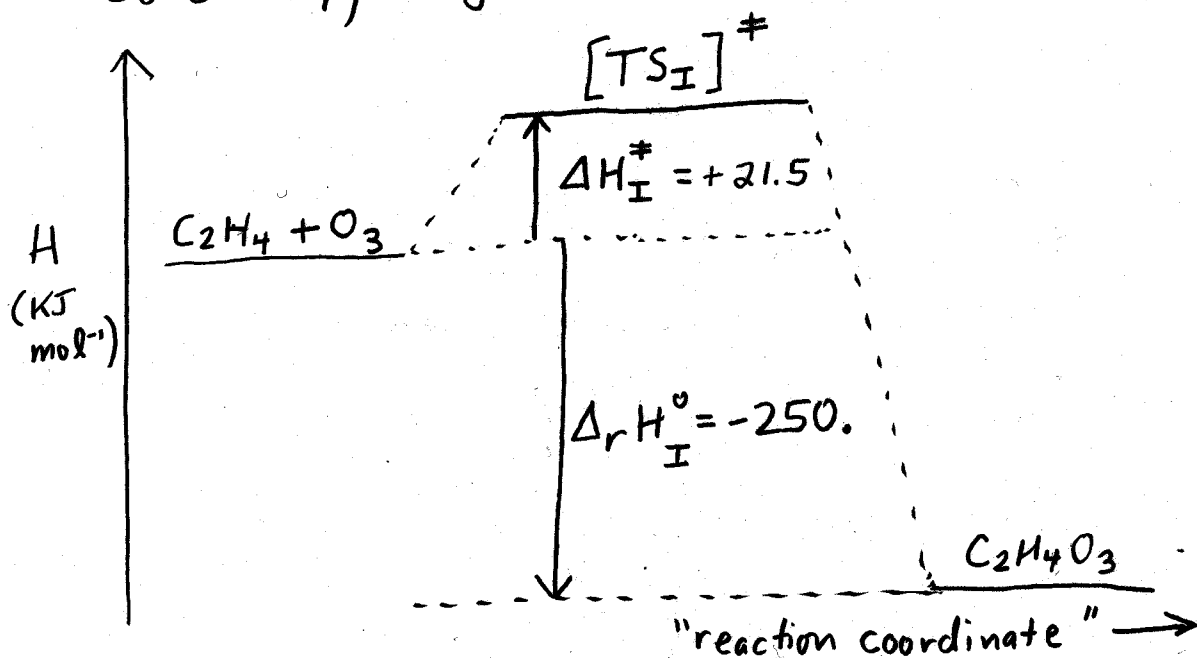


$$\Delta_r H_I^\circ \cong BDE(C=C) + BDE(O=O) - 2BDE(C-O)$$

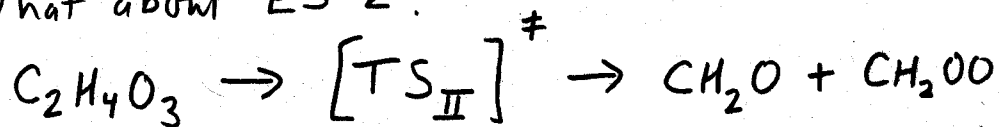
$$\cong [250. + 300. - 2(400.)] \text{ kJ mol}^{-1}$$

$$\Delta_r H_I^\circ \cong -250. \text{ kJ mol}^{-1}$$

So enthalpy diagram for ES I is



What about ES 2?

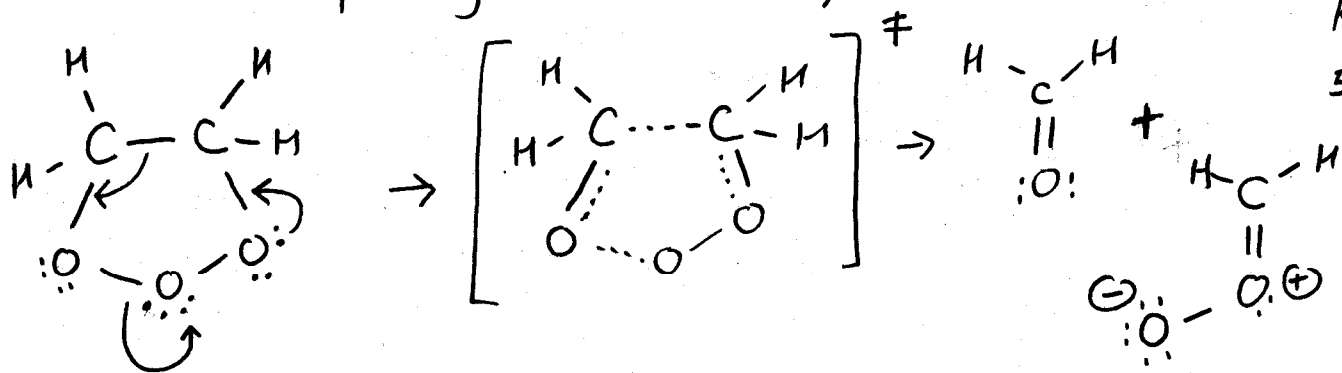


$$\Delta H_{II}^\ddagger = +80. \text{ kJ mol}^{-1} \quad (\text{vs. } BDE(C-C) \cong 400 \text{ kJ mol}^{-1})$$

$\Rightarrow TS_{II}$  also involves simultaneous bond breaking/forming)

$$\Delta_r H_{II}^\circ = +5 \text{ kJ mol}^{-1}$$

More arrow pushing of  $e^-$  density!



Chem 112  
Kinetics  
5/1/06-2

Where does the primary ozonide get the  $80 \text{ kJ mol}^{-1}$ ?

- (1) Collisions with air or solvent molecules  
(high, constant concentrations  $\Rightarrow$  don't appear in rate law)
- (2) Exothermicity of previous elementary step

[ (1) and (2) are true of unimolecular reactions in general ]

Reality check: What overall rate law does our mechanism predict for ozonolysis?

★ The rate law for the slowest step in a mechanism (the "rate-determining" step) is (usually) the rate law for the overall reaction ★

In ozonolysis, ES I is rate-determining

$$\therefore \text{we'd predict } \text{rate} = -\frac{d[\text{C}_2\text{H}_4]}{dt} = k_{\text{I}} [\text{C}_2\text{H}_4] [\text{O}_3]$$

This agrees with experiment!

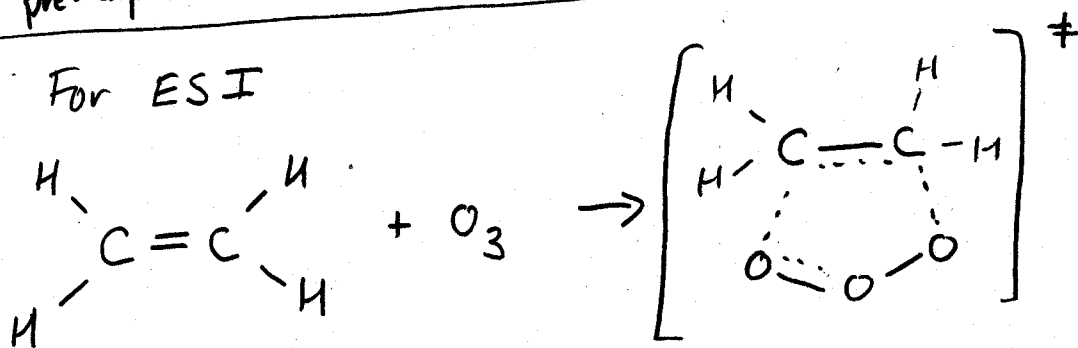
Problem:  $\Delta H_I^\ddagger < \Delta H_{II}^\ddagger$

Chem 112  
Kinetics  
5/1/06-3

Solution: The rate constant is determined by the temporary increase in Gibbs energy ( $\Delta G^\ddagger$ ) required to start a reaction, not just  $\Delta H^\ddagger$ .

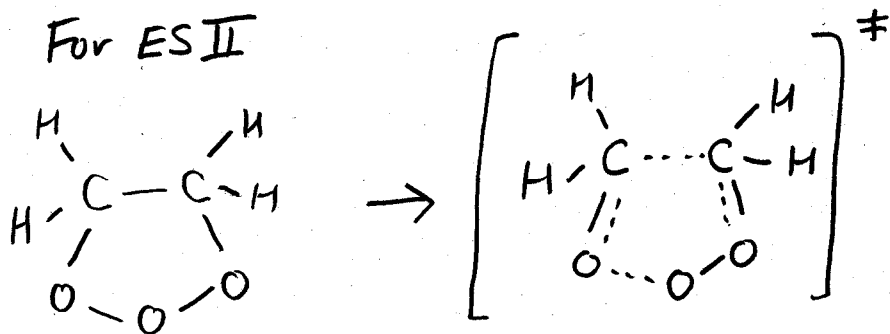
$$\text{i.e. } k = A' e^{-\Delta G^\ddagger/RT} = A' e^{-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT}$$

$$k = \underbrace{A' e^{\Delta S^\ddagger/R}}_{\text{the "customary" pre-exponential factor } A} \underbrace{e^{-\Delta H^\ddagger/RT}}_{\text{Boltzmann distribution}}$$



$$\Delta S_I^\ddagger = -150 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (i.e. very negative)}$$

(typical for bimolecular ES's)



$$\Delta S_{II}^\ddagger = +5 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (i.e. close to zero)}$$

(typical for unimolecular ES's)

Now compare rate<sub>I</sub> and rate<sub>II</sub>. Assume typical reactant concentrations:

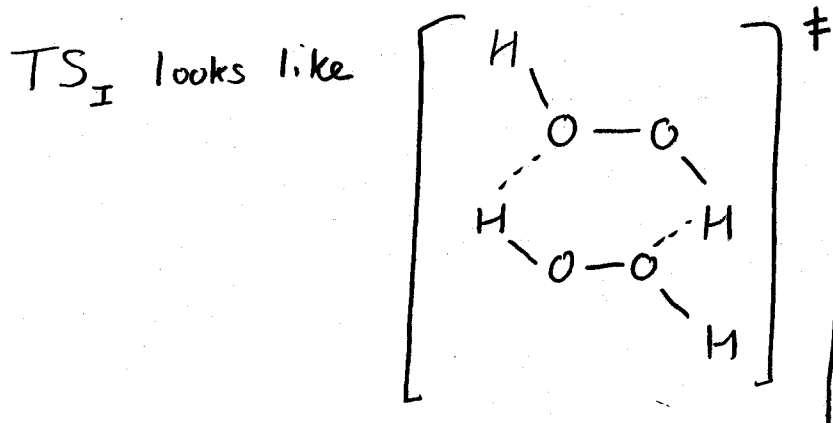
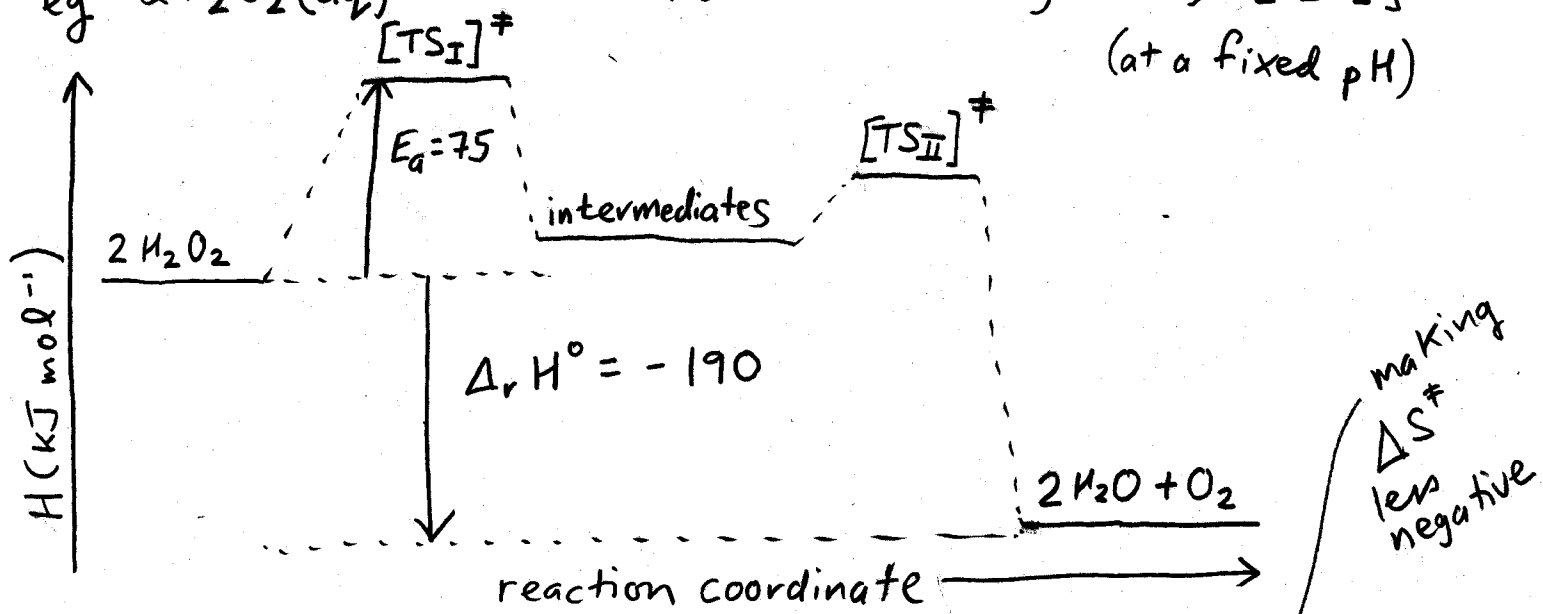
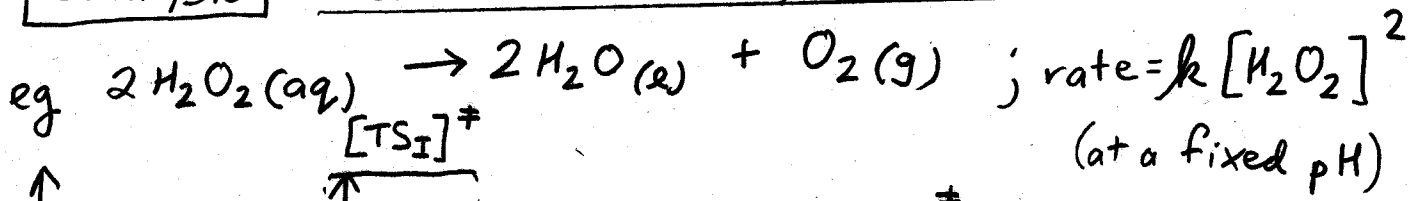
$$[C_2H_4]_0 = 5 \times 10^{-8} M \quad [O_3]_0 = 2 \times 10^{-8} M$$

$$rate_I = - \frac{d[C_2H_4]}{dt} = 5 \times 10^{-9} M s^{-1}$$

$$rate_{II} = - \frac{d[C_2H_4O_3]}{dt} = 5 \times 10^{-8} M s^{-1}$$

Since rate<sub>I</sub> << rate<sub>II</sub>, ES I is the rate-determining step

**Catalysis** - acceleration of rxn by a species not consumed in rxn



A catalyst (eg MnO<sub>2</sub>(s))  
orients reactants  
(~~lowering~~ ΔS<sup>‡</sup>)  
and stabilizes TS  
(lowering ΔH<sup>‡</sup>)