Sn_2 vs. Sn_1

Sn_2	Sn_1
1. 2^{nd} order kinetics	1^{st} order kinetics
2. Complete inversion	
3. Single step i.e. making and breaking bond occurs in a single step.	Two step reaction 1^{st} step rate determining step
4. No rearrangement	Shows rearrangement
5. Reactivity $1^o>2^o>3^o$	Reactivity $3^o>2^o>1^o$
6. Steric factors affect the rate	Electronic factors affect
7. Nucleophile attacks substrate	Nucleophile attacks intermediate

Whether the reaction proceeds by Sn_1 or Sn_2 we need to consider the following factors:

1. The nature of the leaving group; a good leaving group (weak base) speeds up Sn_1 and Sn_2 to the same extent and hence has little effect on Sn_1 and Sn_2.

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 Sn_2 mechanism to take place.

Remember the reactivity of Sn_1

3^o 2^o $1^o>$ CH_3

10^6 1 10^{-4} 10^{-5}

The reactivity of 3^o alkylhalides is 10^6 times the reactivity of 2^o alkylhalides.

Remember rate of formation of carbocation and order of stability

$3^o>2^o>1^o$

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 Sn_2 and has no effect on the Sn_1. The net result is an increase in the concentration of the nucleophile favors Sn_2 and a low concentration of the nucleophile favors Sn_1.

$RO^- + CH_3Br \rightarrow ROCH_3 + Br^-$

S. Base fast reaction

$C_2H_5OH + CH_3Br \rightarrow C_2H_5OCH_3 + Br^-$

W.B very slow

4. Nature of nucleophile

A strong nucleophile attacks the substrate faster and hence favors Sn_2.
A weaker base favors Sn_1.

e.g. neopentyl bromide reacts with the ethoxide ion using Sn_2 and with alcohol using Sn_1.

5. Nature of the solvent

Sn_1 is favored by polar and protic solvents.

In Sn_1 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 Eact.

The effect of polar solvent on Sn_2 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 Eact 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 $3^o > 2^o > 1^o$
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.

Sn_1 vs. E_1
Both have the same 1st step; hydrolysis to form the carbocation; the difference is in the 2nd step.
Reactivity of Sn_1 and E_1 $3^o > 2^o > 1^o$

Notice the attack is on the carbocation.

Sn_1 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 E_2 i.e. use solvent with low polarity and high base concentration.

Sn_2 vs. E_2

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

$$CH_3\text{-}CH_2\text{-}Br + C_2H_5O^-Na^+ \rightarrow \underset{90\%\ Sn_2}{CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3} + \underset{10\%\ E_2}{CH_2{=}CH_2}$$

With 2^o alkylhalide and ethoxide elimination is favored.

$$CH_3\text{-}CHBr\text{-}CH_3 + C_2H_5O^- \rightarrow CH_3\text{-}CH\text{-}CH_3 + CH_2{=}CH\text{-}CH_3$$

79% E_2

21% Sn_2

With 3^o alkylhalide elimination is highly favored.