

Sn₂ vs. Sn₁

Sn₂

1. 2nd order kinetics
2. Complete inversion
3. Single step i.e. making and breaking bond occurs in a single step.
4. No rearrangement
5. Reactivity 1^o>2^o>3^o
6. Steric factors affect the rate
7. Nucleophile attacks substrate

Sn₁

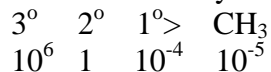
- 1st order kinetics
- Two step reaction
1st step rate determining step
- Shows rearrangement
Reactivity 3^o>2^o>1^o
Electronic factors affect
Nucleophile attacks intermediate

Whether the reaction proceeds by Sn₁ or Sn₂ we need to consider the following factors:

1. The nature of the leaving group; a good leaving group (weak base) speeds up Sn₁ and Sn₂ to the same extent and hence has little effect on Sn₁ and Sn₂.
2. Nature of the alkyl groups.

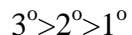
As the number of R groups increases, it becomes more difficult for the nucleophile to reach the substrate, hence more difficult for Sn₂ mechanism to take place.

Remember the reactivity of Sn₁



The reactivity of 3^o alkylhalides is 10⁶ times the reactivity of 2^o alkylhalides.

Remember rate of formation of carbocation and order of stability

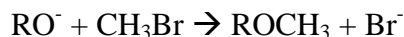


The alkyl groups release e⁻s stabilizing the carbocation and also stabilizing the incipient carbocation in the transition state.

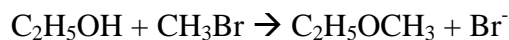
The more stable the transition state leading to the formation of the carbocation the lower the activation energy required and the faster the carbocation formed.

3. Concentration of nucleophile

An increase in the concentration of the nucleophile will increase the Sn₂ and has no effect on the Sn₁. The net result is an increase in the concentration of the nucleophile favors Sn₂ and a low concentration of the nucleophile favors Sn₁.



S. Base fast reaction



W.B very slow

4. Nature of nucleophile

A strong nucleophile attacks the substrate faster and hence favors S_N2 .
A weaker base favors S_N1 .

e.g. neopentyl bromide reacts with the ethoxide ion using S_N2 and with alcohol using S_N1 .

5. Nature of the solvent

S_N1 is favored by polar and protic solvents.

In S_N1 the transition state has stretched C---X bond and hence has a much stronger dipole moment than the reactant which is RX; hence the transition state forms much stronger dipole-dipole bonds to the polar solvent and this stabilizes the transition state more than the reactant and hence lowers the E_{act} .

The effect of polar solvent on S_N2 is that it slows down the reaction enormously by 10^{20} because the polar solvent forms powerful ion-dipole bonds with the base OH^- (the nucleophile). The transition state HO---R---X the charge is divided between the OH^- and X- hence forms weaker ion-dipole bonds i.e. the polar solvent stabilizes the nucleophile more than it stabilizes the transition state and hence E_{act} increases and this slows down the reaction.

E_2 vs. E_1

The rate of reaction (E_1 and E_2) is in this order

E_2 and E_1 $3^\circ > 2^\circ > 1^\circ$

but for different reasons. For E_2 the sequence reflects the relative stabilities of the alkene being formed. For E_1 the order reflects the stabilities of the carbocations formed. The base here plays a very important role.

The base takes part in the rate-determining step of E_2 while in E_1 it does not.

Thus the rate of E_2 depends upon the concentration of the base and E_1 does not. E_2 depends upon the nature of the base but E_1 does not (stronger base pulls a proton faster).

For a given substrate, the stronger the base the more E_2 is favored over E_1 . Normally in dehydrohalogenation, a strong base is used; hence, E_2 is followed.

E_1 mechanism is encountered only with secondary or tertiary substrates and in solutions where the base is low concentration or weak, typically where the base is the solvent.

S_N1 vs. E_1

Both have the same 1st step; hydrolysis to form the carbocation; the difference is in the 2nd step.

Reactivity of S_N1 and E_1 $3^\circ > 2^\circ > 1^\circ$

Notice the attack is on the carbocation.

S_N1 vs. E_1 factors

1. They accompany one another.

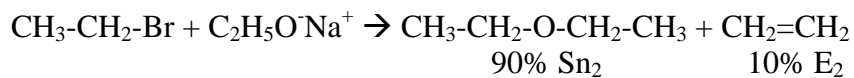
2. They have the same intermediate (carbocation).

E_1 is favored by (1) use of a compound that forms stable carbocation (2) use of a weak base i.e. weak electrophile (3) use of a polar solvent.

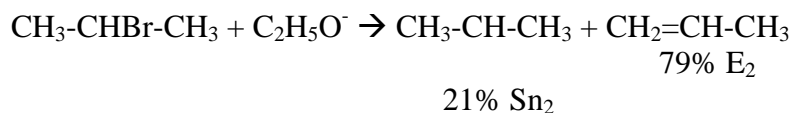
In substitution reactions, elimination is troublesome. Substitution is good with primary alkylhalides and possibly with secondary but with tertiary alkylhalides virtually the result is elimination. When we want elimination we should drive the reaction towards E₂ i.e. use solvent with low polarity and high base concentration.

Sn₂ vs. E₂

When primary alkylhalide and the base is ethoxide ion, substitution is favored.



With 2° alkylhalide and ethoxide elimination is favored.



With 3° alkylhalide elimination is highly favored.