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A Modern Philosopher's Stone

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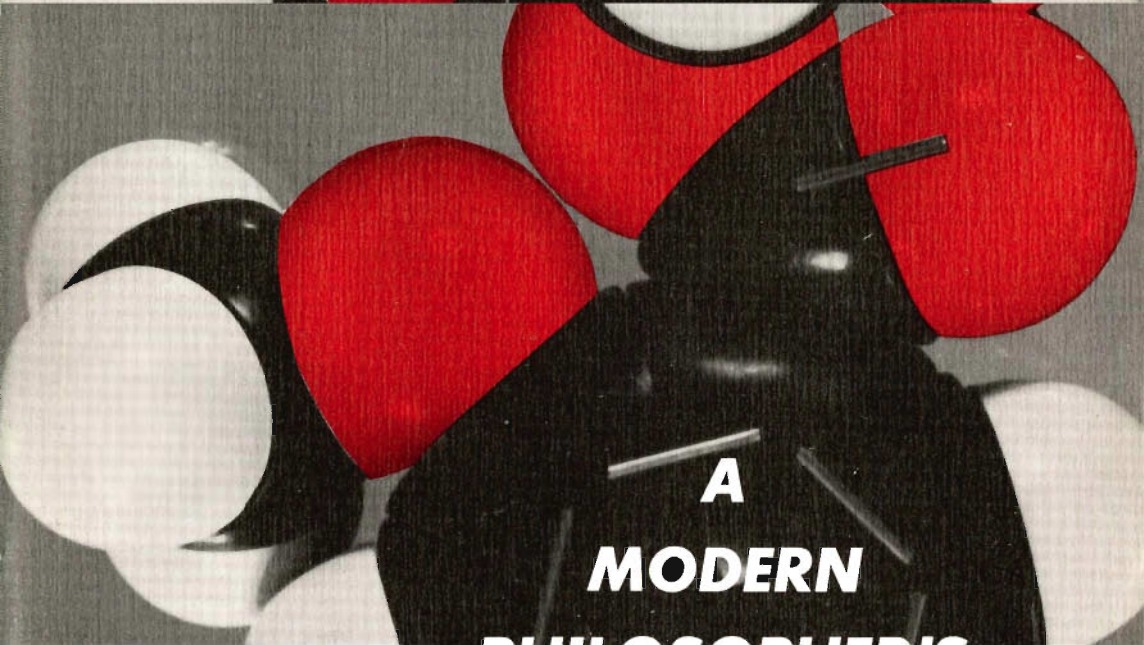
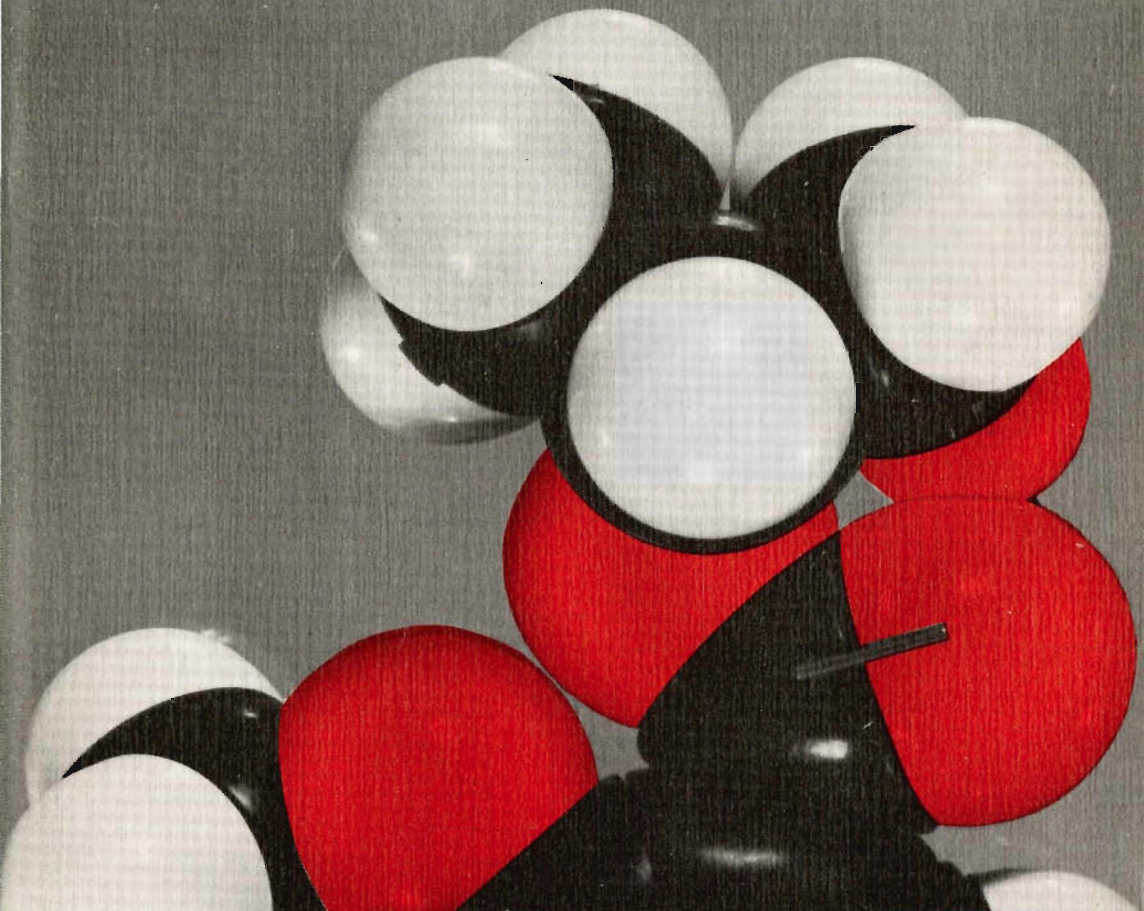
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UTAH STATE UNIVERSITY LOGAN, UTAH



**A
MODERN
PHILOSOPHERIC**

Molecular structure, the language of the chemist, serves as the means by which he formulates ideas and communicates them to his colleagues. Using the theory of molecular structure, chemists attempt to interpret nature—its chemical composition and chemical changes—and synthesize new materials to improve man's living.

Molecules are far too small to be seen even with the most powerful microscope—yet scientists know the atoms which are in molecules, the distances and angles between them and the energy necessary to break the chemical bond that holds the atoms together.

Molecular models are simplified concepts of molecular structure. They attempt to show, in a qualitative way, the arrangement of the atoms one to another in the molecule and their position in space.

The photograph on the front cover illustrates a type of model used by organic chemists in an attempt to describe a molecular structure. The name of the substance is isopropyl, *ortho*-methoxybenzoate, a compound which has been used extensively in carrying on fundamental research at Utah State University in relating molecular structure to chemical reactivity.

THIRTY-FOURTH FACULTY HONOR LECTURE

A
MODERN
PHILOSOPHER'S
STONE

By
GRANT GILL SMITH
Professor, Chemistry Department

THE FACULTY ASSOCIATION
UTAH STATE UNIVERSITY

LOGAN, UTAH
JANUARY 1967

*“So viele Chemiker haben nicht genügend
Phantasie”*

ADOLF BAEYER
NOBEL PRIZE LAUREATE, 1905

A MODERN PHILOSOPHER'S STONE

by
GRANT GILL SMITH

FOREWORD

Alchemists, the forerunners of chemists, for more than a millennium sought the "Philosopher's Stone"—the transmuting agent that could change imperfect base metals such as lead and tin to the noble metals, gold and silver, and also serve as the Elixir of Life to heal the infirmities of man and prolong his existence on earth.

Where alchemy failed, chemistry, in little more than a century, has succeeded in finding the "Philosopher's Stone," for it is now not only possible to transmute one metal into another and heal many of man's infirmities, but scarcely a facet of man's life has not been influenced through chemical research and industry.

Alchemists failed because they sought to solve the problem directly. Chemists succeeded because they first sought to understand the basic principles of nature and directed their efforts to the fundamentals. Industrial applications were the logical and natural outgrowth of these fundamental discoveries.

This lecture centers on the idea that the modern "Philosopher's Stone" is *fundamental research*. The idea is exemplified by chemistry, since its major advances have come not from laboratories seeking solutions to particular problems but rather from creative and imaginative minds that produced such indispensable concepts as the theories of atomic and molecular structure and the nature of chemical bonding, and then defined the relationship of these theories to chemical reactivity.

Some of the impact of chemistry on modern living and our present day economy is mentioned as well as a brief description of our fundamental research at Utah State University.

The author wishes to acknowledge his debts to the authors of the many books and articles which served as source material for a major portion of this lecture. Sincere appreciation is given to the graduate students, postdoctoral research associates, and undergraduates at Utah State University and at Washington State University who made major contributions to the research work briefly referred to in this lecture, to Lois Cox for her helpful suggestions with the manuscript, and to Maradee Siler for typing the manuscript.

The financial support from the National Science Foundation, the Air Force Office of Scientific Research, the Petroleum Research Fund—American Chemical Society, Utah State University and Washington State University which has made this fundamental study possible is gratefully acknowledged by the author.

Particular gratitude is expressed to Dr. Richard T. Arnold, President of Mead Johnson Research Center and former Professor of Chemistry, University of Minnesota, whose inspiring lectures and enthusiasm for research launched the author on a very exciting and rewarding area of research in physical organic chemistry.

And finally many thanks are given to my wife, Phyllis, who has encouraged me during the past 20 years in the pursuit of fundamental research.

MODERN LIVING AND CHEMISTRY

Chemistry, more than any other science, is essential to modern living as we know it today. It has improved our transportation through better road materials, synthetic rubber, high energy fuels and super alloys for supersonic flight. Our shelter has been improved through developments relating to paints, pigments, textiles, plastics, and various other new building materials. Our food, besides being preserved by organic chemicals, is itself organic material, and is made more plentiful by using pesticides, fertilizers, and synthetic hormones.

For centuries, until just a few decades ago, man had to rely on a limited number of fabrics, the raw materials of which were available only from animals and plants, dyes from roots, cleaning agents which were no better than those used by the ancient Assyrians, and a handful of primitive medicine. Today we know that our clothes and household fabrics consist of many new synthetic fibers—*orlon*, *nylon*, *dacron*, and *rayon*, brightened by a myriad of fast synthetic dyes and kept clean by detergents and organic cleaning solvents. Yet, relatively few people realize that nearly every article of commerce is coated, colored, cleaned, protected, stabilized or otherwise modified by chemicals.

Our health and often our lives depend on one or several elixirs of life that fill the pharmacies—*cortisone*, *penicillin*, *tetracycline*, or *insulin*.

Though scientists have been remarkably successful in synthetic organic chemistry, the most efficient synthetic organic factories are not those devised by science and industry. Instead, they are in plants, animals, and human bodies. Through chemistry we are beginning to understand these "factories" which are engaged in chemically breaking down raw organic materials into chemical building blocks, and then transporting the blocks to living cells where they are chemically recombined into new molecular structures according to precise "blueprints" that are now being defined by men.

As chemistry is so deeply involved in every phase of modern living it has become a major factor in the nation's economic growth. Although the chemical industry itself is very large, it represents but a fraction of the total industrial effort of our chemists and chemical engineers. The extent of penetration is emphasized by the fact that the directors of research of some 70 of the 125 largest U.S. corporations are chemists.

What has made this phenomenal advancement in knowledge and industrial progress possible? Have these discoveries been accident—pots boiling over on a hot stove? What seems to have triggered this modern explosion in chemistry?

Most scientists will agree that the theory of molecular structure, which was proposed in the second half of the nineteenth century, was paramount in releasing the potential of chemistry and making it a dynamic factor in modern science and industry. This theory provided chemistry with a foundation, and when coupled with the theories of atomic structure and the nature of the chemical bond, allowed scientists to build the world's fastest growing industry which may become, in a few decades, the second largest industry in the United States.

FUNDAMENTAL THEORIES

In this short lecture it is not feasible to explore in depth very many aspects of the field of organic chemistry. The importance of individual imaginations in developing the theories of molecular structure and of chemical bonding does warrant some discussion, however. First, because these theories are so vital to organic chemistry, and second, because individual imagination and creativity are basic to making advances in all sciences. In addition, these particular theories provide a background for some of our studies at Utah State University of reaction mechanisms and of molecular structural-chemical reactivity relationship.

Molecular Structure

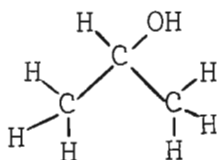
The most renowned contributor to structural organic chemistry was a young German chemist, Friedrich August Kekulé (1829-96), who began to study architecture in the University of Giessen at Munich in 1848, but was attracted to organic chemistry by the brilliant lectures of Justus von Liebig (1803-73). This young man's interest, thus, was turned from the "gross to the molecular aspects of design," and from his brilliant and imaginative mind came the foundations of molecular architecture.

Following a brief stay in Paris where Kekulé benefited greatly from his acquaintance with Dumas, Cahours, Wurtz, Regnault and the then famous Gerhardt, he took a year's position in England. Having contemplated the subject of organic chemistry for many years, Kekulé's discussions with William Odling (1829-1921) and A. W. Williamson (1824-1904) inspired him to conceive his theory of molecular structure during his stay in London. He tells in his own words how the theory came to him while riding a London bus:

"One fine summer evening I was returning by the last omnibus, 'outside,' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie (Traumerei), and lo, the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one even embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain, dragging the smaller ones after them. . . . The cry of the conductor: 'Clapham Road,' awakened me from my dreaming; but I spent a part of the night in putting on paper at least sketches of these dream forms. This was the origin of the Structurtheorie."¹

Kekulé's "dream forms" led to the theory of valence in molecular structure consisting of two fundamental postulates:

the quadrivalence of the carbon atom, that is, that each carbon has four bonds to other atoms, and the capacity of the carbon atoms to join together to form chains of carbon atoms. Since that time organic molecules have been pictured as consisting of a backbone of carbon atoms to which other atoms or groups of atoms (radicals) can be attached, provided each carbon atom maintains its valence of four. These conformations are graphically represented by letters for the atoms and lines illustrating chemical bonds. The graphic formula below is for isopropyl alcohol (rubbing alcohol).



It is important, particularly for those of us who use the theory of structural organic chemistry, to realize the status of organic chemistry when Kekulé set forth his original and novel ideas. At that time chemists referred to organic substances by name and could bring about some chemical transformations. They also knew the elements found in organic substances, but they had no realistic concepts of how the atoms might be linked together into molecules. As a matter of fact, one of the most prominent chemists of that day, Gerhardt, was firmly convinced that it would never be possible to know the structure of the molecule.

Soon after Kekulé published his theory on molecular structure in 1858² he proposed a structure for benzene, an organic substance that had been known to chemists since 1825 when Michael Faraday (1791-1867) first isolated it from an oily condensate found in the coal-gas pipelines in London. The contribution that Kekulé made to chemistry by proposing his structure for benzene was especially notable, for benzene's chemistry differs markedly from that of the other unsaturated hydrocarbons.

Again we will refer to Kekulé's own words to describe his thoughts and theories:

"I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gambling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis."*

Through such insights, the foundation of molecular structure or molecular architecture was proposed by an *imaginative* young chemist who was not seeking to prepare new drugs, to extract essential oils from plants, or to improve on the taste of wine. Yet there is no branch of science which is not indebted to Kekulé's theory and every individual in every developed country of the world has been benefited by his theory.

During the last quarter of the nineteenth century, a large dye industry was built in Germany as a logical and immediate consequence of the newly proposed theory of molecular structure.⁴ This new industry, which used coal tar as raw material, helped to shift the world balance of economic power at that time to Germany. Since then the chemical industry has become a potent factor in all progressive economies.

In the United States today the chemical industry has an

*The snake biting its own tail had played a role earlier in Kekulé's life. In 1847 he had appeared as a witness at a trial in the murder of Countess Gorlitz, who lived next door to his father in Darmstadt; the murder was coupled with a theft of jewelry, including a ring that consisted of two intertwined metal snakes biting their own tails.³

annual sale of more than \$36 billion,* or 5 percent of the gross national product, and a total work force of close to 900,000. There are more practitioners in chemistry than any other natural science.

“Let us learn to dream, gentlemen,” the now-famous Kekulé would say to his students, “and then perhaps we shall learn the truth.” But he was also careful to add a note of warning: “let us beware of publishing our dreams before they have been put to the proof by the waking understanding.”†

Kekulé's imagination and his courage in following it, led him to one of the most useful theories of all chemistry; a theory that stands unsurpassed in the whole history of science as one of the most inclusive and powerful generalizations ever made about the nature of the universe. More recent research has proved that all organic materials depend upon the ability of carbon to form chains and cyclic structures, and that life itself exists because of this ability. Because of the simplicity of the fundamental concepts and the difficulty of predicting the extent of their utility, Kekulé presented his ideas with modesty. He concluded his 1858 paper with the statement: “Finally I have to mention that I myself lay only small value on considerations of this sort . . . but these ideas seem to me to give a simple and rather general expression of recent discoveries, and perhaps their use will help in finding some new facts.”

Little did Kekulé realize that his theory would provide the foundation for all future research in organic chemistry and that within little more than a hundred years, more than

*The gross national product of the chemical industry in the United States was more than the sum of the total gross national product for eleven Asian nations: Malaysia, New Zealand, North Korea, North Vietnam, Pakistan, Phillipines, Singapore, South Korea, South Vietnam, Formosa and Thailand.⁵

†Adolf Baeyer (1835-1917), a pupil of Kekulé's at Heidelberg and the successor of Liebig at Munich, caught from Kekulé one of the secrets of success in chemistry (and in all sciences) for he would say to his students: “So viele Chemiker haben nicht genugend Phantasie (So many chemists suffer from a lack of imagination).”

two million compounds would be isolated or synthesized and described in terms of his theory.

Certainly Kekulé did not claim complete originality for his ideas. He repeatedly referred to others, in particular Gerhardt, Williamson, and Odling, whose theoretical concepts he acknowledged and praised. A. S. Couper (1831-1892), a Scot, working with Wurtz in his Paris laboratory, published a paper in June of 1858, just a few months after Kekulé's first paper, stating many of the same ideas about the quadrivalence of carbon and the linking of carbon atoms.⁶ Unfortunately for Couper, Wurtz was slow to have the paper published, otherwise Couper would have had more credit. In 1861 M. Butlerow (1828-1886) (Russian) published a similar paper on the structural theory. He was first to emphasize that chemical and physical properties could be expressed in terms of molecular structure.⁷ As happens today, Kekulé's ideas were propagated more successfully than comparable ones of other scientists because of his didactic gift as a teacher, orator, and author. His fascinating text-book most effectively brought his work to the attention of a diverse audience.

To illustrate further how imaginative Kekulé was, it was not until 1897, 40 years later, that J. J. Thompson (1856-1940), Cavendish Professor of Physics at Cambridge, discovered and named the electron, the key to all chemical bonds, or the "glue" that holds atoms together. In 1869, 11 years after Kekulé's paper, the most renowned of all Russian chemists, Dmitri Ivanovitsch Mendeleef (1834-1907) proposed the famous Periodic System for classifying the elements.

Louis Pasteur (1822-1895) had noted in 1848 the optical activity of certain organic acids, but it wasn't until the advent of the theory of molecular structure that a suitable explanation was given. Independently in 1874, Jacobus Henricus van't Hoff (1852-1911) and Joseph A. LeBel (1847-1930) proposed the three dimensional asymmetrical concept

of carbon molecules, an extension of Kekulé's theory, which explained this phenomenon.

Scientists now realize that stereochemistry (three dimensional chemistry) is as important to biological activity as other aspects of molecular structure such as elemental composition. Although it has been recognized for many years that the living cell can selectively synthesize a particular stereochemical molecule, chemists are just beginning to acquire the techniques of synthesis in the laboratory. Conformational analysis, a theory recently developed (1950) by D. H. R. Barton (1918-), deals with nonbonded interactions in molecules. When coupled with van't Hoff's and LeBel's theory of asymmetry, Barton's theory helped to make possible a total synthesis of many complicated and important compounds such as reserpine by R. B. Woodward (1917-) and the development of stereospecific polymerization of propylene by K. Zeigler (1898-), creations that contributed to their being awarded Nobel Prizes in chemistry within the last few years.

Atomic Structure

The molecular structure theory proposed by Kekulé and his contemporaries was at best very crude, and not until this century did scientists realize that molecules are a collection of atoms held together by chemical bonds consisting of electrons. A better understanding of molecular structure had to be preceded by more information about atomic structure, and this came in the first quarter of the twentieth century.

After Thompson discovered the electron in 1897, Lord Rutherford (1871-1937) at Cambridge proposed (in 1912) a structure of the atom consisting of a nucleus and planetary electrons. His model was markedly improved upon by a former student, Niels Bohr (1885-1962), of Copenhagen who applied the quantum theory which had been introduced

by Max Planck (1858-1947) in 1900. Despite the success of Bohr's theory of atomic structure relative to small atoms, many important details of physics and chemistry were inconsistent with the theory and could not be explained by it.

During the 1920's, a group of theoretical physicists introduced new mathematical methods of dealing with the atoms. The revolution in mathematics which led to the new quantum mechanics, was initiated largely by Louis Victor de Broglie (1892-) in France and Werner Heisenberg (1901-) in Germany. Heisenberg developed a new matrix mechanics in 1925 to describe the properties of the atom. De Broglie treated electrons not as particles following orbits in Newtonian fashion, but as particles whose motion was governed by the pattern of their standing waves. In essence, all matter was considered as a wave. The wave mechanics theory, which de Broglie proposed, was developed largely by the systematic work of the German physicist Erwin Schrodinger (1887-1961) in 1926.

Wolfgang Pauli (1900-1958) introduced the exclusion principle in 1925, pointing out that no two electrons in a given atom can have all four quantum numbers the same.

Friedrich Hund (1896-) made it clear in 1927 that atomic spectra could be understood in terms of the so-called Aufbau or building-up-process, in which each electron is assigned to an orbital, a term coined by Robert S. Mulliken (1896-).

Chemical Bond

Definition of the nature of the chemical bond began to take shape as a result of the creative thinking of G. N. Lewis (1875-1946), W. Kossel (1888-1956), Irving Langmuir (1881-1957), and N. V. Sidgwick (1873-1952). Their concepts were refined following the development of quantum mechanics in the mid-twenties by H. W. Heitler (1904-) and Fritz London (1900-).

Others who made remarkable contributions to our theoretical understanding of the nature of the chemical bond and gave the chemist a usable pictorial model were Max Born (1882-), John Slater (1900-), E. Huckel (1896-), Linus Pauling (1901-), Robert Robinson (1886-), and Robert S. Mulliken (1896). The last four were principally responsible for applying quantum mechanics to bio- and organic chemistry. The last three of these men received Nobel Prizes largely because of their contributions in this area of chemistry.

Once organic chemists had a better understanding of the electronic theory of structure they could direct their efforts to discovering the role of electrons in organic reactions. Early contributors to this aspect of chemistry were Robert Robinson and Christopher K. Ingold (1893-), who fathered a new specialty known as physical organic chemistry, during the late 1920's. Just as Kekulé's theory of molecular structure had stimulated fundamental research and industry in organic chemistry in the 1860's, physical organic chemistry gave chemistry new impetus in the second quarter of the twentieth century. With the new concepts of physical organic chemistry, chemists soon began to interpret chemical reactivity in light of the electronic theory of molecular structure. They subsequently learned to predict chemical reactivity based on molecular structure and the pathway followed during the reaction course (this is referred to as reaction mechanism). In addition, certain aspects of molecular structure, previously undefinable, could be elucidated or explained in terms of chemical reactivity.

The new approach to organic chemistry was soon coupled with special new techniques such as isotopic labeling, remarkable advancements in instrumentation, and the theory of reaction rates. With the aid of these theories and techniques applied to fundamental research, chemists have created a man-made fiber industry in the United States which amounts

to more than \$2 billion annually, and a new petro-chemical industry which has grown 3.5 times as fast as the growth rate of the gross national product. It now gives a \$10 billion plus annual boost to our economy. Chemists have also synthesized a remarkable number of new drugs such as trifluoroperazine, which has substantially replaced the "talking treatment" once popular in psychiatry. This chemical compound has been a major factor in cutting by half the stay of schizophrenics in mental hospitals. The creation of tolbutamide and chlorpropamide gives relief to approximately one half of the nation's two million diagnosed diabetics by providing oral substitutes for insulin.

Thus, we see the usual pattern of science—each new advance in fundamental knowledge opens the way for practical applications and provides new industrial opportunities of which we are the benefactors.

THE IMPORTANCE OF MOLECULAR STRUCTURE TO CHEMICAL AND BIOLOGICAL ACTIVITY

Much is known about the molecular structure of organic compounds and about the correlation between structure and chemical reactivity. Yet the future growth and development of organic chemistry depend largely upon further basic developments in this area of the science. Our work at Utah State University has not been directed to the solution of any particular problem, the synthesis of a new drug, or the killing

of any particular insect species. We have, instead, studied fundamental theories and details about molecular structure, and the effect of changes in molecular structure on chemical reactivity, thereby hoping to make widely applicable contributions to many sciences. In the author's judgment, such objectives constitute the main justification for university research.

The importance of relating the electronic theory of molecular structure to the chemical reactivity cannot be over-emphasized. When a chemist attempts the synthesis of a new drug, the manufacture of a new fiber, or seeks a cure for cancer he formulates his ideas and communicates them to his colleagues in terms of the molecular architecture of molecules and the electronic distribution within molecules. Changes in molecular structure change the distribution of electrons and alter bond energies, thus altering chemical reactivity. Chemical and biological activity depend on the shape of molecules as well as the electronic distribution, for both of these factors effect bond energy which alters reactivity. To illustrate, special arrangements in molecules are thought to be the basis of the lock to key relationship found in many biological reactions, such as antibodies with their antigens, enzymes with their substrates, and the important desoxyribonucleic acid with the messenger ribonucleic acid. It is also interesting to note that odors are related to the shapes of molecules. Some substances with quite different chemical composition are found to have the same odor. The explanation given for this is that these substances have the same shape. The odor of camphor, $C_{10}H_{16}O$, is possessed by hexachloroethane, C_2Cl_6 , and cyclooctane, C_8H_{16} . The chemical composition of these molecules is completely different, but their three-dimensional properties are very similar.⁸

It is important to chemistry to recognize that many substances that are similarly constituted have similar chemical

reactivity and that once we determine the chemical reactivity-structure relationships in one system we can generally relate or even predict chemical reactivity in closely related substances if certain complicating factors are eliminated. Therefore, the information gained in studying one reaction is very useful in studying other reactions. To illustrate, knowledge gained in the study of explosives might be applied to the study of proteins, drugs, or detergents.

Benzene and its derivatives (substances which have the benzene ring as part of their molecular structure) play an important part in chemistry as noted by the fact that benzene can be converted into fibers, drugs, detergents, explosives, and insecticides, such as dacron, sulfanilamide, trinitrotoluene, and hexachlor, respectively. Hence we recognize that a knowledge of the chemistry of benzene and its derivatives is useful in many phases of organic chemistry.

The goal, therefore, of the organic chemist is to accurately determine molecular structure and chemical reactivity and then be able to relate chemical reactivity to the theory of molecular structure. This, however, is a very challenging objective because of the complexity of molecular structure and the fact that chemical and biological activity are influenced by many other factors as well. For example, these activities are also influenced by temperature, catalysts, solvents, the concentration of various materials which are reacting, and the geometry of the molecule, which may cause important and often undeterminable steric (bulk) effects. Often a reaction does not occur at any measurable rate unless certain metals are present in trace amounts. On the other hand, even when these materials are necessary, if they are provided in high concentrations they poison the system. Non-bonded interactions are some of the most exciting aspects of

chemistry and are attracting the attention of many researchers in this field. We shall attempt to illustrate the importance of electronic distribution and of bulk effects on chemical reactivity in the following way.

The photographs in Figure 1 are of models representing derivatives of benzene, C_6H_4XY . The black ring is for the six carbon atoms, the purple ball is the reacting center, X, the green is for an atom or group of atoms, Y, which alter the reactivity of the reacting center because it changes the electronic density but it itself does not participate in the reaction, and the white balls represent hydrogen atoms, H. Under reacting conditions, the reaction site (purple) changes into a different group. The rate at which this transformation occurs can be used to evaluate the reactivity of the molecule and as mentioned the rate is altered by the other groups attached to the ring (green) as well as the location of the attachment. This is because the nature of the substituent and its location changes the electronic distribution around the reacting site. With two different substituents on the ring there are three different arrangements, as shown, *ortho* (photograph A), *meta* (photograph B), and *para* (photograph C).

Most chemical reactions are bimolecular (two molecule reactions) and occur in solution. Photograph D represents a mixture of reacting molecules and solvent. The brown ball represents the second reacting molecule, and the models of red and white balls represent molecules of the solvent. The solvent molecules surround the two reacting molecules and alter their chemical reactivity and may even determine the course of the reaction. Naturally if the two molecules are to react with one another it is necessary that they come into close proximity. Apparently when the two substances on the ring are separated, (photographs B and C) the attacking

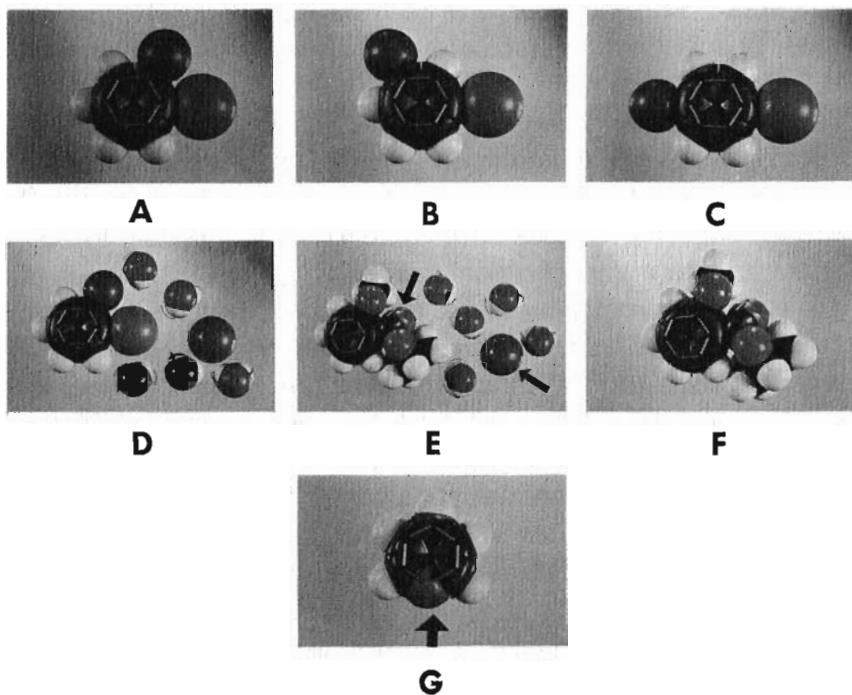


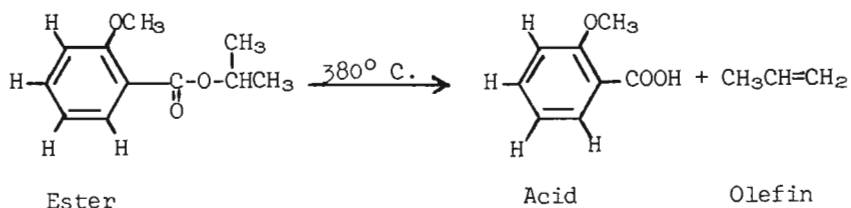
FIGURE 1. A. *ortho*-Disubstituted benzene.
 B. *meta*-Disubstituted benzene.
 C. *para*-Disubstituted benzene.
 D. Bimolecular reaction in the solvent phase with *ortho*-disubstituted benzene.
 E. Bimolecular reaction in the solvent phase with isopropyl *ortho*-methoxybenzoate indicating complexity of condensed phase studies. Arrows pointing to the reactive center and the attacking agent (brown).
 F. Isopropyl *ortho*-methoxybenzoate—An *ortho* substituted benzene derivative used in vapor phase decomposition studies to evaluate *ortho*-polar substituent effects and indicating simplicity of vapor phase studies.
 G. Pyridine—arrow pointing to the most reactive site.

molecule (brown) can come close to the reacting site (purple) and non-bonded interactions between one ring substituent (green) and the attacking molecule (brown) are not important. Many studies have been successfully accomplished when reactivity *vs.* molecular structure have been correlated in *meta* (photograph B) and *para* (photograph C) derivatives of benzene. However, in bimolecular reactions run in solution when the substituent (green) is located in the *ortho* position close to the reacting site (purple, photographs D and E) little success has been obtained in attempting to correlate structure and chemical reactivity. The explanation of this is that the reactivity of the active portion of the molecule (the purple ball in D and black ball indicated in E) is governed by non-bonded interactions between the solvated attacking molecule (brown) and the non-reacting solvated neighboring substituent (green) of the larger molecule in addition to the electronic distribution in the molecule. These non-bonded interactions are not predictable in light of our present knowledge of the electronic theory of molecular structure and therefore the observed reactivity cannot be anticipated or correlated with our knowledge of molecular structure. Until we can understand or eliminate these non-bonded interactions we cannot evaluate the electronic contribution of an *ortho* substituent. The objective, then, is to eliminate non-bonded interactions in order that a true electronic *ortho* substituent constant can be determined.

VAPOR PHASE KINETICS STUDIES

Here at Utah State University we have approached this problem by eliminating as many of these complicating factors as possible with the aim of being able to relate structure to chemical reactivity in cases where attempts have previously failed. We have eliminated the solvent, all trace materials, all catalysts, and the attacking reagent as well, and have

studied the chemical reactivity of the molecule essentially by itself in the vapor phase. This is shown in photograph F by a model of a molecule representing a derivative of benzene, isopropyl *ortho*-methoxybenzoate, one of many substances we have studied in our research. We have chosen a particular substance as a standard and carefully determined how this molecule decomposes into two smaller molecules at high temperature, Reaction 1.



This type of reaction is called "Thermal Decomposition" or "Pyrolysis." The rate of this thermal decomposition was carefully evaluated at several temperatures in order that the energy of activation (the energy necessary to bring about the reaction) and the entropy of activation (a measure of random movement in the molecule) could be calculated. From our studies we were able to formulate a reasonable concept about the nature of the mechanism of this reaction, or in other words, the arrangements of the atoms in the molecule during the course of the thermal decomposition.

We have been able to show that an ester molecule in question decomposes in free space and not on the walls of the reactor; that the molecule must acquire a definite (and measurable) amount of energy (energy of activation) before it will decompose, and furthermore that it must take on a certain arrangement of its atoms before it can decompose into acid and olefin.

The entropy of activation is a measure of the difference in the freedom of motion *within* the molecule in its unactivated and activated states. In the thermal decomposition of

the ester, one molecule breaks into two. One might suppose, therefore, that the molecule would have more freedom of motion just before it splits than it has at the start of the reaction. Our studies show, however, that the molecule must restrict its motion in the activated state which forms just before decomposition. Further, it must take on a particular conformation (restricted arrangement of the atoms) which has fewer degrees of freedom than does the starting material. The presently accepted theory states that substances with less entropy are more ordered and their motion is relatively restricted. Therefore, the negative entropy of activation we have observed indicates less freedom in the activated state.

We initiated this kind of work some 20 years ago. At that time little was known about structure-reactivity relationships in vapor phase reactions and even less about the thermal decomposition of esters to olefins and acids. Our choice of this reaction proved uniquely fortuitous, for once the mechanism (reaction pathway) had been evaluated it was recognized that reactions of this type are less complex than most chemical reactions and therefore, correlations of structure *vs.* reactivity are relatively straight forward.

By knowing the structure of the reacting molecule, and having carefully studied the mechanism of the reaction as well as having eliminated or controlled the complicating factors which were known to alter the rate of the reaction, we concluded that the observed rate was indeed that which could be correlated with the known molecular structure. We then proceeded by preparing new but related structures and carefully determining the rate of their thermal decomposition. Once this was accomplished for a large number of compounds with the substituents located either in the *ortho*, *meta*, or *para* position we were able to develop a pattern on how changes in molecular structure effect chemical reactivity in vapor phase reactions. From this we determined electronic substituent constants for atoms or groups of atoms attached

to the benzene ring, and most important, at the critical *ortho* position, where normally expected non-bonded interactions occur.

What does this mean to have determined an electronic substituent constant for an *ortho* substituent? From this information is it possible to predict the chemical reactivity of new substances which have not yet been studied from a knowledge of their molecular structure? Are these findings in vapor phase studies useful in solution chemistry? Though the conditions of reactions between the vapor phase and solution are very different it is surprising that remarkable predictions have been made of reactions run in solution from data obtained in the vapor phase and on reactions of a quite different nature. This has prompted us to conclude the following:

In those cases where good correlations were obtained, the presence of the solvent and attacking molecule do not cause abnormal influences. However, when marked differences are found in the chemical reactivity from that expected from the electronic theory of molecular structure (the relationship which is now obtainable from our vapor phase studies) we know that the reaction in question is effected by the presence of complicating factors due to non-bonded interactions of the substituent close to the reaction site. These non-bonded complications are difficult to understand, but we are now beginning to at least evaluate the extent of their contribution to chemical reactivity.

To summarize, most structure reactivity studies of benzene derivatives have been on reactions run in solution. These have proven successful in only those cases where the second substituent is located remote from the reacting site, that is, in the *meta* and *para* positions (photographs B and C). Apparently when the second substituent is neighboring the reacting site in the *ortho* position (photographs D and E), the electronic effects of the substituent through the molecule is complicated by bulk effects of the neighboring group, solvent

effects, hydrogen bonding, and many other so-called proximity, or non-bonded interaction effects.

Unimolecular vapor phase reactions, the type we have been studying at Utah State University, are apparently less complicated, for good correlations are obtainable not only for the *meta* and *para* substituted benzene derivatives, but also for those where the substituent is located close to the reaction site in the *ortho* position (photographs A and F).

Our work has provided what appears to be one of the best methods of evaluating the electronic influences of *ortho* substituents on chemical reactivity free from solvent interactions or crowding (bulk) influences normally associated with *ortho* substituted compounds. Information of this type is a necessary precursor to interpreting structure-reactivity relationships in cases involving steric effects, which are so common in large molecules found in proteins or other molecules of nature. These non-bonded interactions constitute a major factor in molecular structure *vs.* chemical and biological activity relationships.

Besides studying substituent effects in crowded molecules, we have investigated the reactivities of a whole class of molecules which have not previously been evaluated because of the inherent difficulties associated with bimolecular reactions in solution. Many molecules have two or more reacting centers, with one being more reactive than the other. In these cases, the first point of attack is at the more reactive site. Any attempt, therefore, to measure the reactivity at another site is doomed to fail because the reaction at the more reactive site modifies the molecular structure of the molecule and in turn, its chemical reactivity. The method developed in our vapor phase unimolecular reaction allows us to measure the reactivity at almost any position on the molecule in question without the danger of the more reactive position being attacked first. In this way we have been able to obtain measurements and comparisons of chemical reactivities never

achieved by other methods. This is particularly true in heterocyclic ring systems of the type illustrated in photograph G.

Precise predictions of the practical applications of such information are difficult to make for it has not been the objective of this research to explore applications but rather to investigate fundamental principles in nature. It is safe to say that the basic data we (and others) are developing on the subtle influences exerted by bond distortion, proximity effects of neighboring groups, and the role of the solvents on reactions, must proceed an understanding of such complex reactions as found in biological reactions such as enzyme action and protein synthesis. Development of diverse basic data is an essential preliminary to many advances that cannot be defined ahead of time.

Apparatus

To study the chemical reactivity of substances of low vapor pressure in the vapor phase at high temperature it was necessary to design and construct suitable equipment as none was commercially available or had been reported in the scientific literature. The apparatus which we have designed and constructed is useful to the study of chemical reactivity of any vapor phase reaction where a change in the number of molecules occurs.

The design of the apparatus centers on a 200 ml cylindrical stainless steel reaction vessel which can be readily evacuated and quickly closed after a liquid sample (or solid sample dissolved in a solvent) is introduced with a hypodermic syringe. The reacting vessel is incased in a large, well-insulated aluminum block whose temperature can be carefully controlled and maintained at any desired temperature between 25-600° C. As the liquid is introduced into the hot

reactor it is immediately vaporized and begins to react (decompose). This causes the pressure to change which is indicated by a null point gauge, a 0.003-inch stainless steel diaphragm that serves as one end of the reacting vessel. Deflection of the diaphragm closes an electric circuit that opens a valve to a source of nitrogen which flows in to maintain a pressure on the outside of the diaphragm equal to the pressure inside the reactor. The changing pressure of the nitrogen is monitored by a pressure transducer, an instrument which converts mechanical energy to electrical energy; this activates a stripchart recorder that continually records the pressure change. From this record of change in pressure with time the rates (rate constants) are readily calculated for the reaction in question and are used by chemists to measure chemical reactivity.

Within a few minutes of operation of the automated instrument a detailed account of the high temperature reaction can be obtained on a very small amount of material (100 μ l). A schematic drawing of the apparatus is shown in Figure 2 indicating the reaction vessel, vacuum system, import valve, null point gauge, pressure transducer nitrogen source, and stripchart recorder.

This equipment has been adapted in a number of different laboratories in this country and abroad for studies similar to the one reported here.

FINANCING FUNDAMENTAL RESEARCH IN THE UNIVERSITY

Time will not permit a worthy discussion of this timely subject but it is surprising and alarming to recognize that though chemistry plays such a vital role to modern living and to our national economy and security that fundamental research in chemistry is not receiving the financial support it

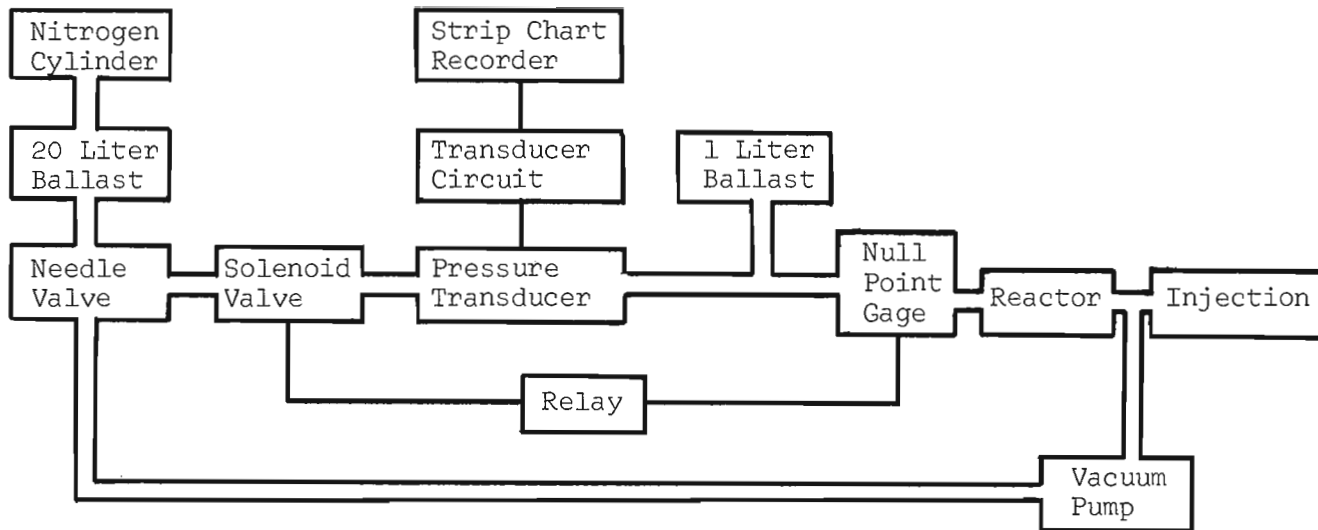


FIGURE 2. Schematic of automatic pressure monitoring system by which the kinetics of vapor-phase reactions involving high-molecular-weight organic compounds can be studied.

warrants. In a report entitled "Opportunities and Needs" by the National Academy of Science, the so-called Westheimer Report, the authors "demonstrate beyond reasonable argument that in federal support of the sciences, chemistry has been the poor relative."

Most of the funds for basic research are now being sponsored by the Federal Government. The National Science Foundation statistics show an increase in support in all the sciences from \$201 million in 1956 to approximately \$1,782 million in 1964. Of the amount spent in 1964, chemistry received only 5-6 percent of the total, and of this only half was for basic chemical research in the universities. A much larger percentage amount was given chemistry in Britain, Germany, and Japan.

It is difficult to estimate the cost of training the 1,377 new Ph.D.'s in chemistry graduated from 125 American universities in the United States granting these degrees in 1965. However, when one considers only the federal support, the amount spent per Ph.D. in chemistry is about the same as for Ph.D.'s in the biological sciences and mathematics and only one fifth to one thirtieth the amount spent per Ph.D. in physics, astronomy, or the earth sciences.

During 1960-63 the total cumulative investment in major instruments by 125 American university chemistry departments was \$55 million. This cost has risen about 20 percent a year because of the need for expensive instruments in chemical research. This is certainly a large sum of money, yet to place this figure in proper perspective, \$55 million is only half the cost of the Stanford linear accelerator.

It is only natural that the major academic activity in chemical research (and most of the expense) is concentrated in the graduate schools of the universities. Because of the limited funds, money is simply not available to support much research in the liberal arts colleges. Serious questions have been raised about what effect this is having on these schools, their science programs, and their chemistry faculties.

Responsible educators in chemistry argue that some research activity is absolutely essential if a young chemistry instructor in a liberal arts college is expected to maintain his enthusiasm for his subject and stay up-to-date in his field. Most of these young teachers are deeply interested in research, not as an end in itself, as may often be the case with university researchers, but as an integral part of effective teaching.

According to Professor A. F. Scott, Head of the Department of Chemistry at one of the best liberal arts colleges in the United States, Reed College, stated, "The education of chemists may present real problems, as it is uncertain whether colleges that do not grant Ph.D.'s will be able to continue their traditional role of training most of the bachelor candidates in chemistry."

The Federal Research and Development Budget for 1967 fiscal was \$14,811.2 million, a 2.4 percent increase over 1966. The National Science Foundation was awarded \$480 million or less than 3.3 percent and the National Institute of Health \$1,412.9 million or less than 10 percent of the total research and development budget.⁹

When one recognizes that these agencies are the major sources of funds for fundamental research in the universities he begins to appreciate percentage-wise the small portion of the Federal Research and Development Budget the universities are getting for the training of our future scientists and discovering new facts. Yet it is estimated that 67-87 percent of the practical discoveries in chemistry originate in laboratories doing fundamental research and that about 60 percent of this work is carried out in university laboratories.

Certainly the whole problem of financing fundamental research in the universities and colleges of this country needs careful review and consideration.

CONCLUSIONS

As we study the developments of science, we see how imaginative and creative minds, working to understand basic concepts of nature have given the world fundamental theories, such as those of molecular and atomic structure, which have set the course for our rapid progress in science and technology. The greatest advances trace most often to men striving to understand the fundamental principles of nature and rarely to those seeking to resolve a particular problem.

Through studies relating molecular architecture and the electronic theory of chemical bonding to chemical reactivity, chemists have learned to foresee the course, the rate, and extent of many chemical reactions in systems that are not too complex. It is not unrealistic to expect that a thorough comprehension of the electronic theory of molecular structure may eventually lead to an understanding of considerable more complicated systems such as life processes and eventually to their control, with all the problems and dangers this Pandora's box may hold. A little knowledge is indeed a dangerous thing, but considerable knowledge can be even more dangerous.

The future of organic chemistry depends upon our achieving a more thorough and detailed exploration of our physical and biological environments. As chemists learn more about the complex organic compounds that occur in nature they may also discover how these compounds influence biological processes. Nucleic acids, proteins, and viruses are beginning to yield their secrets. But before we can hope to understand the behavior of these crucial substances, we must learn more about organic molecules in general.

A special challenge is to learn more about the subtle influences exerted on organic reactions by distortion in bond angles and changes in bond polarities. We must determine, by devising and using model systems that leave no question

as to validity of interpretation, whether our notions about intra- or inter-molecular forces are correct. As better model systems are developed, chemists will be able to relate them more accurately to the complex molecular structures which influence the course of biological processes.

We, at Utah State University, have directed our studies of vapor phase reactions toward these ends by investigating the behavior of isolated molecules, uninfluenced by the presence of other factors. We have defined structure-reactivity relationships by excluding the complications that arise from the co-operative effects of the solvent and catalytic effects which occur in many reactions in solution.

The eventual effects of our research is not known, but the history of chemistry shows that by building on the results of fundamental research, scientists have improved man's standard of living, provided him with many new luxuries of life, better health, and markedly improved the world's economy. Yet, the impact of chemistry on society may be just beginning. Certainly, the effects of fundamental research in chemistry, has already demonstrated that many of the elusive goals of ancient alchemists have been reached. Indeed, fundamental research in Chemistry is a modern Philosopher's Stone.

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