94. *Factors Influencing the Strengths of Bonds.*

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An attempt is made to analyse, for use particularly by chemists, some of the factors influencing the strengths of bonds. The discussion is in qualitative terms under the heads : electronegativity of bonded groups, bond polarity, overlap of atomic orbitals, repulsion of filled atomic orbitals, stability of fission fragments.

There can be few questions of greater importance of chemistry than that of " What factors influence the strengths of bonds? " There are numerous such factors and no theory which tries to explain bond-strength variations in terms of one factor alone can be entertained. We shall here be concerned with factors that the chemist—as distinct from the mathematical physicist—can grasp and apply to the particular molecules in which he is interested. We shall discuss various relevant factors under the five headings noted above, but do not claim that the explanation of varying bond strengths could not be analysed into other and more numerous factors. Nevertheless, we believe these five factors to be of prime utility to chemists.

Distinction between Bond and Dissociation Energies.—It is important to draw a distinction between bond energy and dissociation energy (cf. Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645; Long and Norrish, *Proc. Roy. Soc.*, 1946, *A*, **187**, 337). By bond energy (E) we mean an energy quantity which is a simple measure of the strength of the bond *as it exists in the molecule.* The dissociation energy (D), on the other hand, is the difference of energy between *two* systems, *viz.*, the molecule in its equilibrium configuration and the two portions after fission of the bond under consideration. Clearly, we have no right to expect D to bear a smooth relation to (say) the equilibrium internuclear distance (r) of the bond or to the force constant (k) characterising the curvature of the equilibrium minimum on the potential energy surface. In contrast, E *should* bear such relation. How values are assigned to E is discussed below.

In a diatomic molecule, E is usually equal to D. In some cases, however, the molecule must be regarded as " built " from excited rather than ground-state atoms, so that E is greater than D (Long and Norrish, *loc. cit.*). For example, there are reasons for regarding the oxygen molecule as partly built from excited atoms (see Walsh, this vol., p. 331). In general, however, the bond energy of a diatomic molecule is approximately equal to the dissociation energy. The word "approximately" is used because the act of dissociation must slightly affect the non-bonding electrons in the molecule, so that D is not quite equal to the "true" E characteristic of the molecule in its equilibrium state: H_2 with no non-bonding electrons is an obvious exception here. In general, the difference between D and E arising from this cause will be small and we shall neglect it: it will, however, limit the precision with which E can be defined.

For polyatomic molecules, the dissociation energy of a bond may frequently differ considerably from the bond energy. This is because the strengths of the remaining bonds in the molecule alter at the moment of fission. As an example, the OH bond is known (from length and force-constant data) to be appreciably stronger in the water molecule than in the OH radical. Consequently, energy must be absorbed by the remaining OH bond when one OH bond in water is broken. Hence $D(\text{H}{-}\text{OH})_{\text{H}_2\text{O}} > E(\text{H}{-}\text{OH})_{\text{H}_2\text{O}} > D(\text{O}{-}\text{H})_{\text{OH rad.}}$. $D(\text{H}{-}\text{OH})_{\text{H}_2\text{O}}$ and $D(\text{O}{-}\text{H})_{\text{OH rad.}}$ are respectively $\sim$118 and $\sim$100 kcals./mole (Dwyer and Oldenberg, *J. Chem. Physics*, 1944, **12**, 351); $E(\text{H}{-}\text{OH})_{\text{H}_2\text{O}}$ is 110 kcals./mole.

For molecules of type XY_n, $E(XY) = Q_a/n$ where Q_a is the heat liberated when the atoms, in their appropriate valence states, combine to form the molecule. Thus for the water molecule, if Q_a is taken as 220 kcals./mole, $E(\text{OH})_{\text{H}_2\text{O}}$ is 110 kcals./mole. For CH_4, if we consider the valency state of the carbon atom to be 65 kcals. above the ground state (Long and Norrish, *loc. cit.*), then $Q_a = 416$ kcals./mole and $E(\text{CH})_{\text{CH}_4} = 104$ kcals./mole. In distinction to dissociation energies, bond energies in polyatomic molecules are not capable of definition with complete precision. The concept presupposes a localised-pair bond theory without interaction between different bonds. In fact, as four hydrogen atoms and one carbon atom are brought together to form CH_4, though most of the energy liberated is due to the overlap of electron clouds in the four resulting CH bonds, a little is due to overlap not in the CH bonds. The wave functions for the bonding electrons in methane (Coulson, *Trans. Faraday Soc.*, 1942, **38**, 433) can be expressed as $\psi_A = t_A + k_1 A + k_2(B + C + D)$ where A is one hydrogen atom and B,C,D the others; and where k_2 represents a small non-localisation term, perhaps one-fiftieth of the term $t_A + k_1 A$. In the same way, the "force constant" of a bond in a polyatomic molecule is affected by the neighbouring bonds and cannot be considered in *complete* isolation. Thus, too, the ionisation potential (I) of the electrons in a bond does not solely concern that bond—the bonding effect is not confined to it but is spread a little over all the other bonds. However, the smallness of the non-localisation effect in many molecules still makes "bond quantities" very useful. In molecules like methane the approximation involved in speaking of E, k, I, etc., as referring to a particular bond is not serious, though in carbon tetrachloride it may be more important (Cl–Cl interaction being known to be important in this molecule; Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60). The concept of bond energy has at least as much precision as have the bond diagrams that have been so useful to chemists.

For molecules with different types of bond the definition of E is not so clear. In such cases, the bond energies must be so chosen that (*a*) their sum equals Q_a, (*b*) they serve as useful parameters for interconversion of bond properties, standard points for the interconversion relations being provided by XY_n molecules. For example, in hydrogen peroxide, Q_a may be taken as 256 kcals. Comparison of (*a*) the length and (*b*) the force constant of OH bonds in water, the hydroxyl radical, and hydrogen peroxide shows that the bond is slightly weaker in hydrogen peroxide than in the hydroxyl radical, which in turn is weaker than the OH bond in the water molecule. A choice of 96 kcals./mole for $E(\text{OH})_{\text{H}_2\text{O}_2}$ seems a fair one [that is, a few kcals. less than $E(\text{OH})_{\text{OH rad.}}$; Walsh, this vol. p. 331]. Consequently, $\text{E(OO)}_{\text{H}_2\text{O}_2}$ must be chosen as $\sim$64 kcals./mole, and this may be shown to be roughly consistent with the known strengths and properties of similar bonds.

In view of the foregoing it is unnecessary to stress that bond energies are not constant from molecule to molecule. We have already mentioned as an example the variation in the OH bond energy from water to OH to hydrogen peroxide.

Electronegativities of Bonded Groups.—Since the binding of electrons in a molecular orbital is related to that in the atomic orbitals from which the molecular orbital has been constructed, one expects bond strength to increase (other things being equal) with increase of electronegactivity of one or both of the bonded atoms. There are abundant examples of the truth of this (cf. Gordy, *J. Chem. Physics*, 1946, **14**, 305). Force-constant and energy data show that $E(\text{H}{-}\text{F})_{\text{HF}} > E(\text{H}{-}\text{OH})_{\text{H}_2\text{O}} > E(\text{N}{-}\text{H})_{\text{NH}_3} > E(\text{C}{-}\text{H})_{\text{CH rad.}}$, all these being compounds in which the atom bound to H uses a ground state valency configuration. [$E(\text{H}{-}\text{F})_{\text{HF}} = 148$ kcals./mole (Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645); $k(\text{H}{-}\text{F})_{\text{HF}} = 9{\cdot}62 \times 10^5$ dynes/cm. (Linnett, *ibid.*, 1945, **41**, 223); $E(\text{H–OH})_{\text{H}_2\text{O}} = 110$ kcals./mole (Pauling, " Nature of the Chemical Bond," Cornell, 1940); $k(\text{H–OH})_{\text{H}_2\text{O}} = 7{\cdot}66 \times 10^5$ dynes/cm. (Herzberg, " Infra-red and Raman Spectra," Van Nostrand, 1945); $E(\text{N–H})_{\text{NH}_3} = 93$ kcals./mole, assuming $D(\text{N}_2) = 225$ kcals./mole (Skinner, *loc. cit.*); $k(\text{N–H})_{\text{NH}_3} = 6{\cdot}5 \times 10^5$ dynes/cm. (Linnett, *loc. cit.*); $E(\text{C–H})_{\text{CH rad.}} = 80$ kcals./mole (Herzberg, " Molecular Spectra and Molecular Structure," Prentice Hall, 1939); $k(\text{C–H})_{\text{CH rad.}} = 4{\cdot}09 \times 10^5$ dynes/cm. (Herzberg, 1945, *loc. cit.*).]

Thermochemical and other data show that

$$\begin{array}{ccccc} E(\text{O–O})_{\text{H}_2\text{O}_2} & > & E(\text{S–S})_{\text{S}_8} & > & E(\text{Se–Se})_{\text{Se}_6} \\ 64 & & 54 & & 41 \ \text{kcals./mole} \end{array}$$

(Skinner, *loc. cit.*; Walsh, this vol., p. 331). Similarly,

$$\begin{array}{ccccccc} E(\text{F}_2) & > & E(\text{Cl}_2) & > & E(\text{Br}_2) & > & E(\text{I}_2) \\ 64 & & 58 & & 46 & & 36 \ \text{kcals./mole} \end{array}$$

(Skinner, *loc. cit.*), and, indeed, any bond XX increases in strength as X decreases in atomic weight in any group of the Periodic Table. For example, energy data (Skinner, *loc. cit.*; Walsh, in the press) suggest that

$$\begin{array}{ccccc} E(\text{N–N})_{\text{N}_2\text{H}_4} & > & E(\text{P–P})_{\text{P}_4} & > & E(\text{As–As})_{\text{As}_4} \\ 64 & & 44 & & 34 \ \text{kcals./mole} \end{array}$$

and

$$\begin{array}{ccccc} E(\text{C–C})_{\text{C}_2\text{H}_6} & > & E(\text{Si–Si})_{\text{Si}_2\text{H}_6} & > & E(\text{Ge–Ge})_{\text{Ge}_2\text{H}_6} \\ 95 & & 51 & & 34 \ \text{kcals./mole.} \end{array}$$

Force-constant data show that

$$\begin{array}{ccccc} k(\text{O–H})_{\text{H}_2\text{O}} & > & k(\text{S–H})_{\text{H}_2\text{S}} & > & k(\text{Se–H})_{\text{H}_2\text{Se}} \\ 7{\cdot}7 & & 4{\cdot}1 & & 3{\cdot}2 \times 10^5 \ \text{dynes/cm.} \end{array}$$

(Herzberg, 1945, *loc. cit.*).

An important point that should be considered here is the relation of electronegativity to the hybridisation of the $2s$ and $2p$ atomic orbitals. It is possible to show (Coulson, V. Henri Memorial Vol., Desoer, Liége, in the press) that the average value of the position of an electron lies further from the nucleus for the $2p$ than for the $2s$ orbital. We may therefore state that a carbon atom has a greater electronegativity when exerting a $2s$ than when exerting a $2p$ valency. The same applies to a boron or a nitrogen atom and is to be expected from the drop in first ionisation potential as we pass from beryllium to boron : evidently the $2p$ electrons are less strongly bound than are the $2s$. In a hybrid valency, it therefore follows that the atom concerned has a greater electronegativity the greater the proportion of s character in its valency. Table I shows examples of this.

TABLE I.

Molecule.	Hybridisation state of C valencies used in σ bonds.	
CH radical	pure p	↓ electronegativity of C atom in bonds increasing.
CH_4	sp^3, tetrahedral	
C_2H_4	sp^2, trigonal	
C_2H_2	sp, digonal	

The acidity of acetylene supplies direct confirmation of the present reasoning, as does the finding by Braude and Jones (*J.*, 1946, 128), from studies of reaction velocity (in reactions requiring electron accession at the reaction centre), that an acetylenic carbon atom has a much larger electron-attracting nature than has an ethylenic one. Similarly, propiolic acid ($\text{CH}\vdots\text{C}\cdot\text{CO}_2\text{H}$) has a much higher dissociation constant than has acrylic acid ($\text{CH}_2\text{:CH}\cdot\text{CO}_2\text{H}$). In consequence of the facts embodied in Table I, the CH bond strength should become greater as we descend the table. That this is so is shown by Table II.

TABLE II.

Molecule.	$10^{-5}k(\text{CH})$, dynes/cm.	$r(\text{CH})$, A.	$E(\text{CH})$, kcals./mole.
CH radical	4·09	1·120	80
CH_4	4·97	1·094	104
C_2H_4	5·1	1·087	106
C_2H_2	5·85	1·059	121

The greater strength of the vinyl–Cl bond (shorter length and higher force constant) than of the methyl–Cl bond is usually ascribed exclusively to resonance involving the lone-pair Cl electrons. That this is not satisfactory is seen by the fact that vinyl–H is also strengthened relatively to methyl–H, H having no lone-pair electrons. Instead, a large part of the strengthening is due to the change of electronegativity with increasing *s* character in a hybrid valency. *All* vinyl–X bonds are strengthened relatively to methyl–X.

The CC bond in ethane forms another example of bond strengthening due to admixture of 2*s* with 2*p*. The NN bond in hydrazine, the OO bond in hydrogen peroxide, and the FF bond in fluorine all have closely the same strength (Walsh, this vol., p. 331). We might expect the CC bond in ethane to have a strength very similar to these other bonds. In fact, it is considerably stronger, as shown by its force constant and bond energy. Skinner (*Nature*, 1946, **158**, 592) has shown unambiguously that $D(\mathrm{CC})_{\mathrm{C_2H_6}} = 84{\cdot}3$ kcals./mole. Now the free methyl radical uses sp^2 carbon valencies and therefore each CH should be much as in C_2H_4, that is, $\sim$2 kcals. stronger than in C_2H_6 or CH_4. Hence $E(\mathrm{CC})_{\mathrm{C_2H_6}}$ is certainly greater than 84·3 kcals. and may be as high as 96 kcals.; D is low because CH changes in strength from C_2H_6 to CH_3. In view of the very small interaction of CC or CH bonds attached to the same carbon atom, it seems probable that $E(\mathrm{CC})_{\mathrm{C_2H_6}}$ is close to $E(\mathrm{CC})_{\mathrm{diamond}}$, which is $L_2/2$, where L_2 is the latent heat of sublimation of carbon to the quadrivalent state. Hence if $L_2 \simeq 190$ kcals. (Long and Norrish, *loc. cit.*), $E(\mathrm{CC})_{\mathrm{C_2H_6}} \simeq 95$ kcals.

If two of the hydrogen atoms of ethane are changed to give the compound $CH_2X{\cdot}CH_2X$, where X is a group of higher electronegativity than H, then the strength of the central CC bond should be increased; X may be CO_2H as in succinic acid or a phenyl group as in dibenzyl. Since an unsaturated carbon atom has a high electronegativity, X may also be the group C≡C–. In this way, Bateman and Jeffrey's finding (*Nature*, 1943, **152**, 446; Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 388) that the central bond of the group C≡C—C—C—C≡C is significantly shorter than the CC bond of ethane causes no surprise. The effective electronegativity of the central C atoms is increased without introduction of polarity (see below). This is a particularly good example of the distinction between D and E. The allyl radical is so stable (see below) that there is little doubt that the dissociation energy of the central CC bond of the group C≡C—C—C—C≡C would be abnormally low, whereas the bond energy is abnormally high. Dibenzyl provides a similar example (Jeffrey, *Nature*, 1945, **156**, 82; *Proc. Roy. Soc.*, 1947, *A*, **188**, 222). If X has a lower electronegativity than H, then E(CC) will be less than in ethane. An example is provided by *n*-butane, where the central bond is known to have a low dissociation energy (Skinner, *Nature*, 1946, **158**, 592) and has also a low bond energy. A similar example is seen in *cyclo*hexane, where also the bonds are between secondary carbon atoms and are known to be weaker than in ethane (Walsh, *Trans. Faraday Soc.*, 1946, **42**, 779).* Strain effects (whatever their interpretation in modern orbital theory) of course probably also affect the *cyclo*hexane bonds. In butadiene, even if overlap of π orbitals did not occur, the central CC bond would still be strengthened relatively to ethane, since it is of sp^2–sp^2 type: it is therefore not satisfactory to calculate theoretically the π bond order in the central bond and then to add the ethane CC bond order to this so as to get the total central CC bond order.

Finally, we may point out that the ionisation potentials of non-bonding electrons in the alkyl chlorides and in hydrogen chloride afford a convenient way of assessing relative electronegativities and show that the electronegativity decreases in the series H > Me > Et > Pr^i > Bu^t.

Gordy (*loc. cit.*) has emphasized the importance of electronegativity in determining bond strengths, and has written bond strength as a function of the product (X_AX_B) of the electronegativities of the bonded groups. That other factors cannot be neglected, however, will be stressed in following sections.

The Polarity of Bonds.—If electronegativity were the only factor affecting the strength

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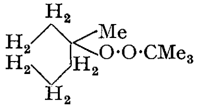
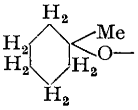
* The decomposition of peroxides supplies much data on relative bond strengths. Peroxides of type R·O·OR break at the O–O bond and then at the weakest bond, other than the C–O, on the α-carbon atom (*idem, ibid.*, p. 269). Thus the peroxide (I) yields the radical (II) and then breaks at a ring C–C

(I).





(II.)

bond in preference to the C–CH_3 bond (Milas and Perry, *J. Amer. Chem. Soc.*, 1946, **68**, 1938). This confirms the weakness of the ring C–C strength. Similarly, in an alkoxy-radical $CR_1R_2R_3{\cdot}O{\cdot}$, the carbon bond to break is that to the alkyl group with the least electronegativity.

of bonds, then on replacing an H in ethane by OH the strength of the CC bond should be increased as a consequence of the increase of electronegativity of one of the carbon atoms. In fact the strength appears, from Bonner's simple, but probably significant, force-constant calculations (*ibid.*, 1937, **5**, 293), to be less in ethyl alcohol. The offsetting factor is to be found in the fact that polarity has been introduced into the CC bond which in ethane was non-polar. Keten affords a similar example : the presence of the oxygen atom and the acetylenic nature of the central carbon atom mean that the $C=C$ bond is polar, whereas that of ethylene is non-polar. Accordingly, the $C=C$ bond does not appear stronger in keten than in ethylene (see Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60), in spite of the raised electronegativity of one of the carbon atoms. In carbon suboxide *all* the carbon atoms are in the acetylenic state : considering the CC bond adjoining a $C=O$, we therefore have a change relative to keten which (*a*) reduces the CC polarity, and (*b*) increases the electronegativity of one of the bonded atoms. These two factors reinforce each other and this CC bond of carbon suboxide, unlike that of keten, becomes stronger than that of ethylene [$k(CC)_{C_2H_4} = 9{\cdot}6 \times 10^5$ dynes/cm. (Herzberg, 1945, *loc. cit.*); $k(CC)_{C_3O_2} = 12{\cdot}7 \times 10^5$ dynes/cm. (Thompson and Linnett, *J.*, 1937, 1376)].

When methyl ether forms its complex with boron trifluoride, $(CH_3)_2O \rightarrow BF_3$, it is clear that the effective electronegativity of the oxygen atom for the C–O bond electrons must increase. Yet the C–O bonds *weaken* on formation of the complex, as a consequence of the increased $\overset{+}{C}-\overset{-}{O}$ polarity. The length of the B–F bonds also increases on formation of the complex. This is partly because their initial $\overset{+}{B}-\overset{-}{F}$ polarity increases and partly because the boron valencies change from trigonal to tetrahedral.

Attachment of a hydroxyl group to the oxygen atom of a second hydroxyl group must increase the effective electronegativity of the oxygen atom of the second group. Yet the indications are that the OH strength in H·O·OH is less and not greater than in the free OH radical.

All these cases are examples where a relation, such as that of Gordy (1946, *loc. cit.*), which relates electronegativity and bond strength without taking into account bond polarity, breaks down.* The breakdown will be likely to occur wherever negative charge is taken out of a bond in such a way as to increase the polarity.

The CH radical utilises a pure *p* carbon valency and has therefore a weaker bond than has CH_4 where the carbon atom utilises hybrid sp^3 valencies. In the same way the NH bond in NH_3 (where nitrogen valencies with probably less *s* character than sp^3 are used) might be expected to be weaker than the NH bond in NH_4^+ (using hybrid sp^3 valencies). However, to expect this is to neglect the importance of the bond polarity which must be much greater in NH_4^+ than in NH_3. Accordingly, it appears that $k(NH)_{NH_4^+}$ is less than $k(NH)_{NH_3}$ (Gordy, *loc. cit.*). Further, the NH strength in NH_4^+ might be expected to be greater than the CH strength in CH_4, since N^+ lies at the end of the series Pb, Sn, Si, C, N^+. Yet if $k(NH)_{NH_4^+} < k(NH)_{NH_3}$, $E(NH)_{NH_4^+}$ must be less than 93 kcals., whereas $E(CH)_{CH_4}$ is $\sim$104 kcals. Again, the explanation must be that the vast increase in bond polarity from CH_4 to NH_4^+ more than offsets the increase of bond strength due to increase in electronegativity product. Gordy has implicitly adopted much the same explanation of the weakness of NH in NH_4^+ by describing the bond polarity in terms of resonance structures and considering the resulting " bond order ".

H_3O^+ presumably uses oxygen valencies of much the same hybridisation type as in H_2O. In this case, therefore, there are no opposing factors and the OH strength should be considerably less in H_3O^+ than in H_2O as a result of the greater bond polarity. The infra-red absorption data appear to accord with this (Gordy, *loc. cit.*). In all cases where H_2O is co-ordinated to, say, a metal ion, the strength of the OH bonds should be decreased [cf. the C–O bonds in the complex $(CH_3)_2O \longrightarrow BF_3$].

In former papers we have given much evidence to justify the statement that bond strength decreases with increasing bond polarity. It is of interest to note that the L.C.A.O. approximation of the molecular orbital theory predicts a result in accord with the facts—namely, that bond strength for a given bond decreases with polarity (Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413). For a single bond between two nuclei A and B, the bonding electrons lie in an orbital of form

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[*] At first sight Gordy's relation suggests that change of polarity would have little effect : it increases X_A but reduces X_B. It is true that Gordy considers a factor *N* allowing for change in " bond order ". One way of making his relation include the bond weakening with polarity increase is to say that increase of polarity causes a decrease in *N* because the charge cloud now extends more and more *outside* the bond; but Gordy himself did not explicitly consider the relation of *N* to polarity increase or to atomic orbital overlap (see below).

$(a\psi_A + b\psi_B)/\sqrt{a^2 + b^2}$. The bond order per electron is then given by the product of the coefficients of ψ_A and ψ_B, *i.e.*, by $ab/(a^2 + b^2)$. This is easily shown to have a maximum value when $a = b$; that is, the binding is a maximum when it is non-polar, but decreases with increasing polarity. (Strictly, the " overlap integral " should be included in the denominator of the expressions for the orbital and the bond order; but its inclusion still leaves the maximum at $a = b$.)

The simple molecular orbital theory thus shows that bonds weaken with increasing polarity. In part, this is because increasing polarity means that the orbitals of the bonding electrons come to extend more and more on the side of one of the atoms away from the bond, where they are lost for bonding purposes and where their screening effect on the repulsion between the nuclei is lost. Nevertheless, this is not the only effect at work. The molecular orbital calculation shows an effect that is too low because it neglects interaction of the bonding electrons with lone-pair electrons on one of the atoms or with electrons in neighbouring bonds. As the polarity of the bond electrons in $>C{=}O$ or $\geq C{-}Cl$ increases, we know that the lone-pair electrons on the oxygen or the chlorine atom suffer more and more repulsion. The bond electrons must suffer an equal repulsion. Hence the bond electrons become more weakly bound the greater the polarity. Hence, by the linkage of bond order and ionisation potential (Walsh, *Trans. Faraday Soc.*, 1946, **42**, 779), the bond weakens to an extent over and above that which would occur in the case of H_2 where no lone pair or neighbouring bond electrons are present. Change of polarity will cause least change of bond strength when (*a*) the nuclear charges are low and (*b*) there are no lone-pair electrons on the more negative atom : CH bonds in quadrivalent carbon compounds fulfil these conditions.

The carbonyl molecules form a particularly excellent series in which the gradation of properties can be correlated with change of carbonyl bond polarity (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 158; *J. Amer. Chem. Soc.*, 1946, **68**, 2408). It would be equivalent in this series to correlate the properties with change in electronegativity of the groups attached to the carbonyl bond. The bond strength increases with increase of electronegativity of these groups partly directly because they increase the effective electronegativity of the carbon atom of the $C{=}O$ group, and partly indirectly because they reduce the bond polarity : it would be difficult to try to separate the two effects.

The Overlap of Atomic Orbitals.—Other things being equal, the greater the overlap of atomic wave functions the greater the strength of the resulting molecular orbital : this is a reason, for example, why π bonds in double and triple bonds are weaker than σ bonds—for the " sideways " overlap of $p\pi$ electrons is less than the " endwise " overlap of $p\sigma$ ones. The principle of " maximum overlapping " is fundamental to both the electron-pair bond and the molecular orbital theory of valency.

Increase of electronegativity of bonded atoms increases the bond strength—but only up to a point. The $2p$ distributions contract inwards towards the nucleus as we pass from N to O to F. Thus, as the electronegativity of bonded atoms increases, there must come a time when, in order to secure appreciable overlap of the atomic wave functions, the atoms must be so close together that appreciable repulsion of the nuclei is likely to result. In other words, beyond a certain point, increase of electronegativity of X in a bond X–X may weaken rather than strengthen the bond.

We only expect to find cases of reduced strength due to reduced overlap in bonds to highly electronegative atoms. We now consider three examples.

(1) *Bond strengths in peroxides.* The author has pointed out (*Trans. Faraday Soc.*, 1946, **42**, 264) that the variations in OO bond strength from molecule to molecule can partly be understood in terms of charge transfer effects established by the study of the ionisation potentials of non-bonding electrons in alkyl halides. The greater the negative charge transfer to the OO group, apparently the greater the OO bond strength (Walsh, this vol., p. 331). This can only be understood in terms of the electronegativity of oxygen atoms being too high to give the overlap that would correspond to the maximum OO bond strength : reduction of their effective electronegativity increases the overlap and strengthens the bond. In this way one can understand the relation between the electronegativity of an element and its tendency to form per-compounds (Walsh, *J. Chem. Physics*, 1947, **15**, 688).

Similarly, it is significant that the NN bond (64 kcals. in N_2H_4) is weaker than the NH (93 kcals. in NH_3), the OO (64 kcals. in H_2O_2) is weaker than the OH (110 kcals. in H_2O), and the FF (64 kcals. in F_2) weaker than the FH (148 kcals. in HF). In all these cases the electronegativity product is greater and the bond polarity is less in XX than in XH. That XX is weaker than XH must therefore be ascribed to a third factor affecting bond strength and this factor we identify with the overlap of atomic orbitals. The interplay of electronegativity product and overlap keeps the NN bond of N_2H_4, the OO bond of H_2O_2 and the FF bond of F_2 remarkably similar in length, force constant, and bond energy. That the CC bond in ethane is markedly stronger than the NN bond in hydrazine ($\sim$95 and $\sim$64 kcals., respectively) is also to be explained as partly due to reduced overlap in the NN bond, though another factor operating here is doubtless the peculiarities of hybridisation. The NN bond of N_2O_4 is even weaker than that of N_2H_4, a fact readily explicable as due to the very high dipoles in the NO_2 groups (Walsh, *J. Chem. Physics, loc. cit.*).

(2) *Halogen compounds.* It is a striking fact that the compound ClF has a greater bond strength (86·5 kcals.) than has F_2 or Cl_2 (64 and 58 kcals., respectively).* The bond strength increase in the series I_2, Br_2, Cl_2, F_2 can be attributed to increase of the electronegativity product in this series, but the FF strength is less than one would expect on this basis, knowing the big jump of electronegativity from Cl to F. The FF strength is probably partly reduced because of reduced overlap consequent upon too great an electronegativity. Replacement of one of the fluorine atoms by Cl enables this overlap to increase and so causes an increase of bond strength, in spite of a polarity effect and a reduced electronegativity product.

(3) *Glyoxal and related compounds.* The conjugation of the two C=O groups in glyoxal should result in a strengthening of the central CC bond relative to ethane, and calculations by Coulson (*Trans. Faraday Soc.*, 1946, **42**, 106) support this expectation. Nevertheless, photochemical data for diacetyl show that the central CC is more easily broken than is that of ethane. The indications are therefore that the CC dissociation energy of glyoxal is less than that of ethane. Even if E(CC) in glyoxal should be greater than D(CC), one is led to the conclusion that there is some factor that offsets the increased strength due to conjugation in glyoxal.† This factor we identify with small σ electron overlap in the CC bond. The small overlap is consequent upon the small size of the carbon orbitals involved, due to the high electronegativity. It is understandable therefore that r(CC) may be as low as $1{\cdot}47 \pm 0{\cdot}02$ A. (the electron-diffraction value) without corresponding to high CC strength. Coulson's calculations do not take into account variation in the bond order of σ CC bonds. If this explanation be true, E(CC) in diacetyl may be greater than E(CC) in glyoxal. Oxalyl chloride should have a lower CC bond strength than glyoxal, in accord with its ready photochemical decomposition and its use by Kharasch and his co-workers as a source of radicals (Waters, *op. cit.*, p. 189). Cyanogen and oxalic acid may prove to be other molecules with a lower CC bond order than simple conjugation theory would expect.

Gordy emphasized the importance of electronegativity, but neglected atomic orbital overlap, in determining bond strength. It is not therefore surprising that his relation fails for H_2O_2 and probably for F_2. It does not account for the increase of strength in FCl relatively to F_2, unless the bond-order term in his expression is specifically related to overlap. Pauling has emphasized the importance of atomic orbital overlap, but has neglected that of electronegativity. As a result, his work (" Nature of the Chemical Bond," Cornell, 1940, p. 86) would lead one to expect that the strength of CH bonds would increase in the series $C_2H_2 < C_2H_4 < C_2H_6$, because the greater the proportion of p character in a hybrid valency, the better can that valency orbital overlap with another atomic orbital. In fact, the CH bond strengths increase in the opposite order, which is explicable as above in terms of varying carbon electronegativity.

Repulsion of Parallel Filled Orbitals.—The fact that the oxygen molecule has two unpaired electrons in its ground state can be reconciled with the pair-bond theory if we make the simple assumption that pairs of electrons in parallel filled atomic orbitals repel each other strongly. This repulsion is the analogue on the pair-bond theory of the "anti-bonding orbitals" of the molecular orbital theory. Suppose the $2p_z$ atomic orbitals overlap to form the first or σ bond. As a result of the repulsion, one oxygen atom twists relatively to the other so that the configuration of one may be written $2p_x^2\ 2p_y\ 2p_z$, and of the other $2p_x\ 2p_y^2\ 2p_z$. This means that repulsion of the parallel lone pairs is avoided, being replaced by the *attractive* interaction of a single electron with a parallel lone pair. A state of the oxygen molecule with two unpaired electrons has thus lower energy than the state represented by the diagram O=O.

The same hypothesis—repulsion of filled parallel orbitals—explains the skew nature of H_2O_2: again, twisting occurs to minimise the repulsion. In a peroxide where twisting is partly prevented by steric factors, the OO strength must be reduced from the value that would otherwise prevail. Di-*tert.*-butyl peroxide probably supplies an example (Walsh, this vol., p. 331).

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* Gaydon ("Dissociation Energies", Chapman and Hall, 1947) favours a value 60·3 for D(FCl) and a consequent value considerably below 64 kcals. for $D(F_2)$.

† This conclusion is confirmed by considerations based upon the measured angles of the molecule and hybridisation theory (Coulson, V. Henri Memorial Vol., Desoer, Liége, in the press).

Repulsion of parallel filled orbitals must be an important factor reducing the bond strength in Cl_2 or in F_2. This is the pair-bond theory analogue of the molecular-orbital theory description of these molecules as containing electrons in anti-bonding orbitals. On either theory, removal of one of the non-bonding electrons should result in an increase of bond strength—an expectation strikingly confirmed by the facts, since the fundamental vibrational frequencies for Cl_2 and Cl_2^+ are 565 and 645 cm.$^{-1}$, respectively (Herzberg, 1939, *loc. cit.*).

Repulsion of adjacent filled atomic orbitals occurs in the carbon tetrachloride molecule (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 158). It probably occurs also in carbon tetrafluoride. In the silicon tetrahalides the much larger size of a silicon than of a carbon atom reduces these repulsions and so

$$E(\text{Si–Cl})_{\text{SiCl}_4} = 90, \text{ whereas } E(\text{C–Cl})_{\text{CCl}_4} = 83 \text{ kcals.}$$

and

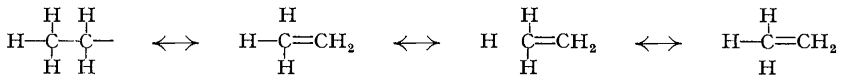
$$E(\text{Si–F})_{\text{SiF}_4} = 147, \text{ whereas } E(\text{C–F})_{\text{CF}_4} = 120 \text{ kcals.}$$

[the latent heats of sublimation of C and Si to their valency states being assumed to be respectively 190 (Long and Norrish, *loc. cit.*) and 102 kcals. (Skinner, 1945, *loc. cit.*)], in spite of the lowered electronegativity of Si relatively to C. Other molecules in which this repulsion of filled atomic orbitals is important comprise *o*-dichlorobenzene, the various halogenated methanes, ethanes, and ethylenes, and the acetyl halides (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 158).

It is clear, therefore, that in assessing probable bond strengths it is always important to consider the pair-bond theory viewpoint of possible repulsion of parallel filled atomic orbitals.

Stability of Fission Fragments.—This is a factor affecting dissociaton, rather than bond, energies. In general the stability of any group X will not be the same in the free state as in the compounds X–H or X–X. If the stability is less in the free state, then $D(\text{X–X}) > E(\text{X–X})$ or $D(\text{X–H}) > E(\text{X–H})$: an example is provided by HO–H. If the stability is greater in the free state, then $D(\text{X–X}) < E(\text{X–X})$: examples are provided by HO–OH and CH_3–CH_3. Further examples are to be seen in those compounds where fission of a bond increases the space available for " delocalisation " of π electrons. Thus if a CH bond in the methyl group of propylene is broken, the carbon atom of the resulting $-CH_2$ assumes the free methyl configuration, *i.e.*, becomes planar with one electron in (originally) a $2p\pi$ orbital at right angles to the plane. This $2p\pi$ orbital must overlap with the π orbital of the double bond, so that the three π electons come to occupy orbitals extending over all three carbon atoms. The effect of this is to lower the energy of the free allyl group relatively to its energy in the propylene molecule. The lowering may be referred to as the resonance energy of the allyl radical. Its effect is to alter the dissociation energy of the allyl–H bond, but not necessarily to affect the bond energy.

Resonance in radicals of the allyl type is very strongly founded in quantum-mechanical theory and there is much evidence to show that it is important quantitatively as well as qualitatively. For example, when a free allyl-type radical is formed, products derived from the two forms —CHR—CH=CH$_2$ and CHR=CH—CH$_2$— appear. It should be regarded as resulting fundamentally from the overlap of atomic *p* orbitals to give inevitably non-localised molecular orbitals. Some workers have supposed resonance to occur in alkyl radicals, for example



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}} \longleftrightarrow \mathrm{H{-}\overset{H}{\underset{H}{C}}{=}CH_2} \longleftrightarrow \mathrm{H\ \ \overset{H}{\underset{H}{C}}{=}CH_2} \longleftrightarrow \mathrm{H{-}\overset{H}{\underset{H}{C}}{=}CH_2}$$

increasing in the series

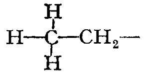
$$\text{Me} < \text{Et} < \text{Pr}^i < \text{Bu}^t \quad . \; . \; . \; . \; . \; . \; . \; . \; . \tag{2}$$

and have supposed the decreases in dissociation energy in the series

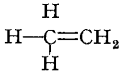
$$\text{Me–X, Et–X, Pr}^i\text{–X, Bu}^t\text{–X} \; . \; . \; . \; . \; . \; . \; . \; . \tag{3}$$

to be attributable to this cause. This type of resonance is much less strongly founded in theory and experiment. It does not correspond to overlap of atomic orbitals with consequent delocalisation of molecular orbitals in the way that does resonance in, say, the benzene molecule or the allyl radical. Nor—if it be granted as likely to occur—is there compelling evidence of its being quantitatively important. One of the main qualitative reasons for supposing it—the decrease of D in the series (3)—has been removed with the realisation that the bond polarity C–X increases in this series and that increase of polarity means weakening of bond strength. Since the ionisation potential of the odd electron does not increase but decreases in the series (2), the alkyl resonance theory has necessitated the further *ad hoc* postulate that resonance in the positive ion increases even more rapidly in series (2) than does resonance in the radical. Further, the theory is not based upon any discussion of the energy that would be necessary to distort the tetrahedral bond angles in (III) and the trigonal angles in (IV) to intermediate positions in

(III.)



$H-\overset{H}{\underset{H}{C}}-CH_2-$



$H-\overset{H}{\underset{H}{C}}=CH_2$

(IV.)

which resonance might be possible : in fact, resonance would only occur if this distortion energy were less than the resonance energy possible after distortion. Unless further evidence is forthcoming, the theory of the importance of resonance in alkyl radicals as a determining factor for dissociation energies should be treated with reserve.

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