

## Nucleophiles in S<sub>N</sub>2 reactions

Relative rates (water = 1) of reaction with MeBr in EtOH

Nucleophile X	pK <sub>a</sub> of HX	Relative rate
HO <sup>-</sup>	15.7	$1.2 \times 10^4$
PhO <sup>-</sup>	10.0	$2.0 \times 10^3$
AcO <sup>-</sup>	4.8	$9 \times 10^2$
H <sub>2</sub> O	-1.7	1.0
ClO <sub>4</sub> <sup>-</sup>	-10	0



*Nucleophilicity parallels basicity*

Relative rates (water = 1) of reaction with MeBr in EtOH

Nucleophile X	pK <sub>a</sub> of HX	Relative rate
PhS <sup>-</sup>	6.4	$5.0 \times 10^7$
PhO <sup>-</sup>	10.0	$2.0 \times 10^3$



*Nucleophilicity does not parallel basicity*

✓ How do we explain these trends?

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Relative rates (water = 1) of  
reaction with MeBr in EtOH

Nucleophile X	$pK_a$ of HX	Relative rate
$\text{HO}^-$	15.7	$1.2 \times 10^4$
$\text{PhO}^-$	10.0	$2.0 \times 10^3$
$\text{AcO}^-$	4.8	$9 \times 10^2$
$\text{H}_2\text{O}$	-1.7	1.0
$\text{ClO}_4^-$	-10	0

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- ✓ If the atom that is forming the new bond to carbon is the same over a range of nucleophiles—it might be oxygen, for example, and the nucleophiles might be  $\text{HO}^-$ ,  $\text{PhO}^-$ ,  $\text{AcO}^-$ , and  $\text{TsO}^-$ , *then nucleophilicity does parallel basicity*

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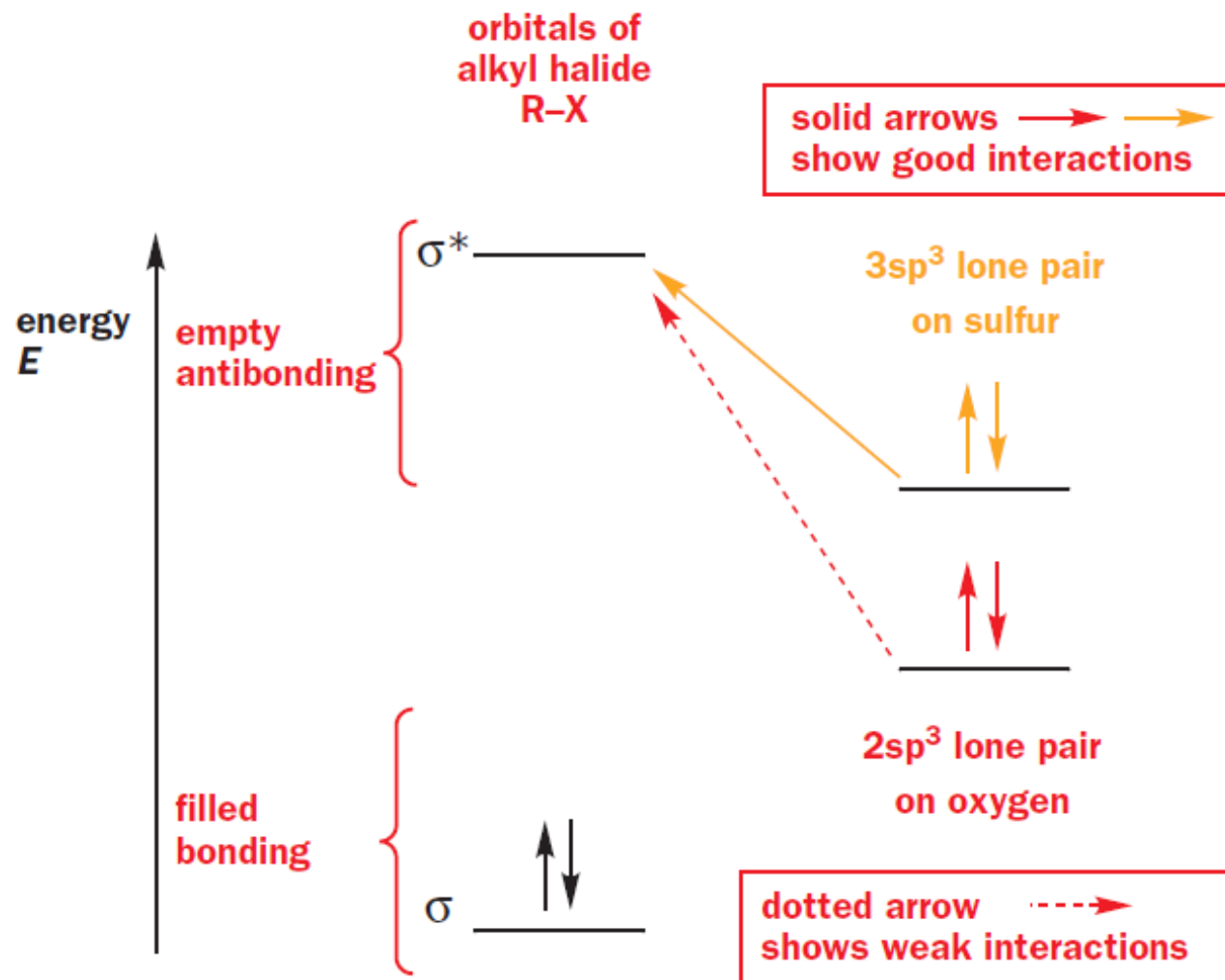
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- ✓ RS<sup>-</sup> is a better nucleophile for saturated carbon than RO<sup>-</sup>
- ✓ How do we relate these apparently opposite trends with the help of MO approach?

**ΔE (interaction energy)** :  $\Sigma \text{sterics} - \Sigma \text{orbital overlap} / (E_{\text{LUMO}} - E_{\text{HOMO}}) + \Sigma \text{charge interaction}$



- ✓ The higher-energy (3sp<sup>3</sup>) lone-pair electrons on S interact better with the  $\sigma^*$  orbital of the C–X bond than do the lower-energy (2sp<sup>3</sup>) lone-pair electrons on oxygen

- ✓ Nucleophiles from lower down the periodic table are more effective in  $S_N2$  reactions than those from the top few rows. Typically, nucleophilic power towards saturated carbon goes like this:



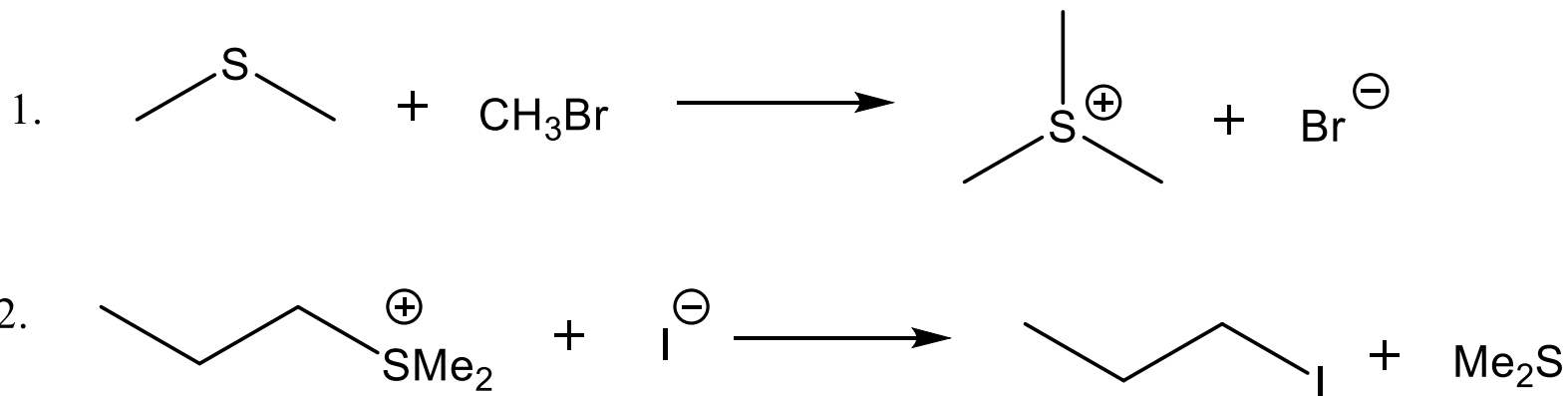
- ✓ *Here, nucleophilicity does not parallel basicity*

## Nucleophiles in S<sub>N</sub>1 Reaction

- ✓ We have established that the nucleophile is not important in the *rate* of an S<sub>N</sub>1 reaction
- ✓ A better nucleophile will not accelerate the S<sub>N</sub>1 reaction but it may determine which product is formed

1. In which solvent the rate for the following  $S_N2$  reactions would be higher, ethanol or diethyl ether?

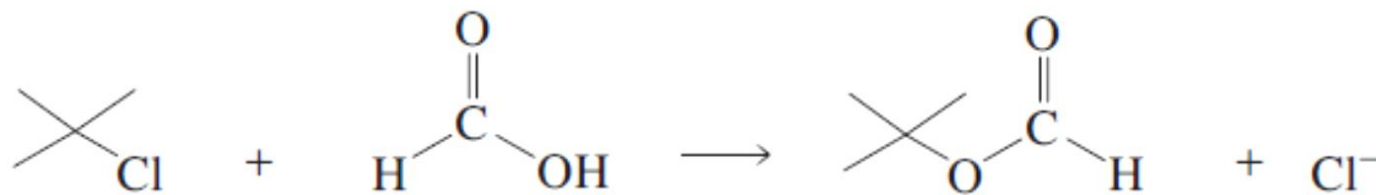
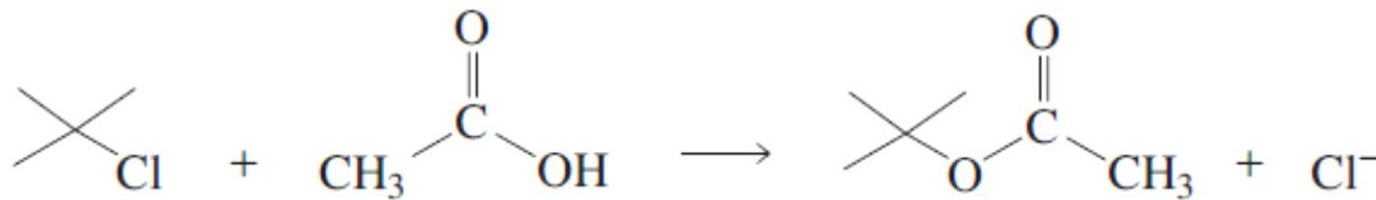
Explain.



Ans. 1. Ethanol since the transition state is more polar than the starting materials. So, ethanol will stabilize the transition state more than the starting materials and hence the activation energy will be lower.

2. Diethyl ether since the transition state is less polar (the charges are dispersed) than the starting materials.

2. *tert*-Butyl chloride undergoes solvolysis in both acetic acid and formic acid.



Solvolysis occurs 5000 times faster in one of the acids than in the other. In which solvent is solvolysis faster? Explain your answer. (Hint: The  $\text{pK}_a$  values of acetic acid and formic acid are 4.76 and 3.77, respectively).

**Ans.** This is an  $\text{S}_{\text{N}}1$  reaction. Formic acid being a stronger acid will produce more amounts of ions through dissociation. The higher ionic strength would lead to the formation of the *t*-butyl cation with a lower activation energy and hence the reaction will be faster than in acetic acid.