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The influence of $(H_2O)_{1\text{-}2}$ in the HOBr + HO_2 Gas-Phase Reaction

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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 HOBr + HO_2 reaction without catalyst, it can occur according to the two-step mechanism proposed in equation 1 and 2:

$$HOBr + HO_2 \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} HOBr \cdots HO_2 \qquad (eq.1)$$

$$HOBr \cdots HO_2 \xrightarrow{k_2} Products \qquad (eq.2)$$

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.

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

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

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

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.

$$k_{eq} = \frac{\sigma Q_{\mathrm{R_1L\ R_2}}}{Q_{\mathrm{R_1}} Q_{\mathrm{R2}}} \exp\left(\frac{E_{\mathrm{HOBr+HO_2}} - E_{\mathrm{HOBrL\ HO_2}}}{RT} \right) \qquad \text{(eq.5)}$$

$$k_2 = \frac{\kappa\sigma}{\beta h} \frac{Q_{TS}}{Q_{RC}} \exp\left(-\frac{E_{TS} - E_{\mathrm{HOBrL\ HO_2}}}{RT} \right) \qquad \text{(eq.6)}$$

The total rate constant k can be obtained as

$$k = k_2 \frac{\sigma Q_{\mathrm{R_1L\ R_2}}}{Q_{\mathrm{R_1}} Q_{\mathrm{R2}}} \exp\left(\frac{E_{\mathrm{HOBr+HO_2}} - E_{\mathrm{HOBrL\ HO_2}}}{RT} \right) \qquad \text{(eq.7)}$$

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.

Table S1. Calculated equilibrium coefficients for the generation of the $HO_2\cdots H_2O$, $H_2O\cdots HOBr$，$HOBr\cdots H_2O$ and $2H_2O\cdots HO_2$ (cm^3 $molecule^{-1}$) in the temperature range of 216.7-298.2 K.

T	$K_{eq(H_2OL\ HO_2)}$	$K_{eq(H_2OL\ HOBr)}$	$K_{eq(HOBrL\ H_2O)}$	$K_{eq(2H_2OL\ HO_2)}$
298.15	3.78×10^{-21}	7.47×10^{-22}	1.62×10^{-24}	8.15×10^{-31}
288.19	5.91×10^{-21}	1.07×10^{-21}	1.93×10^{-24}	8.98×10^{-31}

275.21	1.11×10^{-20}	1.77×10^{-21}	2.49×10^{-24}	1.03×10^{-30}
262.23	2.23×10^{-20}	3.08×10^{-21}	3.29×10^{-24}	1.20×10^{-30}
249.25	4.80×10^{-20}	5.69×10^{-21}	4.48×10^{-24}	1.41×10^{-30}
236.27	1.12×10^{-19}	1.12×10^{-20}	6.30×10^{-24}	1.70×10^{-30}
223.29	2.91×10^{-19}	2.40×10^{-20}	9.23×10^{-24}	2.08×10^{-30}
216.69	4.92×10^{-19}	3.66×10^{-20}	1.14×10^{-23}	2.33×10^{-30}

Table S2. Computed equilibrium coefficients for the generation of the COMR1, COMRW1, COMRW2, COMRW3, COMRW4, COMRW5 and COMRWW2 respectively (cm^{3}molecule^{-1}) in the temperature range of 216.7-298.2 K

T	k_{COMR1}	k_{COMRW1}	k_{COMRW2}	k_{COMRW3}	k_{COMRW4}	k_{COMRW5}	$k_{COMRWW2}$
298.15	9.05×10^{-24}	1.15×10^{-22}	5.73×10^{-22}	6.40×10^{-24}	2.81×10^{-21}	4.37×10^{-24}	4.01×10^{-23}
288.19	1.15×10^{-23}	1.59×10^{-22}	1.01×10^{-21}	8.02×10^{-24}	5.43×10^{-21}	5.35×10^{-24}	6.61×10^{-23}
275.21	1.60×10^{-23}	2.54×10^{-22}	2.25×10^{-21}	1.10×10^{-23}	1.38×10^{-20}	7.14×10^{-24}	1.34×10^{-22}
262.23	2.32×10^{-23}	4.23×10^{-22}	5.41×10^{-21}	1.57×10^{-23}	3.85×10^{-20}	9.81×10^{-24}	2.93×10^{-22}
249.25	3.48×10^{-23}	7.44×10^{-22}	1.43×10^{-20}	2.31×10^{-23}	1.19×10^{-19}	1.39×10^{-23}	6.88×10^{-22}
236.27	5.47×10^{-23}	1.39×10^{-21}	4.20×10^{-20}	3.56×10^{-23}	4.19×10^{-19}	2.05×10^{-23}	1.78×10^{-21}
223.29	9.06×10^{-}	2.80×10^{-}	1.40×10^{-}	5.76×10^{-23}	1.70×10^{-18}	3.17×10^{-23}	5.18×10^{-}

	23	21	19				21
216.69	1.20×10^{-22}	4.13×10^{-21}	2.72×10^{-19}	7.52×10^{-23}	3.71×10^{-18}	4.02×10^{-23}	9.29×10^{-21}

*K*eq(COMR1), *K*eq(COMRW1), *K*eq(COMRW2), *K*eq(COMRW3), *K*eq(COMRW4), *K*eq(COMRW5) and *K*eq(COMRWW2) are the computed equilibrium constants for the formation of binary complexes COMR1, COMRW1, COMRW2, COMRW3, COMRW4, COMRW5 and COMRWW2, respectively.

Table S3. Calculated equilibrium coefficients for the generation of the $H_2O\cdots H_2O_2$, $H_2O\cdots BrO$，$BrO\cdots H_2O$ and $2H_2O\cdots HO_2$ (cm^3 $molecule^{-1}$) in the temperature range of 216.7-298.2 K.

T	$K_{eq(H_2O\cdots H_2O_2)}$	$K_{eq(H_2O\cdots BrO)}$	$K_{eq(BrO\cdots H_2O)}$	$K_{eq(2H_2O\cdots HO_2)}$

298.15	7.99×10^{-21}	1.82×10^{-23}	7.27×10^{-24}	8.15×10^{-31}
288.19	1.11×10^{-20}	2.12×10^{-23}	9.15×10^{-24}	8.98×10^{-31}
275.21	1.76×10^{-20}	2.62×10^{-23}	1.26×10^{-23}	1.03×10^{-30}
262.23	2.93×10^{-20}	3.31×10^{-23}	1.81×10^{-23}	1.20×10^{-30}
249.25	5.14×10^{-20}	4.29×10^{-23}	2.68×10^{-23}	1.41×10^{-30}
236.27	9.58×10^{-20}	5.71×10^{-23}	4.14×10^{-23}	1.70×10^{-30}
223.29	1.92×10^{-19}	7.87×10^{-23}	6.74×10^{-23}	2.08×10^{-30}
216.69	2.83×10^{-19}	9.40×10^{-23}	8.82×10^{-23}	2.33×10^{-30}

Table S4. Computed equilibrium coefficients for the generation of the COMP1, COMPW1, COMPW2, COMPW3 and COMPW5, respectively ($cm^3 molecule^{-1}$) in the temperature range of 216.7-298.2 K

T	k_{COMP1}	k_{COMPW1}	k_{COMPW2}	k_{COMPW3}	k_{COMPW5}
298.15	1.54×10^{-23}	3.52×10^{-23}	3.63×10^{-23}	8.57×10^{-23}	2.08×10^{-23}
288.19	1.94×10^{-23}	5.04×10^{-23}	4.84×10^{-23}	1.37×10^{-22}	2.70×10^{-23}
275.21	2.66×10^{-23}	8.34×10^{-23}	7.29×10^{-23}	2.65×10^{-22}	3.92×10^{-23}
262.23	3.79×10^{-23}	1.45×10^{-22}	1.14×10^{-22}	5.47×10^{-22}	5.91×10^{-23}
249.25	5.59×10^{-23}	2.68×10^{-22}	1.88×10^{-22}	1.22×10^{-21}	9.28×10^{-23}
236.27	8.60×10^{-23}	5.28×10^{-22}	3.25×10^{-22}	2.97×10^{-21}	1.53×10^{-22}
223.29	1.39×10^{-22}	1.12×10^{-21}	6.01×10^{-22}	8.02×10^{-21}	2.68×10^{-22}

216.69	1.82×10^{-22}	1.71×10^{-21}	8.45×10^{-22}	1.39×10^{-20}	3.66×10^{-22}

*K*eq(COMP1), *K*eq(COMPW1), *K*eq(COMPW2), *K*eq(COMPW3) and *K*eq(COMPW5) are the computed equilibrium constants for the formation of binary complexes COMP1, COMPW1, COMPW2, COMPW3 and COMPW5, respectively.

Table S5: The reverse rate constants of the HO_2+ HOBr reaction without water, a single water molecule and two water molecules in the temperature range of 216.7-298.2 K at different heights in the earth atmosphere.

h(km)	T	k_{TS1}	k''_{TS1W1}	k''_{TS1W2}	k''_{TS1W3A}	k''_{TS1W3B}	k''_{TS1W4}	k''_{TS1W5}	k''_{TS1WW2}
0	298.15	4.94×10^{-21}	5.60×10^{-17}	4.50×10^{-20}	3.19×10^{-29}	1.68×10^{-31}	7.34×10^{-18}	2.74×10^{-19}	8.32×10^{-22}
0	288.19	2.99×10^{-21}	4.74×10^{-17}	3.03×10^{-20}	1.26×10^{-29}	5.41×10^{-32}	6.03×10^{-18}	1.91×10^{-19}	5.90×10^{-22}
2	275.21	1.45×10^{-21}	3.76×10^{-17}	1.76×10^{-20}	3.42×10^{-30}	1.09×10^{-32}	4.59×10^{-18}	1.15×10^{-19}	3.64×10^{-22}
4	262.23	6.63×10^{-22}	2.91×10^{-17}	9.60×10^{-21}	8.10×10^{-31}	1.88×10^{-33}	3.41×10^{-18}	6.56×10^{-20}	2.16×10^{-22}
6	249.25	2.80×10^{-22}	2.22×10^{-17}	4.98×10^{-21}	1.67×10^{-31}	2.72×10^{-34}	2.48×10^{-18}	3.56×10^{-20}	1.20×10^{-22}
8	236.27	1.08×10^{-22}	1.64×10^{-17}	2.39×10^{-21}	2.91×10^{-32}	3.18×10^{-35}	1.74×10^{-18}	1.80×10^{-20}	6.34×10^{-23}
10	223.29	3.70×10^{-23}	1.16×10^{-17}	1.06×10^{-21}	4.14×10^{-33}	2.92×10^{-36}	1.18×10^{-18}	8.47×10^{-21}	3.13×10^{-23}

12	216.69	2.06×10^{-23}	9.73×10^{-18}	6.78×10^{-22}	1.40×10^{-33}	7.76×10^{-37}	9.59×10^{-19}	5.60×10^{-21}	2.10×10^{-23}

Table S6: Effective reverse rate constants for the HO_2 + HOBr + H_2O and HO_2 + HOBr + $2H_2O$ reactions in the temperature range of 216.69-298.15 K (cm^3 $molecule^{-1}$ s^{-1}) at different heights in the earth atmosphere.

h(km)	T	$[H_2O]$	$[H_2O]_2$	k'''_{TS1W1}	k'''_{TS1W2}	k'''_{TS1W3A}	k'''_{TS1W3B}	k'''_{TS1W4}	k'''_{TS1W5}	k'''_{TS1WW2}
0	298.15	7.79×10^{17}	3.1×10^{14}	6.72×10^{-22}	2.80×10^{-22}	4.52×10^{-34}	2.38×10^{-36}	2.16×10^{-20}	1.55×10^{-24}	2.10×10^{-37}
0	288.19	4.34×10^{17}	1.2×10^{14}	3.99×10^{-22}	1.46×10^{-22}	1.16×10^{-34}	4.98×10^{-37}	1.55×10^{-20}	7.58×10^{-25}	6.36×10^{-38}

2	275.21	1.89×10^{17}	2.8×10^{13}	1.89×10^{-22}	5.85×10^{-23}	1.69×10^{-35}	5.40×10^{-38}	9.63×10^{-21}	2.74×10^{-25}	1.05×10^{-38}
4	262.23	7.43×10^{16}	5.7×10^{12}	8.19×10^{-23}	2.09×10^{-23}	1.99×10^{-36}	4.62×10^{-39}	5.65×10^{-21}	8.82×10^{-26}	1.48×10^{-39}
6	249.25	2.64×10^{16}	9.6×10^{11}	3.28×10^{-23}	6.76×10^{-24}	1.89×10^{-37}	3.08×10^{-40}	3.14×10^{-21}	2.52×10^{-26}	1.62×10^{-40}
8	236.27	8.15×10^{15}	1.3×10^{11}	1.15×10^{-23}	1.87×10^{-24}	1.35×10^{-38}	1.48×10^{-41}	1.59×10^{-21}	6.07×10^{-27}	1.40×10^{-41}
10	223.29	2.15×10^{15}	1.3×10^{10}	3.47×10^{-24}	4.38×10^{-25}	7.00×10^{-40}	4.94×10^{-43}	7.38×10^{-22}	1.23×10^{-27}	8.46×10^{-43}
12	216.69	1.01×10^{15}	3.7×10^{9}	1.79×10^{-24}	1.94×10^{-25}	1.33×10^{-40}	7.37×10^{-44}	$4.77\times10^{-}$	4.99×10^{-28}	1.81×10^{-43}

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