BOND DISSOCIATION ENERGIES

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ONE of the most interesting problems of chemistry is that of molecular constitution. We describe the structure of a molecule in terms of chemical bonds which link together its various constituents. The abstract and rather vague idea of the chemical bond became more precise when new parameters such as bond length, bond strength, bond dipole, and many others were introduced. It is the concept of bond strength with which we shall be concerned in this Review.

It is usual to describe a chemical bond as being strong or weak. Let us realise exactly what one means by this kind of description. We know that when separate atoms are linked into a molecule, *i.e.*, when chemical bonds are formed, the total energy of the system decreases. Using a quantum-mechanical interpretation of this process, we would say that the electrons which moved previously in atomic orbitals have been directed to molecular orbitals, and consequently the system has passed to a lower energy level—if a stable molecule is formed. The reverse process, the dissociation of a molecule into atoms, would of course require an expenditure of energy, and that required to dissociate a molecule into its constituent atoms is referred to as its heat of atomisation.

The numerical value of the heat of atomisation could be determined in principle by experiment provided one defines the electronic states of the atoms formed in the dissociation process. Usually the lowest, and therefore the most stable state of the atoms, is regarded as the reference state. In such a case we deal with the heat of atomisation referred to the atoms in their ground states. In some instances, however, other reference states are used. For example, in the thermochemistry of organic compounds some authors [1] consider the excited ^5S state of carbon to be more appropriate for reference than the ground state (*i.e.*, ^3P state). Recently, it has been suggested that hypothetical (spectroscopically unobservable) valency states of atoms be used as reference states.[2] However, it is not of great importance which particular state is chosen as long as it is clearly defined.* The choice will depend upon the type of problem involved.

There are many ways of bringing about the dissociation of a molecule into its constituent atoms. Of particular theoretical interest are those processes of dissociation which involve the breakdown of a molecule into two fragments by the rupture of a single chemical bond. This process may be repeated with the fragments formed, until the whole molecule has been ultimately broken down into its separate atoms.

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[1] Long and Norrish, *Proc. Roy. Soc.*, 1946, *A*, **187**, 337.

[2] Pauling, *Z. Naturforsch.*, 1948, **3***a*, 438; *Proc. Nat. Acad. Sci.*, 1949, **35**, 229.

* If the valency state is chosen for reference, then the heat of atomisation cannot be determined from experimental data alone.

Consideration of such a dissociation process leads us to the concept of bond dissociation energy. We define bond dissociation energy as the endothermicity of a process in which a molecule $R_1{\cdot}R_2$ dissociates into fragments R_1 and R_2 produced by the rupture of one chemical bond only, namely, the R_1–R_2 bond. For the sake of accuracy we should add that the above process should take place in the gas phase at 0° K. Denoting bond dissociation energy by a symbol $D(R_1–R_2)$, we can write the following thermochemical equation :

$$R_1{\cdot}R_2 \longrightarrow R_1 + R_2 - D(R_1–R_2) \text{ kcals./mole}$$

The above dissociation process is a phenomenon which is physically possible, and therefore, in principle, observable. The final electronic state of the fragments formed is determined by the condition that the process shall be carried out adiabatically.* The endothermicity of this process, *i.e.*, the bond dissociation energy, is a measurable quantity, and we shall describe later various experimental methods by which one can estimate it.

It is usual to identify the bond strength with bond dissociation energy. We are therefore in a position to give an exact meaning to the statement that a particular bond is either weak or strong. A bond is considered to be strong if its dissociation energy is high ; it is regarded as weak if its dissociation energy is low.

The bond dissociation energy depends not only on the nature of the atoms which are linked together, but also on the nature of its molecular environment. One cannot speak about the C–H bond dissociation energy in general ; it is necessary to be more specific. For example, the C–H bond dissociation energy is different in methane, *i.e.*, $D(CH_3–H)$, from what it is in triphenylmethane, *i.e.*, $D(Ph_3C–H)$. As a further example let us consider the following series of dissociation processes :

$$\begin{aligned} CH_4 &\longrightarrow CH_3 + H - D(CH_3–H) \text{ kcals./mole} \\ CH_3 &\longrightarrow CH_2 + H - D(CH_2–H) \text{ kcals./mole} \\ CH_2 &\longrightarrow CH + H - D(CH–H) \text{ kcals./mole} \\ CH &\longrightarrow C + H - D(C–H) \text{ kcals./mole} \end{aligned}$$

The molecular environment is, of course, different in the molecule of methane from that in the methyl radical or methylene radical. In consequence, we do not expect $D(CH_3–H)$ to be equal to $D(CH_2–H)$ or $D(C–H)$. Indeed, we have evidence that $D(CH_3–H)$ is equal to 101 kcals./mole, while $D(C–H)$ is estimated at 80 kcals./mole. The sum of the four dissociation energies quoted above, *i.e.*,

$$D(CH_3–H) + D(CH_2–H) + D(CH–H) + D(C–H)$$

must however be equal to the heat of atomisation of the molecule of methane with respect to its atoms in their ground states.

It might appear that another quantity which is constant for all identical bonds should be introduced in addition to the concept of bond dissociation

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* An adiabatic change is one in which there is a continuous equilibrium between electrons and nuclei, there being no abrupt electronic rearrangement involving a jump from one electronic level to another.

energy. Since the four C–H bonds in methane are identical, some kind of "bond energy" should exist which would be the same for *all four* C–H bonds. Let us realise, first of all, that the C–H bond dissociation energy in methane is identical for *all four* C–H bonds, *i.e.*, no matter which of them is chosen in the dissociation process $CH_4 \longrightarrow CH_3 + H_2$ *the same* amount of energy has to be spent for its rupture, namely, D(CH_3–H). Similarly D(CH_2–H) is the same for all three C–H bonds in the methyl radical although it need not be equal to D(CH_3–H). The symbols D(CH_3–H) and D(CH_2–H) refer to two different species and that is why they might differ in their magnitude. The main thing which matters, however, is the fact that the value of the C–H bond dissociation energy in methane need not be equal to a quarter of the heat of atomisation of this molecule. Suppose, on the other hand, that the total amount of energy contained in the molecule of methane (*i.e.*, its heat of atomisation) were divided equally amongst the four C–H bonds. One could consider this quantity as the amount of energy invested in each C–H bond in an *undissociated* molecule of methane, and the concept defined in such a way would be called the average bond energy. Its numerical value, of course, depends on the choice of the reference states. This point has been the subject of much discussion recently.

Instead of discussing the pros and cons of the various reference states chosen, let us consider what type of dissociation process is likely to require an amount of energy numerically equal to the average bond energy. One might argue that the process $CH_4 \longrightarrow CH_3 + H$ does not lead to the average C–H bond energy since its endothermicity involves the changes in energy due to the rearrangement of the CH_3 group in methane into a methyl radical. Such an energy change was named by Norrish the reorganisation energy.[1] One would expect, therefore, that the "freezing" of the CH_3 group during the dissociation process should lead to the average bond energy. The average C–H bond energy in the molecule of methane would be measured by the endothermicity of a hypothetical dissociation process in which one C–H bond is ruptured, the products of reaction being a hydrogen atom and a "frozen" methyl group (which could be described as a distorted methyl radical). The whole process is only a fiction; it can never be observed, and therefore its endothermicity can never be measured by any experimental method.

In addition to all these drawbacks, the "bond energy" as defined above does not fulfil the required conditions, since it is *not equal* to a quarter of the heat of atomisation. This condition would be fulfilled only if equal amounts of energy were required for the successive fission of all four C–H bonds in the "frozen" molecule of methane. That is not the case, however. Each hydrogen atom in the molecule of methane interacts not only with the carbon atom but also with the other hydrogen atoms. The chemical bond, like many extremely useful ideas, is based on an over-simplification of the relationships existing in a molecule. A molecule is in reality one indivisible unit in which each component interacts with every other fragment. The separation of one fragment influences, therefore, all the remaining ones. Returning to our example, we have to realise that the removal of the first hydrogen atom from the molecule of methane involves an interaction between this atom and the carbon atom, and in addition a weak interaction with the other three hydrogen atoms. It follows from the above example that the removal of the next hydrogen atom would involve an interaction with two hydrogen atoms only, and so on. Hence we realise that even the " freezing " of the molecule does not ensure that equal amounts of energy would be required for removing successive hydrogen atoms. So one has to abandon the above definition of the average bond energy and look for a better one.

The problem of finding a suitable dissociation process which will lead to the average bond energy was taken up by Szwarc and M. G. Evans.[3] These workers concluded that the average bond energy can be defined as the amount of work required for the rupture of the bond in question in a process in which all the other bonds are stretched independently and simultaneously with the above bond, and thus the molecule swells infinitely without losing its original shape. In the light of this definition the sum of average bond energies is equal to the heat of atomisation of the molecule, and the average bond energies corresponding to identical bonds are equal. It is a corollary of these two properties that in molecules of the type AX_n (*e.g.*, H_2O, NH_3, CH_4) which contain n identical bonds and no others, the average bond energy is equal to $1/n$ of the heat of atomisation of the molecule.

The determination of the average bond energy as defined above requires a knowledge of the potential energy of the molecule as a function of all bond lengths. Our present knowledge of the potential energy of most molecules is far too scanty, so that the computation of average bond energies is not possible yet (molecules of the type AX_n being an obvious exception). There is no other experimental method which would make it possible to determine average bond energies. Hence, the only quantity which can be measured, and about which we may expect new information in the future, is the bond dissociation energy. We proceed now to a discussion of various experimental methods for the determination of bond dissociation energies and of the relationships between these and other observable entities.

A direct estimation of the bond dissociation energy is possible by measuring the amount of energy involved in either the bond-breaking or the bond-forming processes. All the direct methods for estimating bond dissociation energies can, therefore, be classified into two groups : (A) methods in which the process of bond formation is investigated ; (B) methods in which the process of bond rupture is investigated.

It is by no means easy, however, to measure the energy liberated in the bond-formation process. Under ordinary experimental conditions this energy is not liberated in the form of radiation, thus rendering photochemical methods useless ; neither is it liberated in form convertible into electric energy. The only feasible method, therefore, is to measure the amount of heat liberated in the process of recombination of radicals or atoms. This phenomenon has been known for some time and utilised for various purposes ; *e.g.*, the heat liberated in the process of recombination of

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[3] *J. Chem. Physics*, 1950, **18**, 618.

hydrogen atoms has been used for welding purposes (Langmuir torch) and for measuring the concentration of atoms in a gas stream. This effect was used by Bichowsky and Copeland [4] for the estimation of the heat of recombination of hydrogen atoms to hydrogen molecules. The atoms were produced by electric discharge, their concentration was estimated by the effusion method, and the recombination took place on the surface of a calorimeter which was covered by palladium black. The results were satisfactory and D(H–H) was estimated at 105 ± 3·5 kcals./mole. Similar experiments were repeated with oxygen atoms by Copeland [5] and by Rodebush and Troxel.[6] It seems, however, that the method is less reliable in this case. Copeland's preliminary report suggested a very high value for D(O–O), namely, 165 ± 5 kcals./mole. The value finally recommended by Copeland and by Rodebush and Troxel of about 131 kcals./mole is still too high (the value accepted at present is 117 kcals./mole) and seems to indicate some inherent defect of the method. The possibility of the participation of metastable oxygen atoms in the recombination was not definitely refuted.

It is evident from the above that the difficulties associated with the first method are almost unsurmountable, and one turns therefore to techniques in which the process of bond fission is investigated. These methods may be divided into three groups according to the form in which the energy is supplied to the molecule dissociated.

(*a*) *Photochemical methods.* The energy is supplied in the form of radiation. Under this heading we include methods based on investigation of absorption spectra, predissociation phenomena, photo-decompositions, photosensitised decompositions, etc.

(*b*) *Electron-impact methods.* In this type of investigation the energy is supplied in the form of the kinetic energy of a beam of electrons.

(*c*) *Thermal or pyrolytic methods.* Here the energy is supplied in the form of thermal energy. Pyrolytic methods may be subdivided into two classes: equilibrium methods and kinetic methods. The former methods are used for investigations of the equilibrium between the undecomposed molecules and the atoms or radicals produced by the rupture of the bond in question. In the kinetic method one measures the rate of the unimolecular dissociation process in which one bond is ruptured and the molecule splits into two radicals (or atoms).

Photochemical and Spectroscopic Methods

The evaluation of bond dissociation energies from spectroscopic data can be accomplished for simple molecules only, since the spectra of more complex molecules are too intricate for a detailed interpretation. In consequence, we present here only a brief review of methods used for determining dissociation energies of diatomic molecules. A more comprehensive discussion

[4] *J. Amer. Chem. Soc.*, 1928, **50**, 1315.
[5] *Ibid.*, 1930, **52**, 2580; *Phys. Review*, 1930, **36**, 1221.
[6] *J. Amer. Chem. Soc.*, 1930, **52**, 3467.

of these topics can be found in monographs such as those of Herzberg,[7] Sponer,[8] and Gaydon.[9]

Absorption spectra in the visible and ultra-violet region are due to electronic excitation of molecules. An absorption of a suitable quantum of light raises a molecule from its ground state to a higher electronic state. A series of vibrational energy levels corresponds to each electronic state and, therefore, the observed absorption spectrum is usually composed of a series of lines. The relationship between the various vibrational levels of a molecule and the observed lines in the absorption spectrum is shown diagrammatically in Fig. 1. The potential energy of the molecule AB in its ground state is represented by the lower curve. The asymptote of this curve corresponds to the energy level of separated, non-excited atoms A and B which are the products of the adiabatic dissociation of the unexcited molecule AB. The upper curve represents the potential energy of the electronically excited molecule AB*, its asymptote marking the energy level of the separated atoms A and B* (one of which, say B, is in an electronically higher state). The horizontal lines across each potential energy curve represent the various vibrational levels of the ground state and the excited state respectively.

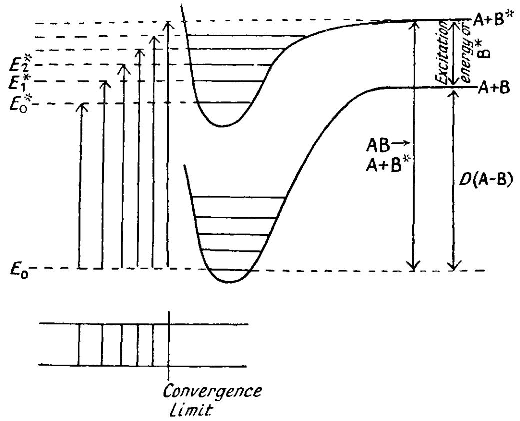

FIG. 1

At room temperature nearly all molecules are in the zero vibrational energy level, E_0, of the ground state. On absorption, these molecules are raised to the corresponding vibrational energy levels $E_n{}^*$ of the higher state, a process shown by the arrows in Fig. 1. The schematic representation of the resulting absorption spectrum is given in the lower part of Fig. 1. The convergence limit of such a series of absorption lines gives the dissociation energy of the molecule AB into a *normal* atom A and an *excited* atom B*.

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[7] " Molecule Spectra and Molecule Structure : Diatomic Molecules ", New York (1939).

[8] " Moleculspektren ", Springer, 1936.

[9] " Dissociation Energies and Spectra of Diatomic Molecules ", Chapman & Hall (1948).

The dissociation energy of the molecule AB into *normal* atoms A and B can be obtained, therefore, from the above dissociation energy by subtracting from it the excitation energy of the products, *i.e.*, the energy required to raise the normal atom B into the excited state B*.

The determination of the convergence limit becomes accurate if a sufficient number of absorption lines can be observed. The results are particularly satisfactory when a continuous absorption, resulting from a direct photo-dissociation process $AB \rightarrow A + B^*$, follows the series of vibrational lines. Often, however, only a small number of lines is observed, and the convergence limit is determined with the help of some extrapolation method. Various extrapolation methods have been devised (see, *e.g.*, Gaydon [9]), but unfortunately the results of calculations depend on the particular extrapolation method used for the computation.

The identification of the dissociation products sometimes presents considerable difficulties. A direct identification is possible when atomic fluorescence can be observed. This phenomenon requires, of course, a photo-dissociation of the molecule which takes place in the continuous absorption region following the respective series of absorption bands. Excited atoms produced in the photo-dissociation process return to their ground state with emission of the fluorescence, which identifies their state of excitation. It is regrettable that this method of identification of products can be applied in only a few cases.

Usually the identification of the products is carried out by applying some correlation rules, *e.g.*, the Wigner–Witmer correlation rule.[7] The properties of absorption bands (including their rotational structure), the selection rules for absorption, and other spectroscopic criteria make it possible to determine the electronic excitation state of the molecule. This, in conjunction with correlation rules, limits the number of permissible excitation states of products. A further elimination is achieved by applying the obvious condition that the excitation energy of the products cannot be greater than the observed dissociation energy. Sometimes this elimination process may leave only one state of excitation compatible with all requirements, and thus the products of dissociation are determined.

The uncertainties due to the difficulties of extrapolation and identification of products often lead to two (or more) possible interpretations of the same spectrum, and consequently to two (or more) values for the respective bond dissociation energy. For example, the spectra of carbon monoxide and nitrogen are differently interpreted by various schools of spectroscopists, each of these suggesting different values for D(C–O) and for D(N–N). It is remarkable that a particular value for D(C–O) or D(N–N) resulting from a particular interpretation is given with high accuracy, although the differences between each set of values are very great.

It is important to realise therefore that the spectroscopic method provides also a means of cross-checking the various values derived for a particular dissociation energy. For example, let us consider a series of absorption spectra resulting from the excitations of the same molecule to different electronic states. Each of the observed band systems leads to a dissociation energy corresponding to the formation of the respective excitation products. The values for these various dissociation energies are, of course, inter-related with each other, since the difference between any two values must be equal to the difference between the excitation energies of the respective products. As the latter values are obtained from atomic spectra, it is possible to examine the consistency of any derived set of dissociation energies.

Further information about dissociation energies can be obtained from studies of continuous absorption spectra and predissociation phenomena. The continuous absorption spectra result from the process of photodissociation in which the molecule is raised either to a high level of a stable excited state (case 1), or to an unstable repulsive state (case 2).

In case 1 we have to distinguish between two possibilities which are illustrated in Figs. 2*a* and 2*b*. Fig. 2*a* represents the appearance of the continuous absorption spectrum following a series of absorption bands. In this instance the long-wave limit of the continuous absorption is identical with the convergence limit of the absorption bands, and it represents the dissociation energy of the relevant photochemical process. This is no longer true, however, in the case illustrated by Fig. 2*b*. Here the long-wave limit of the continuous absorption spectrum is not sharp, and it corresponds to a value which is higher (sometimes considerably higher) than the relevant dissociation energy. Studies of these types of continuous absorption spectra lead, therefore, only to the *upper limits* for the relevant dissociation energies.

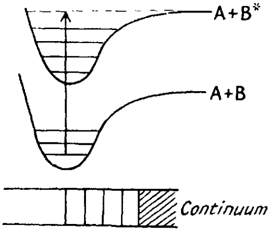

FIG. 2*a*

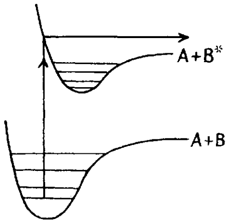

FIG. 2*b*

Case 2 is illustrated by similar diagrams in Figs. 3*a* and 3*b*. The possibility illustrated in Fig. 3*a* corresponds to a flat repulsion curve representing the unstable, repulsive electronic state of the molecule. The continuous absorption spectrum resulting from such a transition is narrow and rather sharp, resembling a narrow absorption band, or even a line. The long-wave limit of such a spectrum gives the required dissociation energy with sufficient accuracy. It is obvious, however, that for a steep repulsion curve, such as is represented in Fig. 3*b*, the resulting continuous absorption spectrum is broad, and its long-wave limit corresponds to a value which is above the required dissociation energy. In this case we can only estimate the upper limit for the dissociation energy.

The phenomenon of predissociation is related to some extent to the processes described in the preceding paragraphs. It is not unusual to ascribe two electronic states to the same energy level, which is then referred to as being degenerate. Sometimes one of these states corresponds to a stable molecule, while the other represents an unstable system tending to a dissociation. Not every possible electronic state can be reached from the ground state by a process of light absorption. Some transitions are forbidden, and the respective absorption lines do not appear in the spectrum. There are cases, therefore, when a transition from the ground state to some *stable* excited state is permissible, whereas a transition to some *unstable* excited state is forbidden, in spite of the fact that both states belong to the same energy level. In this instance, only the line which is characteristic for the transition to the stable discrete state appears in the relevant absorption spectrum; and the continuous absorption region which would be expected for the transition to the unstable state is absent. If, however, a radiationless transition process is permissible in which the molecule passes from the stable electronic state to an unstable electronic state, then a phenomenon called predissociation may be observed. This phenomenon is described therefore by a transition to a stable electronic state due to light absorption, followed by a radiationless transition to an unstable electronic state, and eventually by a dissociation of the molecule.

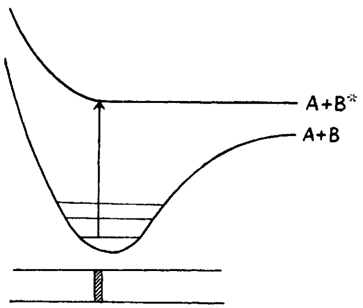

FIG. 3*a*

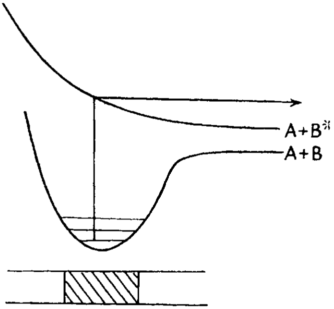

FIG. 3*b*

Predissociation manifests itself by a broadening of the absorption line representing the first transition, by the disappearance of the fine rotational structure of this line, and by a weakening, or even disappearance, of this line in the emission spectrum. The weakening of the respective line in the emission spectra makes it possible to detect this phenomenon even when the probability of the radiationless transition is very small. The energy level in which predissociation takes place gives us the value of the energy of dissociation to the products formed in the predissociation process. The calculation of the energy of dissociation to the normal atoms requires the determination of the state of excitation of the products, and this point has been discussed previously.

In conclusion, it must be stressed that, although very often extremely accurate results for the dissociation energies of diatomic molecules (or radicals) are yielded by spectroscopic methods, yet it is not always possible to give an unique interpretation for each spectrum. In some instances several widely different values have been suggested for the dissociation energy of the same molecule. For example, such an ambiguity in the interpretation of the spectra of carbon monoxide and nitrogen prevents us from getting a final estimate of the values for $D(\text{C–O})$ and $D(\text{N–N})$, and this is most unfortunate since these values are of paramount importance in thermochemistry.

Much valuable information about bond dissociation energies has been provided by the study of photochemical processes. Such information may be obtained from investigations of the products of photolysis and of the kinetics of the overall change without making any reference to the character of the absorption spectrum. If the absorption of quanta of light endowed with an energy $h\nu$ (corresponding to Q kcals./mole) causes the splitting of a molecule R_1R_2 into the fragments R_1R_2 then it follows that

$$D(R_1\text{–}R_2) \leqslant Q \text{ kcals./mole}$$

We need to prove, therefore, that the irradiation of the molecule R_1R_2 with light of frequency ν produces either of the radicals R_1 or R_2 to justify the above inequality. The methods of deduction applied to such problems are illustrated in the following two examples.

(i) Photolysis of mixtures of acetone and iodine gives methyl iodide as one of the products. This result implies that the photolysis of acetone proceeds according to the equation

$$CH_3{\cdot}CO{\cdot}CH_3 + h\nu \longrightarrow CH_3 + CO{\cdot}CH_3$$

and that the methyl radicals, formed in this initial process, react with iodine vapour to give methyl iodide

$$CH_3 + I_2 \longrightarrow CH_3I + I$$

Hence, the formation of methyl iodide in the above reaction can be considered as evidence for the formation of methyl radicals.

(ii) The photolysis of acetaldehyde produces methane and carbon monoxide in the proportion required by the stoicheiometric equation $CH_3{\cdot}CHO = CH_4 + CO$. It has been shown that the number of decomposed acetaldehyde molecules is much greater than the number of absorbed photons ; *i.e.*, the quantum yield for this photolysis is high, and this indicates, of course, a chain process, propagation of which requires the formation of radicals or atoms. The mechanism of a chain reaction accounting for the observed stoicheiometry must be of the following type

$$\begin{array}{rcll}
CH_3{\cdot}CHO + h\nu & \longrightarrow & CH_3 + CHO & \text{. . . . . initiation} \\
CH_3 + CH_3{\cdot}CHO & \longrightarrow & CH_4 + CH_3{\cdot}CO & \rbrace \text{ . . . chain propagation} \\
CH_3{\cdot}CO & \longrightarrow & CH_3 + CO &
\end{array}$$

and finally the chain is broken by some termination step. Knowing that the light of frequency ν (corresponding to Q kcals./mole) is effective in initiating the chain decomposition of acetaldehyde, we deduce that

$$D(CH_3\text{–}CHO) \leqslant Q \text{ kcals./mole}$$

The initiation process of a photodissociation is not always as simple as is implied in the equation

$$R_1{\cdot}R_2 + h\nu \longrightarrow R_1 + R_2$$

We can never observe a process in which the energy of the absorbed quantum of light is used entirely for the vibrational excitation of the molecule, resulting eventually in the rupture of one of the bonds. Such a process would require a transition from some low vibrational energy level to a very high vibrational level, without changing the electronic state of the molecule. These transitions, however, are forbidden by the selection rule which demands the change in the vibrational quantum number to be only ± 1. Hence, the absorption of a visible or ultra-violet light must lead to an electronic excitation of the molecule

$$R_1{\cdot}R_2 + h\nu \longrightarrow R_1{\cdot}R_2{}^*$$

and the eventual dissociation may take place by one of the two distinct processes. The electronically excited molecule is either unstable and dissociates within a short time after absorbing the quantum of light, or this molecule undergoes a radiation-less transition to a lower electronic state in consequence of a collision with some other molecule. The first alternative has already been discussed. It has to be stressed again that in this case the molecule dissociates into excited products, and for calculating the bond dissociation energy the excitation energy of the products should be deducted from the total amount of the absorbed radiant energy. In the case of radiation-less transition induced by a collision, the electronically excited molecule may return to the ground state, the electronic energy being transformed into vibrational and rotational energy. The " hot " molecule formed in this way may decompose into " normal " products, and the energy required for such a dissociation process need not be greater than the bond dissociation energy.

Applications of photochemical methods are limited owing to the obvious reason that a molecule could be photodissociated only by this light which is absorbed by the relevant species. Unfortunately, the energy corresponding to the absorption region is often higher than the dissociation energy of the relevant bonds. The result of such a study is an upper limit for the respective bond dissociation energy and is not of great value for the precise determination of the bond dissociation energy.

For the molecules which do not absorb light in the relevant region, the appropriate amounts of radiant energy may be supplied by photosensitisation. In the photosensitised decomposition the light is absorbed by some suitable species (molecules or atoms) which are not decomposed by the absorbed radiation. These excited species transfer the absorbed radiant energy to the molecules which eventually decompose, the transfer of energy occurring as a result of collision between these two species. For example

$$Hg + h\nu \longrightarrow Hg^*$$
$$Hg^* + H_2 \longrightarrow Hg + 2H$$

The great advantage of the method lies in the fact that a well-defined amount of energy is supplied to the molecule which is dissociating. Unfortunately, there are two drawbacks. There is a limited number of sensitising species which can be used in these studies and which transfer the required amounts of energy. Most of the work has been done with excited atoms of mercury, zinc, and cadmium. Consequently, we cannot vary in a satisfactory way the amount of transferred energy. Additional difficulty is caused by possible exothermic reactions which may take place between the colliding species, *e.g.*

$$\mathrm{Cd}^* + \mathrm{RH} \longrightarrow \mathrm{R} + \mathrm{CdH}$$

The energy liberated in the formation of CdH may be utilised in the dissociation process. Consequently, the amount of available energy is often greater than desired, making the upper limit for the relevant bond dissociation energy much too high.

A full discussion of photodissociation and photosensitised dissociation processes can be found in various publications by Steacie [10] and by West.[10a]

The Electron-impact Method *

This method makes use of the phenomena which occur during collisions between a beam of sufficiently fast electrons and molecules or radicals. Such collisions may cause a variety of effects, two of which are of great interest in connection with the problem of bond dissociation energies: (1) A collision between an electron and a molecule or radical ionises the latter and produces a positive ion, *e.g.*, $CH_3 + e \longrightarrow CH_3^+ + 2e$. (2) A collision is sufficiently violent to break a chemical bond in a molecule and to produce two fragments, one of which is ionised, *e.g.*, $CH_4 + e \longrightarrow CH_3^+ + H + 2e$. The investigation of such reactions consists in observing the appearance of the relevant ions, which are detected by mass-spectrographic techniques.

The description of various techniques applied in mass-spectrographic studies is beyond the scope of this Review, but its essential features must be outlined. The gas under investigation is allowed to leak into an ionisation chamber connected to a pumping system, thereby being kept at a constant, small pressure. Electrons, generated by a hot filament, are accelerated by a known potential—which can be varied during the experiment—and subsequently they are introduced into the ionisation chamber. The collision between the electrons and the molecules of the gas investigated may yield various ions. The latter are directed by electric and magnetic fields to a detector, the arrangement being such that only ions having a chosen charge/mass ratio can reach the detector. The above set-up makes it possible to measure the relative amounts of ions (of a chosen type) produced by the collision with electrons as a function of the kinetic energy of these electrons.

It is obvious that electrons which are able to cause some particular ionisation process must possess a kinetic energy which is greater than, or at least equal to, the endothermicity of this process. For example, if an electron is able to ionise a methyl radical, $CH_3 + e \longrightarrow CH_3^+ + 2e$, its

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[10] "Atomic and Free Radical Reactions", Reinhold Publishing Co., New York (1946); *Research*, 1948, **1**, 541; *Ann. New York Acad. Sci.*, 1941, **41**, 187.

[10a] *Ibid.*, p. 203.

* For detailed discussion of the subject see: [11] Stevenson, *J. Chem. Physics*, 1942, **10**, 291; [12] Hagstrum, *Phys. Review*, 1947, **72**, 947; Hagstrum and Tate, *ibid.*, 1941, **59**, 354.

kinetic energy (measured in volts) must be at least equal to the ionisation potential of this radical. Therefore, CH_3^+ ions appear in the detector only when the potential which accelerates the ionising electrons exceeds some critical value, which thus measures the ionisation potential of methyl radicals.

When the ionisation chamber is fed with methyl radicals, the potential at which CH_3^+ appears (*i.e.*, the critical potential required for the formation of CH_3^+) measures the endothermicity Q_1 of the ionisation process $CH_3 \rightarrow CH_3^+ + e - Q_1$ kcals./mole. However, if the ionisation chamber is fed with methane, the potential at which CH_3^+ appears is higher, and it measures the endothermicity of the process $CH_4 \rightarrow CH_3^+ + H + e - Q_2$ kcals./mole, which accounts for the formation of the CH_3^+ ion from the molecule of methane. It is easy to verify that the difference $Q_2 - Q_1$ is equal to the C–H bond dissociation energy in the molecule of methane.

Generalising the above example, we deduce that the determination of $D(R_1\text{–}R_2)$ by the electron-impact method requires the estimation of the potential at which the R_1^+ ion is formed from the molecule $R_1 \cdot R_2$, in addition to the evaluation of the ionisation potential of the radical R_1. The latter can be determined either by the electron-impact method (feeding the ionisation chamber with R_1 radicals produced independently, say by pyrolysis), or by a spectroscopic method.*

There is, however, another way of determining bond dissociation energies by mass-spectrographic methods which does not require the estimation of the ionisation potential of the relevant radical. The following example illustrates this method. One measures the appearance potentials of CH_3^+ ions produced in the mass-spectrograph when methane and ethane severally are used for the feeding of the ionisation chamber. The observed ionisation potentials represent, therefore, the endothermicities Q_2 and Q_3 of the two processes

$$CH_4 \rightarrow CH_3^+ + H + e - Q_2 \text{ kcals./mole}$$
$$C_2H_6 \rightarrow CH_3^+ + CH_3 + e - Q_3 \text{ kcals./mole}$$

Subtracting the first equation from the second, one obtains

$$\Delta H_f(C_2H_6) - \Delta H_f(CH_4) = \Delta H_f(CH_3) - \Delta H_f(H) + Q_2 - Q_3$$

On the other hand

$$D(CH_3\text{–}H) = \Delta H_f(CH_3) + \Delta H_f(H) - \Delta H_f(CH_4)$$

and

$$D(H\text{–}H) = 2\Delta H_f(H)$$

Solving this set of three equations, one deduces that

$$D(CH_3\text{–}H) = \Delta H_f(C_2H_6) - 2\Delta H_f(CH_4) + D(H\text{–}H) + Q_3 - Q_2$$

The generalisation of this method is obvious. It must be emphasised, however, that this variant of the electron-impact method requires a knowledge of some bond dissociation energies for estimating the other, *e.g.*, $D(H\text{–}H)$ was required for estimating $D(CH_3\text{–}H)$. On the other hand, one of the advantages of this method is that it provides cross-checks for the results.

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* *E.g.*, if R_1 is an atom, this is the most exact and reliable method for determining its ionisation potential.

For example, one can cross-check the value for $D(CH_3–H)$ obtained by measuring the appearance potentials of the CH_3^+ ions produced from methane and ethane, or those of $C_3H_7^+$ ions produced from propane and *iso*butane. Here we measure the endothermicities of reactions

$$C_3H_8 \longrightarrow C_3H_7^+ + H + e - Q_4 \text{ kcals./mole}$$

and

$$iso\text{-}C_4H_{10} \longrightarrow C_3H_7^+ + CH_3 + e - Q_5 \text{ kcals./mole}$$

and a treatment, analogous to the previous one, leads to the result

$$D(CH_3\text{–}H) = \Delta H_f(iso\text{-}C_4H_{10}) - \Delta H_f(C_3H_8) - \Delta H_f(CH_4) + D(H\text{–}H) + Q_5 - Q_4$$

The estimation of the appearance potentials is not as simple as was assumed in the previous paragraphs. Let us consider again the process $CH_4 + e \longrightarrow CH_3^+ + H + 2e$, which takes place in two steps, namely, $CH_4 + e \longrightarrow CH_4^+ + 2e$ and $CH_4^+ \longrightarrow CH_3^+ + H$, and is represented schematically in Fig. 4. The lower curve represents the potential energy of the CH_4 molecule, and the upper curve that of the CH_4^+ ion. Since the ionisation process is much faster than the vibrations of nuclei, the transition takes place in the vertical direction (Frank–Condon principle). Hence, what is observed in the mass-spectrograph is the *vertical* ionisation potential which might be higher than the endothermicity of the relevant process, the excess of energy appearing, of course, as kinetic energy of the particles produced.*

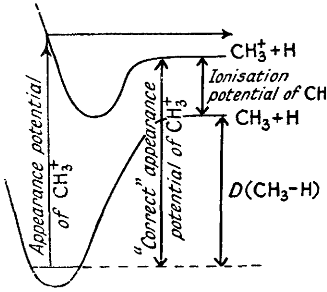

FIG. 4

A further difficulty encountered in the electron-impact method is due to the fact that the " measured " appearance potential depends on the particular mass-spectrograph used in the investigation. One has, therefore, to calibrate the apparatus by measuring some known ionisation potential, *e.g.*, $Ne \longrightarrow Ne^+ + e$. It is doubtful, however, if the correction for standardisation remains unaltered for various types of ionisation processes.

The Pyrolytic Method †

(A) Equilibrium Method.—The determination of bond dissociation energy by the equilibrium method is based on measurement of the equilibrium constants of the gaseous reaction $R_1 \cdot R_2 \rightleftharpoons R_1 + R_2$, where R_1 and R_2 denote the radicals or atoms produced by rupture of the bond in question. These equilibrium constants, determined at various temperatures, enable us to compute the heat of dissociation by applying the van't Hoff isochore, and recalculation of the heat of dissociation to zero pressure and 0° K. yields, by definition, the bond dissociation energy.

The equilibrium method is particularly suitable for estimating the bond

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* See refs. 11 and 12 for further discussion of these points.

† For detailed discussion of the subject see ref. 13.

[13] Szwarc, *Chem. Reviews*, 1950, **47**, 75.

dissociation energies of diatomic molecules of the type X_2. In this case the dissociation process produces the atoms X, and the latter can only recombine into the original molecules X_2. Such a system, therefore, is very simple and cannot be disturbed by any side reactions. However, in the case of molecules of the type R_2, R being a radical, the situation is much more complex owing to the occurrence of various secondary processes such as : (*a*) Reactions between radicals R and molecules R_2, which would lead to products different from R·R ; *e.g.*, in the hypothetical system $CH_3{\cdot}CH_3 \rightleftharpoons 2CH_3$ the CH_3 radicals could be removed by the reaction $CH_3 + CH_3{\cdot}CH_3 \rightarrow CH_4 + CH_2{\cdot}CH_3$. (*b*) Reactions between two radicals R which would lead to products different from R·R ; *e.g.*, in the hypothetical system $C_2H_5{\cdot}C_2H_5 \rightleftharpoons 2C_2H_5$ the radicals C_2H_5 might be removed by a disproportionation $2C_2H_5 \rightarrow C_2H_4 + C_2H_6$. (*c*) Decomposition of radicals R into simpler fragments ; *e.g.*, in the hypothetical system $C_2H_5{\cdot}C_2H_5 \rightleftharpoons 2C_2H_5$, the radicals might decompose according to the equation $C_2H_5 \rightarrow C_2H_4 + H$.

All the side reactions discussed above become more likely at higher temperatures and during longer reaction times, and their participation in the overall process limits the applicability of the equilibrium method. Hence, this method is particularly suitable for dealing with molecules R_2, for which the R–R bond is weak, and the R radical is inert with respect to R_2 and is thermally very stable, *e.g.*, $N_2O_4 \rightleftharpoons 2NO_2$; $Ph_3C{\cdot}CPh_3 \rightleftharpoons 2Ph_3C$.

The most common static method is based on measuring the change of pressure due to the dissociation. In such determinations a known amount of a compound of the type R·R is introduced into a reaction vessel of constant volume and heated to a suitable temperature for the time required. After attainment of equilibrium the final pressure is determined. This method yields the average molecular weight, which in conjunction with the known molecular weight of the undissociated compound R·R enables one to deduce the degree of dissociation α. The equilibrium constant K_e is given by the formula $K_e = P\alpha^2/(1 - \alpha)$, P being the pressure in the system. In order to achieve sufficient accuracy in measuring the pressure increments, these must attain some considerable fraction of the total pressure ; *i.e.*, it is necessary to choose a temperature range over which the degree of dissociation is sufficiently great. The investigation of the equilibrium between I_2 molecules and I atoms is the classical example of the application of the static method.

In order to minimise the occurrence of irreversible processes, it is desirable to reduce the time of heating as much as possible (see above). The application of the flow technique is particularly advantageous in this respect. In this technique the compound investigated passes through a heated reaction vessel, and the " time of contact " (*i.e.*, the time during which the compound investigated is heated) may be varied by adjustment of the rate of flow. The time of contact must be sufficiently long to enable the system under investigation to attain complete equilibrium ; however, this restriction is not a serious one since the equilibrium state is attained very rapidly. Consequently, a stationary state is maintained in the reaction vessel over any required period of time, during which the determination of the relevant concentrations can be accomplished. The normal procedure is to determine the concentration of the radicals (or atoms) produced by the dissociation process by some photometric method. The change of the radical concentration with the temperature makes it possible to determine the heat of dissociation and hence the bond dissociation energy. The method may be illustrated by two examples, the equilibria $(CN)_2 \rightleftharpoons 2CN$ and $2H_2O + O_2 \rightleftharpoons 4OH$.

(B) The Kinetic Method.—In order to estimate the bond dissociation energy by a kinetic method, one must determine the activation energy corresponding to the *unimolecular decomposition* of the molecule into two fragments, R_1 and R_2, produced by the rupture of the bond in question. It is very probable that recombination of the fragments formed in the dissociation process does not require any activation energy, and therefore it is plausible to assume that the activation energy of the dissociation process is equal to the heat of dissociation, *i.e.*, to the bond dissociation energy. It is found that the values of bond dissociation energies obtained by the kinetic method and based on the assumption of zero activation energy for the recombination process are self-consistent and in substantial agreement with results obtained from other direct determinations or from thermochemical data. This provides a valuable justification of the assumption of zero activation energy for the recombination process, and strengthens our confidence in the reliability of the kinetic method. If the activation of the combination process had a finite value, then the value of the bond dissociation energy obtained by the kinetic method would be too high. In such a case it would represent only an upper limit for the "true" dissociation energy.

The required activation energy can be computed in the usual way from the temperature coefficient of the unimolecular dissociation rate constant. Although no absolute values of the rate constants are required for the computation of the temperature coefficient, it is nevertheless essential to obtain a very high degree of accuracy in estimating relative rate constants. The following example illustrates this point. The rate constants of a unimolecular dissociation were determined at two temperatures, T_1 and T_2, for which $1/T_1 - 1/T_2 = 10^{-4}$. This corresponds to a reasonable temperature range of about 50° if the experiments are conducted in the vicinity of 500° K., and to a range of about 100° for those in the region of 1000° K. Let us assume that both rate constants are uncertain by about 20% each, then the maximum experimental error of the computed activation energy is :

$$\Delta E = 2 \times 2{\cdot}3 \times \log(1{\cdot}2/0{\cdot}8)/(10^{-4} \times 1000) = 8{\cdot}1 \text{ kcals./mole}$$

To improve the accuracy of the computed activation energy it is necessary either to extend the temperature range or to increase the accuracy of the estimated rate constants. The extension of the temperature range is limited by technical difficulties. The reaction at high or low temperatures may be unsuitable for experimentation, being either too rapid or too slow. Alternatively, the mean value of the rate constant can be made more reliable by frequent repetition of individual runs, but this leads to an improvement of the results only when the experimental errors are of the haphazard type. On the other hand, if the determination of the rate constant involves a systematic error, which is itself temperature-dependent, then the deviation of the temperature coefficient, and consequently of the " activation energy ", is of a permanent nature and cannot be eliminated by mere repetition of runs. Such a situation is created if, for example, the main reaction under investigation is accompanied by some side reaction the relative extent of which continuously increases or decreases with the temperature.

It is essential, therefore, to find experimental conditions under which all side reactions are suppressed as far as possible. Only in these circumstances can one expect to be able to determine accurately the correct activation energy of the process from the temperature coefficient of the rate constant. If this coefficient has not been estimated, or if it cannot be estimated owing to some technical difficulties, then we are able to calculate the probable activation energy from the absolute value of the rate constant determined at one temperature only, the frequency factor being assumed to be 10^{13} sec.$^{-1}$. Let us illustrate this procedure by a numerical example. The unimolecular rate constant k has been estimated at 10^{-2} sec.$^{-1}$ at a temperature of 800° K. From the equation

$$k = 1 \times 10^{13} e^{-E/\boldsymbol{R}T}$$

we derive

$$E = 2{\cdot}3(13 - \log k)\boldsymbol{R}T/1000 \text{ kcals./mole} \quad . \quad . \quad . \quad (1)$$

i.e.,

$$E = 2{\cdot}3(13 + 2)2 \times 800/1000 \text{ kcals./mole}$$
$$= 55 \text{ kcals./mole}$$

Examination of expression (1) reveals that E is not very sensitive to experimental errors involved in the estimation of k ; *e.g.*, an error in the latter as high as 100% produces an error of only 1·1 kcals./mole in the value of E as computed above. Furthermore, it is apparent that by using data obtained for a very slow reaction, which is carried out at the lowest possible temperature, one can reduce still further the absolute error in E computed by the above method.

It is, of course, very important to use the correct value of ν* in such calculations. It is possible, however, to obtain a reasonably good result for E even though the chosen value of ν is wrong by, say, a factor of 5 : such an error produces in the above example an error of 2·6 kcals./mole in E.

It is instructive to compare the magnitudes of the above errors in E with those which are involved in E calculated from the temperature coefficient of the unimolecular rate constant. In the numerical example discussed in the preceding section errors of 20% in the estimated rate constants produce an error of 8·1 kcals./mole in the activation energy calculated. Therefore, if the experimental and/or theoretical evidence makes it probable that the rate of some process is approximately governed by the unimolecular dissociation, then the activation energy corresponding

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* ν = the frequency factor of a unimolecular reaction.

to this unimolecular decomposition can be estimated fairly accurately by application of the expression

$$E = (13 - \log k) \times 2{\cdot}3RT/1000 \text{ kcals./mole*}$$

particularly if the data used in this computation correspond to a very slow reaction investigated at a comparatively low temperature. On the other hand, the activation energy computed from the temperature coefficient of the rate constant of such a reaction (which involves side reactions or consecutive reactions in addition to the main unimolecular decomposition) may be very different from the former activation energy, which would then be considered to be the more reliable.

In the preceding section it was shown that a fairly reliable estimate of the bond dissociation energy might be attained by a computation based on the assumed value of 10^{13} sec.$^{-1}$ for the frequency factor of the unimolecular decomposition. The absence of more exact knowledge of this frequency factor, however, is the cause of an error in these computed bond dissociation energies, and consequently this method fails in the detection of small variations of bond dissociation energies.

The problem could be considerably simplified by confining ourselves to the study of the variations of the dissociation energy of some particular bond, say C–X, in a series of molecules of the type R·X, where R is a member of some specified class of kindred radicals. There is strong evidence that for such a series of molecules RX, the frequency factors of the unimolecular decompositions $RX \longrightarrow R + X$ are identical. If this is the case then the difference $D(R_1\text{–}X) - D(R_2\text{–}X)$, R_1 and R_2 belonging to the same class of radicals, may be accurately estimated from the ratio of the relevant unimolecular rate constants measured at the same temperature. Thus one obtains the expression

$$D(R_1\text{–}X) - D(R_2\text{–}X) = 2{\cdot}3RT \log (k_2/k_1)$$

k_1 and k_2 denoting the respective unimolecular rate constants, both measured at temperature $T°$.

Examination of the above expression reveals that this method of estimating variations in $D(R\text{–}X)$ requires a knowledge neither of the frequency factor nor of the absolute value of the rate constants. One need only determine, as carefully as possible, the relative rate constants and ascertain that they are actually proportional to the rate constants of the *primary* dissociation process. If the latter condition is fulfilled, then one is able to detect even small differences in the relevant dissociation energies.

Let us consider now the conditions which enable one to measure the rate of the primary unimolecular dissociation $R{\cdot}R_1 \longrightarrow R + R_1$. The experimentation is limited, of course, to the type of decomposition in which the weakest bond of the molecule is ruptured, and it is desirable, therefore, that this bond should be considerably weaker than any other bond in the molecule.

The primary dissociation process is followed by the subsequent reactions

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* The value of 13 was chosen on theoretical grounds.

of the radicals formed, and consequently the investigator is confronted with the possibility of numerous complications which may obscure the kinetics of the decomposition and make their interpretation ambiguous. A straightforward approach would be one based on a direct measurement of the rate of formation of the radicals produced initially. This, however, cannot be achieved by simply estimating the concentration of radicals present in the system. As soon as the radicals are produced by decomposition they begin to react either with each other or with other surrounding molecules. The measured concentration of radicals, therefore, corresponds to their *stationary* concentration, and since this is not proportional to the time of reaction it cannot measure the rate of the dissociation process.

It seems probable that in a flow system in which the reactants pass very rapidly through the furnace, *i.e.*, when the time of contact is extremely short, the radicals produced will have no chance of recombining or reacting in any way. If, in a case like this, one were to count them on their leaving the reaction vessel one would be able to measure the rate of dissociation (% of decomposed molecules divided by time of contact). This idea was developed by Rice and his collaborators.*

The estimation of the rate of initial dissociation is accomplished most satisfactorily in a system in which the radicals are removed as soon as they are formed, without regenerating the original molecules. In such a system we avoid any complications caused by the back reaction, and the rate of formation of the final product from the primary radicals measures the rate of initial dissociation. However, since all reactions between radicals and molecules must produce radicals, there is a danger of starting a chain reaction. It is possible, in principle, to obtain the required information even by investigating a chain reaction, since the determination of both the length of the chain and the overall rate of chain reaction would enable us to compute the rate of initiation. In practice, however, the kinetics of chain reactions are very ambiguous and, in the Reviewer's opinion, these reactions are not to be recommended for the estimation of the rate of initial dissociation.

There are two cases in which the chain reaction might be prevented:

(1) When the radicals are removed rapidly by a recombination which does not produce the original molecules. Such a process generally requires two stages: *e.g.*, the initial decomposition of dimethylmercury takes place according to the equation $Hg(CH_3)_2 \rightarrow Hg{\cdot}CH_3 + CH_3$ and is followed by rapid decomposition of $HgCH_3$, $Hg{\cdot}CH_3 \rightarrow Hg + CH_3$. Thus, the recombination of $Hg{\cdot}CH_3$ and CH_3 radicals into the original molecules of $Hg(CH_3)_2$ is prevented. Now suppose that the recombinations of CH_3 radicals into C_2H_6 molecules is the most effective reaction by which methyl radicals are removed from the system. In this case, the overall process is represented by the equation $Hg(CH_3)_2 \rightarrow Hg + C_2H_6$, and will be governed, kinetically, by the unimolecular rate-determining dissociation $Hg(CH_3)_2 \rightarrow Hg{\cdot}CH_3 + CH_3$.

(2) When radicals initially formed are rapidly removed by some reactions. These eventually produce *stable* radicals which neither decompose into

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* A good summary of studies in which this technique was applied can be found in the monograph, " The Aliphatic Free Radicals " (Baltimore, 1935), by Rice and Rice.

simpler fragments nor react with molecules present in the system. This is illustrated by two examples :

Example (i). Decomposition of benzyl bromide produces reactive Br atoms and relatively inert benzyl radicals : $C_6H_5{\cdot}CH_2Br \rightarrow C_6H_5{\cdot}CH_2 + Br$. If this reaction is carried out in an excess of toluene, then reactive Br atoms are removed rapidly by interaction with toluene : $Br + C_6H_5{\cdot}CH_3 \rightarrow HBr + C_6H_5{\cdot}CH_2$, producing inert benzyl radicals. These radicals may be continuously removed from the reaction vessel and they dimerise eventually in the outlet tube. The rate of the initial dissociation can be measured, therefore, by the rate of formation of either hydrogen bromide or dibenzyl.

Example (ii). Primary decomposition of methyl nitrite takes place according to the equation $CH_3{\cdot}ONO \rightarrow CH_3O + NO$. The reactive CH_3O radical interacts with a molecule of undecomposed nitrite and produces the unstable radical $CH_2{\cdot}ONO$: $CH_3O + CH_3{\cdot}ONO \rightarrow CH_3OH + {\cdot}CH_2{\cdot}ONO$. Finally, the unstable $CH_2{\cdot}ONO$ radical decomposes and a stable NO radical is produced : ${\cdot}CH_2{\cdot}ONO \rightarrow CH_2O + NO$. According to this mechanism the rate of initial decomposition may be measured by the rate of formation of NO.

Thermochemical Methods

Thermochemical methods can be divided into two groups : (*a*) The determination of heats of reactions involving radicals ; (*b*) calculations based on the heat of formation of radicals.

The first method requires investigation of rates and activation energies of reactions involving radicals or atoms, *e.g.*,

$$\begin{aligned} CH_3 + H_2 &\rightarrow CH_4 + H \quad \ldots \; E_1 \\ CH_4 + H &\rightarrow CH_3 + H_2 \quad \ldots \; E_2 \end{aligned}$$

$E_1 - E_2$ gives the heat of reaction $CH_3 + H_2 = CH_4 + H$, which is equal $D(H\text{–}H) - D(CH_3\text{–}H)$.[14] One can therefore calculate $D(CH_3\text{–}H)$ if $D(H\text{–}H)$ is known :

$$D(CH_3\text{–}H) = D(H\text{–}H) + E_2 - E_1$$

The determination of $D(CH_3\text{–}H)$ by Kistiakowsky and his colleagues [15] is based on the same principle. These authors determined activation energies of the reactions

$$\begin{aligned} CH_4 + Br &\rightarrow CH_3 + HBr \quad \ldots \; E_1 \\ CH_3 + HBr &\rightarrow CH_4 + Br \quad \ldots \; E_2 \end{aligned}$$

Since $E_1 - E_2 = D(CH_3\text{–}H) - D(H\text{–}Br)$, the value of $D(CH_3\text{–}H)$ is determined if $D(H\text{–}Br)$ is known, and the latter was obtained from spectroscopic data.

Determination of bond dissociation energies from the heats of formation of radicals is based on the equation

$$D(R_1\text{–}R_2) = \Delta H_f(R_1) + \Delta H_f(R_2) - \Delta H_f(R_1{\cdot}R_2)$$

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[14] The data on E_1 and E_2 have been computed by Wicke, *Ergebn. exakt. Naturwiss.*, 1942, **20**, 1.

[15] Kistiakowsky and Van Artsdalen, *J. Chem. Physics*, 1944, **12**, 469.

However, heats of formation of radicals *must* be obtained from bond dissociation energies which are determined *directly*. A few examples explain the interrelation between bond dissociation energies and heats of formation of radicals. The starting point is provided by symmetrical molecules of the type R·R. If D(R–R) is determined by some direct method, then the equation written above makes it possible to determine the heat of formation of the radical R :

$$D(\mathrm{R{-}R}) = 2\Delta H_f(\mathrm{R}) - \Delta H_f(\mathrm{R{\cdot}R})$$

E.g., having D(H–H) (from spectroscopic studies) and $D(NH_2–NH_2)$ (from pyrolytic studies) we can calculate ΔH_f(H) and $\Delta H_f(NH_2)$:

$$D(\mathrm{H{-}H}) = 2\Delta H_f(\mathrm{H}) - \Delta H\ (\mathrm{H_2})$$

But

$$2\Delta H_f(\mathrm{H}) = 104\ \mathrm{kcals./mole}$$

therefore

$$\Delta H_f(\mathrm{H}) = 52\ \mathrm{kcals./mole}$$

$$D(\mathrm{NH_2{-}NH_2}) = 2\Delta H_f(\mathrm{NH_2}) - \Delta H_f(\mathrm{N_2H_4})$$

But

$$D(\mathrm{NH_2{-}NH_2}) = 60\ \mathrm{kcals./mole} \quad \text{and} \quad \Delta H_f(\mathrm{N_2H_4}) = 22\ \mathrm{kcals./mole}$$

therefore

$$\Delta H_f(\mathrm{NH_2}) = 41\ \mathrm{kcals./mole}$$

Knowing ΔH_f(H) and $\Delta H_f(NH_2)$, we can calculate the *unknown* N–H bond dissociation energy in ammonia :

$$\begin{aligned} D(\mathrm{NH_2{-}H}) &= \Delta H_f(\mathrm{NH_2}) + \Delta H_f(\mathrm{H}) - \Delta H_f(\mathrm{NH_3}) \\ &= 41 + 52 + 11\ \mathrm{kcals./mole} \\ &= 104\ \mathrm{kcals./mole} \end{aligned}$$

Further, knowing heats of formation of some radicals or atoms, we may calculate the heat of formation of other radicals from *directly* determined dissociation energies of the type $D(R_1–R_2)$; *e.g.*, knowing $D(C_6H_5{\cdot}CH_2–H)$ (from pyrolytic studies) we calculate $\Delta H_f(C_6H_5{\cdot}CH_2)$ from the equation

$$\begin{aligned} D(\mathrm{C_6H_5{\cdot}CH_2{-}H}) &= \Delta H_f(\mathrm{C_6H_5{\cdot}CH_2}) + \Delta H_f(\mathrm{H}) - \Delta H_f(\mathrm{C_6H_5{\cdot}CH_3}) \\ 77{\cdot}5\ \mathrm{kcals./mole} &= \Delta H_f(\mathrm{C_6H_5{\cdot}CH_2}) + 52\ \mathrm{kcals./mole} - 12\ \mathrm{kcals./mole} \end{aligned}$$

whence

$$\Delta H_f(\mathrm{C_6H_5{\cdot}CH_2}) = 37{\cdot}5\ \mathrm{kcals./mole}$$

The latter value makes it possible to determine the *unknown* C–C bond dissociation energy in dibenzyl :

$$\begin{aligned} D(\mathrm{C_6H_5{\cdot}CH_2{-}CH_2{\cdot}C_6H_5}) &= 2\Delta H_f(\mathrm{C_6H_5{\cdot}CH_2}) - \Delta H_f(\mathrm{dibenzyl}) \\ &= 2 \times 37{\cdot}5\ \mathrm{kcals./mole} - 27\ \mathrm{kcals./mole} \\ &= 48\ \mathrm{kcals./mole} \end{aligned}$$

One realises, therefore, that direct determination of n bond dissociation energies may lead to the determination of the heats of formation of n radicals, and these in turn enable us to calculate about $\frac{1}{2}n^2$ *unknown* bond dissociation energies, providing the heats of formation of the relevant compounds are known.

Determination of heats of formation of radicals provides us with an important method for checking the consistency of bond dissociation energies determined *directly*. The heat of formation of any one radical can be calculated from several directly determined bond dissociation energies; *e.g.*, $\Delta H_f(C_6H_5{\cdot}CH_2)$ can be calculated from

(*a*) $D(C_6H_5{\cdot}CH_2{-}H)$ by use of the equation

$$\Delta H_f(C_6H_5{\cdot}CH_2) = D(C_6H_5{\cdot}CH_2{-}H) + \Delta H_f(C_6H_5{\cdot}CH_3) - \Delta H_f(H)$$

(*b*) $D(C_6H_5{\cdot}CH_2{-}CH_3)$ by use of

$$\Delta H_f(C_6H_5{\cdot}CH_2) = D(C_6H_5{\cdot}CH_2{-}CH_3) + \Delta H_f(C_2H_5{\cdot}C_6H_5) - \Delta H_f(CH_3)$$

(*c*) $D(C_6H_5{\cdot}CH_2{-}NH_2)$ by use of

$$\Delta H_f(C_6H_5{\cdot}CH_2) = D(C_6H_5{\cdot}CH_2{-}NH_2) + \Delta H_f(C_6H_5{\cdot}CH_2{\cdot}NH_2) - \Delta H_f(NH_2)$$

Since all the bond dissociation energies mentioned above were determined directly (by pyrolytic method) and heats of formation of required radicals (or atoms) were obtained by independent direct methods, the consistent results for $\Delta H_f(C_6H_5{\cdot}CH_2)$ are a guarantee of the consistency of our system of bond dissociation energies.