BOND DISSOCIATION ENERGIES IN SMALL HYDROCARBON MOLECULES[1]

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CONTENTS

I. INTRODUCTION AND DEFINITIONS

With the advent of recent spectroscopic evidence concerning gaseous CH_3 and CH_2 radicals, plus the general acceptance of the "high" value for the heat of sublimation of graphite and the additional mass- and optical-spectroscopic studies of C_2, it seems appropriate to sum up the information on bond dissociation energies in small hydrocarbon molecules as of the present time. In a brief review, a comprehensive summary such as that presented by Szwarc (57) in 1951, or by Cottrell (13) in his 1954 monograph on bond strengths, cannot be attempted. The subject has been restricted to the small molecular species of prime interest to those working with gaseous reactions of relatively simple molecules and radicals.

For the purpose of studying carbon–hydrogen and carbon–carbon bonds in simple hydrocarbons, it is necessary to have a clear understanding of the meaning of the term "bond dissociation energy" and how it differs from the term "bond energy." Bond energy (E) is defined as the strength of a bond as it exists in a molecule, or the contribution of the bond between a particular pair of atoms in a molecule to the total binding energy present in the molecule. On the other hand, the bond dissociation energy (D) (hereafter referred to as dissociation energy) is defined as the difference in energy between the parent molecule (in its equilibrium configuration) and the two fragments (also in their equilibrium configurations) after bond breaking.

In diatomic molecules the bond energy is equal to the dissociation energy. In polyatomic molecules, the strengths of the remaining bonds are changed when bond breaking occurs. Thus, the dissociation energy generally differs considerably from the bond energy. In a molecule of the type AB_n, the bond energy $E(\text{A—B}) = Q_a/n$, where Q_a is the atomic heat of formation of the molecule (the molecule and atoms being in their ground states). In contrast to dissociation energies, the bond energies in most polyatomic molecules cannot be defined with complete precision except in molecules of the type AB_n in which all B's are identical. A precise definition would assume a theory of local pair bonds without interaction between bonds. For example, as one carbon atom and four hydrogen atoms are brought together in the formation of methane, most of the energy liberated is from overlap of electron clouds in the resulting carbon–hydrogen bonds. However, some is due to overlap other than in the carbon–hydrogen bonds. In the same manner, the force constant of a bond in a polyatomic molecule is affected by neighboring bonds and

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cannot be considered as completely isolated. Because these nonlocalization corrections are small for many molecules, the various descriptive qualities of a bond are still useful.

The bond strength should increase with an increase in electronegativity of one or both of the bond atoms, because the binding of electrons in a molecular orbital is certainly related to the binding in the atomic orbitals involved. Walsh (61) has developed this concept in some detail. It predicts a dependence of the electronegativity of carbon on the degree of hybridization of the $2s$ and $2p$ atomic orbitals. The average value of the position of an electron in a $2s$ orbital is closer to the nucleus than that of the $2p$, and a carbon atom has greater electronegativity in a $2s$ than in a $2p$ valence state. As a result, the $2s$ electrons are more strongly bound than the $2p$ electrons. In a hybridized orbital, the greater the s character of the orbital, the greater the electronegativity. As the valence state of the carbon atom changes from pure p to sp^3 to sp^2 to sp, the electronegativity of the carbon atom should increase, and this should result in stronger bonding. Thus one would predict that the C—H bond energies in the molecules CH, CH_4, C_2H_4, and C_2H_2 would increase in the order written, since the hybridization is presumed to shift in this sequence from pure p in CH to sp in C_2H_2. The order is clearly obeyed in the first two molecules, where E(C—H) is unambiguously definable; but in the other two the assignment of E(C—C) also enters into any consideration of E(C—H), so it becomes difficult to test the argument fully.

A second factor that certainly influences bond energies is orbital overlap. The greater the overlap of the atomic wave functions, the stronger the resulting molecular orbital (other things being equal). Thus the π bonds in triple and double bonds are expected to be weaker than the σ bonds, since the lateral overlap of the p orbitals is less than the endwise overlap within the σ bond. There is perhaps some conceptual difficulty here in distinguishing separable contributions from π and σ bonds in the total bond as it exists in a molecule; nevertheless the concept has been very useful and doubtless will continue to be so.

Bond *dissociation* energy as a physical concept has a great advantage over bond energy (or "average" bond energy or bond energy "term"), in that it is unambiguously definable. However, bond dissociation energies in hydrocarbons have not been used as much as bond energies for estimating thermochemical quantities because (*a*) they are difficult to measure; (*b*) they are sensitive to the intramolecular environment, so that "bond additivity" rules are difficult or impossible to formulate; (*c*) when dealing with reactions involving stable reactant and product molecules—i.e., no free radicals—the use of bond energies has been fruitful and of adequate accuracy for many purposes; and (*d*) if all the necessary values of bond dissociation energies were available for a reaction, one would have no need to formulate approximate rules for estimating thermochemical quantities, since exact data would already be available.

The zero-point dissociation energy of a bond (R—R′) is the change in energy (ΔE_0^0) for the reaction $RR' \rightarrow R + R'$. This reaction occurs in the ideal gas state at absolute zero, and the products are in their ground states. The proper designation of the dissociation energy is, therefore, D_0^0, where the superscript refers to products in their ground states and the subscript refers to the zero$^{\text{th}}$ vibrational level. For convenience, the change in enthalpy at some standard temperature is often used. Unfortunately, literature values are not always clearly defined as to which is used. Actually, $\Delta H^0_{25^\circ\text{C.}}$ often does not differ greatly from D_0^0, and much of the enthalpy data is not precise enough to justify a correction. For a dissociation reaction, ΔC_p^0 is generally positive but not large, so that $\Delta H^0_{25^\circ} > D_0^0$, but the difference is rarely more than 1 kcal. When values at 0°K. are used, no distinction between bond dissociation energy and bond dissociation enthalpy is necessary, but a distinction is necessary at other temperatures.

Consider the relationship of the bond dissociation energy to various other properties of the molecule. The heat of atomization (Q_a) of a molecule is equal to the sum of all the dissociation energies involved as the molecule is degraded stepwise into separate atoms (a stepwise atomization of the molecule). It should be noted again that the dissociation energy of a bond between two atoms A and B generally depends not only on the bonded atoms A and B, but on the other atoms attached to A and B, as well as the configuration of the molecule as a whole.

The bond dissociation energy at 0°K. is the difference between the heats of formation of the fragments and the heat of formation of the parent molecule[2]; i.e.,

$$D(\text{AB—C}) = \Delta H_f(\text{AB}) + \Delta H_f(\text{C}) - \Delta H_f(\text{ABC})$$

Conversely, the heat of reaction at 0°K. is the sum of the dissociation energies of bonds formed minus the sum of the dissociation energies of the bonds broken, i.e., for the reaction $AB + C \rightarrow A + BC$:

$$\Delta H = D(\text{B—C}) - D(\text{A—B})$$

Finally, consider the relationship between activation energy and dissociation energy. Generally, a chemical reaction consists in breaking one bond and forming another bond simultaneously, the activation energy being a very complex function of the dissociation energies of the bonds broken and formed. However, in a unimolecular decomposition reaction in which bond

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[2] *From this point on, superscript and subscript ciphers are omitted, with the tacit understanding that the conditions are ideal gases at* 0°K.

breaking produces two atoms or radicals, the true activation energy will be nearly if not exactly equal to the dissociation energy. This is true because a radical recombination process requires little activation energy, if any. For most exothermic reactions between radicals and molecules, activation energies are also very small. It is important to realize that bond energies should not be used in estimating activation energies; only the specific dissociation energies of bonds in a specific molecule under consideration should be used.

II. EXPERIMENTAL METHODS

There are many methods of determining dissociation energies. These are discussed in detail by Cottrell (13). A direct measure of the heat of recombination can sometimes be obtained by calorimetry. By means of the van't Hoff equation, the energy of dissociation can be calculated from known dissociation equilibrium data covering a range of temperatures. In kinetic methods, assuming that the activation energy for radical recombination is zero, the energy of dissociation can be equated to the activation energy for dissociation. Electron-impact studies (17) yield appearance potentials $A(\mathrm{R}^+)$ directly, and, provided that no activation or excess energy is involved, the dissociation energy is the difference between the appearance potential and the ionization potential of one of the fragments:

$$A(R^+) = D(R—R') + I(R)$$

where $I(\mathrm{R})$ is the ionization potential of the fragment R. If the ionization potential is known accurately, the dissociation energy can be calculated directly. If not, then D can be calculated indirectly by measuring several more appearance potentials. Molecular-beam techniques to measure D have also been used. Spectral analysis provides the most accurate method of measuring dissociation energies of diatomic molecules if the states of the dissociation products are known. However, the spectra of polyatomic molecules become extremely complicated, and analysis to determine dissociation energies is nearly impossible. Statistical mechanics can not be used to make independent computations of dissociation energies but can be used to relate molecular spectra to thermodynamic quantities. Quantum-mechanical calculations, although capable of yielding exact results for dissociation energies, have been of very limited success because of their very great mathematical complexity.

These methods, individually or in combination, can yield reliable dissociation energies in most cases where proper measurements can be made. However, different methods sometimes give different answers, or at least they lend the results to different interpretation by different investigators. It is the purpose of this paper to present the various dissociation energies listed in the literature for carbon–carbon and carbon–hydrogen bonds in simple hydrocarbons and to analyze the various results and methods so that the "best" values can be assigned. Two thermochemical quantities are basic to the values assigned: the dissociation energy of the H—H bond in H_2 is 103.24 kcal. at 0°K. and 104.18 kcal. at 298°K. (13); and the heat of sublimation of graphite is 169.6 kcal. at 0°K. (15) and 170.2 kcal. at 298°K. Although there has been considerable controversy over the sublimation energy of graphite, the so-called "high" value quoted here has now gained general acceptance. Literature values of dissociation energies quoted herein have been corrected, where necessary, to bring all numerical quantities onto the basis of the "high" value. The reference temperature is 0°K. unless otherwise indicated.

III. METHANE AND ITS FRAGMENTS

The carbon atom of methane is in an sp^3 hybridized valence state (10, 20), and the molecule is formed by an overlap of *s* orbitals of four hydrogen atoms with the four symmetrical sp^3 hybrid orbitals of the carbon atom. The overlap is very effective in the direction of the bond, and strong bonds result.

A. CH_3—H

There is nearly complete acceptance of the value of D = 101–102 kcal. This has been verified by many different methods. Some of the earliest work was done by Rice and Dooley (42, 43), using their mirror technique. Their original result was about 98 kcal., but this was later modified to 100 ± 6 kcal. Butler and Polanyi (9) obtained a value of about 103 kcal. based on the pyrolysis of methyl iodide. Szwarc (57) criticized the method but arrived at a value of 103 ± 3 kcal. from the pyrolysis of ethylbenzene (56). Photobromination of methane by Kistiakowsky and Van Artsdalen (30) yielded a value of 101 ± 1 kcal.

A great many electron-impact studies have been carried out to determine the energy of dissociation of the first C—H bond in methane. Using indirect electron-impact techniques, Stevenson (52) found the energy to be 101 ± 5 kcal. In conjunction with Hipple (55), he determined a value of 102 ± 4 kcal. In a later paper (27) they confirmed this value by a direct electron-impact method. Langer, Hipple, and Stevenson confirmed this value once again in some direct electron-impact studies of various gases (33). Stevenson (54) tabulated various electron-impact values of the dissociation energy of the first C—H bond in methane and found the average value to be 101.9 ± 1 kcal. Field and Franklin (17) have also reviewed electron-impact studies and concur with Stevenson. Cottrell (13) reviewed the literature and arrived at $D(CH_3—H)$ = 101–102 kcal., a value which is acceptable.

B. C—H

The methine radical has the $^2\pi$ state as its electron configuration of lowest energy (20, 22). The carbon atom is in a pure *p* valence state (62). On the basis of a predissociation in the CH spectrum, Shidei (47) calculated the bond energy to be 80 kcal. This value is now in general acceptance (18, 22). Glockler (20) suggested that the peculiarities in the observed spectrum of CH could be the result of a perturbation instead of a predissociation. His extrapolation of average C—H bond energies versus C—H bond distances for a series of hydrocarbons gave a value of 92.3 kcal. A linear Birge–Sponer extrapolation of the CH vibration spectrum gave 122.5 kcal. The lower value best fits the sequence HF, OH, NH, and CH. However, this argument is weak because the value of the bond energy in NH is not accurately known (13). Gaydon (19) and Porter (40) have challenged the interpretations of Glockler. They believe the predissociation to be strong and real because it involves the complete break-off of rotational structure in several bands, rather than one missing line. Independent support of the spectroscopic value was provided by McDowell and Warren (36). Using electron-impact values of the dissociation energies of the first three C—H bonds in methane, they calculated D(C—H) $\leq$ 83 kcal.

C. CH_2—H *and* CH—H

Because of the uncertainty concerning the structure of these radicals and because of their interdependent dissociation energies, these two radicals will be discussed together.

One possible structure of the methyl radical has the carbon in an sp^3 hybridized valence state (20), and this radical cannot be planar. However, Walsh (62) suggested that the methyl carbon is sp^2 hybridized and the radical planar. In a later paper (63) he discussed the shape of the methyl radical and concluded that it probably is not planar. A computation of the bond angle set the range from 107° to 120°. A recent spectroscopic analysis was reported by Herzberg and Shoosmith (24). They were not able to make a structural analysis, but concluded that the methyl radical is probably planar, or very nearly so.

The structure of methylene is also unknown. Glockler (20) envisioned the carbon atom as an sp^2 hybrid. However, the exact nature of the bonding is not understood. In a recent note, Herzberg and Shoosmith (25) have presented the spectrum of free methylene from the flash photolysis of diazomethane. Because of the zero-point vibration they could not decide between a linear or a nonlinear radical in the ground state. In the lower state of the observed transition the radical has an H—C—H angle between 140° and 180° and a nontotally symmetric electronic structure. Herzberg (48a) has since come to the tentative conclusion that the ground state is linear with a $^3\Sigma_g^-$ structure. This species is long-lived. He also observed a singlet species which is short-lived and probably bent. According to Skell (48), the photolysis of diazomethane produces a short-lived singlet species, and the catalytic decomposition produces a long-lived singlet.

The heat of atomization of methane at 0°K. is 392.0 kcal. Subtracting the dissociation energies of the CH_3—H and C—H bonds from this leaves a remainder equal to the sum of the dissociation energies of the CH_2—H and CH—H bonds, or 210–211 kcal. To assign values to the dissociation energy of these remaining bonds, it is necessary to decide how the energy is partitioned.

McDowell and Warren (36) have studied the dissociation of methane by electron impact. They obtained values of $D(CH_2\text{—}H) = 80 \pm 5$ kcal. and $D(CH\text{—}H) = 78 \pm 5$ kcal. The kinetic energy was not obtained for all fragments; hence these values appear to be upper limits. However, they lead to a low value for the heat of sublimation of carbon and cannot be considered reliable. Cottrell (13) suggested that the appearance potential for CH_2^+ used by McDowell and Warren was in error. The uncertainty arises from a low relative abundance of this ion. A reëvaluation (13) of the work of McDowell and Warren increased the value of $D(CH_2\text{—}H)$ to 86–90 kcal. Smith (49) measured a value of $A(CH_2^+)$ that increased $D(CH_2\text{—}H)$ to 91 kcal. Using this value in the scheme of McDowell and Warren lowers the dissociation energy of CH—H to about 67 kcal. However, Smith obtained a value for $A(CH^+)$ about 23 kcal. larger, which would increase $D(CH\text{—}H)$ to 90 kcal. Because of the lack of agreement and lack of knowledge of the kinetic energies involved, very little weight can be given to these values.

A theoretical calculation was made by Voge (60), using an extended Heitler–London–Pauling–Slater valence calculation in a method developed by Van Vleck and others (59). He used experimental data to correct computed energies and obtain information about L_c. However, the heat of sublimation arrived at in this treatment was 120–140 kcal. On the basis of this value, Voge calculated $D(CH_2\text{—}H) = 90$ kcal. and $D(CH\text{—}H) = 80$ kcal. Using $L_c = 170.4$ kcal., he obtained $D(CH_3\text{—}H) = 109.1$ kcal., $D(CH_2\text{—}H) = 124.0$ kcal., and $D(CH\text{—}H) = 79.6$ kcal. In the light of disagreement with these values, particularly with $D(CH_3\text{—}H)$, in numerous experimental studies, it appears that this interesting treatment is not very useful in determining dissociation energies.

Springall (50) suggests that some of the complications arise from two opposing effects which influence the C—H dissociation energies. The H ⟷ H repulsion force decreases as successive hydrogen atoms are removed, contributing toward an *increase* in successive C—H dissociation energies. At the same time, the orbitals involved in the bonds change from sp^3 hybrids in methane to pure p in methine. This contributes toward a *decrease* in successive C—H dissociation energies.

Laidler and Casey (32) have evaluated and interpreted the kinetic data from the sodium vapor–methylene chloride reaction (5) to give an upper limit for the CH_2—H dissociation energy of 87 kcal. From this they set the lower limit for the energy of dissociation of CH—H at 125 kcal. This implies that CH_2 is more stable than CH_3 with respect to the removal of a hydrogen atom. Assuming that the lowest state of CH_2 is a singlet in which the hydrogen bonds are formed by the p orbitals of the carbon, promotion of a $2s$ electron of carbon to a $2p$ orbital, followed by hybridization to sp^2, results when an additional hydrogen atom is added to CH_2. According to Laidler and Casey, because this stability of hybridization is not large enough to offset the energy required for promotion of the $2s$ electron, CH_3 is less stable than CH_2 with respect to hydrogen removal. This interpretation is in disagreement with Walsh (61), who claims that CH_2 is in a triplet state in which each hydrogen is bonded through a carbon sp hybrid atomic orbital. The promotion of the $2s$ electron occurs during the $H + CH \rightarrow CH_2$ reaction rather than during the $H + CH_2 \rightarrow CH_3$ reaction. In view of the recent spectroscopic work, Walsh may be correct. Laidler and Casey prefer their interpretation because it is consistent with the singlet state of CH_2 and the results of the sodium–methylene chloride reaction. However, they do discuss the existence of a triplet excited state, which is a diradical, and calculate its excitation energy to be at least 19 kcal. Cottrell (13) used more recent thermodynamic data (45) and revised the results of Laidler and Casey to $D(CH_2—H) \leq 90$ kcal. and $D(CH—H) \geq 122$ kcal.

Using heats of formation and *average* bond energies, Glockler (20) computed $D(CH_2—H) = 100.6$ kcal. and $D(CH—H) = 98.5$ kcal. Basic to his calculation was the assumption that the dissociation energy of the carbon–carbon bond in ethylene is 150 kcal. Because of the lack of agreement on the value of this energy and because of the use of average bond energies, there is considerable room for error in this type of calculation. Considering the other evidence discussed, it is difficult to accept a value of the dissociation energy of the carbon–hydrogen bond of the methyl radical larger than that in the methylene radical.

From a kinetic study of the photochemical decomposition of ketene, Kistiakowsky and Rosenberg (29) estimated a lower limit for the dissociation energy of CH_2—H equal to 80 kcal. However, the uncertainty in the method appears to place the value between 80 and 90 kcal. (13).

Electron-impact studies on methane, tetraethyllead, and diazomethane were made by Langer, Hipple, and Stevenson (33). They obtained values of $D(CH_2—H) = 86.5 \pm 7$ kcal. and $D(CH—H) = 92.0 \pm 7$ kcal. They did not make any kinetic energy corrections, and their values lead to a low value of L_c (133 kcal.). Field and Franklin (17) report values of $D(CH_2—H) = 79$ kcal. and $D(CH—H) = 96$ kcal. but give no references to their sources. It is presumed that the values are based on electron-impact studies. These values are also consistent with a low value for the heat of sublimation of carbon.

Cottrell (13) presented in his monograph the values $D(CH_2—H) \cong 88$ kcal. and $D(CH—H) \cong 124$ kcal. The uncertainties in these appear to be 3 or 4 kcal. For consistency with the heat of atomization of methane, a slightly better choice may be 87 kcal. and 123–124 kcal., respectively, for the two values. A definitive structure determination of both methyl and methylene would help greatly to establish the correct values.

IV. ETHANE

A. CH_3CH_2—H

The carbon atoms in ethane are probably sp^3 hybrids, although Walsh (62) has suggested that they are sp^2. In the latter case, ethane might well be regarded as two methyl radicals linked by a p bond, and the C—H dissociation energy should be closer to $D(CH_2—H)$ than to $D(CH_3—H)$.

Much work has been done to determine the dissociation energy of the first C—H bond in ethane. Calculations involving the reaction between an ethyl radical and a hydrogen molecule have been carried out by Wicke (64) and Steacie (51). They obtained values for $D(C_2H_5—H)$ equal to about 102 kcal. and 100 kcal., respectively. Polanyi and coworkers (4) studied the pyrolysis of ethyl iodide and calculated the dissociation energy of the first C—H bond to be 96.4 kcal. This was later revised to 97.5 kcal. (9). Leigh and Szwarc (34) investigated the pyrolysis of n-propylbenzene and evaluated the heat of formation of the ethyl radical as $\Delta H_f = 22$ kcal. This led to several values for the dissociation energy, including $D(C_2H_5—H)$ equal to 94 ± 4 kcal. Semenov (46) lists a value of 26 kcal. for the heat of formation of the ethyl radical at 25°C., and this would increase D to about 96 kcal. However, Semenov does not cite the source for his figure. The photobromination of ethane (1) yielded a value of $D = 98 \pm 2$ kcal., but a later study of this reaction (2) has shown the value to be 97.7 ± 2 kcal.

Several determinations of this dissociation energy have been made using electron-impact techniques. Stevenson (52) evaluated appearance potential data and arrived at a value for the dissociation energy of the first C—H bond equal to 96.2 ± 4.5 kcal. From a subsequent study of the dissociation of 1-butene he calculated a value of about 97 kcal. (53). Later, in conjunction with Hipple (27), he reported a value of 96.8 kcal.

Franklin and Field (17) believe that a value of 97 kcal. is a good figure, while Cottrell (13) considers a value of about 96 kcal. to be reasonable. It appears that either value can be used, while some preference might be given the higher value. Either one appears to support an assumption of sp^3 hybridization in ethane, rather than sp^2.

B. •$\mathrm{CH_2CH_2}$—H

When a hydrogen atom is removed from an ethyl radical, a simultaneous reorganization presumably occurs. To the σ bond between the carbon atoms is added a π bond, and ethylene is formed. Therefore, because of the increased degree of bonding between the two carbon atoms, a much lower dissociation energy is expected for the removal of a hydrogen atom from an ethyl radical than from ethane. Indeed, the experimental results confirm this.

A study of the pyrolysis of *n*-propylbenzene (34) and subsequent evaluation of the heat of formation of the ethyl radical has given a value of 41.5 ± 4 kcal. for the removal of a hydrogen atom from an ethyl radical. Semenov's higher value of the heat of formation of ethyl yields a value of about 38 kcal. (46). Field and Franklin (17) have reported a value of 40 kcal. Since the sum of the dissociation energies of the first two C—H bonds must equal 134 kcal., $D(\mathrm{C_2H_4\text{—}H}) \cong 37$ kcal. This value appears to be the best obtainable from present knowledge.

C. $\mathrm{CH_3}$—$\mathrm{CH_3}$

Breaking the carbon–carbon bond in ethane produces two methyl radicals. The hybridization of the carbon atom presumably changes from sp^3 to sp^2 during this process, so that one cannot well equate the $D(\mathrm{C\text{—}C})$ in ethane to an "intrinsic" σ C—C bond strength of some sort for sp^3-hybridized carbon, as appears to have been done in a recent work on bond energies (7).

The mirror technique of Rice and Dooley (42) gave a value for the dissociation energy equal to 80 ± 6 kcal. Szwarc calculated the value from $D(\mathrm{CH_3\text{—}H})$ and data on the heat of formation and obtained a probable range of 82 to 87 kcal. (57). Using a value of $D(\mathrm{CH_3\text{—}H}) = 102$ kcal., the resulting dissociation energy is about 85 kcal. Cottrell (13) calculated 83 kcal. from thermochemical data. Stevenson (52) evaluated data on appearance potentials and found a value of 82.6 kcal., while Field and Franklin (17) presented an electron-impact value of 84 kcal. Glockler (20) used the heat of atomization of the methyl radical and calculated $D(\mathrm{CH_3\text{—}CH_3}) = 83.5$ kcal.

Thus there is general agreement that the dissociation energy of the C—C bond in ethane is between 83 and 85 kcal.

V. ETHYLENE

The basic structure of the ethylene molecule is usually pictured as two carbon atoms with sp^2 hybrid orbitals, bonded by the endwise overlap of one of the sp^2 orbitals from each carbon, forming a σ bond, and by the lateral overlap of unhybridized p orbitals perpendicular to the plane of the sp^2 orbitals, which results in a π bond. The geometric factors involved make the molecule planar. s orbitals of hydrogen overlap each remaining sp^2 orbital of the carbon atoms, forming four carbon–hydrogen σ bonds.

A. $\mathrm{CH_2CH}$—H

The original electron-impact work on the determination of the dissociation energy of the first C—H bond in ethylene was done by Stevenson (53) in his study of the dissociation of 1-butene. He obtained a value of about 91 kcal., but a reëvaluation of his work (13) produced a value of about 96 kcal. Data on appearance potentials from Dibeler's study of *cis-* and *trans*-2-butenes (14) led to a value of 96 kcal. Laidler (31) calculated $D = 99.9\text{–}102.8$ kcal. from an evaluation of some photosensitized reactions of ethylene. He assumed a slow reaction of the type $\mathrm{A^* + RH_2 \rightarrow AH + RH}$ as the important step. ($\mathrm{A^*}$ is an excited metal atom.) The lower limit was derived from the absence of a reaction with sodium. Cottrell (13) does not believe that the lower limit can be established with the present knowledge of transition states. If there is an activation energy for the reverse reaction, Laidler's deductions are not valid. If a reaction of the type $\mathrm{A^* + RH_2 \rightarrow A + RH_2^*}$ is preferred, then the results of the photosensitized reactions may not apply to $D(\mathrm{C_2H_3\text{—}H})$. In a more recent paper, Field (16) presented electron-impact work in which he obtained appearance potentials for the vinyl ion from eight different compounds. From these he obtained $\Delta H_f(\mathrm{C_2H_3}) = 82.3$ kcal. and $D(\mathrm{C_2H_3\text{—}H}) = 122$ kcal.

Although Field's work was highly self-consistent, the derived value for $D(\mathrm{C_2H_3\text{—}H})$ was based upon what now appears to be an erroneous value for the heat of formation of the tertiary butyl ion. Lampe and Field (32a) recently redetermined this quantity. From it they derived $D(\mathrm{C_2H_3\text{—}H}) = 107$ kcal. There is some uncertainty in the temperature to which this number pertains. It probably is high enough so that about 2 kcal. should be subtracted from the 107 kcal. figure to convert it to 0°K. Taking into account an experimental uncertainty of about 3 kcal., one obtains $D(\mathrm{C_2H_3\text{—}H}) = 105 \pm 3$ kcal. This agrees quite well with still more recent work by Harrison and Lossing (21), in which they determined the ionization potential of the vinyl radical and remeasured the appearance potential of $\mathrm{C_2H_3^+}$ from $\mathrm{C_2H_4}$. The data yielded 65 ± 3 kcal. as the heat of formation of $\mathrm{C_2H_3}$, apparently at 298°K. A correction to 0°K. adds approximately 1 kcal. to this and yields $D(\mathrm{C_2H_3\text{—}H}) = 103 \pm 3$ kcal. The average of these two recent results, viz., 104 ± 3 kcal., may be taken as the best value for $D(C_2H_3—H)$ presently available.

B. •CHCH—H

The removal of a hydrogen atom from the vinyl radical results in a large reorganization within the molecule; i.e., acetylene is formed. It is therefore expected that this dissociation energy will be much smaller than that involved in the removal of a hydrogen atom from ethylene. Field and Franklin (17) give computed values of 54 kcal. and 24 kcal., depending on whether $D(C_2H_3—H) = 91$ kcal. or 121 kcal. With the acceptance of $D(C_2H_3—H) = 104 \pm 3$ kcal., the most probable value of the dissociation energy of a carbon–hydrogen bond in the CH_2 group of the vinyl radical is 39 ± 3 kcal. This is computed by difference, using heat of formation data at 0°K.

C. $CH_2{=}CH_2$

The energy involved in breaking the C=C bond in ethylene is not known precisely. Occurrence of predissociation in the Schumann ultraviolet spectrum led Price (41) to a value of $D < 162$ kcal. and Hilgendorff (26) to a value of $D < 159$ kcal. Because of some of the uncertainties in interpreting the spectrum, these values can only be accepted as upper limits. Using a value of $\Delta H_f(CH_2) = 59$ kcal., Field and Franklin (17) have calculated a dissociation energy of 105 kcal. However, the heat of formation is in some doubt, since it was calculated (17) from uncertain data on the appearance potential for CH_2^+, discussed in Section III,C. Cottrell (13) calculated a dissociation energy of about 125 kcal. from a computed value of $\Delta H_f(CH_2)$. This heat of formation was calculated from the carbon–hydrogen dissociation energies of methine and methylene and the heat of sublimation of carbon, and the value obtained was 69 kcal. Various thermochemical routes may be followed, all involving values that are somewhat in doubt in at least one reaction. The range of values obtained in this way is 120.5–123.5 kcal., or $D(H_2C{=}CH_2) = 122 \pm 1.5$ kcal. A major revision in either $D(CH—H)$ or $D(CH_2—H)$ would have a pronounced effect on this value.

VI. ACETYLENE

The acetylene molecule is envisioned as two *sp*-hybridized carbon atoms and two hydrogen atoms (10). One *sp* hybrid orbital from each carbon atom overlaps the *s* orbital of a hydrogen atom, forming a σ bond. The other *sp* orbitals overlap each other endwise, and the unhybridized *p* orbitals form π bonds by lateral overlap. This results in a carbon–carbon triple bond.

A. CHC—H

Photodecomposition studies of acetylene by Cherton (11) produced a value of $D < 121$ kcal. Steacie and LeRoy (35) studied the mercury-photosensitized polymerization of ethylene. One possible mechanism gave an upper limit of 112.2 kcal. and another gave the limit as 120.7 kcal. Unfortunately, no firm choice could be made between the two mechanisms.

Absence of H⟷H repulsion, the *sp* hybridization, and the strong overlap possible in the C—H bond all lead to an expectation that $D(C_2H—H)$ should be substantially larger than $D(C_2H_3—H)$; however, in the absence of experimental data, it is not possible to set a firm lower limit other than the figure for $D(C_2H_3—H)$, viz., 104 ± 3 kcal. With the experimental upper limit of 120.7 kcal., or 121 to the nearest integral value, the range of possibility becomes $104 \pm 3 \text{ kcal.} \leq D(C_2H—H) < 121$ kcal.

Any efforts to narrow the choice have to rest upon correlations of various sorts, such as a comparison of dissociation energies and vibrational force constants for similar molecules. Among the C—H vibration force constants listed by Cottrell (13) are those for CH, CH_4, C_2H_2, C_2H_4, and C_2H_6. Using the four species of these five for which $D(C—H)$ is adequately established, one finds a rather astonishing constancy of the ratio, D/k, within about 2 per cent. From this ratio and the force constant for the C—H vibration in C_2H_2, one predicts $D(C_2H—H) = 120$ kcal. Furthermore, one predicts for $D(C—H)$ in C_6H_6, HCN, C_3H_8, and C_4H_{10} the respective values 103 kcal., 115 kcal., 96 kcal., and 96 kcal. Cottrell gives best values of 102 kcal. and 114 kcal. for the first two and 100 kcal. and 101 kcal. for the latter two. However, Semenov (46) gives 95 kcal. and 94 kcal. for the latter two. Thus the apparent relationship between D and k finds support; however, Bernstein (6) points out that such a relation assumes identical anharmonicity in all the C—H vibrations, which is not so. His own correlation, taking differing anharmonicity into account and using as principal references the three species CH, CH_4, and HCN, yields a predicted $D(C_2H—H) = 114$ kcal. His relation also predicts $D(C_2H_3—H) = 105$ kcal., in excellent agreement with experiment, as previously discussed. Unfortunately, $D(C—H)$ in HCN is still subject to some question, although the bulk of evidence (13) supports a number within 1 or 2 kcal. of 114 kcal.

Since correlations yield no support for a number as low as 110 kcal. for $D(C_2H—H)$, it can be stated with confidence that $110 \text{ kcal.} < D(C_2H—H) < 121$ kcal., and the result of Bernstein's correlation, 114 kcal., is assigned as the best value.

B. •CC—H

There is no value given for this dissociation energy in the literature. However, the sum of the dissociation energies for the removal of the first and second hydrogen atoms from acetylene must equal about 246 kcal. This is readily computed from data on the heats of formation for C_2H_2, H, and C_2 (discussed below). Therefore, the probable limits are 125 kcal. $< D(C_2H—H) <$ 136 kcal., with a best value of 136 kcal.

C. CH≡CH

Rupture of the carbon–carbon triple bond in acetylene involves the reorganization of the *sp* hybrid orbitals to pure *p* orbitals in the methine radical. Rice and Glasebrook (44) mention a value of D(HC≡CH) = 200 kcal. but give no indication of the source. Price (41) studied the absorption of acetylene in the far ultraviolet region. He interpreted some diffuse band structure to be predissociation and calculated the dissociation energy to be slightly less than 187 kcal. According to Price, a great deal of speculation was involved in the interpretation, but the value obtained was roughly that expected. An analysis of the photodissociation of acetylene was made by Norrish (38). From it he computed two possible values for D(HC≡CH), 220 kcal. and 146 kcal., depending upon the structure of CH. Two different values are reported by Field and Franklin (17). Using a value of ΔH_f(CH) = 103 kcal. they calculated D = 152 kcal., and for ΔH_f(CH) = 140 kcal., they calculated 226 kcal. The larger value is based on L_c = 171 kcal. Cottrell (13) computed a value of 230 kcal. using thermochemical data. 228 kcal. appears to be a better value, on the basis of present data.

VII. C_2

The lowest observed spectroscopic state of the C_2 molecule is $^1\Sigma_g{}^+$. Ballik and Ramsey (3) have recently observed this new band system in the near infrared while studying emission from a carbon furnace. This is about 1.7 kcal. below the previously accepted "ground state" (22). Recent mass-spectrometric studies of the sublimation of graphite by Inghram and coworkers (15) have established the dissociation energy of C_2 as 141 kcal., with an uncertainty of 2 or 3 kcal. From the same work an average value of $\Delta H^0_0(C_2)$ = 197 kcal. is reported for formation from graphite. The uncertainty appears to be about 3 kcal.

In earlier work, an interpretation of the band structure of C_2 led Mulliken (37) to a dissociation energy of about 127 kcal. and a ground state of $^3\pi_u$. The selective emission of the γ' = 6 Swan bands (excited $^3\pi_g \rightarrow$ ground $^3\pi_u$) of C_2 was tentatively explained by Herzberg (23) as caused by an inverse predissociation. This led him to a range for the dissociation energy of 78 to 83 kcal. Gaydon (18) criticized this interpretation and presented a series of possible D values between 92 kcal. and 161 kcal., obtained from Birge–Sponer extrapolations. The value finally accepted by Gaydon was about 113 kcal. He made reference to a study of the vibrational intensity distribution of the Swan bands by Tawde (58), leading to a value of 97 kcal., but he lacked confidence in the principle of the method. A study of the sublimation of graphite by Brewer and coworkers (8) led to a value of 113 kcal. This was later revised to 115.3 kcal. (18). However, there was some question as to the assignment of the correct C_2 ground state. Norrish, Porter, and Thrush (39) believed the actual ground state to be $^1\Sigma_g$, based on interpretation of the Mulliken and Swan bands of C_2. Cottrell (13) calculated a value of $D \simeq$ 143 kcal. based on an assumption of equilibrium conditions in the evaporation studies of Chupka and Inghram (12). In the light of the recent work cited (15), this assumption was probably correct. An extrapolation of bond energy versus bond distance by Glockler (20) yielded D = 135.4 kcal., assuming the ground state of C_2 to be $^3\pi_u$. If a heat of formation of C_2 equal to 233.1 kcal. (45) is used, a value of 107.7 kcal. can be computed. However, this value of the heat of formation is about 36 kcal. too high.

Comparison of the carbon–carbon bond dissociation energies in C_2 (141 kcal.), C_2H_2 (228 kcal.), and C_2H_4 (122 kcal.) makes it seem reasonable to picture the bond in C_2 as a double bond. However, there may be little, if any, hybridization in C_2. The bond may be formed by endwise overlap of $2p_x$ orbitals plus lateral overlap of $2p_y$ orbitals. The difference in carbon–carbon bond dissociation energies in the C_2 and C_2H_4 molecules then would represent principally the difference in endwise overlap energies of *p* orbitals as compared to sp^2 orbitals.

VIII. CONCLUDING REMARKS AND TABLE OF BEST VALUES

The best values of the various dissociation energies at 0°K. discussed in this review are summarized in table 1. For those more interested in values at 298°K., a rough correction can be made by adding 1 kcal. to each listed figure. It may be of interest to the reader to compare these with the bond energy values at 0°K.:

TABLE 1

Best values of dissociation energies

Reaction	ΔH^0_0	
	kcal./mole	
$CH_4 \rightarrow CH_3 + H$	101–102	
$CH_3 \rightarrow CH_2 + H$	87?	Sum must equal 210–211
$CH_2 \rightarrow CH + H$	123–124?	
$CH \rightarrow C + H$	80	
$C_2H_6 \rightarrow C_2H_5 + H$	97	Sum must equal 134
$C_2H_5 \rightarrow C_2H_4 + H$	37	
$C_2H_4 \rightarrow C_2H_3 + H$	104	Sum must equal 143
$C_2H_3 \rightarrow C_2H_2 + H$	39	
$C_2H_2 \rightarrow C_2H + H$	114?	Sum must equal 246
$C_2H \rightarrow C_2 + H$	132?	
$C_2H_6 \rightarrow 2CH_3$	83–85	
$C_2H_4 \rightarrow 2CH_2$	122?	
$C_2H_2 \rightarrow 2CH$	228	
$C_2 \rightarrow 2C$	141	
C(graphite) → C(gas)	169.6	

E(C—H) = 98.0 kcal.; E(C—C) in ethane = 77.3 kcal.; E(C=C) in ethylene = 139.1 kcal.; and E(C≡C) in acetylene = 192.1 kcal.

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