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Supporting Information

for

Molecular Mechanisms for Thermal Degradation of CO_2-loaded Aqueous Monoethanolamine Solution: A First-principles Study

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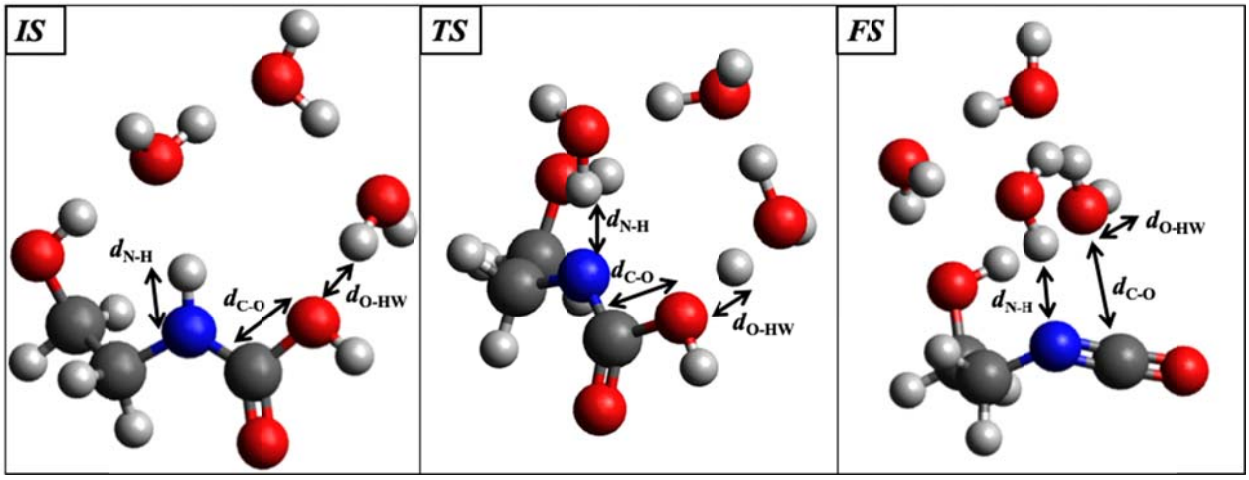

Figure S1. Molecular configurations in the initial (*IS*), transition (*TS*), and final (*FS*) states for dehydration of carbamic acid to isocyanate, i.e., MEACOOH → isocyanate + H_2O, predicted from static QM calculations at the theory level of B3LYP/6-311++G(d,p) with an implicit solvent model. The blue, red, grey, and white balls represent N, O, C, and H atoms, respectively.

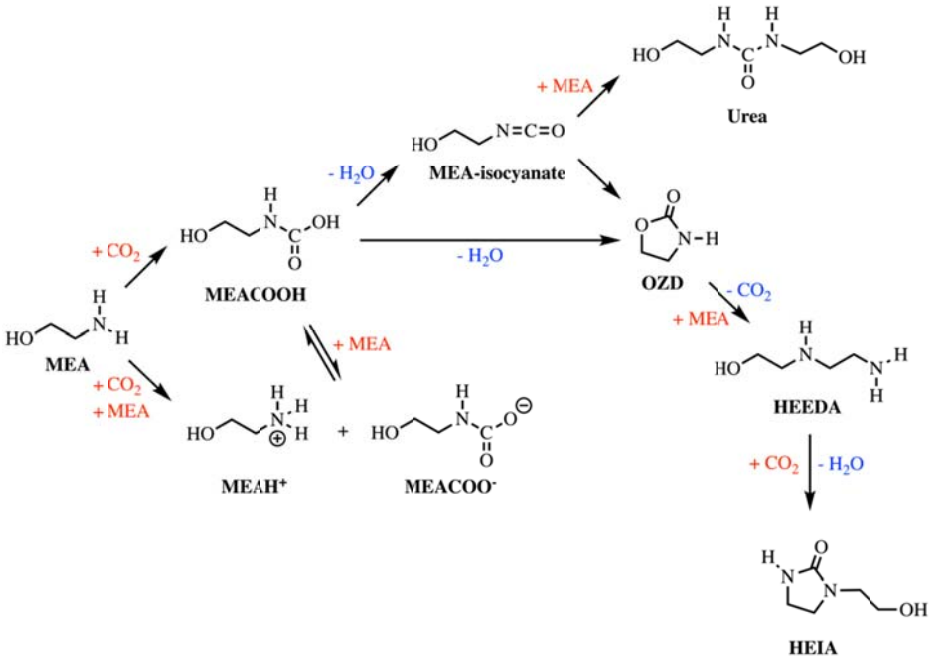

Figure S2. Overall mechanism for thermal degradation of aqueous MEA in CO_2 capture processes.

Table S1. Enthalpies and free energies calculated B3LYP/6-311++G(d,p) level of theory

	H^0_{gas} (kcal/mol)	G^0_{gas} (kcal/mol)	H^0_{solv} (kcal/mol)	G^0_{aq} (kcal/mol)	ΔH^0_{solv} (kcal/mol)	ΔG^0_{solv} (kcal/mol)
MEA	-132001.07	-132022.25	-132010.45	-132031.8	-9.3787495	-11.433784
$MEAH^+$	-132221.25	-132242.38	-132293.24	-132314.78	-71.98846	-72.398223
$MEACOO^-$	-250026.43	-250052.45	-250103.32	-250128.95	-76.888678	-78.388367
MEACOOH	-250367.82	-250394.51	-250384.5	-250410.83	-16.684209	-18.215274
OZD	-202400.12	-202421.69	-202413.02	-202434.64	-12.894055	-14.845551
Urea	-334401.37	-334433.71	-334424.14	-334456.91	-22.762889	-25.09089
HEEDA	-216040.94	-216069.01	-216056.12	-216084.02	-15.178815	-15.018173
HEEDACOOH	-334400.17	-334433.43	-334427.16	-334459.16	-26.51853	-25.727869
HEIA	-286449.37	-286477.23	-286465.51	-286493.63	-16.144552	-18.286183

Table S2. Cartesian coordinates of the key species obtained B3LYP/6-311++G(d,p) level of theory

MEACOOH:

O	0.9649770000	-0.0509550000	0.1189150000
O	1.5581630000	-0.6690900000	2.2229700000
O	1.8217750000	4.4201030000	-0.3910220000
N	2.4837250000	1.1663510000	1.3309680000
C	2.6553400000	2.2505690000	0.3712670000
C	1.6207090000	0.1548840000	1.1380340000
C	1.6340700000	3.3726990000	0.5691940000
H	0.9299630000	-1.3781150000	2.0183010000
H	2.5714090000	1.8453260000	-0.6375140000
H	0.6222180000	2.9938900000	0.4157670000
H	3.6656360000	2.6459970000	0.4927650000
H	2.8993480000	1.2551800000	2.2478630000
H	2.6629840000	4.8562460000	-0.2037090000
H	1.7043870000	3.7701680000	1.5872990000

Isocyanate:

O	1.4020410000	0.1041680000	2.7788000000
O	1.5333620000	3.9573830000	0.8533210000
N	2.6319980000	1.1254840000	1.0240820000
C	1.9545440000	0.6357890000	1.8792560000
C	2.4952480000	1.9329840000	-0.1807450000
C	1.3433930000	2.9237950000	-0.1191340000
H	1.3814620000	3.5885160000	1.7322780000
H	2.3433440000	1.2627820000	-1.0300140000
H	3.4373710000	2.4592620000	-0.3334600000
H	1.2787720000	3.4212450000	-1.0887800000
H	0.4016840000	2.3959850000	0.0651280000

OZD:

O	-4.4840910000	3.3676590000	-0.1904930000
O	-3.5260330000	1.3370530000	-0.4420050000
N	-5.5890970000	1.4059880000	0.3814380000
C	-4.5603250000	2.1516180000	-0.0861480000
C	-3.8721590000	-0.0391790000	-0.0965730000
C	-5.3928140000	-0.0098120000	0.0630520000
H	-3.3637270000	-0.2817980000	0.8373990000
H	-3.5245550000	-0.6863830000	-0.8975500000
H	-5.7320430000	-0.6573690000	0.8695870000
H	-5.9101260000	-0.2795480000	-0.8609700000
H	-6.5080050000	1.8252100000	0.4222630000

Urea:

O	1.1569540000	-2.9862180000	-1.0864770000
O	2.7379770000	-0.1367070000	2.9276670000
O	1.5340880000	4.0675830000	0.1807190000
N	1.8027370000	-0.9376910000	1.0184650000
N	2.2245900000	1.3741170000	1.3097890000
C	0.9177640000	-1.5757480000	-1.2271530000
C	0.6525640000	-0.8882800000	0.1032850000
C	2.2707660000	0.0922320000	1.7899280000
C	2.4379900000	1.7901450000	-0.0848520000
C	1.4383320000	2.8356750000	-0.5544200000
H	1.8942110000	-1.8180450000	1.5093000000
H	2.0428880000	-3.1116940000	-0.7246090000
H	0.0277740000	-1.4811750000	-1.8525860000
H	1.7583900000	-1.1057540000	-1.7471390000
H	0.3680920000	0.1459260000	-0.0804620000
H	-0.1995810000	-1.3734140000	0.5904380000
H	2.6088500000	2.0196570000	1.9879330000
H	1.1442790000	3.9338390000	1.0537090000
H	2.3837640000	0.9250440000	-0.7430100000
H	3.4498720000	2.1986590000	-0.1739640000
H	1.6569680000	3.0861870000	-1.5944330000
H	0.4160800000	2.4482060000	-0.4982710000

HEEDA:

O	1.6417570000	4.6832830000	-0.6457140000
N	3.8538550000	-1.7495010000	2.2691040000
N	2.2789290000	1.5978250000	1.3687430000
C	2.9430120000	-0.5956520000	2.3169920000
C	3.2445010000	0.4929880000	1.2899630000
C	2.5084860000	2.6028550000	0.3251330000
C	1.4817980000	3.7248720000	0.4135230000

H	3.8320020000	-2.1523860000	1.3349790000
H	4.8082520000	-1.4247680000	2.4072870000
H	1.9222220000	-0.9607060000	2.1664130000
H	2.9818250000	-0.1699670000	3.3229770000
H	3.2617540000	0.0377050000	0.2855390000
H	4.2462740000	0.8965390000	1.4724950000
H	1.3518170000	1.2041690000	1.2176350000
H	2.4729930000	2.1679960000	-0.6860830000
H	0.4712120000	3.3242750000	0.3013070000
H	3.5112840000	3.0213880000	0.4608620000
H	2.4926910000	5.1234130000	-0.5259900000
H	1.5447370000	4.2249080000	1.3857330000

HEIA:

O	-8.4110470000	-0.4429040000	0.4684090000
O	-4.9340980000	3.1811500000	0.1820430000
N	-5.8350510000	1.0477350000	-0.0702640000
N	-3.6219170000	1.3180090000	-0.2648920000
C	-8.2590890000	0.9831530000	0.5828240000
C	-7.1983170000	1.4689250000	-0.3855350000
C	-4.8121460000	1.9641170000	-0.0263420000
C	-3.8266710000	-0.1343040000	-0.2035280000
C	-5.3126740000	-0.2415500000	-0.5532030000
H	-9.0747040000	-0.7229210000	1.1102860000
H	-7.9892400000	1.2513810000	1.6095470000
H	-9.2030950000	1.4799910000	0.3317130000
H	-7.2166970000	2.5596670000	-0.3785960000
H	-7.4497280000	1.1370240000	-1.4005200000
H	-2.7962530000	1.7257360000	0.1540050000
H	-5.4681060000	-0.3243050000	-1.6358280000
H	-5.7979880000	-1.0824050000	-0.0628160000
H	-3.6297410000	-0.5149360000	0.8032140000
H	-3.1916700000	-0.6618170000	-0.9132820000