The stereoelectronic theory of hydrolysis -New insights into organic chemistry

Dr. Pierre Deslongchamps of the University of Sherbrooke is studying hydrolysis reactions involving esters and amides. He has postulated that in such reactions, the spatial arrangement of intermediate chemical species determines what compounds are formed. This theory has been verified in a series of experiments based on the synthesis of a number of organic compounds.

The perfume of flowers, the delicate aroma of apples, oranges and bananas, and many familiar compounds such as soap and greases all belong to the chemical family of esters. Nature builds or modifies many compounds essential to life (such as proteins and hormones) through the formation and modification of esters and ester-like molecules. In living systems, this is promoted by a class of proteins called enzymes which are biological catalysts controlling the formation and transformation of esters and related compounds called amides. Thus a detailed study of processes involving esters and amides has great relevance not only for organic chemistry but also for biochemistry where it is essential to understand the complexities of enzymatic catalysis.

Esters, which are represented by the general formula R-COO-R, are formed in the so-called esterification reaction. Chemists express this reversible reaction through the equation:

R-COOH + R'-OH \gtrsim R-COOR' + H₂O Esterification is simply the reaction between an acid (R-COOH) and an alcohol (R'-OH) to produce an ester (R-COOR') and water. The reverse reaction, right to left in the equation, is called the hydrolysis of an ester.



Dr. Pierre Deslongchamps, of the Chemistry Department of the University of Sherbrooke, has shown that the tri-dimensional arrangements of atoms in esters and ester-like compounds determine the type of reactions they take part in, and the final products that are formed. This new theory has relevance in several areas of scientific investigation in chemistry such as understanding how enzymes work. Centre de l'Audio Visuel, Université de Sherbrooke

M. Pierre Deslongchamps, du département de chimie de l'Université de Sherbrooke, a établi que la conformation, c'est-àdire l'arrangement dans l'espace des atomes de composés tels que les esters, détermine la marche des réactions chimiques auxquelles ils participent et la nature des produits formés. La nouvelle théorie du professeur Deslongchamps facilitera l'avancement d'autres travaux de recherche en chimie comme, par example, l'étude de l'action enzymatique.

For the past five years, Dr. Pierre Deslongchamps, from the Chemistry Department of the University of Sherbrooke, has been active in unravelling the mysteries of hydrolysis reactions. According to Dr. Deslongchamps, it is now a well established fact that the hydrolysis reaction is catalyzed by acids and bases and that the reaction proceeds through a tetrahedral intermediate species — shaped like a foursided pyramid of organic groups built around a central atom of carbon.

Dr. Deslongchamps has recently developed a new, socalled stereoelectronic theory on this tetrahedral intermediate. He has postulated that its conformation — the precise spacial arrangement of the atoms — determines the mode of its decomposition and the nature of the final products.

A great deal of effort was required to verify this theory experimentally because the intermediate species present in the hydrolysis reaction decay is less than 10⁻⁷s (.1 millionth of a second). Furthermore, esterification and hydrolysis being reversible reactions, there were many chemical compounds present at the same time, which tended to prevent a full analysis of the reaction mechanism. It thus became necessary to use roundabout methods of organic synthesis to fabricate stable versions of the same intermediate normally present briefly in the hydrolysis of esters. Other methods were used to cleave them and to determine the effect of their conformation on ester formation. Over the past few years, Dr. Deslongchamps and his research team of six graduate students and six post-doctoral scientists have used five different methods of organic synthesis to verify separate facets of the stereoelectronic theory. Much work and ingenuity have been required for these organic syntheses because most of the necessary reactions had to be invented from scratch. However, Dr. Deslongchamps already had considerable expertise in organic synthesis, having worked for several years on the development of "pre-fab" methods to build complex organic molecules in a much smaller number of steps than required by classic synthesis techniques. Such laboratory molecule construction is done in much the same manner as modern house assembly. In recognition of Dr. Deslongchamps' work, the National Research Council of Canada awarded him the E.W.R. Steacie Fellowship in 1971. This award enabled him to conduct uninterrupted research for a period of three years, without teaching or administrative duties. From 1970 to 1972, he was also a Fellow of the New York based A.P. Sloan Foundation.

During 1971, the development of Dr. Deslongchamps' stereoelectronic theory began with his discovery of a new chemical reaction, the oxidation by ozone of the acetal function of an aldehyde into an ester.

Dr. Deslongchamps and his colleagues then studied this system in order to understand the formation of esters, the final product of this reaction. They first showed that there was a direct relationship between the conformation of the acetal group and its reactivity. Dr. Deslongchamps also theorized that the crucial factor in the decomposition of the intermediate into the final product was the orientation in space of free electron pairs or orbitals. Finally, he formed the hypothesis, which was later confirmed, that this oxidation reaction proceeds through the same intermediate as hydrolysis.