The influence of a single water molecule on the reaction of BrO + HO_2

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Table S1. Calculated equilibrium coefficients for the generation of the $HO_2\cdots H_2O$, $H_2O\cdots HO_2$, $BrO\cdots H_2O$ and $H_2O\cdots BrO$ (cm^3 $molecule^{-1}$)

T (K)	K_{eq1}' ($H_2O\cdots HO_2$)	K_{eq2}' ($HO_2\cdots H_2O$)	K_{eq3}' ($BrO\cdots H_2O$)	K_{eq4}' ($H_2O\cdots BrO$)
298.15	8.48×10^{-22}	4.87×10^{-24}	2.73×10^{-23}	2.53×10^{-23}
288.19	1.26×10^{-21}	5.46×10^{-24}	3.32×10^{-23}	3.14×10^{-23}
275.21	2.20×10^{-21}	6.41×10^{-24}	4.19×10^{-23}	4.28×10^{-23}
262.23	4.07×10^{-21}	7.64×10^{-24}	5.42×10^{-23}	6.00×10^{-23}
249.25	8.03×10^{-21}	9.29×10^{-24}	7.20×10^{-23}	8.72×10^{-23}
236.27	1.70×10^{-20}	1.15×10^{-23}	9.87×10^{-23}	1.32×10^{-22}
223.29	3.95×10^{-20}	1.46×10^{-23}	1.40×10^{-22}	2.10×10^{-22}
216.69	6.29×10^{-20}	1.68×10^{-23}	1.71×10^{-22}	2.71×10^{-22}

Table S2. Computed equilibrium rate coefficients for the generation of the COMRW1, COMRW2, COMRW3 and COMRW4, respectively ($cm^3molecule^{-1}$).

T (K)	$[H_2O]^a$	K_{eq}(COMRW1)	K_{eq}(COMRW2)	K_{eq}(COMRW3)	K_{eq}(COMRW4)
298.15	7.79×10^{17}	2.19×10^{-22}	3.66×10^{-14}	6.16×10^{-21}	2.10×10^{-12}
288.19	4.34×10^{17}	4.03×10^{-22}	1.33×10^{-13}	1.41×10^{-20}	6.99×10^{-12}
275.21	1.89×10^{17}	9.51×10^{-22}	8.21×10^{-13}	4.54×10^{-20}	3.82×10^{-11}
262.23	7.43×10^{16}	2.44×10^{-21}	6.07×10^{-12}	1.64×10^{-19}	2.46×10^{-10}
249.25	2.64×10^{16}	6.92×10^{-21}	5.52×10^{-11}	6.78×10^{-19}	1.93×10^{-9}
236.27	8.15×10^{15}	2.20×10^{-20}	6.41×10^{-10}	3.28×10^{-18}	1.90×10^{-8}
223.29	2.15×10^{15}	8.00×10^{-20}	9.88×10^{-9}	1.90×10^{-17}	2.43×10^{-7}
216.69	1.01×10^{15}	1.64×10^{-19}	4.51×10^{-8}	5.04×10^{-17}	1.00×10^{-6}

K_{eq}(COMRW1), K_{eq}(COMRW2), K_{eq}(COMRW3) and K_{eq}(COMRW4) are the computed equilibrium rate coefficients for the generation of binary complexes COMRW1, COMRW2, COMRW3 and COMRW4, respectively. [a]Water concentrations are taken from Ref 1.[1]

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

$$BrO + HO_2 \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} BrO\cdots HO_2$$

$$BrO\cdots HO_2 \xrightarrow{k_2} Products$$

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.

$$k = \frac{k_1 k_2}{k_{-1} + k_2}$$

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,[2-5] and a pseudo equilibrium assumption can be used in the formation of the reactant complex. Hence, eq.3 can be represented as

$$k = \frac{k_1}{k_{-1} + k_2} k_2 = k_{eq} k_2$$

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.

$$k_{eq} = \frac{\sigma Q_{R_1\cdots R_2} k_1 k_2}{Q_{R_1} Q_{R2}} \exp\left(\frac{E_{BrO+HO_2} - E_{BrO\cdots HO_2}}{RT} \right)$$

$$k_2 = \frac{\kappa\sigma}{\beta h}\frac{Q_{TS}}{Q_{RC}}\exp\left(-\frac{E_{TS} - E_{\mathrm{BrO}\cdots\mathrm{HO_2}}}{RT}\right)$$

The total rate constant *k* can be obtained as

$$k = k_2\frac{\sigma Q_{\mathrm{R_1}\cdots\mathrm{R_2}}}{Q_{\mathrm{R_1}}Q_{\mathrm{R}2}}\exp\left(\frac{E_{\mathrm{BrO+HO_2}} - E_{\mathrm{BrO}\cdots\mathrm{HO_2}}}{RT}\right)$$

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.

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