Supporting Information

for

On the Mechanism of Predominant Urea Formation from Thermal Degradation of

CO₂-loaded Aqueous Ethylenediamine

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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., EDACOOH \rightarrow isocyanate + H₂O, predicted by implicit-solvent QM calculations at a theory level of B3LYP/6-311++G(d,p). The blue, red, grey, and white balls represent N, O, C, and H atoms, respectively.



Figure S2. AIMD snapshots demonstrating rehydration of isocyanate to carbamic acid (a-c) at 1000 K. Systems contain 16 H_2O , 3 EDA and 1 EDA-isocyanate in a cubic simulation box of edge length 9.98 Å with periodic boundary conditions. The blue, red, grey, and white balls represent N, O, C, and H atoms, respectively.

Hydrogen bond dynamics:

The continuous hydrogen bond correlation function S(t) and the intermittent hydrogen bond correlation function C(t) for the pairs *i*, *j* of hydrogen bonded molecules are defined as

$$S(t) = \frac{\langle h_{ij}(0) * H_{ij}(t) \rangle}{\langle h_{ij} \rangle}$$

$$C(t) = \frac{\langle h_{ij}(0) * h_{ij}(t) \rangle}{\langle h_{ij} \rangle}$$

The population variable $H_{ij}(t)$ is unity if the *i*,*j* pair remains continuously hydrogen bonded from t = 0 to time *t* within a first solvation shell of 2.5 Å and zero otherwise, whereas $h_{ij}(t)$ is unity if the pair *i*,*j* is hydrogen bonded at time *t* and zero otherwise; <...> represents an average over all hydrogen bond pairs. S(t) depicts the probability that initial hydrogen bond between *i* and *j* pair molecules remains bonded at all times up to *t*. C(t) describes the probability that of pair *i* and *j* molecules remaining hydrogen-bonded at time *t* given that the pair was hydrogen-bonded at time 0 and is independent of the breaking of hydrogen bonds at any intermediate time instant and allows for the re-formation of broken bonds. The corresponding average lifetime ($\tau_{S,ij}$ and $\tau_{C,ij}$) of a hydrogen bond between molecules *i* and *j* can be obtained as

$$\tau_{S,ij} = \int_0^\infty S(t)dt$$
$$\tau_{C,ij} = \int_0^\infty C(t)dt$$

 $\tau_{S,ij}$ and $\tau_{C,ij}$ essentially represent the residence time of pair *i* and *j* molecules remain hydrogen bonded. Since the isocyanates of EDA and MEA only differ on their end group, we investigated intermolecular hydrogen bond from terminal base N atom of EDA-isocyanate, represented as N_t, and terminal O atom of MEA-isocyanate, represented as O_t, to H of surrounding water molecules, represented as H_w; in other words, pair *i* and *j* are N_t (O_t) and H_w, for the case of EDA (MEA) respectively. The system contains 1 isocyanate and 30 H₂O molecules in a cubic simulation box of edge length 10.54 Å.

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

	$H^0_{\rm gas}$	$G^0_{\rm gas}$	$H^0_{ m solv}$	G^0_{aq}	$\Delta H^0_{ m solv}$	$\Delta G^0_{ m solv}$
	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)
EDA	-119521.16	-119542.69	-119530.74	-119552.22	-9.58	-11.42
$EDAH^+$	-119738.08	-119760.16	-119813.22	-119834.92	-75.15	-74.75
EDACOO-	-237545.37	-237571.67	-237623.47	-237649.41	-78.10	-79.62
EDACOOH	-237882.18	-237908.96	-237902.98	-237929.35	-20.80	-22.27
Isocyanate	-189911.86	-189936.68	-189917.92	-189942.27	-6.07	-7.48
Urea	-309445.51	-309478.16	-309465.27	-309498.07	-19.76	-21.79
IZD	-189925.37	-189947.01	-189939.75	-189961.39	-14.38	-16.26

		$\Delta H_{\rm gas}$	$\Delta H_{ m aq}$	$\Delta G_{\rm gas}$	$\Delta G_{ m aq}$
а	$2 EDA + CO_2 \rightarrow EDACOO^- + EDAH^+$	126.74	-10.06	137.03	-1.02
b	$\begin{array}{c} 2 \text{ EDA} + \text{CO}_2 \rightarrow \\ \text{EDACOOH} + \text{EDA} \end{array}$	6.94	-8.73	16.91	1.90
c	$EDACOO^{-} + EDAH^{+} \rightarrow IZD + EDA + H_{2}O$	-125.70	-4.93	-134.70	-12.70
d	$EDACOOH + EDA \rightarrow IZD + EDA + H_2O$	-5.90	-8.26	-14.58	-15.63
e	$EDACOO^{-} + EDAH^{+} \rightarrow EDA-Urea + H_{2}O$	-127.97	-5.14	-127.39	-4.21
f	EDACOOH+ EDA → EDA-Urea + H ₂ O	-8.17	-8.48	-7.27	-7.13
g	EDACOOH \rightarrow EDA-isocyanate + H ₂ O	8.53	13.67	-4.05	3.12
h	EDA-isocyanate \rightarrow IZD	-14.43	-21.94	-10.53	-18.75
i	EDA-isocyanate + EDA → EDA-Urea	-16.70	-22.15	-3.22	-10.25

Table S2. Predicted enthalpy (ΔH) and free energy (ΔG) changes in kcal/mol for selected reactions during thermal degradation of EDA from static QM calculations at a theory level of B3LYP/6-311++G(d,p) in the gas-phase and aqueous solution (with an implicit solvent model) as indicated.

Table S3. Predicted enthalpy (ΔH) and free energy (ΔG) changes in kcal/mol for selected reactions during thermal degradation of EDA from static QM calculations at a theory level of PBE-D3/6-311++G(d,p) in the gas-phase and aqueous solution (with an implicit solvent model) as indicated.

		$\Delta H_{\rm gas}$	$\Delta H_{ m aq}$	$\Delta G_{\rm gas}$	$\Delta G_{ m aq}$
a	$2 EDA + CO_2 \rightarrow EDACOO^- + EDAH^+$	124.86	-12.21	135.16	-2.11
b	$2 EDA + CO_2 \rightarrow EDACOOH + EDA$	5.29	-9.05	14.97	1.30
c	$\begin{array}{c} \text{EDACOO}^{-} + \text{EDAH}^{+} \rightarrow \\ \text{IZD} + \text{EDA} + \text{H}_2\text{O} \end{array}$	-123.97	-4.47	-132.91	-12.14
d	$\begin{array}{l} \text{EDACOOH} + \text{EDA} \rightarrow \\ \text{IZD} + \text{EDA} + \text{H}_2\text{O} \end{array}$	-5.40	-7.63	-14.02	-14.72
e	$EDACOO^{-} + EDAH^{+} \rightarrow EDA-Urea + H_{2}O$	-126.82	-5.17	-126.21	-4.30
f	EDACOOH+ EDA → EDA-Urea + H ₂ O	-8.26	-8.32	-7.32	-6.88
g	EDACOOH \rightarrow EDA-isocyanate + H ₂ O	9.64	15.01	-3.12	4.99
h	EDA-isocyanate \rightarrow IZD	-16.44	-23.63	-12.90	-19.91
i	EDA-isocyanate + EDA \rightarrow EDA-Urea	-18.30	-24.33	-4.89	-11.97



Figure S3. Predicted Gibbs free energy changes (ΔG_{aq}) for the elementary reactions involved in ethylenediamine (EDA) degradation in aqueous solution. Isolated EDA and CO₂ in aqueous solution with B3LYP/6-311++G(d,p) are chosen as reference. Error bars represent statistical variance due to different functionals (i.e. PBE+D3).

Table S4. Cartesian coordinates of the key species obtained B3LYP/6-311++G(d,p) level of theory

EDACOOH:

0	0.1327180000	3.1379670000	0.2715850000
0	-1.3697740000	2.8723220000	1.8924840000
Ν	-1.8166350000	1.9858230000	-0.1679370000
Ν	-5.5728250000	1.9404550000	0.1319240000
С	-3.1595800000	1.4971520000	0.1410770000
С	-4.2524890000	2.5234190000	-0.1505290000
С	-1.0679170000	2.6656070000	0.7202970000
Н	-3.3234440000	0.5995590000	-0.4593150000
Н	-3.1866820000	1.2035370000	1.1903300000
Н	-1.5201420000	1.9591330000	-1.1346250000
Н	-4.1483790000	2.8681340000	-1.1878750000
Н	-4.1117320000	3.3922420000	0.4960180000
Н	-5.7919190000	1.2493650000	-0.5819140000
Н	-6.2815090000	2.6639240000	0.0503380000
Η	0.3048380000	2.9019960000	-0.6525380000
Isoc	evanate:		
0	-0.5021110000	3.7075180000	0.5220670000
Ň	-5.5442850000	1.9598600000	-0.1032450000
Ν	-1.8521740000	1.7538110000	0.5194120000
С	-1.2293920000	2.7755140000	0.5068390000
С	-4.1884860000	2.4750680000	0.1211170000
С	-3.2281980000	1.3116170000	0.3401200000

Н	-6.2028750000	2.7331820000	-0.0888620000
Н	-5.6001730000	1.5569570000	-1.0353250000
Н	-4.1977400000	3.1037980000	1.0143380000
Н	-3.8136470000	3.0885050000	-0.7091080000
Н	-3.5137250000	0.7380120000	1.2225580000
Н	-3.2499760000	0.6315430000	-0.5141890000
IZD:	:		
0	-2.5877000000	2.6699900000	-2.0842080000
Ν	-1.5213030000	0.7987510000	-1.2039890000
Ν	-3.6674490000	1.1360540000	-0.7085140000
С	-3.3642920000	-0.2230750000	-0.2371580000
С	-1.8360290000	-0.1670090000	-0.1415460000
С	-2.5914290000	1.6363500000	-1.3990270000
Н	-1.3681180000	-1.1328430000	-0.3232650000
Н	-1.5148520000	0.2094140000	0.8345050000
Н	-0.5983130000	1.2093380000	-1.2594630000
Н	-3.8364370000	-0.4328360000	0.7208320000
Н	-3.6880810000	-0.9702470000	-0.9682130000
Н	-4.5870010000	1.3550500000	-1.0689390000
Urea	Ľ		
0	-7.0684010000	3.4284990000	1.4115420000
Ň	-5.8900350000	1.7080530000	0.4671960000
N	-2.3110710000	2.4032650000	-0.3574330000
N	-8.1858740000	1.5543050000	0.7287890000
N	-11.8130410000	1.3507770000	1.6140580000
С	-4.6752320000	2.4997010000	0.2784760000
Ċ	-3.5060900000	1.5923290000	-0.0797030000
Č	-7.0501220000	2.2931480000	0.8960400000
Ċ	-9.4369220000	1.9192970000	1.3903610000
Ċ	-10.5644200000	1.0139530000	0.9136060000
H	-5.9846690000	0.8956790000	-0.1299720000
Н	-4.4566850000	3.0409610000	1.1995290000
Н	-4.8158140000	3.2431090000	-0.5169310000
Н	-1.5251050000	1.7847600000	-0.5369870000
Н	-2.4589120000	2.9243460000	-1.2188160000
Н	-3.2863730000	0.9282530000	0.7594690000
Н	-3.7926810000	0.9561970000	-0.9292730000
Н	-8.0698280000	0.5777040000	0.4898530000
Н	-9.6732360000	2.9583980000	1.1574570000
Н	-9.3375580000	1.8377080000	2.4803680000
Н	-10.2657370000	-0.0343680000	1.0556240000
Н	-10.7218260000	1.1624560000	-0.1571270000
Н	-11.7338470000	1.0748650000	2.5901460000
Η	-12.5690100000	0.7933520000	1.2266180000

K-point set sensitivity:

The total energy changes for a reaction between the cases using either only gamma point or $(2 \times 2 \times 2)$ k-point mesh are compared; as shown in Table S5, the difference is only 15 meV, while the latter is 8 times more expensive. This indicates that our simulations based on only gamma point suffice, and our results are insensitive on the choice of k-point set.

Table S5. Predicted total energy (*E*) and changes in total energy (ΔE) in eV for selected reactions during thermal degradation of EDA using different k-point sets as indicated.

		E_1	E_2	$\Delta E_{1 \rightarrow 2}$
а	Gamma	-527.930	-528.328	0.398
b	2×2×2	-527.914	-528.297	0.383

Convergence of metadynamics and veracity of transition state:

We have implemented well-tempered algorithm based metadynamics for the reactions, indicated as **R3**, **R4**, **R5**, **R6** in the manuscript. Once the metadynamics runs are fully converged, the free-energy barrier should plateau, as shown in Figure S4. Moreover, in well-tempered algorithm, the gaussian heights deposited on to free-energy surface (FES) must decay to zero, indicating that no more bias gaussian hills are added once the FES is fully converged, thereby representing a true FES (as shown in Figure S5).

Once a true reactive trajectory has been found (i.e. FES), we have performed a big number of unbiased MD simulations where at least 20 different configurations around identified transition state region are started with random Boltzmann distributed velocities. We thereafter identified and confirmed that the unbiased MD simulations reached either reactant or product states, as indicated along our chosen CV space.



Figure S4. Convergence of free-energy barrier along well-tempered metadynamics runs for the reactions: R3, R4, R5, R6



Figure S5. Convergence of deposited gaussian height during well-tempered metadynamics runs