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ELECTRONIC SUPPLEMENTARY INFORMATION

A novel assessment of the role of the methyl radical and water formation channel in the $CH_3OH + H$ reaction

Flávio O. Sanches-Neto[a], Nayara D. Coutinho[b], Valter H. Carvalho-Silva.[a*]

[a.] *Grupo de Química Teórica e Estrutural de Anápolis, Campus de Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás, Caixa Postal 459, 75001-970, Anápolis, GO, Brazil.*

[b.] *Laboratório de Estrutura Eletrônica e Dinâmica Molecular (LEEDMOL), Instituto de Química, Universidade de Brasília, Caixa Postal 4478, 70904-970, Brasília, Brazil.*

**E-mail:fatioleg@gmail.com.*

Table S1. Geometries and imaginary frequencies of the transition states for R1, R2 and R3 channels at different levels of calculations. Distances are in Å; bond angles are in degrees.

Methods	TS1				TS2				TS3			
	C1-H2	H2-H3	C1-H2-H3	ω_i	O4-H4	H5-H3	OH-H5-H3	ω_i	C1-O4	O4-H3	C1-O4-H3	ω_i
M06HF/6-31G*	1.2419	1.0739	174.7197	1399.0	1.2733	0.8583	168.4204	2044.1	1.6876	1.2519	157.5179	1.614.5
M06HF/6-311++G**	1.2369	1.0756	173.3204	1407.7	1.2223	0.8818	168.8221	1984.0	...	...	...	...
M06HF/aug-cc-pVDZ	1.254	1.0553	173.7696	1144.8	1.2628	0.8665	166.1412	80452.5	...	...	...	...
M06/6-311++g**	1.2979	1.0024	178.7053	2064.2568	1.1967	0.9094	169.9688	1805.931	1.4757	1.1814	113.2512	1454.27
M06/6-311+g*	1.3088	0.9963	178.583	1880.931	1.18	0.9319	171.3791	2380.65	1.6286	1.2269	146.4673	1566.524
M06/6-311+g	1.299	1.0002	179.4563	1672.4708	1.1633	0.9516	169.2276	2123.072	1.5182	1.1844	123.477	1263.189
B2PLYP/6-311+G	1.3445	0.9486	178.9187	1533.6059	1.2016	0.9142	170.4614	1772.584	1.4909	1.1771	113.6076	1501.973
B2PLYP/6-311++G**	1.3164	0.9697	178.4115	1425.2411	1.2487	0.868	169.4177	1605.056	1.4909	1.1771	113.6076	1501.973
PBEH1PBE/6-311++G(3df, 3pd)	1.3123	0.9788	178.0255	1201.741	1.244	0.8777	169.6902	1398.63	...	...	...	...
PBEH1PBE/6-311+G	1.3494	0.9468	178.861	1238.664	1.1747	0.9383	170.3263	1509.796	1.53031	1.16132	123.9174	1074.7
MP2/6-311++G**	1.34403	0.92614	177.20788	1815.3744	1.26618	0.84098	167.54243	2217.6	1.4784	1.1784	112.3065	1633.549
QCISD/6-311G	1.35556	0.96581	179.543	1861.76	1.19626	0.94065	168.9216	2226	1.5394	1.1818	119.2211	1516.424

CCSD/6-311++G**	1.319	0.9649	176.8455	1657.7	1.2225	0.8821	168.7947	1987.3	1.4771	1.1742	112.3074	1641.196

Table S2 Energy parameters (kcal/mol) of the three channels obtained at different levels of theory. E_0 is the barrier height, ΔE is the classical energy of reaction and ΔH^0 is standard enthalpy change. Experimental and other theoretical data are also presented for comparison.

Methods	R1			R2			R3		
	E_0	ΔE	ΔH^0	E_0	ΔE	ΔH^0	E_0	ΔE	ΔH^0
M06HF/6-311++G**	9.6	-6.7	-9,4	16.7	3.7	1.5	...	...	...
M06HF/6-31G*	9.6	-3.6	-6,2	12	0.03	-2.2	27.5	-14.9	-16.7
M06HF/aug-cc-pVDZ	9.3	-4.0	-6,7	16.5	7.1	4.7	...	...	...
M06/6-311++G**	7.1	-4,9	-7,6	10	2.1	-4.0	21.3	-25.6	-25.8
M06/6-311+G*	8.0	-4.0	-6,5	10	-1.15	-7.3	24.4	-19.9	-20.3
M06/6-311+G	8.3	-3.8	-6,9	7.3	-3.1	-8.6	15.5	-24.4	-24.9
PBEH1PBE/6-311++G(3df, 3pd)	4,2	-5.5	-8.0	8.4	2.3	-0.9	...	...	...
PBEH1PBE/6-311++G**	4,2	-5.2	-7.7	-1.3	1.6	-1.6	...	...	...
PBEH1PBE/6-311+G	6,2	-3.2	-6.1	4.3	-3.5	-6.2	...	...	...
B2PLYP/ 6-311+G	8.6	-5.16	-7.9	7.1	-4,17	-6.5	...	...	...
B2PLYP/6-311++G**	6.7	-6.2	-8.6	10.8	1.77	-2.2	17.6	-27.7	-27.9
MP2/6-311++G**	13.7	-1.6	-3.9	23.3	11.0	8.4	22.5	-24.2	-24.3
QCISD/6-311G	13.3	-4.8	-7.3	12.2	-4.7	-7.3	14.0	-23.7	-24.0
CCSD/6-311++G**	9.8	-6.1	-8.5	14.1	-0.9	-1.9	21.5	-27.3	-28.5
CCSD(T, full)/cc-pVTZ	9.8	-6.1	-8,5	14.8	2.3	-0.7	...	...	...
WIBD	9.6	-6.0	-8.4	15.2	3.7	0.7	...	...	...
Experimental[C]			-8,9 $\pm$ 0.9			-0,3 $\pm$ 0.9			-27.1

[C]NIST Chemistry Web Book

Table S3. Fitting parameters for the d-TST total ($k_{Total} = k_{R1} + k_{R2} + k_{R3}$) rate constants computed at the B2PLYP/6-311++G(d,p) level (see Eq 5 in main manuscript). In parenthesis is the fitting parameter for the reserve reaction rate constant.

Parameters	Reaction			
	$k_{R1} + k_{R2} + k_{R3}$	k_{R1} (k_{-R1})	k_{R2} (k_{-R2})	k_{R3} (k_{-R3})
A_{Fit} ($cm^3\ s^{-1}$ $molecule^{-1}$)	2.31626E-09	1.05585E-09 (1.02990E-10)	7.52967E-10 (2.78222E-10)	1.92264E-10 (3.17795E-9)
d_{Fit}	-0.09751	-0.09027 (-0.0202)	-0.03781 (-0.03793)	-0.01099 (-0.00284)
E_{Fit} (kJ mol^{-1})	77.20885	65.54169 (87.28056)	72.49604 (82.05231)	93.20427 (220.23279)

Calculated atomic coordinates (in angstroms), frequencies (in cm^{-1}) and energies (a.u.) for all optimized structures of CH_3OH + H reaction at b2plyp/6-311++g(d,p) level

1. $CH_3OH + H \rightarrow CH_2OH + H_2$ (R1)

CH_3OH

12	0.66649200	-0.01993900	0.00001000
1	1.08110100	0.98690400	-0.00226200
1	1.02688100	-0.54225200	0.89274000
1	1.02637000	-0.54592800	-0.89072200
16	-0.74906900	0.12189200	0.00002700
1	-1.14075500	-0.75422500	-0.00003700

H

1	0.00000000	0.00000000	0.37055700

CH_2OH

12	-0.68521900	0.02785200	-0.06607000
1	-1.23143900	-0.88725800	0.10026500
1	-1.11646500	0.99084300	0.17726800
16	0.67067400	-0.12532300	0.02371900
1	1.09382300	0.73188600	-0.07086200

H_2

1	0.00000000	0.00000000	0.37055700
1	0.00000000	0.00000000	-0.37055700

TS1

12	-0.48444100	-0.32627300	0.03961200
1	-0.75113900	-0.97389600	-0.79125500
1	-0.70826100	-0.76127300	1.01667800
16	0.81857600	0.12188100	-0.11958400
1	1.08351500	0.60707600	0.66641300
1	-1.93474000	1.43347300	-0.11900700
1	-1.33133800	0.67721000	-0.05382900

<u>Frequencies:</u>

CH_3OH: 307.6;1057.5;1081.7;1182.4;1370.6;1496.9; 1510.0;1522.4;3023.4;3078.5;3149.9;3878.7

CH_2OH:430.5;600.8;1063.6;1204.6;1365.7;1499.3; 3153.6;3302.5;3874.4.

H_2: 4470.1

TS1: 306.2;366.8;558.7;1082.9;1108.1;1145.2;1289.5; 1297.1;1382.1;1483.2;1499.2;3066.3;3190.2;3865.2; 1425.2*i*

<u>Energies in atomic units (a.u.):</u>

CH3OH =-115.65008700; H= -0.4986643; CH2OH = -114.99153700; H2 = -1.16829500; TS1 = -116.13695900

2. $CH_3OH + H \rightarrow CH_3O + H_2$ (R2)

CH_3O

12 0.57758200 -0.00034500 0.01251200
1 0.86904400 0.01375800 -1.05403800
1 1.00240000 0.90205300 0.46983500
1 1.00321900 -0.91279100 0.44838500
16 -0.79252000 -0.00011900 0.00759400

TS2

12 0.73169300 0.15388300 -0.00000800
1 1.42317300 -0.69595200 0.00008100
1 0.92276100 0.74970800 -0.89789900
1 0.92284700 0.74982800 0.89780900
16 -0.54873200 -0.42835400 0.00000000
1 -1.40143700 0.48387900 0.00005500
1 -1.86764000 1.21606800 -0.00000200

Frequencies:

CH3O: 749.7;967.5;1115.8;1387.5;1392.5;1529.4;2943.8;
3022.1;3065.9

TS2:199.4;394.2;678.4;1001.4;1038.6;1176.0;1181.5;
1449.6;1454.9;1523.6;2065.4;3017.4;3092.7;3095.3;
1605.0*i*

Energies in atomic units (a.u.):

CH3O = -114.97878800; TS2 = -116.12969700

3. $CH_3OH + H \rightarrow CH_3 + H_2O$ (R3)

CH_3

12 0.00000000 0.00000000 0.00000000
1 0.00000000 1.07941200 0.00000000
1 0.93479900 -0.53970600 0.00000000
1 -0.93479900 -0.53970600 0.00000000

H_2O

16 0.00000000 0.00000000 0.1174330
1 0.00000000 0.75942600 -0.46973300
1 0.00000000 -0.75942600 -0.46973300

TS3

12 0.77875600 0.01195800 -0.02069600
1 1.06911000 0.93708800 0.46703600
1 1.05113800 0.01941100 -1.07324200
1 1.17900300 -0.85189200 0.49841600
16 -0.70529000 -0.03712400 0.11317600
1 -1.08246500 -0.80695200 -0.38485600
1 -1.24699800 0.92759300 -0.28858300

Frequencies:

CH3: 516.7;1425.9;1425.9;3131.6;3316.0;3316.0
H2O:1616.6;3851.3;3962.1.,
TS3:181.1;587.0;746.8;907.5;1086.0;1126.3;1281.5;
1417.3;1494.2;1500.7;3105.0;3205.9;3225.6;3241.3;
1501.9*i*

Energies in atomic units (a.u.):

CH3 = -39.80001700; H2O = -76.39297500;
TS3 = -116.12181400

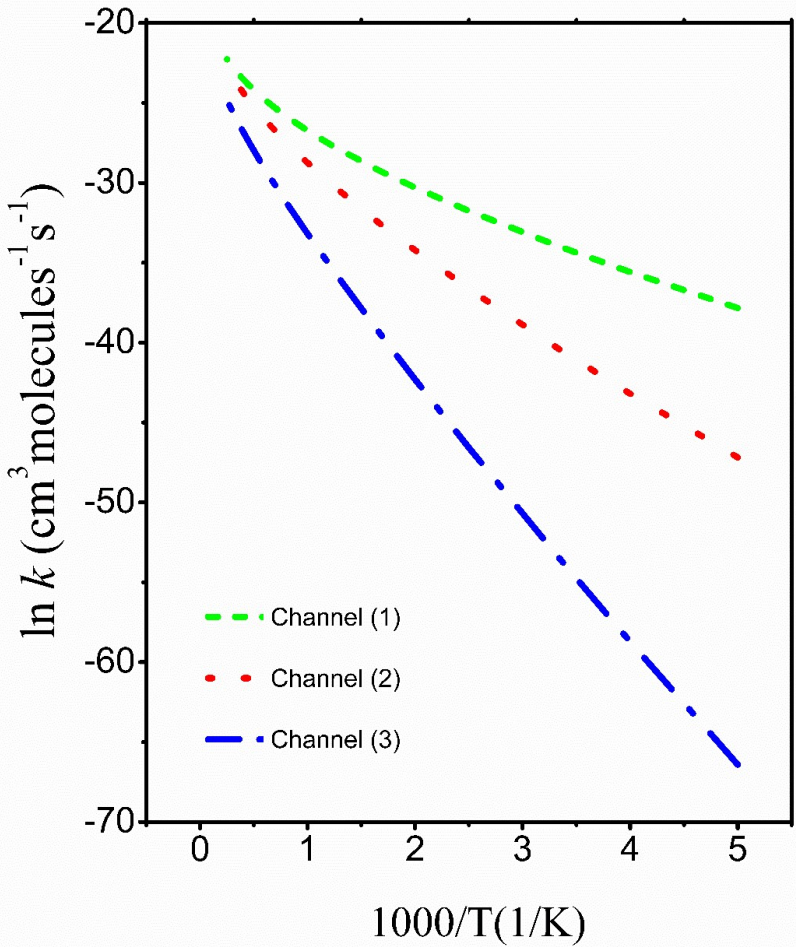

Figure S1. Arrhenius plot of the rate constants of the three channels calculated separately at B2PLYP/6-311++G(d,p) level.

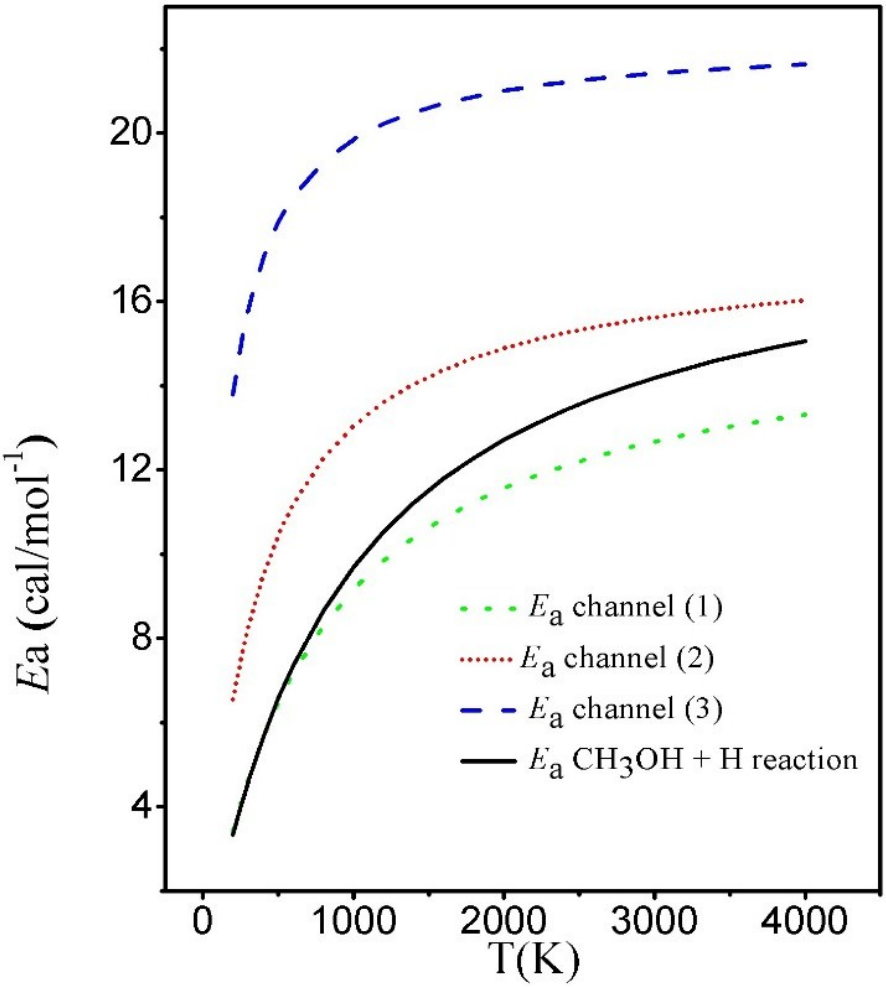

Figure S2. Temperature dependence of the activation energy (in kcal/mol) for three reaction channels (R1, R2 and R3) and for the total CH_3OH + H reaction (R1 + R2 + R3).