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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 / cm^3 $molecule^{-1}$ s^{-1}
R2	$AlO + O_2$ (+ N_2) → $OAlO_2$	5.3	192	$(2.44 \pm 0.31) \times 10^{-12}$
			300	$(1.58 \pm 0.03) \times 10^{-12}$
		10		$(2.43 \pm 0.07) \times 10^{-12}$
		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	$AlO + CO_2$ (+ N_2) → $AlCO_3$	5.4	193	$(8.09 \pm 1.81) \times 10^{-13}$
			300	$(3.61 \pm 0.44) \times 10^{-13}$
		9.9		$(6.13 \pm 0.21) \times 10^{-13}$
		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	$AlO + O_3 \rightarrow AlO_2 + O_2$	5.8	295	$(1.25 \pm 0.19) \times 10^{-10}$
R5	$AlO + CO \rightarrow Al + CO_2$	1.0	295	(1.95 ± 0.35) x 10^{-12}
R6	$OAlO + CO \rightarrow AlO + CO_2$	1.0	295	(2.6 ± 0.7) x 10^{-11}
R7	$OAlO + O \rightarrow AlO + O_2$	1.0	295	$(1.9 \pm 0.8) \times 10^{-10}$

Table S2. Molecular properties and heats of formation (at 0 K) of AlO, $OAlO_2$, AlO_3, OAlO, and $AlCO_3$, and the stationary points on the AlO + O_2 and AlO + CO_2 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]	$\Delta_f H^o$(0 K) (kJ mol^{-1}) [b]
AlO ($^2\Sigma^+$)	Al, 0., 0., -0.008 O, 0., 0., 1.623	18.916	946 [c]	70 [d]
$OAlO_2$ ($^2A_2$)	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	339*i*, 183, 218, 645, 783, 987	-83
AlO_3 ($^2B_2$)	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) ($^2A_2$)	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 ($^2\Pi_g$)	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	-223*i*, 116, 206, 281, 559, 655, 930, 1276, 2305	-335 [e]
$AlCO_3$ ($^3B_1$)	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	383*i*, 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 $\Delta_f H^o$(Al) = 327.3 kJ mol^{-1}, $\Delta_f H^o$(O) = 246.8 kJ mol^{-1}, $\Delta_f H^o$(CO) = -113.8 kJ mol^{-1}, $\Delta_f H^o$(CO_2) = -393.2 kJ mol^{-1} and $\Delta_f H^o$(H_2O) = -238.9 kJ mol^{-1} at 0 K. [3]

[c] Experimental values: r_e(Al-O) = 1.6179 Å; ω_e = 979 cm^{-1} [4]

[d] Calculated using D_0(AlO) = 502.8 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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