

# Solvents and Solvolysis Reactions

## Classification of Solvents

- (1) Bronsted protic vs aprotic
- (2) Lewis donor vs non-donor
- (3) polar vs apolar

### (1) Bronsted protic vs aprotic

- protic solvents are good hydrogen bond donors

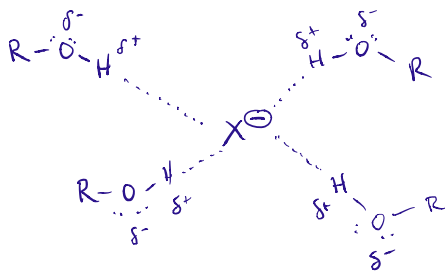
Ex:  $H_2O$ , alcohols, carboxylic acids

- aprotic solvents cannot act as hydrogen bond donors

Ex: ether, dichloromethane (DCM) =  $CH_2Cl_2$ , hexanes

protic solvents stabilize anions:

\* prof  
Ganem's  
lec



Solvation = favorable interaction of a dissolved molecule with solvent.

### (2) Lewis donor vs non-donor

- donor solvents = molecules containing oxygens or nitrogens that can donate unshared electron pairs (molecules that can act as Lewis bases)

Ex: Ether, THF,  $H_2O$ , alcohols



- non-donor solvents = molecules that cannot act as Lewis bases

Ex: alkanes, benzene, DCM, chloroform  
 $CHCl_3$



NOTE: even though DCM & chloroform have halogen atoms with unshared e<sup>-</sup> pairs, they are very poor LBs and are considered non-donors

(3) polar vs apolar

- polar solvents have dielectric constant  $\geq 15$
- apolar solvents have dielectric constant  $\leq 15$

dielectric constant,  $\epsilon \equiv$  interaction energy between two ions with respective charges  $q_1$  &  $q_2$ , separated by distance  $r$  (measures ease of separating charges)

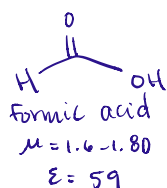
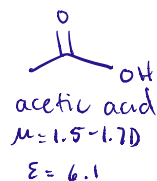
$$E = k \frac{q_1 q_2}{\epsilon r}$$

dielectric constant  $\swarrow$

\* large  $\epsilon$ , magnitude of interaction  $E$  is small; this means attractive and repulsive forces between charges are weak.

\* oppositely charged ions tend to associate less in a polar solvent than apolar.

— All polar solvents consist of dipolar molecules, but not all dipolar molecules are polar solvents —



**TABLE 8.2 Properties of Some Common Organic Solvents**  
(Listed in order of increasing dielectric constant)

Solvent	Structure	Common abbreviation	Boiling point, °C	Dielectric constant $\epsilon^*$	Dipole moment	Class		
						Polar	Protic	Donor
hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	—	68.7	1.9	0.08			
1,4-dioxane <sup>†</sup>		—	101.3	2.2	0.4			x
benzene <sup>†</sup>		—	80.1	2.3	0.1			
diethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$	$\text{Et}_2\text{O}$	34.6	4.3	1.2			x
chloroform	$\text{CHCl}_3$	—	61.2	4.8	1.2			
ethyl acetate		$\text{EtOAc}$	77.1	6.0	1.6			x
acetic acid		$\text{HOAc}$	117.9	6.1	1.6		x	x
tetrahydrofuran		THF	66	7.6	1.7			x
dichloromethane	$\text{CH}_2\text{Cl}_2$	DCM	39.8	8.9	1.1			
acetone		$\text{Me}_2\text{CO}$	56.3	21	2.7	x		x
ethanol	$\text{C}_2\text{H}_5\text{OH}$	$\text{EtOH}$	78.3	25	1.7	x	x	x
<i>N</i> -methylpyrrolidone		NMP	202	32	4.0	x		x
methanol	$\text{CH}_3\text{OH}$	$\text{MeOH}$	64.7	33	2.9	x	x	x
nitromethane	$\text{CH}_3\text{NO}_2$	$\text{MeNO}_2$	101.2	36	3.4	x		x
<i>N,N</i> -dimethylformamide		DMF	153.0	37	3.9	x		x
acetonitrile	$\text{CH}_3\text{C}\equiv\text{N}$	$\text{MeCN}$	81.6	38	3.4	x		x
sulfolane		—	287 (dec)	43	4.7	x		x
dimethyl sulfoxide		DMSO	189	47	4.0	x		x
formic acid		—	100.6	59	1.7	x	x	x
water	$\text{H}_2\text{O}$	—	100.0	78	1.9	x	x	x
formamide		—	211 (dec)	111	3.9	x	x	x

\* Most values are at or near 25 °C † Known carcinogen

Fill out form

# SOLVENT CHEAT SHEET

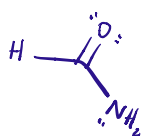
\* should know \*  
how to draw,  
use in rxn

\* All polar solvents are donors

## POLAR SOLVENTS

Protic

$H_2O, CH_3OH$   
 $CH_3CH_2OH$

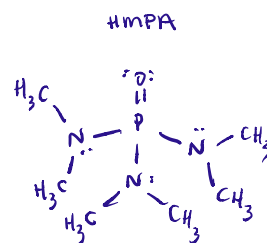
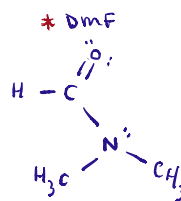
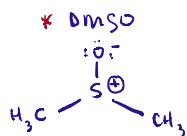


excellent  $\oplus$  &  $\ominus$  solvation

Aprotic

DMSO, HMPA, DMF,  
 $CH_3C\equiv N:$

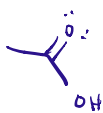
excellent  $\oplus$  stabilization  
no  $\ominus$  solvation



## NONPOLAR SOLVENTS

Protic, Donors

moderate  $\oplus/\ominus$  solvation



$\epsilon = 6.1$



$\epsilon = 10.9$

Aprotic

Donor

moderate  $\oplus$  solvation  
NO  $\ominus$

diethyl ether  
THF

NON DONOR

hexanes  
pentanes  
 $CH_2Cl_2$   
 $CHCl_3$   
benzene

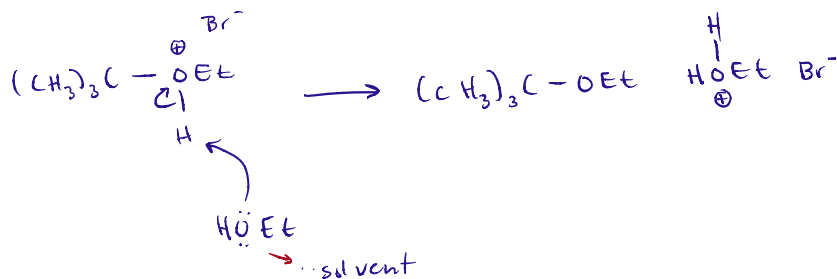
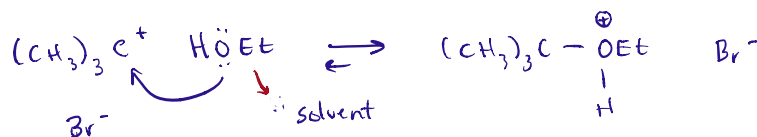


solvent choice important for  $S_N1/E1$ ,  $S_N2/E2$  reactions

Solvolysis reactions

solvolysis: the reaction of an alkyl halide with a solvent in which no other base or nucleophile has been added.

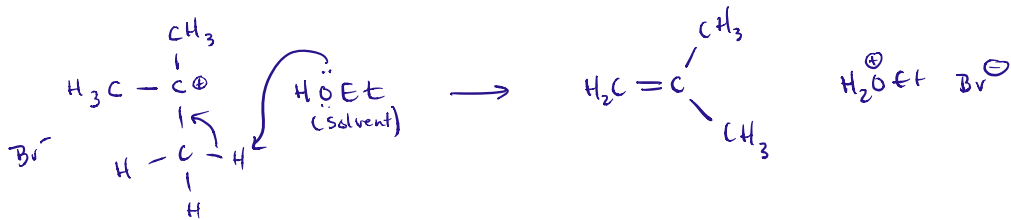
solvolysis of tert-butyl bromide



Reaction Summary:

- tert-butyl bromide in polar protic solvent forms carbocation intermediate
- bromine is substituted by the solvent
- the solvent that formed a new covalent bond with the carbocation is deprotonated by another solvent molecule
- this followed an  $S_N1$  reaction mechanism

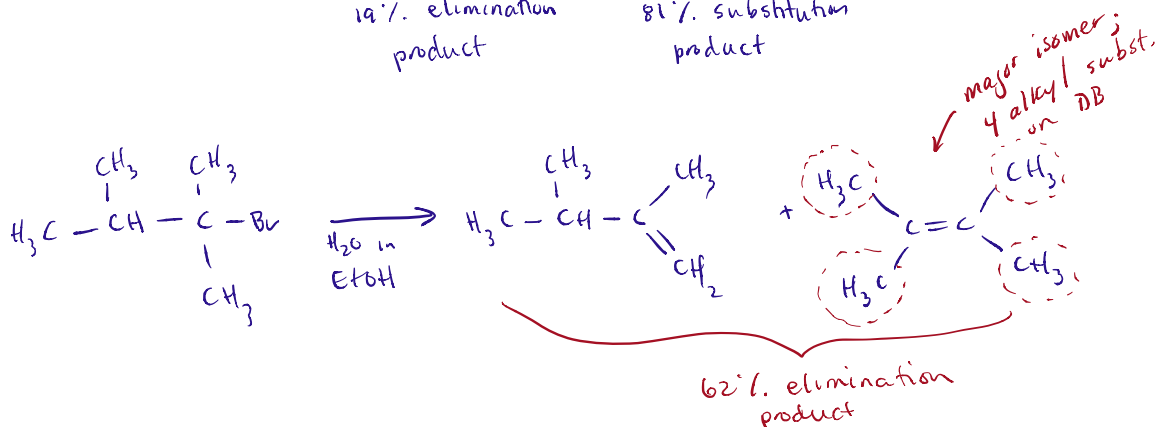
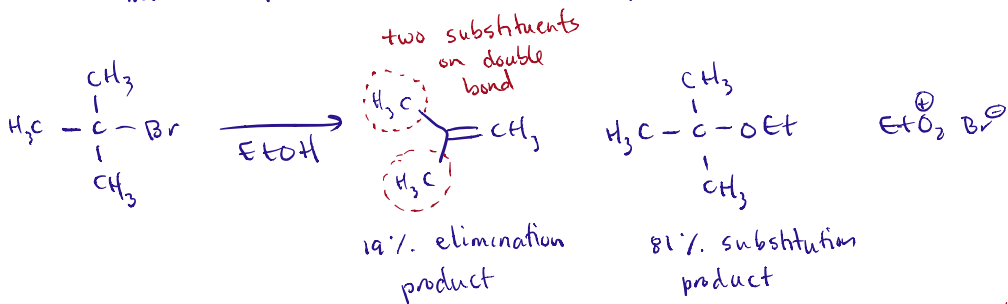
Polar protic solvent stabilizes carbocation

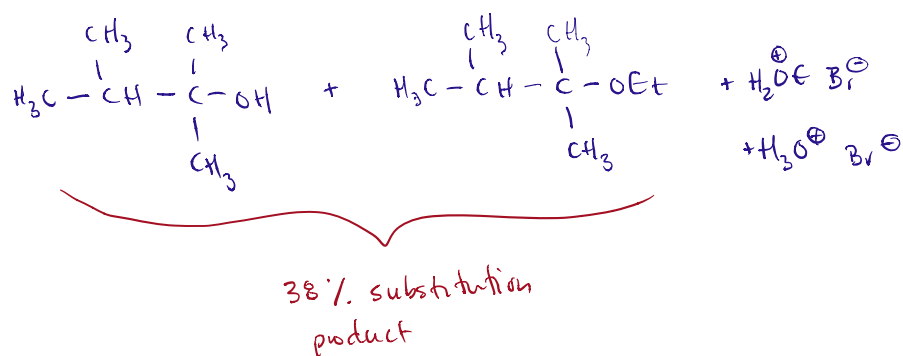


Reaction Summary:

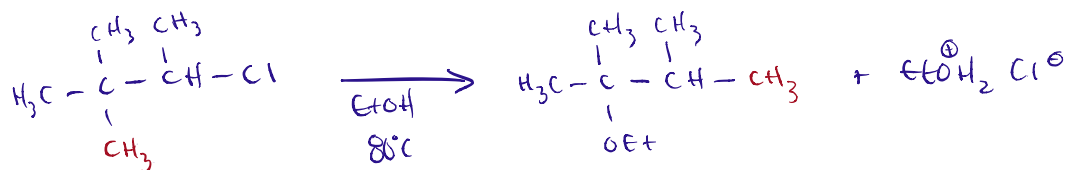
- tert-butyl bromide in polar protic solvent forms carbocation intermediate
- solvent reacts with a  $\beta$ -hydrogen to form an alkene
- This follows the E1 reaction mechanism

Important note:  
Alkyl halide structure and nucleophile strength have more influence on which type of reaction predominates





Rearrangements are also possible in some solvolysis rxns



$\text{S}_{\text{N}}1$ - $\text{E}1$  reactions fastest in polar, protic, donor solvents.

polar (high  $\epsilon$ ) allows for separation of ions

protic, donor stabilizes both  $\oplus$  and  $\ominus$  species.

- carbocation intermediate stabilized and halide anion stabilized

For  $\text{S}_{\text{N}}2$ - $\text{E}2$  reactions, polar aprotic solvents preferred  
 polar protic solvents stabilize the nucleophile, reducing its effective negative charge and therefore its nucleophilicity.

Substrate	Protic Solv.	Aprotic Solv.	Strong B	Bulky B
CH <sub>3</sub> -Br	S <sub>N</sub> 2	S <sub>N</sub> 2	S <sub>N</sub> 2	S <sub>N</sub> 2
1°	S <sub>N</sub> 2	S <sub>N</sub> 2	S <sub>N</sub> 2/E2	E2
2°	S <sub>N</sub> 1/E1	S <sub>N</sub> 2	E2/S <sub>N</sub> 2	E2
3°	S <sub>N</sub> 1/E1	S <sub>N</sub> 1/E1	E2	E2

\* B = Base  
Solv. = Solvent

\* From Organic Chemistry Tutor