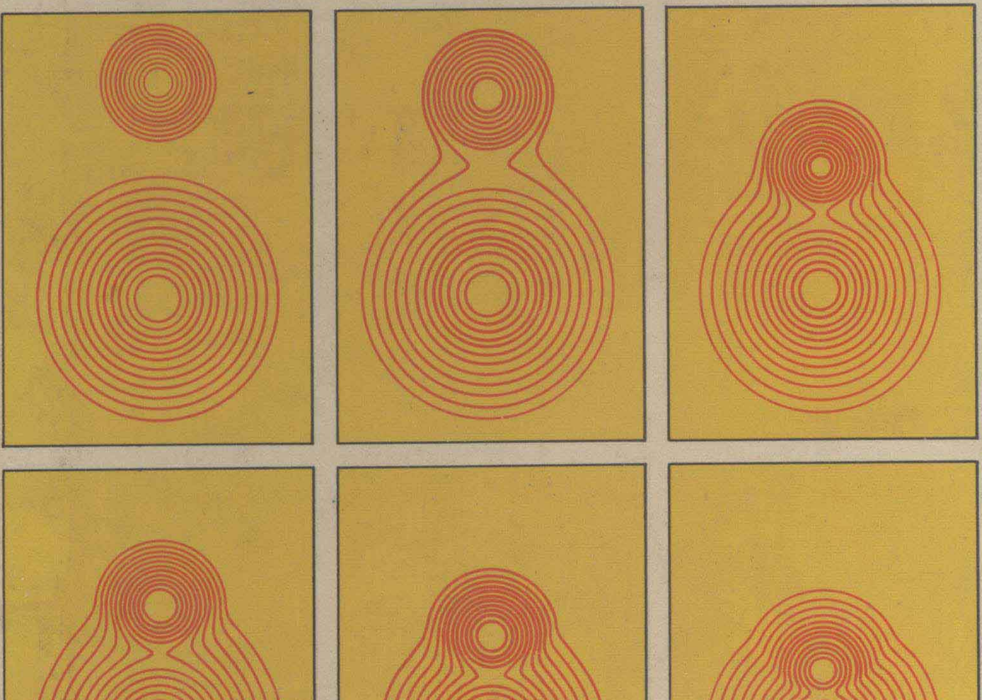
hydrogen bonding



Vinogradov | Linnell

Hydrogen Bonding

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Preface

Latimer and Rodebush were the first to recognize explicitly the existence of hydrogen bonding in 1920. The number of research papers dealing with its nature and manifestations that have appeared since then is in the thousands and continues to grow rapidly. The only reference text, "The Hydrogen Bond" by Pimentel and McClellan (Freeman and Co., 1959), contains a complete bibliography through 1956 of some 2242 papers. The proceedings of a symposium on hydrogen bonding held in Ljubljana in 1957, (Hadzi and Thompson, eds., "Hydrogen Bonding," Pergamon Press, 1959), provide an important landmark in the development of the subject and many of its ramifications. The proceedings of a symposium held in Moscow in 1962 are available in Russian (Sokolov and Chulanovskii, eds., "Vodorodnaya Svyaz," Akad. Nauk SSSR, 1964). A comprehensive monograph on hydrogen bonding in solids has been published recently (Hamilton and Ibers, "Hydrogen Bonding in Solids," Benjamin, 1968). Four chapters in the volume dedicated to Pauling (Rich and Davidson, eds., "Structural Chemistry and Molecular Biology," Freeman and Co., 1968) provide an up-to-date coverage of several important topics in hydrogen bonding. A monograph by Davis ("Acid-Base Behavior in Aprotic Organic Solvents", National Bureau of Standards Monograph No. 105, 1968) includes a review of hydrogen bonding in nonpolar solvents. Finally, the proceedings of a symposium on equilibria and reaction kinetics in hydrogen bonded solvent systems (Covington and Jones, eds., "Hydrogen Bonded Solvents" Taylor and Francis Ltd., 1968) are also available. However, conspicuously lacking is a book on hydrogen bonding suitable for undergraduate students and nonspecialists. We have attempted to remedy the situation by presenting an elementary account of the manifestations of hydrogen bonding. Included at the end of each chapter are the leading references from the literature through 1968, and including some from 1969 and 1970. The coverage of the recent literature on hydrogen bonding is by no means complete. Our aim has been to provide a reasonable coverage of this specialty topic, intermediate between that of a monograph useful only to a few, and the brief discussions generally found in textbooks.

We hope that the ensuing presentation will be of value to undergraduates majoring in chemistry and biology and to graduate students in physical chemistry, biochemistry, and biology. In addition, research workers in the life sciences should find the text and recent references a useful starting point for developing an appreciation of the range and importance of the manifestations of hydrogen bonding.

Serge N. Vinogradov

November, 1970

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Molecular Interactions and Chemical Bonds

1-1 INTRODUCTION

Much of the science of chemistry is concerned with the making and breaking of chemical bonds. Chemical reactions occur when the overall changes of bonds broken and bonds formed make the reaction thermodynamically possible. But what do we mean by the term chemical bond? Pauling[1] has defined the chemical bond as follows: "There is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species." This definition emphasizes the word stability but leaves its meaning somewhat vague. We will focus our attention on the strengths of chemical bonds as given by bond energies and their relationships to the stability of the chemical bonds involved. Bond strengths are usually expressed in kilocalories per mole (kcal/mole), or Avogadro's number (6.023×10^{23}) times larger than the bond strength of the individual chemical bond.* The translational energy (e.g., energy of motion) of gaseous molecules averages $\frac{3}{2}RT$ (where $R =$ gas constant $= 1.98$ cal/deg mole and $T =$ absolute temperature) so that at room temperature the average translational energy of a molecule is 0.9 kcal/mole. Since there are three degrees of freedom for translational energy (corresponding to the usual Cartesian coordinate system x, y, z), each has an average energy of $\frac{1}{2}RT$ or 0.3 kcal/mole at room temperature. Not all molecules have the same velocity since the distribution of molecular speeds follows the Boltzmann distribution. In Fig. 1-1 the fractional number of molecules with energy of E or greater is plotted against the kinetic energy. As the temperature is increased the average kinetic energy increases, because the number of slow moving molecules decreases and the numbers of fast moving molecules increases. A simplified expression for the fractional number of molecules possessing translational energy E or greater, in two degrees of freedom, is

$$\frac{n_E}{n_0} = e^{-E/RT}$$

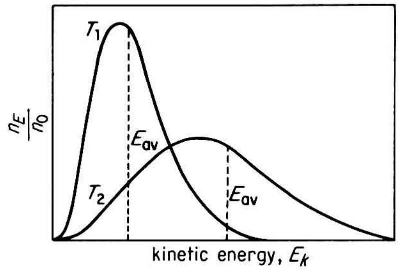

Fig. 1-1 Boltzmann distribution of translational energy ($T_1 < T_2$). Here n_E is the number of molecules with energy E or greater, and n_0 is the total number of molecules.

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* Strictly speaking, we are using the term bond strength to mean bond enthalpy. This is the energy which must be added to the particular compound in the ideal gaseous state at 1 atm pressure and the stated temperature in order to rupture the relevant bond. For the electron-pair covalent bond, bond breaking can be homolytic (yielding two neutral species) or heterolytic (yielding charged species or ions), and the bond enthalpies are not usually the same. Bond enthalpies also depend on the nature of the nearby atomic environment.

The molecules are moving in a three-dimensional space, but if two of them collide, then it is reasonable to assume that the combined translational energy along the lines of collision (two degrees of freedom) represents translational energy available for a chemical reaction (e.g., breaking a chemical bond). Such a collision is shown schematically in Fig. 1-2. We can now look at the stability of chemical bonds by computing n_E/n_0 at a given temperature for different values of E. The results are shown in Table 1-1. Bond strengths of typical chemical bonds are listed in Table 1-2.

TABLE 1-1 Fractional Number of Molecules with Energy E or Greater in Two Degrees of Freedom

n_E/n_0	T (°K)	E (kcal/mole)	n_E/n_0	T (°K)	E (kcal/mole)
0.368	300	0.6	0.607	600	0.6
0.135	300	1.2	0.368	600	1.2
0.0067	300	3.0	0.082	600	3.0
0.00005	300	6.0	0.0067	600	6.0
3.7×10^{-44}	300	60.0	1.93×10^{-22}	600	60.0

Inspection shows that hydrogen (H) bonds are very weak, being only 1/10 to 1/50 as strong as the more familiar chemical bonds. Comparison with Table 1-1 indicates that at room temperature (27°C) almost 1% (0.67%) of bimolecular collisions involve 3.0 kcal/mole or more in two degrees of translational freedom; a negligible number of collisions (10^{-42}%) have energy equal to or greater than 60 kcal/mole. This illustrates an important characteristic of H bonds: They can be experimentally detected by several techniques (to be discussed later), but because of their

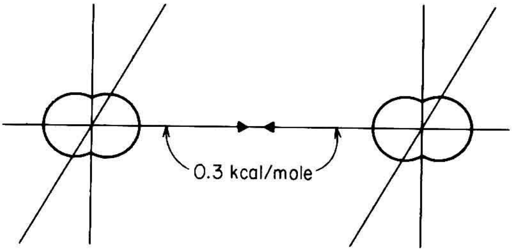

Fig. 1-2 Collision of two diatomic molecules. At room temperature the average translational energy in one degree of freedom is 0.3 kcal/mole.

weakness and the large number of collisions taking place in molecular systems even at as low a concentration as $0.05M$ (a gas at STP), many H bonds are breaking and new H bonds are forming at any one instant.

TABLE 1-2 Some Representative Bond Strengths and Reaction Heats (Enthalpies at 25°C, 1 atm)[a]

Bond	*Enthalpy (kcal/mole)*	*Bond*	*Enthalpy (kcal/mole)*
$C—C$	83	$C—H$	99
$C=C$	146	$O—H$	111
$C\equiv C$	200	$N—H$	93
$C—Cl$	81	$C_6H_5NH_2{-}{-}{-}NC_5H_5$[b]	3.4
$C—Br$	68	$R—OH{-}{-}{-}\underset{\substack{\vert \\ H}}{O}—R$ (gas)	4–6[c]
$C=O$	176	$HOH{-}{-}{-}\underset{\substack{\vert \\ H}}{O}—H$ (gas)	3–6[c]
$Na—Cl$	98	$(CH_3)_3N\cdots B(CH_3)_3$ (gas)[d]	17.6
$H—H$	104	$H_3O^+ + OH^- \rightarrow 2H_2O$ (aq)[e]	13.5 ± 0.05

[a] Detailed treatments of bond strengths and reaction heats can be found in the texts by Cottrel[2] and Mortimer.[3]

[b] The notation --- is used to indicate a H bond.

[c] A range of H bond strengths is indicated because different self-associated species present, besides the isolated 1 : 1 complex indicated in the table, possess H bonds of varying strengths.

[d] Molecular addition complex.

[e] Heats of neutralization of sulfuric and hydrochloric acids at infinite dilution.

The term *association* is frequently applied to these phenomena and *H bonded complex* to the entities held together by H bonds. In such H bonded systems a dynamic equilibrium exists, such that at any moment in time some molecules are free and some bonded. Under these circumstances, one or more equilibrium constants may be determined, depending on the number of different H bonded species present. Ordinary chemical bonds, with bond strengths of the order of 50–200 kcal/mole, do not behave in this manner and no significant or detectable fraction of bonds are being broken at temperatures at or near room temperature. Thus the dynamic equilibria, characteristic of H bonded and other weakly complexed systems at normal temperatures, are not present in chemical systems with the usual chemical bonds.

1-2 CHEMICAL BONDS[1]

Three major types of chemical bonds are generally recognized: covalent bonds, ionic bonds, and metallic bonds. There is some arbitrariness in this classification system and many chemical bonds are intermediate in type. Hydrogen bonds can be better discussed and described within the context of chemical bonds in general.

The simplest atom, hydrogen (one proton and one extranuclear electron) has a 1*s* orbital, the wave function of lowest energy. In this orbital the electron cloud is spherically symmetrical about the central nucleus. Ordinary hydrogen gas consists of diatomic molecules and the H—H bond is the simplest case of a covalent bond. The overlap of the 1*s* orbitals of two H atoms form a stable covalent bond (Fig. 1-3a). Using the electron dot formulation, we write $H\cdot + H\cdot \rightarrow H : H$. The covalent bond is sometimes referred to as an electron-pair bond. All electrons have the property of spin, with two possible spins allowed. If the electron spins of the two electrons associated with two hydrogen atoms are the same, there is repulsion and no bond formation, whereas opposite spins lead to bond formation (the electrons are said to "pair up") with the liberation of about 104 kcal/mole of H_2 molecules (Fig. 1-3b). Since the two H atoms in a H_2 molecule are identical, the electron pair is shared equally and the

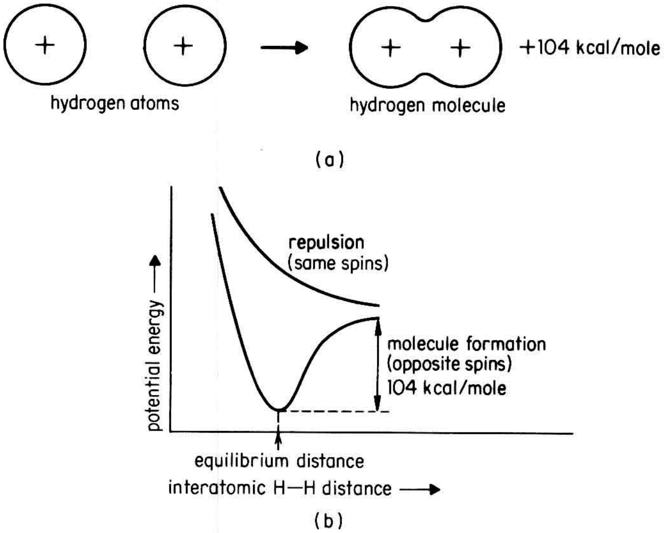

Fig. 1-3 Formation of a hydrogen molecule.