

University of Tikrit
College of science
Department of Chemistry



A Scientific Essay

on

Aliphatic Nucleophilic Substitution

(SN₁ & SN₂ Reactions)

Papered by PhD students

Emaad Mohammed Alawsaj

Anahed Abdulghaffar Yaseen

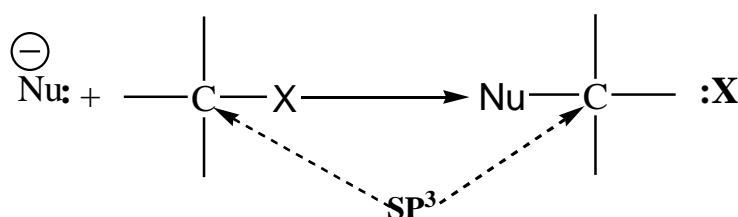
Supervised by

Prof. Dr. Hanaa .Kaain. Salih

Introduction:

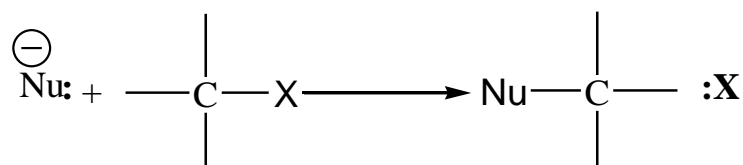
❖ Nucleophilic substitution

Nucleophilic substitution at carbon is of broad synthetic utility and has received exceptionally detailed mechanistic study by organic chemists. The goal developing a coherent mechanistic interpretation was first undertaken by C. K. Ingold and E. D. Hughes in England in the 1930s. Their studies laid the basis for current understanding. Nucleophilic substitution reactions may involve several different combinations of charged and uncharged species as reactants of.



❖ **Aliphatic Substitution:-**

In nucleophilic aliphatic substitution the attacking (electron donating) reagent (the nucleophile) brings an electron pair to the substrate, using this pair to form the new bond, and the leaving group (the nucleofuge) comes away with an electron pair:-



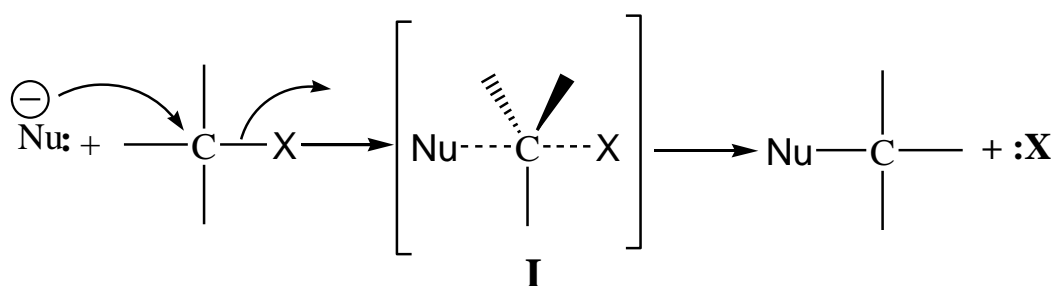
This equation says nothing about charges. Nucleophile Y may be neutral or negatively charged.

❖ **Mechanism of Aliphatic Substitution:**

Several distinct mechanisms are possible for aliphatic nucleophilic substitution reactions, depending on the substrate, nucleophile, leaving group, and reaction conditions. In all of them, however, the attacking reagent carries the electron pair with it, so that the similarities are greater than the differences. There for these reactions can be classified as bellow :

- **The S_N2 Mechanism:**

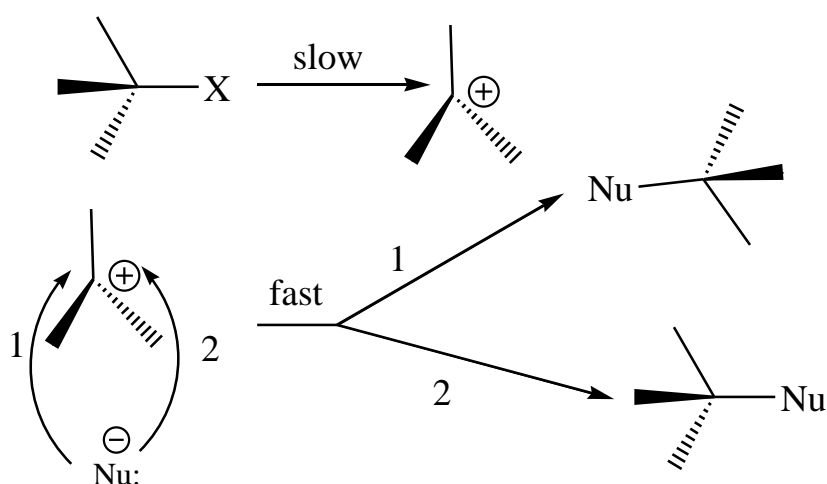
The designation S_N2 stands for *substitution nucleophilic bimolecular*. In this mechanism, there is backside attack, the nucleophile approaches the substrate from a position 180 away from the leaving group. The reaction is a one-step process with no intermediate. The C-Y bond is formed as the C-X bond is broken to generate transition state(I):



The energy necessary to break the C-X bond is supplied by simultaneous formation of the C-Y bond. The position of the atoms at the top of the curve of free energy of activation is represented as transition state **I**. Of course, the reaction does not stop here since this is the transition state. The group X must leave as the group Y comes in, because at no time can the carbon have more than eight electrons in its outer shell. When the transition state is reached, the central carbon atom has gone from its initial sp³ hybridization to an sp² state with an approximately perpendicular *p* orbital. One lobe of this *p* orbital overlaps with the nucleophile and the other with the leaving group.

- **The S_N1 Mechanism:**

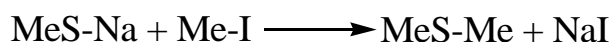
The most ideal version of the S_N1 mechanism (*substitutional nucleophilic unimolecular*) consists of two steps, (once again, possible charges on the substrate and nucleophile are not shown):



❖ **The effect of Concentration [R-X] and [Nu] on S_N1 & S_N2 (Kinetics for the mechanisms):**

1-S_N2 mechanism:

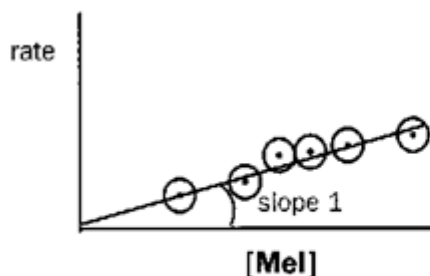
The reaction between [SMe] (as Nucleophile) and Me-I were indeed S_N2 as we would expect:



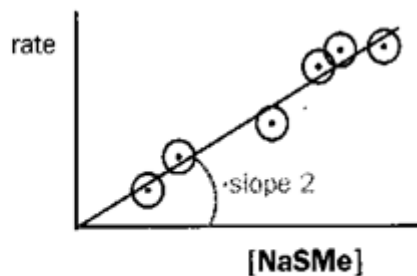
First we would keep the concentration of [SMe] constant and vary that of [MeI] and see what happened to the rate. Then we would keep the concentration of [MeI] constant and vary that of [MeS] and see what happened to the rate. If the reaction is indeed S_N2 we should get linear relationships in both cases. The first graph tells us that the rate is proportional to [MeI], that is **rate = k₁[MeI]** and the second graph that is proportional to [MeSNa], that is **rate = k₂[MeSNa]**.

The Question

Why are the slopes different?



First Graph



Second Graph

If you look at the rate equation for the reaction you will see that we have incorporated a constant concentration of one of the reagents into what appears to be the rate constant for the reaction. the true rate equation is :

$$\text{Rate} = k_2[\text{MeSNa}][\text{MeI}]$$

If [MeSNa] constant the equation becomes:

$$\text{Rate} = k_1[\text{MeI}] \text{ where } k_1 = k_2[\text{MeSNa}]$$

If [MeI] constant the equation becomes:

$$\text{Rate} = k_2[\text{MeSNa}] \text{ where } k_2 = k_1[\text{MeI}]$$

$$\text{Slope 1} = k_1 = k_2[\text{MeSNa}], \text{ but slope 2} = k_2 = k_1[\text{MeI}].$$

We can easily measure the true rate constant k_2 from these slope because we know the constant values for [MeSNa] in the first experiment and the for [MeI] in the second .

2 -S_N1 mechanism:

In this mechanism the starting material tertiary alkyl halide [t-BuBr] with base [NaOH] the mechanism following below :

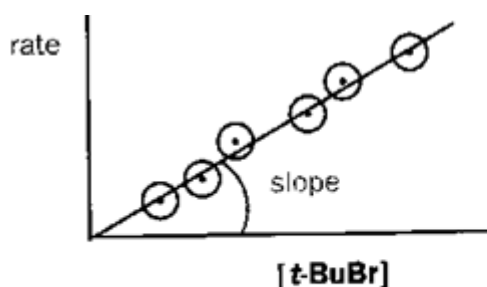
The formation of Cation is the rate determining and the Nucleophile attacks the carbon cation. The rate of disappearance of t-BuBr is simply the rate of slow step is called the (**the rate determining**) step. It's a Unimolecular reaction with simple rate of equation :

$$\text{Rate} = k_1[\text{t-BuBr}]$$

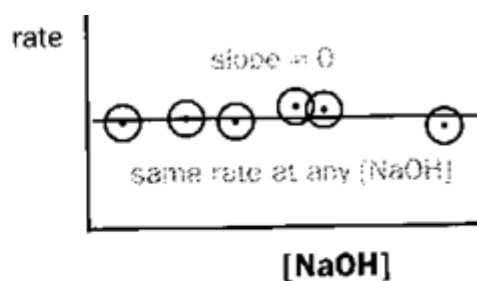
They look like this when we vary [t-BuBr] at constant [NaOH] and then vary [NaOH] at constant [t-BuBr]. The slope of the first graph is simply the first order constant because :

$$\text{Rate} = k_1[\text{t-BuBr}]$$

But the second graph is zero, the rate determining step does not involve NaOH adding more of it does not speed up the reaction. The reaction shows first order kinetics .



first graph



second graph

SUMMARY

<i>Reaction</i>	<i>S_N2</i>	<i>S_N1</i>
R-x	Methyle > Primary...	Tertiary > Secondary...
Nucleophile	Strong Nucleophile	Poor Nucleophile
Mechanism	One step	Two steps
Rate limiting step	Bimolecular T.S	Carbon cation
Rate Law	Rate=k[R-X][Nu]	Rate=k[R-X]
Stereochemistry	<i>Inversion of configuration</i>	Mixed configuration
Solvent	Polar a protic	Polar protic

References

- ❖ **Advanced Organic Chemistry ,fourth edition ,(Francis A.Carey &Richard J.Sudberg),University of Virginia.**
- ❖ **Michael B. Smith and Jerry March March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Sixth Edition.**
- ❖ **Morrison and Boyd Organic Chemistry, Sixth Edition.**