8.7

Nucleophiles and Nucleophilicity

Nucleophiles

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Not all nucleophiles are anions. Many are neutral.

HOH CH_3OH $:NH_3$ for example

All nucleophiles, however, are Lewis bases.

Nucleophiles

Many of the solvents in which nucleophilic substitutions are carried out are themselves nucleophiles.

$H\ddot{\underset{..}{O}}H$ $\qquad$ $CH_3\ddot{\underset{..}{O}}H$ $\qquad$ for example

Solvolysis

The term *solvolysis* refers to a nucleophilic substitution in which the nucleophile is the solvent.

Solvolysis

substitution by an anionic nucleophile

$$\mathrm{R{-}X} + \mathbf{:}\mathrm{Nu}^{-} \longrightarrow \mathrm{R{-}Nu} + \mathbf{:}\mathrm{X}^{-}$$

solvolysis

$$\mathrm{R{-}X} + \mathbf{:}\mathrm{Nu{-}H} \longrightarrow \mathrm{R{-}}\overset{+}{\mathrm{Nu}}\mathrm{{-}H} + \mathbf{:}\mathrm{X}^{-}$$

step in which nucleophilic substitution occurs

Solvolysis

substitution by an anionic nucleophile

$$R—X + :Nu^{-} \longrightarrow R—Nu + :X^{-}$$

solvolysis

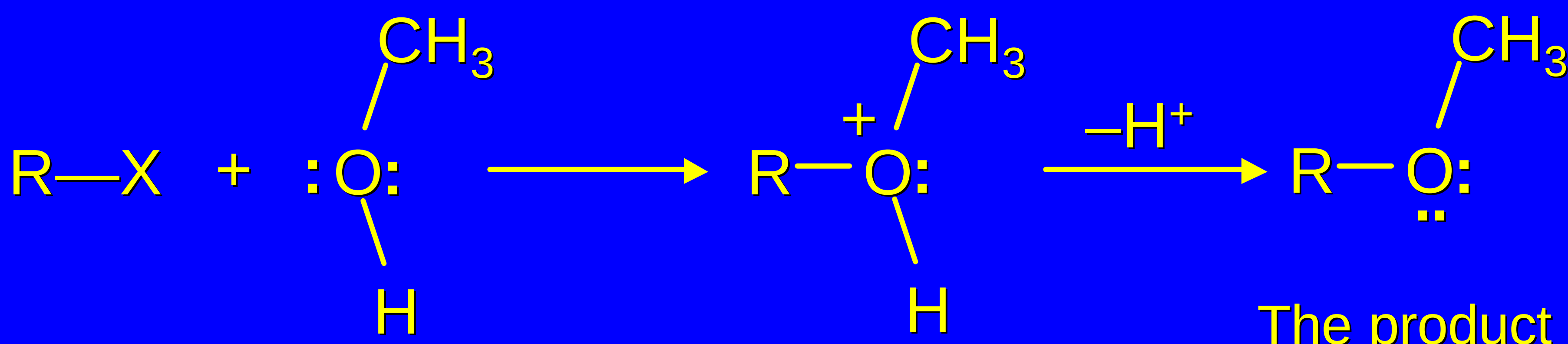
$$R—X + :Nu—H \longrightarrow R—\overset{+}{Nu}—H + :X^{-}$$

$$\downarrow$$

products of overall reaction — $R—Nu + HX$

Example: Methanolysis

Methanolysis is a nucleophilic substitution in which methanol acts as both the solvent and the nucleophile.



The product is a methyl ether.

Typical solvents in solvolysis

solvent	product from RX
water (HOH)	ROH
methanol (CH_3OH)	$ROCH_3$
ethanol (CH_3CH_2OH)	$ROCH_2CH_3$
formic acid ($H\overset{\overset{O}{\|}}{C}OH$)	$RO\overset{\overset{O}{\|}}{C}H$
acetic acid ($CH_3\overset{\overset{O}{\|}}{C}OH$)	$RO\overset{\overset{O}{\|}}{C}CH_3$

Nucleophilicity is a measure of the reactivity of a nucleophile

Table 8.4 compares the relative rates of nucleophilic substitution of a variety of nucleophiles toward methyl iodide as the substrate. The standard of comparison is methanol, which is assigned a relative rate of 1.0.

Table 8.4 Nucleophilicity

Rank	Nucleophile	Relative rate
strong	I^-, HS^-, RS^-	$>10^5$
good	Br^-, HO^-, RO^-, CN^-, N_3^-	10^4
fair	NH_3, Cl^-, F^-, RCO_2^-	10^3
weak	H_2O, ROH	1
very weak	RCO_2H	10^{-2}

Major factors that control nucleophilicity

basicity

solvation

- small negative ions are highly solvated in protic solvents
- large negative ions are less solvated

polarizability

Table 8.4 Nucleophilicity

Rank	Nucleophile	Relative rate
good	HO^-, RO^-	10^4
fair	RCO_2^-	10^3
weak	H_2O, ROH	1

When the attacking atom is the same (oxygen in this case), nucleophilicity increases with increasing basicity.

Major factors that control nucleophilicity

basicity

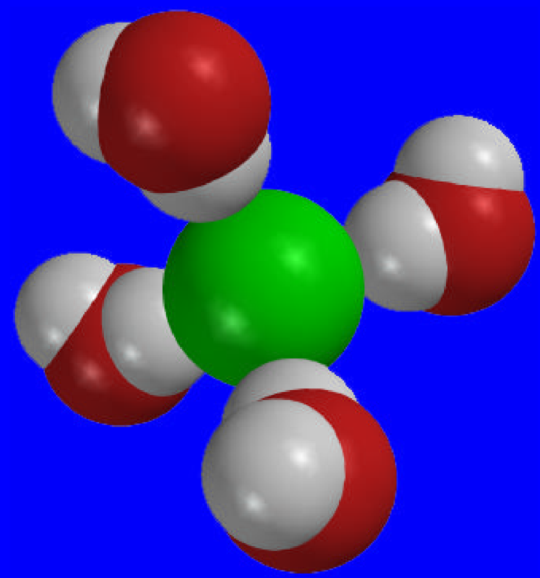
solvation

small negative ions are highly solvated in protic solvents

large negative ions are less solvated

polarizability

Figure 8.4



Solvation of a chloride ion by ion-dipole attractive forces with water. The negatively charged chloride ion interacts with the positively polarized hydrogens of water.

Table 8.4 Nucleophilicity

Rank	Nucleophile	Relative rate
strong	I^-	$>10^5$
good	Br^-	10^4
fair	Cl^-, F^-	10^3

A tight solvent shell around an ion makes it less reactive. Larger ions are less solvated than smaller ones and are more nucleophilic.

Major factors that control nucleophilicity

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solvation

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large negative ions are less solvated

polarizability

Table 8.4 Nucleophilicity

Rank	Nucleophile	Relative reactivity
strong	I^-	$>10^5$
good	Br^-	10^4
fair	Cl^-, F^-	10^3

More polarizable ions are more nucleophilic than less polarizable ones. Polarizability increases with increasing ionic size.