Supplementary Information for:

Barrierless methane-to-methanol conversion: The unique mechanism of AlO^+

Brendan C. Sweeny,[a] David C. McDonald II,[a] Shaun G. Ard,[b] Albert A. Viggiano,[b] and Nicholas S. Shuman[b]

[a] *NRC postdoc at Air Force Research Laboratory, Space Vehicles Directorate, Kirtland Air Force Base, New Mexico 87117*

[b] *Air Force Research Laboratory, Space Vehicles Directorate, Kirtland Air Force Base, New Mexico 87117*

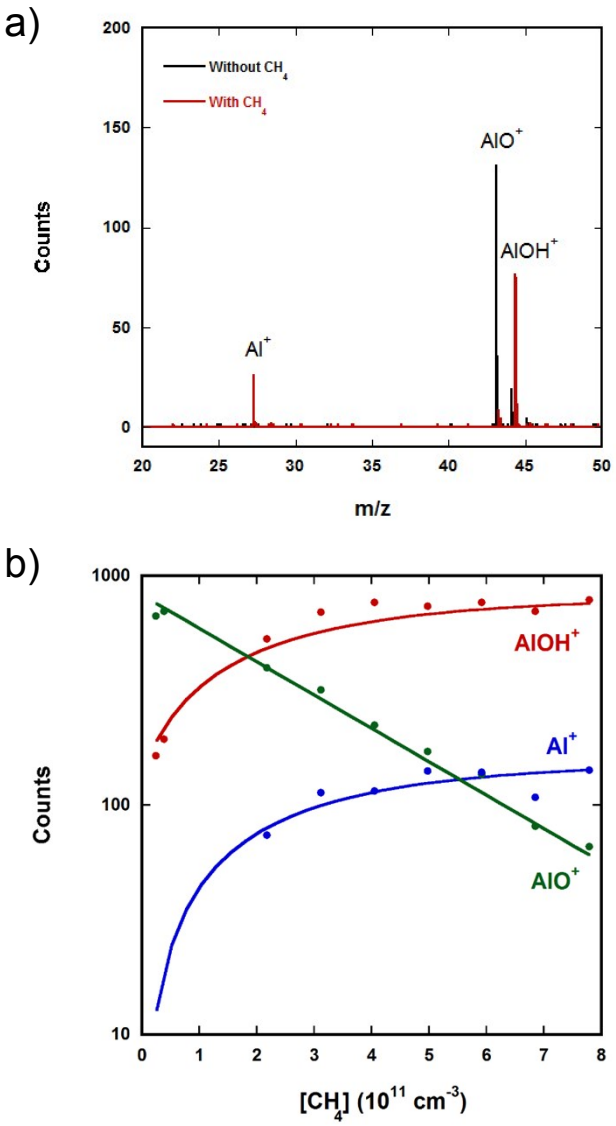

Figure S1. a) A typical mass spectrum before introducing CH_4 (black) and after (red, spectrum is shifted +0.5 m/z). The only two products observed are Al^+ and $AlOH^+$. Note: the black spectra is offset from the

red by ~0.5 m/z for clarity. b) Depletion of AlO^+ as a function of CH_4 concentration, with products $AlOH^+$ and Al^+ making up 86% ± 5% and 14% ± 5%, respectively.

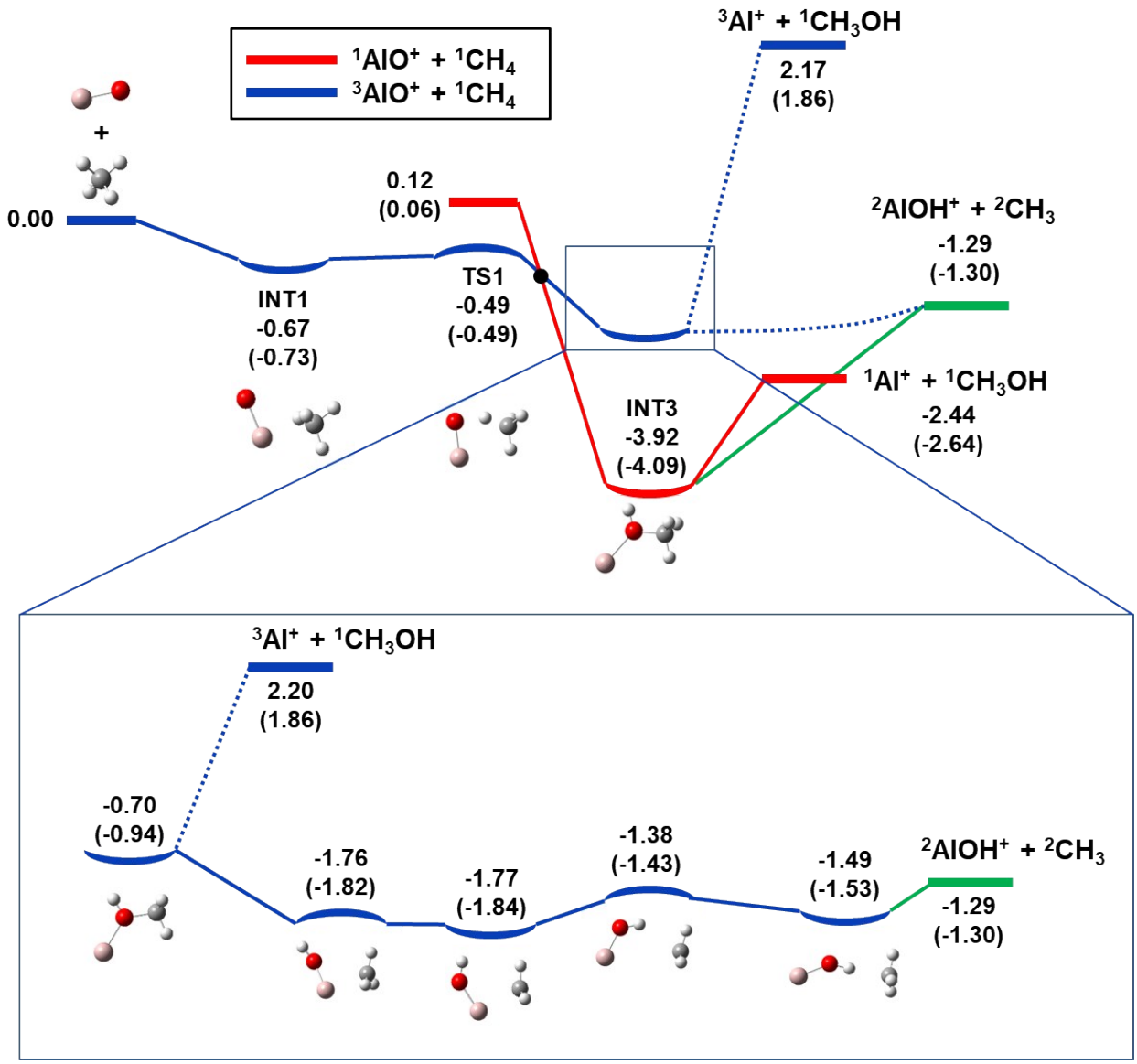

Figure S2. The reaction coordinate for $AlO^+ + CH_4$ calculated at B2PLYP/def2-TZVP describing more detail for the region near INT2* on the triplet surface. Singlet point energies calculated at CCSD(T)/aug-cc-pvtz are included in parentheses.

Ligand	RAl-O(H)CH_3^+ NBA (eV)	RAl^+-CH_3OH BDE (eV)	R$AlOH^+$-CH_3 BDE (eV)
-	0.97	1.75	2.63
AlO_2	1.57	3.04	1.98
F	1.67	2.59	1.39
NO	0.94	1.34	1.73
Al	0.50	1.06	-0.13
O	2.06	3.41	2.15
O_2	2.18	3.95	1.38
CH_3	1.42	1.83	0.48
NH_3	0.88	1.00	1.23
NH_2	1.54	2.10	0.79
H	1.29	2.13	0.75
Cl	1.42	2.31	1.06
Cl_2	1.79	2.76	4.44
F_2	2.34	3.40	5.16

Table S1. Natural bond analysis partial charge for Al atoms bound to the indicated ligands, R, and the resulting methanol bond dissociation energy (RAl^+-CH_3OH) and the competing CH_3 dissociation channel, R$AlOH^+$-CH_3. RAl^+-CH_3OH correlates linearly (Figure 6) to partial charge on the Al atom with $R^2 = 0.88$, while R$AlOH^+$-CH_3 correlates more weakly with an $R^2 = 0.24$. Stationary points were calculated using B2PLYP/def2tzvp.

Estimation of uncertainty in calculated BDE

We estimate the uncertainty in the B2PLYP/def2-TZVP calculated bond energies appearing in Table 1 by comparison to a modest available set of reliable experimental aluminum-containing species thermochemistry. Most of the available BDE are for neutral species, and we also compare to available ionization energies.

	0 K BDE (kJ mol^{-1})	
Species	Literature[1]	Calculated
Al_2-O	917 ± 20	920
AlO-Al	539 ± 19	541
Al-O_2	413 ± 32	368
AlO-O	399 ± 32	374
Al-Al	128 ± 7	118
Al-H	284 ± 4	288
Al-F	670 ± 4	666
Al-Cl	499 ± 4	494
Al^+-O	145 ± 12	125
	Ionization Energy (eV)	
Species	Literature[1]	Calculated

Al	5.98577	5.88
AlO	9.82 ± 0.06	9.85
AlCl	9.4 ± 0.3	9.12
AlF	9.73 ±0.09	9.55

Table S2. Comparison of literature experimental and B2PLYP/def2-TZVP calculated thermochemistry for Al-containing species

The root mean squared (RMSE) deviation of the BDE is 19 kJ mol^{-1} and of the ionization energies is 17 kJ mol^{-1}. RMSE is typically about one half the 2σ uncertainty. Considering average uncertainties in the experimental values of 15 kJ mol^{-1} for the BDE and 9 kJ mol^{-1} (assuming these reported uncertainties are intended to be 2σ) for the ionization energies are much smaller, most of the deviation is assumed to be in the calculation. We estimate then a 2σ uncertainty in the calculated values of ±35 kJ mol^{-1}, represented in Figure 7 of the main text (implicitly assuming an unbiased normal distribution in calculation error; we note that the signed average deviation is somewhat biased at +12 kJ mol^{-1}). While 35 kJ mol^{-1} may seem like a large uncertainty, we note that uncertainty in calculated values is much more commonly represented by RMSE (about 1σ) or mean average deviation (about ¾σ), so more typically this result would be reported as ~ ±15 kJ mol^{-1}, but we feel that the 2σ value is the more useful representation.

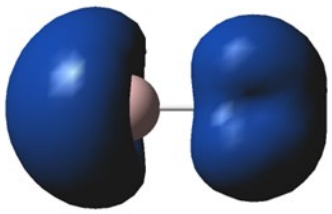

Figure S3. Spin density of $^3AlO^+$ (contour = 0.005 e/$Bohr^3$).

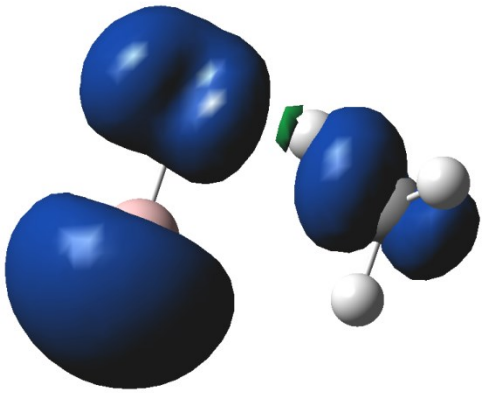

Figure S4. Spin density of ^{3}TS1 (contour = 0.005 e/Bohr^3).

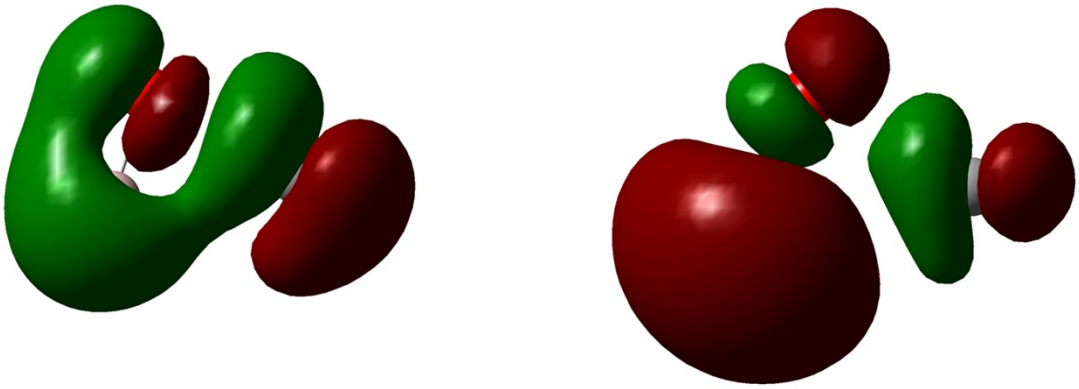

Figure S5. Spin natural orbitals for ^{3}TS1 calculated at the B2PLYP/def2-TZVP level.

Atom	^{3}INT1	^{3}TS1
Al	0.85065	0.81812
O	1.11178	0.94382
C	0.0056	0.28737
H	0.00189	-0.01207
H_t	0.0019	-0.0364
H	0.02603	-0.00042

Table S3. Natural bond orbital spin densities calculated for ^{3}INT1 and ^{3}TS1, where the spin densities are represented as the difference between alpha and beta total electron population calculated at the B2PLYP/def2-TZVP level. H atom being transferred is denoted as H_t.

Optimized geometries (B2PLYP/def2tzvp)
Electronic energy (Hartree)

B2PLYP/def2tzvp
CCSD(T)/aug-cc-pvtz//B2PLYP/def2tzvp
Vibrational frequencies (cm^{-1})
Rotational constants (GHz)
S^2 (for open shell species)

$^3AlO^+$
Al 0.0 0.0 0.660662
O   0.0 0.0 -1.073576
-317.1313948
-316.7327827
780
0.0;16.7;16.7
2.0001

$^1AlO^+$
Al 0.0 0.0 0.608334
O   0.0 0.0 -0.988542
-317.1277893
-316.731108
1082
0.0;19.7;19.7

$^1CH_4$
C 0.000000 0.000000 0.000000
H 0.627938 0.627938 0.627938
H -0.627938 -0.627938 0.627938
H -0.627938 0.627938 -0.627938
H 0.627938 -0.627938 -0.627938
-40.4826528
-40.4409171
1355;1355;1355;1574;1574;3054;3168;3168;3168
159.0;159.0;159.0

INT1
Al -0.448307 -0.682644 -0.000006
O -1.398512 0.764934 0.000009
C   1.683204 0.254314 -0.000006
H   1.148853 0.508458 0.931690
H   1.147503 0.510772 -0.930306
H   2.518039 0.962604 0.000200
H   2.102470 -0.752827 -0.001535
-357.6397655
-357.2014928
60;146;169;302;324;802;1199;1346;1383;1530;1540;2924;3016;3074;3138
19.2;5.9;4.7
2.0000

TS1
Al -1.350434 -0.512296 -0.000002
O -0.599080 0.953096 0.000001

C 2.406629 -0.226920 0.000007
H 2.431476 -0.771150 -0.931957
H 0.356811 1.119779 -0.000029
H 2.431725 -0.768662 0.933412
H 2.688499 0.816627 -0.001451
-357.6624497
-357.2237625
121*i*;23;107;205;227;390;525;778;947;1424;1424;3116;3287;3300;3720
18.7;3.5;3.0
2.0000

INT2*, Leftmost Intermediate
Al -1.414141 -0.153388 -0.000121
O 0.324171 0.464136 0.000174
C 1.611860 -0.292513 0.000031
H 2.150302 -0.022765 0.901717
H 0.484803 1.420652 0.000012
H 2.150468 -0.022085 -0.901351
H 1.333732 -1.339768 -0.000393
-357.6467659
-357.2151213
96;260;428;550;880;1111;1170;1356;1482;1496;1507;3106;3225;3228;3736
47.8;5.1;4.8
2.0000

INT2*, Leftmost Transition State
Al 0.356604 -0.726265 -0.016452
O 1.256743 0.646380 0.069861
C -1.785069 0.328690 -0.000723
H -1.762005 -0.070382 1.017110
H 1.783988 1.269957 -0.433864
H -2.116598 -0.300897 -0.823599
H -1.884763 1.399583 -0.100319
-357.6759979
-357.2380053
255*i*;73;133;188;219;286;382;924;954;1352;1433;3027;3182;3277;3899
18.2;6.1;4.7
2.0000

INT2*, Middle Intermediate
Al -0.359421 -0.726236 0.000009
O -1.316192 0.625099 -0.000007
C 1.772696 0.312378 0.000004
H 1.962582 -0.203137 -0.941414
H -1.208927 1.580453 0.000066
H 1.962772 -0.201629 0.942179
H 1.849401 1.390321 -0.000906
-357.6775229
-357.2394994
58;138;208;211;293;397;455;910;964;1362;1432;3039;3187;3269;3871
18.2;6.1;4.7

2.0000

INT2*, Rightmost Transition State
Al -1.350434 -0.512296 -0.000002
O -0.599080 0.953096 0.000001
C   2.406629 -0.226920 0.000007
H   2.431476 -0.771150 -0.931957
H   0.356811 1.119779 -0.000029
H   2.431725 -0.768662 0.933412
H   2.688499 0.816627 -0.001451
-357.6624497
-357.2237625
121*i*;23;107;205;227;390;525;778;947;1424;1424;3116;3287;3300;3720
18.7;3.5;3.0
2.0000

INT2*, Rightmost Intermediate
Al -1.817486 -0.101144 -0.000024
O -0.247002 0.242659 0.000065
C   2.727048 -0.081582 0.000003
H   2.807683 -0.876650 -0.726188
H   0.726907 0.119906 -0.000039
H   2.829146 -0.318510 1.048660
H   2.877309 0.938344 -0.322651
-357.6666161
-357.2276112
16;20;159;201;203;525;538;823;1042;1426;1426;3117;3295;3297;3412
104.9;2.5;2.5
2.0000

INT3
Al 1.487043 -0.147917 0.000004
O -0.395281 0.489237 -0.000024
C -1.637975 -0.316481 0.000010
H -2.197970 -0.084616 -0.899565
H -0.615381 1.435012 0.000078
H -2.197486 -0.085284 0.900057
H -1.330616 -1.357197 -0.000480
-357.7646109
-357.3303216
118;166;365;395;902;1095;1173;1363;1490;1500;1519;3101;3208;3215;3718
45.2;4.7;4.4

$^{2}AlOH^{+}$
Al 0.0 0.0 0.698915
O   0.0 0.0 -0.903122
H   0.0 0.0 -1.860919
-317.8477911
-317.4526914
110;110;1052;3921
0.0;17.1;17.1

0.7500

$^{2}CH_3$
C 0.000000 0.00000 0.00031
H 0.000000 1.07702 -0.00062
H -0.932727 -0.53851 -0.00062
H 0.932727 -0.53851 -0.00062
-39.8084171
-39.7636486
524;1427;1427;3142;3324;3324
288.2;288.2;144.1
0.7500

$^{3}Al^{+}$
Al 0.0 0.0 0.0
-241.8624233
-241.5475977
2.0000

$^{1}Al^{+}$
Al 0.0 0.0 0.0
-242.0320131
-241.7130017

$^{1}CH_3OH$
O 0.748077 0.122214 0.000005
C -0.665245 -0.019914 0.000004
H -1.026184 -0.542411 0.890416
H 1.140642 -0.755411 0.000023
H -1.025950 -0.544954 -0.888997
H -1.081660 0.984548 -0.001501
-115.6764481
-115.5623591
305;1054;1089;1182;1378;1496;1513;1527;3023;3075;3146;3834
128.6;24.8;23.9

References

1. P. J. Linstrom and W. G. Mallard, eds., *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg MD, 20899.