

Supporting Information for:

New insights into 3M3M1B: roles of water on the ·OH-initiated degradation and aerosol formation in the presence of NO_x (X=1, 2) and alkali

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Table S1. Calculated rate constants at different temperatures (in K) and heights (in km) in the Earth atmosphere (in $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$).

T	Altitude	k_1	k_2	k_3	k_4	k_5	k_6	k
200	12	5.40E-14	6.43E-12	3.54E-13	2.10E-13	2.36E-12	6.23E-12	1.56E-11
217	10	5.50E-14	6.72E-12	3.83E-13	2.10E-13	2.65E-12	6.06E-12	1.61E-11
223	9	5.55E-14	6.83E-12	3.94E-13	2.10E-13	2.77E-12	6.02E-12	1.63E-11
230	8	5.61E-14	6.97E-12	4.06E-13	2.10E-13	2.90E-12	6.00E-12	1.65E-11
236	7	5.66E-14	7.10E-12	4.18E-13	2.11E-13	3.02E-12	5.99E-12	1.68E-11
243	6	5.73E-14	7.25E-12	4.31E-13	2.12E-13	3.17E-12	5.99E-12	1.71E-11
249	5	5.79E-14	7.38E-12	4.42E-13	2.12E-13	3.30E-12	6.00E-12	1.74E-11
256	4	5.86E-14	7.55E-12	4.56E-13	2.13E-13	3.45E-12	6.02E-12	1.77E-11
262	3	5.93E-14	7.69E-12	4.68E-13	2.14E-13	3.59E-12	6.05E-12	1.81E-11
269	2	6.02E-14	7.87E-12	4.83E-13	2.16E-13	3.76E-12	6.09E-12	1.85E-11
275	1	6.09E-14	8.02E-12	4.96E-13	2.17E-13	3.90E-12	6.13E-12	1.88E-11
282	0	6.18E-14	8.21E-12	5.11E-13	2.19E-13	4.08E-12	6.19E-12	1.93E-11
288	0	6.26E-14	8.38E-12	5.24E-13	2.20E-13	4.23E-12	6.24E-12	1.97E-11
296	0	6.37E-14	8.60E-12	5.42E-13	2.23E-13	4.45E-12	6.32E-12	2.02E-11
								(1.64±0.18)E-11
298	0	6.40E-14	8.66E-12	5.47E-13	2.23E-13	6.34E-12	4.5E-12	2.03E-11

Table S2. Predicted acute and chronic toxicity of 3M3M1B and the main products of hydroxylation of 3M3M1B. The GHS classification LC₅₀, EC₅₀, and ChV units are mgL⁻¹.

Compound	Acute toxicity (mg/L)			Chronic toxicity (ChV) (mg/L)		
	Fish (LC ₅₀)	Daphnid (LC ₅₀)	Green Algae (EC ₅₀)	Fish	Daphnid	Green Algae
3M3M1B	2367.28	1165.51	481.44	195.57	76.43	91.77
CH ₃ OC(CH ₃) ₂ CH ₂ CHO	44.03	155.36	166.18	12.36	16.85	42.57
CH ₃ OC(CH ₃) ₂ CH ₂ COOH	16521.57	8307.30	3743.55	1399.20	577.62	747.86

^A R=-C(CH₃)₂OCH₃

Not harmful
 Harmful
 Toxic

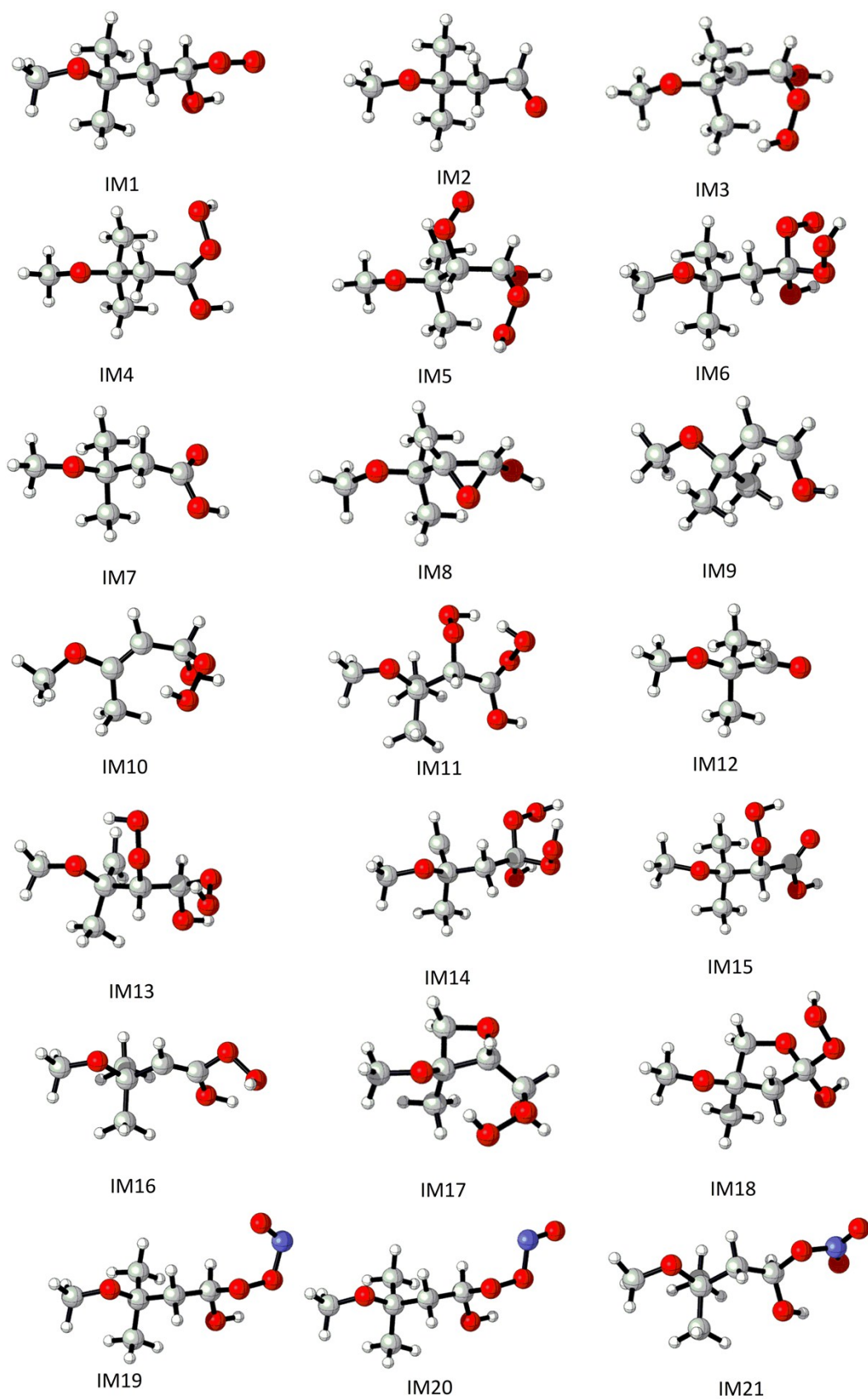


Figure S1. The geometries for the stationary points and transition states in gaseous phase involving the subsequent degradation of subsequent behaviors of peroxy radical in the absence and presence of NO.

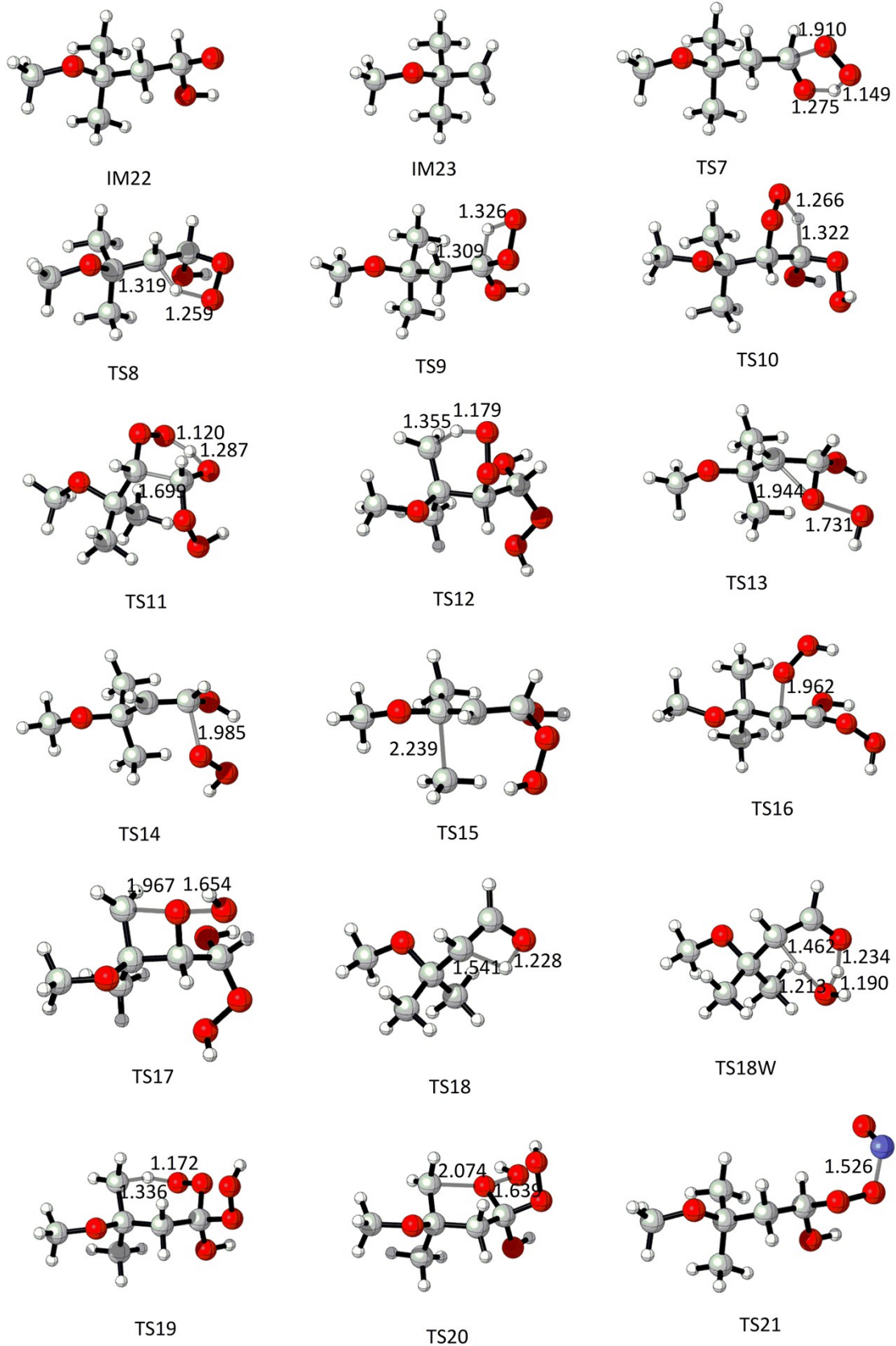


Figure S1. (Continued)

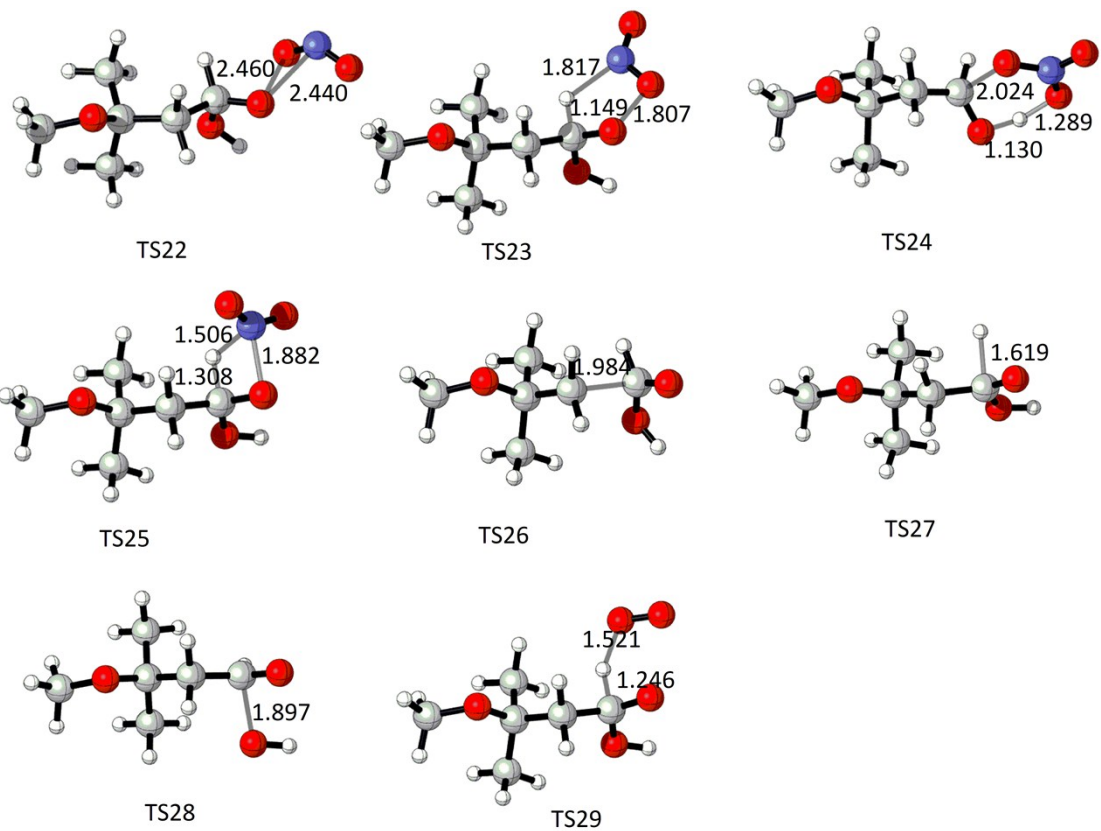


Figure S1. (Continued)

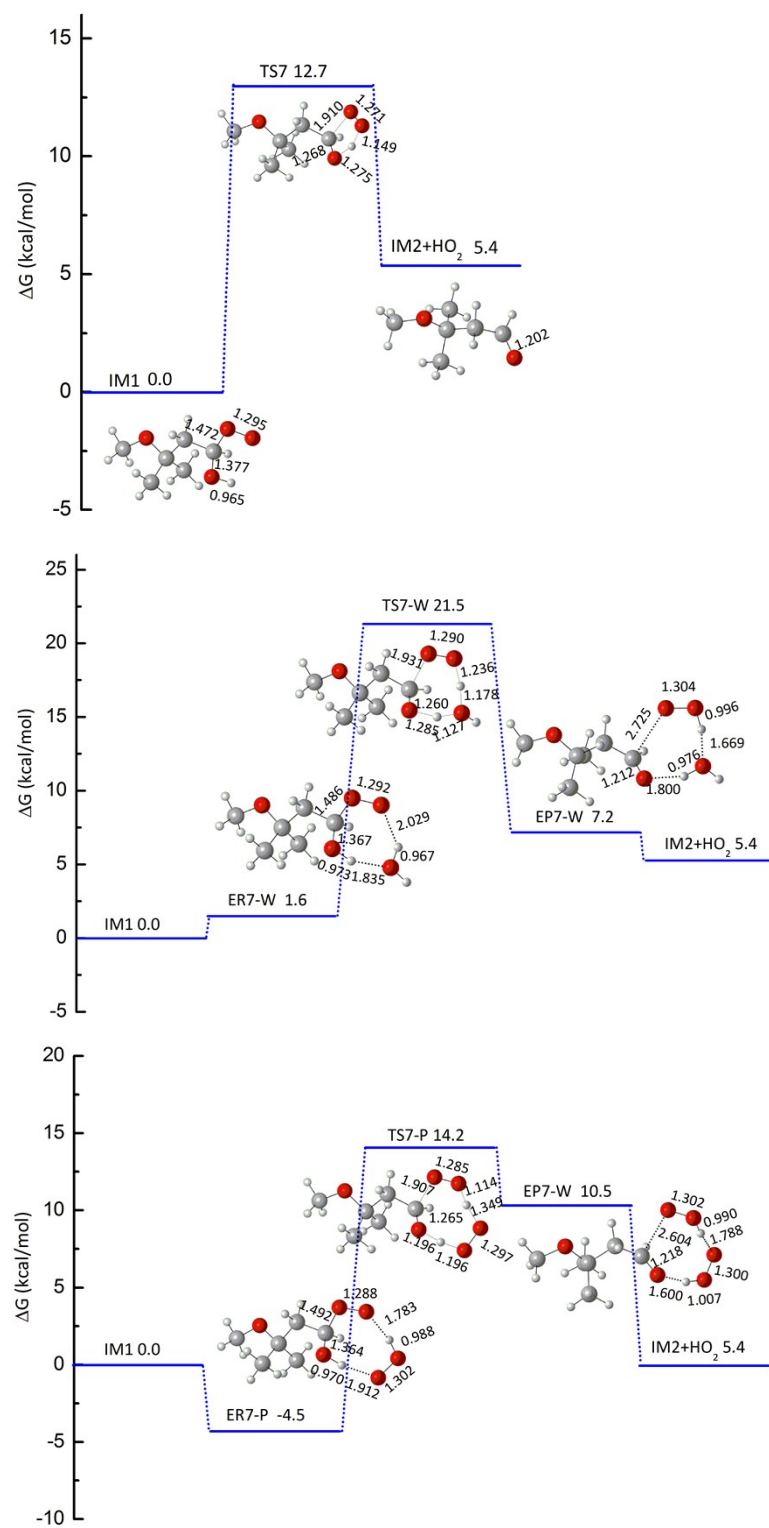
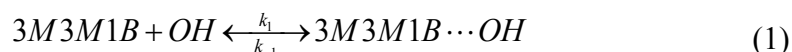


Figure S2. Gibbs free energies potential surfaces for the decomposition of the $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{OO}\cdot)\text{HOH}$ (IM1) in the absence and presence of H_2O and $\text{HO}_2\cdot$ radical. The optimized geometries of the primary species together with certain bond distances (in Å) are also listed.

The expression equation for calculating the rate constants of the reactions. The concentration of the particular catalyst is considered and the catalytic effect of the catalyst on the reaction is measured by the effective rate constant. The specific calculation formula is as follows:

In fact, for the 3M3M1B + OH reaction without catalyst, it can occur according to the two-step mechanism proposed in eqs 1 and 2:



If k_1 and k_{-1} are the forward and reverse rate constants for the first step, respectively, and k_2 corresponds to the second step, the rate constant for this process is shown by eq. 3 according to the steady-state conditions.¹

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \quad (3)$$

Due to the very loose transition state, the entropy change in k_{-1} is much larger than in the formation of products. Therefore, k_{-1} is considerably larger than k_2 ,¹⁻⁴ and a pseudo equilibrium assumption can be used in the formation of the reactant complex. Hence, eq. 3 can be represented as

$$k = \frac{k_1}{k_{-1} + k_2} k_2 = k_{eq} k_2 \quad (4)$$

where K_{eq} and k_2 are the equilibrium constant of the first step and the rate constant of the second step in the reactions, and they can be displayed by eq. 5 and 6, respectively.

$$k_{eq} = \frac{\sigma Q_{R_1 \cdots R_2}}{Q_{R_1} Q_{R_2}} \exp\left(\frac{E_{3M3M1B+OH} - E_{3M3M1B \cdots OH}}{RT}\right) \quad (5)$$

$$k_2 = \frac{\kappa \sigma}{\beta h} \frac{Q_{TS}}{Q_{RC}} \exp\left(-\frac{E_{TS} - E_{3M3M1B \cdots OH}}{RT}\right) \quad (6)$$

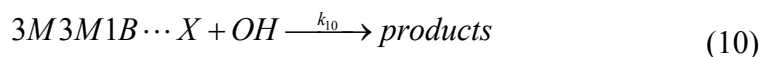
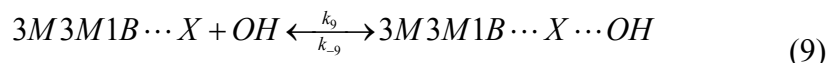
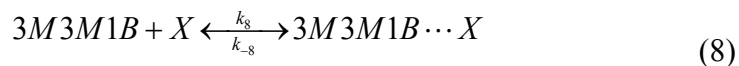
The total rate constant k can be obtained as

$$k = k_2 \frac{\sigma Q_{R_1 \cdots R_2}}{Q_{R_1} Q_{R_2}} \exp\left(\frac{E_{3M3M1B+OH} - E_{3M3M1B \cdots OH}}{RT}\right) \quad (7)$$

where σ is the symmetry factor; β equals the reciprocal of Boltzmann's constant; h

is Planck's constant; κ is the tunneling factor; Q_{ER} and Q_{TS} are partition functions for the reactant complexes and transition state, respectively.

For the reaction assisted by water, ammonia, formic acid or sulfur acid, the following three steps have been taken into account:



According to Fliegl⁵ and Sinha⁶, the above reaction sequence is typically viewed as one involving the formation of the three-body complex prereactive collision complex, which then undergoes unimolecular reaction. From the energy information, it can be concluded that reaction 10 is the rate-determining step, and the rate can be expressed as

$$\frac{d[p]}{dt} = k_{10}[3M3M1B \cdots X \cdots OH] \quad (11)$$

Applying a steady-state approximation to $3M3M1B \cdots X \cdots OH$ and assuming that it is in equilibrium with the reactants and by assuming that the equilibrium of reaction 6 is not inferred by reaction 9, then

$$[3M3M1B \cdots X \cdots OH] = \frac{k_9[3M3M1B \cdots X][OH]}{k_{-9} + k_{10}} \quad (12)$$

where $[3M3M1B \cdots X] = K_{eq8}[3M3M1B][X]$. Because k_{-9} is larger than k_{10} , eq 12 can be expressed as

$$[3M3M1B \cdots X \cdots OH] = \frac{k_9 K_{eq8}[3M3M1B][X][OH]}{k_{-9}} \quad (13)$$

$$[3M3M1B \cdots X \cdots OH] = K_{eq8}K_{eq9}[3M3M1B][X][OH] \quad (14)$$

Consequently, eq. 11 can be given as

$$\frac{d[p]}{dt} = k_{10} K_{eq8}K_{eq9}[3M3M1B][X][OH] \quad (15)$$

In the end,, the rate constant k for the total reaction is obtained by eq. 16

$$k = k_{10} K_{\text{eq}8} K_{\text{eq}9} [X] \quad (16)$$

where $K_{\text{eq}8}$ and $K_{\text{eq}9}$ are the equilibrium constants for reactions 8 and 9, respectively, k_{10} is the rate constant of reaction 10, and $[X]$ is the atmospheric concentration of catalyst.

If reaction 8 is not taken into account, the rate constants for the title reaction assisted by catalyst can be represented as

$$k' = K_{\text{eq}9} k_{10} \quad (17)$$

References

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