STRUCTURE AND MECHANISM IN
ORGANIC CHEMISTRY

* BY C. K. INGOLD *

中外科學書社

Structure and Mechanism in Organic Chemistry

By C. K. INGOLD

Professor of Chemistry, University College
University of London

Structure and Mechanism
in Organic Chemistry, 1953

原 著 者：C. K. Ingold,

影印發行者：中外科學書社
上海淮海中路671號　電話：79088

印 刷 者：天成印書局

裝 訂 者：根記裝訂所

定　　價：¥ 72,000元　銅版圖55¼"

1954年12月初次化學印　31"×43"　1/22　印數：001—300

Preface

THIS book records, and in its later chapters extends, a course of lectures which, as George Fisher Baker Non-resident Lecturer in Chemistry, I gave in the Baker Laboratory, Cornell University, during the Fall Term of 1950–51.

I should like to express my sincere gratitude to Professor F. A. Long for all the trouble he took to make my duties easy and my visit enjoyable. I am deeply grateful to him and to all the staff of the Baker Laboratory for the generosity of their welcome and the great kindness they extended to me throughout my stay. I wish to thank their colleagues and students also for their acceptance of me into their congenial society.

I am much indebted to a number of friends, most of them on this side of the water, who have in various ways shared with me the task of preparing the present manuscript. Professor E. D. Hughes gave me his private notes on a number of subjects: the substance of Chapter XI in particular is due essentially to him. That of Chapter XV is similarly due to Professor J. F. Bunnett of Reed College, Portland, Oregon, whose co-operation I enjoyed during his tenure of a Fulbright Fellowship in London. Dr. A. Wassermann gave me the same kind of aid in the composition of part of Chapter XII. Dr. R. A. Buckingham helped me with part of Chapter II. Among those, not of my own College nor of Cornell University, who were kind enough to give me important new information in advance of its publication were Dr. J. W. Baker of the University of Leeds, Dr. H. M. E. Cardwell of the University of Oxford, Dr. M. Magat of the University of Paris, Dr. A. K. Mills of Guinness's Brewery, Dublin, Dr. J. D. Roberts of the Massachusetts Institute of Technology, and Professor F. H. Westheimer of the University of Chicago. It seems hardly necessary to say that my friends of the Baker Laboratory, and my colleagues here, have contributed largely to my education in many matters which have affected this book. I am grateful for the permission which several investigators have given me to reproduce diagrams from their original papers, as is indicated by the references under the reproductions. I feel much indebted to the writers of the books and reviews, to which reference is given in the text on the numerous occasions on which I have made use of them.

When this manuscript was written, Professor E. D. Hughes read the whole of it, Dr. A. Maccoll most of it, Dr. D. P. Craig and Dr. A. Wassermann large portions of it, and Dr. J. N. E. Day, Dr. P. B. D. de la Mare, and Dr. J. F. J. Dippy selected chapters. I thank these good friends for the time they have devoted to this work. They have given me much expert criticism and many valuable suggestions, of which I have been glad to take advantage. I thank my wife, who has done most of the heavy routine work involved in the composition. I believe that, had I not accepted her doctrine that it is better to finish an imperfect book than never to finish a perfect one, this particular book would never have appeared.

As its title indicates, it deals with the structure of molecules and the mechanism of reactions in organic chemistry. However, the wide scope of this subject has necessitated the imposition of limitations. As to structure, attention has concentrated on molecules in their normal states. As to reactions, discussion has been restricted substantially to those classes of homogeneous molecular reactions on which the present broad pattern of organic chemistry mainly depends. Thus a very appreciable fraction of the field indicated by the title remains uncovered. But I have been writing chiefly for the university student, and, rightly or wrongly, I have adopted the policy of limitation by selection.

University College, London C. K. INGOLD
December, 1951

POSTSCRIPT (February, 1953).—During the passage of this book through processes of publication, Dr. John R. Johnson has very kindly co-operated with the staff of the Cornell University Press in solving the numerous problems that have arisen. I am sincerely grateful both to him and to them.—C. K. I.

Contents

CHAPTER I

Valency and Molecular Structure

(1) DEVELOPMENT OF THE THEORY OF MOLECULAR STRUCTURE

IN 1808 Dalton published his atomic theory; and in 1812 Berzelius advanced the earliest theory of chemical combination. This so-called dualistic theory of combination was based on the study of inorganic substances, and envisaged binding as an electrostatic attraction between oppositely charged atoms. About 1840 the dualistic theory was overthrown as a result of the work of Dumas and others, who showed it to be incompatible with the accumulating facts of organic chemistry. Much later, following the announcement of Arrhenius's theory of electrolytic dissociation in 1887, the idea of electrostatic binding was revived, but now only in relation to ionising compounds.

In the meantime, mainly between 1840 and 1860, the work of Gerhardt, Laurent, Cannizzaro, Frankland, Williamson, Kekulé, and many others had clarified the numerical aspect of valency. Largely as part of the same work, the unitary theory of molecular constitution was developed, through its transitional forms, the radical and type theories, into the structural theory. This made no attempt to specify the physical nature of the forces holding atoms. It assumed binding power as an intrinsic property of atoms, the number of bonds formed by an atom, its valency, being characteristic for each kind of atom.

The idea that chemical binding must also have a geometrical aspect was not at once accepted as axiomatic; but it became accepted as a result of van't Hoff and Le Bel's recognition in 1874 of the specific geometrical arrangement of carbon bonds.

At the close of the last century the single term valency was used to mean both the charge on an element in its ionic form and the number of bonds by which an atom holds others in a structure. The circumstance that these numbers are often identical facilitated the dual usage. However, there was considerable confusion, structural bonds being frequently assumed where none had been shown to exist. In this period Werner was foremost in maintaining a clear distinction between an electrically neutral assembly of kinetically separable ions, and a kinetically individual molecular or ionic structure; and therefore between the charge number of an ion, and the co-ordination number, as he called it, of an atom, that is, the number of atoms bound by it structurally.

Regularities concerning the valency numbers of elements had attracted attention from an early time. Mendeléjeff, when formulating his periodic law in 1869, pointed out that valency is closely related to the numbers of the periodic groups, and normally changes by one unit from one group to the next. After the discovery of the electron by Thomson and Wiechert in 1897, several attempts were made to express the connexion between valency and group number in electronic terms. Thus Abegg assigned to each element a positive valency, equal to the group number, and a negative valency, such that the sum of the two, neglecting signs, was always eight; and he designated as the normal valency of an element, whichever, apart from signs, was the smaller. His interpretation was that all atoms have eight places for electrons, the positive valency, that is, the periodic group number, being the number of such places actually occupied in the neutral atom.[1] As Drude expressed the matter, Abegg's normal valency, when positive, represented the number of easily detached electrons, and, when negative, the number of easily added electrons.[2] The theory of octet stability could hardly have been rendered in a clearer form than this before 1913, when, as a result of the work of Fajans and Soddy, and especially of Moseley, the numbers of electrons in the atoms became known.

Already in 1911, Rutherford had established the nuclear theory of the atom. In 1916 the celebrated papers by Kössel[3] and by Lewis[4] appeared, which outlined the grouping of atomic electrons in concentric *shells*, the first a shell of two electrons, a *duplet*, the second a shell of eight, the third of eight, and the higher shells of less regular character, but always ending in a shell of eight, an *octet*, in the atoms of the inert gases. These assignments have since proved correct, though they were made before the rules of quantisation were understood. The specific geometrical ideas with which they were associated in the two theories were different, but inessential. It was essential in both theories that the electron shells reach their highest degree of stability and completeness in the inert gases, helium with its shell of two, neon with its shells of two and eight, and so on; and also that atoms having a few electrons more or less than in an inert gas would tend to lose or acquire electrons, in such a way as to produce the electronic structure of the inert gas. The formation of many stable ions, those of potassium, calcium, sulphide, and chloride, for example, could thus be understood.

---

[1] R. Abegg, *Z. anorg. Chem.*, 1904, **39**, 330.

[2] P. Drude, *Ann. Physik*, 1904, **14**, 722.

[3] W. Kössel, *Ann. Physik*, 1916, **49**, 229.

[4] G. N. Lewis, *J. Am. Chem. Soc.*, 1916, **38**, 762.

Lewis's theory involved a further step of quite fundamental importance, inasmuch as he recognised the *sharing* of electrons as a second process by which stable electron groups could be produced. Thus he achieved an electronic interpretation of the structural bond of chemistry. His hypothesis was that the bond consisted of a pair of electrons belonging jointly to two atoms and contributing to the completion of the electron shells of each. Sharing economises electrons, so that atoms, which, when free, had insufficient, could, when combined, have sufficient electrons to complete their shells. A bond satisfied one unit of combining power, normally represented by one electron, of each of two atoms, and therefore the content of a bond was two electrons, which themselves constituted a stable group. Lewis regarded the electron *pair*, or duplet, as the most fundamental of electron groups, and considered valency octets to consist of four duplets, whether all the electrons are shared or not. This idea has also proved correct, although it was advanced a decade before the discovery of electron spin and of Pauli's principle.

The bond of two shared electrons is much the most important type of bond on which molecular structure depends: it is the bond of the classical structural theory of chemistry. Langmuir gave it the name *covalent bond.* A weaker form of bond is known which depends on the sharing of a single electron. Binding by the sharing of electrons generally is called *homopolar binding.*

The electrostatic attraction between ions was termed *electrovalency* by Langmuir. It constitutes a strong force; yet it very often fails to hold ions together in solution, because of the similarly strong, competing electrostatic attraction between the ions and the solvent. In general, electrostatic attraction may arise between oppositely charged ions, between ions and permanent or induced dipoles, and between two dipoles. Electrostatic attraction is a factor of considerable importance for molecular structure; and a measure of such *electrostatic binding* is often associated with covalent binding.

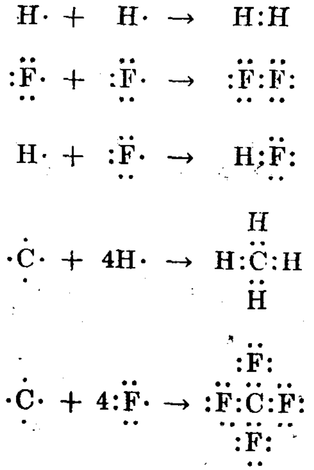
(2) ELECTRONIC CHARACTER OF COVALENCY[5]

(2a) Atomic Binding.—Lewis assumed that when two hydrogen atoms, a hydrogen and a fluorine atom, or two fluorine atoms combined, each atom, being one electron short of the number needed to complete its valency shell, supplies one electron to the shared duplet constituting the bond, each hydrogen atom thus completing its duplet, and each fluorine atom its octet; and that other atoms would similarly combine to complete their stable valency shells; so that carbon, for example,

---

[5] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923.

would form four bonds with hydrogen or fluorine. He expressed these ideas in formulae in which the electrons of the valency shells are represented by dots, while the literal symbols for the elements are allowed to stand, not as previously for neutral atoms, but for the positively charged kernels of atoms, that is, the atomic nuclei together with any completed inner shells of electrons:



$$\mathrm{H}\cdot + \mathrm{H}\cdot \rightarrow \mathrm{H}:\mathrm{H}$$

$$:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\cdot + :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\cdot \rightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$$

$$\mathrm{H}\cdot + :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\cdot \rightarrow \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$$

$$\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot + 4\mathrm{H}\cdot \rightarrow \mathrm{H}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{C}}}}:\mathrm{H}$$

$$\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot + 4:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\cdot \rightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:\overset{:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:}{\overset{\cdot\cdot}{\underset{\underset{:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:}{\cdot\cdot}}{\mathrm{C}}}}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$$

The process of forming a covalent bond by means of one electron of each of the combining atoms will be called *colligation*:[6] the atoms may be said to colligate with each other. It is to be distinguished from the alternative way of forming a two-electron bond, co-ordination, which is to be discussed in the next Section; and the distinction is to be maintained, even when the formed bond is exactly the same.

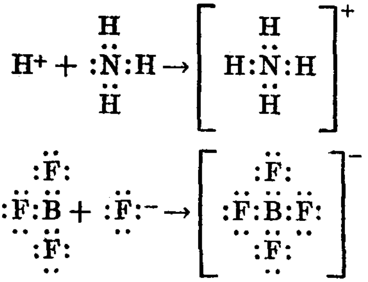
By reversing equations such as the foregoing, we obtain a picture of one way in which the covalent bond can be broken, namely, so that one of the electrons which constituted the bond is retained by each of the atoms which had formed the bond. This mode of bond fission is called *homolysis*. It is the prevalent form of bond fission in reactions which take place in the gaseous phase.

(2b) Co-ordination.—Although the above-written formulae completely correspond in the number and arrangement of their bonds to the formulae of the classical structural theory, such correspondence, as Lewis pointed out, is not universal: the theory of the electron-pair bond and of the valency octet leads to a number of structures which differ significantly from those previously accepted. Moreover, the

---

[6] There does not seem to be any generally accepted short name for this fundamental chemical process; yet it is inconvenient always to be forced back upon the periphrase "homopolar formation of a covalent bond"; and no customary phrase much shorter than this will express what is intended and no more.

new formulae abolish some unsatisfactory features of the old, including a number to which Werner had directed attention.[7] Indeed, the electronic theory includes and interprets Werner's theory, also going beyond it by eliminating some unreal distinctions which it had retained. Thus, Werner discussed the formation and structure of ammonium salts, and of fluoroborates: according to him, nitrogen used its three principal valencies in ammonia, and employed a subsidiary valency, which was in some way qualitatively different, to hold the fourth hydrogen atom of ammonium salts: a similar description was applied to the formation of fluoroborates. Lewis admitted no distinction between the bonds holding the four hydrogen atoms, or the four fluorine atoms: he expressed the formation of the ammonium and fluoroborate ions as follows:



$$H^+ + \begin{array}{c}H\\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:H\\ H\end{array} \rightarrow \left[\begin{array}{c}H\\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:H\\ H\end{array}\right]^+$$

$$\begin{array}{c}:\overset{\cdot\cdot}{F}:\\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}}\\ :\underset{\cdot\cdot}{F}:\end{array} + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:^- \rightarrow \left[\begin{array}{c}:\overset{\cdot\cdot}{F}:\\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\\ :\underset{\cdot\cdot}{F}:\end{array}\right]^-$$

Werner called the process of binding by the use of a subsidiary valency *co-ordination*. In its electronic interpretation, this process evidently constitutes another general method of producing a two-electron bond, namely, through the acceptance by one atom, which must have room for two additional electrons in its valency shell, of a share of a pair of unshared electrons of another atom. All the reactions by which Werner illustrated binding by subsidiary valencies retain this feature in their electronic interpretation. No distinction being now admitted between Werner's two kinds of valency, it is natural that even bonds which he would have classified as principal valencies can be formed in the same way. Thus the hydrogen molecule might be formed, not only from two hydrogen atoms, but also from a proton and a hydride ion; just as a hydrogen fluoride molecule may be, and commonly is, formed from a proton and a fluoride ion:

$$H^+ + H:^- \rightarrow H:H$$

$$H^+ + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:^- \rightarrow H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

---

[7] A. Werner, "Neuere Anschauungen auf den Gebiete der Anorganischen Chemie," Vieweg, Braunschweig, 1905.

Following Sidgwick, it is customary to summarise all such processes of bond formation under the term co-ordination.

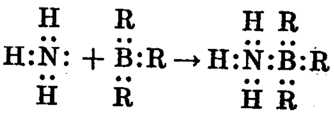
By reversing the last four equations, we obtain illustrations of the second method by which a covalent bond can be broken, namely, so that both the electrons of the bond are retained by one of the separating atoms. This process is termed *heterolysis*. It is the common mode of bond fission in reactions in solution, although homolysis also has some importance in such reactions.

(2c) Multiple Bonds.—The electronic interpretation of a number of the double and triple bonds of classical structural formulae is completely straightforward. The double bond of ethylene and of carbonyl compounds is represented as containing two shared pairs of electrons, and the triple bond of acetylene and of cyanides, three shared pairs:

$$\begin{matrix} H. & & .H \\ & \dot{}\!\!:C::C:\!\!\dot{} & \\ H\cdot & & \cdot H \end{matrix} \qquad \begin{matrix} H. & & \cdot \\ & :C::O: & \\ H\cdot & & \cdot \end{matrix} \qquad H:C:::C:H \qquad H:C:::N:$$

What these formulae do not indicate is that one of the shared pairs in a double bond is not equivalent to the other, and that one pair in a triple bond is not equivalent to either of the other two pairs. These situations only became apparent after the development of the physical theory of binding (Section 3).

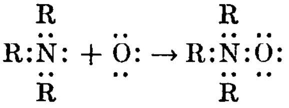
(2d) Dipolar Bonds.—Two examples will serve to demonstrate the character of these bonds. Consider first the compound of ammonia with trimethylborane. It was formerly classified as a "molecular" compound. Werner considered the nitrogen and boron atoms to be linked with a subsidiary valency, and he wrote the compound $H_3N \cdots BMe_3$. The electronic theory regards this valency as a covalent bond, and the formation of the compound as a process of co-ordination:



$$H:\overset{H}{\overset{\cdot\cdot}{\underset{H}{\underset{\cdot\cdot}{N}}}}: + \overset{R}{\overset{\cdot\cdot}{\underset{R}{\underset{\cdot\cdot}{B}}}}:R \rightarrow H:\overset{H}{\overset{\cdot\cdot}{\underset{H}{\underset{\cdot\cdot}{N}}}}:\overset{R}{\overset{\cdot\cdot}{\underset{R}{\underset{\cdot\cdot}{B}}}}:R$$

The electronic formula shows, however, that the nitrogen atom is in the quadricovalent condition characteristic of an ammonium ion: so far as concerns the nitrogen atom, the compound is indeed a substituted ammonium ion. Again, the boron atom is in the quadricovalent condition obtaining, for instance, in the fluoroborate ion: so far as concerns this atom, the compound is a substituted borate ion. In order to signalise these analogies, it is convenient to attach sign-labels to the nitrogen and boron atoms, the compound being regarded as a dipolar ion, $H_3N^{+}B^{-}R_3$.

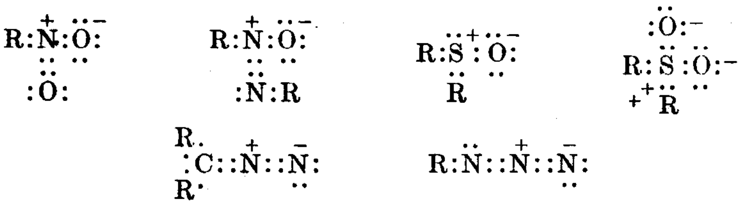
As the second example, consider trimethylamine-oxide, which was formerly written with a double bond, $Me_3N{=}O$. However, the electronic theory formulates this bond as a single covalent bond. It could be formed by co-ordination between the trimethylamine molecule and an atom of oxygen:



$$\mathrm{R}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\underset{\cdot\cdot}{\ddot{\mathrm{N}}}}}: + \underset{\cdot\cdot}{\ddot{\mathrm{O}}}: \rightarrow \mathrm{R}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\underset{\cdot\cdot}{\ddot{\mathrm{N}}}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:$$

Here the nitrogen atom is again bound as in ammonium ions. The oxygen atom is in the unicovalent condition characteristic of hydroxide, phenoxide, or other 'oxide ions. Again it is convenient to signalise these conditions by the use of sign labels, the compound being considered as a dipolar ion, $R_3N^+O^-$.

The kind of bond illustrated, that is, a single covalent bond between atoms constituting a formal dipole, may be called a *dipolar bond.* The theory of the shared duplet and the valency octet places many such bonds in simple inorganic molecules, including most of the oxy-acids, together with their halides, anhydrides, and other derivatives. The theory places one such bond in the nitro-group, one in the azoxy-group, one in sulphoxides, and two in sulphones. It places what may be called a *dipolar double bond,* that is, a covalent double bond between atoms constituting a formal dipole, in the diazo-group, and in the azido-group:[8]



$$\mathrm{R}:\overset{+}{\underset{\cdot\cdot}{\mathrm{N}}}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{\mathrm{O}}}: \quad \mathrm{R}:\overset{+}{\underset{\cdot\cdot}{\mathrm{N}}}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{\mathrm{O}}}: \quad \mathrm{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}\overset{+}{:}\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{\mathrm{O}}}: \quad \begin{array}{c}:\ddot{\mathrm{O}}:^-\\ \mathrm{R}:\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^-\end{array}$$

$$:\ddot{\mathrm{O}}: \qquad :\ddot{\mathrm{N}}:\mathrm{R} \qquad \mathrm{R} \qquad {}^{++}\mathrm{R}$$

$$\begin{matrix}\mathrm{R}\cdot\\ \mathrm{R}\cdot\end{matrix}\!\!:\mathrm{C}::\overset{+}{\mathrm{N}}::\overset{-}{\underset{\cdot\cdot}{\mathrm{N}}}: \qquad \mathrm{R}:\ddot{\mathrm{N}}::\overset{+}{\mathrm{N}}::\overset{-}{\underset{\cdot\cdot}{\mathrm{N}}}:$$

During the growth of the physical theory of binding, the concepts underlying these structures have been modified, largely, however, in ways that can best be treated by reading added significance into the structures, which remain the correct starting point from which to pursue these developments.

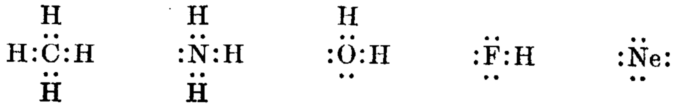
(2e) Polarity of Bonds.—Polarity enters into molecular constitution

---

[8] The bond here called a *dipolar bond* has previously been termed a *semipolar double bond* and a *co-ordinate bond.* The name used in the text is preferred, because some of the bonds concerned have never been regarded as double, and because co-ordination by no means always produces charges. Lewis considered that the bond should not receive a distinctive name, but it seems not to have proved convenient to do without one.

in more subtle ways than those which depend on formal charges. Consider again the covalent bond between formally uncharged atoms. As Lewis was careful to point out, the hypothesis of sharing does not imply a general equality of possession of the shared electrons by the atoms concerned. In the hydrogen molecule, or the fluorine molecule, the electrons must, for obvious reasons, be equally shared between the atoms. But in hydrogen fluoride, the shared electrons should be considered to belong much more to the fluorine atom than to the hydrogen atom. Therefore the molecule should possess a dipole moment, with hydrogen at the positive and fluorine at the negative end of the dipole. Furthermore, such electrical dissymmetry should reduce the energy needed to split the molecule into hydrogen and fluoride ions.

The following *isoelectronic* series will serve as the basis for a more detailed discussion:



$$\mathrm{H}:\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{C}}}:\mathrm{H} \qquad :\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\mathrm{H} \qquad :\underset{\cdot\cdot}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}:\mathrm{H} \qquad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:\mathrm{H} \qquad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Ne}}}:$$

In all these molecules, the total nuclear charge, to the combined field of which all the electrons must be subject, is the same, namely, ten units. However, on passing towards the right, successive units of positive charge are removed from their peripheral situations to the central position, from which they must be expected to exert a firmer general control over the octet of electrons. Therefore, comparing in several molecules a particular shared pair, say, that binding the hydrogen atom written on the right in each of the first four formulae, it can be deduced that this pair will belong progressively more to the central atom, and less to hydrogen, along the series CH_4, NH_3, OH_2, FH. The hydrogen atom should become increasingly positive; and this should affect physical properties, such as dipole moments, and chemical reactions, such as the ionic dissociation of the compounds as acids. If the electron-pair under consideration were in each case binding some other common atom, say, carbon, instead of hydrogen, then, increasingly along the series, electrons should be withdrawn from carbon. This likewise should influence the physical properties of the compounds, and also their chemical reactions, as we shall have occasion later to illustrate.

The above series may also be used for comparisons with respect to an unshared electron-pair, say, that written on the left in each of the last four formulae. This electron-pair should be progressively more strongly bound along the series NH_3, OH_2, FH, Ne. The effect of this should likewise be apparent in physical properties, such as polarisability, and chemical properties, such as basicity.

The terms *electronegative* and *electropositive* have been applied to atoms and atomic groups throughout the whole history of chemical molecular theory. On account of a chain of ideas originating with Berzelius, atoms and groups have been classified as electronegative if they conferred or enhanced acidic properties, and electropositive if they behaved in the opposite way. The groups $—CH_3$, $—NH_2$, $—OH$, $—F$, or, if we prefer, the central atoms of those groups, form a series in order of increasing electronegativity. The preceding explanation shows that the term *electronegativity* summarises those properties which result from the power of an atom to *attract* electrons from attached atoms, that is, from the strength of the *positive* electrical field of the atom. Conversely, *electropositivity* implies the *repulsion* of electrons, and a dominating *negative* electrical field.

It is to be expected that electronegativity will, quite generally, increase as an atom, or the central atom of a group, is displaced, in successive units of atomic number, towards the right-hand side of Mendeléjeff's periodic table. This applies so long as the atoms compared are all formally neutral, or at least possess the same formal charge. It should be noted that atoms and groups carrying a *positive* ionic charge are, by virtue of that fact, *electronegative*: they are among the most strongly electronegative groups known. Thus, the group $—NH_3^+$ is much more strongly electronegative than $—NH_2$, or, indeed, than any group of the series $—CH_3$, $—NH_2$, $—OH$, $—F$. Similarly, atoms and groups bearing a *negative* ionic charge are *electropositive*. Thus the group $—O^-$ is much more strongly electropositive than $—OH$, or than any of the series of neutral groups.

(2f) The Binding of Hydrogen.—As the hydrogen atom is small compared to other bound atoms, its nucleus can be approached especially closely by the unshared electron-pairs of other atoms, with the consequence that electrostatic attraction plays a particularly large part in determining the behaviour of bound hydrogen. Two effects of this are of outstanding importance.

The first relates to the great *mobility, as proton,* of hydrogen bound to electronegative atoms, which also possess unshared electrons, particularly atoms of the nitrogen, oxygen, and fluorine families. In bonds with such atoms, the proton is so little screened that the close approach, thereby permitted, of an active unshared electron-pair of another atom, can lead to the development of an electrostatic attraction for the proton strong enough to be competitive with the original bond. Thus only a very small energy barrier resists proton-transfers between electronegative atoms in such an example as the following:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:H + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:^- \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:^- + H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

It is for this reason that isomerism depending on differences in the position of attachment of protons to electronegative atoms, for instance, among the inorganic oxy-acids, is unknown. Proton transfers between electronegative atoms, whether these be in the same or in different molecules, have never been shown to limit the rate of a chemical reaction.

The second effect arises from the circumstance that, during the period in which two molecules are close enough together to permit facile proton-transfer, the proton is strongly attracted, by one kind of force or another, to *both* the atoms between which it can be transferred: the bond may switch, and even switch repeatedly, but *forces* in both directions remain; and they will tend to hold the species together. This form of association of two atoms through hydrogen is called a ***hydrogen bond.*** Three types of phenomena depending on hydrogen bonds may be mentioned. (1) The hydrogen bonding may be strong enough to maintain the combination of species as a kinetically individual particle of long life in solution. Thus the hydrogen difluoride ion $(FHF)^-$ is a kinetically stable entity. (2) Weaker forms of hydrogen bonding can produce striking effects in condensed systems, in which hydrogen bonds can be formed with such frequency that, despite a short individual life, the number of such bonds present is always large. This is the interpretation given to the association, manifested by reduced volatility, raised viscosity, and other altered physical properties, which is recognised in many pure liquids, notably, ammonia, water, hydrogen fluoride, primary and secondary amines, alcohols, phenols, and inorganic and organic acids. (3) When the components of a hydrogen bond are present in the same molecule, and are suitably articulated by the structure, intramolecular hydrogen bonds of considerable permanence may be established. Such bonds affect physical properties by repressing the intermolecular hydrogen bonding in which the groups concerned would otherwise have engaged. They also affect chemical properties by resisting the normal functional behaviour of the groups, for example, the acidic ionisation of the proton. To cite but one of the many available examples of these effects, salicylaldehyde is notably more volatile than *p*-hydroxybenzaldehyde.

(3) PHYSICAL INTERPRETATION OF COVALENCY

Lewis discovered the material constitution of the covalent bond. But he could not describe the forces involved, because they were of a nature unknown in classical physics. Their discovery was one of the achievements of quantum mechanics.

(3a) Quantum Mechanics.[9]—In 1900 Planck introduced the quan-

---

[9] V. Rojansky, "Introductory Quantum Mechanics," Prentice-Hall, New York, 1946.