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1 **Kinetic study of the reactions of AIO and OAIO relevant to planetary mesospheres**

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16 **Abstract**

17 Aluminium atoms are injected into planetary upper atmospheres by meteoric ablation. Rapid
18 oxidation by O₂ to AlO is then likely to be followed by reactions with O₃, O₂ and CO₂ to
19 form larger oxides and carbonates, which can also be reduced by atomic O and CO. The
20 reactions listed below were investigated experimentally using both pulsed laser photolysis of
21 an Al precursor in a slow flow reactor, and pulsed laser ablation of an Al target in a fast flow
22 tube, with laser induced fluorescence detection of AlO. The experimental results were
23 interpreted using electronic structure theory calculations and Rice-Ramsperger-Kassel-
24 Marcus theory. The low-pressure limiting rate coefficients for the two recombination
25 reactions are: $\log_{10}(k_{\text{rec},0}(\text{AlO} + \text{O}_2 + \text{N}_2, 192\text{-}812 \text{ K})) = -35.137 + 6.1052 \log_{10}(T) - 1.4089$
26 $(\log_{10}(T))^2$; and $\log_{10}(k_{\text{rec},0}(\text{AlO} + \text{CO}_2 + \text{N}_2, 193\text{-}813 \text{ K})) = -38.736 + 8.7342 \log_{10}(T) - 2.0202$
27 $(\log_{10}(T))^2 \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, with a $\pm 20\%$ uncertainty over the experimental temperature
28 range. The following bimolecular reactions were also studied at 295 K: $k(\text{AlO} + \text{O}_3 \rightarrow \text{OAlO}$
29 $+ \text{O}_2) = (1.25 \pm 0.19) \times 10^{-10}$; $k(\text{AlO} + \text{CO} \rightarrow \text{Al} + \text{CO}_2) = (1.95 \pm 0.35) \times 10^{-12}$; $k(\text{OAlO} +$
30 $\text{CO} \rightarrow \text{AlO} + \text{CO}_2) = (2.6 \pm 0.7) \times 10^{-11}$ and $k(\text{OAlO} + \text{O} \rightarrow \text{AlO} + \text{O}_2) = (1.9 \pm 0.8) \times 10^{-10}$
31 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In the terrestrial atmosphere between 65 and 110 km, AlO is mostly
32 removed by recombination with O₂ below 85 km, and reaction with O₃ above 90 km. On
33 Mars recombination with CO₂ is much more important than with O₂, although reduction of
34 AlO by CO should maintain a significant density of Al atoms. Here we show that in both
35 atmospheres, AlOH is likely to be an important reservoir.

36

37 **Keywords:** Gas-phase Kinetics, Metal Oxides, Aluminum, Aluminum Oxide, Earth upper
38 atmosphere, Mars Upper Atmosphere, Meteoric Ablation.

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43 **1. Introduction**

44 Metal atom layers in the mesosphere-lower thermosphere (MLT) altitude region (70 – 110 km)
 45 are produced by ablation of the 28 ± 16 tonnes of cosmic dust that enters the terrestrial
 46 atmosphere every day.¹ Aluminium (Al) is present in cosmic dust with a relative mass
 47 abundance of 9.2×10^{-3} , and an Al:Fe ratio of 0.096.¹ A recent study¹ of cosmic dust sources
 48 in the solar system estimates that 14% of the Al in this dust ablates as Al atoms (compared with
 49 36% of Fe). Because Al is mainly present in cosmic dust as a highly refractory oxide, 94% of
 50 the ablated Al comes from fast-moving Halley-Type Comets which undergo heating to
 51 relatively high temperatures (>2300 K) during atmospheric entry.¹

52 Figure 1 shows a partial reaction scheme involving neutral Al species in the MLT (we have
 53 investigated the ion-molecule chemistry of Al^+ elsewhere²). Ablated Al atoms will be very
 54 short-lived in the MLT, because of the rapid reaction with O_2 :



56 which has a rate coefficient of $k_1(298 \text{ K}) = (1.68 \pm 0.24) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³ AlO can
 57 then go on to react with O_2 , CO_2 and O_3 in the MLT:



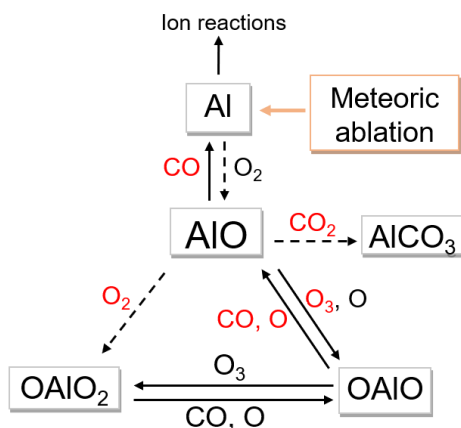
61 where M is the bath gas. AlO can also be reduced back to Al by CO (potentially important in
 62 a CO_2 -rich atmosphere such as Mars and Venus), and OAlO can be reduced back to AlO by
 63 either O or CO:



67 The enthalpy changes (at 0 K) in these reactions are calculated at the CBS-QB3 level of theory⁴
 68 (see Section 4). Reactions R4 - R7 do not appear to have been studied previously. The rate
 69 coefficient for R2 ($\text{AlO} + \text{O}_2$) has been measured by Belyung and Fontijn,⁵ although Ar bath
 70 gas was used and the study focused on high temperatures (305 - 1690 K). Above 1000 K, the
 71 reaction became second-order and this was postulated to be due to a bimolecular channel
 72 opening up to form $\text{OAlO} + \text{O}$. R3 ($\text{AlO} + \text{CO}_2$) was studied by Parnis *et al.*,⁶ though in a
 73 relatively high pressure regime (200 - 700 Torr) with N_2O as the bath gas. In the same study, a
 74 slow third-order reaction between AlO and CO was reported.

75 In the present study we report kinetic measurements of R2 – R7 (depicted in red in Figure 1).
 76 Electronic structure calculations are then be used to elucidate the reaction pathways and
 77 extrapolate to the low temperatures (120 - 240 K) and pressures (< 5 Pa) in the MLT. In the
 78 final part of the paper, the relative rates of the reactions involving AlO are examined as a
 79 function of altitude in the atmospheres of Earth and Mars.

80



81
 82 **Figure 1.** Partial reaction scheme for the neutral chemistry of Al in the MLT. Meteoric ablation
 83 provides the initial source of Al. Previously measured reactions are shown by dashed lines,
 84 with red species indicating reactions measured in the present study.

85
 86

87 2. Experimental

88 Reactions R2–R4 were studied using the pulsed laser photolysis–laser-induced fluorescence
 89 (PLP-LIF) technique within a temperature-controlled reactor. This reactor has been used
 90 previously⁷ to study the kinetics of a range of mesospheric metals (e.g. Si, Mg, Ca, Fe). For a
 91 recent schematic diagram of the experimental layout, see Figure 2 of Mangan *et al.*⁸ The
 92 stainless steel reactor comprises a central chamber with five side arms and a temperature range
 93 of 192 - 1100 K. AlO molecules were produced in the reactor by multiphoton dissociation of
 94 aluminium acetylacetonate ($\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$, also known as $\text{Al}(\text{acac})_3$) vapor by a loosely focused
 95 KrF excimer laser (Physik COMPLEX 102) at 248 nm, with a typical pulse energy of 40 mJ at
 96 10 Hz (< 5 mJ in the reactor). Solid $\text{Al}(\text{acac})_3$ powder was inserted into one of the chamber
 97 arms in a steel boat attached to the end of a thermocouple (K-type) and heated to ~ 340 K using
 98 heating tape around the reactor arm, in order to achieve a sufficient $\text{Al}(\text{acac})_3$ vapour pressure,
 99 estimated to be 4.6×10^{-4} Torr.⁹ A flow of N_2 over the steel boat entrained and transported the
 100 $\text{Al}(\text{acac})_3$ vapour into the main reactor volume. Experiments were conducted up to a maximum
 101 temperature around 810 K; above this temperature the LIF signal degraded, presumably due to
 102 decomposition of the $\text{Al}(\text{acac})_3$ precursor on the timescale of its residence in the reactor (~ 1 s).

103 The transition probed by LIF was the AlO ($\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+(0,0)$) band at 484.23 nm,¹⁰ using a
 104 Nd:YAG (Quantel Q smart 850 at 355 nm) pumped dye laser (Sirah Cobra-stretch CBST-G-
 105 18) with Coumarin 102 laser dye. The time delay between the counter-propagating dye laser
 106 (probe) and excimer laser (photolysis, $t = 0$) beams was varied to produce scans of the relative
 107 AlO concentration with time. Typical kinetic traces were produced from 1000 laser shots, with
 108 an accumulation time of 100 s. The AlO LIF signal was collected using a photomultiplier tube
 109 (Electron Tubes, model 9816QB) positioned orthogonal to the laser beams, through an
 110 interference filter ($\lambda_{\text{max}} = 480$ nm, fwhm = 10 nm).

111 A total gas flow through the reactor of 180 sccm included the entrained $\text{Al}(\text{acac})_3$ vapor in N_2 ,
 112 reactant gas (O_2 , CO_2 or O_3 in N_2) and a balancing flow of the N_2 bath gas. These flows were
 113 set using calibrated mass controllers, and the pressure in the reactor (5 – 18 Torr) measured
 114 with a capacitance manometer. O_3 was generated by flowing O_2 through a commercial ozoniser
 115 and the concentration measured downstream of the reactor by optical absorption at 254 nm (for
 116 details see Mangan *et al.*⁸).

117 Reactions R5 - R7 were studied using a stainless steel fast flow tube reactor (for a schematic
118 diagram see Figure 1 in Daly *et al.*²). Pulses of Al atoms were generated in the N₂ carrier gas
119 flow by the laser ablation of a rotating Al rod positioned centrally within the upstream section
120 of the tube, using a loosely focused 532 nm Nd:YAG laser (Continuum Minilite, pulse rate =
121 10 Hz, pulse energy = 8 mJ). At the downstream end of the tube, AlO was probed by LIF using
122 a Nd:YAG (Continuum Surelite SL1-10 at 355 nm) pumped dye laser (Sirah Cobra). The LIF
123 signal was collected using a boxcar integrator (Stanford Research Systems SR200), and the
124 digital signal transferred via a National Instruments CompactRIO interface. Each experimental
125 data point was produced by an average of 600 laser shots.

126 Experiments were carried out with a total laminar flow of 3 slm, using a throttled roots blower
127 (Edwards EH500A) backed by an Edwards E2M80 rotary pump to maintain a pressure of 1
128 Torr at 295 K. The distance from the Al rod to LIF detection point was 455 mm. O₂ and O₃
129 were introduced through a side-arm in the flow tube, 230 mm upstream from the detection
130 point, while CO and O were introduced at the same distance via a sliding injector. The flow
131 velocity in the tube was set to 67 m s⁻¹, giving a flow time from reactant injection to LIF
132 detection of 3.5 ms. A mixing time for the reactants of 1.5 ms was used, estimated as the time
133 taken for O₃ to diffuse 1 cm across the tube in a laminar flow, with $D(\text{O}_3\text{-N}_2) = 134 \text{ cm}^2 \text{ s}^{-1}$ at
134 1 Torr.¹¹ Atomic O was produced by the microwave dissociation of N₂ followed by titration
135 with NO. We have described previously¹² the method used to determine the absolute O atom
136 concentration at the point of injection, and the subsequent rate of loss on the flow tube walls.

137 **Materials.** N₂ (99.9999% pure, Air Products), O₂ (99.999%, pure Air Products), CO₂ (99.995%
138 pure, Air Products) and CO (99.5% pure, Argo International) were used without any further
139 purification. NO (99.95%, Air products) was purified via freeze-pump-thaw cycles before
140 dilution in N₂. Al(acac)₃ (99% pure, Sigma Aldrich) was warmed gently under vacuum in the
141 reactor prior to experiments. The Al rod (Alfa Aesar) was 99.999% pure.

142

143 3. Results

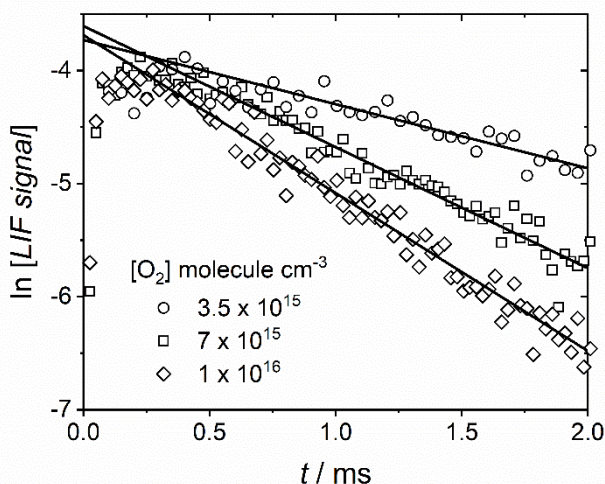
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145 3.1 AlO + O₂ and CO₂

146 The time-resolved LIF signals of AlO are described by a single exponential form $A\exp(-k't)$,
147 where the pseudo first-order decay coefficient k' (taking R2 as an example, where O₂ is the
148 reactant) is given by:

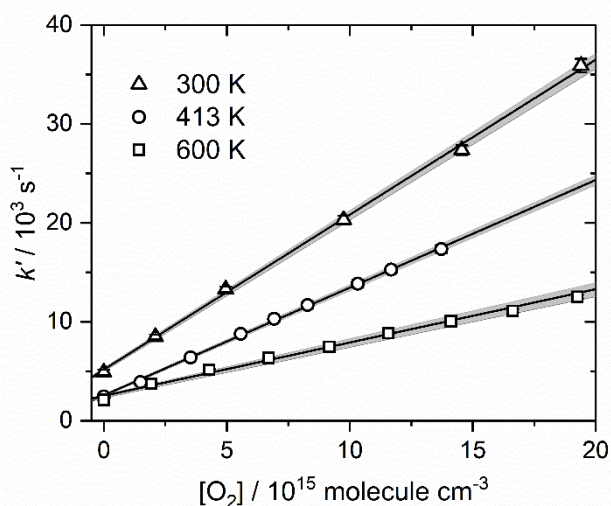
$$149 \quad k' = k_{diff} + k_2[\text{O}_2][\text{N}_2] \quad (\text{E1})$$

150 k_{diff} is the rate of diffusion of AlO molecules out of the photolysis volume observed by the
151 PMT. Figure 2 shows kinetic traces over a range of [O₂] as a natural logarithm of the raw LIF
152 signal against time, confirming the pseudo first-order behaviour after the first ~200 μs. AlO is
153 produced rapidly after photolysis of the precursor, either directly or by R1 (with an e-folding
154 lifetime of < 2 μs at the O₂ concentrations employed). The small rise and plateau in LIF signal
155 before 200 μs is most likely caused by quenching of vibrationally excited AlO, as reported by
156 Parnis *et al.*⁶ The time-resolved decays of AlO were fitted at reaction times longer than 300 μs,
157 to ensure that quenching did not affect the retrieved value of k_2 . Beginning the analysis at even
158 longer times did not change the retrieved first-order rate within error, but was avoided in order
159 to maximise the number of datapoints with good signal-to-noise in each fit, thereby reducing
160 the error.



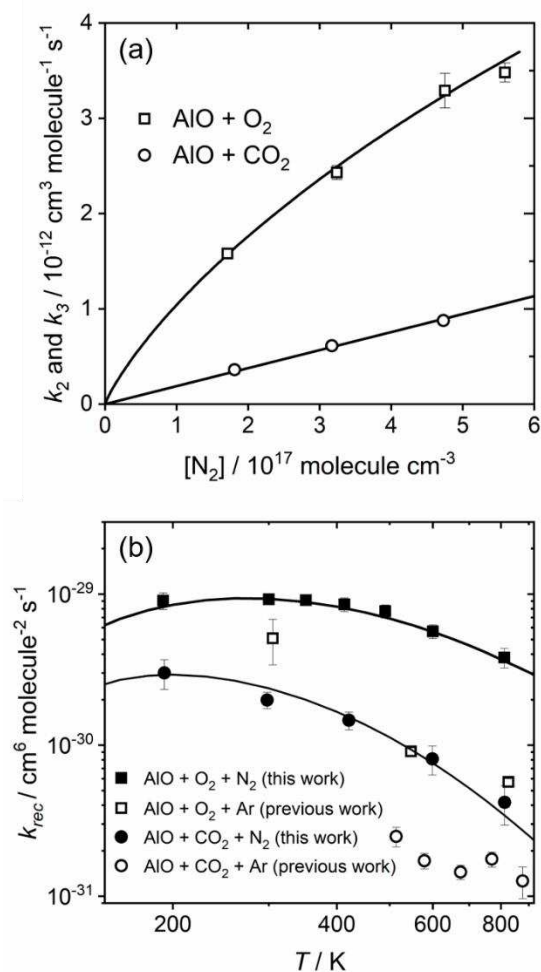
161
 162 **Figure 2.** Kinetic decays of AlO reacting with different $[O_2]$ (total pressure = 5.3 Torr). The
 163 lines are linear regressions through each decay from ~ 0.3 ms onwards.

164
 165 Example plots of k' against $[O_2]$ at temperatures between 300 and 600 K are shown in Figure
 166 3, with the slope providing the second order-rate coefficient at a specific pressure of N_2 . The
 167 profiles in Figure 3 show non-zero intercepts, with the measured loss rate of AlO in the absence
 168 of a reactant typically between $2000 - 5000 \text{ s}^{-1}$. This is several times higher than typical
 169 diffusion rates of metal oxides under the experimental conditions of this study and is likely due
 170 to removal of AlO by the precursor $Al(acac)_3$, or a precursor fragment produced by thermal
 171 decomposition of the precursor.⁸ This loss rate was monitored at the start and end of each
 172 experimental run, and found to be constant within error.



173
 174 **Figure 3.** Plots of k' against $[O_2]$ for R2 at 5.3 Torr total pressure for 300 – 600 K. The shaded
 175 area indicates the 95% confidence limits for each fit.

176 Figure 4a shows the pressure dependence of the second-order rate coefficients for R2 and R3
 177 at room temperature. R2 is clearly in the fall-off region over the pressure range studied (5 - 17
 178 Torr) while R3 is linearly pressure-dependent. Figure 4b illustrates the overall negative
 179 temperature dependences of R2 and R3. The flattening out of the rate coefficients below 400
 180 K is discussed in Section 4.



181

182 **Figure 4.** (a) Pressure dependence of k_2 ($AIO + O_2$) and k_3 ($AIO + CO_2$) at 300 K in N_2 bath
 183 gas. The symbols are experimental values, and the lines are RRKM fits. (b) Third-order rate
 184 coefficients for R2 and R3 as a function of temperature. Solid symbols are measurements from
 185 the present study at in N_2 pressures of 5.3 and 5.4 torr, respectively. The previous
 186 measurements of R2 by Belyung and Fontijn⁵ and R3 by Rogowski *et al.*¹³ were at Ar pressures
 187 between 10 and 20 Torr.

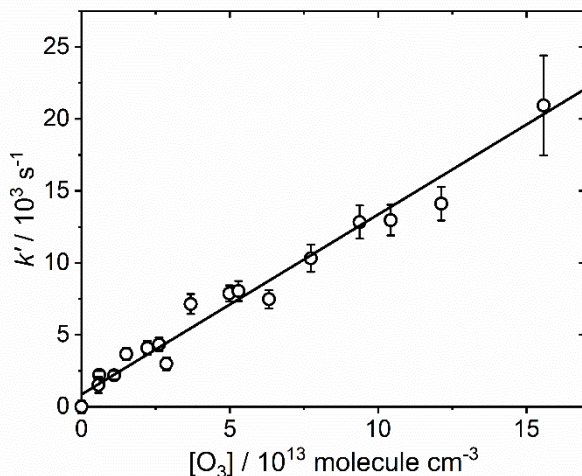
188

189 3.2 $AIO + O_3$

190 The decay of AIO in the presence of O_3 and O_2 can be described by:

$$191 \quad k' = k_{diff} + k_4[O_3] + k_2[O_2] \quad (E2)$$

192 A plot of k' as a function of $[O_3]$ is shown in Figure 5. The contribution from R2 (up to 50% at
 193 low $[O_3]$) and the remaining contribution from the non-zero intercept has been subtracted from
 194 k' to leave the contribution from R4. The linear dependence of k' with $[O_3]$ indicates the
 195 absence of a recycling reaction back to Al , which has been observed for other metal oxides
 196 such as NaO and NiO .^{7, 8} This is unsurprising, given the very strong bond energy of AIO (503
 197 kJ mol^{-1} ¹⁴). A linear regression fit yields $k_4(295 \text{ K}) = (1.25 \pm 0.19) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.



198

199 **Figure 5.** Plot of k' against $[O_3]$ for the reaction of $AlO + O_3$ (R4) at 295 K. The line is a
 200 linear regression through the dataset.

201

202 3.3 Flow tube kinetics

203 R5, R6 and R7 were studied at 295 K and 1 Torr total pressure of N_2 , using the flow tube
 204 apparatus described in Section 2. AlO was formed from ablated Al atoms via R1 ($Al + O_2$) in
 205 the upstream section of the flow tube where further reagents (e.g. CO , O_3 and O) were also
 206 added. Unlike the chemistry in the PLP-LIF system which involved simple pseudo first-order
 207 kinetics, the more complex chemistry in the flow tube requires a kinetic model to extract useful
 208 kinetic data. For this model a set of coupled ordinary differential equations describing the time-
 209 dependent behaviour of the Al species (Al , AlO , $OAlO$ etc.) in the flow tube were solved in
 210 order to fit to the experimental data. This flow tube model has been described in detail
 211 elsewhere.¹⁵ The rate coefficients for R2 and R4 measured in the present study, and k_1 from
 212 our previous study,³ were used.

213 **Table 1.** Parameters and estimated diffusion coefficients for Al species in N_2 at 295 K.

Species	Dipole moment / Debye	Polarizability / 10^{-24} cm^3	Ionization energy / eV	Diffusion coefficient / Torr $\text{cm}^2 \text{ s}^{-1}$
Al	-	6.8 ^a	5.99 ^a	121
AlO	4.45 ^b	8.6 ^c	9.82 ^d	90.9
OAlO	-	9.0 ^c	9.71 ^c	84.2

^aLide *et al.*¹⁶ ^bBei and Steimle.¹⁷ ^cCalculated at the B3LYP/6-311+g(2d,p) level.⁴

^dClemmer *et al.*¹⁸

214

215 The diffusional loss rates of Al, AlO and OAlO to the walls of the flow tube were also required,
 216 and these were calculated (the diffusion coefficient of AlO could not be measured because of
 217 the need for O_2 to be present in the flow tube to produce AlO from ablated Al, so that removal
 218 of AlO via R2 was unavoidable). The diffusion coefficients in N_2 and hence wall loss rates
 219 (assuming an uptake coefficient on the walls close to unity) for Al, AlO and OAlO were
 220 estimated from the long-range capture forces between these species and N_2 , a method we have

221 described elsewhere.¹² The relevant parameters and resulting diffusion coefficients are listed
222 in Table 1.

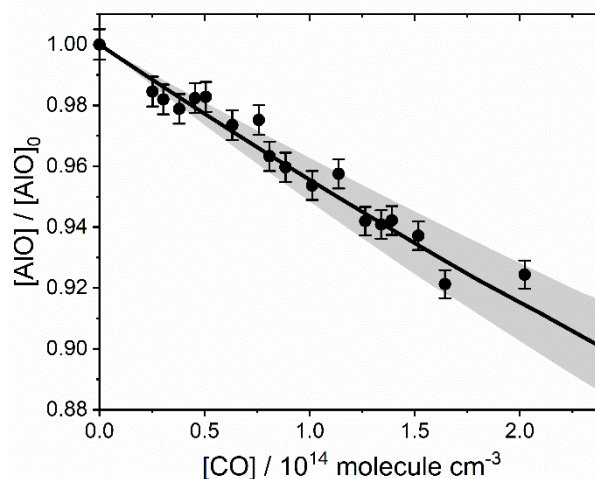
223 Time zero in the model is the point where the reactants are mixed into the flow tube, and the
224 model end point is the time when the metal pulse reaches the LIF detection point (~2 ms). The
225 model is initialised by fitting [AlO] to the experimental AlO LIF signal in the absence of the
226 reactant being studied (CO or O) by constraining the initial model [Al]. This is done using the
227 independently measured rate coefficients, reactant concentrations and the calculated diffusion
228 rates at 1 Torr. Due to the fast Al + O₂ reaction, Al is essentially completely converted to AlO
229 within 0.5 ms of O₂ addition. [AlO] reaches a peak at this point in the flow tube and then
230 decreases due to diffusion to the flow tube walls and chemical loss. After initializing the model,
231 the model is run to simulate the conditions of each experimental data point by turning on the
232 CO or O and optimizing the appropriate rate coefficient (k_5 , k_6 or k_7) to best fit the AlO LIF
233 signal of that data point. The mean of these optimized fits gives the overall value and standard
234 error of the rate coefficient.

235 The sensitivity of the model-fitted rate coefficients to realistic uncertainties in the diffusion
236 rates of the Al species, and the uncertainties of previously measured reaction rate coefficients,
237 is not significant. Varying k_1 and k_2 in the case of fitting k_5 , and also k_4 for fitting k_6 and k_7 ,
238 within their respective error limits still produces model simulations that lie well within the
239 scatter of the experimental data. Concerning diffusion, changing the diffusion coefficients for
240 the Al species by an unrealistically large factor of 2 from their calculated values primarily
241 causes a change in the [Al] required to initialize the model, but the model fits remain within
242 the scatter of the experimental data over the range of reactant concentrations. Since the fitting
243 procedure is primarily sensitive to the scatter in the experimental data, the uncertainty in each
244 determined rate coefficient is given by the standard deviation ($\pm 1\sigma$) of the mean of the fitted
245 values to each of the datapoints.

246

247 3.4 AlO + CO

248 This reaction was studied first as k_5 needed to be added to the kinetic model for the subsequent
249 fitting of R6 (OAlO + CO). Just sufficient O₂ was added ($[O_2] = 2.4 \times 10^{13}$ molecule cm⁻³) to
250 maximise the AlO LIF signal at the downstream detection point, but minimise further reaction
251 with O₂ to produce OAlO₂ (R2), or overwhelm recycling of AlO back to Al by R5. This
252 procedure also avoids significant recycling from OAlO₂ by CO which would then interfere
253 with the observed AlO as a function of CO. The points in Figure 6 shows the measured AlO
254 signal as a function of added CO, normalised against the signal in the absence of [CO] (i.e., the
255 ratio $[AlO]/[AlO]_0$). The addition of sufficient CO (2.2×10^{14} molecule cm⁻³) causes an 8.6%
256 reduction in AlO via recycling to Al by R4, which is partially offset by re-oxidation of Al to
257 AlO by R1. The model fit to the dataset (solid line in Figure 6) yields $k_5(295\text{ K}) = (1.95 \pm 0.35)$
258 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.



259

260 **Figure 6.** Plot of $[\text{AlO}]/[\text{AlO}]_0$ against $[\text{CO}]$ for the reaction of $\text{AlO} + \text{CO}$ ($[\text{O}_2] = 2.44 \times 10^{13}$
 261 molecule cm^{-3} , 295 K and 1 Torr). The line is the kinetic model fit to the dataset, with the
 262 shaded area showing the associated error in the fit ($\pm 1\sigma$).

263

264 3.5 OAIO + CO

265 Once k_5 had been measured, R6 ($\text{OAIO} + \text{CO}$) could be investigated. This required the addition
 266 of a fixed $[\text{O}_3]$ to produce OAIO via R4, while $[\text{CO}]$ was varied. The corona discharge
 267 converted 1.5% of O_2 into O_3 , so that $[\text{O}_2]$ (1.01×10^{14} molecule cm^{-3}) was ~ 33 times larger
 268 than the $[\text{O}_3]$ (3.28×10^{12} molecule cm^{-3}). Figure 7 shows the observed $[\text{AlO}]$ as a function of
 269 CO, normalized by $[\text{AlO}]_0$, the signal when $[\text{CO}] = 0$. There is a marked increase in the
 270 $[\text{AlO}]/[\text{AlO}]_0$ ratio as $[\text{CO}]$ is increased, clear evidence for reduction of OAIO by CO.

271 However, based on our experience with other metal dioxides,¹² O_3 should in turn oxidize
 272 OAIO:



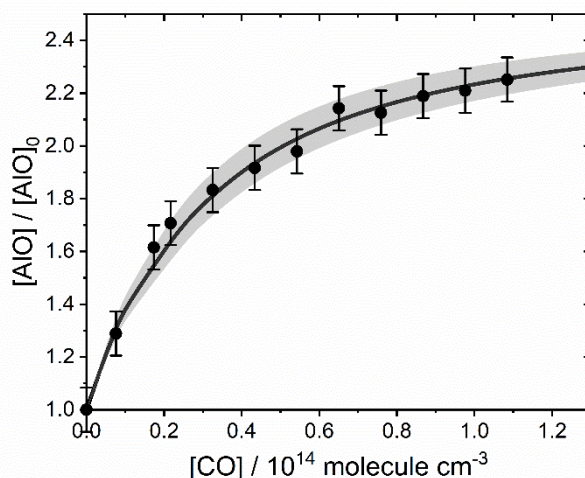
274 R8, as well as affecting the concentration of OAIO if the rate were sufficiently fast, would also
 275 contribute a kinetically relevant concentration of OAIO_2 , particularly in combination with
 276 direct formation of OAIO_2 via R2 ($\text{AlO} + \text{O}_2$). This makes the flow tube kinetics sensitive to
 277 another potential reaction between OAIO_2 and CO:



279 The sensitivity of the value of k_6 retrieved from the model fit to the experimental data was
 280 therefore tested with respect to k_8 and k_9 . The overall shape of the modelled variation of
 281 $[\text{AlO}]/[\text{AlO}]_0$ with $[\text{CO}]$ was not influenced by varying k_8 , but an increase in k_8 caused an
 282 increase in the fitted value of k_6 . As an upper limit to k_8 could therefore not be constrained
 283 experimentally, it was set to the measured value for $\text{AlO} + \text{O}_3$ (i.e. $k_8 \leq 1.25 \times 10^{-10}$ cm^3
 284 molecule $^{-1}$ s $^{-1}$). This is based on our previous work on Fe oxides which showed a monotonic
 285 decrease in the rate coefficients for Fe, FeO and $\text{OFeO} + \text{O}_3$,¹² and the fact that in this case
 286 OAIO is a linear molecule¹⁹ with no dipole moment and hence will have weaker long-range
 287 interactions with O_3 compared to AlO.

288 In contrast, the shape of the modelled variation of $[\text{AlO}]/[\text{AlO}]_0$ with $[\text{CO}]$ is sensitive to k_9 : if
 289 too large, the model underestimated the AlO signal recovery at low $[\text{CO}]$ and overestimated
 290 the recovery at high $[\text{CO}]$. This enabled an upper limit of k_9 (295K) $\leq 5 \times 10^{-12}$ cm^3 molecule $^{-1}$

291 s^{-1} to be obtained. The final fit to k_6 (solid line in Figure 7) was achieved by varying k_8 and k_9
 292 from 0 to their respective upper limits. This produced a 28% uncertainty in the fit to k_6 , so that
 293 $k_6(295\text{ K}) = (2.6 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

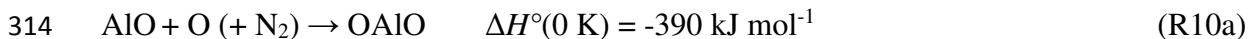


294
 295 **Figure 7.** Plot of $[\text{AlO}]/[\text{AlO}]_0$ against $[\text{CO}]$ for the reaction of $\text{AlO}_2 + \text{CO}$ ($[\text{O}_2] = 1.08 \times 10^{14}$
 296 molecule cm^{-3} , $[\text{O}_3] = 3.28 \times 10^{12} \text{ molecule cm}^{-3}$, 295 K and 1 Torr). The line is the kinetic
 297 model fit to the dataset, with the shaded area showing the associated error in the fit ($\pm 1\sigma$),
 298 caused by the variability in R7 and R8 (see text).

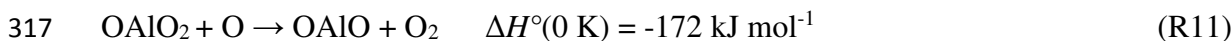
299

300 3.6 OAIO + O

301 OAIO was produced in the same way as for studying R6, and the same upper limit for k_8 was
 302 used in the kinetic model. However, instead of varying the reactant of interest (in this case O),
 303 $[\text{O}_3]$ was varied while $[\text{O}]$ was fixed to $7.02 \times 10^{12} \text{ molecule cm}^{-3}$ at the point of injection. This
 304 procedure was adopted because it is considerably easier to vary $[\text{O}_3]$, which was continuously
 305 monitored by optical absorption, than to vary $[\text{O}]$ and carry out a new titration with NO_2 at
 306 each point. This would require turning off the ozoniser and the Al ablation laser, making the
 307 $[\text{O}]$ measurement, restarting ablation and O_3 production, and waiting for the signals to stabilize,
 308 a process which would take in excess of 30 min and lead to significant signal drift. Figure 8
 309 shows the AlO signal as a function of $[\text{O}_3]$ ($0.2 - 3.7 \times 10^{12} \text{ molecule cm}^{-3}$), in the absence of
 310 $[\text{O}]$ (open circles) or at fixed $[\text{O}]$ (black circles). The measured wall loss of O was $150 \pm 22 \text{ s}^{-1}$.
 311 O was added from the sliding injector close to the centre of the flow, while the O_3 was added
 312 through a side port of the flow tube. As well as the reaction of interest (R7) there are two other
 313 possible reactions involving O that could occur in the flow tube:



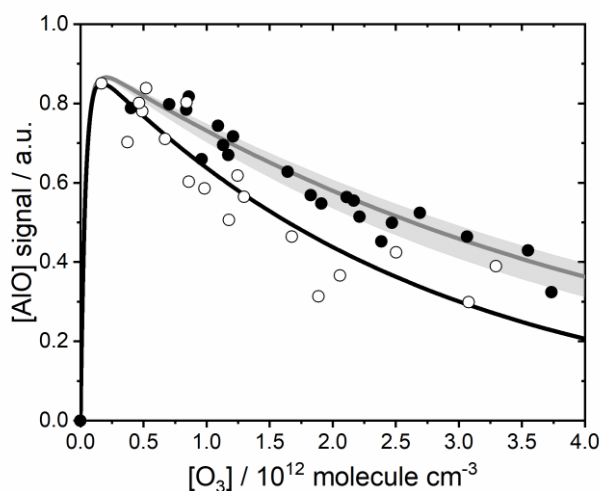
316



318 R10a is a termolecular reaction and its rate coefficient is estimated to be $k_{10}(295\text{ K}) = 7.2 \times$
 319 $10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, using the RRKM Master Equation method described in Section 4;
 320 hence, this channel is relatively slow at the 1 Torr pressure in the flow tube. The radiative
 321 recombination channel R10b, discussed below, also appears to be minor: when O was added
 322 to a flow of AlO (and O_2), no change in the AlO LIF signal was observed, suggesting that R10

323 is too slow to compete with rapid recycling by the bimolecular reaction R7 back to AIO and so
 324 was not included in the kinetic model. This cycling between R7 and R10 also makes an
 325 independent measurement of R10 difficult in this experimental system. The effect of R11 in
 326 the model was well within the scatter of the experimental data points when k_{11} was set to an
 327 upper limit $\leq 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. If a higher value for k_{11} was used, the model failed
 328 to reproduce the slope of the experimental data in Figure 8. Indeed, the closest comparable
 329 reaction previously studied, $\text{OFeO}_2 + \text{O}$, was too slow to measure ($< 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
 330 below 466 K.¹² The sensitivity to the O diffusion rate was also investigated, with a doubling
 331 of the rate to 300 s^{-1} causing only a 20% increase in the fitted value of k_7 . The final model fit
 332 through the experimental points, shown by the solid lines in Figure 8, yields $k_7(294 \text{ K}) = (1.9$
 333 $\pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

334



335

336 **Figure 8.** Plots of [AIO] as a function of [O₃] at 1 Torr and 294 K. Solid black circles are
 337 experimental data with a fixed addition of O ($[\text{O}] = 7.02 \times 10^{12} \text{ molecule cm}^{-3}$ at the injection
 338 point) and open circles are in the absence of [O]. The solid grey and black lines are the model
 339 fits with and without [O], respectively, with the shaded grey area of the model fit representing
 340 $\pm 1\sigma$ uncertainty in k_7 .

341

342 3.6.1 Chemiluminescence from AIO + O

343

344 Chemiluminescence produced by R10b was also investigated. This reaction, followed by
 345 recycling of OAIO back to AIO (R7) has been hypothesised to explain observations of broad
 346 visible emission when Tri-Methyl Aluminium (TMA) grenades are released in the upper
 347 atmosphere above 90 km.^{20, 21} The LIF detection system was modified by replacing the 480 nm
 348 band pass filter with a monochromator, and the PMT used in the photon-counting mode with a
 349 multichannel scaler. In order to observe sufficient signal, the slit width of the monochromator
 350 had to be set to a width giving a wavelength accuracy of only $\pm 30 \text{ nm}$, calibrated at 532 nm
 351 using a laser diode (Thorlabs CPS532).

352 The experimental conditions were the same as those used to study the kinetics of R7, but
 353 without the addition of O₃ to the flow. A broad emission was seen across the detectable
 354 wavelength range (300 – 800 nm) reducing to almost zero at 300 nm, still present at 800 nm,
 355 and peaking between 500 - 600 nm. The same profile was observed with just Al and O₂ in the

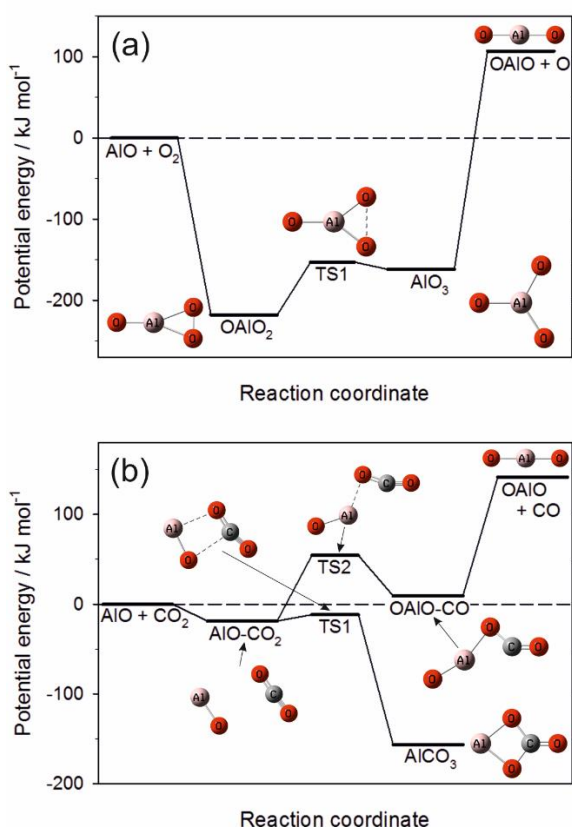
356 system, but the raw signal was an order of magnitude higher when [O] was also present and
357 scaled linearly with increasing [O]. A peak observed on top of the broad emission at
358 approximately 400 nm (still present with only Al + N₂ in the flow tube) was attributed to
359 emission from the long lived Al(²S) state, produced by laser ablation of the Al rod, relaxing to
360 the ground state Al(²P).

361

362 4 Discussion

363 The measured second-order rate coefficients as a function of temperature and pressure for R2
364 – R7 are listed in Table S1 (in the Supporting Information). To understand the unusual
365 behaviour of some of the measured reactions, and to extrapolate the recombination reactions
366 to MLT pressures and temperatures, electronic structure calculations were combined where
367 appropriate with Rice-Ramsperger-Kassel-Markus (RRKM) theory. The geometries of the Al-
368 containing molecules were first optimized at the B3LYP/6-311+g(2d,p) level of theory within
369 the Gaussian 16 suite of programs.⁴ More accurate energies were then determined using the
370 Complete Basis Set (CBS-QB3) method.²² The Cartesian coordinates, rotational constants,
371 vibrational frequencies and heats of formation of the relevant molecules are listed in Table S2.
372 Most of the geometries are illustrated in Figure 9, which shows the potential energy surfaces
373 for R2 (AlO + O₂) and R3 (AlO + CO₂).

374 The results obtained here are generally in good agreement with previous theoretical work.²³⁻²⁷
375 In particular, the most stable isomer of AlO₂ is linear OAlO(²Π_g), as demonstrated in a
376 photoelectron spectroscopy experiment by Desai *et al.*¹⁹ This study measured the symmetric
377 vibrational frequency to be 810 cm⁻¹, in excellent agreement with our calculated value of 830
378 cm⁻¹ (Table S2). A matrix isolation study by Andrews *et al.*²⁸ attributed a vibrational
379 frequency at 1129 cm⁻¹ to OAlO, but this assignment does not seem to be correct. In contrast,
380 their frequency at 496 cm⁻¹ attributed to cyclic AlO₂ agrees well with our calculated value of
381 504 cm⁻¹. In the case of AlO₃, four absorptions at 838, 850, 853 and 861 cm⁻¹ attributed to
382 this isomer are consistent with our calculated values of 859 and 868 cm⁻¹. The matrix study²⁸
383 reported an absorption at 964 cm⁻¹ for the C_{2v} OAlO₂ isomer, which seems quite low
384 compared with our closest vibrational mode at 1109 cm⁻¹.



385
 386 **Figure 9.** Potential energy surfaces calculated at the CBS-QB3 level of theory: (a) AIO +
 387 O₂; (b) AIO + CO₂, where the barrier height of TS1 has been increased by 13 kJ mol⁻¹ to
 388 optimise the RRKM fit.

389
 390 **4.1 AIO + O₂ and AIO + CO₂**

391
 392 The reaction between AIO and O₂ has been studied previously by Belyung and Fontijn⁵ over
 393 a wide range of temperature (305 – 1689 K) and pressure (5 – 75 Torr). They found that the
 394 reaction was pressure-dependent below 1010 K and, as in the present study, observed clear
 395 fall-off behaviour at 305 K. As shown in Figure 4(b), their reported third-order rate
 396 coefficients are somewhat slower (e.g. 44% slower around 300 K) than in the present study,
 397 which is probably explained by the use of Ar rather N₂ as the bath gas. Above 1000 K, R2
 398 became pressure independent, which was attributed to the bimolecular reaction dominating
 399 the kinetics:



401 The measured rate coefficient was reported to be $k_{12}(1010 - 1689 \text{ K}) = 7.7 \times 10^{-10} \exp(-83.1$
 402 $\text{kJ mol}^{-1}/RT)$. Inspection of the Arrhenius plot (Figure 6 in Belyung and Fontijn⁵) shows that
 403 the uncertainty in the activation energy is around 23 kJ mol⁻¹, so that the activation energy is
 404 consistent with the reaction endothermicity of 107 kJ mol⁻¹ at the CBS-QB3 level (Figure 9),
 405 where the uncertainty in the theoretical estimate is probably 15 kJ mol⁻¹.²⁹ It should be noted
 406 that OAIO has a well-known problem with symmetry breaking in its wavefunction, and a
 407 high-level theoretical study (at the partially spin-restricted RCCSD(T)/aug-cc-pvqz level of
 408 theory) indicates that the linear OAIO (²Π) state is around 121 kJ mol⁻¹ lower than the lowest

409 state of cyclic AlO_2 ($^2\text{A}_2$).²⁵ This would decrease the endothermicity of R12 to 87 kJ mol^{-1} , in
410 even better agreement with the experimental activation energy.

411 The reaction between AlO and CO_2 has been studied previously in Ar bath gas by Rogowski
412 *et al.*¹³ between 500 and 1300 K. Those authors assumed that the reaction was bimolecular:



414 and did not consider the possible recombination reaction leading to AlCO_3 , despite obtaining
415 a small negative temperature dependence for the second-order rate coefficient. Dividing their
416 second-order rate coefficients by their respective Ar concentrations yields the points plotted
417 in Figure 4(b), which are in sensible accord with the present study considering the different
418 bath gas. More recently, Parnis *et al.*⁶ studied the $\text{AlO} + \text{CO}_2$ reaction at high pressures (200 -
419 700 Torr) of N_2O . They reported rate coefficients between $(1.1 - 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$
420 s^{-1} at 296 K, and a slight pressure dependence indicating the reaction was well into the fall-
421 off region.

422 We now describe using RRKM theory to fit the experimental rate coefficients for reactions
423 R2 – R3. The Master Equation Solver for Multi-Energy well Reactions (MESMER)
424 program³⁰ was used. Each reaction is assumed to proceed via the formation of an excited
425 adduct, which can either dissociate or be stabilized by collision with the N_2 third body. The
426 internal energy of this adduct was divided into a contiguous set of grains (typical width = 110
427 cm^{-1}) containing a bundle of rovibrational states. Each grain was then assigned a set of
428 microcanonical rate coefficients for dissociation, which were determined using inverse
429 Laplace transformation to link them directly to $k_{\text{rec},\infty}$, the high pressure limiting
430 recombination coefficient. The density of states of each adduct was calculated with the
431 vibrational frequencies and rotational constants listed in Table S2, without making a
432 correction for anharmonicity, and a classical densities of states treatment for the rotational
433 modes. The probability of collisional transfer between grains was estimated using the
434 exponential down model, where the average energy for downward transitions is designated
435 $\langle \Delta E \rangle_{\text{down}}$, and the probabilities for upward transitions are determined by detailed balance.³¹
436 $\langle \Delta E \rangle_{\text{down}}$ was assigned a small temperature dependence of the form T^β . The collision rate of
437 N_2 with the adduct as a function of temperature, $Z(T)$, was calculated using Lennard-Jones
438 parameters (σ and ε) to characterise the intermolecular potential. The ME, which describes
439 the evolution with time of the adduct grain populations, was then expressed in matrix form
440 and solved to yield the recombination rate constant at a specified pressure and temperature.

441 The adjustable parameters used to perform a global fit to all the experimental data points for
442 each reaction (Table S1) were $k_{\text{rec},\infty}$, σ , $\langle \Delta E \rangle_{\text{down}}$ and β . Table 3 summarises the results. The
443 fitted values of $\langle \Delta E \rangle_{\text{down}}$ lie between 310 and 330 cm^{-1} i.e. within the expected range for
444 N_2 .³¹ Although the value of β is usually between -0.5 and 0.5,³¹ the somewhat larger values
445 here are needed to capture the decrease in k_2 and k_3 at temperatures above 450 K. $k_{\text{rec},\infty}$ for
446 reaction R3 is essentially the capture rate between AlO and CO_2 , with a small positive
447 temperature. In contrast, $k_{\text{rec},\infty}$ for R2 is a factor of 6 smaller than the capture rate, with the
448 slightly higher temperature dependence. This is explained in Figure 9(a), which shows the
449 potential energy surface for R2 as the AlO approaches the O_2 at different angles of attack.
450 Near-orthogonal reactions, where the angle α (defined in the figure legend) is between 90 and
451 118° , and near-end-on reactions where α is between 145 and 180° , involve significant
452 barriers. Successful collisions are thus quite sterically constrained. This also justifies the
453 small activation energy (2.3 kJ mol^{-1}) for $k_{\text{rec},\infty}$. For both reactions, the expressions for $Z(T)$
454 (the values for σ and ε are given in the footnotes to Table 3) are essentially at their collision
455 frequencies.

456

457 **Table 2.** Parameters used in RRKM fits to the kinetics of reactions R2 and R3.

Reaction	$\langle \Delta E \rangle_{\text{down}}$ cm ⁻¹ at 298 K	β^a	$k_{\text{rec},\infty}$ cm ³ molecule ⁻¹ s ⁻¹	$Z(T)^b$ cm ³ molecule ⁻¹ s ⁻¹
AlO + O ₂	330	1.8	$8.5 \times 10^{-11} \exp(-277 / T)$	$3.4 \times 10^{-10} (T/300)^{0.5}$
AlO + CO ₂	310	1.9	$5.0 \times 10^{-10} \exp(-230 / T)$	$2.4 \times 10^{-10} (T/300)^{0.5}$

458 ^a $\langle \Delta E \rangle_{\text{down}}(T) = \langle \Delta E \rangle_{\text{down}}(T / 298)^\beta$ 459 ^b Collision frequency between the adduct and N₂. For AlO-O₂, $\sigma = 3.6 \text{ \AA}$ and $\mathcal{E}/k_B = 250 \text{ K}$.460 For AlO-CO₂, $\sigma = 3.0 \text{ \AA}$ and $\mathcal{E}/k_B = 250 \text{ K}$.

461

462 Satisfactory fits of the bimolecular rate coefficients for R2 and R3 at 296 K are shown in
 463 Figure 4a, and the termolecular rate coefficients $k_{2,\text{rec}}$ and $k_{3,\text{rec}}$ (at the experimental pressure)
 464 are compared in Figure 4b. Figure 9a shows that both OAlO₂ and AlO₃ are stable with respect
 465 to AlO + O₂, and connected by a transition state 153 kJ mol⁻¹ below the reactant entrance
 466 channel. Since OAlO₂ is 56 kJ mol⁻¹ lower in energy than AlO₃, this is the major product
 467 below 1000 K. Above 1000 K, the formation of OAlO dominates over recombination even at
 468 a pressure of 10 Torr, in accord with the experiments of Belyung and Fontijn.⁵

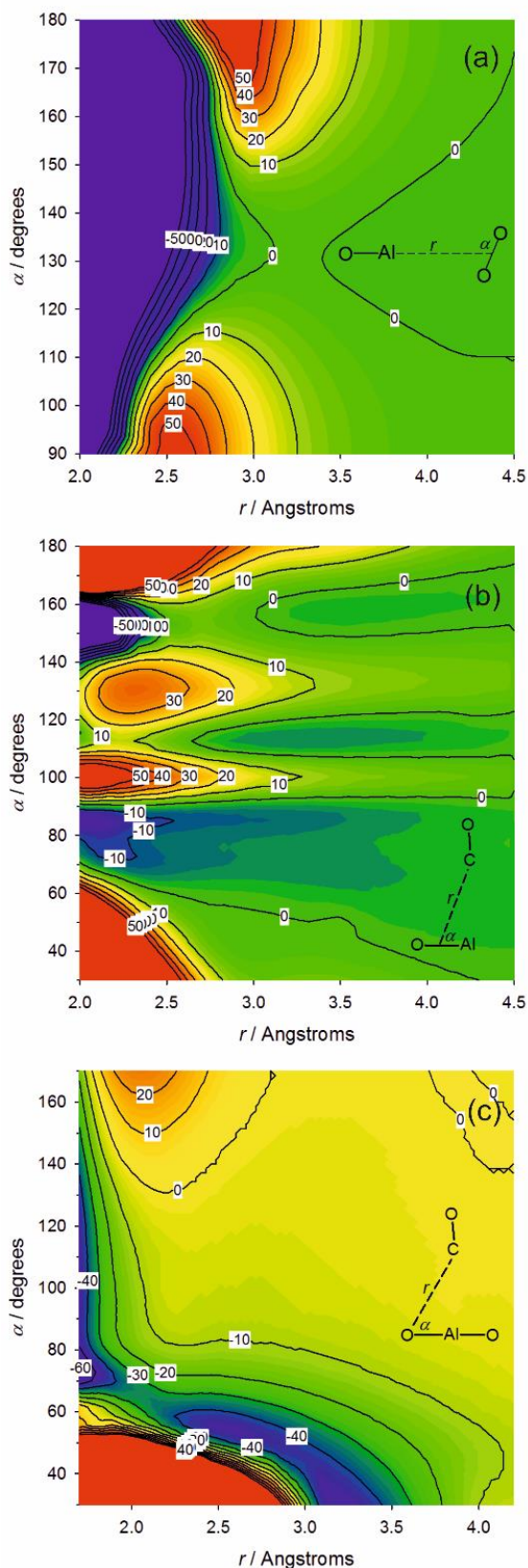
469 In the case of R3 (AlO + CO₂), Figure 9b shows that a very weakly bound AlO-CO₂ cluster
 470 rearranges over a small barrier to form AlCO₃. The height of this barrier needed to be
 471 increased by 13 kJ mol⁻¹ above the CBS-QB3 value to optimise the RRKM fit at temperatures
 472 below 350 K, where the negative temperature dependence of $k_{3,\text{rec}}$ becomes smaller. This
 473 change in energy is within the expected uncertainty at this level of theory.³¹ The alternative
 474 rearrangement to OAlO-CO and then OAlO + CO involves a significant barrier that is 54 kJ
 475 mol⁻¹ above the reactant entrance channel; hence the carbonate is the only product that should
 476 form below 1000 K.

477 $k_{2,\text{rec}}$ and $k_{3,\text{rec}}$ can now be extrapolated to the low pressure limiting values appropriate for
 478 modelling in planetary upper atmospheres. The temperature-dependent rate coefficients are
 479 well-fitted by second-order polynomials (note that the coefficients are given to 5 significant
 480 figures to preserve numerical precision, not to imply accuracy):

481
$$\log_{10}(k_{2,\text{rec}0}) = -35.137 + 6.1052 \log_{10}(T) - 1.4089 (\log_{10}(T))^2$$

482
$$\log_{10}(k_{3,\text{rec}0}) = -38.736 + 8.7342 \log_{10}(T) - 2.0202 (\log_{10}(T))^2$$

483 The uncertainty over the experimental temperature range (190 – 812 K) is $\pm 20\%$, based on
 484 the experimental uncertainties at the temperature extremes.



485

486 **Figure 10.** Potential energy surfaces for (a) AlO + O₂, (b) AlO + CO and (c) OAlO + CO,
 487 plotted as a function of bond angle α and bond distance r (defined on each figure). Calculations
 488 at the B3LYP/6-311+g(2d,p) level of theory. At each (r, α) point on the surface the geometry
 489 was optimized with α and r fixed.

490 4.2 AlO + O₃, CO and O

491 The reaction between AlO and O₃ is relatively fast: $k_4(295\text{ K}) = (1.3 \pm 0.2) \times 10^{-10}\text{ cm}^3$
492 $\text{molecule}^{-1}\text{ s}^{-1}$ is within a factor of 2 of the rate coefficients for the metal oxides CaO, FeO,
493 KO and NaO which we have studied previously, and 3.7 times faster than MgO + O₃.⁷

494 The reaction AlO + CO was studied previously by Parnis *et al.*⁶ in a high pressure (200 –
495 700 Torr) of N₂O. They reported a pressure-dependent reaction with a third-order rate
496 coefficient of $4.3 \times 10^{-32}\text{ cm}^6\text{ molecule}^{-2}\text{ s}^{-1}$. AlO does indeed form an AlO-CO complex, but
497 this is only bound by 104 kJ mol⁻¹ with respect to AlO + CO (at the CBS-QB3 level), and this
498 should then dissociate to Al + CO₂ in a reaction that is overall 34 kJ mol⁻¹ exothermic,
499 consistent with our observation of a bimolecular reaction. Insufficient detail is provided in the
500 Parnis *et al.* paper⁶ to comment further on this apparent discrepancy. Figure 9b shows the
501 potential energy surface for the approach of AlO to CO. This shows that there are limited
502 angles of attack which allow formation of the AlO-CO complex; this most likely explains
503 why the rate coefficient $k_5(295\text{ K}) = (1.95 \pm 0.35) \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ is significantly
504 slower than the collision frequency.

505 Garland *et al.*³² studied the reverse reaction and found that it was bimolecular above 700 K,
506 obtaining $k(\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}) = 2.9 \times 10^{-10}\text{ exp}(-26.8 \pm 1.7\text{ kJ mol}^{-1}/RT)\text{ cm}^3$
507 $\text{molecule}^{-1}\text{ s}^{-1}$. This activation energy is close to our calculated reaction endothermicity of 34
508 kJ mol⁻¹ at the CBS-QB3 level. This compares well (within the expected uncertainty²⁹) with a
509 recent higher level (CCSD(T)/cc-pV(Q+d)) calculation of 21 kJ mol⁻¹,³³ and a value of 19 ± 9
510 kJ mol⁻¹ using the currently recommended experimental bond energy (at 0 K) for AlO of 507
511 $\pm 9\text{ kJ mol}^{-1}$.³⁴ Sun *et al.*³³ showed that there is a submerged barrier on the potential surface
512 connecting AlO with CO, consistent with two crossed molecular beam studies^{35,36} and in
513 disagreement with a previous theoretical study by Sakai³⁷ who predicted the barrier to lie 79
514 kJ mol⁻¹ above Al + CO₂.

515 The addition of AlO to O is 390 kJ mol⁻¹ exothermic, so that chemiluminescence could
516 potentially be observed down to 306 nm. The broad emission observed in this study is
517 comparable to that seen previously by Golomb and Brown,³⁸ who added O atoms to a flow of
518 TMA and recorded peak emission at 540 nm. The present study therefore confirms that the
519 emission is produced by reaction 10b.

520

521 4.3 OAlO + CO and O

522 Reaction R6 (OAlO + CO) is relatively fast, about 1 order of magnitude slower than the
523 collision frequency and an order of magnitude faster than R5 (AlO + CO). This is explained
524 by the potential energy surface in Figure 10c, which shows that the reaction is much less
525 sterically constrained compared with R5: attack by CO over a wide range of C-O-Al angles
526 from 60 – 140° should lead to successful reaction.

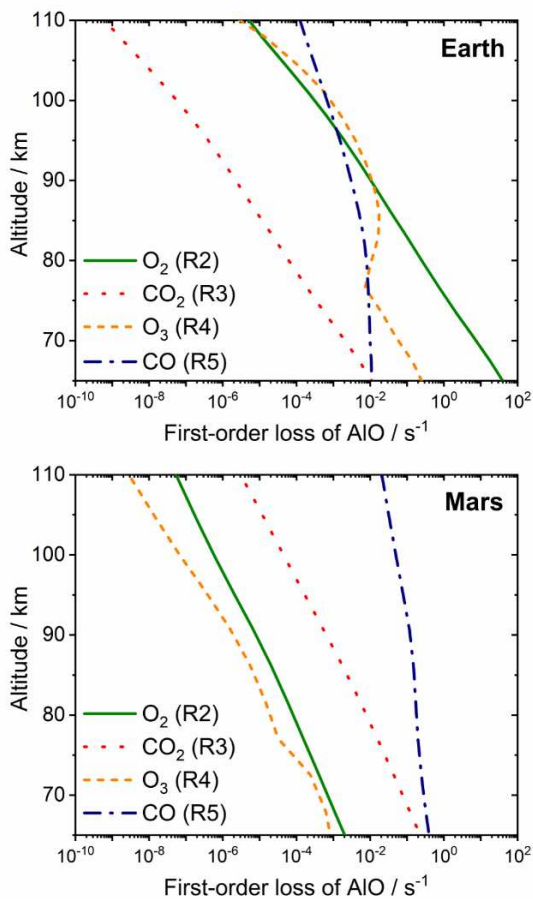
527 Reaction R7 (OAlO + O) is close to the collision frequency ($k_7 = (1.9 \pm 0.8) \times 10^{-10}\text{ cm}^3$
528 $\text{molecule}^{-1}\text{ s}^{-1}$), and inspection of Figure 9a shows that there are no barriers for this reaction
529 (the reverse of R12). Interestingly, k_7 is a factor 2.3 times faster than the room temperature
530 rate coefficients for the analogous reaction of OMgO, and an order of magnitude faster than
531 the reactions of NaO₂, FeO₂ and CaO₂ with O.⁷

532

533 5 Atmospheric Implications for Earth and Mars

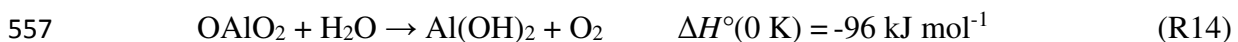
534 The measured rate coefficients for R2 – R5 can now be used to calculate the first-order removal
 535 rates of AIO in the atmospheres of Earth and Mars between 65 and 110 km, where Al ablates
 536 from cosmic dust particles¹ and has been observed as Al⁺ ions on both planets.² For Earth, the
 537 vertical profiles of T , pressure and the mixing ratios of relevant species (O₃, O₂, CO₂ and CO)
 538 were taken from the Whole Atmosphere Community Climate Model (WACCM4),³⁹ and for
 539 Mars from the Mars Climate Database v5.3 ((http://wwwmars.lmd.jussieu.fr/mcd_python/)).⁴⁰
 540 For R4 and R5, a $T^{1/6}$ temperature dependence is assumed, typical of a reaction governed by
 541 long-range attractive forces. For the recombination reactions in Mars' atmosphere, k_2 and k_3
 542 are multiplied by 2 to account for the increased efficiency of CO₂ compared with N₂.³¹

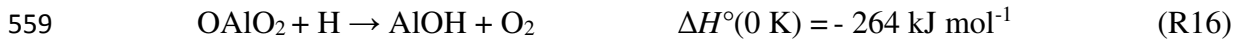
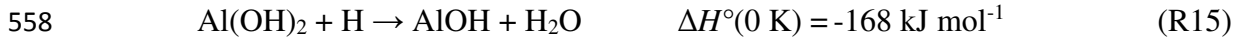
543 Figure 11 (top panel) shows that the recombination of AIO with O₂ is the most important loss
 544 process below 90 km in the Earth's atmosphere. Above 85 km in the region of the tertiary O₃
 545 maximum,⁴¹ R4 (AIO + O₃) becomes slightly faster as the increasingly low pressure slows
 546 down the recombination reaction. Although reduction of AIO back to Al by CO (R5) also
 547 becomes competitive above 90 km, the Al product will rapidly be re-oxidized by O₂ (R1), so
 548 that this represents a null cycle. The relatively low CO₂ abundance means that R3 (AIO + CO₂)
 549 is the slowest of these AIO loss processes between 65 and 110 km.



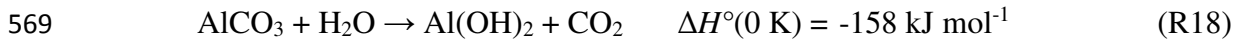
550
 551 **Figure 11.** First-order loss rates of AIO by reaction with O₂, O₃, CO₂ and CO (R2 – R5) as a
 552 function of altitude in planetary atmospheres: Earth, 40°N, January, local midnight (top panel);
 553 Mars, 60°N, solar longitude Ls = 90 (summer solstice), local midnight (bottom panel).

554 Although this comparison suggests that a primary Al reservoir will be OAlO₂, reactions with
 555 H₂O and H (which have similar concentrations between 80 and 100 km⁷) will most likely
 556 produce AIOH:





560 On Mars, the situation is quite different. Figure 11 (bottom panel) shows that recombination of
 561 AlO with CO₂ is about 2 orders of magnitude faster than recombination with O₂, and R4 is the
 562 slowest reaction because of the relatively low O₃ abundance in Mars' atmosphere. Strikingly,
 563 R5 (AlO + CO) dominates AlO removal in the meteor ablation region around 80 km and above.
 564 Although the resulting Al atoms will be re-oxidized by O₂, the CO/O₂ ratio is ~3 so that atomic
 565 Al should be a significant atmospheric species, with an Al:AlO ratio of ~19. Nevertheless,
 566 AlO will still be converted to AlCO₃, albeit more slowly because of the recycling between Al
 567 and AlO. AlCO₃ is then likely to react with O₂, H₂O or H, again producing AlOH:



571 This makes an interesting contrast with the two major metal carbonates, MgCO₃ and FeCO₃,
 572 that should be produced in Mars' atmosphere through meteoric ablation.¹ These carbonates are
 573 calculated to have very large dipole moments (11.6 and 9.2 Debye, respectively⁴²), so that they
 574 bind with up to four CO₂ molecules at the sub-200 K temperatures around 80 km. H₂O then
 575 switches with the CO₂ ligands to produce an unreactive hydrated carbonate.⁴² The calculated
 576 dipole moment of AlCO₃ from the present is only 6.5 D; the resulting CO₂ binding energy (32
 577 kJ mol⁻¹) is not strong enough for significant CO₂ cluster formation which would prevent
 578 AlCO₃ from undergoing reactions R17 – R19.

579 Finally, unlike other metal hydroxides such as FeOH, NaOH and CaOH,^{7, 12, 43} AlOH is stable
 580 with respect to reaction with H and O atoms:



583



585 and is thus likely to be the major reservoir for ablated Al in both planetary atmospheres.

586

587 **6. Conclusions**

588 The reactions of AlO with O₂, CO₂ and O₃ were studied using the PLP-LIF technique, and the
 589 reactions of AlO with CO, and OAlO with CO and O, using pulsed laser ablation in a fast flow
 590 tube. The temperature dependences of the recombination reactions of AlO with O₂ and CO₂
 591 become less negative at temperatures below 350 K, which is explained by small barriers on
 592 their potential surfaces. RRKM fits were used to extrapolate the experimental data for these
 593 reactions to pressures (< 5 Pa) and temperatures (< 240 K) appropriate for modelling planetary
 594 atmospheres. A summary of the measured rate coefficients is provided in Table 3.
 595 Chemiluminescence over a broad wavelength range (305 – > 800 nm) was observed from the
 596 radiative recombination of AlO with O, presumably by production of electronically excited
 597 OAlO. In terms of atmospheric implications, in the Earth's MLT region AlO should be
 598 removed most rapidly by O₃ above 85 km and with O₂ below 85 km, with O recycling OAlO
 599 to AlO. On Mars, reduction of AlO to Al by CO should maintain a significant Al:AlO ratio.
 600 However, in both atmospheres AlOH is predicted to be the major reservoir for meteor-ablated
 601 Al.

602

603 **Table 3.** Summary of rate coefficients measured in this study

Reaction	Rate coefficient ^a
R2 AlO + O ₂ (+ N ₂) → OAlO ₂	$k_{\text{rec},0} = 10^{-35.137 + 6.1052\log_{10}(T) - 1.4089(\log_{10}(T))^2}$
R3 AlO + CO ₂ (+ N ₂) → AlCO ₃	$k_{\text{rec},0} = 10^{-38.736 + 8.7342\log_{10}(T) - 2.0202(\log_{10}(T))^2}$
R4 AlO + O ₃ → OAlO + O ₂	$(1.25 \pm 0.05) \times 10^{-10} (T/295)^{1/6}$
R5 AlO + CO → Al + CO ₂	$(1.95 \pm 0.35) \times 10^{-12} (T/295)^{1/6}$
R6 OAlO + CO → AlO + CO ₂	$(2.55 \pm 0.7) \times 10^{-11} (T/295)^{1/6}$
R7 OAlO + O → AlO + O ₂	$(1.9 \pm 0.8) \times 10^{-10} (T/295)^{1/6}$

604 ^a Units for termolecular reactions: cm⁶ molecule⁻² s⁻¹ (see section 4.1 for uncertainties). Units
 605 for bimolecular reactions: cm³ molecule⁻¹ s⁻¹.

606

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 610 Supporting Information.

611

612 **Supporting Information**

613 Table S1: list of second-order rate coefficients for reactions R2 – R7, as a function of
 614 temperature and pressure. Table S2: molecular properties and heats of formation (at 0 K) of
 615 AlO, OAlO₂, AlO₃, OAlO, and AlCO₃, and the stationary points on the AlO + O₂ and AlO +
 616 CO₂ potential energy surfaces.

617

618 **References**

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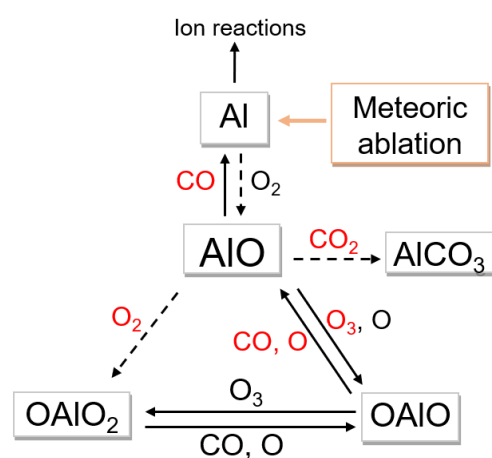
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728

729 **Graphical abstract:**



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