

Factors affecting the rate of reaction:

Four factors affect the rate of the reaction are as follows

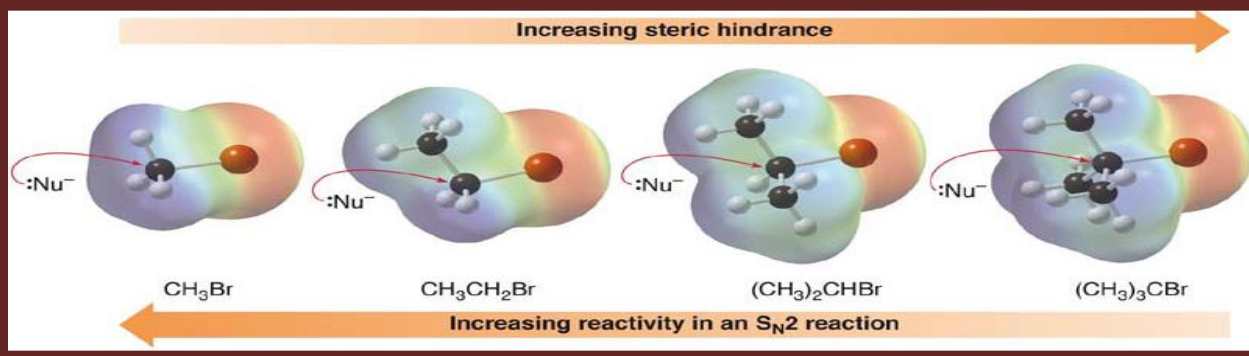
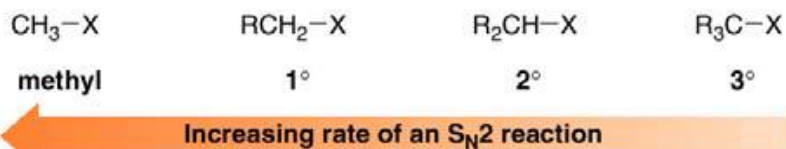
- 1)The substrate
- 2)The nucleophile
- 3)The leaving group
- 4)The solvent

Nature of the substrate:

The substrate plays the most important part in determining the rate of the reaction. Methyl and 1° alkyl halides undergo S_N2 reactions with ease. 2° Alkyl halides react more slowly. 3° Alkyl halides do not undergo S_N2 reactions. This order of reactivity can be explained by steric effects. Steric hindrance caused by bulky R groups makes nucleophilic attack from the backside more difficult, slowing the reaction rate. Therefore, to maximise the rate of the S_N2 reaction, the back of the substrate must be as unhindered as possible.

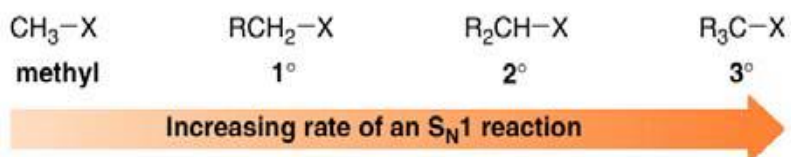
Moreover, compounds like '1-chloro 1-ethene' too do not undergo nucleophilic substitution easily because the carbon to chlorine bond is said to be of partial double bond character, thus is harder to break. Another factor leading to an S_N2 reaction due to substrate involves the stability and ease by which the carbocation is formed after removing the leaving group. This means the more stable the carbocation is after removing the leaving group, the more likely it is an S_N1 reaction will occur instead of an S_N2. Among the stabilization methods to be considered are: resonance stabilization, hyper-conjugative stabilization, inductive effect stabilization, or the formation of an aromatic ring molecule (as in the case of 7-chloro cyclohept-1, 3, 5-triene, as it will form a tropylium carbocation which is aromatic).

- As the number of R groups on the carbon with the leaving group *increases*, the rate of an S_N2 reaction *decreases*.



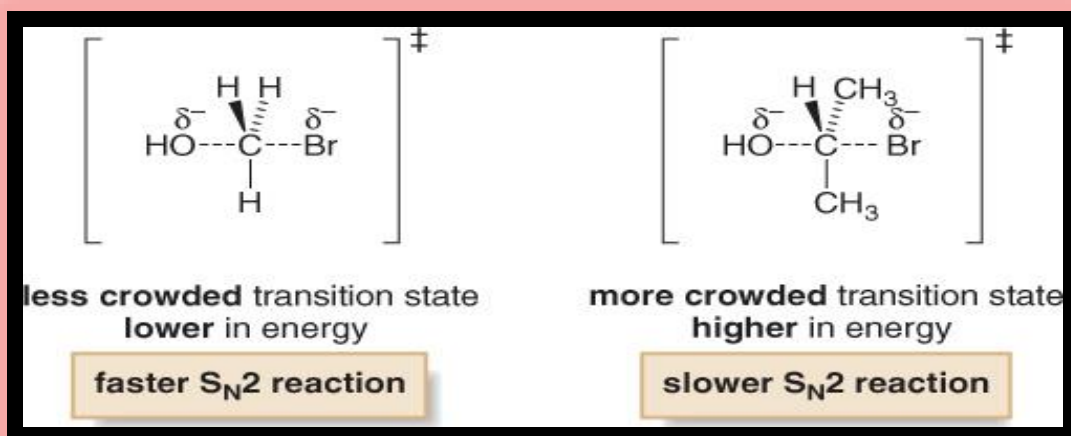
The rate of an S_N1 reaction is affected by the type of alkyl halide involved

- As the number of R groups on the carbon with the leaving group *increases*, the rate of an S_N1 reaction *increases*.



This trend is exactly opposite to that observed in S_N2 reactions.

Increasing the number of R groups on the carbon with the leaving group increases crowding in the transition state, thereby decreasing the reaction rate. The S_N2 reaction is fastest with unhindered halides.



Carbocation Stability

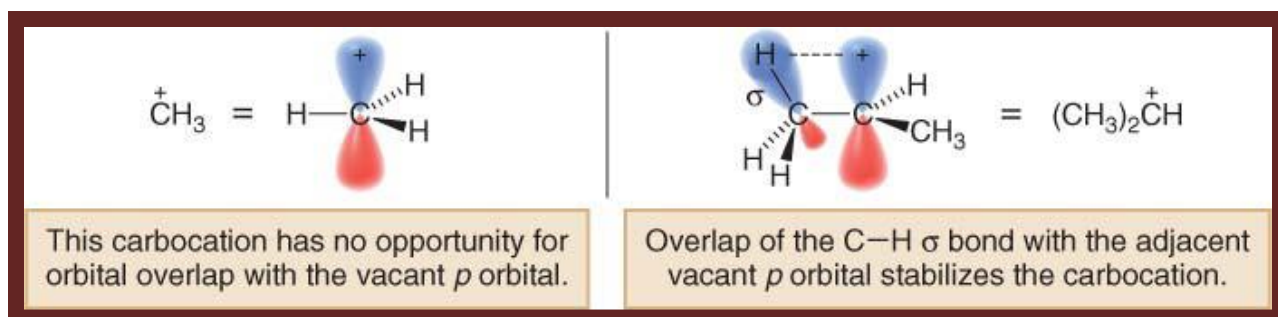
- The effect of the type of alkyl halide on S_N1 reaction rates can be explained by considering carbocation stability. Carbocations are classified as primary (1°), secondary (2°), or tertiary (3°), based on the number of R groups bonded to the charged carbon atom. As the number of R groups increases, carbocation stability increases.

Inductive Effect

Carbocation stability depends upon inductive effects & hyperconjugation. Inductive effects are electronic effects that occur through σ bonds. The inductive effect is the pull of electron density through σ bonds caused by EN differences between Atoms. Alkyl groups are electron donating groups that stabilize a positive charge. Since an alkyl group has several σ bonds, each containing electron density, it is more polarizable than a hydrogen atom, and better able to donate electron density. The greater the no. of alkyl groups attached to a carbon with a positive charge, the more stable will be the cation.

Hyperconjugation

The order of carbocation stability is also a consequence of hyperconjugation. It is the spreading out of charge by the overlap of an empty p orbital with an adjacent σ bond. This overlap (hyperconjugation) delocalizes the positive charge on the carbocation, spreading it over a larger volume, and this stabilizes the carbocation. Example: CH_3^+ cannot be stabilized by hyperconjugation, but $(\text{CH}_3)_2\text{CH}^+$ can.



Relative reaction rates of halogen exchange.

Alkyl halide	Structure	Class	Relative reaction rate
Methyl bromide	CH ₃ Br	Methyl	163
Ethyl bromide	CH ₃ CH ₂ Br	Primary	1
Isopropyl bromide	(CH ₃) ₂ CHBr	Secondary	0.00074
<i>tert</i> -butyl bromide	(CH ₃) ₃ CBr	Tertiary	negligible small

The cause of the reaction rate's large decrease in the halogen exchanges with different alkyl bromides is the increasing steric shielding of the central carbon. In an S_N2 reaction, the nucleophile has to approach the central carbon from the side opposite to the leaving group (here: bromide). This approach is more sterically hindered the more alkyl substituents the central carbon carries. In the three-dimensional, interactive molecular models below, the steric effects of alkyl substituents are illustrated, in particular, when the spacefill presentation is activated.

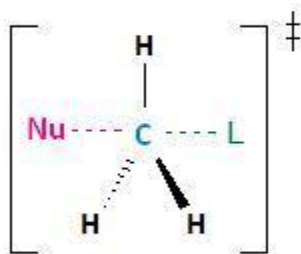
Due to extremely low steric shielding by hydrogen atoms, methyl halides are particularly reactive in S_N2 reactions. Primary substrates react considerably more rapidly than secondary and tertiary substrates do. In *tert*-butyl bromide, the reaction center is almost completely blocked by the three methyl substituents. Therefore, the S_N2 reaction with *tert*-butyl bromide can only proceed extremely slowly.

Sterically Hindered Substrates Will Reduce the S_N2 Reaction Rate

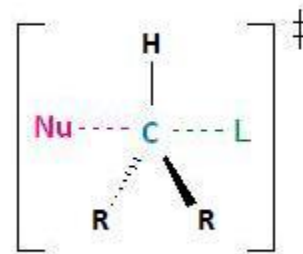
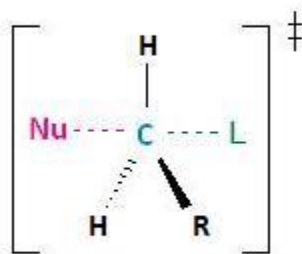
Although the substrate, in the case of nucleophilic substitution of haloalkanes, is considered to be the entire molecule circled below, we will be paying particular attention to the alkyl portion of the substrate. In other words, we are most interested in the electrophilic center that bears the leaving group.

If each of the three substituents in this transition state were small hydrogen atoms, as illustrated in the first example below, there would be little steric repulsion between the incoming nucleophile and the electrophilic center, thereby increasing the ease at which the nucleophilic substitution reaction can occur. Remember, for the S_N2 reaction to occur, the nucleophile must be able to attack the electrophilic center, resulting in the expulsion of the leaving group. If one of the hydrogens, however, were replaced with an R group, such as a methyl or ethyl group, there would be an increase in steric repulsion with the incoming nucleophile. If two of the hydrogens were replaced by R groups, there would be an even greater increase in steric repulsion with the incoming nucleophile.

S_N2 Transition State



Least Steric Repulsion



Greater Steric Repulsion

How does steric hindrance affect the rate at which an S_N2 reaction will occur? As each hydrogen is replaced by an R group, the rate of reaction is significantly diminished. This is because the addition of one or two R groups shields the backside of the electrophilic carbon, impeding nucleophilic attack.

The diagram below illustrates this concept, showing that electrophilic carbons attached to three hydrogen atoms results in faster nucleophilic substitution reactions, in comparison to primary and secondary haloalkanes, which result in nucleophilic substitution reactions that occur at slower or much slower rates, respectively. Notice that a tertiary haloalkane, that which has three R groups attached, does not undergo nucleophilic substitution reactions at all. The addition of a third R group to this molecule creates a carbon that is entirely blocked.

SN₂ Displacement Reactivity of Haloalkanes

