Supporting Information: Thermal kinetics of $Al_n^- + O_2$ (n=2-30): Measurable reactivity of Al_{13}^-

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Comparison with previous results

As described in the main text, quantitative rate constants for $Al_n^- + O_2$ have been reported previously in multiple ICR experiments as well as in a flow tube experiment lacking mass analysis. Figure S1 compares the present results to those previously published. Although the plot is quite busy, this is supporting information and if you're reading this, you're happy to stare at the data for one or two extra moments to extract the useful information. The more recent ICR results (Neumaier et al.) for n = 8, 10, 12, 14, 16 are in quantitative agreement with the present results. The older ICR results (Cooper et al.) for n = 3 – 23 show a similar trend to the present results, but are biased to lower values. The prior flow tube results (Woodward et al.) for n = 5 – 37 have large uncertainties, but are in generally good agreement with the present results, with the notable exception of Al_9^-.

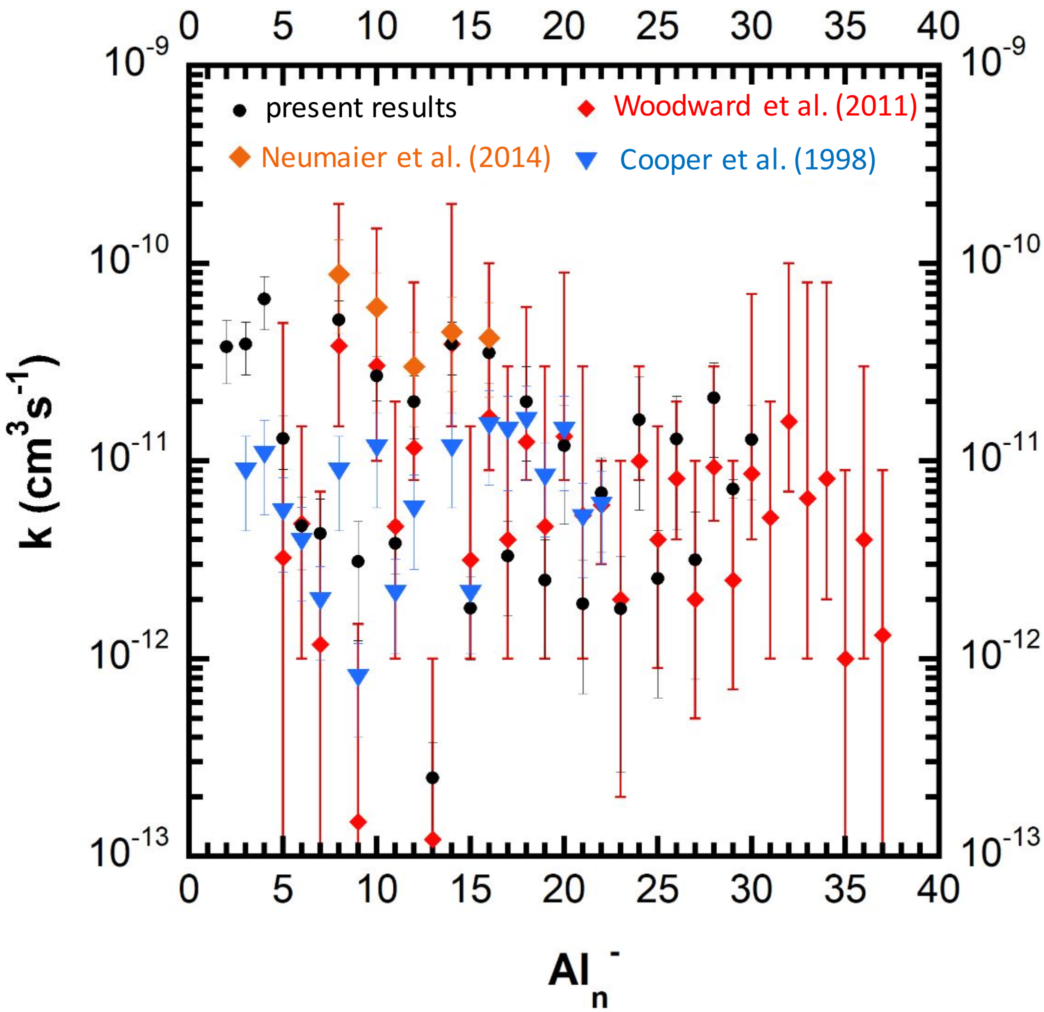

Figure S1. Measured rate constants as a function of cluster size from the current work (black), as well as those by Woodward et al. Ref. [1] (red), Neumaier et al. Ref. [2] (orange), and Cooper et al. Ref. [3] (blue).

Evaluated thermochemistry for Al_n^-

Thermochemistry for small ($n \leq 4$) Al_n and Al_n^- clusters have been determined experimentally. High level calculations have been applied up to n = 14, while thermochemistry of larger clusters has been limited to density functional methods. Below, we compile the experimental and calculated literature to estimate the exothermicities of possible product channels of Al_n^- + O_2.

Table S1. Literature experimental enthalpies of formation

	ΔH^o_{0K} (kJ mol^{-1})
Al	327 ± 4[a]
Al^-	285 ± 4[a,b]

Al_2	487 ± 4[c]
Al_2^-	385 ± 4[b,c]
Al_3	624 ± 10[d]
Al_3^-	439 ± 10[e]
Al_4	753 ± 15[b,f]
Al_4^-	540 ± 12[f]
AlO	67 ± 8[a]
AlO^-	-184 ± 17[a,g]
AlO_2	-86 ± 32[a]
AlO_2^-	-494 ± 32[a,g]
Al_2O	-145 ± 17[a]

[a] Ref. [4]
[b] Ref. [5]
[c] Ref. [6]
[d] Ref. [7]
[e] Ref. [8]
[f] Ref. [9]
[g] Ref. [10]

Table S2. Literature calculated enthalpies of formation of Al_n

	ΔH^o_{0K} (kJ mol^{-1})								
n	CCSD(T)/ CBS[a]	CCSD(T)/ def2-QZVPP //PBE0/ def2-TZVPP[b]	B3LYP/ 6-311G(d)[c]	BPW91/ LANL2DZ[d]	BP86/ SVP[e]	PBE/ 6-311G++ (2d,2p)[f]	Diffusion Monte Carlo[f]	CCSD(T)/ CBS[g]	BP86/ Defs-TZVP[h]
2	494	519	529		503	497	517	520	
3	578	616	674		608	598	611	619	
4	688	741	828	790	728	706	739	747	
5	769	820	941	897	807	783	822		758
6	766	845	1050	1009	869	803	852		784
7	825	837	1098	1062	873	796	853		772
8		941	1237	1184	985	897	955		871
9		1007	1365	1314	1080	952	1026		921
10		1070	1466	1397	1154	1016	1081		975
11			1574	1499	1197	1042	1138		1004
12			1654	1536	1210	1072	1154		1025
13			1727	1612	1208	1010	1138		990
14			1820	1701	1259				1027
15			1951	1830	1345				1096
16			2043						1130
17			2163						1177
18									1228
19									1296
20									1254
21									1338
22									1341

23									1379
24									1422
25									1473
26									1496
27									1525
28									1553
29									1628
30									1643
31									1666
32									1687
33									1728
34									1698

[a] Ref. [11]
[b] Ref. [12]
[c] Ref. [13]
[d] Ref. [14]
[e] Ref. [15]
[f] Ref. [16]
[g] Ref. [17]
[h] Ref. [18]

Table S3. Literature calculated enthalpies of formation of Al_n^-

	ΔH^o_{0K} (kJ mol^{-1})								
n	CCSD(T)/ CBS[a]	CCSD(T)/ def2-QZVPP //PBE0/ def2-TZVPP[b]	B3LYP/ 6-311G(d)[c,i]	BPW91/ LANL2DZ[d]	BP86/ SVP[e,i]	PBE/ 6-311G++ (2d,2p)[f]	Diffusion Monte Carlo[f]	CCSD(T)/ CBS[g]	BP86/ Defs-TZVP[h,i]
2	363	363	388		362	360	362	374	
3	422	427	492		425	440	437	437	
4	515	521	616	554	515	512	527	536	
5	585	609	724	663	590	589	611		541
6	570	606	796	750	615	570	594		530
7	553	633	864	827	639	599	637		537
8		760	1010	933	758	700	757		644
9		765	1090	1014	805	708	761		646
10		845	1206	1116	894	775	841		715
11			1297	1184	920	796	871		727
12			1388	1265	945	822	914		760
13			1378	1272	859	696	789		641
14			1569	1430	1008				776
15			1671	1527	1065				816
16									853
17									897

18									980
19									995
20									978
21									1020
22									1031
23									1046
24									1152
25									1150
26									1218
27									1205
28									1273
29									1308
30									1349
31									1355
32									1401
33									1400
34									1397

[a] Ref. [11]
[b] Ref. [12]
[c] Ref. [13]
[d] Ref. [14]
[e] Ref. [15]
[f] Ref. [16]
[g] Ref. [17]
[h] Ref. [18]
[i] ΔH^o_{0K} from Table 2 adjusted by the electron affinity from Ref. [5]

Table S4. Evaluated enthalpies of formation

	ΔH^o_{0K} (kJ mol^{-1})		$E_{cohesion}$ (kJ mol^{-1})	
n	Al_n	Al_n^-	Al_n	Al_n^-
2	525 ± 10	288		
3	624 ± 10	385		
4	756 ± 15	439 ± 12		
5	820 ± 30	543		
6	860 ± 50	603		
7	870 ± 50	606		
8	970 ± 50	636		
9	1040 ± 50	743		
10	1105 ± 50	765		
11	1170 ± 75	844		
12	1190 ± 75	893		
13	1180 ± 75	925		
14	1224 ± 100	831		
15	1306 ± 100	973		
16	1300 ± 100	1026		
17	1354 ± 100	1023		

18	1412 ± 100	1074		
19	1490 ± 100	1164		
20	1442 ± 100	1189		
21	1539 ± 100	1166		
22	1543 ± 100	1221		
23	1586 ± 100	1232		
24	1635 ± 100	1253		
25	1694 ± 100	1365		
26	1720 ± 100	1371		
27	1754 ± 100	1442		
28	1786 ± 100	1434		
29	1873 ± 100	1506		
30	1890 ± 100	1552		
31	1916 ± 100	1595		
32	1940 ± 100	1605		
33	1987 ± 100	1654		
34	1953 ± 100	1659		

[a] Uncertainties are equal to those for Al_n^- except where noted

Table S5. $Al_n^- + O_2$ reaction channel exothermicities

	$\Delta H^o_{0K,r}$ (kJ mol^{-1})									
n	$AlO^- + Al_{n-1}O$	$AlO + Al_{n-1}O + e^-$	$AlO_2^- + Al_{n-1}$	$Al^-_{n-2} + Al_2O$	$Al^-_{n-2} + Al_2O + e^-$	$Al^-_{n-4} + 2Al_2O$	$Al_{n-4} + 2Al_2O + e^-$	$Al^-_{n-5} + 2Al_2O + Al$	$Al^-_{n-6} + 2Al_2O + 2Al$	$Al^-_{n-6} + 2Al_2O + Al_2$
2	-502	-251	-549							
3	-768	-517	-408	-546	-503					
4	-667	-416	-413	-553	-412					
5	-612	-361	-341	-559	-373	-605	-563			
6	-470	-219	-280	-458	-244	-511	-371	-278		
7	-454	-204	-270	-428	-210	-487	-302	-211	16	-151
8	-472	-221	-367	-532	-277	-490	-277	-264	6	-161
9	-509	-258	-289	-524	-289	-452	-235	-182	38	-129
10	-473	-222	-299	-496	-268	-528	-274	-202	63	-104
11			-282	-523	-247	-548	-313	-247	74	-93
12			-249	-475	-214	-471	-245	-249	46	-121
13			-135	-333	-55	-356	-81	-47	169	2
14			-287	-443	-177	-419	-158	-168	134	-33
15			-296	-590	-240	-423	-146	-142	103	-64
16			-211	-444	-193	-388	-123	-90	186	19
17			-269	-443	-162	-533	-184	-109	183	16
18			-304	-536	-259	-481	-230	-293	125	-42
19			-272	-510	-230	-453	-173	-176	5	-162
20			-170	-397	-148	-434	-157	-100	171	4
21			-273	-426	-124	-437	-157	-158	169	2
22			-187	-461	-184	-358	-110	-118	155	-12

23			-204	-427	-107	-353	-52	-49	185	18
24			-274	-528	-217	-489	-213	-136	163	-4
25			-230	-514	-180	-441	-122	-165	182	15
26			-243	-472	-201	-500	-190	-182	88	-79
27			-208	-458	-134	-471	-138	-162	151	-16
28			-246	-459	-180	-431	-161	-213	90	-77
29			-261	-513	-192	-471	-149	-147	64	-103
30			-217	-484	-204	-443	-165	-184	134	-33
31			-210	-448	-126	-461	-141	-123	130	-37
32			-232	-454	-158	-438	-158	-180	152	-15
33			-214	-449	-137	-397	-76	-113	139	-28
34			-159	-393	-106	-347	-52	-60	218	51

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