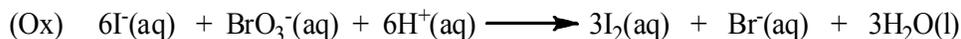


Creating an Energy Profile
For the
Aqueous Oxidation of Iodide by Bromate in Acid

The net ionic equation for the process we are investigating (Ox) is depicted below.



Before we begin to study of the kinetics of this process we need to understand the thermodynamics of the reaction. In this case the information we need is be found in the thermodynamic data tables in the back of freshman chemistry books. The thermodynamic properties of the spectator ions do not change in the reaction so we only have to consider the net ionic equation in our calculations.

$$6I^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightleftharpoons 3I_2(aq) + Br^-(aq) + 3H_2O(l)$$

| | | | | | | |
|----------------------------|---------|--------|-----|-------|---------|---------|
| $\Delta H_f^\circ(kJ/mol)$ | - 55.19 | -67.07 | 0.0 | 22.6 | -121.55 | -285.83 |
| $S^\circ (J/molK)$ | 111.3 | 161.71 | 0.0 | 137.2 | 82.4 | 69.91 |
| $\Delta G_f^\circ(kJ/mol)$ | - 51.57 | 18.60 | 0.0 | 16.40 | -103.96 | -237.18 |

Thermodynamic data from tables in Principles of Modern Chemistry, 4thEd. ; Oxtoby, Gillis, Nachtrieb

The Gibbs free energy change for the process is

$$\Delta G^\circ_{(Ox)} = 3\text{mol}I_2 \left(\frac{16.4\text{kJ}}{\text{mol}I_2} \right) + 1\text{mol}Br^- \left(\frac{-103.96\text{kJ}}{\text{mol}Br^-} \right) + 3\text{mol}H_2O \left(\frac{-237.18\text{kJ}}{\text{mol}H_2O} \right) \\ - 6\text{mol}I^- \left(\frac{-51.57\text{kJ}}{\text{mol}I^-} \right) - 1\text{mol}BrO_3^- \left(\frac{18.60\text{kJ}}{\text{mol}BrO_3^-} \right) - 6\text{mol}H^+ \left(\frac{0\text{kJ}}{\text{mol}H^+} \right)$$

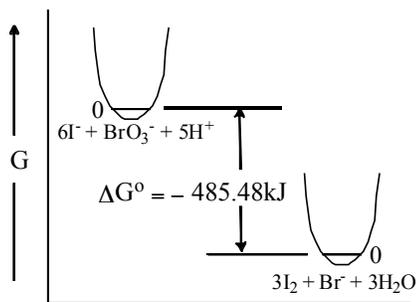
$$\Delta G^\circ_{(Ox)} = -485.48\text{kJ}$$

Similar calculations reveal

$$\Delta H^\circ_{(1)} = -513.03\text{kJmol}^{-1} \quad \text{and}$$

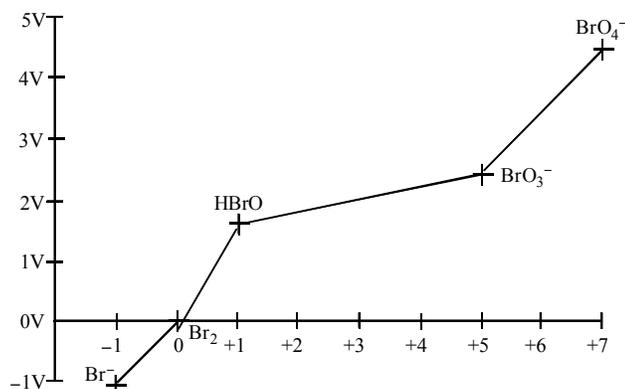
$$\Delta S^\circ_{(1)} = -125.77\text{JK}^{-1}\text{mol}^{-1}$$

The free energy of the reactants is 485.48kJ higher than the free energy of the products in the energy profile for the reaction



The oxidation state of bromine goes from +5 in bromate to -1 in bromide in this 6 electron reduction. The average free energy change is $-485.48\text{kJ}/6e^- \approx -80.9\text{kJ}$ per e^- transferred. This average change in the free energy will provide an estimate for the free energy of some of the intermediates in the proposed mechanisms. The Frost diagram for an element is a plot (on the y-axis) of the oxidation state multiplied by the reduction potential between the oxidation state under consideration to the zero oxidation state. The oxidation state is plotted on the x-axis. The Frost diagram for bromine in aqueous acid (depicted below) reveals an approximately linear increase in the free energy with increasing oxidation state.

The bond dissociation enthalpy for the bromine-iodine bond is 175kJmol^{-1} . The formation of a I-Br bond corresponds to a two electron reduction (since the oxidation state of bromine is lowered by two units). Our approximation suggests that the free energy change for such a process is $\approx 160\text{kJmol}^{-1}$ which implies that the approximation provides a reasonable estimate. A reasonable estimate is one that is qualitatively accurate. We are estimating the energy profile for the entire mechanism and the only experimentally measured energy is the activation energy of the rate-determining (slowest) step so qualitative accuracy will be sufficient for all the other steps.



Frost diagram for bromine in aqueous acid

When using bond dissociation enthalpy in our estimates we will only need to consider the bonds that are made or broken in each process. The following bonds will be made or broken in our proposed mechanisms.

$$\Delta H_{(\text{I-Br})} = 175\text{kJmol}^{-1}, \Delta H_{(\text{Br-Br})} = 190\text{kJmol}^{-1}, \Delta H_{(\text{Br-O})} = 201\text{kJmol}^{-1}, \Delta H_{(\text{O-H})} = 459\text{kJmol}^{-1}$$

Proposing a mechanism from the rate data:

The experiment revealed the following rate law

$$\text{rate} = k[\text{I}^-][\text{BrO}_3^-][\text{H}^+]^2$$

All proposed mechanisms must agree with the experimental rate law.

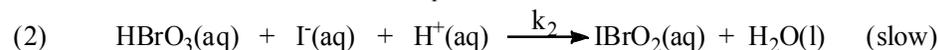
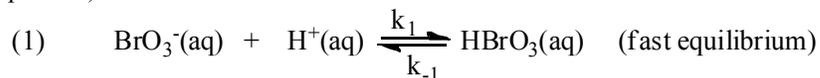
Each iodide ion undergoes a $1e^-$ oxidation while $6e^-$ s are needed to reduce the BrO_3^- ion to Br^- . This mismatch between the reducing agent (the iodide ions) and the oxidizing agent (the bromate ions) suggests a multi-step mechanism. The oxygen atoms in oxoanions and oxides are generally acid labile since they can be protonated to form water that is easily displaced by an atom or molecule that is entering the coordination sphere of the bromine atom.

The order of each concentration in the rate law is the number of times that each ion must occur by the rate-determining (slowest) step. Thus iodide and bromate must occur once and two hydrogen ions are required. The first step cannot be the rate-determining step since it would have to be a tetra-molecular elementary reaction and the probability for that is negligible. A plausible possibility is one or more fast equilibrium process followed by a slow (rate-determining) step. There are many plausible mechanisms that will agree with the rate law, we will only consider three of these.

Case1:

1st A bromate ion is protonated to form a bromic acid intermediate in a fast equilibrium (a bimolecular process)

2nd The bromic acid intermediate combines simultaneously with another proton and an iodide ion to produce the IBrO_2 intermediate and a water molecule in the slow rate determining step. (a termolecular process)



The rate of the slowest step is what is measured in the experiment. So the slowest step determines the rate law. The rate-determining step can be preceded or followed by any number of faster steps without changing the predicted rate law. The rate law given by the slow step is

$$\text{Rate} = k_2[\text{I}^-][\text{HBrO}_3][\text{H}^+]$$

This expression contains the concentration of the bromic acid intermediate and this does not correspond to an experimentally measured quantity. The bromic acid concentration is expressed in terms of observable (controllable) quantities by rearranging the rate expression for the first step.

The first step is an equilibrium therefore the rate of the forward reaction must be equal to the rate of the reverse reaction

$$k_1[\text{BrO}_3^-][\text{H}^+] = k_{-1}[\text{HBrO}_3]$$

The concentration of the bromic acid intermediate is

$$[\text{HBrO}_3] = \left(\frac{k_1}{k_{-1}}\right)[\text{BrO}_3^-][\text{H}^+] = K_1[\text{BrO}_3^-][\text{H}^+]$$

Where K_1 is the equilibrium constant for the equilibrium. Substituting this in the rate law expression

$$\text{rate} = k_2 \left(\frac{k_1}{k_{-1}}\right) [\text{I}^-][\text{BrO}_3^-][\text{H}^+]^2 = k_{\text{obs}}[\text{I}^-][\text{BrO}_3^-][\text{H}^+]^2$$

where $k_{\text{obs}} = k_2 \left(\frac{k_1}{k_{-1}}\right)$

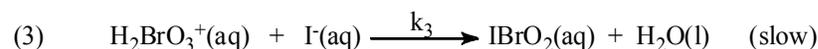
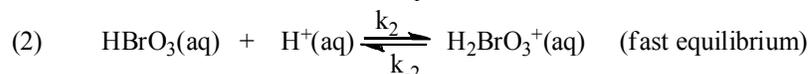
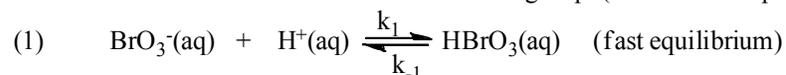
This agrees with the experimental rate law so the first two steps are plausible. The remaining steps do not impact the rate since they are all proposed to be faster than the second step.

Case2:

1st A bromate ion is protonated to form a bromic acid intermediate in a fast equilibrium (a bimolecular process)

2nd The bromic acid intermediate is protonated to form the H_2BrO_3^+ intermediate ion in a fast equilibrium (a bimolecular process).

3rd The H_2BrO_3^+ intermediate ion combines with an iodide ion to produce the IBrO_2 intermediate and a water molecule in the slow rate determining step. (a bimolecular process)



The rate law given by the slow step (step (3)) is

$$\text{rate} = k_3[\text{I}^-][\text{H}_2\text{BrO}_3^+]$$

This expression contains the concentration of the H_2BrO_3^+ intermediate ion and this does not correspond to an experimentally measured quantity. The $[\text{H}_2\text{BrO}_3^+]$ concentration is expressed in terms of observable quantities by rearranging the rate expression for the first two steps.

The second step is a fast equilibrium. The rate law for this step is

$$k_2[\text{HBrO}_3][\text{H}^+] = k_{-2}[\text{H}_2\text{BrO}_3^+]$$

Where the concentration of the H_2BrO_3^+ intermediate ion is given by the expression

$$[\text{H}_2\text{BrO}_3^+] = \left(\frac{k_2}{k_{-2}}\right)[\text{HBrO}_3][\text{H}^+] = K_2[\text{HBrO}_3][\text{H}^+]$$

Where K_2 is the equilibrium constant for this fast equilibrium. Substituting this in the rate law expression for the rate determining step

$$\text{rate} = k_3 \left(\frac{k_2}{k_{-2}}\right) [\text{I}^-][\text{HBrO}_3][\text{H}^+] = k_3 K_2 [\text{I}^-][\text{HBrO}_3][\text{H}^+]$$

The concentration of the bromic acid intermediate $[\text{HBrO}_3]$ can be expressed in terms of controllable concentrations by rearranging the rate law for the first step.

The first step is a fast equilibrium

$$k_1[\text{BrO}_3^-][\text{H}^+] = k_{-1}[\text{HBrO}_3]$$

The concentration of the bromic acid intermediate is

$$[\text{HBrO}_3] = \left(\frac{k_1}{k_{-1}}\right)[\text{BrO}_3^-][\text{H}^+] = K_1[\text{BrO}_3^-][\text{H}^+]$$

Where K_1 is the equilibrium constant for this fast equilibrium.

Substituting this in the rate law expression for step (3)

$$\text{rate} = k_3 K_2 \left(\frac{k_1}{k_{-1}} \right) [\text{I}^-][\text{BrO}_3^-][\text{H}^+]^2 = k_3 K_2 K_1 [\text{I}^-][\text{BrO}_3^-][\text{H}^+]^2 = k_{\text{obs}} [\text{I}^-][\text{BrO}_3^-][\text{H}^+]^2$$

$$\text{where } k_{\text{obs}} = k_3 K_2 K_1$$

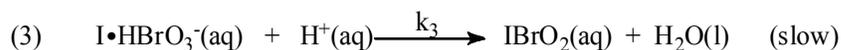
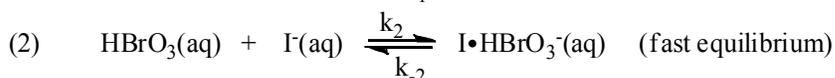
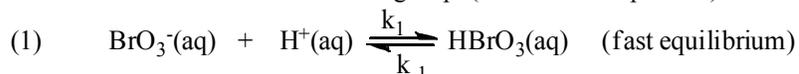
This agrees with the experimental rate law.

Case3:

1st A bromate ion is protonated to form a bromic acid intermediate in a fast equilibrium (a bimolecular process)

2nd The bromic acid intermediate combines with an iodide ion to produce the $\text{I}\cdot\text{HBrO}_3^-$ intermediate ion (a bimolecular process).

3rd The $\text{I}\cdot\text{HBrO}_3^-$ intermediate ion is protonated to produce the IBrO_2 intermediate and a water molecule in the slow rate determining step. (a bimolecular process)



The rate law given by the slow step is

$$\text{rate} = k_3 [\text{I}\cdot\text{HBrO}_3^-][\text{H}^+]$$

Exercise 1: Show that the proposed sequence in case 3 agrees with the experimental rate law.

These three cases illustrate the fact that any mechanism that agrees with the observed rate law is a plausible mechanism. Experimental evidence can verify the rate law but that's all, no mechanism can be proved. Conversely a mechanism can be proven wrong experimentally so the scientific approach to the study of mechanisms is to try to prove them wrong in the lab. The activation energy (E_a) and the frequency factor (A) are also measured in this experiment and other kinetic experiments. This information does not prove or refute any mechanism but it should be taken into consideration and can provide insight into how reasonable a proposed mechanism is. The following data was obtained in this experiment

$$E_a \approx 43.3 \text{ kJ mol}^{-1}, \quad A \approx 5.0 \times 10^9 \text{ M}^{-3} \text{ s}^{-1}$$

Our proposed mechanisms have to be continuously questioned. Plausibility does not imply reasonability. Consider the three mechanisms that we are proposing

Case1: (Termolecular rate determining step)

The most remarkable feature in this case is the termolecular step. A termolecular process is a lot less likely (has a much smaller probability) than bimolecular process. It is reasonable to expect a termolecular process to be slower and therefore rate determining but it is not reasonable to expect it to exclude more likely possibilities. A bimolecular process has a greater probability so if a reaction path involving bimolecular steps is available then the reaction is more likely to proceed in that fashion.

Consider the overall partition function for the process (Z)

$$q_{\text{H}^+} = f_t^3 = q_{\text{I}^-}, \quad q_{\text{HBrO}_3} = f_t^3 f_r^3 f_v^9, \quad q_{\ddagger} = f_t^3 f_r^3 f_v^{12}$$

$$Z = \frac{q_{\ddagger}}{q_{\text{H}^+} q_{\text{I}^-} q_{\text{HBrO}_3}} = \frac{f_t^3 f_r^3 f_v^{12}}{f_t^3 f_t^3 f_r^3 f_r^3 f_v^9} = \frac{f_v^3}{f_t^6} = \frac{(10^0)^3}{(10^9)^6} = 10^{-54}$$

The reactants lose 6 translational degrees of freedom and gain 3 vibrational degrees of freedom upon forming the activated complex. Translational degrees of freedom make by far the greatest contribution to the molecular motions (the contribution from vibrational motions is negligible at room temperature). The entropy of activation is negative because of the loss of translational degrees of freedom.

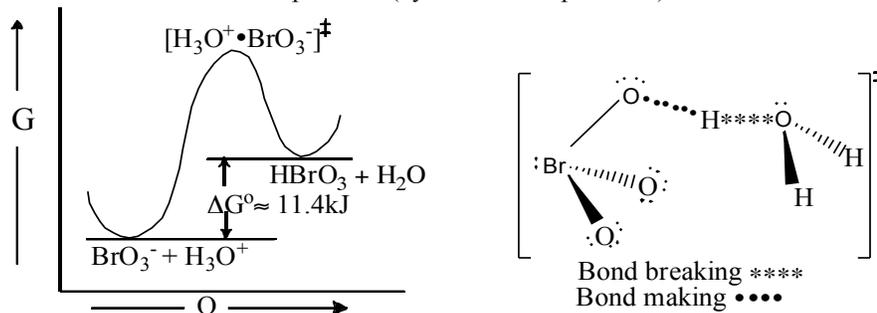
The order of magnitude estimate of the frequency factor we calculated in the kinetic exercises for this termolecular process is

$$A \sim 10^6 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

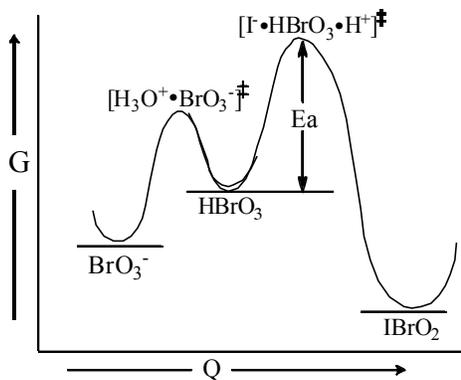
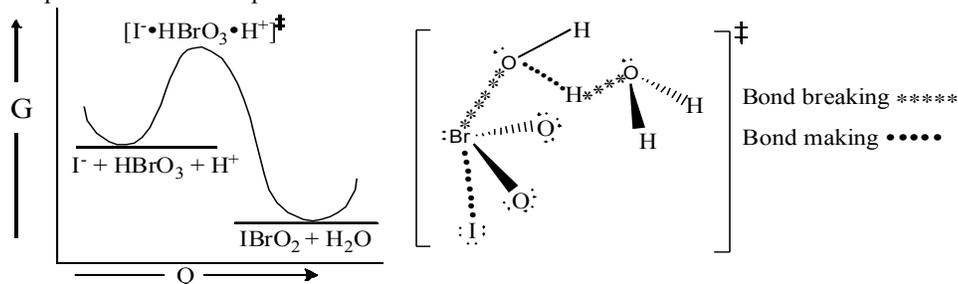
This is only an order of magnitude estimate accurate within 2 orders of magnitude (multiplied or divided by 10^2). Any quantitative conclusions drawn from this number is weak at best. The estimate does provide sound qualitative insight into the process. Inspection of the partition function for the process (Z) reveals which degrees of freedom are lost or gained in the process.

Energy Profile:

Step (1) in this proposed mechanism is expected to have a late transition state. The Pauling rules for estimating (a priori) the pKa of oxy-acids estimate the pKa ≈ -2 for bromic acid (we calculated this in the kinetic exercises). The HBrO₃ intermediate is ≈ 11.4 kJ higher in energy than the reactants so the transition state should resemble the products (by Hammonds postulate).



Step (2) is expected to have an early transition state. The free energy of the IBrO₂ product (+3 oxidation state) is estimated to be ≈ 160 kJmol⁻¹ lower than the Bromate ion BrO₃⁻ (+5 oxidation state). The transition state in this step should look like the reactants. The proton in this transition state has to be added to the oxygen that is bonded to a hydrogen atom so that it can depart bromines coordination sphere as the water produced in this step.



The energy profile for case1. The reaction coordinate Q corresponds to a vibrational degree of freedom of the activated complex. This is the vibrational degree of freedom that is lost to the reaction. The activation energy Ea that is measured experimentally is the height of the energy barrier for the rate determining step.

Case 2: (Combination of I⁻ anion with protonated bromic acid cation rate determining step)

The attractive feature in this case is the electrostatic attraction between the cation and anion in the rate-determining step. This will make the slow step more favorable (lower activation energy Ea). This is a bimolecular reaction between the H₂BrO₃⁺ intermediate cation and an I⁻ anion. There is intra-molecular transfer of a hydrogen atom in the transition state. The partition function for the process Z is

$$Z = \frac{q_{\ddagger}}{q_{I^-} q_{H_2BrO_3^+}} \approx \frac{f_t^3 f_r^3 f_v^{14}}{f_t^3 f_t^3 f_r^3 f_v^{12}} = \frac{f_v^2}{f_t^3} = \frac{(10^0)^2}{(10^9)^3} = 10^{-27}$$

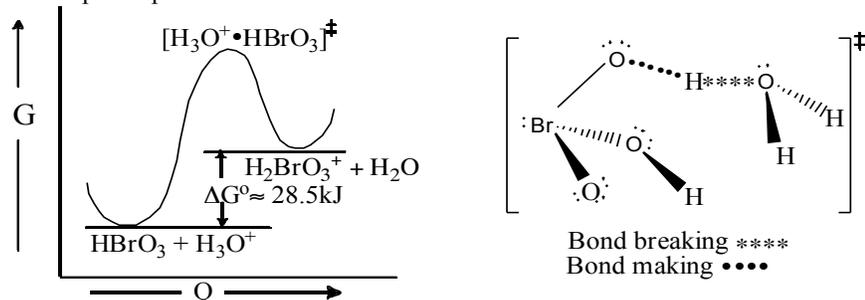
The reactants gain 2 vibrational degrees of freedom and lose 3 translational degrees of freedom upon forming the activated complex.

The order of magnitude estimate of the frequency factor we calculated in the kinetic exercises for this bimolecular process is

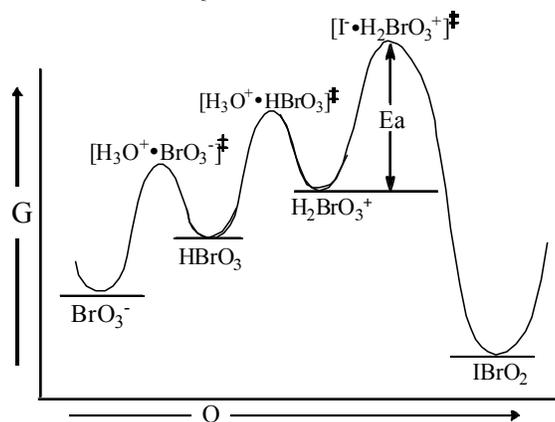
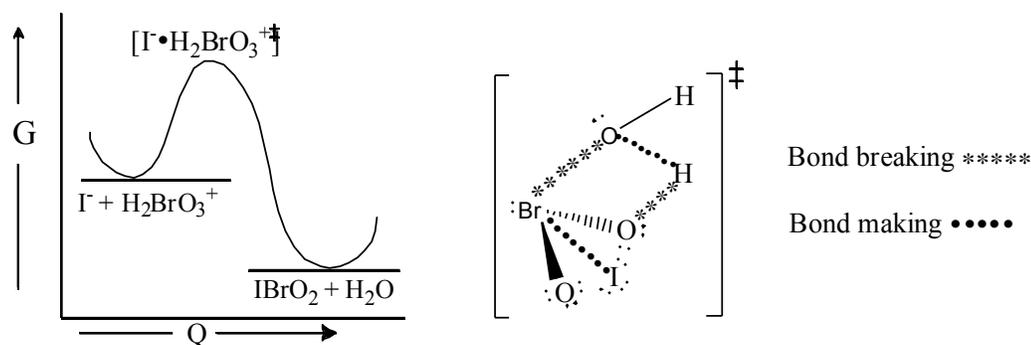
$$A \sim 10^9 \text{Lmol}^{-1}\text{s}^{-1}$$

Step (1) in this case is identical to step (1) in case 1.

Step (2) in this case is the protonation of the HBrO_3 intermediate. The Pauling rules for poly-protic acids require the pK_a of the second proton to be 5pK units higher than the first. We will estimate that the free energy of H_2BrO_3^+ is $5 \times 5.7 \text{kJmol}^{-1} = 28.5 \text{kJmol}^{-1}$ higher than the free energy of HBrO_3 . This step is expected to have a late transition state.



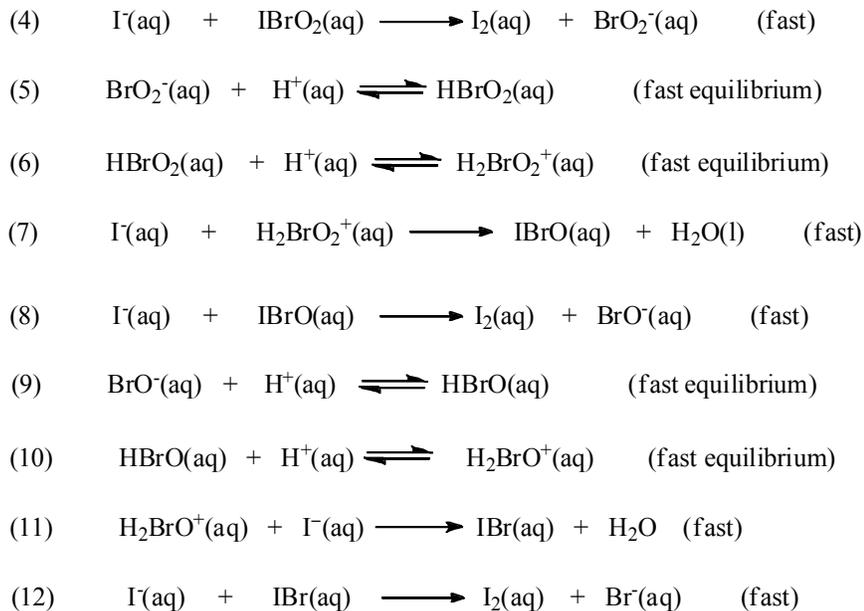
Step (3) is again expected to have an early transition state for the same reasons as the rate determining step in case 1. In this case there is intramolecular proton transfer within the $\text{I} \cdot \text{H}_2\text{BrO}_3^+$ transition state.



The energy profile for case 2. Note that activation energy that is measured experimentally E_a is the largest activation energy of any of the steps. This corresponds to the slowest step of the mechanism. All kinetic experiments measure the activation energy and frequency factor of the slowest step (the rate determining step)

Exercise 2: Estimate the energy profile for case 3. Sketch all three transition states.

A possible sequence for the rest of the reaction (assuming the rate determining step is step (3) as in case 2 and case 3). The steps of the sequence (3) – (8) are assumed to be faster than the rate determining step and therefore cannot be measured by this kinetic experiment.



Exercise 3:

- Verify that the above sequence combines with any of our proposed mechanisms to give the overall reaction (Ox).
- Assuming that $\Delta G^\circ = 0$ for steps (4), (8), and (12) draw the energy profile and sketch the transition state for these steps.
- How many intermediates are there in the overall sequence in each of the three proposed mechanisms?
- How many transition states are there in the overall sequence in each of the three proposed mechanisms?
- How many activated complexes are there in the overall sequence in each of the three proposed mechanisms?
- Draw the energy profile and sketch the transition state for all of the remaining steps.
- Draw the energy profile for the overall sequence for one of the proposed mechanisms.
- Calculate ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger from the experimental E_a and A .

Activation energy E_a :

The relation between the activation energy and bond formation and destruction in the transition state is simple. Recall that bond making is exothermic (energy releasing) while bond breaking is endothermic (energy consuming).

Bond making in the transition state releases energy and lowers the activation energy.

Bond breaking in the transition state consumes energy and raises the activation energy.

Consider the three cases we are studying.

