Semester IV

CHE-HC-4014: INORGANIC CHEMISTRY-III

Topic: Coordination Chemistry

Chelate Effect

Chelate Effect

- The enhanced stability of polydentate complexes compared to their monodentate counterparts is known as the ***chelate effect***. It is chiefly an entropy effect common to all chelate systems, but often addition stabilization results from enthalpy changes.
- Let us consider the following reaction:

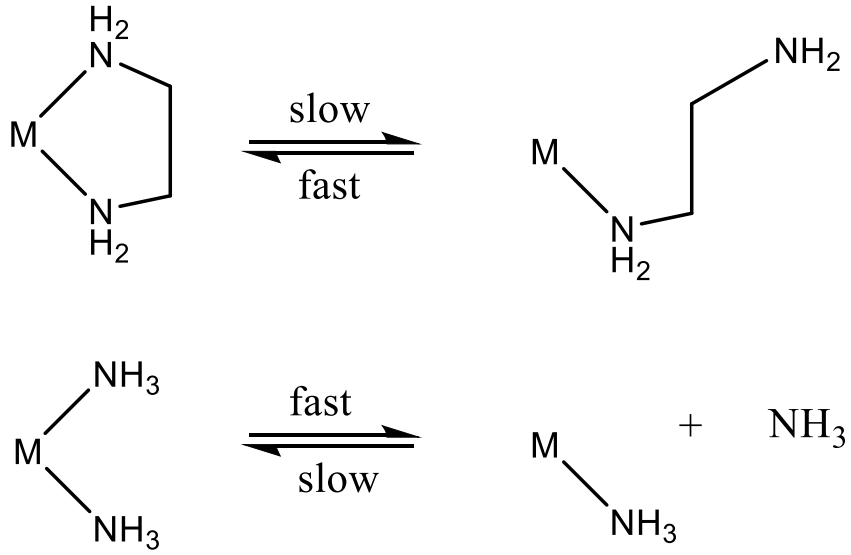
$$[Ni(NH_3)_6] + 3\ en \rightleftharpoons [Ni(en)_3] + 6\ NH_3$$

- In the above reaction, ΔH is expected to be small as the bonding characteristics of **en** and **NH_3** would be similar.
- Again, ΔS could be considered proportional to the change in the no. of particles at the beginning and end of the reaction.
- Since, ΔS is +ve, the translational entropy favours the formation of the chelate system instead of the hexamine system.

Chelate Effect

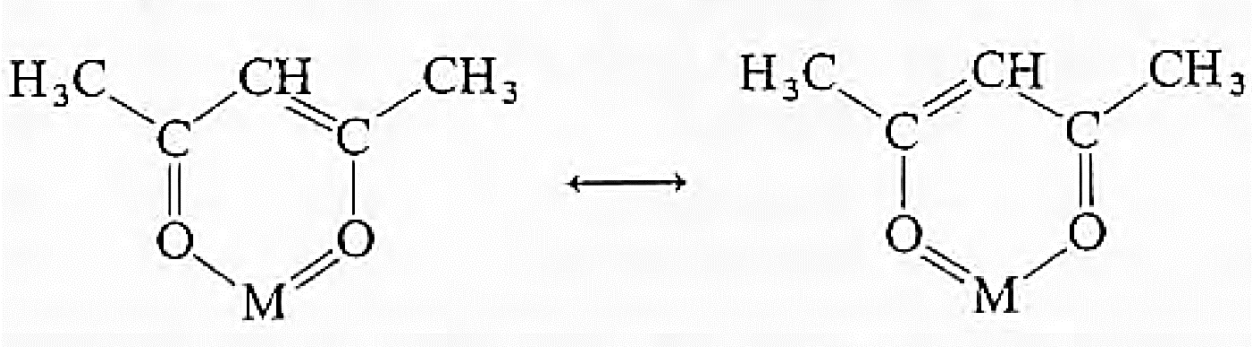
- It was again observed that substitution for a chelated ligand is generally a slower reaction than that for a similar monodentate ligand.
- This kinetic chelate effect can be explained as follows:

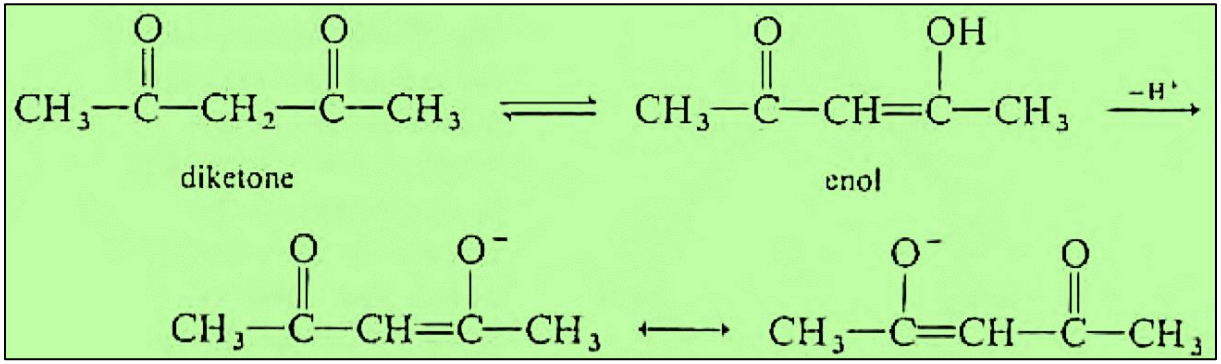
First, the ΔH associated with removal of the first bound atom is larger than for a related monodentate ligand. If this atom does separate from the metal center, its kinetic barrier for subsequent reattachment is lower than for a related monodentate ligand since the former remains in close proximity to the metal center.



Chelate Effect

- **Resonance stabilization**: Chelating ligand such as ‘acac’ enjoys resonance stabilization due to the formation of six-membered chelate rings having some aromatic character. Thus, with M^{3+} metals, acac forms neutral tris complexes. As a result of resonance, the two M-O bonds, the two C-O bonds, and the two ring C-C bonds are equal in length. E.g.: $[Cr(acac)_3]$, $[Co(acac)_3]$, etc.





Chelate Effect

- The chelate effect is amplified in the case of polydentate ligands that forms several chelate rings upon coordination to single metal center. For. e.g., **edta** with six ligating atoms forms extremely stable metal complexes.
- Unlike organic ring system, maximum stability in chelate rings arises from five membered rings because the metal atom is larger than a carbon atom and the bond angles at the metal (L-M-L) will be 90° in square planar and octahedral complexes in contrast to an optimum angle of ca. 109 ° for tetrahedral carbon.
- For rings exhibiting significant resonance effects, such as **acac**, six-membered rings are quite stable.
- Larger and smaller chelate rings are known but they are not nearly as **stable** as that of five and six-membered rings.