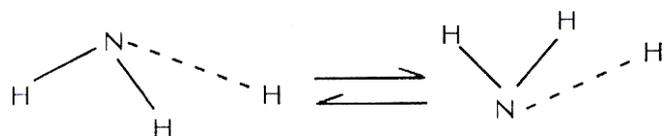

SOME SIMPLE REACTIONS OF COVALENTLY BONDED MOLECULES

One of the major differences between organic and inorganic chemistry is the relative emphasis placed on structure and reactivity. Structural organic chemistry is relatively simple, as it is based on diagonal, trigonal or tetrahedral carbon. Thus organic chemistry has turned to the various mechanisms of reaction as one of the more exciting aspects of the subject, to contrast, inorganic chemistry has a wide variety of structural types to consider, and even for a given element there are many factors to consider. Inorganic chemistry has been, and to a large extent still is more concerned with the static structure of reactants or products than with the way in which they interconvert. This has also been largely a result of the paucity of unambiguous data on reaction mechanisms. However, this situation is changing. Interest is increasingly centring on how inorganic molecules change and react. Most of this work has been done on coordinate chemistry, and much of it will be considered later on, but a few simple reactions of covalent molecules will be discussed here.

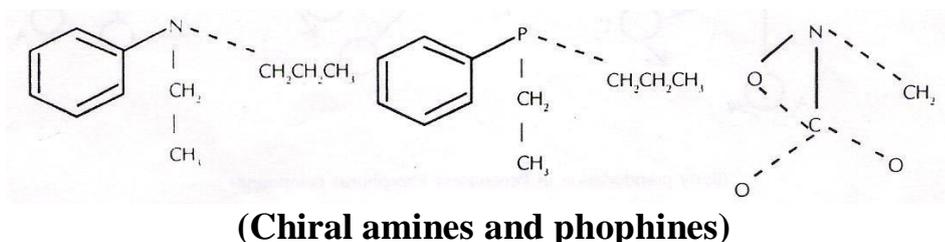
1.6.1 Atomic Inversion

The simplest reaction is seen in a molecule of ammonia. This can undergo the simple inversion of the hydrogen atoms about the nitrogen atom. This is analogous to the inversion of an umbrella in a high wind.



One might argue that above equation does not represent a reaction because the product is identical to the reactant and no bonds were formed or broken in the process. Leaving aside, the process illustrated above is of chemical interest and worthy of chemical study.

Consider the trisubstituted amines and phosphines shown in the figure below.

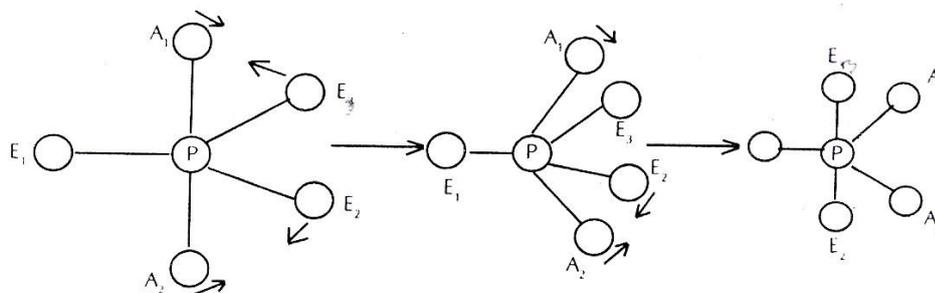


Because these molecules are non superimposable upon their mirror images (i.e. they are chiral) they are potentially optically active, and separation of the enantiomers is at least theoretically possible. Racemization of the optically active material can take place as shown in mechanism of NH_3 . It is of interest to note that the energy barrier to inversion is strongly dependent on the nature of the central atom and that of subsequent. For example, the barrier to inversion of methyl propyl phenylphosphine is about 120 MJ Mol^{-1} . This is sufficient to allow the separation of optical isomers, and their racemization may be followed by classical techniques. In contrast, the barrier to inversion in most amines is low (-40 KJ mol) with such low barriers to inversion, optical isomers cannot be separated because racemization takes place faster than the resolution can be affected. Since traditional chemical separations cannot effect the resolution of the racemic mixture, the chemist must turn to spectroscopy to study the rate of interconversion of the enantiomers.

1.6.2 Berry Pseudo Rotation

In PF_5 the fluorine atoms are indistinguishable by means of NMR of F. This means that they are exchanging with each other faster than the NMR instrument can distinguish them. The mechanism for this exchange is related to the inversion reaction we have seen for amines and phosphines. The mechanism for this exchange is believed to take place through conversion of the ground state trigonal bipyramidal into a square pyramidal transition state and back to a new trigonal bipyramidal structure. This process results in complete scrambling of the fluorine atoms at the equatorial and axial positions in phosphorus pentafluoride. If it occurs faster than the time scale of NMR experiment, all the fluorine atoms appear to be identical. Because it was first suggested by Berry, and because, if all of the substituents are the same as in PF_5 , the two trigonal

bipyramidal arrangements are related to each other by simple rotation, the entire process is called a **Berry pseudorotation**. Note that the process can take place very readily because of the similarity in energy between trigonal bipyramidal and square pyramidal structures.

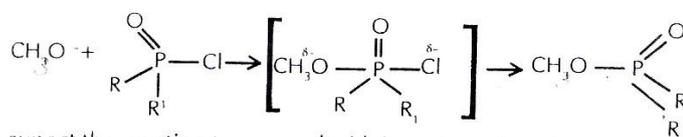


(Berry pseudorotation in Pentavalent Phosphorus Compound)

In fact the series of 5-coordinated structures collected by Muettterties and Guggenberger, which are intermediate between trigonal bipyramidal and square pyramidal geometrically effectively provides a reaction coordinate between the extreme structures in the Berry pseudorotation.

1.6.3 Nucleophilic Substitution

The simplest reaction path for nucleophilic displacement may be illustrated by solvolysis of a chlorodialkylphosphine oxide.



We would expect the reaction to proceed with inversion of configuration of the phosphorus atom. This is generally observed especially when the entering and leaving groups are highly electronegative and is thus favorably disposed at the axial positions, and when the leaving group is one that is easily displaced. In contrast in some cases when the leaving group is a poor one, it appears as though front

side attack takes place because there is retention of configuration. In either case, the common inversion or the less common retention, there is a contrast with the loss of stereochemistry associated with a carbonium ion mechanism.

1.6.4 Free Radical Mechanism

In the atmosphere there are many free radical reactions initiated by sunlight. One of the most important and controversial sets of atmospheric reactions at present is that revolving around stratospheric ozone. The importance of ozone and the effect of ultraviolet radiation on life will be discussed later, but we may note briefly that only a small portion of the sun's spectrum reaches the surface of the earth and that parts of UV portion that are largely screened can cause various ill effects to living systems.

The earth is screened from extremely high energy UV radiation cleaves the oxygen molecule to form two free radicals of oxygen atoms.



The oxygen atoms can then attack oxygen molecules to form ozone.



The neutral body m carries off some of the kinetic energy of the oxygen atoms. This reduces the energy of the system and allows the bond to form to make ozone. The net reaction is therefore:



The process protects the earth from the very energetic, short wavelength UV radiation and at the same time produces ozone, which absorbs somewhat longer wavelength radiation by similar process:



Thus the process is repeated
