CO_2 Absorption in an Alcoholic Solution of Heavily Hindered Alkanolamine: The Reaction Mechanism of 2-(*tert*-butylamino)-ethanol with CO_2 Revisited

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Four texts, three Tables and one Figure.

1. Computational details for global minimum search

Density functional theory (DFT) with the BLYP-D functional along with the SVP basis set within the resolution-of-the-identity approximation[1] was used to carry out the AIMD calculations. The temperature was set to 500 K in order to sample a large number of different configurations. A time step of 2 fs was used. The total length of AIMD simulation was 10 ps (5000 time steps). The calculation was carried out using the TURBOMOLE package.[2] The configurations from the AIMD run were used as starting points to obtain the global minimum of TBAE at the B3LYP/6-311++G(d,p) level with the SMD solvation model. Single point energy calculation was then performed at the B3LYP-D/6-311++G(3df,2pd) level to obtain accurate total energies for each of the sample configurations.

2. Overall activation free energy for carbamate mechanism

For the carbamate pathway, we start from the following reaction scheme according to the free energy surface.

$$\text{amine} + CO_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} \text{Zwitterion} \tag{S1}$$

$$\text{Zwitterion} + \text{amine} \xrightarrow{k_{\text{Base}}} \text{Carbamate} \tag{S2}$$

Invoking the pseudo steady-state approximation, the zwitterion concentration can be expressed as:

$$[\text{zwitterion}] = \frac{k_2[\text{amine}][CO_2]}{k_{-1} + k_{\text{Base}}[\text{amine}]} \tag{S3}$$

The overall rate of consumption of CO_2 is therefore

$$r_{CO_2} = \frac{k_{\text{Base}} k_2 [\text{amine}]^2 [CO_2]}{k_{-1} + k_{\text{Base}}[\text{amine}]} \tag{S4}$$

Then, it can be rewritten eq.(S4) as:

$$r_{CO_2} = k_c[CO_2] \quad \text{(S5)}$$

where the pseudo-first-order reaction rate coefficient k_c is defined as:

$$k_c = \frac{k_{Base}k_2[amine]^2}{k_{-1} + k_{Base}[amine]} \quad \text{(S6)}$$

The reaction rate constant (k) for elementary reactions was calculated by the transition state theory:

$$k = (c^o)^{\Delta n}\frac{k_B T}{h}\exp(-\frac{\Delta G^+}{RT}) \quad \text{(S7)}$$

where $c°$ is the standard-state concentration (1 molL^{-1}), Δn is the change of the number of moles from reactants to the transition states, h is the Planck constant, ΔG^+ (activation free energies) is the difference in the Gibbs free energy between the reactants and the transition states, and R is the gas constant.

In the carbamate channel, the ΔG^+ of pathway that zwitterion returns back to reactants is much smaller than that of the second step (eq. S2). Therefore, k_{-1} is >>k_{Base}. Then, we can approximate eq.(S6) as:

$$k_c = \frac{k_{Base}k_2[amine]^2}{k_{-1}} \quad \text{(S8)}$$

When k_{Base}, k_2 and k_{-1} are presented by eq.S7, respectively, we can rewrite eq.(S8) as:

$$k_c = (c^o)^{\Delta n}\frac{k_B T}{h}\exp(-\frac{\Delta G_{all}^+}{RT})[amine]^2 \quad \text{(S9)}$$

Where ΔG_{all}^+ is the overall activation free energy, which is equal to the sum of activation free energy (ΔG_{Sec}^+) for the second step (eq.S2) and the relative free energy of zwitterion.

3. The possible reason that inter-molecular proton transfer of TBAE (pathway

E) is a little more favorable than its intra-molecular proton transfer (pathway B).

A possible reason could be the stabilization of hydrogen bond between HO- of TBAE and O-atom of the other TBAE (TS-5) on the transition state of inter-molecular proton transfer of TBAE in pathway E. We also try to consider the role of a hydrogen bond on the intra-molecular proton transfer in pathway B by introducing an EG molecule to form an inter-molecular hydrogen bond with –OH of TBAE (as shown in Figure 1S). The computed ΔG^{+} value that CO_2 attack on –OH of TBAE is 16.3 kcal/mol, which is lower than that (19.9 kcal/mol) of pathway B by taking the structure in Figure 1S as the reactant. This indicates that the formation of hydrogen bond does stabilize the transition state. Even though, the ΔG^{+} values for the pathways via the attack of CO_2 on –OH of TBAE is about 2 kcal/mol higher than that of most favorable pathway C.

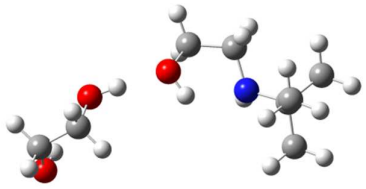

Figure 1S. The hydrogen bond complex between TBAE and EG.

4. Reliability evaluation calculations

We have carried out additional calculations to confirm the revealed the reaction mechanism of CO_2 with TBAE in EG solution. High-level quantum chemical methods, B3LYP-D/6-311++G(3df,2pd) and MP2/aug-cc-pVDZ method with the SMD solvent model were firstly used to calculate the single point energies based on the geometries at the B3LYP/6-311++G(d,p) level with the SMD model. Reliability evaluation

calculations were performed on all the pathways except pathway A because it has no any competition with the others due to its high ΔG^{+}. As shown in Table S1, the ΔG^{+} values at the B3LYP-D/6-311++G(3df,2pd) and MP2/aug-cc-pVDZ levels are generally 3~6 kcal/mol lower than those at the B3LYP/6-311++G(d,p) level for pathways B~F. In addition, the trend in the ΔG^{+} values at the B3LYP/6-311++G(d,p) level for these pathways agree well with that obtained at the B3LYP-D/6-311++G(3df,2pd)//B3LYP/6-311++G(d,p) and MP2/aug-cc-pVDZ// B3LYP/ 6-311++G(d,p) level. More importantly, pathway C is still the most favorable at the B3LYP-D/6-311++G(3df,2pd)//B3LYP/6-311++G(d,p) and MP2/aug-cc-pVDZ //B3LYP/6-311++G(d,p) level. Therefore, the B3LYP/6-311++G(d,p) method provides a qualitatively accurate picture of the reaction mechanism with an acceptable level of computational cost.

Table S1. Activation free energies (kcal/mol) for pathways B~F at the B3LYP/6-311++G(d,p), B3LYP-D/6-311++G(3df,2pd) and MP2/aug-cc-pVDZ level.

	B	C	D	E	F
B3LYP/6-311++G(d,p)	19.9	14.2	19.2	16.2	18.7
B3LYP-D/6-311++G(3df,2pd)	16.4	9.3	15.8	11.3	15.7
MP2/aug-cc-pVDZ	15.3	8.0	16.0	9.4	15.8

The conductor-like polarizable continuum model (CPCM)[3,4] formalism with Bondi and Pauling atomic radii, which was proved to reliably predict the reaction mechanism of MEA with CO_2,[5] was also used to calculate the ΔG^{+} for pathways B~F at the B3LYP/6-311++G(d,p) level, to confirm the reliability of the SMD model. As shown in Table S2, the CPCM model with Bondi and Pauling atomic radii predicts that the ΔG^{+} values for pathways C and E are lower than those of pathways B, D and F, and the ΔG^{+} values of pathways B, D and F are close to each other. This trend agrees

well with the findings using the SMD solvent model at the B3LYP/6-311++G(d,p) level, although the ΔG^{+} values from the Bondi and Pauling atomic radii are systematically higher than those from the SMD model. Therefore, the SMD model can reasonably treat the reaction of CO_2 with EG solution of TBAE. All in all, the theoretical method used here can reliably reveal the reaction mechanism of the titled reaction.

Table S2. Activation free energies for pathways B~F at the B3LYP/6-311++G(d,p) level using SMD, CPCM with Bondi and Pauling atomic radiis.

Solvent models	B	C	D	E	F
SMD	19.9	14.2	19.2	16.2	18.7
CPCM(Bondi)	24.1	18.9	24.0	21.0	24.2
CPCM(Pauling)	23.7	18.9	25.0	19.6	24.2

References:

1. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R., Auxiliary basis sets to approximate Coulomb potentials. *Chem. Phys. Lett.* **1995,** *240*, (4), 283-290.

2. Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C., Electronic structure calculations on workstation computers: The program system turbomole. *Chem. Phys. Lett.* **1989,** *162*, (3), 165-169.

3. Barone, V.; Cossi, M., Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. J. Phys. Chem. A 1998, 102, (11), 1995-2001.

4. Cossi, M.; Rega, N.; Scalmani, G.; Barone, V., Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. J. Comput.Chem. 2003, 24, (6), 669-681.

5. Xie, H.-B.; Zhou, Y.; Zhang, Y.; Johnson, J. K., Reaction Mechanism of Monoethanolamine with CO_2 in Aqueous Solution from Molecular Modeling. J. Phys. Chem. A 2010, 114, (43), 11844-11852.

Table S3. Accurate mass measurements for TABE, EG and their CO_2 absorption products.

Compound	Proposed formula	Experimental mass (m/z)	Calculated mass (m/z)	Error (ppm)	DBE[a]
TABE	$[C_6H_{15}NO + H]^+$	118.1220	118.1226	5.47	0
EG	$[C_2H_6O_2 - H]^-$	61.0297	61.0295	−3.18	0
Product	$[C_3H_6O_4 - H]^-$	105.0194	105.0193	−0.64	1
	$[C_2H_6O_2 - H]^-$	61.0296	61.0295	−1.56	0
	$[C_2H_4O_2 - H]^-$	59.0140	59.0139	−2.45	1

[a] DBE stands for double bond equivalents.

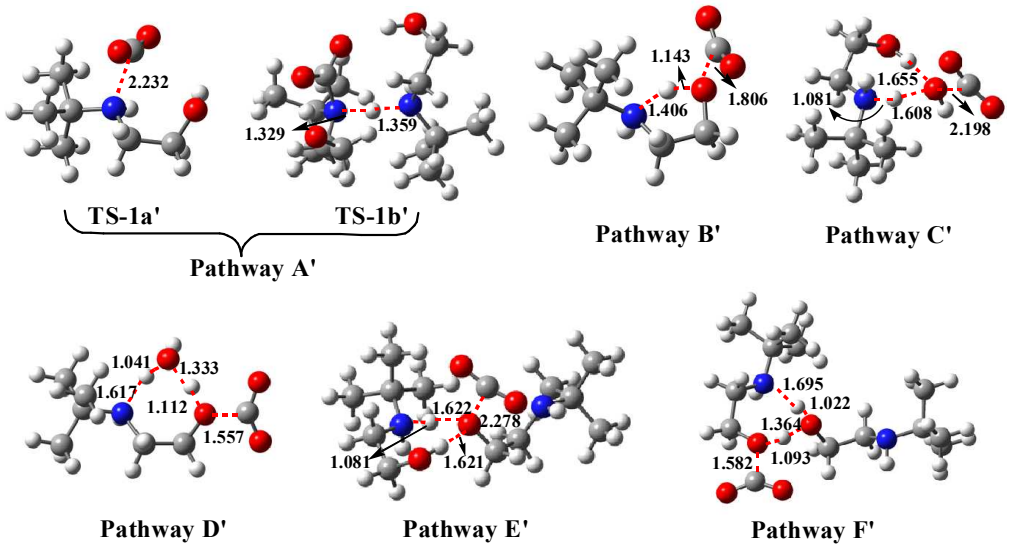

Figure S1. B3LYP/6-311++G(d,p)-optimized geometries for the transition states of pathways A'~F' for the reaction of CO_2 with TBAE in aqueous solution (The distances are in Å)