

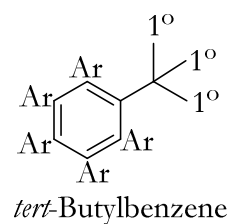
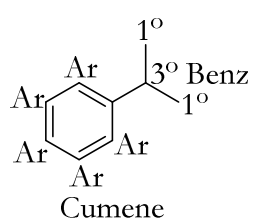
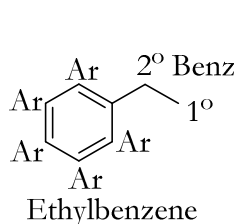
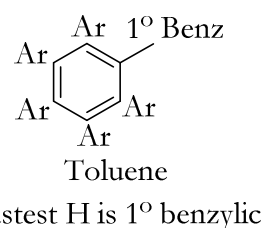
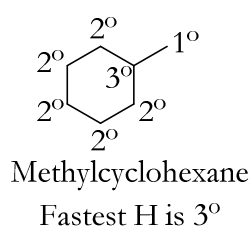
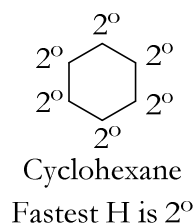
# Experiment 31

## Halogenation of Alkanes: Relative Rates of Free-Radical Bromination

### Study Questions

- 1) Draw the structures of the six hydrocarbons used in this study and classify all the hydrogen atoms according to the scheme above. Predict the reactivity order of the hydrocarbons toward bromine.

**Answer:**



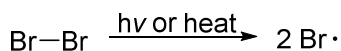
Fastest to slowest, the order should be cumene (3° benzylic), ethylbenzene (2° benzylic), toluene (1° benzylic), methylcyclohexane (3° aliphatic), cyclohexane (2° aliphatic), and *tert*-butylbenzene (1° aliphatic).

- 2) Write the initiation, propagation, and termination steps for the free radical bromination of methylcyclohexane (assume that only the most reactive hydrogen will be substituted).

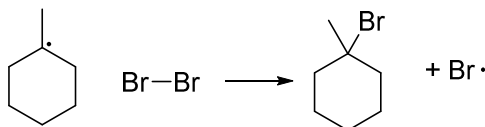
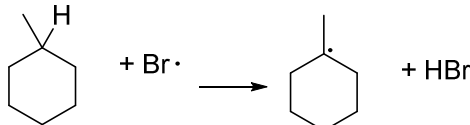
**Answer:**

## Experiment 31: Halogenation of Alkanes

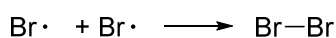
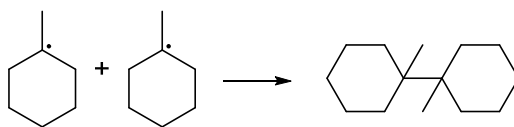
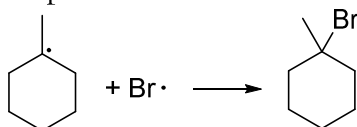
### Step 1: Initiation



### Step 2: Propagation



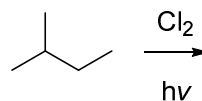
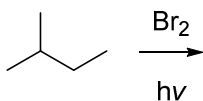
### Step 3: Termination



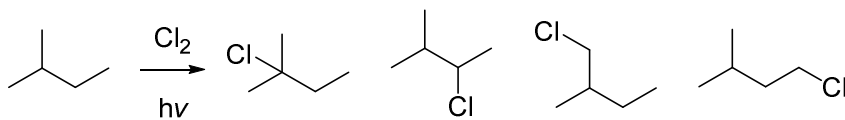
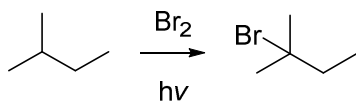
- 3) When first mixed together, the reaction mixtures of hydrocarbons, bromine, and methylene chloride are brown. In time, however, they become clear. What causes this decolorization?

**Answer:** The bromine (which causes the brown color) is being consumed by the reaction with the hydrocarbon.

- 4) What would be the monohalogenation product(s) of the following reactions?



**Answer:**



- 5) If the bromine solution is left uncapped too long, then the DCM will partially evaporate out of the bottle. What effect will this have on your observed reaction times? **Answer:** Evaporation of DCM will increase the concentration of the bromine, which means that when a given volume of

bromine solution is dispensed, it will contain more actual bromine than expected. This means that the bromine will take longer to decolorize, since there is more of it to be reacted. If the bromine is concentrated enough, the solution might never decolorize, since there may be too much bromine to be used up by reacting stoichiometrically with the hydrocarbon.