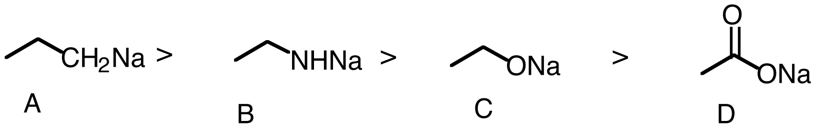
Stability/Reactivity/Selectivity Principles

1. **Reactant Stability/Reactivity**: The more stable the reactant, the less reactive it will be. In terms of rates, this means that the more stable the reactant, the slower it will react. (The concept here is that the more stable the reactant, the more content it is to stay as is, and the less motivated it is to react and change into something different)

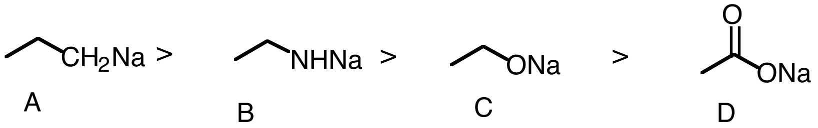
   Key note: Often the "reactant" that's relevant in this context will not be the original reactant of the reaction, but will be the "reactant" involved in the rate determining step.

- **Basicity**



Why: As anion stability increases from A to D, the reactivity decreases

- **Nucleophilicity**



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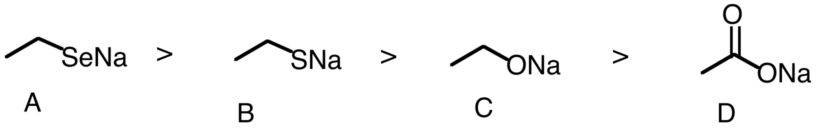

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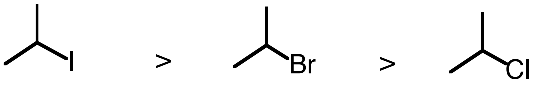
- **Reactivity toward alkanes via radical halogenation**

$F_2 > Cl_2 > Br_2 > I_2$ because F• > Cl• > Br• > I•

Why: Chlorine is more reactive the bromine because chlorine radical is less stable then bromine radical.

- **Electrophilicity (Reactivity in S_N2, S_N1, E2, E1 Reactions)**

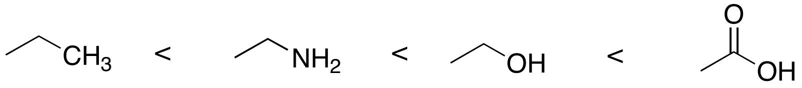


Why: As carbon-halogen bond stability increases, the reactivity decreases

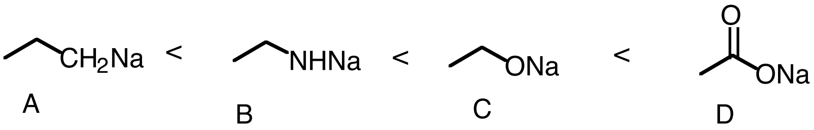
2. **Product Stability/Reactivity**: The more stable the product, the more favorable its formation will be. In terms of rates, this means that the more stable the product, the faster the reaction. (The concept here is that the more stable the product, the more favorable it will be to make that product.)

   Key note: Often the "product" that's relevant in this context will not be the final product of the reaction, but will be the "product" of the rate determining step.

- Acidity

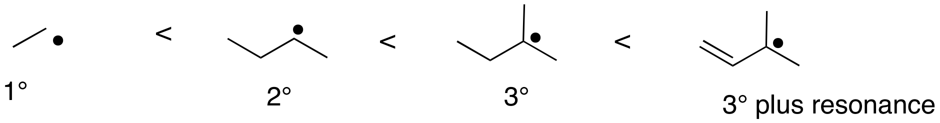


Why: Because as the stability of the anion products increases from A to D, the reactivity of the parent acids increase

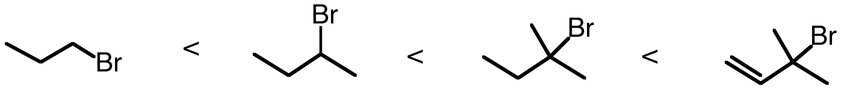


- **Reactivity of alkanes toward radical halogenation**

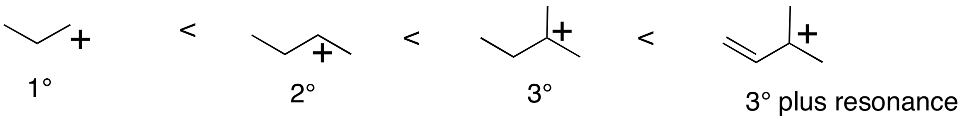
Why: Because as the stability of the radical produced during the rate-determining-step increases, the reactivity of the parent alkane increases



- **S_N1, E1 Reactivity**

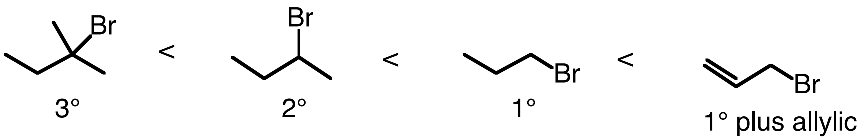


Why: Because as the stability of the cation produced in the rate-determining step increases, the reactivity of the parent halide increases as well



3. **Transition-State Stability/Reactivity**: The more stable the transition state, the faster the reaction will be. (The concept here is that the lower the transition state, the more easily it will be crossed.)

- **S_N2 Reactivity**

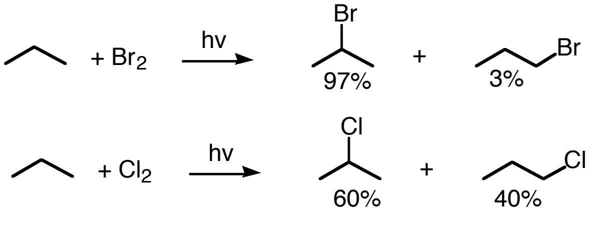


Why: The pattern reflects the relative stability of the transition states. In the case of 3˚ versus 2˚ versus 1˚, the issue is steric congestion in the transition state. The transition states for the more highly substituted halides are destabilized. In the case of allylic halides, the transition state is stabilized for orbital reasons, not steric reasons.

4. **Reactant Stability/Reactivity/Selectivity**: Often a reaction can proceed to give either of two products, of unequal stability. The pathway leading to the more stable product will be preferred. However, the selectivity between formation of the more stable and less stable product will vary depending on the stability of the reactant. The more stable the reactant, the less reactive it will be and the more selective it will be. (The concept here is that a more stable reactant is less desperate to react, and is more choosy, better able to select the best possible pathway without using a less favorable pathway that would result in a less stable product. A more sophisticated picture is that a more stable reactant will have larger activation barriers to cross; it has a hard enough time crossing even the lowest transition state leading to the best possible product, and is much less likely to have the surplus energy required to cross the high transition state leading to the less stable product.)

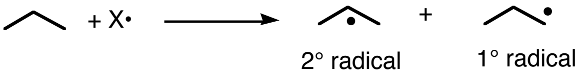
   Key note: The "reactant" and "products" involved are those for the rate-determing step.

- **Selectivity in the reaction of bromine versus chlorine with alkanes via radical halogenation**



Bromine is much more selective
Chlorine is much less selective

Why?



Formation of the secondary radical is more favorable then formation of the primary radical, in the rate determining step. Bromine radical, being less reactive, is more selective for the 2° radical. Cl•, being less stable and more reactive, is less choosy and less selective.