Theoretical Study on the Kinetics of Rubisco Carboxylase Reaction by a Model based on Quantum Chemistry and Absolute Reaction Rate Theory

Shin’ichiro Okude,1,* Junwei Shen1, Makoto Hatakeyama1,2 and Shinichiro Nakamura1,*

1Cluster for Science, Technology and Innovation Hub, Nakamura Laboratory, RIKEN, Wako, Saitama 351-0198, Japan
2Department of Pharmacy, Sanyo-Onoda City University, Onoda Yamaguchi 756-0884, Japan

KEYWORDS Enzyme Reaction, Absolute Rate, CO2, Rubisco, Global Warming, Catalyst.
Nomenclatures

Section 3

TS: The transition state

$N_{TS}$ : The population of the transition states.

$\delta$ : The length of the plateau of the transition state.

$\nu_T$ : The thermal velocity of the moving active part of the transition state.

$R_P$ : The reaction rate with which products are produced.

$N_{ENZYME}$ : The total number of the enzyme molecules.

TON : The turnover number

Section 4-1

$N_{RS}$ : The number of RS’s.

$N_{CO2}$: The number of gas phase $CO_2$ molecules.

$N_{VM,II}$: The total number of the vibration normal modes of the transition state II.

$P_{CO2}$: The partial pressure of $CO_2$ gas.

$K_B$ : The Boltsmann constant

$T$ : The temperature

$m_{CO2}$ : The mass of a $CO_2$ molecule.

$h$ : Planck constant

$H_{ACT,ADD}$ : The activation energy of the addition of a gaseous $CO_2$ molecule to form Structure III, which is the energy level of II measured from the energy level of $CO_2$ gaseous molecules and RS’s.

$N_{VM,CO2}$: The total number of the vibration normal modes of a $CO_2$ molecule.

$N_I$ : The population of cluster I.

$<N_I>$ : The average value of thermally fluctuating $N_I$. 
$N_{VM,II}$: The total number of the vibration normal modes of a cluster II.

$H_{ADD,I}$: The heat generated when one gaseous CO$_2$ molecule is weakly captured by a RS and to form I.

$N_{II}$: The population of the transition state II.

**Section 4-2**

$N_{III}$: The population of the Structure III.

$N_{IV}$: The population of the transition state IV.

**Section 4-3**

$N_{V}$: The population of the Structure V.

$N_{VI}$: The population of the transition state VI.

$v_{TSUBSTATE/2}$: The thermal velocity of one of the fragments of the divided substrate molecule.

**Section 4-4**

$N_{VIII}$: The population of the transition state VIII.

**Supplements**

$V_{T,CO2}$: Thermal velocity of CO$_2$ at the transition state of CO$_2$ capture.

RS: The complex consists of (1) simplified reaction center of Rubisco, (2) substrate (RuBP).

$V$: The volume of gas phase CO$_2$ molecules.

II: A transition state II of the addition of CO$_2$.

$E_{\ell_{CO2}}$: The energy level of $\ell_{CO2}$. 
\( E_{C.E}(N_{TS,II}) \): Total energy of the canonical ensemble when the number of the transition state is \( N_{TS,II} \).

\( Z_{C.E}(N_{TS,II}) \): The partition function of the canonical ensemble to be used to calculate the Reaction Rate of addition of \( \text{CO}_2 \), which is a function of \( N_{TS,II} \).

\( N_{VM,R} \): The number of vibration normal mode of the reactant of a single cluster reaction or single substrate reaction.

\( N_{VM,III} \): The number of vibration normal modes of the product of the addition of \( \text{CO}_2 \). That is the number of vibration normal modes of Structure III.

\( \Xi_{CAP} \): The grand canonical function for addition of \( \text{CO}_2 \).

\( H_{ACT,ADD} \): The activation energy of addition of \( \text{CO}_2 \).

\( N_{VM,RS} \): The number of vibration normal mode of the RS

\( R_{ADD} \): The number of the \( \text{CO}_2 \) molecules added to form Structure III in one second to produce a reaction product.

\( N_{R,1C} \): The number of single cluster reactants.

\( N_{TS,1C} \): The number of single cluster transition states.

\( E_{C.E}(N_{TS,1C}) \): Total energy of the canonical ensemble when the number of the single cluster transition state is \( N_{TS,1C} \).

\( E_{C.E}(N_{TS,1C}) \): Total energy of the canonical ensemble when the number of the single cluster transition state is \( N_{TS,1C} \).

\( \Xi_{1C} \): The grand canonical function for a single cluster reaction.

\( R_{P,1C} \): the number of the product that is produced in one second in a single cluster reaction

\( m_{\text{SUBSTRATE/2}} \): the thermal velocity of one of the fragments of the divided substrate molecule.

\( H_{ACT,1C} \): The activation energy of a single substrate reaction.
S.I  THE DERIVATION OF $TON$ OF THE REACTION OF ADDITION OF $CO_2$

S.I.1  CANONICAL ENSEMBLE FOR THE CALCULATION OF $TON$ FOR THE REACTION OF ADDITION of $CO_2$

We assume that there were originally $N_{RS}$ RS.’s and $N_{CO2}$ gaseous molecules, before the addition reaction occurs. In an absolute reaction rate theory, the reactants (RS’s and gaseous $CO_2$ molecules) and the transition states (Structure II) are assumed to be in a thermal equilibrium after the addition reaction occurs. Let the total number of the transition states (i.e., the total number of Structure II), be $N_{II}$. The value of $N_{II}$ fluctuates by thermal noise. The $<N_{II}>$ is the statistical average number of $N_{II}$. Equation (4.1-1) shows that the derivation of $<N_{II}>$ must be obtained before obtaining the derivation of the turnover number of the addition reaction, $TON(Addition of CO_2)$. Here, we neglect the precursor states, i.e., we neglect Structure I. Then, in the thermal equilibrium, $(N_{RS} - N_{II})$ RS’s remain uncombined with $CO_2$, and $(N_{CO2} - N_{II}) CO_2$ molecules remain uncombined with a RS. We assume that the volume of $CO_2$ remains $V$ in the thermal equilibrium. The energy and the entropy of the total system is given as a function of $N_{II}$. The RS’s, the gaseous $CO_2$ molecules and the transition states (Structure II) form a canonical ensemble. If the value of $N_{II}$ is averaged in the canonical ensemble with the average value, $<N_{II}>$.

S.I.2  PARTITION FUNCTIONS FOR $TON(ADDITION of CO_2)$ CALCULATION
One CO$_2$ molecule has three types of micro states: translational degree of freedom, rotational degree of freedom, and vibration degree of freedom. Thus, one CO$_2$ molecule has micro states, $\ell_{CO2} = 0, 1, 2, 3, \ldots$, which are a combination of three types of micro states.

One RS has only vibrational states, $\ell_{RS} = 0, 1, 2, 3, \ldots$.

One transition state has vibrational states, $\ell_{II} = 0, 1, 2, 3, \ldots$.

The total energy of the canonical ensemble, which is a function of $N_{II}$, is given by

$$E_{C,E}(N_{II}) =$$

$$\sum_{\ell_{RS}}^{N_{RS} - N_{II}} E_{\ell_{RS}} + \sum_{\ell_{CO2}}^{N_{CO2} - N_{II}} E_{\ell_{CO2}} + \sum_{\ell_{II}}^{N_{II}} E_{\ell_{II}}$$

$$= (N_{RS} - N_{II}) \cdot \sum_{\ell_{RS}} E_{\ell_{RS}} + (N_{CO2} - N_{II}) \cdot \sum_{\ell_{CO2}} E_{\ell_{CO2}} + (N_{II}) \cdot \sum_{\ell_{II}} E_{\ell_{II}}$$

Where $E_{\ell_{RS}}$ is the energy level of $\ell_{RS}$, $E_{\ell_{CO2}}$ is the energy level of $\ell_{CO2}$ and $E_{\ell_{II}}$ is the energy level of $\ell_{II}$.

There are

$$\frac{N_{RS}!}{N_{II}! \cdot (N_{RS} - N_{II})!}$$

ways to select $N_{II}$ RUB.SUBs that capture CO$_2$ out of total $N_{RS}$ RSs. Therefore, the partition function of the canonical ensemble, which is a function of $N_{II}$, is given by
\[ Z_{C.E.}(N_{II}) \]
\[ = \left( \frac{N_{RS}!}{N_{II}! \cdot (N_{RS} - N_{II})!} \right) \cdot \left( \sum_{E_{RS}} e^{-\frac{E_{RS}}{k_B \cdot T}} \right) \cdot \left( \sum_{E_{CO2}} e^{-\frac{E_{CO2}}{k_B \cdot T}} \right) \cdot \left( \sum_{E_{II}} e^{-\frac{E_{II}}{k_B \cdot T}} \right) \]
\[ (S.I.2-1) \]

where \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. The partition function of a CO\(_2\) molecule is given by\(^{15} \)

\[ \left( \sum_{E_{CO2}} e^{-\frac{E_{CO2}}{k_B \cdot T}} \right)^{N_{CO2}} = \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot k_B \cdot T}{\hbar^2} \right)^{\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{V_{CO2}^{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}}, \]
\[ (S.I.2-2) \]

Where, \( \hbar \) is the Plank constant, and \( m_{CO2} \) is the mass of a CO\(_2\) molecule.

\( j(T) \) is given by

\[ j(T) = \left( \frac{4 \cdot \pi^2 \cdot I_{CO2} \cdot k_B \cdot T}{\hbar^2} \right) \cdot \prod_{i=1}^{N_{V.M.CO2}} \left( 1 - e^{-\frac{\hbar \cdot v_i}{k_B \cdot T}} \right)^{-1}, \]
\[ (S.I.2-3) \]

Where, \( I_{CO2} \) is the moment of inertia of a CO\(_2\) molecule, \( N_{V.M.CO2} \) is the number of the vibration normal modes of a CO\(_2\) molecule, and \( v_i \) is the frequency of the \( i \)th vibration normal mode.

By inserting (S.I.2-2) to (S.I.2-1), we get...
\[ Z_{C.E.}(N_{II}) = \]
\[
\left( \frac{N_{RS}}{N_{II} \cdot (N_{RS} - N_{II})} \right) \cdot \left( \sum_{l_{RS}} e^{-\frac{e_{l_{RS}}}{k_{B} \cdot T}} \right)^{N_{RS} - N_{II}} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_{B} \cdot T}{h^{2}} \right)^{\frac{3 \cdot (N_{CO2} - N_{II})}{2}} \cdot \frac{V^{N_{CO2} - N_{II}}}{(N_{CO2} - N_{II})}.
\]

\[ j(T)^{N_{CO2} - N_{II}} \cdot \left( \sum_{l_{TS,CAP}} e^{-\frac{e_{l_{II}}}{k_{B} \cdot T}} \right)^{N_{II}}.
\]  

(S.I.2-4)

If the supply of CO\(_2\) gas to a Rubisco from atmosphere is complete (Full ventilation condition), the relation,

\[ N_{CO2} \gg N_{II} \]

holds. In this case, \((N_{CO2} - N_{II})!\) is approximated by

\[ (N_{CO2} - N_{II})! = \frac{N_{CO2}!}{(N_{CO2}) \cdot (N_{CO2} - 1) \cdots (N_{CO2} - N_{II} + 1)} \]

\[ = \frac{N_{CO2}!}{N_{CO2}^{N_{II}} \cdot \left(1 - \frac{1 + 2 + \cdots + N_{II}}{N_{CO2}} + \cdots \right)} \]

\[ \approx \frac{N_{CO2}!}{N_{CO2}^{N_{II}}} \quad \text{(S.I.2-5)} \]
By inserting eq. (S.I.2-5) to eq. (S.I.2-4), we get

\[
Z_{C,E}(N_{II}) \\
\approx \\
\left( \frac{N_{RS}!}{N_{II}! \cdot (N_{RS}-N_{II})!} \right) \cdot \left( \sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{k_B \cdot T}} \right)^{N_{RS}-N_{II}} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{\frac{3 \cdot (N_{CO2}-N_{II})}{2}} \cdot \frac{V^{N_{CO2}-N_{II}} \cdot N_{CO2}^{N_{II}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{k_B \cdot T}} \right)^{N_{II}},
\]

\[
= \\
\left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{V^{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \cdot \left( \frac{N_{RS}!}{N_{II}! \cdot (N_{RS}-N_{II})!} \right) \cdot \left( \sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{k_B \cdot T}} \right)^{N_{RS}-N_{II}} \cdot \\
\left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-3 \cdot N_{II}} \cdot V^{-N_{II}} \cdot N_{CO2}^{N_{II}} \cdot j(T)^{-N_{II}} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{k_B \cdot T}} \right)^{N_{II}}.
\]
S.I.2.6 GRAND CANONICAL FUNCTION for \( \text{TG}(\text{ADDITION of } \text{CO}_2) \) CALCULATION

The grand canonical function for addition of \( \text{CO}_2 \) reaction, \( \Xi_{\text{ADD}} \), is given by definition,

\[
\Xi_{\text{ADD}} = \sum_{N_{II}}^{N_{RS}} Z_{C.E.}(N_{II}) \quad (\text{S.I.3-1})
\]

By inserting eq. (S.I.2-6) to eq. (S.I.3-1), we get
\[ E_{ADD} = \sum_{N_{II} = 1}^{N_{RS}} \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{V^{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \cdot \left( \frac{N_{RS}!}{N_{II}! \cdot (N_{RS} - N_{II})!} \right) \]

\[ \cdot \left( \sum e^{-\frac{E_{\ell RS}}{K_B \cdot T}} \right) \]

\[ \cdot \left\{ \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{N_{CO2}}{V} \cdot j(T)^{-1} \cdot \left( \sum e^{-\frac{E_{\ell II}}{K_B \cdot T}} \right)^{N_{II}} \right\} \]

\[ = \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{V^{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \]

\[ \cdot \sum_{N_{II} = 1}^{N_{RS}} \left( \frac{N_{RS}!}{N_{II}! \cdot (N_{RS} - N_{II})!} \right) \cdot \left( \sum e^{-\frac{E_{\ell RS}}{K_B \cdot T}} \right)^{N_{RS} - N_{II}} \]

\[ \cdot \left\{ \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{N_{CO2}}{V} \cdot j(T)^{-1} \cdot \left( \sum e^{-\frac{E_{\ell II}}{K_B \cdot T}} \right)^{N_{II}} \right\} \]

\[ = \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{V^{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \]

\[ \cdot \left\{ \sum e^{-\frac{E_{\ell RS}}{K_B \cdot T}} \right\} + \left\{ \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{N_{CO2}}{V} \cdot j(T)^{-1} \cdot \left( \sum e^{-\frac{E_{\ell II}}{K_B \cdot T}} \right)^{N_{II}} \right\} \]
S.I.4 AVERAGE POPULATION of the TRANSITION STATES of the ADDITION of CO$_2$, $< N_{II} >$

The number $N_{II}$ fluctuates as the result of thermal fluctuation. The average of the value of $N_{II}$ is given by

$$< N_{II} > = \sum_{N_{II}=1}^{N_{RS}} \frac{N_{II} \cdot Z_{C.E}(N_{II})}{\varepsilon_{ADD}}$$

$$= \frac{1}{\varepsilon_{ADD}} \cdot \sum_{N_{II}=1}^{N_{RS}} N_{II} \cdot Z_{C.E}(N_{II})$$

(S.I.4-1)

By inserting eq. (S.I.2-6) to eq (S.I.4-1), we get

$$< N_{II} >$$

$$= \frac{1}{\varepsilon_{ADD}} \cdot \sum_{N_{II}=1}^{N_{RS}} N_{II} \cdot Z_{C.E}(N_{II})$$
\[
\frac{1}{\bar{E}_{ADD}} \cdot \sum_{N_{RS}}^{N_{II}} (2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T) \cdot \frac{3 \cdot N_{CO2}}{h^2} \cdot \frac{V_{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \cdot \left(\frac{N_{RS}}{(N_{II}! \cdot (N_{RS} - N_{II})!)}\right) \cdot \left(\sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{K_B \cdot T}}\right) \cdot \left(\frac{N_{RS} - N_{II}}{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T} \right)
\]

\[
= \frac{1}{\bar{E}_{ADD}} \cdot \left(\frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2}\right)^{\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{V_{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \cdot N_{RS} \cdot \left(\frac{(N_{RS} - 1)!}{(N_{II} - 1)! \cdot (N_{RS} - N_{II})!}\right) \cdot \left(\sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{K_B \cdot T}}\right) \cdot \left(\frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2}\right)^{-\frac{3}{2}} \cdot \frac{N_{CO2}}{V} \cdot j(T)^{-1} \cdot \left(\sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}}\right) \cdot N_{RS} - N_{II}
\]

\[
= \frac{1}{\bar{E}_{ADD}} \cdot \left(\frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2}\right)^{\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{V_{N_{CO2}}}{N_{CO2}!} \cdot j(T)^{N_{CO2}} \cdot N_{RS} \cdot \left(\frac{(N_{RS} - 1)!}{(N_{II} - 1)! \cdot (N_{RS} - N_{II})!}\right) \cdot \left(\sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{K_B \cdot T}}\right) \cdot \left(\frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2}\right)^{-\frac{3}{2}} \cdot \frac{N_{CO2}}{V} \cdot j(T)^{-1} \cdot \left(\sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}}\right) \cdot N_{RS} - N_{II}
\]
By inserting eq. (S.I.3-2) to eq. (S.I.4-2), we get

\[
< N_{II} > 
\approx \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{\hbar^2} \right)^{-\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{N_{CO2}!}{V^{N_{CO2}}} \cdot j(T)^{-N_{CO2}} \cdot \left[ \left( \sum_{\ell_{RS}} \frac{E_{\ell_{RS}}}{K_B \cdot T} \right) \right]^{-N_{RS}} 
\]

\[
+ \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{\hbar^2} \right)^{-\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{N_{CO2}!}{V^{N_{CO2}}} \cdot j(T)^{-N_{CO2}} \cdot N_{RS} \cdot \left[ \left( \sum_{\ell_{II}} \frac{E_{\ell_{II}}}{K_B \cdot T} \right) \right]^{-N_{RS} - 1} 
\]

\[
\left[ \left( \sum_{\ell_{RS}} \frac{E_{\ell_{RS}}}{K_B \cdot T} \right) \right] + \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{\hbar^2} \right)^{-\frac{3 \cdot N_{CO2}}{2}} \cdot \frac{N_{CO2}!}{V^{N_{CO2}}} \cdot j(T)^{-1} \cdot \left( \sum_{\ell_{II}} \frac{E_{\ell_{II}}}{K_B \cdot T} \right) \right]^{N_{RS} - 1} 
\]

=
\[ N_{RS} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{N_{CO2}}{V} \cdot j(T)^{-1} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}} \right) \cdot \left[ \sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{K_B \cdot T}} \right] + \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{N_{CO2}}{V} \cdot j(T)^{-1} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}} \right) \cdot \left[ \sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{K_B \cdot T}} \right]^{-1} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}} \right)^{-1} \right] \]

(S.I.4-3)

The partial pressure of \( CO_2 \) gas, \( P_{CO2} \) satisfies

\[ \frac{N_{CO2}}{V} = \frac{P_{CO2}}{K_B \cdot T} \quad \text{(S.I.4-4)} \]

By inserting eq. (S.I.4-4) to eq. (S.I.4-3), we get

\[ < N_{II} > = \]

\[ N_{RS} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T)^{-1} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}} \right) \cdot \left[ \sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{K_B \cdot T}} \right] + \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T)^{-1} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}} \right) \cdot \left[ \sum_{\ell_{RS}} e^{-\frac{E_{\ell_{RS}}}{K_B \cdot T}} \right]^{-1} \cdot \left( \sum_{\ell_{II}} e^{-\frac{E_{\ell_{II}}}{K_B \cdot T}} \right)^{-1} \right] \]

(S.I.4-5)
One vibrational mode of the transition sate has imaginary number frequency. So,

\[
\sum_{\ell_{II}} e^{\frac{E_{\ell_{II}}}{k_B \cdot T}} = \left(\frac{(2 \cdot \pi \cdot m_{CO_2} \cdot k_B \cdot T)^{\frac{1}{2}}}{h}\right)^{\delta} \cdot \delta \cdot \prod_{i_{II}=1}^{N_{VM,II}} -1 \left(1 - e^{-\frac{h \cdot v_{i_{II}}}{k_B \cdot T}}\right)^{-1} \cdot e^{-\frac{H_{ACT,ADD}}{k_B \cdot T}}.
\]

(S.I.4-6)

Where \( \delta \) is the typical length of the plateau of the transition state, and is usually

\( \delta \approx 10^{-10} \text{ m} \),

\[
\left(\frac{(2 \cdot \pi \cdot m_{CO_2} \cdot k_B \cdot T)^{\frac{1}{2}}}{h}\right)^{\delta} \cdot \delta \quad \text{is the partition function of the one dimensional translational motion}^{27} \text{ in within the span } \delta. N_{VM,II} \text{ is the number of vibration normal mode of the transition state, and } v_{i_{II}} \text{ is the frequency of the } i_{II} \text{'th vibration normal mode that has real number frequency, and } H_{ACT,ADD} \text{ is the activation energy of addiion of } CO_2. \]

Rubisco substrate complex has only real number frequencies. So,

\[
\sum_{\ell_{RS}} e^{\frac{E_{\ell_{RS}}}{k_B \cdot T}} = \prod_{i_{RS}=1}^{N_{VM,RS}} \left(1 - e^{-\frac{h \cdot v_{i_{RS}}}{k_B \cdot T}}\right)^{-1},
\]
where $N_{VM,RS.}$ is the number of vibration normal mode of the Rubisco substrate complex, and $\nu_{i_RS}$ is the frequency of the $i_{RS}$th vibration normal mode, which has only real number frequencies.

By inserting eqs. (S.I.4-6) and (S.I.4-7) to eq. (S.I.4-5), we get

\[
<N_{II}>
\]

\[
= N_{RS} \cdot P_{CO2} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{\hbar^2} \right)^{\frac{3}{2}} \cdot K_B \cdot T \cdot j(T) \cdot \left( \frac{(2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T)^{\frac{1}{2}}}{h} \right) \cdot \delta \cdot \prod_{i_{II} = 1}^{N_{VM,II} - 1} \left( 1 - e^{-\frac{\hbar \cdot \nu_{i_{II}}}{K_B \cdot T}} \right)
\]

\[
= N_{RS} \cdot P_{CO2} \cdot \frac{(2 \cdot \pi \cdot m_{CO2}) \cdot (K_B \cdot T)^2}{\hbar^2} \cdot j(T) \cdot \left( \delta \cdot \prod_{i_{II} = 1}^{N_{VM,II} - 1} \left( 1 - e^{-\frac{\hbar \cdot \nu_{i_{II}}}{K_B \cdot T}} \right) \right) \cdot \prod_{i_{RS} = 1}^{N_{VM,RS}} \left( 1 - e^{-\frac{\hbar \cdot \nu_{i_{RS}}}{K_B \cdot T}} \right)
\]

(S.I.4-8)
According to the absolute reaction rate theory, the number of the CO₂ molecules added in one second to produce a reaction product is given by

\[ R_{ADD} = <N_{II}> \cdot \frac{V_{T,CO₂}}{\delta} \quad \text{(S.I.4-9)} \]

and \( V_{T,CO₂} \) is the thermal velocity of the captured CO₂ molecule and is given by

\[ V_{T,CO₂} = \left( \frac{K_B \cdot T}{2 \cdot \pi \cdot m_{CO₂}} \right)^{\frac{1}{2}} \quad \text{(S.I.4-10)} \]

By inserting eqs. (S.I.4-8) and (S.I.4-10) to eq. (S.I.4-9), we get

\[
R_{ADD} = N_{RS} \cdot P_{CO₂} \cdot \left( \frac{K_B \cdot T}{2 \cdot \pi \cdot m_{CO₂}} \right)^{\frac{1}{2}} \cdot \delta^{-1} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO₂} \cdot (K_B \cdot T)^2}{h^2} \right) \cdot j(T) \cdot \left( \delta \cdot \prod_{i_{II}=1}^{N_{VM,II}} \left( 1 - e^{-\frac{h \cdot v_{i_{II}}}{K_B \cdot T}} \right) \right)^{-1} \cdot \left( \prod_{i_{RS}=1}^{N_{V,RS}} \left( 1 - e^{-\frac{h \cdot v_{i_{RS}}}{K_B \cdot T}} \right) \right)^{-1} \cdot e^{H_{ACT,ADD}} \cdot \left( \prod_{CO₂} \right) + \{P \}
\]
Where \( j(T) \) was given by eq. (S.I.2-3).

The turnover number of Rubisco for \( \text{CO}_2 \) capture reaction is given by

\[
TON = \frac{V_{\text{CAP}}}{N_{\text{R.S.}}} \quad (\text{S.I.4-11})
\]

By inserting eq. (S.I.4-8) to eq. (S.I.4-11), we get

\[
TON = P_{\text{CO}_2} \cdot \delta^{-1} \cdot \left( \frac{K_B \cdot T}{2 \cdot \pi \cdot m_{\text{CO}_2}} \right)^{1/2} \cdot \left[ \frac{(2 \cdot \pi \cdot m_{\text{CO}_2}) \cdot (K_B \cdot T)^2}{h^2} \right] \cdot j(T) \cdot \left( \delta \cdot \prod_{i_{\text{II}} = 1}^{N_{\text{VM,II}}} \left( 1 - e^{-\frac{h \cdot v_{i_{\text{II}}}}{K_B \cdot T}} \right) \right)^{-1} \cdot \left\{ \prod_{i_{\text{RS}} = 1}^{N_{\text{VM,RS}}} \left( 1 - e^{-\frac{h \cdot v_{i_{\text{RS}}}}{K_B \cdot T}} \right) \right\}^{-1} \cdot e^{\frac{H_{\text{ACT,ADD}}}{K_B \cdot T}} + \left\{ P_{\text{CO}_2} \right\}^{-1}, \quad (\text{S.I.4-12})
\]

S.II ABSOLUTE REACTION RATE THEORY for RUBISCO FUNDAMENTAL REACTION other than ADDITION of \( \text{CO}_2 \)
S.II.1 DEFINITION of RUBISCO FUNDAMENTAL REACTION other than ADDITION of CO₂

Kannappan et. al introduced Structures I to IX in the RuBiScO reaction. In our present paper, we added the second phosphate base to each of the structures so as for each structure to have two phosphate bases.

S.II.2 The CANONICAL ENSEMBLE to be used to CALCULATE the Rate of REACTIONS other than ADDITION of CO₂

In an absolute reaction rate theory, the reactants and the transition states are assumed to be in a thermal equilibrium. In a system of the present section, there are $N_{R,1C}$ single cluster reactants and $N_{TS,1C}$ single cluster transition states.

S.II.3 The PARTITION FUNCTION of the CANONICAL ENSEMBLE to be USED to CALCULATE the RATE of REACTIONS other than ADDITION of CO₂

Out of $N_{RS,1C}$ Rubisco substrate complexes, $N_{TS,1C}$ transition states are assumed to be formed. One reactant has vibrational states, $\ell_{R,1C} = 0, 1, 2, 3, \ldots \ldots \ldots$. One transition state has vibrational states, $\ell_{TS,1C} = 0, 1, 2, 3, \ldots \ldots \ldots$.

The total energy of the canonical ensemble to be used to calculate the rate of reactions other than Addition of CO₂, $E_{C,E}(N_{TS,1C})$, is given by

$$E_{C,E}(N_{TS,1C}) = \sum_{l=1}^{N_{RS,1C}} \sum_{\ell_{R,1C}} E_{\ell_{R,1C}} + \sum_{m=1}^{N_{TS,1C}} \sum_{\ell_{TS,1C}} E_{\ell_{TS,1C}}$$
\[(N_{R.S.} - N_{TS.1C}) \cdot \sum_{\ell_{R.1C}} E_{\ell_{R.1C}} + N_{TS.1C} \cdot \sum_{\ell_{TS.1C}} E_{\ell_{TS.1C}},\]

Where \(E_{\ell_{R.1C}}\) is the energy level of \(\ell_{R.1C}\) and \(E_{\ell_{TS.1C}}\) is the energy level of \(\ell_{TS.1C}\).

There are

\[\frac{N_{R.S}!}{N_{TS.1C}! \cdot (N_{R.S} - N_{TS.1C})!}\]

ways to select \(N_{TS.1C}\) RUB.SUBs that becomes a transition state out of total \(N_{RS}\) RUB.SUBs. Therefore, the partition function of the canonical ensemble to be used to calculate the rate of reaction other than \(\text{CO}_2\) capture, \(Z_{c.e.}(N_{TS.1C})\) is given by

\[Z_{c.e.}(N_{TS.1C}) =\]
\[\left(\frac{N_{R.S}!}{N_{TS.1C}! \cdot (N_{R.S} - N_{TS.1C})!}\right) \cdot \left(\sum_{\ell_{R.1C}} e^{-\frac{E_{\ell_{R.1C}}}{k_B T}}\right)^{N_{RS} - N_{TS.1C}} \cdot \left(\sum_{\ell_{TS}} e^{-\frac{E_{\ell_{TS.1C}}}{k_B T}}\right)^{N_{TS.1C}},\]

(S.II.3-1)

Where \(k_B\) is the Boltzmann constant.

S.II.4 Grand Canonical Function of the Canonical Ensemble to be used to calculate the Rate of Reactions other than Addition of \(\text{CO}_2\)
The grand canonical function for a single cluster reaction, \( \Xi_{1c} \), is given by definition,

\[
\Xi_{1c} = \sum_{N_{TS,1c}=1}^{N_{RS}} Z_{c.e.}(N_{TS,1c}) \quad (S.II.4-1)
\]

By inserting eq. (S.II.3-1) to eq. (S.II.4-1), we get

\[
\Xi_{1c} \approx \sum_{N_{TS}=1}^{N_{RS}} \left( \frac{N_{R.S.}!}{N_{TS,1c}! \cdot (N_{R.S.} - N_{TS,1c})!} \right) \cdot \left( \sum e^{-\frac{E_{\ell,1c}}{k_B \cdot T}} \right)^{N_{RS} - N_{TS,1c}} \cdot \left( \sum e^{-\frac{E_{\ell,TS,1c}}{k_B \cdot T}} \right)^{N_{TS,1c}}
\]

\[
= \left[ \left( \sum e^{-\frac{E_{\ell,1c}}{k_B \cdot T}} \right) + \left( \sum e^{-\frac{E_{\ell,TS,1c}}{k_B \cdot T}} \right) \right]^{N_{RS}}
\]

(S.II.4-2)

S.II.5 POPULATION of the TRANSITION STATES of REACTIONS other than \( \text{CO}_2 \) CAPTURE REACTION

The number \( N_{TS,1c} \) fluctuates as the result of thermal fluctuation. The average of the value of \( N_{TS} \) is given by
\[
\langle N_{TS.1C} \rangle = \sum_{N_{TS.1C}}^{N_{RS}} \frac{N_{TS.1C} \cdot Z_{c.e.}(N_{TS.1C})}{\mathcal{E}_{1C}}
\]

\[
= \frac{1}{\mathcal{E}_{1C}} \cdot \sum_{N_{TS.1C}}^{N_{RS}} N_{TS.1C} \cdot Z_{c.e.}(N_{TS.1C})
\]

(S.II.5-1)

By inserting eq. (S.II.3-1) to eq. (S.II.5-1), we get

\[
\langle N_{TS.1C} \rangle = \frac{1}{\mathcal{E}_{1C}} \cdot \sum_{N_{TS.1C}}^{N_{RS}} N_{TS.1C} \cdot \left( \sum_{\ell_{R.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{R.1C}}}{K_{B} \cdot T}} \right) \cdot \left( \sum_{\ell_{TS.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{TS.1C}}}{K_{B} \cdot T}} \right) N_{RS} - N_{TS.1C}
\]

\[
= \frac{\left( \sum_{\ell_{TS.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{TS.1C}}}{K_{B} \cdot T}} \right) \cdot N_{RS}}{\mathcal{E}_{1C}} \cdot \sum_{N_{TS.1C}}^{N_{RS}} \left( \frac{(N_{RS} - 1)!}{(N_{TS.1C} - 1) \cdot (N_{RS} - N_{TS.1C})!} \right) \cdot \left( \sum_{\ell_{R.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{R.1C}}}{K_{B} \cdot T}} \right) N_{RS} - N_{TS.1C}
\]

\[
= \frac{\left( \sum_{\ell_{TS.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{TS.1C}}}{K_{B} \cdot T}} \right) \cdot N_{RS} - N_{TS.1C}}{\mathcal{E}_{1C}} \cdot \sum_{N_{TS.1C}}^{N_{RS}} \left( \frac{(N_{RS} - 1)!}{(N_{TS.1C} - 1) \cdot (N_{RS} - N_{TS.1C})!} \right) \cdot \left( \sum_{\ell_{R.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{R.1C}}}{K_{B} \cdot T}} \right) N_{RS} - N_{TS.1C}
\]

\[
= \frac{\left( \sum_{\ell_{TS.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{TS.1C}}}{K_{B} \cdot T}} \right) \cdot N_{RS} - N_{TS.1C}}{\mathcal{E}_{1C}} \cdot \sum_{N_{TS.1C}}^{N_{RS}} \left( \frac{(N_{RS} - 1)!}{(N_{TS.1C} - 1) \cdot (N_{RS} - N_{TS.1C})!} \right) \cdot \left( \sum_{\ell_{R.1C}}^{N_{RS}} e^{-\frac{E_{\ell_{R.1C}}}{K_{B} \cdot T}} \right) N_{RS} - N_{TS.1C}
\]
\[
\left( \sum_{\ell_{\text{TS.1C}}} \frac{e^{-\frac{E_{\ell_{\text{TS.1C}}}}{K_{\text{B}} \cdot T}}}{E_{1C}} \right) \cdot N_{RS} \cdot \left( \sum_{\ell_{\text{R.1C}}} e^{-\frac{E_{\ell_{\text{R.1C}}}}{K_{\text{B}} \cdot T}} + \sum_{\ell_{\text{TS.1C}}} e^{-\frac{E_{\ell_{\text{TS.1C}}}}{K_{\text{B}} \cdot T}} \right)^{N_{RS} - 1}.
\]

(S.II.5-2)

By inserting eq. (S.II.4-2) to eq. (S.II.5-2), we get

\[
< N_{\text{TS.1C}} > =
\left( \sum_{\ell_{\text{R.1C}}} e^{-\frac{E_{\ell_{\text{R.1C}}}}{K_{\text{B}} \cdot T}} \right) + \left( \sum_{\ell_{\text{TS.1C}}} e^{-\frac{E_{\ell_{\text{TS.1C}}}}{K_{\text{B}} \cdot T}} \right)^{-N_{RS}} \cdot \left( \sum_{\ell_{\text{R.1C}}} e^{-\frac{E_{\ell_{\text{R.1C}}}}{K_{\text{B}} \cdot T}} + \sum_{\ell_{\text{TS.1C}}} e^{-\frac{E_{\ell_{\text{TS.1C}}}}{K_{\text{B}} \cdot T}} \right)^{N_{RS} - 1}
\]

\[
= \left( \sum_{\ell_{\text{TS.1C}}} e^{-\frac{E_{\ell_{\text{TS.1C}}}}{K_{\text{B}} \cdot T}} \right) \cdot N_{RS} \cdot \left( \sum_{\ell_{\text{R.1C}}} e^{-\frac{E_{\ell_{\text{R.1C}}}}{K_{\text{B}} \cdot T}} \right) + \left( \sum_{\ell_{\text{TS.1C}}} e^{-\frac{E_{\ell_{\text{TS.1C}}}}{K_{\text{B}} \cdot T}} \right)^{-1}
\]

(S.II.5-3)
According to the absolute reaction rate theory, the number of the product that is produced in one second in a single cluster reaction is given by

\[ R_{1C} = < N_{TS.1C} > \cdot \frac{V_{T, SUB}}{\delta} \quad \text{(S.II.5-4)} \]

Where \( \delta \) is the typical length of the plateau of the transition state, and is usually

\[ \delta \approx 10^{-10} \text{ m} \]

and \( V_{T, SUB} \) is the thermal velocity of the reacting substrate and is given by

\[ V_{T, SUB} = \left( \frac{K_B \cdot T}{2 \cdot \pi \cdot m_{SUB}} \right)^{1/2} \quad \text{(S.II.5-5)} \]

Where \( m_{SUB} \) is the mass of the reacting substrate.

By inserting eq. (S.II.5-3) to eq. (S.II.5-4), we get

\[
R_{1C} = \delta^{-1} \cdot \left( \sum_{\ell_{TS.1C}} e^{-\frac{E_{\ell_{TS.1C}}}{K_B \cdot T}} \right) \cdot N_{RS} \cdot V_{T, SUB} \cdot \left[ \left( \sum_{\ell_{R.1C}} e^{-\frac{E_{\ell_{R.1C}}}{K_B \cdot T}} \right) + \left( \sum_{\ell_{TS.1C}} e^{-\frac{E_{\ell_{TS.1C}}}{K_B \cdot T}} \right) \right]^{-1}
\]

\[ \text{(S.II.5-6)} \]

The turnover number of Rubisco reaction other than \( \text{CO}_2 \) capture is given by
\[ TON = \frac{R_{1C}}{N_{RS}} \quad \text{(S.II.5-7)} \]

By inserting eqs. (S.II.5-6) and (S.II.5-5) to eq. (S.II.5-7), we get

\[
TON = \delta^{-1} \cdot \left( \sum_{\ell_{TS.1C}} e^{-\frac{E_{\ell_{TS.1C}}}{K_BT}} \right) \cdot \left( \frac{K_BT}{2\pi m_{SUB}} \right)^{\frac{1}{2}} \cdot \left[ \left( \sum_{\ell_{R.1C}} e^{-\frac{E_{\ell_{R.1C}}}{K_BT}} \right) + \left( \sum_{\ell_{TS.1C}} e^{-\frac{E_{\ell_{TS.1C}}}{K_BT}} \right) \right]^{-1} \quad \text{(S.II.5-8)}
\]

One vibrational mode of the transition state has imaginary number frequency. So,

\[
\sum_{\ell_{TS.1C}} e^{-\frac{E_{\ell_{TS.1C}}}{K_BT}} = \frac{(2\pi m_{SUB}K_BT)^{\frac{1}{2}}}{h} \cdot \delta \cdot e^{-\frac{H_{ACT.1C}}{K_BT}} \cdot \prod_{i_R=1}^{N_{VM.TS}} \left( 1 - e^{-\frac{h\nu_i}{K_BT}} \right)^{-1} \quad \text{(S.II.5-9)}
\]
Where $H_{\text{ACT.1C}}$ is the activation energy, and $N_{\text{VM.TS}}$ is the number of vibration normal mode of the transition state, and $\nu_{i_r}$ is the frequency of the $i_r$'th vibration normal mode that has real number frequency. $\delta$ was given by eq. (S.1.7-4).

Reactant complex has only real number frequency. So,

$$
\sum \frac{e^{\frac{-E_{R.1C}}{k_B T}}}{\prod_{i=1}^{N_{\text{VM.R.}}}} - 1
$$

(S.II.5-10)

where $N_{\text{VIB.MOD.REACTANT}}$ is the number of vibration normal mode of the reactant, and $\nu_i$ is the frequency of the $i$'th vibration normal mode, which has only real number frequency.

By inserting eqs (S.II.5-9) and (S.II.5-10) to eq. (S.II.5-8), we obtain

$$
TON
$$

= 


\[
\delta^{-1} \cdot \left( \frac{2 \cdot \pi \cdot m_{\text{SUB}} \cdot K_B \cdot T}{h} \right)^2 \cdot \delta \cdot e^{-\frac{H_{\text{ACT,1C}}}{K_B \cdot T}} \cdot \left( \frac{K_B \cdot T}{2 \cdot \pi \cdot m_{\text{SUB}}} \right)^{\frac{1}{2}} \cdot \prod_{i_R = 1}^{N_{\text{VM,TS}} - 1} \left( 1 - e^{-\frac{h \cdot \nu_i}{K_B \cdot T}} \right) \\
\left[ \sum_{\ell_R, iC} \frac{E_{\ell_R, iC}}{K_B \cdot T} \right]^{-1} \cdot \left[ \left( \frac{2 \cdot \pi \cdot m_{\text{SUB}} \cdot K_B \cdot T}{h} \right)^2 \cdot \delta \cdot \prod_{i_R = 1}^{N_{\text{VM,TS}} - 1} \left( 1 - e^{-\frac{h \cdot \nu_i}{K_B \cdot T}} \right) \right]^{-1} \\
\left[ \prod_{i = 1}^{N_{\text{VM,R}}} \left( 1 - e^{-\frac{h \cdot \nu_i}{K_B \cdot T}} \right) \right]^{-1} \cdot e^{-\frac{H_{\text{ACT,1C}}}{K_B \cdot T}} \\
\left[ \prod_{i_R = 1}^{N_{\text{VM,TS}} - 1} \left( 1 - e^{-\frac{h \cdot \nu_i}{K_B \cdot T}} \right) \right]^{-1} \cdot e^{-\frac{H_{\text{ACT,1C}}}{K_B \cdot T}} \right]^{-1}
\]

\[TON\]

\[=\]
\[
\begin{align*}
\frac{K_B \cdot T}{h} \cdot e^{\frac{H_{ACT.1C}}{k_B \cdot T}} \cdot \prod_{i_R=1}^{N_{VM.TS}} \left(1 - e^{\frac{h \cdot v_{i_R}}{k_B \cdot T}}\right)^{-1} \\
\left[ \left( \sum e^{\frac{E_{E.R.1C}}{k_B \cdot T}} \right) + \frac{(2 \cdot \pi \cdot m_{SUB} \cdot K_B \cdot T)^2}{h} \cdot \delta \cdot \prod_{i_R=1}^{N_{VM.TS}} \left(1 - e^{\frac{h \cdot v_{i_R}}{k_B \cdot T}}\right)^{-1} \right]^{-1} \\
\frac{H_{ACT.1C}}{k_B \cdot T}
\end{align*}
\]

(S.II.5-11)

S.III ABSOLUTE REACTION RATE THEORY for COVERAGE of CO2 MOLECULES CAPTURED on Structure I of our present paper

S.III.1 DEFINITION of GASEOUS CO2 CAPTURE REACTION to form Structure I

Structure I of our present paper consists of (1) simplified reaction center of Rubisco, (2) substrate and (3) CO2. We calculated the rate of chemical adsorption of CO2 to the complex consists of simplified reaction center of Rubisco and substrate. We call (1) and (2) complex RS complex.

S.III.2 DEFINITION of the REACTANT

We call the number of RS \(N_{RS}\). We assume that there are \(N_{CO2}\) CO2 molecules in volume V. These RS’s and CO2 molecules are the reactant of the CO2 capture reaction.
S.III.3 DEFINITION of the TRANSITION STATE

The product, Structure I, is a loosely bound complex combined by intermolecular interactions such as Van-Der-Waals force. The activation energy of a physical adsorption is very low and the transition state is not expected to be important.

S.III.4 DEFINITION of the PRODUCT

Structure I is the product. In this paper, Structure I is assumed to be in a thermal equilibrium with the reactant (RS's and \( \text{CO}_2 \) gaseous molecules in volume \( V \)).

S.III.5 The CANONICAL ENSEMBLE to be USED to CALCULATE the REACTION RATE of \( \text{CO}_2 \) CAPTURE

In the present paper, the reactants and the products are assumed to be in a thermal equilibrium. In the case of chemical adsorption, the transition states are ignored. In that system, there are \( N_I \) products. \((N_{RS} - N_I)\) RS's remain uncombined with \( \text{CO}_2 \), and \((N_{CO2} - N_I)\) \( \text{CO}_2 \) molecules remain uncombined with a RS. We assume that the volume of \( \text{CO}_2 \) remains \( V \). RS's, \( \text{CO}_2 \) gaseous molecules and the products (Structure I) are the canonical ensemble to be treated in the absolute reaction rate theory.

S.III.6 COVERAGE

The value of \( N_I \) fluctuates thermally. Just like the way we got eq. (3.1.7-4),

\(< N_I >\)
\[
N_{RS} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-3/2} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T)^{-1} \cdot \left( \sum \frac{E_{\ell_i}}{K_B \cdot T} \right).
\]

\[
\left\{ \sum \frac{E_{\ell_{RS}}}{K_B \cdot T} \right\} + \left\{ \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right\}^{-3/2} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T)^{-1} \cdot \left( \sum \frac{E_{\ell_i}}{K_B \cdot T} \right)^{-1}.
\]

(S.III.6-1)

where,
\[
\sum_{\ell_{RS}} \frac{E_{\ell_{RS}}}{K_B \cdot T} = \prod_{i=1}^{N_{VM,RS}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right)^{-1}, \quad (S.III.6-2)
\]

And
\[
\sum_{\ell_i} \frac{E_{\ell_i}}{K_B \cdot T} = \prod_{i=1}^{N_{VM,I}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right)^{-1} \cdot e^{\frac{H_{CAPI}}{K_B \cdot T}}, \quad (S.III.6-3)
\]

Where \(N_{VM,PI}\) is the number of the normal mode of the product of physical adsorption (the number of the normal mode of Structure I), \(H_{CAPI}\) is the heat mitted when one \(CO_2\) molecule is captured and a cluster in the Structure I is formed. By inserting eqs. (S.III.6-2) and (S.III.6-3) to eq. (S.III.6-1), we get

\[
< N_I > =
\]

\[
N_{RS} \cdot \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-3/2} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T)^{-1} \cdot \left( \prod_{i=1}^{N_{VM,I}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right)^{-1} \cdot e^{\frac{H_{CAPI}}{K_B \cdot T}} \right).
\]
\[
\left\{ \prod_{i=1}^{N_{VM,RS}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right) \right\}^{-1} + \left\{ \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T) \right\}^{-1} \cdot \left( \prod_{i=1}^{N_{VM,I}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right) \right) \cdot e^{\frac{H_{CAP}}{K_B \cdot T}} \right) \\
\]  

\[
(S.III.6-4)
\]

The ratio $\theta$ is defined by

\[
\theta = \frac{<N_{PRO,CAP_I}>}{N_{RS}} \quad (S.III.6-5)
\]

By inserting (S.III.6-4) to (S.III.6-5), we get

\[
\theta = \left\{ \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T) \right\}^{-1} \cdot \left( \prod_{i=1}^{N_{VM,I}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right) \right) \cdot e^{\frac{H_{CAP}}{K_B \cdot T}} \right\} \\
\]

\[
\left\{ \prod_{i=1}^{N_{VM,RS}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right) \right\}^{-1} + \left\{ \left( \frac{2 \cdot \pi \cdot m_{CO2} \cdot K_B \cdot T}{h^2} \right)^{-\frac{3}{2}} \cdot \frac{P_{CO2}}{K_B \cdot T} \cdot j(T) \right\}^{-1} \cdot \left( \prod_{i=1}^{N_{VM,I}} \left( 1 - e^{-\frac{h \cdot v_i}{K_B \cdot T}} \right) \right) \cdot e^{\frac{H_{CAP}}{K_B \cdot T}} \right\}^{-1} \\
\]

\[
(S.III.6-6)
\]

S.IV THE ROLE OF PHOSPHATE BASIS TO ACCELERATE REACTION RATES

The phosphate basis in the substrate of the Rubisco reaction is originated from adenosine triphosphate (ATP), ATP is well known that it activates varieties of biochemical reactions. In the case of the present paper, the C2-C3 bond scission is,
for example, activated by both of the two phosphate bases originated from ATP, but the distance from the second phosphate base and C2-C3 bond is distant. We suggest the following “Phosphate Base Conjugation Mechanism”.

Scheme S1 Phosphate Base Conjugation Mechanism.