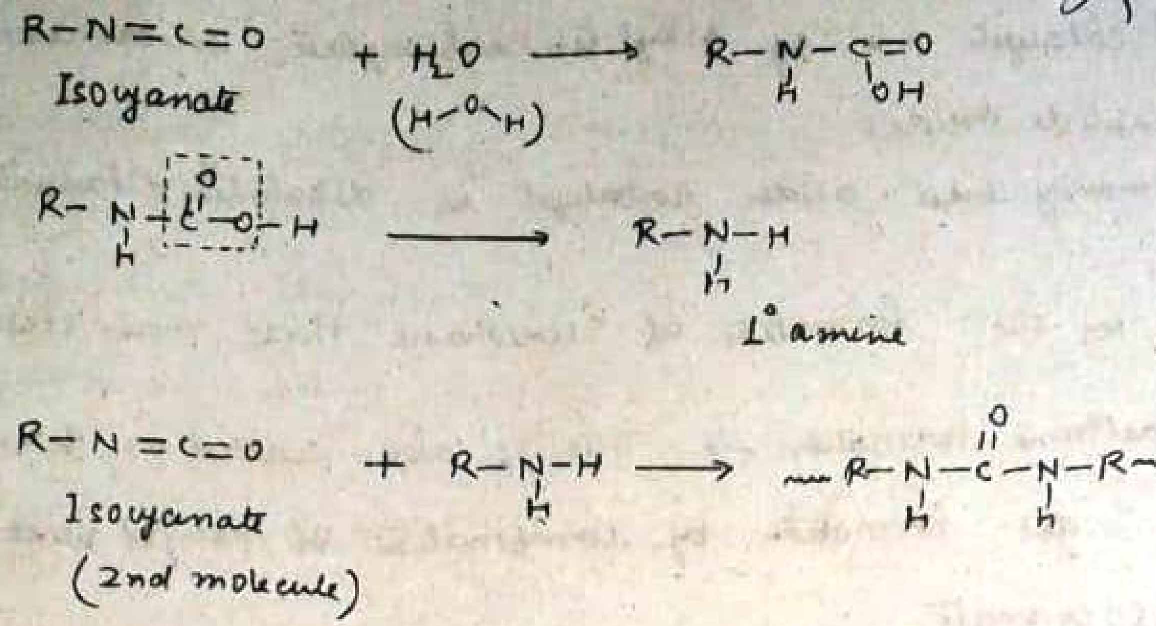
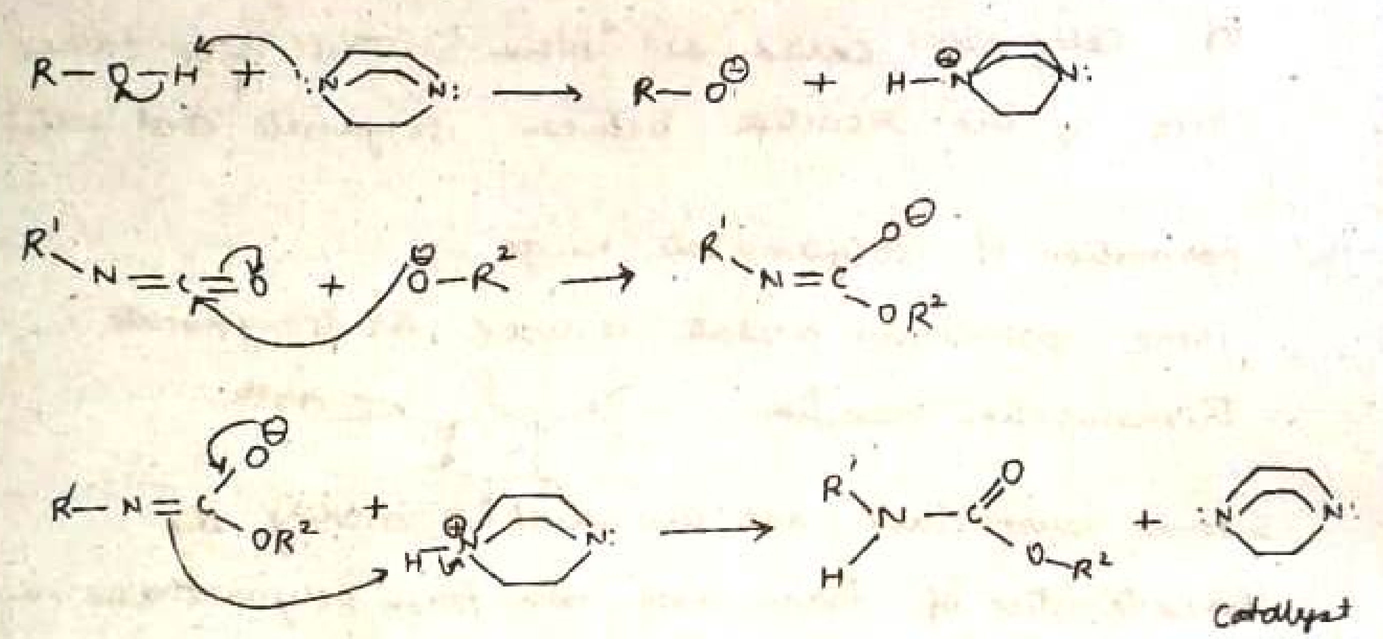
ii)



Action of Catalyst (3° amine)



Overall reaction →

$$R_1-N=C=O + R_2-O-H \longrightarrow R_1-N(H)-C(=O)-O-R_2$$

The use of CO_2 gas formed in step(ii) is for making foam (cells). However this reaction may be replaced by using a volatile liquid eg n-pentane.

Heat generated during polymerisation cause vaporisation of volatile liquid

Here the isocyanate used is very much hazardous because.

i) It is powerful irritant

ii) It can cause breathing problem

iii) It is dangerous for eyes and skin if not handled cautiously.

Therefore, green methods are required for the valuable polymer.

This product was first made made by Otto Bayer in 1937 and it became commercially available in 1952.

Since then its use has stepped in various walks of our lives. Some important uses are

a) Flexible foam for seating

b) Rigid foam for insulation panels

c) Microcellular foam for seals and gaskets

d) Durable elastomeric wheels eg for escalator, rollercoaster

e) As adhesive

f) Synthetic fibres eg spandex

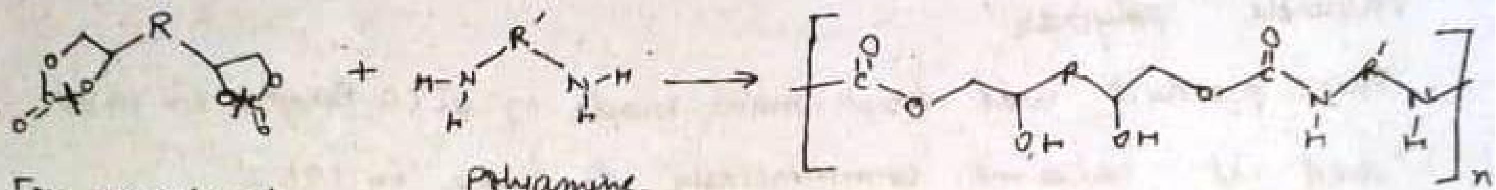
g) Hard plastic parts for electronic instrument etc.

For green methods,

polyols are derived from vegetable oils eg soyabean, cotton seed, neem seed, castor oil etc.

In recent years, intensive research has been carried out to prepare isocyanate free or urethane by the reaction between polyamines and cyclic carbonate to produce polyhydroxy urethanes

The basic reaction is as follows:-

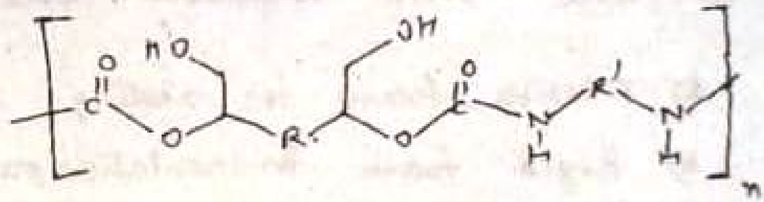


Five membered cyclic carbonate

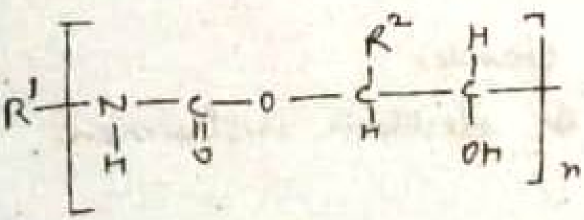
Polyamine

β-hydroxy urethane

or,



Thus basic structure of hydroxy urethane modified (HUM) is



10 BY

Application of microwave for synthesis of a compound

conventional methods for synthesis of organic compounds require longer heating time, complex apparatus, use of solvent and reagent in large amount. These arrangement result a little higher cost of production.

In spite of these problems, there are problems which include safety and health of workers and then a sufficient amount of waste is generated which are disposed in some cases but, in general, they are left as it is, which causes environment problems in a very serious way.

However, when green chemistry principles are applied then it increases the efficiency of synthetic methods, less toxic reagents and solvents are used, the number of stages of the reaction is decreased and at last the waste which is formed, is minimised.

Microwave synthesis is regarded as an important tool for the chemists which is much more eco friendly. Microwave radiation directly affects the reacting molecules and by passing thermal conductivity causes rapid rise in temperature. As a result of uniform heating, the reaction is completed in a very less amount of time and a good yield of product is obtained.

In microwave synthesis, the time required for completion of a reaction is in seconds not in hours also, in many cases no solvent is required, thus the problem of waste disposal is eliminated with a clean chemical process, higher yields and greater selectivity

Microwave radiations are electromagnetic waves which is located between radio wave and IR (infrared) radiations. Microwaves have a wavelength of 1 mm to 1 m and corresponds to frequencies between 0.3 G.Hz and 300 G.Hz. Microwave uses the ability of some liquids and solids to transform the radiation into heat which causes a reaction to occur.

Mechanism of microwave heating :-

When microwave is irradiated to a substance than different substance exhibit different behaviour towards microwave. Their behaviour can be classified as

i) Substances which can absorb microwave radiation eg. water

ii) Substances which reflect microwave eg copper
These have high conductivity.

iii) Substances which are transparent to microwave eg sulphur.

Three different mechanisms are involved for the heating tendency

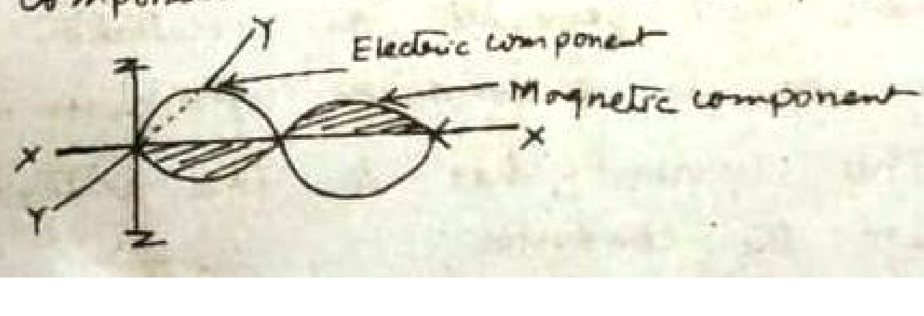
a) Dipolar polarisation

b) Conduction mechanism

c) Interfacial polarisation

a) Dipolar polarisation →

For a substance to generate heat when irradiated with microwave must possess a dipole moment. We know that similar to all other electromagnetic radiation, microwave radiation has also a magnetic field component and an electric field component



when microwave is irradiated on a substance (dipole) having dipole moment then its dipole tries to reorient itself with the alternating electric field component of radiation, & it loses its energy in the form of heat by molecular friction.

Dipolar polarization can generate heat either by interaction between polar solvent molecules eg water, methyl alcohol, ethyl alcohol or by interaction between polar solute molecules such as ammonia etc.

Here it should be noted that the frequency range of oscillation must be approximately equal to the interparticle interaction. If the frequency range is very high than the required value then inter-molecular forces will stop the motion of polar molecules and if the frequency range is less than the required value then the polar molecules will take much time to align itself with the electric field.

b) Conduction mechanism →

The conduction mechanism generates heat through resistance to an electric current. The oscillating electromagnetic field generates an oscillation of electrons or ions in a conductor, giving an electric current. This current has to face internal resistance, which heats the conductor.

Thus a solution containing ion or ions will move through the solution under the influence of electric field at the cost of expenditure of energy and hence, more polar the solvent, more readily the microwave radiation is absorbed and higher the temperature.
Also, when the sample is electrical conductor, the charge carrier i.e. electrons or ion etc are moved through the material under the influence of electric field, causing polarisation. These induced current in the sample causes heating due to any electrical resistance.
However, materials with high conductivity will reflect most of the microwave radiation energy fall on them. This is one of the limitations of this method.

c) Interfacial polarisation ⟶

Interfacial polarisation method may be considered as a combination of both the two methods above discussed. In this method, the ultimate -quirement is that, the heating system must be conducting material dispersed in a non-conducting material.
For example dispersion of metal particles in sulphur. Sulphur does not respond to microwave and metals reflect most of microwave energy incident on it. However, when both these two are combined together

they form a good absorber of microwave radiation. But the metal must be in powder form because metal powder is good microwave absorbing material but metal surface is not.

The environment of metal powder acts as a solvent for polar molecules and restricts the motion of ions by forces that are equivalent to inter-particle interaction in polar solvent. These restricting forces under the effect of an oscillating field induce a phase lag in the motion of ions, causing a random motion of ions and heating of system occurs.

For achieving this result specific apparatus for synthesis has been devised which are called as

i) Single mode microwave apparatus
ii) Multi mode microwave apparatus.

i) Single mode microwave apparatus → It has ability to create a standing wave pattern. This interface generates a no of nodes where microwave energy intensity is zero and a no of nodes (array) of antinodes where the intensity of microwave energy is maximum. It has high rate of heating because the sample is always placed at the antinode where intensity of microway radiation is highest.

In sealed-vessel condition the apparatus can process the volume from 0.2 to about 50 ml whereas in open-vessel condition about 150 ml can be processed.

Limitation— Only one vessel can be irradiated at a time

ii) Multimode microwave apparatus →

In this apparatus, generation of a standing wave pattern is avoided so that a chaos is created inside the apparatus. Greater the chaos, higher is the dispersion of radiation and hence large area can be heated and hence a number of samples can be kept for heating simultaneously.

Limitation → Heating samples can not be controlled due to lack of temperature uniformity