Supplementary Materials

Effect of Water and Formic acid on OH+CH_4 Reaction :An Ab Initio/DFT study

Mohamad Akbar Ali [1,*] and Balaganesh Muthiah [2]

[1] Department of Chemistry, College of Science, King Faisal University, Al-Ahsa 31982, Saudi Arabia

[2] Department of Chemistry, National Taiwan University, Taipei 10617, Taiwa

*corresponding author: aamohamad@kfu.edu.sa

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Table S1: Redundant internal coordinates of reactants, complexes, products and transition states obtained using M06-2X/6-311++G(3df,3pd) taken from gaussian checkpoint file.

(a) CH_4 + OH==> CH_3 + H_2O

CH_4
Charge = 0 Multiplicity = 1
C,0,-0.337477789,-0.523978723,0.
H,0,0.0246335578,-1.5482237771,-0.0000008724
H,0,0.0246528899,-0.0118632827,0.8870184359
H,0,0.0246514653,-0.0118622754,-0.8870184359
H,0,-1.4238490691,-0.5239655568,0.0000008724

OH
Charge = 0 Multiplicity = 2
O,0,0.810535131,0.88541678,0.
H,0,1.781409489,0.88541678,0.

RC_1
Charge = 0 Multiplicity = 2
C,0,-0.0716501175,-0.1373135994,0.1048992586
H,0,0.5407457641,0.5051417438,0.7329206314
H,0,-0.8958317822,-0.5345528544,0.6908068576
H,0,-0.4662033757,0.4395912865,-0.7279848883
H,0,0.5266768832,-0.9648556735,-0.2703759148
O,0,1.7404026462,1.7890540302,-1.2304861072
H,0,2.015270442,0.8697317268,-1.3785266373

TS
Charge = 0 Multiplicity = 2
H,0,-1.7166476928,0.973299368,-0.0306501525
C,0,-1.3130425097,-0.0333870269,-0.0009414347
H,0,-0.13537831,0.1170911133,-0.0089439299
H,0,-1.5690075288,-0.6060915651,-0.885357394
H,0,-1.5638478656,-0.5507791483,0.9183512088
O,0,1.2155332824,0.0844365949,-0.0114930261
H,0,1.3265036245,-0.8775163358,0.0181407284

Post-RC
Charge = 0 Multiplicity = 2
H,0,1.637983879,1.0522484011,-0.07432975
C,0,1.6175631533,-0.0230500733,-0.0167815204
H,0,-0.7258543326,0.0572501213,0.1326126645
H,0,1.7255455433,-0.5083935423,0.9386813072
H,0,1.6673342409,-0.6054328218,-0.9214328674
O,0,-1.6868024427,0.0724441391,0.1807524576
H,0,-1.9674607612,-0.7421292841,-0.2395091415

CH_3

Charge = 0 Multiplicity = 2
C,0,-0.0219175165,0.9324605817,0.0000494797
H,0,0.4855755461,1.1121142883,0.9320053078
H,0,0.4855264844,1.1120957527,-0.9320080402
H,0,-1.0366245116,0.5739610957,-0.0000467472

H_2O
Charge = 0 Multiplicity = 1
O,0,-1.4346366202,0.2446432413,0.01863449
H,0,-0.4767523973,0.2816161171,0.01863449
H,0,-1.7195327818,1.1599264517,0.01863449

Table S1: Redundant internal coordinates of complexes, post products and transition states obtained using M06-2X/6-311++G(3df,3pd) taken from gaussian checkpoint file.

(b) CH_4 + OH + (HCOOH) ==> CH_3 + H_2O+ HCOOH

HCOOH-1

Charge = 0 Multiplicity = 1
C,0,-1.4446753947,-0.4817068094,0.
H,0,-2.536423369,-0.5621299045,0.
O,0,-0.894144081,-1.6990326503,0.
O,0,-0.8343335076,0.5413536227,0.
H,0,0.0665675323,-1.5883758085,0.

HCOOH-2
Charge = 0 Multiplicity = 1
C,0,-1.4531097868,-0.4963886076,0.
H,0,-2.5475832312,-0.6147511195,0.
O,0,-0.7832273307,-1.6601967899,0.
O,0,-0.9039507257,0.5534327929,0.
H,0,-1.3967814657,-2.4005186959,0.

OH---HCOOH-1
Charge = 0 Multiplicity = 2
O,0,1.1617552669,0.1249418511,0.1787037385
O,0,-1.0479956695,1.8587363147,-0.2397184094
H,0,-0.2842454132,2.4282721811,0.0000694125
C,0,1.9493365655,1.146814571,0.4614422996
H,0,2.9640450272,0.8091518273,0.6909625909

O,0,1.6181154057,2.3025044491,0.4716861663
H,0,0.2644770473,0.4585028658,-0.0214127185

OH---HCOOH-2

Charge = 0 Multiplicity = 2
O,0,1.1793650718,0.1402906507,0.2319681998
H,0,1.6328904259,-0.7067053976,0.2818220975
O,0,-1.2026580441,2.071465149,-0.1872761081
H,0,-0.294510862,2.3498545083,0.0363771205
C,0,2.0105392977,1.1524667035,0.4845706492
H,0,3.0454611172,0.8555724817,0.7011546424
O,0,1.6430026535,2.2848451245,0.4722450086
H,0,-1.2838319403,0.4443714859,-0.031276744
H,0,-2.4812335201,0.1444157908,-1.0996767646
N,0,-2.0325573431,-0.2022275385,-0.2608616072
H,0,-2.7177333793,-0.1432299156,0.4822090913

PRC_{FA-1}

Charge = 0 Multiplicity = 2
C,0,2.1147924898,-1.1312752165,0.4789440791
H,0,2.7270803315,-1.8882838527,0.961722122
H,0,2.7427061954,-0.2871950165,0.2009626637
H,0,1.6577615592,-1.5530493249,-0.4128853895
H,0,1.3400944252,-0.8044798998,1.1695410737
O,0,1.1030125391,1.3740118221,-0.6079541022
H,0,0.6091034226,1.3273760776,0.2392420266
O,0,-0.9779950942,-0.4978359341,-1.0246431308
H,0,-0.1910949471,0.0707856312,-1.1501597086
C,0,-1.4551098672,-0.308374656,0.1916271501
H,0,-2.3380911391,-0.9290852546,0.3701345268
O,0,-0.9968139151,0.4410566242,1.0129806891

PRC_{FA-2}

Charge = 0 Multiplicity = 2
C,0,1.4432056513,1.3285733255,-2.1169538233
H,0,1.8015557103,0.970394673,-3.0788348483
H,0,1.7970993403,2.3420693603,-1.9475290958
H,0,0.3555962478,1.3273588186,-2.106873334
H,0,1.8166962131,0.6847926926,-1.3241876471
O,0,0.3377925416,2.8135403039,0.1768491282
H,0,0.2152985749,1.8669645346,0.3845680009
O,0,-1.6477060071,-0.0570493604,-0.8436483771
C,0,-0.8131607436,-0.6630622137,0.0013552966
H,0,-0.905409454,-1.756969149,0.0323531471
O,0,-0.033668851,-0.0551935616,0.6651703252
H,0,-2.2019363746,-0.6966403891,-1.3015763753

$TS1_{FA1}$

Charge = 0 Multiplicity = 2
C,0,1.1450680881,-0.9042889436,0.230780792
H,0,2.19846656,-0.8843384777,0.4897565299
H,0,0.9271573863,0.131872409,-0.2809039191
H,0,0.9115123993,-1.6571825177,-0.514993685
H,0,0.5015419507,-0.9722610705,1.1012285774
O,0,0.318131222,1.3053997405,-0.7117885421
H,0,-0.2018961708,1.4427923729,0.1040203976
O,0,-1.9146830953,-0.1845079577,-1.2918319398
H,0,-1.0816892709,0.340699979,-1.3164033068
C,0,-2.431395113,-0.0962539163,-0.0808806972
H,0,-3.361437723,-0.6685712218,-0.0052463296
O,0,-1.9614386035,0.5229630739,0.8364194728

$TS2_{FA2}$

Charge = 0 Multiplicity = 2
C,0,-2.2673651778,-0.8421338,0.3213972464
H,0,-2.1689927717,-1.1645571381,-0.7094140695
H,0,-1.6117332227,0.1567411201,0.4372560001
H,0,-3.2825635633,-0.5526501999,0.5713820701
H,0,-1.8456981531,-1.5561737374,1.0200500362
O,0,-0.7875840084,1.178802288,0.3124007284
H,0,-0.3704959584,0.8795941755,-0.5140134565
O,0,0.7431744921,-1.8646223252,-0.685920601
C,0,0.9453835554,-1.2084100793,-1.8311137825
H,0,1.6134490743,-1.7204303923,-2.5375777592
O,0,0.4357530076,-0.1578206151,-2.0577966873
H,0,1.2422897259,-2.6869342962,-0.6691137254

Post-PRC_{FA-1}

Charge = 0 Multiplicity = 2

C,0,1.9909191959,-1.3504694931,0.6228580972

H,0,3.066688296,-1.2878578936,0.6218877983

H,0,1.9200551224,1.042398512,-0.4877079479

H,0,1.4867324193,-1.8498364341,-0.1879379896

H,0,1.4371572908,-1.0733161377,1.5041568965

O,0,1.0705629504,1.4789183555,-0.5997531355

H,0,0.6437965273,1.4118723763,0.2679213942

O,0,-0.8839341734,-0.3155281657,-1.1091752917

H,0,-0.1275434117,0.3194500538,-1.1492495821

C,0,-1.3546274097,-0.3293253974,0.1215039047

H,0,-2.1968069344,-1.0225329234,0.2170392763

O,0,-0.9314138729,0.3219461473,1.0407305797

Post-PRC$_{FA-2}$

C,0,-1.8283023568,1.2425333841,0.7330823144

H,0,-1.1102043415,1.9415524338,0.3357167023

H,0,-1.367204111,-0.2688808918,-1.0705284701

H,0,-1.5898961092,0.7018587863,1.6344209642

H,0,-2.8504580413,1.2755611491,0.3911734181

O,0,-0.6400295025,-0.5422341898,-1.641324359

H,0,-0.8594120825,-1.4136226333,-1.9757742741

O,0,1.4015132171,0.7575019949,-0.3265141504

C,0,1.2982770885,0.1744997767,0.8651848172

H,0,0.6841430639,-0.7404695851,0.8508754212

O,0,1.8141518817,0.5972720372,1.8512487829

H,0,0.8440952937,0.276564738,-0.9622361666

Table S1: Redundant internal coordinates of complexes, post products and transition states obtained using M06-2X/6-311++G(3df,3pd) taken from gaussian checkpoint file.

(c) $CH_4 + OH + (H_2O) ==> CH_3 + 2H_2O$

HO---H_2O

Charge = 0 Multiplicity = 2

Charge = 0 Multiplicity = 2

O,0,-0.0867222707,0.0638158913,-0.0625109564

H,0,-0.0855411999,0.0669486052,0.8968432747

H,0,0.8353560523,0.0855566692,-0.3264631354

O,0,-1.9094150871,1.8252379147,-1.4087937283

H,0,-1.3084124014,1.1943728933,-0.9653882769

PRCw-1

C,0,2.2484316441,-0.5220585519,-0.0061850482

H,0,2.3765059964,0.1421786807,-0.8595746331

H,0,3.0500875493,-1.2547356163,-0.0155222189

H,0,2.3043343056,0.0444851729,0.9216746985

H,0,1.2902947498,-1.0327039644,-0.0713708845

O,0,-0.3517449646,1.3712543188,0.2122806271

H,0,-0.5935975177,2.1189631172,-0.3377601546

H,0,0.5848807633,1.218133304,0.0581279986

O,0,-1.391270053,-1.250911728,-0.1447115122

H,0,-1.1581754732,-0.3145827331,0.0211291273

PRCw-2

Charge = 0 Multiplicity = 2

C,0,-3.419129772,-0.3546597595,0.2043304016

H,0,-2.9836336668,-0.8714642927,1.0577786461

H,0,-3.4338723369,0.7205211588,0.3768062118

H,0,-2.8532881171,-0.5778363263,-0.6988276717

H,0,-4.4411485696,-0.6954218709,0.0653718696

O,0,-0.319480255,0.5269187315,0.8620309038

H,0,-1.2326529918,0.3724367267,0.5577154238

O,0,-1.1859344226,-1.6279235966,2.5732806783

H,0,-0.5606980052,-0.9794652143,2.2319710341

H,0,-0.7229185732,-2.1053990166,3.2627997824

TSaw

Charge = 0 Multiplicity = 2

C,0,-0.108437038,-0.6352602796,0.1441548721

H,0,-0.4480360387,-1.6652162887,0.1012610916

H,0,0.1866284946,-0.4558715031,1.2587385702

H,0,0.7984797798,-0.4638136722,-0.4255432309

H,0,-0.8974679715,0.065160511,-0.1081583062

O,0,0.6161947303,0.0667958023,2.5053101237

H,0,0.1255417568,0.9018860923,2.4525817142

O,0,2.8966677846,0.5194812835,0.76354131

H,0,2.2919343007,0.353937333,1.4978917452

H,0,3.7773214514,0.4654885314,1.13637446

Post-PRCw

C,0,1.6297069173,-1.2888643458,0.0001583833

H,0,2.1695310693,-1.2693935131,-0.9327342875

H,0,0.9111338027,0.9054884768,-0.1010501211

H,0,0.5704110967,-1.4943233815,0.0060334282

H,0,2.1835685237,-1.2936843687,0.9247829629

O,0,0.232727829,1.5924198271,-0.0877854395

H,0,0.3691264427,2.0665195875,0.735208413

O,0,-1.6529328714,-0.5381404259,0.0990028102

H,0,-1.1974710941,0.3077159661,-0.0137310518

H,0,-2.4932627159,-0.4450028226,-0.3510140978

Table S2 (a): Rotational (GHZ) -vibrational (cm^{-1}) parameters obtained from vibrational analysis.

Rot-GHZ	**OH**	**H2O**	**OH--H2O**	**HCOOH-1**	**HCOOH-2**	**OH--HCOOH-1**	**OH--HCOOH-2**
	3767.4	1633.0	121.1	650.2	516.6	168.1	44.8
		3888.9	149.0	676.1	678.4	187.4	55.0
		3992.1	198.0	1071.6	1050.9	207.6	163.7
			400.8	1165.6	1143.8	439.1	406.2
			620.8	1323.3	1295.5	641.4	486.8
			1619.2	1409.0	1436.9	701.8	517.8
			3659.5	1874.2	1927.2	767.0	690.2
			3880.7	3119.5	3058.9	1081.0	1057.9
			3980.9	3808.9	3896.5	1230.8	1157.4
						1384.8	1291.2
						1432.9	1438.7
						1831.9	1900.5
						3128.4	3072.6
						3561.0	3689.6
						3621.5	3887.0
K-rotor		833.2896	357.7404	78.21913	88.12876	12.04534	11.98386
2D1-rotor		434.6283	6.90608	12.23954	11.83197	5.14977	4.34726
2D2-rotor		285.6425	6.81752	10.43146	1.91211	3.60746	3.19004
2D-rotor	565.5135	352.3469	6.861657	11.10967	2.089529	3.96012204	2.709395569

Table S2 (b): Rotational (GHZ) -vibrational (cm^{-1}) parameters obtained from vibrational analysis.

PRCFA1	**PRCFA2**	**TS1FA-1**	**TS2FA-2**	**Post-PRCFA1**	**PostPRCFA2**	**RC**	**TSw**	**Post-PRCw**
47.2	34.6	***-827.2***	***-1204.5***	45.3	45.4	67.7	***-732.1***	99.3
64.7	54.3	42.0	25.8	66.7	75.6	88.9	69.1	100.3
96.7	55.9	61.7	49.7	123.5	98.8	105.6	102.1	146.9
116.8	78.6	80.2	52.1	141.5	134.5	116.3	159.9	166.3
146.6	95.4	177.6	74.3	174.9	172.6	141.1	175.7	196.4
175.5	125.2	204.9	97.1	191.5	181.4	155.0	213.2	220.1
198.1	159.4	210.6	157.0	218.0	205.8	185.3	284.2	244.8
206.6	166.3	327.6	307.8	227.5	213.8	208.2	319.7	268.9
212.6	175.6	339.5	360.1	258.0	231.1	212.5	399.9	281.2
509.6	475.0	590.1	467.0	291.7	287.9	399.3	570.2	325.8
627.1	479.8	709.6	532.9	405.6	329.6	461.0	822.4	495.9
703.6	516.7	887.9	686.5	563.4	385.0	1338.6	1074.8	623.9
836.6	688.9	914.0	783.9	633.4	660.6	1351.2	1252.3	663.9
1083.2	1061.7	1056.5	974.1	721.2	694.9	1355.1	1340.6	1410.3
1235.0	1163.1	1098.3	1063.9	962.7	840.8	1572.6	1458.8	1432.6
1337.0	1296.7	1243.7	1158.9	1086.5	1075.1	1577.5	1472.9	1623.0

1345.3	1335.4	1248.2	1198.3	1255.7	1197.1	1623.6	1523.0	1635.1
1349.6	1343.1	1336.0	1278.2	1406.9	1381.5	3023.7	1638.8	3116.2
1388.5	1354.3	1402.7	1296.9	1411.3	1413.8	3133.3	3075.2	3289.0
1434.5	1434.4	1439.0	1388.0	1425.3	1432.3	3143.4	3189.1	3304.5
1563.6	1564.4	1454.1	1437.8	1466.5	1440.5	3152.1	3207.2	3752.2
1572.1	1568.7	1474.7	1464.7	1639.9	1607.4	3732.7	3790.3	3802.3
1829.5	1896.4	1509.8	1479.8	1827.1	1905.0	3843.1	3807.6	3953.1
3036.7	3051.1	1832.5	1904.8	3115.7	3023.8	3981.1	3970.6	3970.6
3144.7	3052.1	3080.5	3071.7	3132.2	3128.6			
3149.3	3162.2	3120.4	3076.3	3304.6	3299.3			
3150.7	3164.4	3200.7	3189.2	3321.9	3316.7			
3155.5	3169.0	3207.4	3202.3	3342.0	3648.8			
3546.4	3678.1	3421.4	3740.0	3765.3	3830.3			
3610.9	3879.9	3681.0	3880.5	3911.0	3972.2			
4.62653	4.36956	5.3932	5.24621	4.11026	4.43162	6.9791	9.07504	6.9791
2.53881	2.28341	2.47946	2.30117	2.79933	2.35947	4.48154	5.00699	4.48154
10.58346	2.2828	2.36872	1.85952	2.31368	1.70761	2.77714	3.33884	2.77714
11.38141828	2.407404301	2.3256739	2.147232	2.29849517	2.1863586	3.52787	4.088709	3.5278696

Table S3: Electronic Energies (E_o), Zero-point correction (ZPE), Thermal Correction (E_T), Thermal Correction to Enthalpy (H_T),Free energy correction (G), Entropy (cal/mol-K) of all the species involved in the reactions. All Energies are in Hartree/Particle.

Species	Eo	ZPE	Et	Ht	G	S
OH	-75.6398532	0.008583	0.010943	0.011887	-0.008336	42.564
CH4	-40.4381924	0.044959	0.047827	0.048771	0.027653	44.447
TS	-116.0682119	0.051652	0.056138	0.057082	0.026207	64.982
H_2O	-76.337435	0.021649	0.024485	0.025429	0.004017	45.065
OH--H_2O	-151.9868574	0.033329	0.038526	0.039471	0.007279	67.754
HCOOH-1	-189.5061299	0.034397	0.037552	0.038496	0.010339	59.262
HCOOH-2	-189.4994147	0.034183	0.037419	0.038363	0.010119	59.446
OH--HCOOH-1	-265.1539342	0.046440	0.051684	0.052628	0.017865	73.165
OH--HCOOH-2	-265.147875	0.045242	0.051299	0.052243	0.014376	79.698
PRC_{FA1}	-305.6004388	0.093118	0.102579	0.103523	0.057780	96.274
PRC_{FA2}	-305.5887088	0.091766	0.102079	0.103023	0.054113	102.940
$TS1_{FA-1}$	-305.5910306	0.089651	0.097879	0.098823	0.055645	90.875
$TS2_{FA-2}$	-305.5755387	0.087480	0.096590	0.097535	0.050954	98.037
Post-PRC_{FA1}	-305.6244939	0.092121	0.101926	0.102870	0.057066	96.404
PostPRC_{FA2}	-305.6150261	0.091651	0.101850	0.102795	0.055977	98.537
PRCw-1	-192.4249461	0.079665	0.089049	0.089993	0.045903	92.797
PRCw-2	-192.42767	0.080489	0.089492	0.090436	0.047255	90.882
TSw	-192.4150057	0.077269	0.084859	0.085803	0.046160	83.437
Post-PRCw	-192.4496651	0.080015	0.088987	0.089931	0.047852	88.564
CH_3	-39.7612982	0.029672	0.032784	0.033728	0.009860	50.235
Post-RC	-116.101624	0.054062	0.060613	0.061558	0.026044	74.744

Table S4: Calculated unimolecular rate constant (k_2 in s^{-1})

T (K)	$k_{2(w)}$ ($\rightarrow PRC_w$) $\rightarrow TSw$	$k_{2(FA-1)}$ (PRC_{FA-1}) $\rightarrow TS2_{FA-1}$	$k_{2(FA-2)}$ (PRC_{FA-2}) $\rightarrow TS2_{FA-2}$
200	8.03×10^{5}	5.58×10^{8}	5.66×10^{6}
225	2.55×10^{6}	1.09×10^{9}	2.60×10^{7}
250	5.33×10^{6}	1.91×10^{9}	8.72×10^{7}
275	1.22×10^{7}	3.10×10^{9}	2.34×10^{8}
300	2.45×10^{7}	4.68×10^{9}	5.32×10^{8}
325	4.45×10^{7}	6.69×10^{9}	1.06×10^{9}
350	7.47×10^{7}	9.13×10^{9}	1.92×10^{9}
375	1.17×10^{8}	1.20×10^{10}	3.22×10^{9}
400	1.74×10^{8}	1.53×10^{10}	5.04×10^{9}

Table S5: Calculated equilibrium constants (K_{eq} in cm^3 $molecule^{-1}$) for the formation of two-body complexes.

T(K)	$K_{eq(3)}$ (OH+ H_2O $\rightarrow$RC2w)	$K_{eq(1)}$ (OH+ FA-1 $\rightarrow RC_{4FA1}$)	$K_{eq(2)}$ OH+ FA-2 $\rightarrow RC_{4FA2}$)
200	1.38×10^{-19}	7.00×10^{-22}	9.06×10^{-21}
225	4.23×10^{-20}	3.12×10^{-22}	$3.03\times10^{-}$
250	1.66×10^{-20}	1.67×10^{-22}	1.28×10^{-21}
275	7.80×10^{-21}	1.01×10^{-22}	6.41×10^{-22}
300	4.19×10^{-21} *5.7×10^{-21}*	6.74×10^{-23}	3.64×10^{-22}
325	2.50×10^{-21}	4.85×10^{-23}	2.28×10^{-22}
350	1.62×10^{-21}	3.69×10^{-23}	1.54×10^{-22}
375	1.12×10^{-21}	2.95×10^{-23}	1.11×10^{-22}
400	8.19×10^{-22}	2.44×10^{-23}	8.40×10^{-23}

Table S6: Calculated equilibrium constants (K_{eq} in cm^3 $molecule^{-1}$) for the formation of three-body complex

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T (K)	$K_{eq(A)}$ (CH_4 + RC_{2w} $\rightarrow PRC_w$)	$K_{eq(E)}$ (CH_4 + RC_{4FA1} $\rightarrow PRC_{FA1}$)	$K_{eq(F)}$ CH_4 + RC_{4FA2} $\rightarrow PRC_{FA2}$)
200	3.75×10^{-20}	1.82×10^{-18}	3.16×10^{-20}
225	1.18×10^{-20}	2.61×10^{-19}	1.00×10^{-20}
250	4.82×10^{-21}	5.64×10^{-20}	4.13×10^{-21}
275	2.37×10^{-21}	1.64×10^{-20}	2.04×10^{-21}
300	1.34×10^{-21}	5.93×10^{-21}	1.16×10^{-21}
325	8.37×10^{-22}	2.54×10^{-21}	7.33×10^{-22}
350	5.69×10^{-22}	1.24×10^{-21}	5.01×10^{-22}
375	4.13×10^{-22}	6.77×10^{-22}	3.66×10^{-22}
400	3.16×10^{-22}	4.01×10^{-22}	2.81×10^{-22}

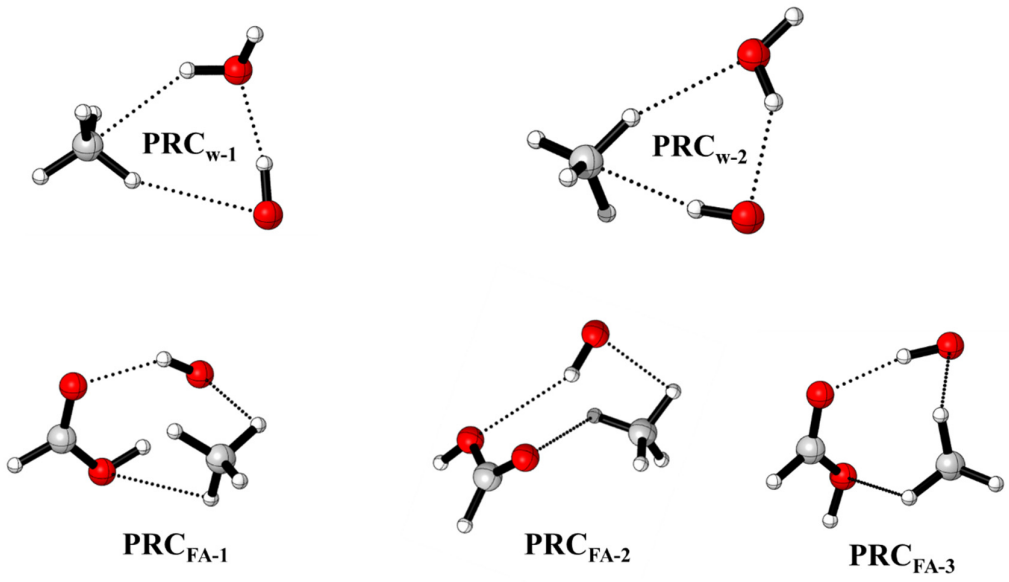

Figure S1. Three body complexes for the effect of FA/H_2O on OH+CH_4 reaction.

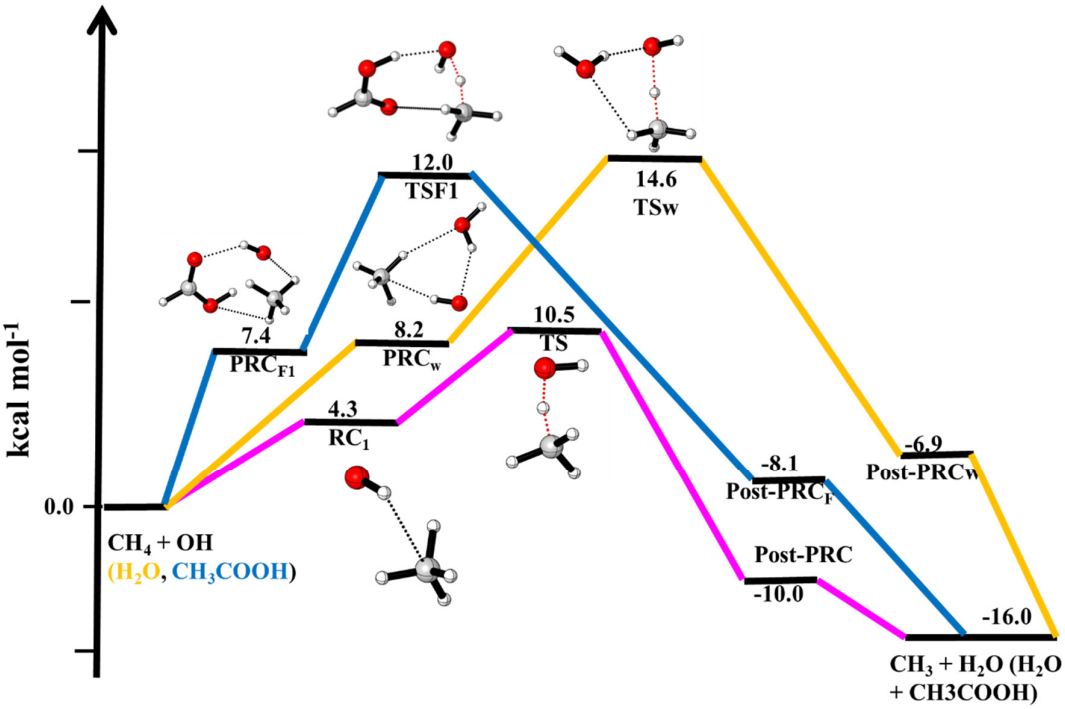

Figure S2. Free energy profiles for the CH_4+OH (____), CH_4+OH+H_2O (____) and CH_4+OH +HCOOH (____) reactions.