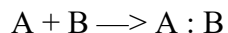


# Reaction mechanism CC13

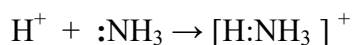
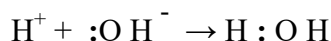
## Types of Reactions

There are thousands of different chemical reactions. However these can largely be classified into one of three different categories on the basis of how the valency electrons are involved during reactions.

### (1) *Acid-Base Reactions*



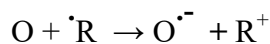
acid + base  $\longrightarrow$  coordinate bond



Here the generalized or Lewis definition of an acid and a base is applied. Thus an *acid* is a substance that can accept a pair of electrons and a *base* is a substance that donates a pair of electrons. It follows then that a metal ion, like hydrogen ion, is an acid and a ligand with its pair of electrons is a base. The formation of metal complexes and the replacement of one ligand by another or one metal by another in these systems then are examples of acid-base reactions.

### (2) *Oxidation-Reduction Reactions*

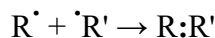
Oxidation-reduction reactions differ from acid-base reactions in that electron interchange occurs instead of electron sharing. Since metals generally have more than one oxidation state, redox reactions of metal complexes are very common.



oxidizing agent + reducing agent  $\longrightarrow$  electron interchange

### (3) *Free Radical Reactions*

Many reactions are known to proceed by a free radical process. This type of reaction may be considered as something between Acid-Base Reactions and Oxidation-Reduction Reactions. For metal complexes such reactions are often classified as oxidation-reduction reactions.

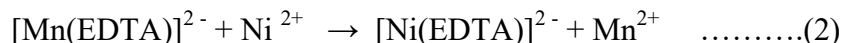


radical 1 + radical 2  $\longrightarrow$  chemical bond

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## SUBSTITUTION REACTIONS

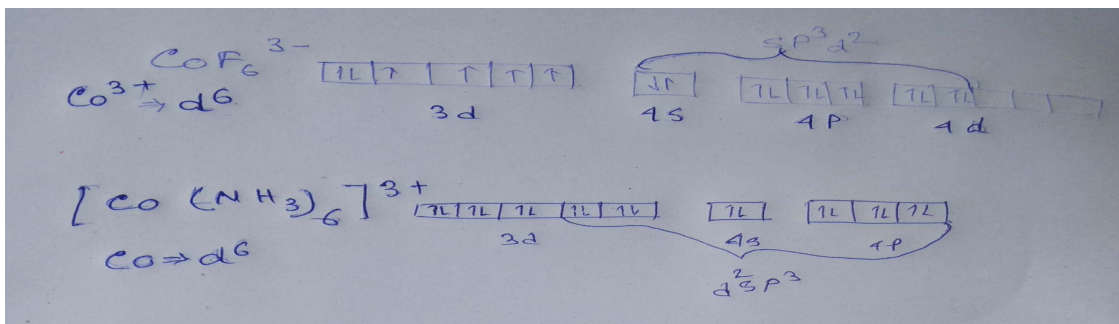
Substitution reactions are reactions in which one ligand in a complex is replaced by another as shown by Eqs. (1), or in which one metal is replaced by another as in Eqs. (2).



These reactions are all of the acid-base type where the weaker base (coordinated ligand) is replaced by a stronger base (entering ligand) or the weaker acid (coordinated metal ion) is replaced by a stronger acid (entering metal ion). Following usual organic terminology, ligand-replacement reactions are examples of nucleophilic substitution reactions. This term is used to designate that the reagent (entering ligand) or nucleophile is electron rich and seeks the nucleus of the substrate (metal ion of the complex). Metal ion-replacement reactions are examples of electrophilic substitution reactions. The reagent (entering metal ion) is an electrophile which seeks the electrons of the substrate (ligands of the complex).

Any attempt to understand and predict something about the relative reactivities of metal complexes requires some knowledge about the nature and the energy of the metal-ligand bond. In recent years the valence bond theory as applied to these systems has been largely replaced, in chronological order, by the crystal field, the ligand field, and the molecular orbital theories.

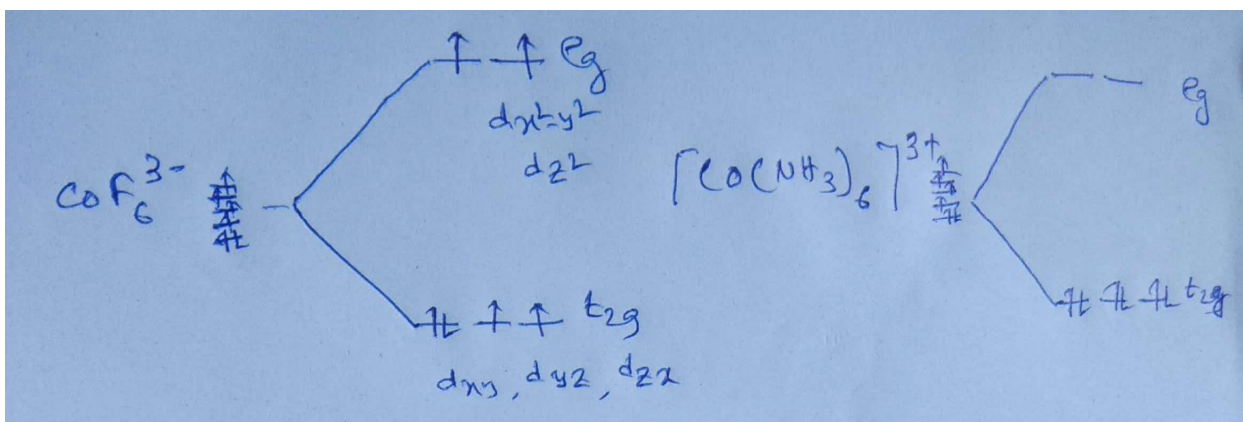
Restricting ourselves to a six-coordinated system and to the valence bond theory and crystal field theory, it is possible to illustrate the bonding in complexes and to designate the nomenclature using  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  as examples. It is first necessary to know that  $[\text{CoF}_6]^{3-}$  is paramagnetic with four unpaired electrons, whereas  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic. On the basis of the valence bond theory the electronic structures are designated as  $sp^3d^2$  or  $d^2sp^3$  hybridizations.



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Thus  $[\text{CoF}_6]^{3-}$  is called an outer-orbital (uses  $nd$  orbitals) or a spin-free or high-spin (electrons are not paired) complex, and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is called an inner-orbital (uses  $(n-1)d$  orbitals) or a spin-paired or low-spin (electrons are paired) complex.

The crystal field theory considers the metal-ligand bond to be ionic and worries only about the effect that the negative point charges at the corners of the octahedron have on the energy levels of the  $d$  orbitals. Because of the geometry of the  $d$  orbitals the  $d_{x^2-y^2}$  and the  $d_{z^2}$  orbitals which point directly at the ligands become higher in energy. On the other hand, the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ , with lobes oriented between the  $x$ ,  $y$ , and  $z$  axes, become of lower energy. This difference in energy level between the two sets of  $d$  orbitals is called the crystal field splitting. The electronic structures for  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  are designated by the following diagram.



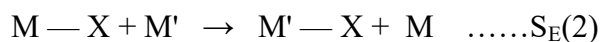
Relative to a random distribution of electrons, the lower energy level orbitals stabilize the system by  $4Dq$  units per electron, whereas the higher energy orbitals represent a destabilization of  $6Dq$  units. Thus the crystal field stabilization energy, (CFSE) for  $[\text{CoF}_6]^{3-}$  is  $4 \times 4 - 2 \times 6 = 4Dq$ , and that for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is  $6 \times 4 - 0 \times 6 = 24Dq$ .

Taube's classification designates complexes as *labile* if they react completely at room temperatures within the time of mixing  $0.1 M$  solutions, and as *inert* if under these conditions the rate of reaction can be followed by conventional kinetic techniques. For six-coordinated complexes on the basis of the valence bond theory it is possible to classify labile systems as being either outer-orbital complexes (e.g.  $[\text{CoF}_6]^{3-}$ ) or inner-orbital complexes having at least one vacant  $d$  orbital. Only the inner-orbital complexes containing no vacant  $d$  orbitals are inert, e.g.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

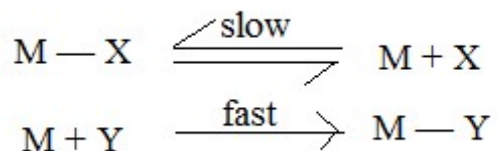
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## CLASSIFICATION OF REACTION MECHANISMS

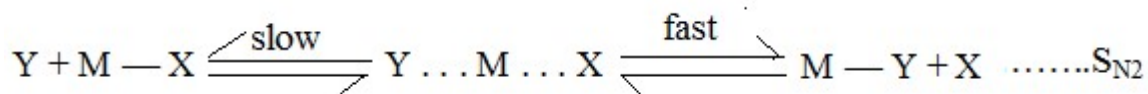
Substitution reactions of metal complexes may involve the replacement either of one ligand by another (X by Y) or of one metal by another (M by M'). Following the terminology of Hughes and Ingold, developed for organic reactions, these are assigned the symbols  $S_N$  (*substitution nucleophilic*) and  $S_E$  (*substitution electrophilic*), Eqs. (1) and (2), respectively



Each of these reaction processes may be considered to involve two fundamentally different reaction paths. For example,  $S_N$  reactions (the same is true for  $S_E$  reactions) may take place by the prior slow removal of X, followed by the rapid addition of Y.



Such a process is called a *dissociation* mechanism and is given the symbol  $S_{N1}$  (**substitution nucleophilic unimolecular**). An alternative reaction path is one in which Y is directly involved in assisting the removal of X,



This is called a *displacement* mechanism and is designated by the symbol  $S_{N2}$  (substitution, nucleophilic, bimolecular). It must be recognized that mechanisms other than  $S_{N1}$  and  $S_{N2}$  (similarly  $S_{E1}$  and  $S_{E2}$ ) are known.

Suitably designed experiments often provide information which permits the classification of substitution reactions as either  $S_{N1}$  or  $S_{N2}$ . However it should be noted that the evidence is usually indirect and requires some interpretation. Unfortunately it is difficult to obtain direct, unequivocal evidence as to the exact reaction mechanism. For example, proof of an  $S_{N1}$  process

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may be obtained by detecting the active intermediate of lower coordination number, M. Direct detection of M is often impossible because it is so very reactive and its presence or absence is usually judged on the basis of indirect means.

Chemical kinetics plays a major role in investigations of reaction mechanisms. In principle, the kinetic order or rate law of a reaction helps establish its mechanism. Thus an  $S_{NI}$  process is expected to have a rate law of the form,

$$\text{rate} = k [M-X]$$
 where  $k$  is the first-order rate constant.

This follows from the fact that the rate-determining step, depends only on the complex, M-X, since the reagent, Y, is involved only in the subsequent fast step. The rate of reaction is then proportional to the first power of the concentration of M-X and to the zero power of the concentration of Y, i.e., first-order in M-X and zero-order in Y.

In contrast to this, a rate law of the form

$$\text{rate} = k [M-X][Y]$$
 where  $k$  is a second-order rate constant, is expected for an  $S_{N2}$  reaction.

This follows from the fact that both the complex, M-X, and the reagent, Y, are used in the rate-determining step.

From this brief discussion of chemical kinetics it appears that the mechanism of a reaction is readily established by experimentally determining its rate law. Such need not be the case. For example, the rate law of a solvolysis reaction, where Y is the solvent as well as the reagent, is first-order or, better, pseudo first-order. This results from the fact that the concentration of the solvent remains the same during the reaction and its effect, if any, is contained in the rate constant. Such an experiment then gives no information as to whether the solvent is a passive reagent, as in a dissociation process, or if it participates in a bimolecular displacement process. Thus it is necessary to use some indirect approach to get information on the role of the solvent in solvolysis reactions.

**Conclusions** as to the mechanism of reaction can sometimes be reached on the basis of changes in rates of reaction accompanying certain systematic changes in the metal complexes. A brief summary of the expected rate trends with specific changes in the complex is shown in the Table (below) for the two mechanisms being considered. These predictions can be understood in terms

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of the essential difference between the two reaction processes. Keep in mind that the important feature of an  $S_{\text{N}1}$  mechanism is bond breaking, charge separation, whereas for an  $S_{\text{N}2}$  process both bond breaking and bond making are important. It then follows that, providing all other factors are kept the same, an **increase in the positive charge on the metal of a metal complex makes it more difficult to break the metal-ligand bond** and conversely **makes it easier to form such a bond**. The result is that the rate of substitution decreases for a dissociative process of charge separation but the rate does not change for a displacement mechanism because the decreased bond-breaking tendency is compensated for by an increased bond making tendency. Regardless of mechanism, an increase in the size of the metal is expected to result in an increase in rate of reaction. Because of its greater size, the metal-ligand bond is weaker and, also, the larger metal can more readily accommodate an entering ligand. Changes in charge or size of the entering nucleophile have no effect on the rate of an  $S_{\text{N}1}$  reaction because the rate-controlling step does not involve the entering group. The rate of reaction decreases for both mechanisms with an increase in the negative charge of the departing ligand, since the bond rupture is more difficult, as is also bond making, due to the smaller effective positive charge on the metal. However an increase in size of the leaving group makes bond cleavage easier so that a more rapid rate is expected for a dissociation process. This effect is compensated for in part by the fact that the larger size of the ligand makes an expansion in coordination number more difficult, resulting in a smaller net effect on the rate for a displacement mechanism. Finally, changes in the "inert" ligands, those not undergoing substitution, are also expected to alter the rates of reaction. With increased negative charge it becomes easier for a negative ligand or dipole to break away from the complex; hence the rate increases for a dissociative process. By the same reasoning, it becomes more difficult for a negative reagent to enter the complex, an opposing effect which causes the rates to be comparable for displacement-type reactions. The steric strain due to an increase in the size of the inert ligands favors a mechanism involving a decrease in coordination number rather than an increase. Thus the rate of an  $S_{\text{N}1}$  reaction increases, whereas that of an  $S_{\text{N}2}$  reaction decreases. This indirect approach to the assignment of reaction mechanisms clearly has its limitations and must be used with caution. However it is often the only method available and it has been used both for organic and inorganic reactions. The degree of confidence in this approach is enhanced whenever several changes in the system are found to affect the rate in a manner consistent with one mechanism but not the other.

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**Table: Effect of charges and sizes on rates of  $S_{N1}$  and  $S_{N2}$  reactions**

Changes made	$S_{N1}$ rate	$S_{N2}$ rate
Increase positive charge of central metal	Decrease	Opposing effects
Increase size of central metal	Increase	Increase
Increase negative charge of entering group	No effect	Increase
Increase size of entering group	No effect	Decrease
Increase negative charge of leaving ligand	Decrease	Decrease
Increase size of leaving ligand	Increase	Opposing effects
Increase negative charge of other ligands	Increase	Opposing effects
Increase size of other ligands	Increase	Decrease