D., and Uy, O.M., "Mass Spectrometric Determination of the Heat of Formation of the AlO_2 Molecule," J. Chem. Phys. 55, 4142 (1971).
 - ⁶ Zare, R.N., "Fluorescence of Free Radicals: A Method for Determining Dissociation Energy Limits," Ber. Bunsengesell. Phys. Chem. (to be published).

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I. INTRODUCTION

For several problems related to disturbed atmospheres, the identity and atmospheric lifetimes of metal oxides (particularly those of Al) need to be established. To obtain such knowledge one needs kinetic information not only on the reaction



(which we have provided under the preceding Advanced Research Projects Agency/Defense Nuclear Agency contract⁷) but also on subsequent reactions resulting from the presence of AlO in the atmosphere.

AlO is known to form following upper atmospheric releases of Al⁷ and Al compounds.⁸ Additionally, the presence of AlO₂ may be anticipated. Since release experiments cannot provide the information computer codes need to predict the time-space history of these species and the processes in which they are involved, laboratory measurements are necessary. However, other than the measurements of the rate coefficient of Reaction (2) and its temperature dependence² and the recent work of Linevsky on the global kinetics of the TMA/O-atom system, there is no laboratory kinetic information available on the fate of AlO and AlO₂ in O/O₂/inert gas atmospheres. The purpose of the present work is to provide kinetic information (in the form of relative, and where possible absolute, rate coefficients) on these reactions.

In this report we discuss the initial measurements of the absolute rate coefficient of



near 1200 K and the apparatus and methods developed to make these measurements.

⁷ Golomb, D., "Results of AFCRL ALADDIN October 1973 Releases," Project IVY OWL Technical Progress Review Meeting, 12 February 1974.

⁸ Rosenberg, N.W., Golomb, D., and Allen, E.F., Jr., "Resonance Radiation of AlO from Trimethyl Aluminum Released in the Upper Atmosphere," J. Geophys. Res. 69, 145 (1964).

II. EXPERIMENTAL

A. Apparatus

The 'metal oxide' high-temperature fast-flow reactor, shown schematically in Fig. 1, is similar to the reactor used in our studies of metal atom disappearance kinetics^{1,2,3} (the 'metal atom' reactor). However, while the reaction tube i.d. in the present work has been kept at 2.5 cm, the vacuum furnace 'can' of the metal oxide reactor has been reduced to 15 cm i.d. The smaller furnace leads to an increase by about a factor of 4 in fluorescence light flux arriving at the observation window. Such an increase in flux is desired since AlO is a molecular species, the measurement of which requires much higher light intensities than does Al, an atomic species. While a further decrease in size would have been beneficial, such a decrease would have been incompatible with the insulation requirements of the high-temperature reactor. The new reactor also allows for the use of a second O₂ inlet, or an O-atom source, and a fourth observation port. These options are not needed in the initial experiments discussed here, but will be required in the course of the work.

The light source for AlO fluorescence excitation is the 0.3 W 488.0 nm Ar⁺ line from a Coherent Radiation Model 52 cw Ar/Kr mixed gas ion laser, the beam of which is chopped at 140 Hz. The fluorescence at $\approx$ 465 nm (1,0 band) is collected through a port at right angles to the laser beam by an f/2 lens and focused on the 2.5 mm slit of a Spex Minimate monochromator (4.0 nm mm⁻¹ dispersion). The dispersed radiation falls on a HTV R212 photomultiplier tube (PMT), the signal from which is fed across a 1 M Ω resistor to a PAR 120 lock-in amplifier. The signal to noise ratio (S/N) obtained at the maximum [AlO] in a given experiment has been found to be in the 10-100 range.[†] A S/N of 10 may be considered a minimum requirement for kinetic measurements. Initial [Al] is monitored in absorption using the 396.2 nm Al radiation from an Al hollow cathode lamp. This radiation is also chopped at 140 Hz and detected by the same monochromator/PMT combination as the AlO radiation; however, a 0.25 mm slit is used in these measurements. When measuring AlO fluorescence at 465 nm the Al lamp radiation is blocked out to avoid interference from the Ne hollow cathode lamp filler gas radiation near 462 nm; AlO fluorescence does not interfere with the [Al] measurements.

[†] An increase in the initial [Al] would, of course, increase the [AlO]; however, large concentrations of [AlO] could result in self-absorption of the fluorescence, thus seriously affecting the accuracy of the method for kinetic measurements.

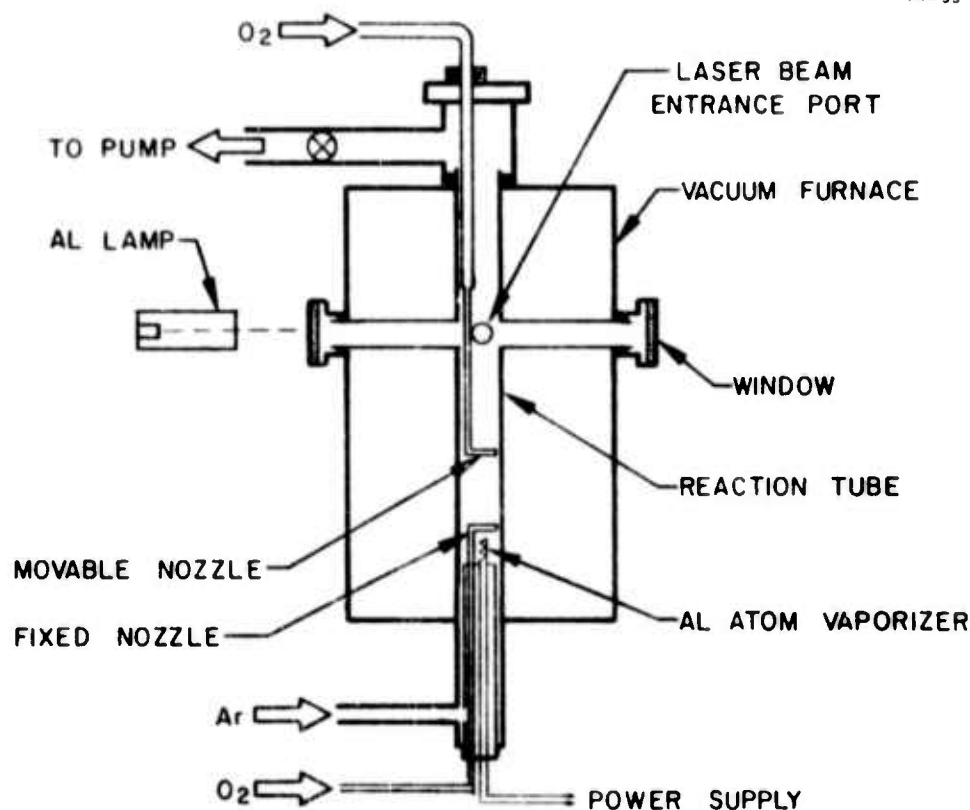


Figure 1. Schematic of the AeroChem High-Temperature Fast-Flow Reactor modified for the study of metal oxide kinetics.

B. Fluorescence Measurement of Relative $[AlO]$

Figure 2 shows a summary diagram of the $AlO(B^2\Sigma^+ - X^2\Sigma^+)$ system transitions observed in our $[AlO]_{rel}$ fluorescence measurements. The Ar^+ 488.0 nm laser line pumps the $K = 49$ line of $AlO X(v'' = 0)$ to the $AlO B(v' = 0, K = 48)$ line). The observable fluorescence emission from this level falls at ≈ 507.9 nm. However, $AlO X(v'' = 1)$ radicals present in our system are also pumped by the 488.0 nm laser line, causing fluorescence at 510.2 and 464.8 nm. (The numbers indicating this accidental double pumping mechanism are given in Table I from the work of Johnson, Capelle and Broida.⁹) The slit width required to separate 510.2 and 507.9 nm is such that a $S/N < 10$ was obtained in the initial experiments, unsuitable for kinetic measurements. We therefore chose to use the 464.8 nm fluorescence for the present experiments. The rate coefficient data obtained thus pertain to $AlO X(v = 1)$.

⁹ Johnson, S.E., Capelle, G., and Broida, H.P., "Laser Excited Fluorescence and Radiative Lifetimes of $AlO(B^2\Sigma^+ - X^2\Sigma^+)$," J. Chem. Phys. **56**, 663 (1972).

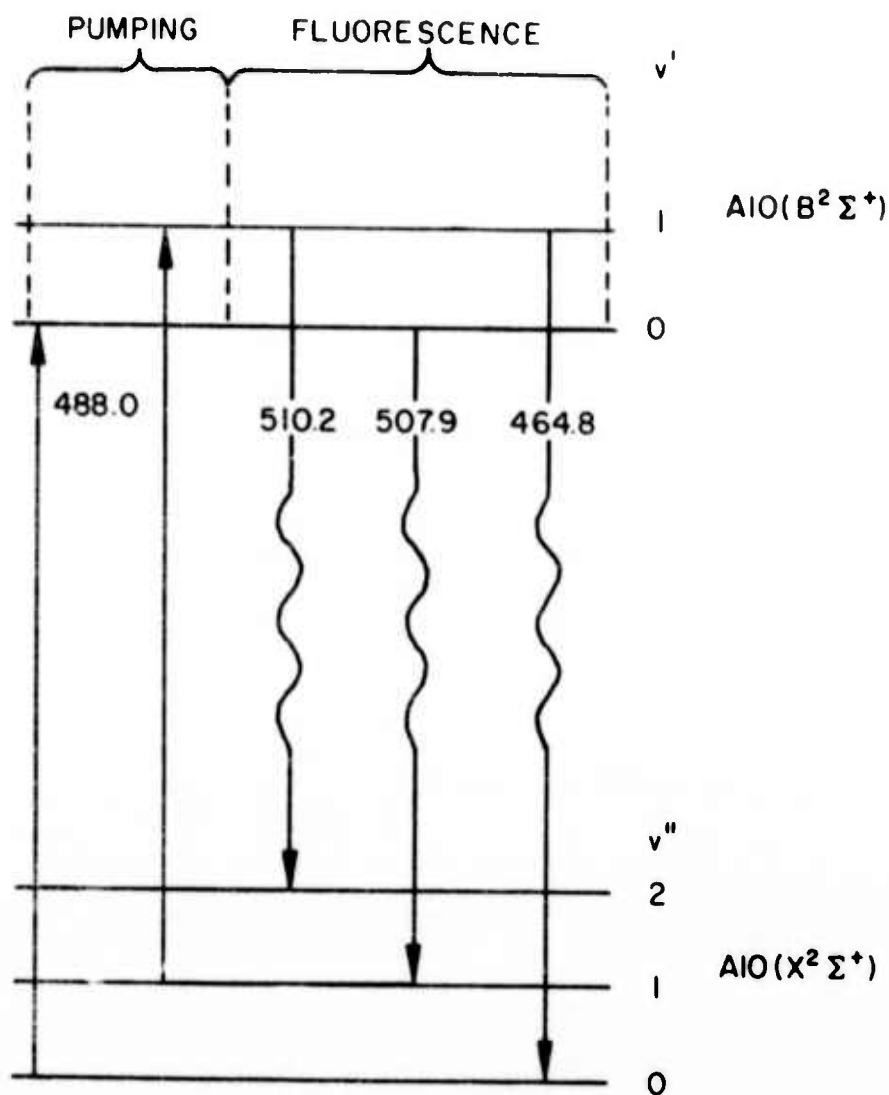


Figure 2. Summary diagram of AlO (B-X) system showing Ar⁺ laser pumping and observed fluorescence transitions.

TABLE I. TRANSITION ASSIGNMENTS OF AlO (B²Σ⁺-X²Σ⁺) RESONANCE FLUORESCENCE EXCITED BY THE 488.0 nm LASER LINE^a

Excited Transitions				ν_{laser} (cm ⁻¹)	ν_{calc}^b (cm ⁻¹)
v'	K'	v''	K''		
0	48	0	49	20486.7	20486.9 20486.2
1	57	1	56		20487.2 20486.4

^a

From Johnson, S.E., Capelle, G., and Broida, H.P.⁹

^bValues are given for both spin components, $J = K + 1$ and $J = K - 1$, respectively.

Since Reaction (1) may be substantially endothermic it is quite possible that the approximately 0.12 eV difference between $v = 1$ and 0 will considerably affect the rate coefficient.¹⁰ It therefore is important to obtain a fairly accurate idea of this difference in rate coefficients. Zare¹¹ has shown that Reaction (2) produces (for Al $\approx$ 1700 K, O₂ $\approx$ 300 K) $\approx$ 70% AlO ($v = 0$) and 23% $v = 1$ which corresponds to the equilibrium population at 1400 K. Lower temperatures are likely to increase the relative $v = 0$ population, especially if vibrational relaxation is sufficiently rapid.[†] It thus appears quite possible that the rate observations near 510 nm are dominated by AlO ($v = 0$). In order to test this we are attempting to improve the S/N so that the 507.9 nm fluorescence (pumped from $v = 0$, cf. Fig. 2) can be resolved from the 510.2 nm fluorescence (pumped from $v = 1$). With the improvements in S/N (e.g. by using a more sensitive PMT and lock-in amplifier) it may additionally be possible to resolve the 484.2 nm (0,0) and 486.6 nm (1,1) fluorescence bands from each other and from scattered 488.0 nm pumping radiation.

In the initial measurements to define running conditions for obtaining sufficient [AlO] for kinetic measurements, a high pressure Xe/Hg arc lamp and high-pass monochromator were used as the pumping source. However, the fluorescence intensities in any band obtained using this source were too small to be of use in making measurements (where we require S/N of at least 10). From a comparison of the fluorescence intensities obtained using the laser and the arc lamp, it appears that the laser is about 200 times more effective as a pumping source than the arc lamp.

¹⁰

Douglas, D.J., Polanyi, J.C., and Sloan, J.J., "Effect of Reagent Vibrational Excitation on the Rate of a Substantially Endothermic Reaction: $\text{HCl}(v' = 1-4) + \text{Br} \rightarrow \text{Cl} + \text{HBr}$," J. Chem. Phys. 59, 6679 (1973).

¹¹ Zare, R.N., Columbia University, Private communication to A. Fontijn, January 1974.

[†]

The vibrational relaxation of AlO ($v = 1 \rightarrow 0$) ($\omega_e \approx 1000 \text{ cm}^{-1}$) has not been studied; molecules such as O₂ ($\omega_e \approx 1500 \text{ cm}^{-1}$) and Cl₂ ($\omega_e \approx 550 \text{ cm}^{-1}$) are relaxed by Ar at 1000 K ($v = 1 \rightarrow 0$) in about 2×10^4 and 1×10^4 gas kinetic collisions, respectively.¹² The average number of Ar-AlO collisions in the present system ($\approx 1 \text{ msec}$ residence time) at 10 Torr and 1000 K is about 3×10^6 suggesting that vibrational relaxation should be sufficiently fast to bring the AlO vibrational distribution to equilibrium throughout the reaction zone.

¹²

Stevens, B., Collisional Activation in Gases, Volume 3 International Encyclopedia of Physical Chemistry and Chemical Physics, ed. A.F. Trotman-Dickenson (Pergamon Press, New York, 1967), p. 201.

C. Procedures

The basic procedures used to obtain rate coefficients from the measurements are similar to those used in the metal atom reactor work.^{2,3} In this work, both [Al] and [AlO] are monitored. [Al] is determined before and after each experiment to insure that it has not changed significantly over the course of the measurement; the agreement between the pre- and post-experiment measurements is generally better than $\approx 5\%$. Experience has shown that [Al] corresponding to $\approx 50\%$ absorption is necessary to obtain sufficient [AlO] for kinetic measurements (cf. Section II.A). Figure 3 shows a typical plot of the AlO fluorescence data obtained in the stationary inlet mode.² Rate coefficients can also be obtained by using a traversing O₂ inlet.³ Values of k_1 and k_2 can be simultaneously obtained in the experiments in either mode as the following analysis demonstrates:

Consider only Reactions (1) and (2) (the back reactions and subsequent reactions involving O atoms may be neglected because [O] is negligible compared to [O₂]) and assume that wall losses for AlO are either negligible or zero-order in O₂. Under these assumptions, and when k_2 differs[†] sufficiently from k_1 , it is shown in Appendix A that

$$[\text{AlO}]_{\text{rel}} \sim \pm [\exp(-k_1[\text{O}_2]t) - \exp(-k_2[\text{O}_2]t)] \quad (3)$$

where the (+) sign pertains to the case $k_2 \gg k_1$ and the (-) sign to $k_1 \gg k_2$. In Eqs. (3) t is the reaction time defined, as in our previous work,² by $t = x/\eta\bar{v}$ in which x is the distance from the point of O₂ introduction to the observation plane, $\bar{v}$ is the bulk gas flow velocity and η is a factor which is equal to 1 for plug flow and ≈ 1.6 for parabolic flow.¹³ We have taken η to be 1.3 (± 0.3) as in our previous work.^{2,3} Hence, for the stationary mode the variable in Eqs. (3) is [O₂], while for the traverse mode, the variable is x . Eqs. (3) always separate into two distinct regions of AlO increase and decrease as a function of [O₂]t. We give below the limiting values of [AlO]_{rel} when [O₂]t is large and when it is small for the two cases, $k_2 \gg k_1$ and $k_1 \gg k_2$.

[†] The present results show that k_2 is greatly different from k_1 . Therefore we do not further consider the case $k_2 \approx k_1$ which would require use of the full expressions derived in the appendix.

¹³ Ferguson, E.E., Fehsenfeld, F.C., and Schmeltekopf, A.L., "Flowing Afterglow Measurements of Ion-Neutral Reactions," *Advances in Atomic and Molecular Physics* 5, 1 (1969).

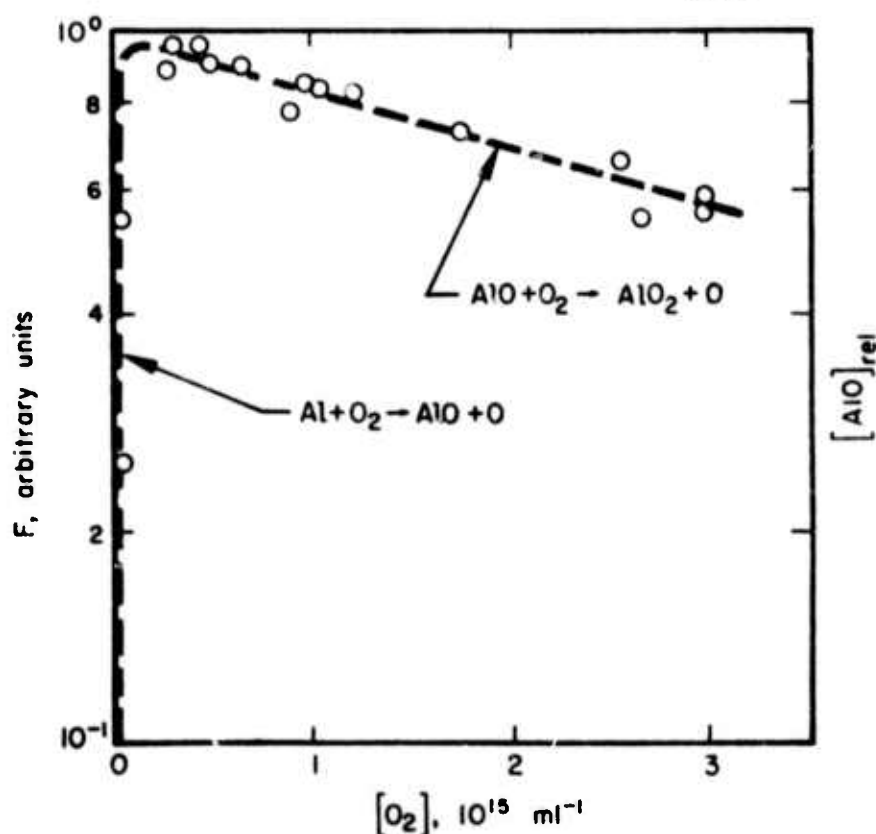


Figure 3. Al/O₂ and AlO/O₂ kinetics from stationary mode data using laser induced fluorescence. $\bar{T} = 1185$ K, $\bar{v} = 97$ m sec⁻¹; $[M] = 8.2 \times 10^{16}$ ml⁻¹; $t = 0.8 \times 10^{-3}$ sec; fluorescence $\lambda = 465$ nm. The plot gives $k_2 t = 2.4 \times 10^{-14}$ ml molecule⁻¹, $k_2 = 3 \times 10^{-11}$ ml molecule⁻¹ sec⁻¹; $k_1 t = 1.8 \times 10^{-16}$ ml molecule⁻¹; $k_1 = 2.3 \times 10^{-13}$ ml molecule⁻¹ sec⁻¹.

Case 1: $k_2 \gg k_1$

$$[AlO]_{rel} \sim [\exp(-k_1[O_2]t) - \exp(-k_2[O_2]t)] \quad (3+)$$

a. Ascending portion, $k_1[O_2]t \ll k_2[O_2]t \ll 1$

$$[AlO]_{rel} \sim 1 - \exp(-k_2[O_2]t) \sim 1 - (1 - k_2[O_2]t) \sim k_2[O_2]t \quad (4a)$$

b. Descending portion, $1 < k_1[O_2]t \ll k_2[O_2]t$

$$[AlO]_{rel} \sim \exp(-k_1[O_2]t)$$

$$\ln[AlO]_{rel} \sim -k_1[O_2]t \quad (4b)$$

Case 2: $k_1 \gg k_2$

$$[AlO]_{rel} \sim [\exp(-k_2[O_2]t) - \exp(-k_1[O_2]t)] \quad (3-)$$

a. Ascending portion, $k_2[O_2]t \ll k_1[O_2]t \ll 1$

$$[AlO]_{rel} \sim 1 - \exp(-k_1[O_2]t) \sim k_1[O_2]t \quad (5a)$$

b. Descending portion, $1 < k_2[O_2]t \ll k_1[O_2]t$

$$[AlO]_{rel} \sim \exp(-k_2[O_2]t)$$

$$\ln[AlO]_{rel} \sim -k_2[O_2]t \quad (5b)$$

Thus, the initial positive slopes of plots of $[AlO]_{rel}$ against $[O_2]$ (stationary mode)² or t (traverse mode)² can be used to obtain a value of k_2 when $k_2 \gg k_1$ or a value of k_1 when $k_1 \gg k_2$ (Eqs. (4a) and (5a) respectively). The descending slopes of plots of $\ln[AlO]_{rel}$ against $[O_2]$ or t yield a value for k_1 when $k_2 \gg k_1$ or a value for k_2 when $k_1 \gg k_2$ (Eqs. (4b) and (5b) respectively). The two cases, $k_2 \gg k_1$ and $k_1 \gg k_2$, although giving curves of identical shape, can be distinguished since k_2 is known.² The ascending portion of the curve in Fig. 3 is indicative of a reaction with rate coefficient $\approx 10^{-11}$; the descending portion, of a reaction with rate coefficient $\approx 10^{-13}$. Since we know that k_2 is of the former magnitude,² it follows that k_1 is of the latter. Thus, the experiments show that $k_2 \gg k_1$. Actually, since k_2 is already about one tenth of the gas kinetic collision frequency rate factor, it is a priori highly unlikely that $k_1 \gg k_2$ in any case. A consequence of this analysis is that while the AlO observations provide another measurement of k_2 , such a measurement depends on prior knowledge of the magnitude of k_2 .

III. RESULTS AND DISCUSSION

The values of k_2 and k_1 extracted from Fig. 3 are 3×10^{-11} and 2×10^{-13} , respectively in units of $\text{ml molecule}^{-1} \text{sec}^{-1}$. Additional measurements at 1200 K have been made, but the raw data show large scatter. We have therefore increased the reactor temperature to 1400 K where the experimental problems of transporting and producing AlO and Al are less severe and where the rate of Reaction (1) is somewhat increased. Initial experiments at 1400 K show that these problems have been reduced and that better quality raw data are obtained. It is anticipated that when we have completed the 1400 K experiments, enough experience with producing and transporting AlO will have been gained to allow us to return to lower temperatures. The value of k_2 thus obtained in this initial work is completely consistent with our previous measurement.² To our knowledge, this is the first measurement of k_1 .

The thermochemistry of Reaction (1) is not well known. Farber et al.³ determined a value of ~ 0 eV for the heat of reaction based on Knudsen cell effusion-mass spectrometer measurements. Linevsky⁴ has suggested that the reaction could be as much as 1.7 eV endothermic based on the onset of the 'AlO₂ continuum' observed in his studies of the O atom/TMA system. Since the pre-exponential of k_1 cannot exceed the collision frequency rate factor ($\approx 3 \times 10^{-10}$ ml molecule⁻¹ sec⁻¹) the above value of k_1 suggests that $\Delta H \leq 0.9$ eV. Subsequent data obtained at a number of temperatures will allow an accurate determination of the activation energy and hence an upper limit for ΔH .

The heat of reaction of Reaction (2) is somewhat better known. Zare and coworkers⁶ have placed a lower limit of 5.2 eV on the dissociation energy of AlO from their chemiluminescence and laser-induced fluorescence studies of the Al/O₃ and Al/O₂ reactions under single collision conditions. The upper limit of 5.3 eV has been provided by the work of Drowart and collaborators¹⁴ using conventional mass spectrometric measurements of Al₂O₃ thermal decomposition products. Thus, the exothermicity of Reaction (1) appears to be 0.1 to 0.2 eV.

We can compute the relative effectiveness of Reactions (1) and (-2) in removing AlO in O/O₂ atmospheres at 1200 K by using the previously measured² value of k_2 and the equilibrium constant, K_2 for Reaction (2), by adjusting the values of K_2 given in the JANAF compilation¹⁵ to take account of the limits given for ΔH above.[†] The values of k_{-2}/k_1 thus obtained are ~ 30 or ~ 12 for $\Delta H = 0.1$ or 0.2 eV, respectively, implying that Reaction (-2) dominates when $[O_2]/[O] < 30$ or $[O_2]/[O] < 12$ respectively.

¹⁴ Drowart, J., Private communication to R.N. Zare, quoted in Ref. 6.

¹⁵ JANAF Thermochemical Tables (Dow Chemical Company, Midland, Michigan) continuously updated.

[†] Since the present work deals in general with the reactions of Al oxides, we present in Table II calculated values of K_2 and k_{-2} in the temperature range of interest.

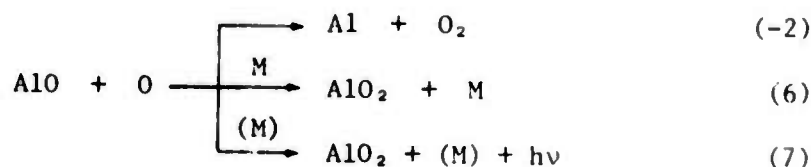
TABLE II. CALCULATED VALUES OF k_{-2} (in $\text{ml molecule}^{-1} \text{sec}^{-1}$) AND k_2 USING THE LIMITING EXOTHERMICITIES OF 0.1 AND 0.2 eV, GIVEN BY ZARE (REF. 6) TO ADJUST THE VALUES OF k_2 GIVEN IN THE JANAF COMPILATION (REF. 15). k_2 FROM REF. 2.

$$\text{Al} + \text{O}_2 \xrightleftharpoons[-2]{2} \text{AlO} + \text{O}$$

T(K)	$\Delta H = -0.1 \text{ eV}$		$\Delta H = -0.2 \text{ eV}$	
	k_{-2}	k_2	k_{-2}	k_2
300	1.2×10^{-13}	120	2.5×10^{-13}	5570
1000	2.4×10^{-12}	10.7	7.7×10^{-13}	33.9
1200	3.0×10^{-12}	9.29	1.2×10^{-12}	24.3
1700	4.2×10^{-12}	7.82	2.1×10^{-12}	15.4

IV. PLANS

We will continue the studies of k_1 at 1400 K by determining its value over a range of $[M]$, $\bar{V}$ and t using both the stationary nozzle and nozzle traverse techniques. We will attempt to make these measurements not only for AlO ($v = 1$) but also for AlO ($v = 0$). The kinetics of Reaction (2) will simultaneously be checked. In further experiments T will be varied to determine the activation energy of Reaction (1). We will also continue preparation for work with O-atoms as reactant in follow-up studies of the AlO/O atom system. Such studies should include kinetic measurements on the competing reactions



There now exists considerable doubt¹⁶ whether Reaction (7) is responsible for the apparent continuum emission observed in upper atmospheric Al releases. This makes a direct study of emission from AlO/O , and/or its suggested alternatives,¹⁶ all the more important. In fact the preliminary value for $\Delta H(k_2) < 0.9 \text{ eV}$ obtained in this work would predict a $D(\text{AlO-O}) > 4.2 \text{ eV}$ and hence an onset for the continuum of $\leq 300 \text{ nm}$, which may be inconsistent with Linevsky's observations placing the onset at $\approx 340 \text{ nm}$. However, these two values are sufficiently close that it appears premature to draw any definitive conclusion from this comparison.

¹⁶ Kolb, C.E., Herschbach, D.R., and Gersh, M.E., "An Analysis of the Visible Chemiluminescence Observed in the Gas-Phase Oxidation of Aluminum and Its Compounds," Project IVY OWL Technical Progress Review Meeting, 12 February 1974.

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APPENDIX

DERIVATION OF THE GOVERNING EQUATIONS FOR AlO/O_2 KINETICS

We wish to obtain an expression for relative $[\text{AlO}]$ based on Reactions (1) and (2). Thus, we define

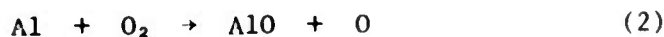
$$[\text{AlO}]_{\text{rel}} = [\text{AlO}]/[\text{AlO}]_i$$

and

$$[\text{Al}]_{\text{rel}} = [\text{Al}]/[\text{Al}]_i$$

where the subscripts i denote maximum values. In the analysis, we wish to generate expressions for $[\text{AlO}]_{\text{rel}}$ in terms of derived expressions for $[\text{AlO}]_i$ which, in turn, depend upon the relative magnitudes of k_1 and k_2 .

1. Derivation of the general expression for $[\text{AlO}]$.



Under the assumptions given on p. 9, the rate expressions for $[\text{Al}]$ and $[\text{AlO}]$ can be written as,

$$d[\text{AlO}]/dt = -k_2[\text{O}_2][\text{Al}] \quad (\text{A1})$$

$$d[\text{AlO}]/dt = k_2[\text{O}_2][\text{Al}] - k_1[\text{O}_2][\text{AlO}] \quad (\text{A2})$$

Substituting the solution of Eq. (A1) into Eq. (A2) and rearranging gives:

$$d[\text{AlO}]/dt + k_1[\text{O}_2][\text{AlO}] = k_2[\text{O}_2][\text{Al}]_i \exp(-k_2[\text{O}_2]t) \quad (\text{A3})$$

Multiplying both sides of Eq. (A3) by the integrating factor, $\exp(k_1[\text{O}_2]t)$, and integrating using the boundary condition $[\text{AlO}] = 0$ at $t = 0$ gives,

$$[\text{AlO}] = \left[k_2[\text{Al}]_i / (k_1 - k_2) \right] \left[\exp(-k_2[\text{O}_2]t) - \exp(-k_1[\text{O}_2]t) \right] \quad (\text{A4})$$

2. Derivation of $[\text{AlO}]_i$. The maximum value of $[\text{AlO}]$ can be determined by setting $d[\text{AlO}]/dt = 0$. Thus, using Eq. (A4)

$$d[\text{AlO}]/dt = 0 = \left[k_2[\text{Al}]_i / (k_1 - k_2) \right] \left[-k_2[\text{O}_2] \exp(-k_2[\text{O}_2]t) + k_1[\text{O}_2] \exp(-k_1[\text{O}_2]t) \right]$$

we solve for t^* , the value at which $[\text{AlO}] = [\text{AlO}]_i$

$$k_2[\text{O}_2] \exp(-k_2[\text{O}_2]t^*) = k_1[\text{O}_2] \exp(-k_1[\text{O}_2]t^*)$$

or

$$\ln(k_2/k_1) = (k_2 - k_1)[O_2]t^*$$

$$\left[1/(k_2 - k_1)\right] \ln(k_2/k_1) = [O_2]t^* \quad (A5)$$

Substituting Eq. (A5) into Eq. (A4) we obtain

$$[A10]_1 = \left[k_2 [A1]_1 / (k_1 - k_2) \right] \left[\exp(-k_2 \ln[k_2/k_1] / [k_2 - k_1]) - \exp(-k_1 \ln[k_2/k_1] / [k_2 - k_1]) \right] \quad (A6)$$

$[A10]_{rel}$ can now be approximated for the two cases of interest as follows:

a. $k_2 \gg k_1$, Eq. (A6) becomes

$$\begin{aligned} [A10]_1 &\approx -[A1]_1 \left[\exp(-\ln[k_2/k_1]) - \exp(-(k_1/k_2) \ln[k_2/k_1]) \right] \\ [A10]_1 &\approx -[A1]_1 \left[(k_1/k_2) - (k_1/k_2)^{k_1/k_2} \right] \\ [A10]_1 &\sim -[A1]_1 \left[0 - (k_1/k_2)^{k_1/k_2} \right] \\ [A10]_1 &\sim [A1]_1 (k_1/k_2)^{k_1/k_2} \end{aligned} \quad (A7)$$

The form $(k_1/k_2)^{k_1/k_2}$ can be evaluated as shown in Ref. 17.

$$\lim_{k_1/k_2 \rightarrow 0} (k_1/k_2)^{k_1/k_2} = 1$$

hence

$$[A10]_1 \sim [A1]_1 \quad (A8)$$

Dividing Eq. (A4) by Eq. (A8) and making the $k_2 \gg k_1$ approximation in (A4) gives Eq. (3+) of p.10.

$$[A10]_{rel} \sim \left[\exp(-k_1[O_2]t) - \exp(-k_2[O_2]t) \right] \quad (3+)$$

¹⁷ Johnson, R.E. and Fokemeister, F.L., Calculus with Analytic Geometry, Second Edition (Allyn and Bacon, Boston, 1962), p. 378.

b. $k_1 \gg k_2$, Eq. (A6) becomes

$$\begin{aligned}
 [A10]_i &\approx (k_2[A1]_i/k_1) \left[\exp(-(-k_2/k_1) \ln[k_2/k_1]) - \exp(\ln k_2/k_1) \right] \\
 [A10]_i &\approx (k_2[A1]_i/k_1) \left[(k_2/k_1)^{k_2/k_1} - (k_2/k_1) \right] \\
 [A10]_i &\sim (k_2[A1]_i/k_1) [1 - 0] \\
 [A10]_i &\sim k_2[A1]_i/k_1
 \end{aligned} \tag{A9}$$

and, by the same procedure as used to arrive at Eq. (3+)

$$[A10]_{rel} \sim \left[\exp(-k_2[O_2]t) - \exp(-k_1[O_2]t) \right] \tag{3-}$$