



# ADVANCED CHEMISTRY BLOC

## (THERMAL DECOMPOSITION)

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Temperature, relative humidity, pressure and chemical constituents all exert a modifying influence on the compounds. They just try to adapt to new conditions just like living beings. Stability plays a key role, after all steps move towards more stable state in thermodynamic sense. In this context, thermal decomposition is a significant area, both in organic and inorganic chemistry.

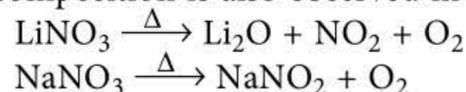
$\text{Be}^{2+}$  ion has very high polarising power. It polarises  $\text{CO}_3^{2-}$  ion to such an extent that  $\text{BeCO}_3$  has high degree of covalent character or low lattice energy. On the other hand,  $\text{BeO}$  has high lattice energy owing to small sized ions. This difference in lattice energy between  $\text{BeCO}_3$  and  $\text{BeO}$  acts as the driving force in their thermal decomposition. Practically,  $\text{BeCO}_3$  decomposes even under room temperature. It appears as if  $\text{BeCO}_3$  is eager to move towards  $\text{BeO}$ , which has higher lattice energy. Thermal stability of group-2 carbonates changes as :  $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$

In a similar way, you easily understand the following observations :

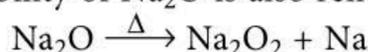
- Thermal stability of group-1 carbonates :  
 $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{CO}_2$   
 $\text{Na}_2\text{CO}_3$  is stable to even red heat.
- Thermal stability of group-1 hydroxides :  
 $\text{LiOH} \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{H}_2\text{O}$   
 $\text{NaOH}$  is stable to heat.

Similarly, thermal stability of hydroxides increases as for group-2 :

$\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$   
 Decomposition is also observed in nitrates :

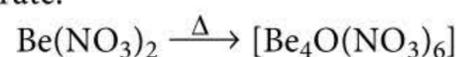


A possible explanation can be :  $\text{Li}_2\text{O}$  has high lattice energy but  $\text{Na}_2\text{O}$  is thermally less stable. Poor thermal stability of  $\text{Na}_2\text{O}$  is also reflected in the reaction :

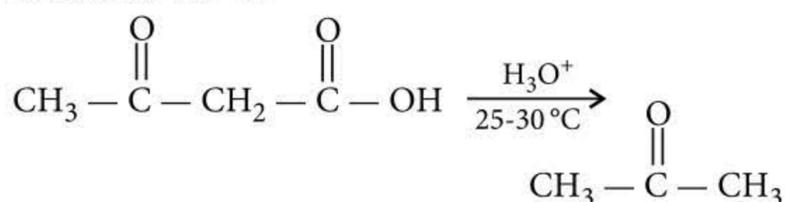


This is also the reason why on heating in air Na forms  $\text{Na}_2\text{O}_2$  but Li forms  $\text{Li}_2\text{O}$ .

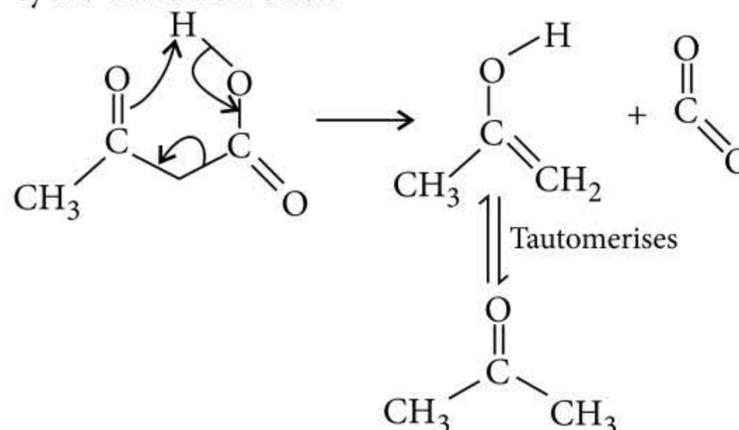
$\text{Mg}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  behave like  $\text{LiNO}_3$ ,  $\text{Be}(\text{NO}_3)_2$  however, on heating at  $125^\circ\text{C}$  forms basic beryllium nitrate.



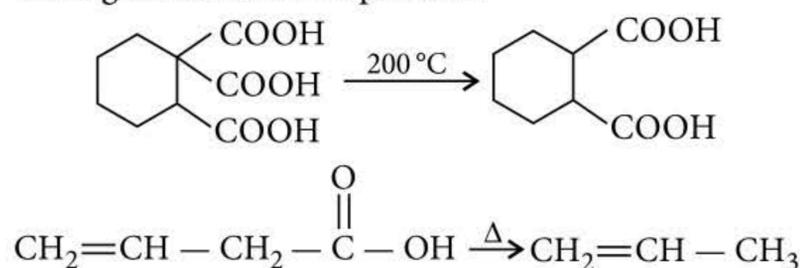
Complexing ability of Be is responsible for this pattern. Thermal decomposition in organic compounds are also very common, particularly in carboxylic acids.  $\beta$ -keto acids undergo decomposition in acidic medium even at  $25\text{-}30^\circ\text{C}$ .



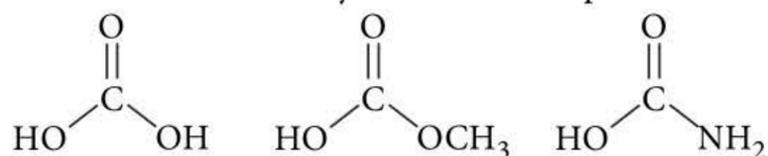
The compound, however, resists thermal decomposition in basic medium. This implies presence of acidic proton is necessary for the decomposition, which involves a cyclic transition state.



$\beta$ -diacids,  $\beta$ -cyano acids,  $\beta$ ,  $\gamma$ -unsaturated acids also undergo similar decomposition.

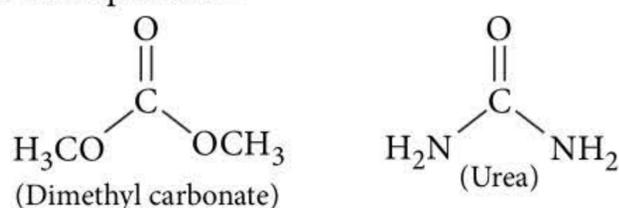


There are few compounds, which undergo spontaneous decompositions. You prepare them and they just decompose. Following are three such compounds. Carbonic acid is a very common example.



There is one thing common : An acid functional group whose  $-\text{CO}-$  is also a part of another acid or acid derivative functional group.

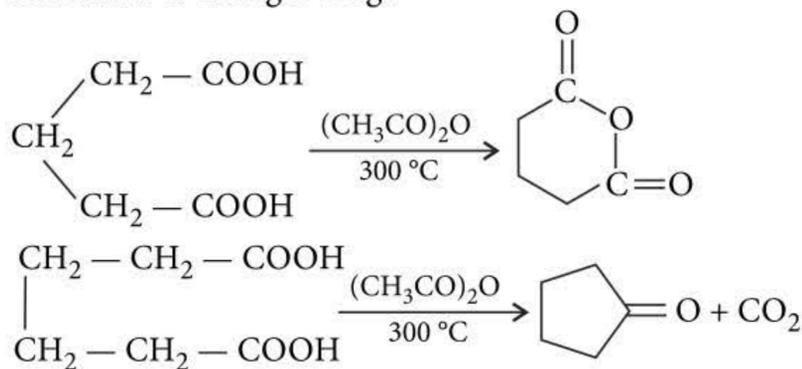
When you have two acid derivative functional groups, sharing one  $-\text{CO}-$  group, the compound is thermally stable. Examples are :



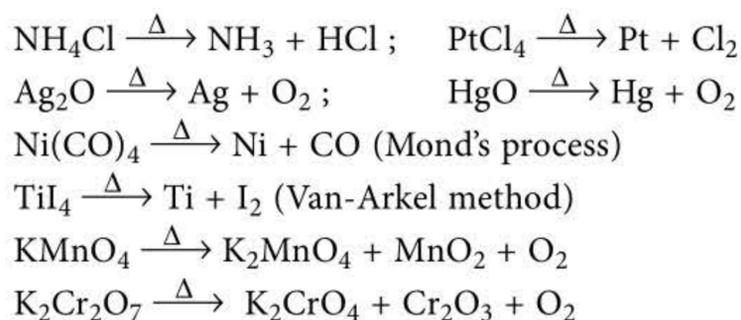
In all the above decomposition reactions, formation of  $\text{CO}_2$  is the driving force.

1, 5-dicarboxylic acid when heated to  $300^\circ\text{C}$  in presence of acetic anhydride gives cyclic anhydride. Under similar conditions 1,6-dicarboxylic acid prefers to give cyclic

ketone, probably because formation of anhydride would have lead to a larger ring.



Many such thermal decompositions are part of your syllabus.

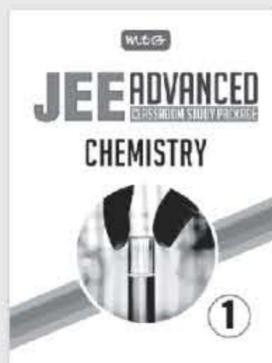
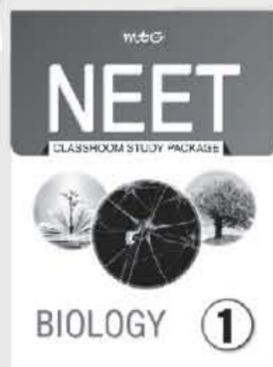


Never hesitate to remember these reactions. Studying chemistry is like maintaining a delicate balance between informations and concepts.



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