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Supporting Information

Kinetic study of the reactions of AlO and OAlO relevant to planetary mesospheres

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Table S1. List of measured second-order rate coefficients for reactions R2 – R7, as a function of temperature and pressure.

Reaction No.	Reaction	Pressure / torr	T / K	Rate coefficient / $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
R2	$\text{AlO} + \text{O}_2 (+ \text{N}_2) \rightarrow \text{OAlO}_2$	5.3	192	$(2.44 \pm 0.31) \times 10^{-12}$
		10	300	$(2.43 \pm 0.07) \times 10^{-12}$
		14.7		$(3.29 \pm 0.18) \times 10^{-12}$
		17.3		$(3.48 \pm 0.1) \times 10^{-12}$
		5.3	351	$(1.34 \pm 0.04) \times 10^{-12}$
			413	$(1.06 \pm 0.11) \times 10^{-12}$
			491	$(8.03 \pm 0.8) \times 10^{-13}$
			600	$(4.89 \pm 0.51) \times 10^{-13}$
			812	$(2.44 \pm 0.36) \times 10^{-13}$
R3	$\text{AlO} + \text{CO}_2 (+ \text{N}_2) \rightarrow \text{AlCO}_3$	5.4	193	$(8.09 \pm 1.81) \times 10^{-13}$
		9.9	300	$(6.13 \pm 0.21) \times 10^{-13}$
		14.8		$(8.77 \pm 0.3) \times 10^{-13}$
		5.4	421	$(1.77 \pm 0.24) \times 10^{-13}$
			599	$(6.94 \pm 1.54) \times 10^{-14}$
813	$(2.68 \pm 0.79) \times 10^{-14}$			
R4	$\text{AlO} + \text{O}_3 \rightarrow \text{AlO}_2 + \text{O}_2$	5.8	295	$(1.25 \pm 0.19) \times 10^{-10}$
R5	$\text{AlO} + \text{CO} \rightarrow \text{Al} + \text{CO}_2$	1.0	295	$(1.95 \pm 0.35) \times 10^{-12}$
R6	$\text{OAlO} + \text{CO} \rightarrow \text{AlO} + \text{CO}_2$	1.0	295	$(2.6 \pm 0.7) \times 10^{-11}$
R7	$\text{OAlO} + \text{O} \rightarrow \text{AlO} + \text{O}_2$	1.0	295	$(1.9 \pm 0.8) \times 10^{-10}$

Table S2. Molecular properties and heats of formation (at 0 K) of AlO, OAlO₂, AlO₃, OAlO, and AlCO₃, and the stationary points on the AlO + O₂ and AlO + CO₂ potential energy surfaces. The geometries are illustrated in Figure 10 in the main paper.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) ^a	Rotational constants (GHz) ^a	Vibrational frequencies (cm ⁻¹) ^a	$\Delta_f H^\circ(0\text{ K})$ (kJ mol ⁻¹) ^b
AlO (² Σ^+)	Al, 0., 0., -0.008 O, 0., 0., 1.623	18.916	946 ^c	70 ^d
OAlO ₂ (² A ₂)	Al, 0., 0., -0.394 O, 0., -0.684, 1.318 O, 0., 0.685, 1.318 O, 0., 0., -1.994	33.702 4.0970 3.6530	189, 192, 454, 556, 1109, 1157	-148
TS from OAlO ₂ to AlO ₃ (TS1)	Al, 0.931, 0.120, 0.567 O, -0.537, 0.973, 0.744 O, -0.239, -1.084, 0.877 O, 2.621, 0.349, 0.253	14.560 4.8875 3.6592	339i, 183, 218, 645, 783, 987	-83
AlO ₃ (² B ₂)	Al, 0.432, 0.281, -0.002 O, 2.034, 0.951, 0.088 O, 0.257, -1.450, -0.057 O, -0.925, 1.370, -0.031	7.1732 6.7640 3.4813	170, 190, 256, 644, 859, 868	-92
AlO ₂ (cyclic) (² A ₂)	Al, 0., 0., 1.010 O, 0., 0.673, -0.822 O, 0., -0.673, -0.822	34.8353 10.2871 7.9418	336, 504, 1180	32
OAlO (² Π_g)	Al, 0.0, 0.072, -0.0 O, 1.653, 0.071, -0.0 O, -1.654, 0.072, 0.0	5.7786	183, 214, 773, 830	-69
AlO-CO ₂	C, 1.432, 0.072, 0.043 O, 0.343, -0.213, -0.266 O, 2.522, 0.307, 0.344 Al, -1.125, 2.435, -0.230 O, 0.389, 2.863, 0.205	9.1531 2.0912 1.7023	37, 57, 64, 141, 650, 675, 944, 1360, 2394	-342
TS from AlO- CO ₂ to AlCO ₃ (TS1)	Al, 1.445, 0.820, -0.004 O, -0.736, 1.075, 0.049 C, -1.071, -0.074, 0.015 O, -1.662, -1.059, -0.008 O, 1.154, -0.797, -0.054	9.7093 3.2467 2.4331	-223i, 116, 206, 281, 559, 655, 930, 1276, 2305	-335 ^e
AlCO ₃ (³ B ₁)	Al, 0.0, -1.589, 0. O, -1.111, -0.219, 0. C, -0.0, 0.605, 0. O, 0.0, 1.792, 0.0 O, 1.111, -0.219, 0.	12.789 4.1025 3.1061	189, 500, 577, 658, 794, 862, 911, 1016, 1862	-480
TS from AlO- CO ₂ to OAlO- CO (TS2)	Al, 0.973, -0.3215, 0.0 O, -0.660, 0.937, 0.0 O, 2.537, 0.092, 0.0 C, -1.385, -0.0446, 0.0	21.5321 2.03810 1.86187	383i, 86, 125, 185, 494, 511, 996, 1168,	-269

	O, -2.358, -0.671, 0.0		2184	
OAlO-CO	Al, -0.891, -0.004, 0.0 O, 0.618, 0.996, 0.001 O, -2.463, -0.329, 0.002 C, 1.253, -0.148, 0.0 O, 2.35, -0.549, 0.0	22.2861 2.17845 1.98447	140, 155, 193, 366, 474, 725, 1039, 1112, 1925	-314

^a Calculated at the B3LYP/6-311+g(2d,p) level of theory ¹

^b Calculated at the CBS-QB3 level of theory, ² with reference values for $\Delta_f H^0(\text{Al}) = 327.3 \text{ kJ mol}^{-1}$, $\Delta_f H^0(\text{O}) = 246.8 \text{ kJ mol}^{-1}$, $\Delta_f H^0(\text{CO}) = -113.8 \text{ kJ mol}^{-1}$, $\Delta_f H^0(\text{CO}_2) = -393.2 \text{ kJ mol}^{-1}$ and $\Delta_f H^0(\text{H}_2\text{O}) = -238.9 \text{ kJ mol}^{-1}$ at 0 K. ³

^c Experimental values: $r_e(\text{Al-O}) = 1.6179 \text{ \AA}$; $\omega_e = 979 \text{ cm}^{-1}$ ⁴

^d Calculated using $D_0(\text{AlO}) = 502.8 \text{ kJ mol}^{-1}$ determined with the very accurate W1BD complete basis set method. ¹

^e RRKM fit of the barrier (see text in the main paper). The CBS-QB3 energy is 13 kJ mol^{-1} lower.

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