Catalyzed-like water enhanced mechanism of CO_2 conversion to methanol

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Supplementary Information

Contents

Structural parameters of the intermediate molecules:

1. CO_2 (A):

	X	Y	Z
C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16013100
O	0.00000000	0.00000000	-1.16013100

2. H_2CO_3 (B):

	X	Y	Z
C	-0.05280300	-0.12604600	-0.00002600
O	-0.55986000	1.11803400	0.00001000
H	-1.52521300	1.05324300	0.00003100
O	1.28171900	-0.11025200	0.00000200
H	1.60801800	0.80047800	0.00000600
O	-0.69441900	-1.14248500	0.00000900

3. $HC(OH)_3$ (C) :

	X	Y	Z
C	0.01038900	-0.02504300	0.36269000
O	-1.00380000	-0.89500000	-0.05895900
H	-1.05408800	-0.86038400	-1.02412500
O	-0.19454200	1.27221800	-0.13448200
H	-1.10954200	1.52155100	0.04148900
O	1.28391600	-0.41635700	-0.03127400
H	-0.01259000	-0.06325700	1.45224700
H	1.41534000	-0.13670800	-0.94737400

4. HCOOH (D) :

	X	Y	Z
O	1.11221800	-0.09511900	0.00023900
H	1.06064500	-1.06506800	-0.00006100
C	-0.13001900	0.39935100	0.00036400
H	-0.09632600	1.49343900	0.00047400
O	-1.13803800	-0.25638300	-0.00006300

5. $HCOOH_2^+$ (E) :

	X	Y	Z
C	0.00637800	0.42488000	-0.00032400
H	0.05569200	1.50851700	-0.00063800
O	-1.14631900	-0.09495600	-0.00000800
O	1.04514700	-0.30292800	-0.00028800
H	-1.13704200	-1.07384500	0.00024600
H	1.87582800	0.20726200	-0.00054800

6. H_2COH^+-H_2O (F) :

	X	Y	Z
C	-0.22390200	0.57546300	-0.03339900
H	-0.13576300	1.18216300	0.86046700
O	1.17501500	-0.26280000	0.07905200
O	-1.20267800	-0.31567800	-0.07784700
H	1.30341200	-0.83509200	-0.69859700
H	-1.45315400	-0.61614600	0.80728800
H	-0.11465700	1.10346500	-0.97167500
H	1.95705300	0.31222100	0.16385200

7. H_2COH^+ (G) :

	X	Y	Z
C	-0.62388100	0.03263700	0.00000800
H	-1.06544100	1.02492500	0.00000900
O	0.61023800	-0.12819900	0.00001000
H	1.13418300	0.70100300	0.00000900
H	-1.22262000	-0.87156900	0.00001600

8. $H_3COH_2^+$ (H) :

	X	Y	Z
C	0.78519100	-0.00000100	0.01955200
H	1.10000300	-0.89701600	-0.49655600
H	1.10000200	0.89700400	-0.49657400
H	1.04979600	0.00001000	1.06960000
O	-0.71335100	-0.00000200	-0.08962100
H	-1.12540900	0.79240500	0.30043500

H	-1.12540900	-0.79240200	0.30044900

9. H_3COH (I) :

	X	Y	Z
O	0.74953200	0.11629200	-0.00003500
H	1.13342600	-0.76536900	0.00009900
C	-0.66910800	-0.01925500	0.00000600
H	-1.03231500	-0.54274000	0.88875100
H	-1.08572000	0.98639300	-0.00026200
H	-1.03232200	-0.54321500	-0.88845500

10. HCO_2^+ (J) :

	X	Y	Z
C	-0.10291900	0.01495600	0.00085000
O	1.10282000	-0.11316100	0.00017500
O	-1.22708800	0.01841300	0.00013200
H	1.68082000	0.68937500	-0.00189600

11. $H_3CO_3^+$ (K) :

	X	Y	Z
C	0.20879400	0.14488800	0.00059600
O	0.50515200	1.27487900	0.00178000
O	0.79647500	-1.00348000	0.00679700
H	1.76460300	-0.90306600	0.02616500
O	-1.25643300	-0.19658800	-0.06322000
H	-1.84024600	0.53509300	0.21803100
H	-1.52961400	-1.06392500	0.29779200

12. $C(OH)_3^+$ (L):

	X	Y	Z
C	0.00006600	-0.00045000	0.00001500
O	-1.08052100	-0.68633000	0.00013600
H	-0.92265400	-1.64754400	0.00016900
O	-0.05436200	1.27838200	-0.00005800
H	-0.96650100	1.62061600	0.00000800
O	1.13497800	-0.59226300	-0.00007000

H	1.88701800	0.02749000	-0.00015700

13. H_2CO_3-H (B*) :

	X	Y	Z
C	0.00047600	-0.00053700	0.18243400
O	-1.06754700	-0.76164600	-0.22196000
H	-0.97678800	-1.64249600	0.16129600
O	-0.12526500	1.30593000	-0.21862200
H	-0.93826000	1.66335500	0.15866100
O	1.19448500	-0.54357500	-0.22118700
H	1.91092300	-0.02112900	0.15942000

14. $HCOOH^+$-H_2O (L_1*) :

	X	Y	Z
C	-0.26960600	-0.04862800	0.33401400
O	1.43848200	0.18557500	-0.47770900
H	2.07993800	0.43926900	0.20540900
O	-0.85473600	1.09060700	0.38131800
H	-0.40866000	1.73151900	0.96084900
O	-0.79400800	-1.02370200	-0.29785300
H	-1.62682700	-0.79761400	-0.76024800
H	1.71591500	-0.68882400	-0.79575000

15. $HOCOH^+$ (L_2*) :

	X	Y	Z
C	-0.35698300	-0.01966000	0.32169100
O	-0.85416200	1.12426500	0.42292400
H	-0.34104200	1.74930700	0.97610500
O	-0.77788800	-1.00365000	-0.30264200
H	-1.62376200	-0.89808000	-0.79999800

16. $H_2CO_2^+$ (J*) :

	X	Y	Z
O	1.08810700	-0.11597000	0.00024800
H	1.10125400	-1.09641600	-0.00002100
C	-0.06836700	0.40337700	0.00025600

H	-0.15752800	1.50024700	0.00053800
O	-1.15498600	-0.21501800	-0.00006900

17. $HCOH^{+}$-H_2O (E*) :

	X	Y	Z
C	-0.18689500	0.54156200	-0.15753800
H	-0.10526700	1.49373900	0.34879300
O	-1.17548400	-0.23735300	0.18501300
O	1.13839600	-0.19993200	-0.14073400
H	-1.23569600	-1.04226500	-0.35594900
H	1.80105200	0.21552700	-0.72378900
H	1.52526300	-0.34444600	0.74815300

18. H_2COH^{+}-H (G_1*) :

	X	Y	Z
C	-0.63039300	0.06981400	-0.00000200
H	-0.96525700	1.09785500	-0.00006300
O	0.70866100	-0.12500000	-0.00002400
H	1.22355800	0.71271600	-0.00005400
H	-1.04982900	-0.57042700	-0.82165700
H	-1.04976500	-0.57028700	0.82180400

19. $H3COH^{+}$ (G_2*) :

	X	Y	Z
C	-0.79598700	-0.00000100	-0.07248800
H	-1.21932200	-0.96386800	0.14475400
O	0.63233600	0.00000100	0.07781300
H	1.08535900	-0.80486800	-0.23979400
H	-1.21932500	0.96386500	0.14475100
H	1.08535600	0.80487300	-0.23978800

20. H_2:

	X	Y	Z
H	0.00000000	0.00000000	0.37168100
H	0.00000000	0.00000000	-0.37168100

21. H_2O:

	X	Y	Z
O	0.00000000	0.00000000	0.11324700
H	0.00000000	0.75857700	-0.47938100
H	0.00000000	-0.75857700	-0.47938100

22. H_3O^+:

	X	Y	Z
O	-0.00003500	-0.00020800	-0.07490100
H	-0.91790200	-0.12900500	0.23570700
H	0.34639300	0.85927200	0.23574700
H	0.57154800	-0.72985300	0.23570600

Structural parameters of transition states:

1. TS_{AB}:

	X	Y	Z
C	0.30723500	0.08059100	-0.00448700
O	-0.22591500	1.22670600	0.01620500
H	-1.26212500	0.47860200	0.02940700
O	-1.06434900	-0.72176100	-0.09611300
H	-1.21233300	-1.29550100	0.67181100
O	1.35764100	-0.45657000	0.00201500

2. TS_{BB*}:

	X	Y	Z
C	0.02794300	-0.00571900	-0.13815100
O	1.14303600	0.72512200	0.02061100
H	1.91172400	0.14182700	-0.04537900
O	-1.09351600	0.70408600	0.00251200
H	-0.88590200	1.64675900	0.07348000
O	0.00214800	-1.25327400	-0.11685400
H	-0.06626000	-1.81511100	1.07373700

3. TS_{CD}

	X	Y	Z
C	-0.25494100	0.12742600	0.42247000
O	0.15118900	1.22947200	-0.16032300
H	1.11845300	0.51594900	-0.40654300
O	1.26838200	-0.65279400	-0.00592400
H	1.11317800	-1.31011600	-0.69882800
O	-1.30233200	-0.53439100	-0.08464200
H	-0.20701100	0.00170300	1.50167300
H	-1.43995400	-0.22764000	-0.99493300

4. TS_{LL^*}:

	X	Y	Z
C	-0.08895700	-0.00956600	0.15539300
O	1.24982100	0.05556200	0.07263000
H	1.67752400	-0.73916900	0.45121900
O	-0.76588700	1.07771000	-0.05271400
H	-0.27876300	1.87985400	0.19941800
O	-0.63911000	-1.16755500	-0.05353600
H	-1.60765500	-1.10533200	-0.11891600
H	1.87814500	0.16073100	-1.10626500

5. TS_{JJ^*}:

	X	Y	Z
C	-0.09979000	0.03647000	-0.00000800
O	-1.21848900	-0.14507400	0.00000000
O	1.12574700	0.01538100	-0.00001700
H	-0.10652700	1.99887600	-0.00000300
H	1.55665200	-0.87580900	-0.00002100
C	-0.09979000	0.03647000	-0.00000800

6. TS_{EE^*}:

	X	Y	Z
C	-0.10698500	0.49279100	0.00166600
H	-0.11616000	1.52428400	0.32287000
O	-1.20859400	-0.16668100	0.02272900

O	1.02717600	-0.17407000	-0.13207200
H	-1.12486600	-1.08850600	-0.28345500
H	1.78909300	0.42065900	-0.28546700
H	1.53613700	-0.98050900	0.89277000

7. TS_{GG1*}:

	X	Y	Z
C	-0.72859500	0.03367400	0.03468100
H	-1.24532700	-0.79650300	0.49746400
O	0.53921100	-0.02223600	-0.16361400
H	0.92257900	-0.90743500	0.01731700
H	-1.20018500	0.97145400	-0.22036700
H	1.58368900	0.76269900	0.73496800

1. TS_{G1*G2*}:

	X	Y	Z
C	0.73592000	0.03088600	-0.00701200
H	1.13301700	1.03293200	0.01674400
O	-0.69354700	-0.10607500	0.09327700
H	-1.14034300	0.76561700	0.02532900
H	1.24445600	-0.86731500	0.30537400
H	-0.13848600	-0.29069400	-0.97322900

2. TS_{KL}

	X	Y	Z
C	0.12015900	0.09102200	-0.00280000
O	-0.37811700	1.21262000	0.01432500
H	-1.44859200	0.34894900	0.05134000
O	-0.95954700	-0.77659100	-0.07404200
H	-1.00215100	-1.55464900	0.52025500
O	1.29539500	-0.38370500	-0.00211400
H	1.98053400	0.30918700	0.05268700

Structural parameters of molecular complexes involved in the barrierless reactions:

1. M_{AJ}:

	X	Y	Z
C	1.19757400	0.08290800	-0.00237500
O	0.12587500	0.54447300	-0.02726300
O	2.26300600	-0.35211200	0.02104600
H	-1.46014500	0.08110700	-0.00336000
O	-2.43940200	-0.12357000	0.00271700
H	-2.69382400	-0.58117200	0.82587800
H	-2.68534100	-0.66703000	-0.76915100

2. M_{BK}:

	X	Y	Z
C	0.00649100	-0.18148100	-1.44789500
O	-0.34760700	1.08804400	-1.29545700
H	-0.36572900	1.51917700	-2.16303700
O	0.04171800	-0.80028800	-0.23231600
H	0.28514600	-2.27186500	-0.07670700
O	0.27137300	-0.76696700	-2.45313000
O	0.45614500	-3.28847700	-0.00723200
H	-0.21033900	-0.21601300	0.49882500
H	1.22722300	-3.48099800	0.55466800
H	-0.32374800	-3.75586300	0.34042300

3. M_{BL}:

	X	Y	Z
C	-0.76534300	-0.01715500	0.00007900
O	-0.53037800	1.25529100	0.00100400
H	-1.34988900	1.77823100	0.00107000
O	0.17399800	-0.84780000	-0.00011900
H	1.18415800	-0.43991700	0.00025500
O	-2.00453900	-0.39552400	-0.00065600
H	-2.07936100	-1.36488700	-0.00143900

O	2.45904600	0.04145200	0.00018700
H	2.96985600	-0.22663400	0.77541000
H	2.96894600	-0.22880700	-0.77489700

4. M_{DE}:

	X	Y	Z
O	-2.12203000	0.11435000	-0.00010400
H	-2.31907600	-0.84139500	0.00020300
C	-0.85927000	0.34624700	-0.00013700
H	-0.59258400	1.39974500	-0.00043700
O	-0.01416600	-0.56720700	0.00020000
O	2.30845600	0.16576400	0.00019900
H	2.80352700	-0.12703400	-0.77685400
H	1.04620000	-0.24079800	0.00021900
H	2.80354900	-0.12712700	0.77720300

5. M_{HI}:

	X	Y	Z
C	-1.52425400	-0.45922500	0.02155500
H	-2.49158100	-0.01253200	-0.17402000
H	-1.26734100	-1.17713500	-0.74773300
H	-1.47808900	-0.90208400	1.01098400
O	-0.52465700	0.61633400	-0.08539900
H	0.50848100	0.27590600	-0.01989300
H	-0.68895000	1.32541700	0.55491800
O	1.81374000	-0.09067200	0.01842300
H	2.02986900	-0.71129600	0.72676400
H	2.13387400	-0.48358000	-0.80436300