Supplementary Materials

Theoretical Study on Gas Phase Reaction of CH_2O+NH_3: Formation of $CH_2O\cdots NH_3$, NH_2CH_2OH, or $CH_2NH + H_2O$

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$CH_2O+NH_3 \rightarrow$PRODUCTS

$OHCH_2NH_2+OH \rightarrow$PRODUCTS

$CH_2O + NH_3 \rightarrow$ Products

Table S1: Optimized geometries of reactants, complexes, products and transition states obtained using M06-2X/6-311++G(3df,3pd).

CH_2O

C	0.00000000	-0.52447100	0.00000000
H	-0.93797900	-1.10444600	0.00000000
H	0.93797800	-1.10444800	0.00000000
O	0.00000000	0.66946500	0.00000000

NH_3

N	0.00000000	0.00000000	0.11344200
H	0.00000000	0.93915700	-0.26469800
H	-0.81333400	-0.46957900	-0.26469800
H	0.81333400	-0.46957900	-0.26469800

CH_2O--NH_3

C	0.00000000	1.10058500	0.00000000
H	0.58057500	1.15742200	0.93373000
H	0.58057500	1.15742200	-0.93373000
N	0.86970200	-1.57900100	0.00000000
H	1.21429200	-2.07357000	-0.81381200
H	1.21429200	-2.07357000	0.81381200
O	-1.19226400	0.99458000	0.00000000
H	-0.13953600	-1.67484600	0.00000000

NH_2CH_2OH-1

C	0.04291000	0.53866700	0.01615000
H	0.03012400	1.19291300	-0.85997400
H	0.08716800	1.16186200	0.91177900
N	-1.12467700	-0.31425600	-0.06016000

H	-1.34225400	-0.72495800	0.83867400
H	-1.93757000	0.18982900	-0.38714400
O	1.20850400	-0.24093200	0.05448200
H	1.10978500	-0.92440300	-0.61497200

NH_2CH_2OH-2

C	-0.03408900	0.53637700	0.04810600
H	-0.07386700	1.07583700	0.99620800
H	-0.07886200	1.25906300	-0.76295800
N	1.22008500	-0.15859300	-0.01980500
H	1.35295500	-0.78152900	0.76613300
H	1.28647300	-0.70238700	-0.87072100
O	-1.19277200	-0.26399400	-0.11507500
H	-1.28058700	-0.84714400	0.64193400

CH_2NH--H_2O

C	-1.25287800	-0.56100700	0.02006900
H	-2.29015400	-0.89421300	-0.02315300
H	-0.47861700	-1.32268900	0.07987300
N	-0.90210100	0.65073100	0.00389800
H	-1.69982300	1.28064600	-0.05584700
H	1.05442400	0.43647600	-0.03364900
O	1.84392400	-0.12431000	-0.07451100
H	2.49475100	0.30519200	0.48116300

CH_2NH

C	0.05628700	0.58142600	0.00000000
H	-0.84429800	1.19842500	0.00000000
H	1.00853600	1.10768700	0.00000000
N	0.05628700	-0.67872600	0.00000000

H	-0.89596400	-1.04359100	0.00000000

H_2O

H	0.00000000	0.76099200	-0.46653800
O	0.00000000	0.00000000	0.11663500
H	0.00000000	-0.76099200	-0.46653800

TS1

C	0.00000000	0.66943500	0.00000000
H	0.27911700	1.24168300	0.89795900
H	0.27911700	1.24168300	-0.89795900
N	0.89042000	-0.62874600	0.00000000
H	1.44033500	-0.79699100	-0.83597100
H	1.44033500	-0.79699100	0.83597100
O	-1.18311200	0.06227600	0.00000000
H	-0.20694900	-1.00297100	0.00000000

TS2

C	-0.03598900	0.54626600	0.04282600
H	-0.14847100	1.12461600	0.96255600
H	-0.01039800	1.24136800	-0.79573100
N	1.19209500	-0.24374900	0.11077200
H	0.95820500	-1.20847200	-0.08967400
H	1.85018300	0.04433400	-0.60086700
O	-1.16909100	-0.26590200	-0.15009100
H	-1.42553000	-0.64598700	0.69208700

TS3

C	0.33637300	0.67471600	0.02082100
H	0.29127600	1.23488300	0.95406000
H	0.16603700	1.27530300	-0.86564000
N	1.07737800	-0.44447500	-0.12130200
H	1.40511100	-0.77001800	0.78306100
H	-0.21668600	-0.86183800	-0.24843300
O	-1.20368200	-0.18360000	-0.08593900
H	-1.57616600	-0.34649600	0.78864700

Table S2: Vibrational frequencies of reactants, complexes, products and transition states obtained using M06-2X/6-311++G(3df,3pd).

CH2O	**NH3**	**CH2O--NH3**	**AM-1**	**AM-2**	**CH2NH--H2O**	**CH2NH**	**H_2O**	**TS1**	**TS2**	**TS3**
1219.95	1049.9	45.79	265.52	281.53	118.71	1076.99	1619.24	**1384*i***	**320*i***	**1900.7*i***
1277.9	1661.9	91.0	352.5	396.2	165.9	1122.4	3889.6	267.3	342.8	433.4
1540.6	1661.9	157.4	539.1	488.8	208.1	1169.7	3990.6	706.8	504.3	471.0
1884.1	3513.4	185.1	820.9	814.7	209.9	1370.4		789.4	845.7	666.2
2959.7	3637.3	298.1	974.0	915.0	371.3	1501.1		814.0	985.0	723.1
3030.2	3637.3	299.7	1031.3	1054.9	618.4	1745.0		1030.9	1079.1	764.4
		1077.7	1143.5	1120.6	1081.5	3068.8		1198.5	1118.5	1028.4
		1202.8	1227.9	1172.8	1132.4	3153.0		1215.2	1197.4	1082.9
		1273.5	1308.3	1372.2	1158.3	3471.7		1271.9	1295.9	1254.9
		1539.1	1391.1	1391.0	1378.3			1377.3	1396.4	1286.0
		1658.7	1465.5	1433.1	1503.0			1482.9	1449.8	1377.4
		1663.8	1543.1	1517.5	1642.3			1543.6	1545.9	1475.0
		1865.7	1643.9	1658.8	1749.6			1566.0	1646.3	1552.4
		2988.6	3049.6	3062.1	3076.3			2226.0	3047.6	1835.0
		3059.3	3089.3	3133.0	3177.9			2970.4	3097.1	3091.9
		3503.4	3546.7	3542.3	3496.4			2992.1	3547.4	3188.1
		3625.5	3637.1	3627.5	3719.1			3493.8	3625.3	3540.7
		3632.1	3880.6	3909.5	3971.1			3605.5	3915.7	3858.3

Table S3: Electronic energies + ZPE (E_e + ZPE) of reactants, complexes, products and transition states obtained using CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd).

Species	ZPE	CCSDT	CCSDT+ZPE
CH_2O	0.027139	-114.335966	-114.308827
NH_3	0.034541	-56.476677	-56.4421364
CH_2O--NH_3	0.06417	-170.817930	-170.75376
TS1	0.065045	-170.766318	-170.701273
AM-1	0.070418	-170.834942	-170.764524
TS2	0.069803	-170.828417	-170.758614
AM-2	0.070376	-170.836058	-170.765682
TS3	0.062943	-170.739401	-170.676458
CH_2NH---H_2O	0.065563	-170.822989	-170.757426
CH_2NH	0.040276	-94.474849	-94.4345734
H_2O	0.021641	-76.337436	-76.3157951

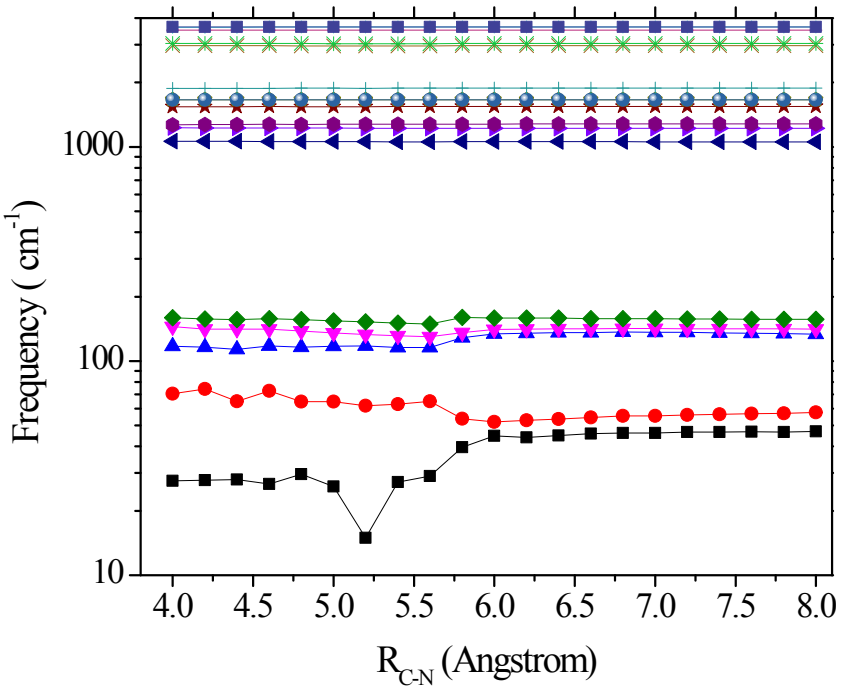

Figure S1(a). Harmonic vibrational frequencies, as a function of C−N distances.

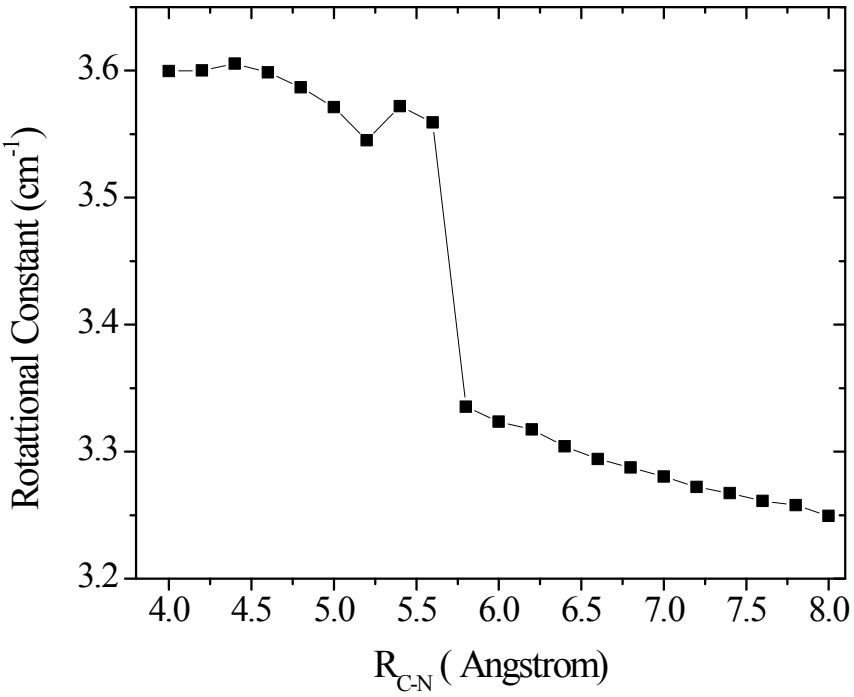

Figure S2 (a). 1D rotational constants as a function of C−N distances.

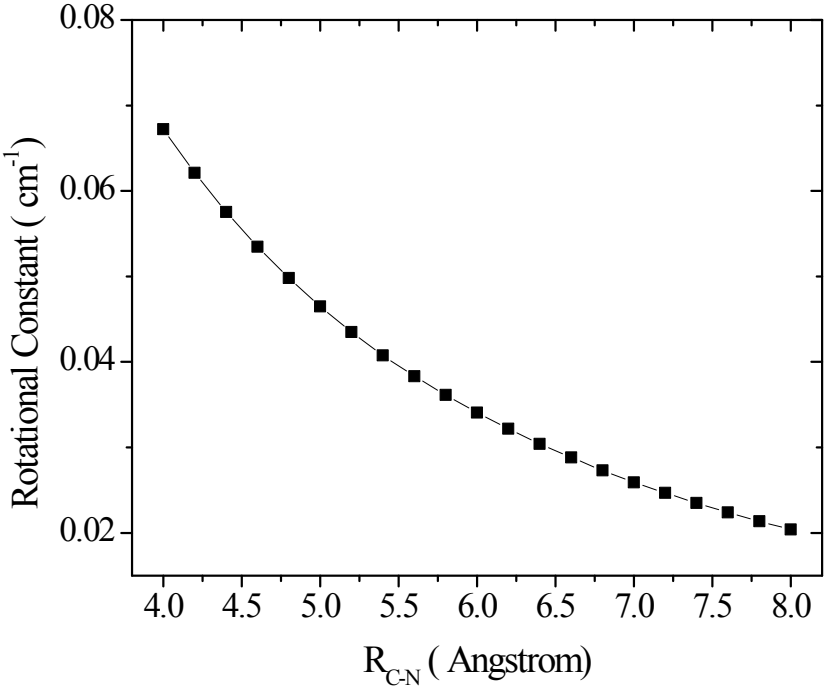

Figure S3 (a). 2D rotational constants as a function of C−N distances

Location of Transition State for Barrierless Reactions using CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd) level.

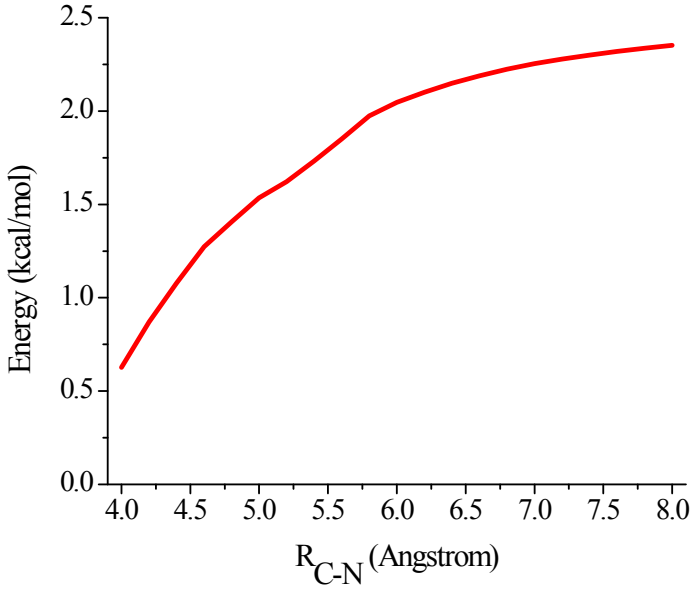

Figure S4(a). ZPE corrected potential energy surface relative to energies of the pre-reactive complex as functions of R_{N-C} distances along the reaction pathway.

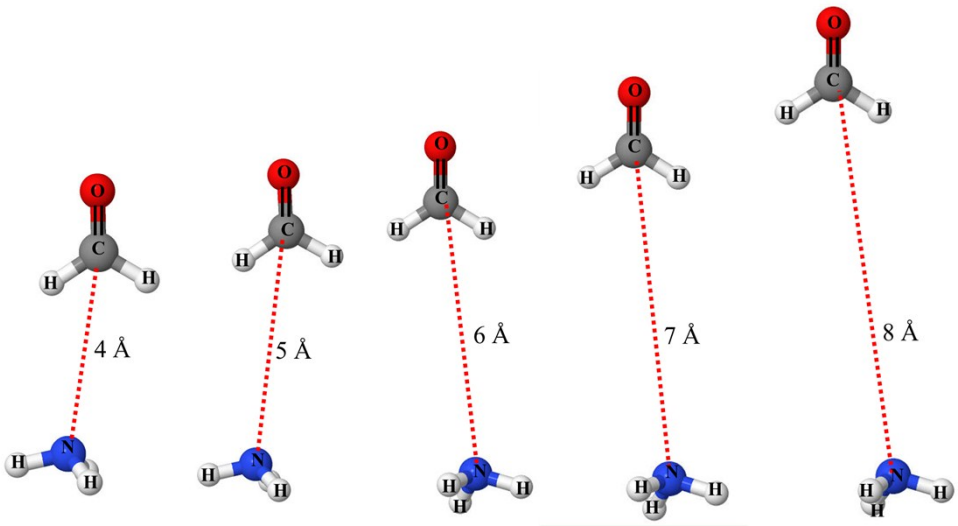

Figure S5. Optimized geometries at several R_{N-C} distances along the reaction pathway.

The CVTST "trial" rate constants computed using the potential energy, harmonic frequencies, and rotational constants along the reaction path are shown in **Figure S6** for different temperature 100K, 200K, 300K and 400K. Two minima in the "trial" rate constants are clearly present on each curve. Crudely speaking, each minimum is associated with staggered and eclipsed form of the $CH_2O\cdots NH_3$ complex. Thus, a two-transition-state (2-TS) model is needed to describe this single entrance channel. In previous works, Greenwald et al.[70], Senosiain et al.[71] and Ali and Barker[23, 54] have also shown multiple transition states for

similar atmospheric and combustion reaction systems and they used 2-TS model for the effective rate constants calculations. In this work, we used Miller [56] 2-TS model to compute the effective microcanonical (k_{eff}^{micro}) rate constants as given in Eq. 6:

$$k_{eff}^{micro} = \left[\frac{1}{k_1(E,J)} + \frac{1}{k_2(E,J)} \right]^{-1}$$

where $k_1(E,J)$ and $k_2(E,J)$ are microcanonical rate constants for transition states 1 and 2.

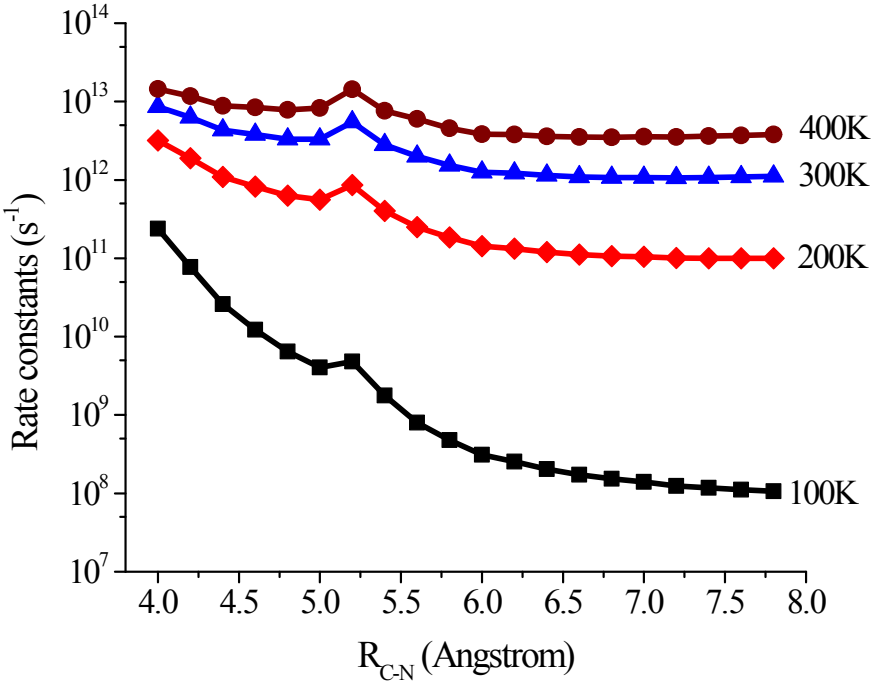

Figure S6 (a): Trial CVTST rate constants for dissociation of $CH_2O\cdots NH_3$ complex as functions of $R_{C\text{-}N}$ bond distances.

Location of Transition State for Barrierless Reactions using CCSD(T)/6-311++G(3df,3pd)// ωB97XD/6-311++G(3df,3pd) level.

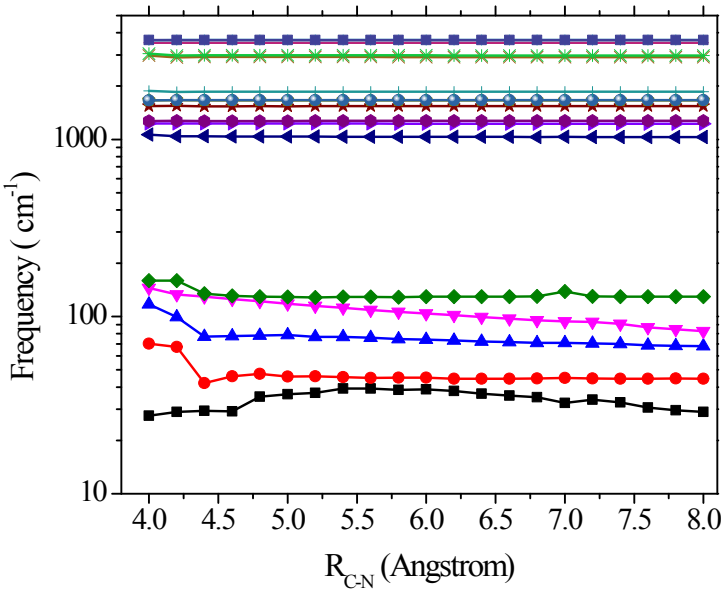

Figure S1(b). Harmonic vibrational frequencies, as a function of C−N distances

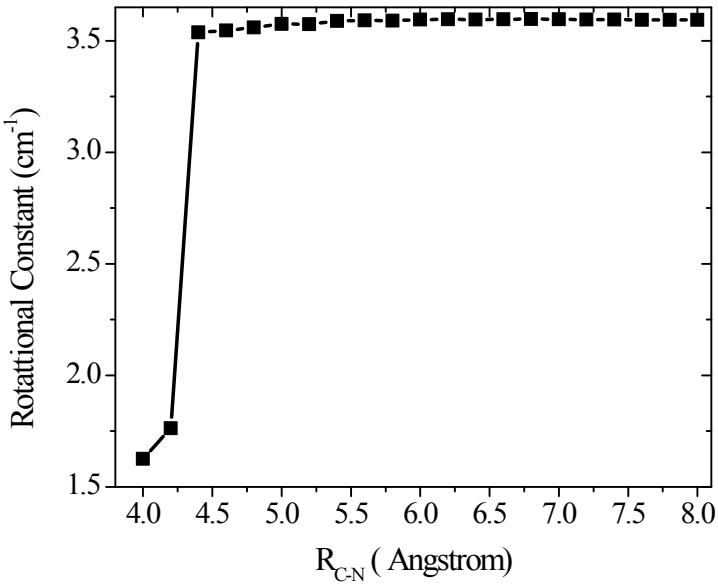

Figure S2 (b). 1D rotational constants as a function of C−N distances.

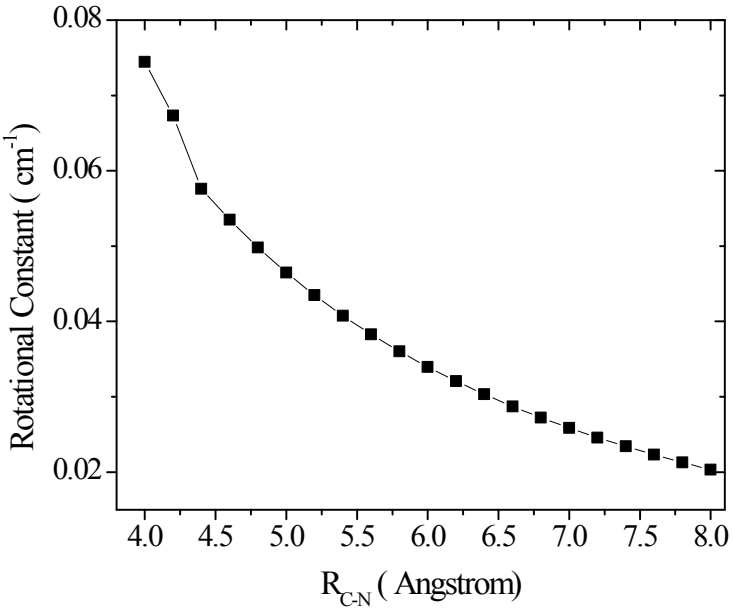

Figure S3(b). 2D rotational constants as a function of C−N distances

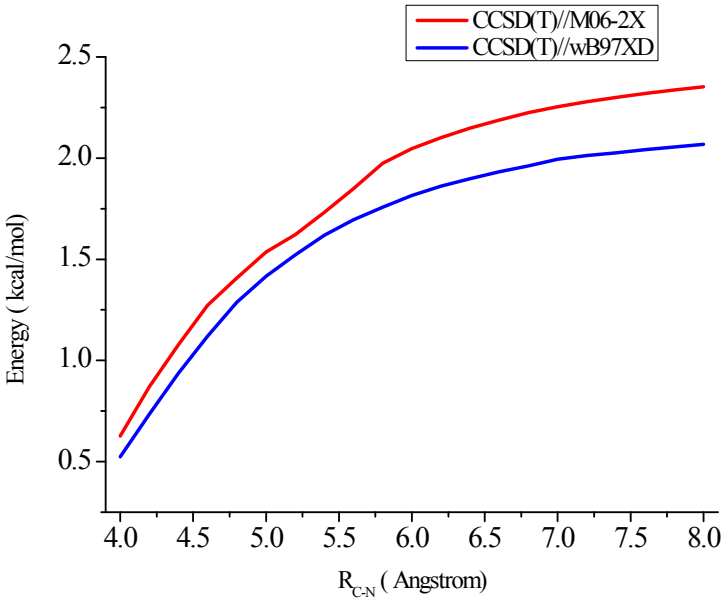

Figure S4 (b). ZPE corrected potential energy surface relative to energies of the pre-reactive complex as functions of R_{N-C} distances along the reaction pathway.

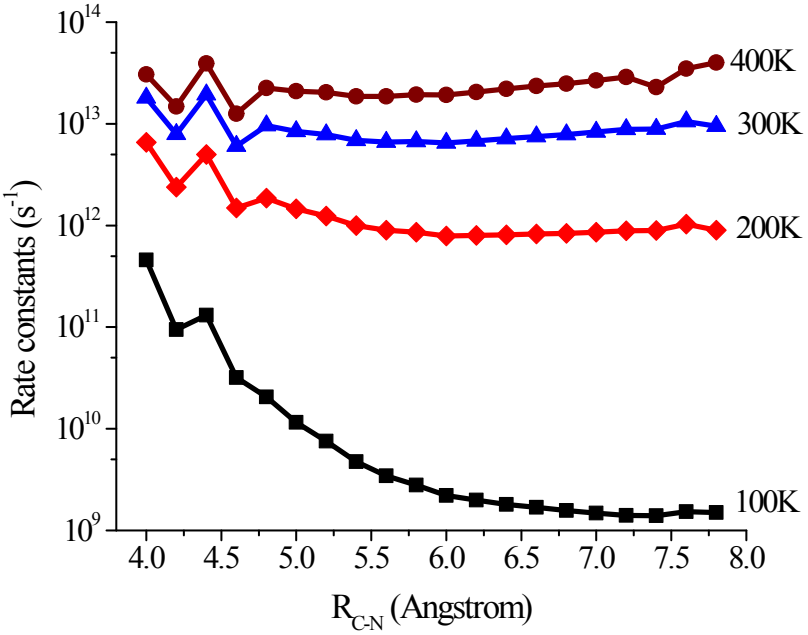

Figure S6(b): Trial CVTST rate constants for dissociation of $CH_2O\cdots NH_3$ complex as functions of $R_{C\text{-}N}$ bond distances.

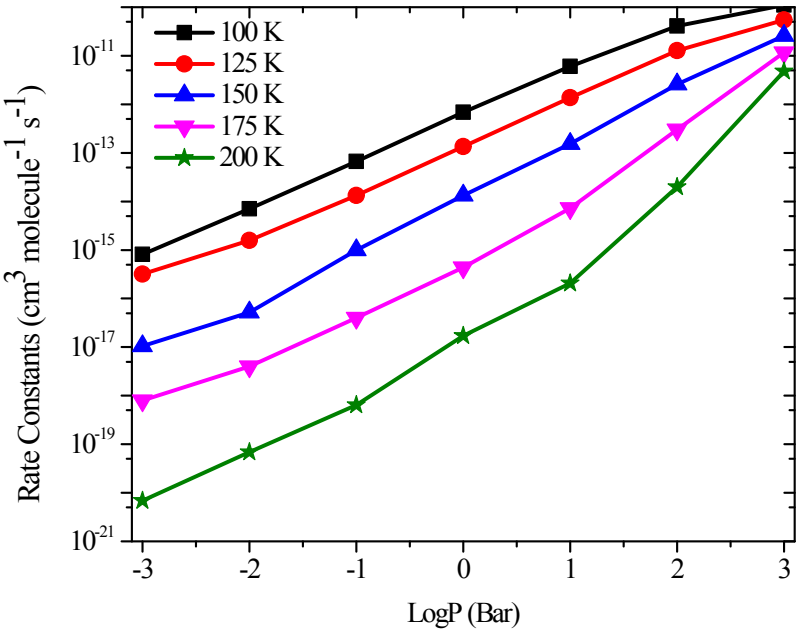

Figure S6(c). Calculated rate constants in the falloff region for $CH_2O+NH_3 \rightarrow CH_2O\cdots NH_3$. The unified sum of states of the transition state are obtained from CCSD(T)/6-311++G(3df,3pd)//ωB97XD/6-311++G(3df,3pd) level used in ME calculation.

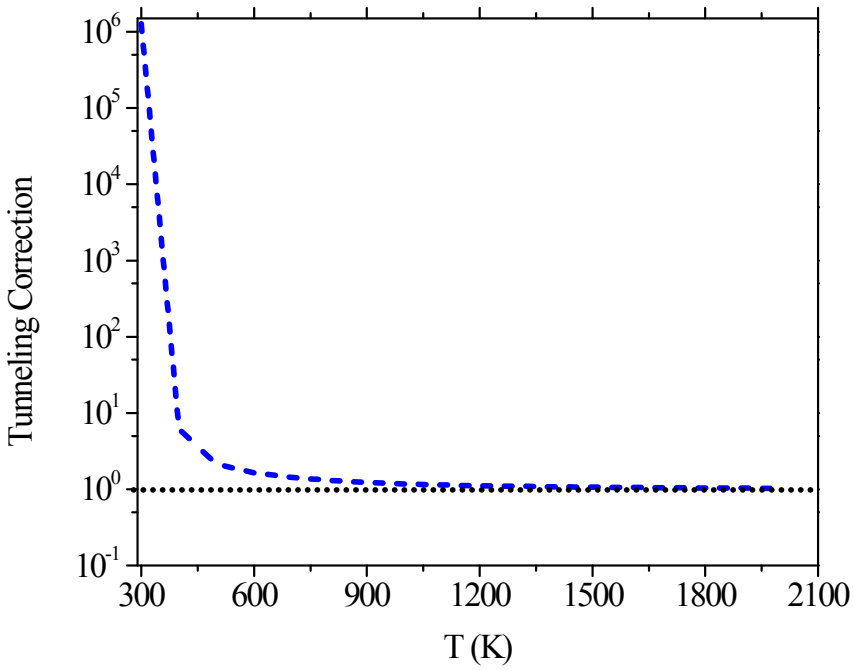

Figure S7. SCT tunnelling correction as a function of temperatures.

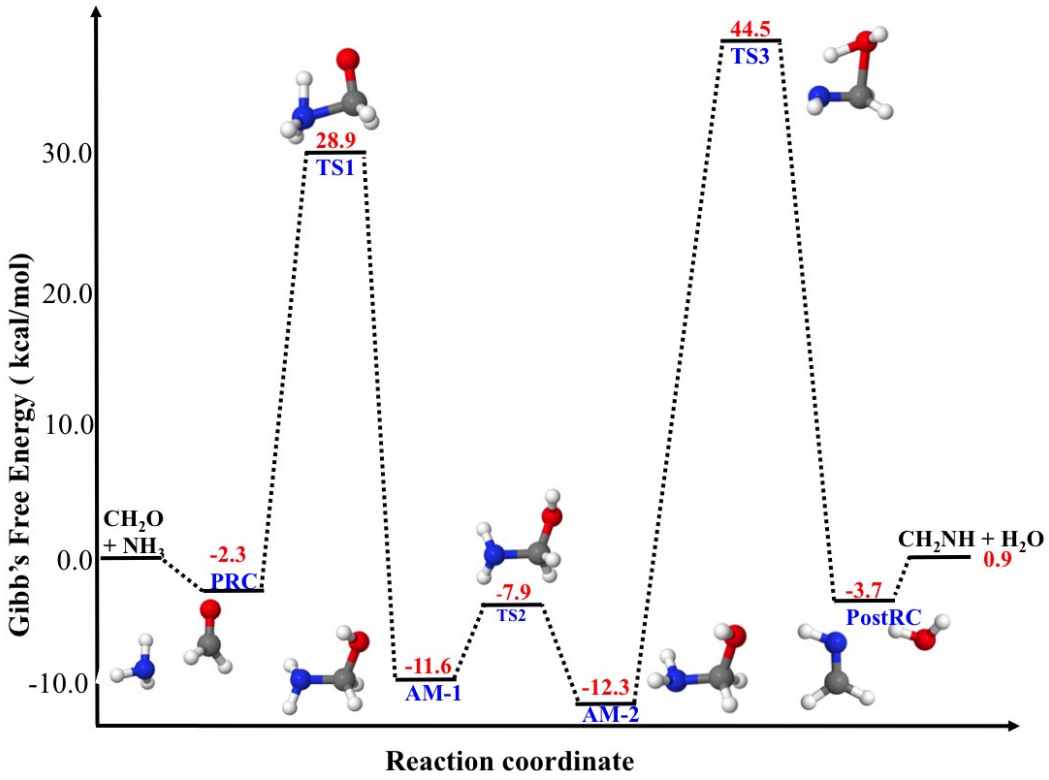

Figure S8. Gibb free energy corrected PES of CH_2O+NH_3 reaction computed at CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd).

$OHCH_2NH_2$+OH →PRODUCTS

Table S4. Optimized geometries of complexes, products and transition states obtained using M06-2X/6-311++G(3df,3pd)**.**

PRC

C	1.07344100	-0.08806500	0.35028700
H	2.13231900	-0.26762500	0.14023500
H	0.91549700	-0.11373300	1.42934100
N	0.71131800	1.20051600	-0.14140500
H	0.87235500	1.32449100	-1.13366800
H	-0.23860900	1.46644600	0.09898200
O	0.30577900	-1.20054200	-0.14760000
H	0.55894100	-1.38443800	-1.05975300
O	-2.07777800	0.16548700	0.06576300
H	-1.48438400	-0.61991700	0.06767600

TS1

C	-0.41612800	0.00337800	0.45747900
H	-0.67609500	0.10388600	1.51217500
H	0.66884600	-0.41113100	0.42559900
N	-1.26738900	-0.93301600	-0.17074400
H	-2.24533400	-0.84589200	0.06479500
H	-1.13053700	-0.98398800	-1.17023400
O	-0.27807400	1.25798500	-0.17319600
H	-1.14327600	1.66874800	-0.25367300
O	2.01591200	-0.44261400	-0.04199800
H	1.99218000	0.45626300	-0.40677300

TS2

C	-0.48598000	-0.01623800	0.49029200
H	0.62715200	-0.27579500	0.60393900
H	-0.92046400	0.02612000	1.48647300
N	-0.53324700	1.26940800	-0.13202700
H	-0.08932200	1.24895500	-1.04218400
H	-1.48770100	1.58872700	-0.24543400
O	-1.09952400	-1.07632800	-0.17876000
H	-0.62836800	-1.23892600	-1.00143900
O	1.97182100	-0.27189500	-0.06960500
H	2.16893600	0.64826800	0.16799900

TS3

C	0.91394500	0.32162500	0.40309000
H	1.84969100	0.89090500	0.40421400
H	0.60445800	0.16146500	1.43796900
N	-0.05346600	1.06094800	-0.37804400
H	-0.96225500	0.47757200	-0.49999800
H	-0.31027700	1.92193600	0.09765900
O	1.08433900	-0.95650200	-0.14277200
H	1.30813500	-0.85871000	-1.07315900
O	-1.87515700	-0.39319600	0.10382400
H	-1.27261600	-1.15197800	0.17267300

TS4

C	-0.65424600	-0.44660700	0.02145600
H	-0.43533100	-1.08009700	-0.83908300
H	-0.45129800	-1.00926100	0.93223100

N	0.16017000	0.75036800	-0.09891700
H	0.14259300	1.28390100	0.76619500
H	1.18969900	0.51914700	-0.39613500
O	-2.00550500	-0.08021000	0.08741200
H	-2.21967900	0.42158100	-0.70403700
O	2.26169700	-0.25920400	-0.08717200
H	2.52877300	0.00711000	0.80258400

$OHCHNH_2$

C	0.04818200	0.50811700	-0.16222000
H	0.12702700	1.53438900	0.16329900
N	-1.19284000	-0.11323000	-0.01129700
H	-1.31345600	-0.95403200	-0.55787700
H	-1.50070000	-0.26480100	0.94448200
O	1.21194200	-0.18125300	0.06865900
H	1.05238100	-1.12162500	-0.04677500

$OHCH_2NH$

C	0.05602700	0.50837300	0.00724800
H	0.09661000	1.15843000	-0.87506000
N	1.27021900	-0.23453200	0.04105600
H	1.04448600	-1.19120400	-0.24477200
O	-1.13167400	-0.24019500	-0.10528900
H	-1.34629600	-0.62103800	0.74856200
H	0.03089800	1.16685300	0.88270200

Table S5: Vibrational frequencies of complexes, products and transition states obtained using M06-2X/6-311++G(3df,3pd).

PRC	TS1	TS2	TS3	TS4	$OHCHNH_2$	$OHCH_2NH$
23.1	-951.6	-867.6	-815.9	-861.7	205.3	246.0
85.3	77.3	106.9	71.4	75.7	331.4	286.2
172.4	131.9	192.0	149.6	149.4	511.0	492.8
212.3	234.4	349.6	223.9	192.2	913.3	654.8
356.7	327.9	364.3	365.8	321.2	995.1	710.8
435.3	402.1	499.4	449.8	354.9	1121.6	1071.1
514.6	494.4	517.3	505.1	481.2	1198.3	1122.7
580.6	721.0	661.7	678.8	656.4	1244.7	1239.4
780.6	798.1	845.4	776.7	728.9	1374.9	1294.9
910.9	976.2	1006.1	851.6	868.6	1404.4	1426.1
996.6	1040.4	1036.3	1064.6	1007.4	1462.4	1634.5
1125.7	1118.6	1134.8	1146.4	1132.5	3022.4	3217.0
1166.3	1187.8	1228.3	1155.3	1176.6	3053.7	3480.5
1368.4	1307.0	1230.6	1299.4	1235.4	3456.9	3611.8
1389.9	1382.3	1389.5	1383.6	1303.5	3912.2	3900.5
1422.6	1430.0	1431.7	1393.7	1364.6		
1513.0	1529.0	1526.1	1423.3	1416.0		
1651.6	1559.1	1550.1	1644.3	1635.9		
3089.0	1950.8	1907.7	1900.0	1721.6		
3152.5	3073.7	3026.8	3129.6	3087.8		
3536.1	3120.0	3081.0	3529.9	3562.9		
3572.2	3534.8	3535.3	3615.3	3662.9		
3634.3	3845.4	3770.2	3797.1	3786.4		
3874.6	3887.7	3880.8	3880.3	3877.4		

Table S6: Electronic energies + ZPE (E_e + ZPE) of reactants, complexes, products and transition states obtained using CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd).

Species	ZPE	CCSDT	CCSDT+ZPE
NH_2CH_2OH	0.070376	-170.8360575	-170.7656815
OH	0.008583	-75.6398532	-75.6312702
PRC	0.081023	-246.4866351	-246.4008051
TS1	0.077001	-246.4866801	-246.4056571
TS2	0.07845	-246.471968	-246.394967
TS3	0.078076	-246.4751797	-246.3967297
TS4	0.077753	-246.4737091	-246.3956331
$OHCHNH_2$	0.055562	-246.4723021	-246.3945491
OHCH2NH	0.055149	-170.1705642	-170.1150022
H_2O	0.021641	-170.1625501	-170.1074011

Table S7: Rate constants (cm^3 $molecule^{-1}$ s^{-1}) for OH + NH_2CH_2OH→ Products

Temp	k1_TS1	k2_TS2	k3_TS3	k4_TS4	k_{total}
200	1.20E-13	8.19E-12	1.53E-13	8.05E-14	8.54E-12
225	1.06E-13	2.24E-12	1.13E-13	6.55E-14	2.52E-12
250	1.05E-13	9.29E-13	9.50E-14	6.18E-14	1.19E-12
275	1.10E-13	5.33E-13	8.67E-14	6.29E-14	7.92E-13
300	1.18E-13	3.91E-13	8.31E-14	6.63E-14	6.58E-13
325	1.19E-13	3.83E-13	8.29E-14	6.67E-14	6.52E-13