

Comparisons within a column of the periodic table are less uniform, and there can be a strong solvent effect that depends on whether the Lewis base is charged or uncharged. Three generalizations are typically made.

(1) For uncharged Lewis bases in the same column of the periodic table, the larger atom is faster (more nucleophilic); its electrons are less tightly held by the nucleus, and they can more readily undergo the distortion needed to form a new bond. This property of the larger atom's electrons is called polarizability. For example, H<sub>2</sub>S is a better nucleophile than H<sub>2</sub>O, and (CH<sub>3</sub>)<sub>3</sub>P is a better nucleophile than (CH<sub>3</sub>)<sub>3</sub>N.

(2) For charged Lewis bases in the same column of the periodic table, the larger atom is faster (more nucleophilic) in protic solvents; a larger, less basic atom is not as strongly hydrogen bonded as the smaller, more basic atom. In water or methanol, NaI is more nucleophilic than NaBr, which is more nucleophilic than NaCl.

(3) For charged Lewis bases in the same column of the periodic table, the smaller atom is faster (more nucleophilic) in aprotic solvents; without the hydrogen bonding to slow it down, the smaller, more basic atoms are faster than their larger counterparts. In dimethylformamide (DMF) or dimethylsulfoxide (DMSO), for instance, NaCl is more nucleophilic than NaBr, which is more nucleophilic than NaI.

Figure 0757 summarizes these trends. The rates for the chloride/bromide/iodide comparisons in methanol versus dimethylformamide (DMF) are reported on the same scale as a reminder that the solvent effect is also operating here. Despite the order of reactivity, note that all three of the rates of the "naked ions" in DMF are significantly faster than all of the rates in methanol, where hydrogen bonding occurs.

$$\text{I-CH}_3 + \text{Nu:} \xrightarrow{\text{[solvent]}} \text{CH}_3\text{Nu} + \text{NaI}$$

identity of Nu	[CH <sub>3</sub> OH] rate relative to Nu = NaBr in CH <sub>3</sub> OH	[DMF] rate relative to Nu = NaBr in CH <sub>3</sub> OH
H <sub>2</sub> O, ROH	1.7 × 10 <sup>-5</sup>	
NaCl	4.2 × 10 <sup>-1</sup> slower	4.3 × 10 <sup>5</sup> faster
H <sub>2</sub> S, R <sub>2</sub> S	2.1 × 10 <sup>-1</sup>	
NaBr	1	2.1 × 10 <sup>4</sup>
NaOCH <sub>3</sub>	3.3	
(CH <sub>3</sub> ) <sub>3</sub> N	5.3	
NaI	4.2 × 10 <sup>2</sup> faster	6.3 × 10 <sup>3</sup> slower
NaSCH <sub>3</sub>	1.7 × 10 <sup>3</sup>	
(CH <sub>3</sub> ) <sub>3</sub> P	1.3 × 10 <sup>3</sup>	

**Figure 0757**

**Summary for nucleophilicity comparisons.**

#### D. Heteroatom Electrophiles

Carbon atoms are not the only sites where substitution and elimination reactions can take place. Many different tetrahedral atoms with an attached leaving group can undergo these reactions.

Earlier in this chapter (Figure 0722), two of the mechanisms for forming a tosylate were shown as an S<sub>N</sub>2 reaction at a tetrahedral sulfur atom, and this is repeated in Figure 0758 on the next page, along with a few other known examples of substitution and elimination reactions where there are heteroatom electrophiles. There can be a lot of variation in these reactions, so no good general statement can be made. The purpose of this short section is to remind you that the fundamental chemistry of many different atoms is being introduced here, not just the chemistry of carbon.