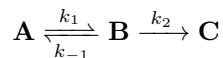


4 Isotope Effects and Kinetics

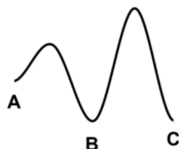
11/26: The questions pertain to the material covered from Thermodynamic Isotope Effects (Nov 5) to Kinetic Rate Laws (Nov 14).

1. The following schematic illustrates the six possible kinetic scenarios for the reaction

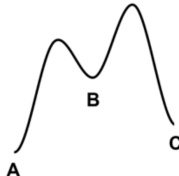


of **A** to **C** via **B**.

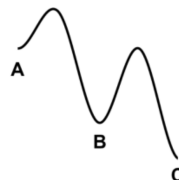
i.



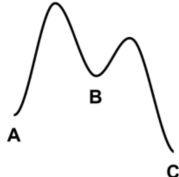
ii.



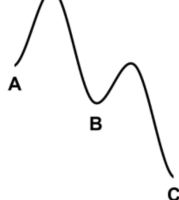
iii.



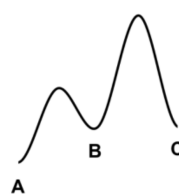
iv.



v.

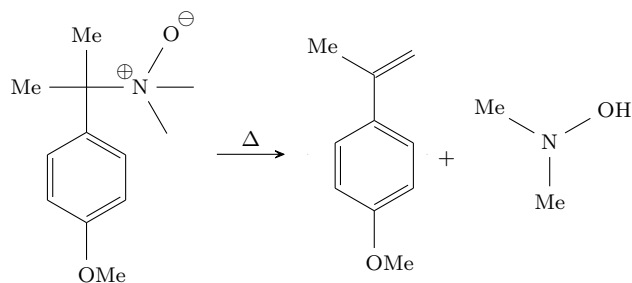


vi.



- In which of these scenarios would the steady-state approximation *not* be valid? Provide a brief explanation for your answers.
- In which of these scenarios would the quasi-equilibrium assumption *not* be valid? Provide a brief explanation for your answers.
- Consider a situation where **A** is isotopically labeled. If isotopic substitution affects only the rate of conversion of **B** to **C** (and not from **A** to **B**), in which scenarios might you expect to observe an independent rate kinetic isotope effect (KIE)? Please explain.
- In which scenarios might you expect to observe an independent rate KIE if isotopic substitution affects only the step involving formation of **B** from **A** (and not from **B** to **C**)?

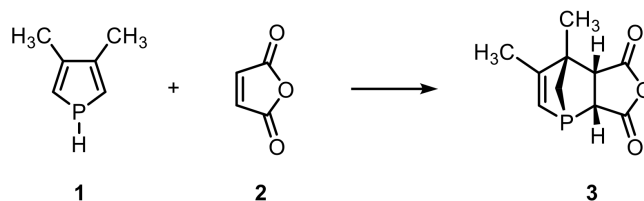
2. Consider the following reaction.



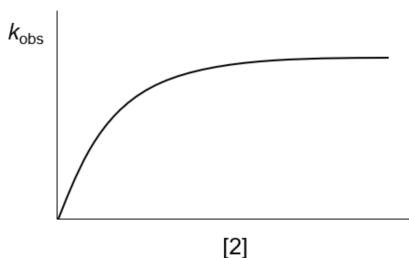
- a) The mechanism for this reaction could proceed via a concerted pathway or a stepwise pathway. Provide arrow-pushing mechanisms for both processes.
- b) When the two benzylic methyl groups were deuterated, kinetic isotope effects (KIEs) of 5 and 1.2 were measured in toluene and DMF respectively. Suggest a possible explanation for the observed KIEs.
- c) When the reaction was run at two different temperatures and in two different solvents, the following rate data were obtained. Compare the activation enthalpy (ΔH^\ddagger) and activation entropy (ΔS^\ddagger) of the reactions in toluene and in DMF. Suggest a possible explanation for the observed differences.

T (°C)	k_{rel} in toluene	k_{rel} in DMF
60	1	10
110	50	500,000

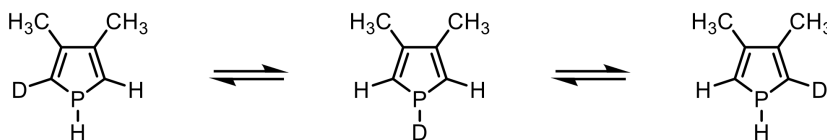
3. In nonpolar solvents, compound **1** reacts thermally with **2** to give only *endo* **3**.



Using small amounts of **1** and ‘flooding’ with **2**, it has been established that the rate is pseudo-first-order in [**1**]. Measuring the pseudo-first-order rate constant k_{obs} at several different concentrations of excess **2** gives a plot of the type shown below.

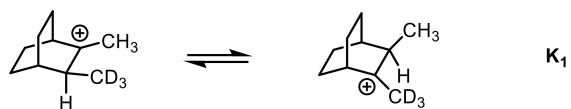


Compound **1**, deuterated at phosphorus, undergoes exchange of D with both α -hydrogens, as shown below. At low concentrations of **2**, the H/D exchange rate is rapid compared to the rate of formation of **3**. At ‘saturating’ concentrations of **2**, the formation of **3** occurs faster than H/D exchange.



- Write a full mechanism and a rate law for the formation of **3** that is consistent with these observations.
- Explain how your mechanism accounts for the labeling and kinetic behavior.
- Draw reaction coordinate energy diagrams at the limiting cases where [**2**] is ...
 - Very low;
 - Very high.

4. a) Estimate the magnitudes of the equilibrium constants (K_1 , K_2) for the following reactions. Provide explanations.



- b) Estimate the magnitudes of KIE_1 and KIE_2 for the following solvolysis reactions. Provide explanations.

