THE DETERMINATION OF BOND DISSOCIATION ENERGIES BY PYROLYTIC METHODS

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Received January 9, 1950

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I. INTRODUCTION

A. Synopsis

The determination of dissociation energies of various chemical bonds is of fundamental importance for the quantitative treatment of chemical processes. In chemical reactions bonds are broken and formed, and in many reactions both processes occur simultaneously. In consequence the magnitudes of dissociation energies are of prime importance for both chemical kinetics and chemical equilibria.

At the outset of this review the definition of the bond dissociation energy is given, which is followed by a brief discussion of the various relationships between this entity and other related quantities: namely, the heat of atomization, the average bond energy, the heat of radical formation, the heat of reaction, and the activation energy of the reaction. This discussion is followed by a short review of various direct methods which may be applied for the estimation of bond dissociation energies.

The main theme of this paper, however, is a critical survey of various pyrolytic methods used for the determination of bond dissociation energies, the examination of principles applied in the interpretation of the experimental material and in computation of the results, and finally a review of the actual results obtained by various workers. This part is divided into two sections, the first dealing with the equilibrium method and the second with the kinetic method.

The paper then concludes with a discussion of some unexplored reactions which might be used for the determination of bond dissociation energies, and with a description of various new methods which might prove useful in this type of work. Tables of bond dissociation energies and heats of formation of various radicals are given in the appendix.

B. The definition of bond dissociation energy

The dissociation energy of the bond A—B in the molecule (or radical) M is the endothermicity of the reaction in which M is decomposed into two fragments R′ and R″ formed by breaking the bond A—B.[1]

$$\mathrm{M} \rightarrow \mathrm{R'} + \mathrm{R''} - D(\mathrm{R'}\text{—}\mathrm{R''})\ \text{kcal./mole}$$

It must be stressed that this endothermicity must be computed for the state in which the reactant M and the products R′ and R″ are in the gaseous phase, at

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[1] In cyclic molecules the breaking of certain bonds might lead to the formation of one fragment only.

zero pressure and at 0°K. It follows from the above definition that the dissociation energy of the bond is defined unambiguously by the description of the initial state, i.e., the molecule (or radical) M, and the final state, i.e., the fragments R′ and R″, M, R′, and R″ being in certain specified electronic states. It is also obvious that no restriction need be imposed on the path of the reaction which leads to this dissociation, since variation of this path does not change the endothermicity of the process.

C. The relationship between the bond dissociation energy and the heat of atomization of a molecule

The rupture of the "first" bond in a polyatomic molecule M requires an expenditure of energy equal to the dissociation energy of the particular bond in the original molecule. As a result of this process new fragments are formed and the breaking of an additional bond requires an amount of work equal to the dissociation energy of this bond referred to the appropriate fragment. The work expended in splitting a further bond is in turn equal to the dissociation energy of this bond in the newly formed fragment. This process is continued stepwise until ultimate atomization of the molecule takes place. Hence, the heat of atomization of the original molecule is equal to the sum of the dissociation energies of all the bonds as they are broken successively until the whole molecule is finally degraded into separate atoms.

This relationship is illustrated by the following two examples:

Example 1

$$H_2O \rightarrow H + OH - D(\text{H—OH})$$

$$OH \rightarrow O + H - D(\text{O—H})$$

$D(\text{H—OH}) = D(\text{O—H})_{\text{in } H_2O}$ = the dissociation energy of the "first" O—H bond in H_2O

$D(\text{O—H}) = D(\text{O—H})_{\text{in OH}}$ = the dissociation energy of the "second" O—H bond in H_2O or the O—H bond dissociation energy in the OH radical

$$Q_a = D(\text{H—OH}) + D(\text{O—H})$$

Q_a denotes here the heat of atomization of the original molecule.

It should be emphasized that the dissociation energies of a bond between any two given atoms, but referred to different fragments, will not usually be equal; e.g.:

$$D(\text{O—H})_{\text{in } H_2O} = D(\text{H—OH}) = 118 \text{ kcal./mole}$$

$$D(\text{O—H})_{\text{in OH}} = D(\text{O—H}) = 100 \text{ kcal./mole}$$

In this particular case, the dissociation energy of the "first" O—H bond is greater than the dissociation energy of the "second" O—H bond in H_2O by 18 kcal./mole.

Example 2

$$\begin{aligned}
CH_3Cl &\rightarrow CH_3 + Cl - D(CH_3\text{—}Cl)\\
CH_3 &\rightarrow CH_2 + H - D(CH_2\text{—}H)\\
CH_2 &\rightarrow CH + H - D(CH\text{—}H)\\
CH &\rightarrow C + H - D(C\text{—}H)
\end{aligned}$$

Thus

$$Q_a = D(CH_3\text{—}Cl) + D(CH_2\text{—}H) + D(CH\text{—}H) + D(C\text{—}H)$$

It is permissible, however, to visualize other paths for the atomization process of the methyl chloride molecule, e.g.:

$$\begin{aligned}
CH_3Cl &\rightarrow CH_2Cl + H - D(CH_2Cl\text{—}H)\\
CH_2Cl &\rightarrow CH_2 + Cl - D(CH_2\text{—}Cl)\\
CH_2 &\rightarrow CH + H - D(CH\text{—}H)\\
CH &\rightarrow C + H - D(C\text{—}H)
\end{aligned}$$

Thus

$$Q_a = D(CH_2Cl\text{—}H) + D(CH_2\text{—}Cl) + D(CH\text{—}H) + D(C\text{—}H)$$

Both modes of atomization must lead, of course, to the same value for the heat of atomization, although the component dissociation energies need not necessarily be the same; e.g.:

$$\begin{aligned}
D(CH_3\text{—}Cl) &\neq D(CH_2\text{—}Cl)\\
D(CH_2Cl\text{—}H) &\neq D(CH_2\text{—}H)
\end{aligned}$$

D. The relationship between the bond dissociation energy and the "average bond energy"

The bond dissociation energy is to be distinguished from another quantity which will be referred to in this paper as "average bond energy."[2] The latter is defined for a molecule of the type AX_n as $1/n$ of its heat of atomization. The absence of a clear definition of the "average bond energy" was recently stressed in a paper by M. G. Evans and M. Szwarc (56). These authors proposed a purely formal and unequivocal definition of the "average bond energy" which can be expressed in nonmathematical language as follows: The "average bond energy" of a bond between two atoms A and B is equal to the work done in separating these two atoms in a process during which all the other bonds are independently and simultaneously extended in such a way that the molecule as a whole swells infinitely whilst preserving its original geometrical form.

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[2] See, for example, L. H. Long and R. G. W. Norrish: Proc. Roy. Soc. (London) **A187**, 337 (1946).

The mathematical representation of the "average bond energy" described in this manner is given, therefore, by the integral

$$\bar{q}_{a_k} = \int_{r_{k_0}, L}^{\infty} \frac{\partial E}{\partial r_k} \cdot dr_k$$

where E denotes the potential energy of the molecule expressed as a function of all the bond lengths (r_k) and of other required coördinates (α_i), the latter being chosen as the required angles between the bonds; r_{k_0} denotes the value of r_k in the original molecule; L denotes the integration path, which is defined by the following set of equations:

$$\alpha_i = \alpha_{i_0} = \text{const. for all } i$$

$$r_k = \gamma r_{k_0} \qquad \text{for all } k$$

γ being a variable which increases from 1 to ∞. The potential energy E is measured from the zero level represented by the set of separate atoms, each of them being in a specified electronic state.

The following example illustrates the numerical difference between the bond dissociation energy and the "average bond energy."

$$D(\text{H—OH}) = 118 \text{ kcal./mole}: D(\text{O—H}) = 100 \text{ kcal./mole}$$

"Average bond energy = 109 kcal./mole"

i.e., in molecules of the type AX_n the "average bond energy" is the arithmetic mean of all the bond dissociation energies.

The relationship between D and $\bar{q}_a$ in various molecules of the type AX_n has been discussed more fully in papers by M. Wehrli and G. Milazzo (212) and by H. A. Skinner (164).

E. The relationship between the bond dissociation energy and the heat of formation of radicals

The determination of the dissociation energy of a bond, the rupture of which produces two *identical* radicals (or atoms), enables one to compute the heat of formation of these radicals (or atoms):

$$\Delta H_f \text{ (radical or atom R)} = \tfrac{1}{2}[\Delta H_f(\text{R}_2) + D(\text{R—R})]$$

Example 1: The dissociation energy of the H—H bond in hydrogen is 104 kcal./mole; hence the heat of formation of hydrogen atoms (from the element in its standard state) is 52 kcal./mole.

$$\Delta H_f(\text{H}) = \tfrac{1}{2}[D(\text{H—H})] = \tfrac{1}{2} \times 104 \text{ kcal./mole}$$

Example 2: The dissociation energy of the N—N bond in hydrazine is 60 kcal./mole and the heat of formation of gaseous hydrazine (from the elements in their standard states) is 22 kcal./mole; hence the heat of formation of the NH_2 radical (from the elements in their standard states) is 41 kcal./mole.

$$\Delta H_f(\mathrm{NH_2}) = \tfrac{1}{2}[\Delta H_f(\mathrm{N_2H_4}) + D(\mathrm{NH_2{-}NH_2})]$$
$$= \tfrac{1}{2}(22 + 60)\ \text{kcal./mole} = 41\ \text{kcal./mole}$$

If the heats of formation of various radicals or atoms are known it is possible to calculate the related dissociation energies, provided the heats of formation of the required compounds are known. For instance, the heat of formation of gaseous ammonia (from the elements in their standard states) is -11 kcal./mole, and the heats of formation of H atoms and NH_2 radicals have been computed in the examples given above at 52 kcal./mole and 41 kcal./mole, respectively. Thus we can calculate the dissociation energy of the "first" N—H bond in ammonia as follows:

$$D(\mathrm{NH_2{-}H}) = \Delta H_f(\mathrm{NH_2}) + \Delta H_f(\mathrm{H}) - \Delta H_f(\mathrm{NH_3})$$
$$= (52 + 41 + 11)\ \text{kcal./mole} = 104\ \text{kcal./mole}$$

The above example illustrates the use of the principle which enables one to derive bond dissociation energies from thermochemical data, provided the heats of formation of the required radicals, or atoms, are known, i.e., if the bond dissociation energies on which these latter quantities are based have been independently determined by some direct methods. It must be stressed that it is by no means possible to compute a bond dissociation energy from purely thermochemical data, without recourse to other bond dissociation energies which have been determined by direct measurements. It is obvious, therefore, that a bond dissociation energy calculated on the basis of thermochemical data and in terms of directly estimated dissociation energies entails the uncertainty and the experimental errors involved in the determination of the latter.[3]

If the value of the dissociation energy of a bond the rupture of which produces two *different* radicals or atoms is known, then one is able to compute the heat of formation of a radical by reversing the above method. For instance, $D(\mathrm{C_6H_5CH_2{-}H}) = 77.5$ kcal./mole, the heat of formation of toluene in the gaseous state is 12 kcal./mole, and that of hydrogen atoms is 52 kcal./mole. Thus, the heat of formation of the benzyl radical is found to be 37.5 kcal./mole.

$$\Delta H_f(\mathrm{C_6H_5CH_2}) = \Delta H_f(\mathrm{C_6H_5CH_3}) + D(\mathrm{C_6H_5CH_2{-}H}) - \Delta H_f(\mathrm{H})$$
$$= (12 + 77.5 - 52)\ \text{kcal./mole} = 37.5\ \text{kcal./mole}$$

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[3] For example, the C—F bond dissociation energy in acetyl fluoride was computed by A. S. Carson and H. A. Skinner (37) at 110 kcal./mole. The above authors measured calorimetrically the heat of hydrolysis of acetyl fluoride and their experimental error was ±0.6 kcal./mole only. The computation of $D(\mathrm{CH_3CO{-}F})$ involves, however, the values of $D(\mathrm{F{-}F})$ and $D(\mathrm{CH_3{-}CO})$ in addition to their experimental data. These two bond dissociation energies involve considerable uncertainties, owing to the interpretation of experimental data used for their calculation (for example, $D(\mathrm{F{-}F})$ has been accepted at 60–65 kcal./mole and at present the new evidence seems to suggest a value of 35–45 kcal./mole) and to experimental errors of measurements. Hence, the uncertainty in $D(\mathrm{CH_3O{-}F})$ is probably of the order of ± 10 kcal./mole, although the experimental error of calorimetric determination of Carson and Skinner is only 0.6 kcal./mole.

It must be emphasized again that this calculation requires a knowledge of both the heat of formation of the second fragment and the dissociation energy.

F. The relationship between the bond dissociation energy and the heat of reaction

The heat of reaction is equal to the sum of the dissociation energies of the bonds which are formed minus the sum of the dissociation energies of the bonds which are broken. This relationship is particularly simple for reactions of the type

$$AX + Y \rightarrow A + XY$$

where Y denotes either an atom or a radical. The heat of this reaction is given as $D(X—Y) - D(A—X)$. Hence, if $D(X—Y)$ is known, the determination of the heat of reaction will enable one to compute the value of $D(A—X)$.

G. B. Kistiakowsky and his collaborators (88) applied this principle in a very ingenious manner to the problem of the estimation of the dissociation energy of the C—H bond in methane. They determined the activation energies of the two reactions

$$CH_4 + Br \rightarrow CH_3{\cdot} + HBr$$

$$CH_3{\cdot} + HBr \rightarrow CH_4 + Br$$

as 18 kcal./mole and 2 kcal./mole, respectively. The difference between these activation energies gave the heat of reaction for

$$CH_4 + Br = CH_3{\cdot} + HBr - 16 \text{ kcal./mole at } 453°K.$$

their own recalculation for 0°K. leading to $\Delta H_0^0 = 15$ kcal./mole. On applying the above principle, and taking the $D(H—Br)$ at 85.8 kcal./mole they concluded:

$$D(CH_3—H) = D(H—Br) + 15 \text{ kcal./mole} = 101 \text{ kcal./mole}$$

G. The relationship between the bond dissociation energy and the energy of activation

In most chemical reactions two processes occur simultaneously: the existing bond is broken and a new bond is formed. The activation energy of such a reaction is, of course, a function of the dissociation energies of both the bond which is broken and that which is formed. The relationship between the activation energy and the relevant dissociation energies is, in most instances, of a complex nature. It is not an easy task, therefore, to obtain information concerning the magnitude of the dissociation energies involved in a reaction from a knowledge of the corresponding activation energy of the process.

In some cases, however, these relationships are greatly simplified. Firstly, let us consider the unimolecular decomposition of a molecule in which the fission of one bond results in the production of two radicals or atoms. The activation energy of this process will be equal to the dissociation energy of the broken bond if the reverse process, i.e., the recombination of the radicals, corresponds to zero activation energy. Although there are few experimental data available from which we may calculate the activation energy of the recombination process, the evidence so far accumulated strongly suggests that this activation energy is negligible. There is no theoretical justification whatever to anticipate repulsion forces between two colliding radicals or atoms.[4] Furthermore, observed spectroscopic data seem to conform closely to potential energy curves which do not show humps. Finally, most reactions between radicals and molecules, if exothermic, seem to have very low activation energies.

One should notice, however, that the recombination of two triphenylmethyl radicals involves an activation energy of about 7–8 kcal./mole (227). This reaction is an obvious exception, and the calculation by M. Szwarc (184) demonstrates that there are repulsion forces, due to the interaction between the hydrogen atoms of the approaching phenyl groups. These repulsion forces begin to operate when the distance separating the central carbon atoms is still greater than 4 Å., i.e., before the development of any appreciable attraction between these centers.

It seems reasonable, therefore, to make the general assumption that the recombination of radicals or atoms does not involve any activation energy; hence it follows that the activation energy of the discussed dissociation process is equal to the respective bond dissociation energy.

The second case which we shall consider involves a series of reactions of the type:

$$\mathrm{RX} + \mathrm{A} \rightarrow \mathrm{R} + \mathrm{XA}$$

In each series the radical R is varied, while X and A remain constant. The variation of R changes the bond which is subsequently broken, giving rise to different R—X dissociation energies. On the other hand, it will be noticed that the same bond is formed in every reaction. For such reactions we should expect some systematic increase of the activation energy with the increase of the dissociation energy of the R—X bond. As an example we may quote a series of reactions of the type:

$$\mathrm{RCl} + \mathrm{Na} \rightarrow \mathrm{R} + \mathrm{NaCl}$$

For this series a relationship between the activation energy and the dissociation energy of the R—Cl bond was first proposed by R. A. Ogg, Jr., and M. Polanyi (124) and further developed by M. G. Evans and M. Polanyi (54). It was shown by the above authors that in such a series the increase in activation energy is proportional to the increase in the dissociation energy of the R—Cl bond.

$$\Delta E_a = \alpha \cdot \Delta D$$

On the basis of theoretical considerations a value of about 0.3 was attributed to α, and the experimental justification of the above relationship was presented in a paper by E. T. Butler and M. Polanyi (35).

Similar relationships have been reported for other series of reactions, e.g.,

$$\mathrm{RH} + \mathrm{CH_3}^{\bullet} \rightarrow \mathrm{R} + \mathrm{CH_4}$$

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[4] See, however, W. Heitler and G. Rumer (75).

given by H. S. Taylor and J. O. Smith (202), and

$$RH + Cl \rightarrow R + HCl$$

given by H. Steiner and H. R. Watson (176).

This type of relationship does not provide information as to the absolute magnitude of the bond dissociation energy; nevertheless it is valuable for the estimation of the gradation in bond dissociation energies. However, the results obtained from this type of investigation cannot be accepted always with complete confidence.

II. THE DIRECT DETERMINATION OF BOND DISSOCIATION ENERGIES

The principles of the evaluation of bond dissociation energies from thermochemical data have already been described in Sections I, E and I, F. In Section II various direct methods applicable to the determination of bond dissociation energies are presented.

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 estimation of 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 the energy liberated in bond formation converted 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 utilized for various purposes; e.g., the heat liberated in the process of recombination of 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 F. R. Bichowsky and L. C. Copeland (19) 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 kcal./mole. Similar experiments were repeated with oxygen atoms by L. C. Copeland (43) and by W. H. Rodebush and S. M. Troxel (154). It seems, however, that the method is less reliable in this case. The preliminary report of Copeland suggested a very high value for $D(O—O)$: namely, 165 ± 5 kcal./mole. The value finally recommended by Copeland and by Rodebush and Troxel of about 131 kcal./mole is still too high (the value accepted at present is 117 kcal./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 refuted in a decisive way.

All the other direct estimations hitherto completed have been based on the bond-splitting process. This method, included in group B, can in turn be divided into three subclasses according to the form in which the energy is supplied for the fission of the bond.

(*a*) *Photochemical methods:* The energy is supplied in the form of radiation. Under this heading we include the methods based on the investigation of absorption spectra, predissociation phenomena, photodecomposition, photosensitized decomposition, etc.

(*b*) *Electron impact methods:* The energy in this type of investigation is supplied by the kinetic energy of a beam of electrons. This method was used successfully by D. P. Stevenson.

(*c*) *Thermal or pyrolytic methods:* Here the energy is supplied in the form of thermal energy. These methods are discussed in detail in the following sections. They are described under two main headings: (*1*) the equilibrium method and (*2*) the kinetic method. The former deals with those investigations in which equilibrium is attained between the undissociated molecules and the fragments resulting from the fission of the bond in question, and leads to the computation of the heat of dissociation. The latter is based on the kinetics of the bond-breaking process and leads to the determination of the activation energy of the dissociation process. It is shown later that this activation energy might be identified with the bond dissociation energy.

III. DETERMINATION OF BOND DISSOCIATION ENERGIES BY THE EQUILIBRIUM METHOD

A. Principle

The determination of bond dissociation energies by the equilibrium method is based on the measurement of the equilibrium constants of the gaseous reaction:

$$R'R'' \rightleftharpoons R' + R''$$

where R′ and R″ denote the radicals or atoms produced by the rupture of the bond in question. These equilibrium constants, estimated at various temperatures, enable us to compute the heat of dissociation by applying the van't Hoff isochore, and the recalculation of the heat of dissociation to zero pressure and 0°K. yields, by definition, the bond dissociation energy.

The experimenter who wishes to determine a bond dissociation energy by the equilibrium method has to consider the problems of: (*a*) selecting a system in which the required equilibrium may be established and maintained throughout the period necessary for the appropriate measurements to be made; (*b*) selecting, or devising, a method which will enable him to determine the equilibrium constant with a sufficient degree of accuracy.

The equilibrium method is particularly suitable for estimating the bond dissociation energies of diatomic molecules of the X_2 type. 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.[5] However, in the case of molecules of the type

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[5] There were speculations about the formation of molecules of the X_3 type. Such a situation is encountered, e.g., in the system O, O_2, and O_3 at very high temperatures. It was definitely proved, however, that no molecules of the I_3 type exist in the system $I_2 \rightleftharpoons 2I$ (133), and probably no molecules of the Br_3 type disturb the equilibrium $Br_2 \rightleftharpoons 2Br$.

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 RR; e.g., in the hypothetical system $CH_3CH_3 \rightleftharpoons 2CH_3\cdot$ the CH_3 radicals could be removed by the reaction:

$$CH_3\cdot + CH_3CH_3 \rightarrow CH_4 + \cdot CH_2CH_3$$

(b) Reactions between two radicals R which would lead to products different from RR; e.g., in the hypothetical system $C_2H_5C_2H_5 \rightleftharpoons 2C_2H_5\cdot$ the radicals $C_2H_5\cdot$ might be removed by a disproportionation:

$$2C_2H_5\cdot \rightarrow C_2H_4 + C_2H_6$$

(c) Decomposition of radicals R into simpler fragments; e.g., in the hypothetical system $C_2H_5C_2H_5 \rightleftharpoons 2C_2H_5\cdot$ the radicals might decompose according to the equation:

$$C_2H_5\cdot \rightarrow C_2H_4 + H$$

All the side reactions discussed above become more likely at higher temperatures and for longer reaction times, and their participation in the overall process limits the applicability of the equilibrium method; therefore the equilibrium method is particularly suitable for dealing with molecules R_2, for which the R—R bond is weak, the R radical is inert with respect to R_2, and thermally very stable, e.g., $N_2O_4 \rightleftharpoons 2NO_2$; $(C_6H_5)_3CC(C_6H_5)_3 \rightleftharpoons 2(C_6H_5)_3C\cdot$.

It is possible, in principle, to calculate the heat of reaction even if the equilibrium constant was measured at one temperature only. These calculations, however, require a knowledge of the partition functions of the molecule R′R″ and of the radicals or atoms, R′ and R″. Since partition functions are known accurately only for relatively simple molecules and they are not available for radicals, the method is limited to the estimation of dissociation energies of diatomic molecules.[6]

B. *Static manometric method*

A known amount of a compound of the type RR 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 RR enables one to deduce the degree of dissociation, α. The equilibrium constant K_e is given by the formula:

$$K_e = \frac{\alpha^2}{1 - \alpha} \cdot P$$

P being the pressure in the system.

In order to achieve sufficient accuracy in measuring the pressure increments,

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[6] For further details see, for example, R. H. Fowler and E. A. Guggenheim: *Statistical Thermodynamics*. Macmillan Company, New York (1940).

the latter 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 adequately large. Table 1, taken from E. W. R. Steacie's monograph (168), gives the temperatures at which a dissociation of 1 per cent is attained for various diatomic molecules at a pressure of 1 mm. of mercury. It is scarcely possible to detect sufficiently accurately the increase of pressure corresponding to 1 per cent of dissociation, and a glance at table 1 shows that a high temperature is required for the determination of bond dissociation energies greater than about 50 kcal./mole. Work at such high temperatures presents many technical difficulties, making the static manometric method very inconvenient.

The difficulties associated with experimentation at high temperatures might be avoided by working at extremely low pressures. This, however, presents new problems, such as the measurement of very low pressures, estimation of minute quantities of material, and, above all, an estimation of the amount of material adsorbed on the walls of the reaction vessel. The latter information is required for estimating the amount of material present in the gas phase, as at very low pressures the amount of adsorbed material may rise to a considerable fraction of the total amount of compound introduced. Obviously, accurate estimation of the adsorbed material would present formidable difficulty.

TABLE 1

Dissociation of diatomic molecules at a pressure of 1 mm. of mercury

COMPOUND	DISSOCIATION ENERGY	T	COMPOUND	DISSOCIATION ENERGY	T
	kcal./mole	°C.		*kcal./mole*	°C.
K_2	11.8	270	Br_2	45.2	850
Na_2	17.0	390	Cl_2	56.9	1040
Li_2	26.7	590	H_2	104	1920
I_2	35.2	680	O_2	117.4	2000

C. Dissociation energies determined by the static manometric method

(1) I—I bond dissociation energy in the iodine molecule

The first accurate data on the equilibrium $I_2 \rightleftharpoons 2I$ were obtained by G. Starck and M. Bodenstein in 1910 (166). The equilibrium was investigated over a wide temperature range from 800° to 1200°C. The results are self-consistent and the accuracy of the measurements appears to be satisfactory. The heat of dissociation of iodine, recalculated by these authors for 0°K., was estimated at 35.5 kcal./mole.

These investigations were repeated in 1922 by H. Braune and H. Ramstetter (26), and by lowering the total pressure in the reaction vessel to a few millimeters of mercury they succeeded in measuring the equilibria at lower temperatures, i.e., 640–1100°C. The final results, however, seem less satisfactory than those of Starck and Bodenstein, and the value of 35.1 kcal./mole recommended by Braune and Ramstetter is definitely too low.

The most elaborate study of the equilibrium $I_2 \rightleftharpoons 2I$ was undertaken by M. L. Perlman and G. K. Rollefson in 1941 (133). A modern technique was applied and the experiments were carried out over a temperature range of 450° to 1000°C. Perlman and Rollefson achieved an extremely high degree of accuracy and estimated the dissociation energy of the iodine molecule at 35.514 ± 0.050 kcal./mole. In computing this value a correction was introduced to allow for a deviation of iodine vapor from the perfect gas law. It should be emphasized that the accuracy of this estimation is of the same order as that obtained in the best spectroscopic determinations of $D(\text{I—I})$. The best spectroscopic value, 35.547 ± 0.023 kcal./mole obtained by W. G. Brown (31), agrees excellently with the value 35.514 ± 0.050 kcal./mole recommended by Perlman and Rollefson.

(2) Br—Br bond dissociation energy in the bromine molecule

Values of the dissociation energy of bromine obtained by the static manometric method are much less reliable than those obtained for $D(\text{I—I})$. These studies had to be carried out at temperatures still higher than those required in the study of the iodine system and the investigators were obliged to overcome increasing technical difficulties.

E. P. Parman and G. A. S. Atkinson (131) were the first to show that the apparent molecular weight of bromine vapors varied with temperature, thus indicating the occurrence of the dissociation process. The observed change was, however, too small (80.0 at about 650°C. and 74.3 at about 1050°C.) and their experimental technique too crude to justify any calculations of the heat of the dissociation process.

In 1916 M. Bodenstein and P. Cramer (22) repeated these experiments, using a much more refined technique. Bromine vapor was heated up to 1300°C. in a silica reaction vessel (a platinum reaction vessel was attacked at these temperatures by bromine). Since silica starts to soften at 1300°C., the reaction vessel might be deformed as a result of the differences between the outside and inside pressures. The silica reaction vessel was enclosed therefore in a platinum container, the pressure in the latter being continually adjusted to the pressure in the former. The highest percentage of decomposition observed was 18.3 per cent at 1300°C. and 770 mm. of mercury. The uncorrected value for the Br—Br bond dissociation energy was computed by Bodenstein at 46.5 kcal./mole (compared with the accepted value at present of 45.4 kcal./mole).

The percentage of decomposition of bromine molecule into bromine atoms was estimated experimentally by H. von Wartenberg and F. A. Henglein (211). These authors measured the dissociation at extremely low pressures, of the order of 10^{-3} mm. of mercury, and in consequence could observe the dissociation over a much lower temperature range: namely, 560–730°C. It is interesting to note that the percentage of decomposition computed from Bodenstein and Cramer's equation for log K agreed closely with that observed directly by von Wartenberg and Henglein.

(3) Cl—Cl bond dissociation energy in the chlorine molecule

The technical difficulties associated with work at extremely high temperatures became serious and manifested themselves in the investigations of the dissociation process $Cl_2 \rightleftharpoons 2Cl$. The early workers were unable to observe any dissociation, even at temperatures as high as 1200°C. (e.g., see V. Mayer: Ber. **11,** 1426 (1879)). M. Trautz and W. Stäckel (205), who investigated the dissociation of chlorine under atmospheric pressure by heating it in a porcelain reaction vessel up to 1300°C., recorded 1.5 per cent decomposition at 1200°C. and 3 per cent decomposition at 1280°C. They calculated from these data the Cl—Cl bond dissociation energy at 70 kcal./mole, a value which is widely different from that accepted nowadays (57 kcal./mole). Undoubtedly, the degree of dissociation observed by them was too small to render the results accurate enough.

Much better results were obtained by F. A. Henglein (76), who carried out the investigation of the dissociation process of chlorine at pressures of the order of 10^{-3} mm. of mercury. Chlorine was heated in a silica reaction vessel which was enclosed in an evacuated platinum container. This arrangement was required in order to prevent the diffusion of hydrogen into the silica vessel.[7] The experiments were performed over a temperature range of 700° to 900°C. and the pressure was measured by the Haber–Kerschbaum fiber manometer. The Cl—Cl bond dissociation energy was estimated at 54 kcal./mole.

It is rather strange that in a preliminary communication H. von Wartenberg and F. A. Henglein (211), reporting the above studies, claimed the value of 70 kcal./mole for D(Cl—Cl).

(4) N—N bond dissociation energy in N_2O_4

The first experimental data on the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ were reported by E. Natanson and L. Natanson (120) in 1886, and used by K. Schreber (160) for the calculation of the heat of dissociation of N_2O_4, estimated by him at 13.1 kcal./mole.

E. Wourtzel (224) reinvestigated this equilibrium in 1919. His results, concordant with those of E. and L. Natanson, led to a slightly smaller value for the heat of dissociation: namely, 12.85 kcal./mole. About the same time M. Bodenstein *et al.* (21) reëxamined thoroughly the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$. The experimental technique was considerably improved by using an all-glass apparatus and a spiral manometer.[8] The final results were given for two sets of pressures, the so-called "higher" and "lower" constants. The results at the lower pressures were considered to be more reliable, since N_2O_4 does not follow the ideal gas law at pressures of the order of 1 atm. The heat of dissociation was estimated at 12.90 kcal./mole, showing a good agreement with results obtained by Wourtzel.

Bodenstein observed some displacement in the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ at higher temperatures (about 500°C.), and succeeded in proving that this was due to the reversible reaction $2NO_2 \rightleftharpoons 2NO + O_2$, which became appreciable at these temperatures.

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[7] Hydrogen was formed by the decomposition of water vapor present in the laboratory air, while in contact with the hot silica surface.

[8] The previous workers used greased stopcocks, rubber tubing for connections, and mercury manometers. All these materials are attacked by nitrogen dioxide vapor, and therefore their presence in the system introduces a considerable element of uncertainty in the interpretation of results.

The deviation of N_2O_4 from the ideal gas behavior is the source of some error in Bodenstein's computation of the heat of dissociation of N_2O_4. In order to remove this uncertainty F. Verhoek and F. Daniels (207) reinvestigated the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$, using a very sensitive glass-membrane manometer, and measured the equilibrium constants for decreasing pressures. They extrapolated the results to zero pressure, thus computing the heat of dissociation at zero pressure. The measurements were taken at 25.0°, 35.0°, and 45.0°C., in order to avoid any complications due to the decomposition of nitrogen dioxide. It was definitely proved that the presence of inert gases was without any influence on the equilibrium constant. The "corrected" heat of dissociation was estimated at 14.5–14.7 kcal./mole, i.e., considerably higher than the values proposed by previous workers.

Lastly it is necessary to consider which of the bonds is ruptured during the decomposition of the N_2O_4 molecule into NO_2. From the study of symmetry properties of the infrared absorption spectrum of N_2O_4 L. Harris and G. W. King (73) concluded that only those models where the NO_2 groups are joined by the nitrogen atoms would be compatible with the observed pattern. This conclusion is further supported by investigation of the electron diffraction of N_2O_4, which indicates that the N—N distance in the model $O_2N—NO_2$ is 1.6–1.7 Å. (L. R. Maxwell, V. M. Mosley, and L. S. Deming (109)). The results were confirmed by recent x-ray studies of N_2O_4 crystals (28). It is reasonable to conclude, therefore, that the fission takes place at the N—N bond and the observed heat of dissociation measures the N—N bond dissociation energy in N_2O_4.

(5) N—N bond dissociation energy in N_2O_3

The equilibrium $N_2O_3 \rightleftharpoons NO + NO_2$ was investigated at about the same time by E. Abel and J. Proisl (1) and by F. Verhoek and F. Daniels (207). The investigation was complicated by the fact that the above equilibrium takes place simultaneously with the equilibrium $2NO_2 \rightleftharpoons N_2O_4$, the system investigated being thus composed of the four species NO, NO_2, N_2O_3, and N_2O_4.

The heat of dissociation of N_2O_3, calculated from the van't Hoff isochore on the basis of data at 25°C. and 35°C. and extrapolated to zero pressure, was estimated by Verhoek and Daniels at 10 kcal./mole. The results obtained by Abel and Proisl pointed to the same value (9.5 kcal./mole).

D. Other static methods used for the determination of bond dissociation energies

It was shown in Section II that the static manometric method is not suitable for the determination of very small fractions of decomposition, since the results of computation are obtained as minute differences of large numbers derived from the direct measurements. To measure accurately the small extent of dissociation it is necessary to determine, by some direct method, the concentrations of the fragments formed in the process. This can be achieved either by a colorimetric method (if the respective fragment has an intense color) or by a magnetic method (utilizing the fact that the radicals are paramagnetic). Hexaphenylethane can serve as an example for both methods.

The first colorimetric estimation of the degree of dissociation of hexaphenylethane was due to J. Piccard (134) in 1911. The method was further elaborated and improved by K. Ziegler and L. Ewald (228), who determined the dissociation constants of the equilibrium

$$(C_6H_5)_3C{-}C(C_6H_5)_3 \rightleftharpoons 2(C_6H_5)_3C\cdot$$

in various solvents and over a range of temperature. Their results are listed in table 2.

Since the heat of dissociation appeared to be constant in all solvents it was concluded that it corresponds to the C—C bond dissociation energy in hexaphenylethane: $D[(C_6H_5)_3C{-}C(C_6H_5)_3] = 11.3 \pm 1$ kcal./mole. It must be emphasized, however, that the conclusions drawn from experiments carried out in the liquid phase are always uncertain, owing to the thermal effects connected with the solvation phenomena.

TABLE 2

Dissociation of hexaphenylethane

SOLVENT	DISSOCIATION CONSTANT AT 20°C.	HEAT OF DISSOCIATION
		kcal./mole
Propionitrile	1.2×10^{-4}	11.1
Ethyl benzoate	1.67×10^{-4}	12.0
Acetophenone	1.70×10^{-4}	11.5
Dioxane	2.5×10^{-4}	11.6
Bromobenzene	3.7×10^{-4}	11.5
Ethylene dibromide	3.9×10^{-4}	11.4
Benzene	4.1×10^{-4}	11.3
Chloroform	6.9×10^{-4}	10.5
Carbon disulfide	19.2×10^{-4}	11.0

TABLE 3

Dissociation of hexaphenylethane

TEMPERATURE	DISSOCIATION CONSTANT	HEAT OF DISSOCIATION
°C.		*kcal./mole*
23	1.5×10^{-4}	11.6 ± 1.7
75	53×10^{-4}	

E. Müller and I. Müller-Rodloff (117) investigated the equilibrium $(C_6H_5)_3CC(C_6H_5)_3 \rightleftharpoons 2(C_6H_5)_3C\cdot$ by measuring the magnetic susceptibility of the benzene solution. Although the equilibrium constants determined by these workers were smaller than those reported by Ziegler and Ewald, the heat of dissociation was found to be the same as that given by Ziegler (see table 3).

M. F. Roy and C. S. Marvel (158) reinvestigated the above dissociation process, using a magnetic method. Their results were in good agreement with Müller's observations, but later investigations of Marvel *et al.* (108) proved that the dissociation processes of many derivatives of hexaphenylethane were followed by some irreversible reactions which consumed the radicals produced. Thus, it was found that the paramagnetic susceptibility of solutions of these compounds was falling gradually with time, attaining eventually zero value. The true estimation of the degree of dissociation required, therefore, the determination of the magnetic susceptibility as a function of time and its extrapolation to zero time. In this way the degree of dissociation of a number of hexaphenylethane derivatives was determined. It is worth mentioning that although the paramagnetic susceptibility of the solutions disappeared, their color persisted. This observation casts doubt on the results obtained by the colorimetric method. Hexaphenylethane seems to be an exceptional case, since the triphenylmethyl radicals are not removed by the irreversible process mentioned above.

The studies of Marvel were continued by R. Preckel and P. W. Selwood (139). These workers estimated the heat of dissociation of several hexaphenylethane derivatives, measuring the degree of dissociation at various temperatures by a magnetic method and extrapolating the results to zero time. Their results are listed in table 4. They confirmed the great stability of triphenylmethyl radicals, although they found that at 100°C. even these radicals began to disappear, and thus the paramagnetic susceptibility was approaching zero after solution had been heated for 24 hr.

TABLE 4

Dissociation of hexaphenylethane derivatives

ETHANE DERIVATIVE	TEMPERATURE RANGE	ΔH	STABILITY
	°C.	*kcal./mole*	
Hexaphenyl	30–80	9.9	Stable
Di(*o*-tolyl)tetraphenyl	10–50	11.4	Labile
Di(α-naphthyl)tetraphenyl	−10–50	11.5	Labile

E. The bond dissociation energies of some diatomic metallic molecules

The dissociation energy of a variety of diatomic molecules composed of metal atoms has been estimated by measuring the changes in the intensity of the absorption bands of these molecules caused by the variation of the temperature. In principle, there is no difference between this method and the colorimetric method discussed in connection with the dissociation process of hexaphenylethane. The only peculiarity of the metal vapor system is the minute concentration of molecules as compared with the concentration of the atoms, and the former would therefore be considered as the labile species. Owing to the low dissociation energies of such molecules the measurements must be carried out over a large temperature range, of several hundred degrees. Difficulties are frequently caused by the low volatility of metals (e.g., cadmium) and compel the investigators to resort to long absorption cells. The type of investigation which has been carried out is illustrated by the following examples.

In 1925 E. Koernicke (92) published his results of the investigation of the 2540 Å. band which appears in the absorption spectrum of mercury. He demonstrated that this band is due to the presence of Hg_2 molecules in the mercury vapor, and by measuring the intensity of the band at various temperatures and under different pressures of mercury he estimated D(Hg—Hg) at 1.4 kcal./mole.

His work was repeated by H. Kuhn and K. Freudenberg (94), who measured the intensity of the 2540 Å. band at temperatures ranging from 500°C. to 1150°C. Their results were essentially concordant with those of Koernicke, and they recommended the value of 1.6 kcal./mole for D(Hg—Hg).

In 1944 this work was investigated again by J. G. Winans and M. P. Heitz (220), who calculated the dissociation energy of Hg_2 from measurements of the intensity of the 2345 bands by applying the Gibson–Heitler equation (64). This result was in agreement with those of previous investigators and yielded D(Hg—Hg) $= 1.38 \pm 0.07$ kcal./mole.

Following the work of S. Mrozowski (116), who demonstrated that the absorption band at 3178 Å. is due to the Cd_2 molecule, H. Kuhn and S. Arrhenius (93) measured the changes of the intensity of this band in the temperature region 1000–1450°K. The cadmium vapor was contained in a silica tube 60 cm. long heated by a special electric furnace. Their conclusion was that D(Cd—Cd) $= 2 \pm 0.5$ kcal./mole.

For some metallic molecules it was possible to deduce the heat of dissociation from the measurements of the vapor pressure and density of the respective metal vapors. For example, the investigations of the sodium vapor pressure–temperature relationship by W. H. Rodebush and E. G. Walters (155) and by R. Ladenburg and E. Thiele (95) proved the existence of Na_2 molecules in the vapor phase and according to E. Thiele (204) $P_{Na_2} = 119$ mm. of mercury at the boiling point of sodium. From these measurements D(Na—Na) was estimated at about 18 kcal./mole.

F. The equilibrium flow technique

It was mentioned in Section III,A that the occurrence of various irreversible processes, which may take place in an investigated system, is the source of the main difficulties encountered in the determination of bond dissociation energies by an equilibrium method. These processes are particularly likely to occur at high temperatures and when the period of heating is long. It is desirable, therefore, to reduce the time of heating as much as possible. The application of the flow technique is particularly advantageous in this respect.

In the flow 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 the proper adjustment of the rate of flow. The time of contact must be sufficiently long to enable the system under investigation to attain full equilibrium; however, this restriction is not a serious one, since the equilibrium state is attained in an extremely short period of time. 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 by some photometric method the concentration of the radicals (or atoms) produced by the dissociation process. 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 study of the equilibrium between $(CN)_2$ and CN radicals and the study of the system $2H_2O + O_2 \rightleftharpoons 4OH$.

G. B. Kistiakowsky and H. Gershinowitz were the first to investigate the equilibrium $(CN)_2 \rightleftharpoons 2CN$ (87). Cyanogen was made to flow through a silica tube 60 cm. long heated electrically to the required temperature. The concentration of CN radicals was measured by the intensity of the $0 \rightarrow 0$ band at 3883 Å., due to the transition $2\Sigma \rightarrow 2\Sigma^*$. The measurements were carried out over a temperature range of about 110°C. (1124–1238°C.). The heat of dissociation was calculated at 77 ± 4 kcal./mole.

The problem was reinvestigated by J. U. White (216), who pointed out how misleading the photometric determination of the CN concentration would be if the results were not corrected for the incomplete resolution of the spectrograph. From the lower limit of the absolute absorption coefficient of CN radicals he calculated their partial pressure at 1500°K. and from this data the equilibrium constant $K_{1500°\text{K.}} = 1.1 \times 10^{-12}$. A lower limit for the heat of reaction follows directly from calculations based on the partition functions of $(CN)_2$ and CN radicals. Thus the most probable value of the heat of dissociation of cyanogen was computed from these data at 146 ± 4 kcal./mole, a value which is obviously widely different from that obtained by Kistiakowsky and Gershinowitz.

There is little doubt that the Kistiakowsky and Gershinowitz value is too low, but it is by no means certain that White's value is correct. White's results have been criticized by G. Herzberg (79), who pointed out that they are less direct than those obtained by Kistiakowsky and Gershinowitz, as they are dependent on the determination of the partition function of $(CN)_2$. The investigations of the kinetics of hydrogenation of cyanogen by N. C. Robertson and R. N. Pease (152) seem to point to some value in between the two earlier ones, i.e., 120–130 kcal./mole; this is further supported by some photochemical studies of T. R. Hogness and Liu-Sheng Ts'ai (84). The whole controversy has recently been reviewed by H. D. Springall (165) and by L. H. Long (104).

The equilibrium $2H_2O + O_2 \rightleftharpoons 4OH$ was investigated for the first time by K. F. Bonhoeffer and H. Reichardt (25). This work followed the study of K. F. Bonhoeffer (23), who demonstrated qualitatively that the dissociation of water vapor takes place according to the equation $2H_2O \rightarrow H_2 + 2OH$ (the presence of OH radicals was demonstrated by the appearance of their absorption bands). They found that the latter equilibrium could be shifted by introducing oxygen into the heated steam, and thus they were able to maintain a constant concentration of OH radicals at various temperatures of the reaction vessel, by adjusting properly the partial pressure of oxygen. Using this technique Bonhoeffer and Reichardt estimated the relative equilibrium constants of the above reaction over temperatures ranging from 1200°C. to 1600°C. They concluded that $D(\text{HO—H})$ is about 115 ± 2.5 kcal./mole.

The above work was repeated very carefully by R. J. Dwyer and O. Oldenberg (50). Also these workers pointed out the systematic errors due to the lack of the resolving power of the spectrograph. For a quantitative test by the absorption spectrum rather weak absorption is desired, and although the average absorption observed with a spectrograph of poor resolving power may be weak, the actual absorption band contains many lines, each one of which at its middle almost completely absorbs the incident radiation. The above workers used, therefore, in their studies a spectrograph of high resolving power which allowed them to measure the absorption of single lines, and by matching the absorptions of two lines of equal intensity they tested the two reacting mixtures for equal density of OH radicals. The measurement of the intensity of a single line made it possible to observe the OH radicals at lower temperatures than those used by Bonhoeffer and Reichardt (the highest temperature being brought down from 1590°C. to 1100°C.), and thus to reduce considerably many technical difficulties caused by the extremely high temperatures.

The results were corrected for (*a*) the nonuniform temperature distribution, (*b*) the difference in the Boltzmann distribution between the two temperatures, i.e., the change in the population of the various rotational levels caused by the change of temperature, and (*c*) the variation ΔH_T over the temperature range T_1–T_2. The only source of systematic error which was known to the above workers was due to variations in the width of the line. The Doppler effect was responsible for one-third of the observed width of the line (126), the other two-thirds representing the pressure broadening. The pressure was of the order of 1 atm., but it was due to a mixture of water vapor and oxygen in various proportions. The observations, however, showed that the broadening effect of O_2 and H_2O on the absorption lines of OH was practically the same.

As a result of this very careful piece of work Dwyer and Oldenberg were led to conclude that

$$H_2 + 2(OH) = 2H_2O(g) - 133.8 \pm 1.3 \text{ kcal./mole}$$

This result, in conjunction with $D(\text{H—H}) = 102.48$ kcal./mole as computed by H. Beutler (18), led them to $D(\text{HO—H}) = 118.2 \pm 0.7$ kcal./mole. If instead we use $D(\text{H—H}) = 103.22$, as recommended by A. G. Gaydon (60), we obtain $D(\text{HO—H}) = 118.5 \pm 0.7$ kcal./mole. This value leads to $D(\text{O—H}) = 101$ kcal./mole.

The various methods of determination of $D(\text{H—OH})$ have been reviewed recently by O. Oldenberg (125).

G. The effusion method

The laws of gas effusion through an orifice the diameter of which is small in comparison with the mean free path of a molecule have been worked out by Knudsen (89), who deduced that the mass m of a gas which effuses in time t through an orifice of cross-sectional area A is given by

$$m = \frac{1}{4}(N_1 - N_2) \cdot \frac{M}{N_0} \cdot \bar{u}At$$

where N_1 and N_2 denote the number of molecules per milliliter present on each side of a membrane, respectively, M is the molecular weight of the gas, N_0 is the Avogadro number, and $\bar{u}$ is the mean thermal velocity of the molecules. Where the gas concentration on one side of an orifice may be neglected in comparison with the concentration on the other side, then:

$$m = \frac{1}{4} \cdot N_1 \cdot \frac{M}{N_0} \cdot \bar{u}At$$

A determination of the rate of effusion makes it possible therefore to estimate the pressure of the gas (which is proportional to N_1) if the molecular weight is known, or to estimate the molecular weight if the pressure is known. Thus, for example, Knudsen determined the vapor pressure of mercury (90), and by means of similar measurements the vapor pressures of zinc, cadmium, and other metals (see, for example, Egerton (51)) were measured.

It is simple to prove that for a mixture of gases effusing through an orifice, the rate of effusion of each component is equal to its rate of effusion if it were present alone and at a pressure equal to its partial pressure in the mixture. This relationship holds, of course, only if the mean free path of the molecules in the mixture is large in comparison to the diameter of the orifice. It is possible, therefore, to use the phenomenon of effusion to estimate the mean molecular weight of partially dissociated gas. Consideration of Knudsen's formula shows that the rate of effusion is proportional to the average thermal velocity of the molecules and the latter is inversely proportional to the square root of its molecular weight. Therefore, if the pressure of the gas is kept constant, then the rates of effusion of an undissociated and fully dissociated gas would be in the ratio of $1:\sqrt{2}$. It must be pointed out that the greatest possible change in the rate of effusion, due to the dissociation process, amounts to about 40 per cent only. Hence it is essential to determine the rates of effusion very accurately if we are to obtain reliable data on the degree of dissociation. The latter can be evaluated by using a formula which is derived from Knudsen's formula:

$$m = (M/2\pi \cdot RT)^{1/2} \cdot AtP \cdot (1 - \alpha + \sqrt{2}\alpha)/(1 + \alpha)$$

m, M, A, and t have the meanings given before, while R denotes the gas constant, T the absolute temperature of the space surrounding the orifice, P the total pressure of the gas (assuming that its pressure on the other side of the orifice is negligible), and α the degree of dissociation.

The actual performance of the experiment requires the fulfillment of several conditions which have been discussed by H. Weide and F. R. Bichowsky (213): (*1*) the hole must be small in comparison with the mean free path of the gas and the thickness of the plate in which it is made must be small in comparison with the diameter of the hole (the recommended thickness of the plate is 0.1 of the diameter of the orifice); (*2*) the chamber on the high-pressure side of the hole must be large in comparison with the mean free path of the gas; (*3*) the gas on the high-pressure side must be in thermal and pressure equilibrium over a region which is in the neighborhood of the hole and large in comparison with the mean free path of the gas.

The last condition requires that the rate of effusion should be small in comparison with the rate of diffusion of the gas from its source to the space which is near the orifice. This means that the "time of contact," i.e., the average time spent by the molecules of the gas in the heated chamber which is near the hole, cannot be too short. This is rather unfortunate, because it favors the occurrence of the side reactions discussed in Section III,A.

The effusion method is, therefore, less suitable than the equilibrium flow technique in the investigations of the dissociation process $R_2 \rightleftharpoons 2R$, in which R is a radical, particularly if the temperature required to break the R—R bond is high and the radical R has not a great thermal stability. It is worth noting that the low pressure which is used in the effusion technique makes it possible to work at lower temperatures, but on the other hand it is necessary to have a high degree of dissociation (not less than about 30 per cent) in order to obtain reliable results, and that requires higher temperatures. However, the effusion method seems to compete well with the static manometric method in the region of low pressures. It was mentioned earlier (see page 86) that the great difficulty encountered in the static manometric method in the low-pressure region is due to the adsorption of radicals or molecules on the walls of the reaction vessel, and this difficulty is amplified if there is some corrosion of the wall. These effects are of no importance in the effusion method,[9] since only the amount of substance which effuses is measured and one is not concerned with the amount of substance introduced into the reaction vessel. The following example makes this point clearer. Let us say that the heat of dissociation of fluorine is to be measured. The gas attacks the walls of most reaction vessels, particularly at high temperature. The investigation should be carried out, therefore, at low temperatures (let us say in the region of 400°C.), and in order to obtain a measurable degree of dissociation it is necessary to work at very low pressures. The manometric method seems to be of no great use, because of the corrosion of the wall which is unavoidable in this case. On the other hand, the effusion method may be used, since it requires only that a constant low pressure be maintained on one side of the hole and that the quantity of effused fluorine be measured. The corrosion of the vessel walls is of no importance, with the exception of the slight change in diameter of the orifice, for which a correction may be introduced based on measurements of its cross-sectional area before and after each experiment.

The effusion method was used by T. DeVries and W. H. Rodebush (45) in the determination of the dissociation energies of iodine and bromine. Great stress was laid upon the necessity of maintaining a constant pressure in the apparatus. For example, the pressure of iodine was kept constant by having a reservoir of iodine crystals maintained at a constant temperature of ice water, and it was pointed out that variations of temperature of a few hundredths of a degree would change the vapor pressure sufficiently to make a determination worthless.

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[9] In the case when corrosion of the wall produces volatile materials the required correction must be introduced by analyzing the composition of the substance which has effused.

Special precautions were taken to avoid changes of vapor pressure caused by the distillation of the smaller crystals on to the larger ones, and attention was called to the conditions under which there is satisfactory thermal contact between the crystals and the external wall of the reservoir.

The various technical difficulties were adequately resolved in the case of iodine, but a less satisfactory solution was achieved in the case of bromine. These authors estimated D(I—I) at 31.6 kcal./mole and D(Br—Br) at 41.2 kcal./mole. Both values seem to be too low by a few kilocalories per mole.

E. Wrede (223) suggested the following modification of the effusion method: Two compartments are divided by a wall perforated by one or several orifices. Owing to some dissociation process, there is a mixture of undissociated and dissociated species in one compartment, while there is a full recombination in the second compartment. In consequence, there is a stationary difference in pressures on both sides of the orifice which measures the degree of dissociation. This method is not suitable for the estimation of the degree of thermal dissociation, since by keeping both compartments at different temperatures additional difference of pressures is introduced which decreases the sensitivity of the method.

H. The hot wire method

The characteristic feature of the hot wire method is the mode by which the heat is supplied to the molecules which eventually dissociate. In the experimental arrangement the molecules of the gas investigated strike the surface of a hot wire, heated to the required temperature, and in consequence of these impacts they may dissociate into some fragments. The actual process of dissociation is investigated either by measuring the amount of heat carried away from the wire (the conductometric method), or by determining the rate of the dissociation process (the thermal equilibrium method).

The conductometric method was developed by the pioneer work of I. Langmuir (97), who made the observation that a layer of stationary gas seems to surround a hot wire, and that the heat carried away from the wire through this layer is transferred by a pure conduction process and not by a convection process. The amount of heat removed by conduction is determined as the difference between the amounts of heat lost by the wire when surrounded by the gas investigated and when heated in the high vacuum, provided of course that the temperature of the wire is the same in both cases. According to Langmuir the heat carried away by the conduction process may be calculated by the following formula

$$W_c = S(\varphi_2 - \varphi_1)$$

where W_c denotes the rate of heat loss from a unit surface of the wire, S (called by Langmuir the shape factor) is a coefficient which depends on the geometry of the lamp and the nature of the gas, and φ_2 and φ_1 are functions of the temperatures of the wire and the cooling agent, respectively. Further considerations of this phenomenon led Langmuir to the following expressions for S, φ_2, and φ_1:

$$S = \text{const. } 2\pi/\ln (b/a)$$

b denoting the thickness of the stationary layer of gas which surrounds the wire and a denoting the diameter of the wire, while the constant depends on the units used in the computation.

$$\varphi_2 = \int_0^{T_2} k \, \mathrm{d}T; \qquad \varphi_1 = \int_0^{T_1} k \, \mathrm{d}T$$

where T_2 and T_1 denote the temperatures of the wire and the cooling agent, respectively, and k denotes the specific conductivity of the gas investigated.

Langmuir deduced also that $b \ln (b/a)$ is a constant which depends on the nature and pressure of the gas investigated but is independent of the diameter and the temperature of the wire. All these theoretical deductions he confirmed by a series of accurate measurements of the heat lost by wires maintained at various temperatures and surrounded by a variety of gases under various pressures.

The above treatment requires, however, some modification if the gas investigated dissociates on the surface of the wire. The theory of the heat conduction in a dissociating gas was also developed by Langmuir and reported in a subsequent paper (98). The heat carried away from the wire (deducting the loss due to radiation) was represented by:

$$W = W_c + W_D$$

W_c having the same meaning as before, while W_D represents the amount of heat carried away by the dissociating particles during the process of dissociation. This heat is subsequently transferred to the cooling agent during the recombination process. For the sake of clarity we restrict this discussion to the dissociation of hydrogen on a hot wire. The hydrogen atoms produced in the dissociation process diffuse away from the immediate vicinity of the wire to the outside, the rate of the diffusion being dependent on the gradient of concentration, $\mathrm{d}c/\mathrm{d}x$. Assuming that c is given by the *equilibrium concentration* of hydrogen atoms determined by the temperature corresponding to the appropriate point in the stationary layer of the gas surrounding the hot wire, and taking into account that each gram-atom of hydrogen disappearing from the gas phase produced $\frac{1}{2}Q$ kcal. (Q being the heat of dissociation $H_2 \rightleftharpoons 2H$), Langmuir concluded that

$$W_D = \tfrac{1}{2}QSc_0D$$

c_0 denoting the initial concentration of hydrogen atoms in the immediate vicinity of the wire and D being the diffusion constant of hydrogen atoms in a medium of hydrogen molecules. W_D is calculated from the total observable heat lost (W) and the extrapolated value of W_c, using for the extrapolation the values obtained for $W \approx W_c$ in the temperature region in which the dissociation is negligible.

If c_0 is equal to the equilibrium concentration of hydrogen atoms corresponding to the temperature of the wire, then it is possible to calculate Q from the temperature dependence of W_D. This type of calculation led Langmuir to the conclusion that $D(\mathrm{H—H})$ is about 130 kcal./mole.

The method described here was criticized by Langmuir (99) himself, who emphasized the doubtful nature of two assumptions involved in the deduction: (*a*) the assumption that the gas in the vicinity of the wire attains the same temperature as the wire and that c_0 is equal to the equilibrium concentration of hydrogen atoms at this temperature; and (*b*) the assumption that the shape factor S remains the same over the whole temperature range, the latter assumption being a particularly great source of error, since the calculated value of Q is extremely sensitive to small changes in S (it affects both the calculated value of W_D from $W - W_c$, and the value of dW_D/dT). Langmuir developed therefore an alternative treatment (99), in which allowances were made for accommodation coefficients different from 1 by introducing two constants α_1 and α_2, which denote the fractions of hydrogen atoms and hydrogen molecules adsorbed on the wire. Assumption (*b*) was also avoided by deriving a formula for the equilibrium constant

$$K = \frac{(W/Q)^2(P/D + 1/\alpha_1)^2}{P - (W/Q)(P/D - 1/\alpha_2)^2}$$

and choosing the "best" set of values for the constants K, D, α_1, and α_2, i.e., for which the best agreement was obtained between the calculated and observed values of W corresponding to various pressures P. This treatment yielded a value of 84 kcal./mole for Q (at constant volume) and 90 kcal./mole (for constant pressure).

The method can be simplified considerably if one determines directly the rate of the dissociation process. This can be achieved if every atom produced by the dissociation process is trapped and removed from the system. This was the case in the experiments performed by G. Bryce (32). A tungsten wire was heated in hydrogen maintained under a pressure sufficiently low to enable every hydrogen atom emitted from the hot wire to be adsorbed on the surface of molybdenum oxide. Thus the rate of dissociation was measured by the rate of decrease of pressure due to the adsorption of hydrogen atoms.

The data obtained in this way may be utilized in two ways. One determines the loss of heat from the wire and by extrapolation estimates the loss due to the undissociated molecules (using for the extrapolation the data obtained at the temperatures at which the dissociation is negligible). Thus the heat transferred by the atoms is computable, and, their number being known, the dissociation energy may be deduced. The calculation requires, however, a correction for the kinetic energy of the atoms, which would only be calculable if the accommodation coefficient is 1.

The second possibility is to assume that the accommodation coefficient is 1. The numbers of molecules and atoms leaving the wire would then obey the equilibrium condition. Since the total mass of particles leaving the wire must be equal to the mass of hydrogen molecules striking the wire, and the latter is given by the kinetic theory if we know the pressure and temperature of the gas in the tube, then the estimation of the mass of hydrogen atoms produced leads directly to the equilibrium constant for $H_2 \rightleftharpoons 2H$ dissociation at the temperature of the wire. P. M. Doty (47), using the experimental results of Bryce (32), demonstrated that the calculated equilibrium constant, on the assumption of an accommodation coefficient equal to 1, agreed fairly well with the value derived from spectroscopic data. He concluded, therefore, that in this case the accommodation coefficient is indeed equal to 1. The equilibrium constant being known, the heat of dissociation may be calculated by applying the equation of the van't Hoff isochore.

An interesting modification of the hot wire technique was introduced by P. P. Sutton and J. E. Mayer (181). They developed a device which made it possible to measure the current due to the flow of electrons and negative ions emitted from the hot wire. Moreover, this device enabled them to estimate separately the extent to which both species participated in the current measured. The results obtained in this way were used by Mayer and his colleagues for the estimation of the electron affinity of chlorine (105, 115), bromine (49), iodine (181), and oxygen (112, 208). The method of computation was based on the *assumption* that the accommodation coefficient of the molecules used in these experiments was equal to 1, and the final results provided a fair *a posteriori* justification for this assumption.

P. M. Doty (48) applied the above method to the determination of the C—Cl bond dissociation energy in methyl chloride and carbon tetrachloride. If the accommodation coefficient is 1, then the molecules of methyl chloride striking the surface of the hot wire would attain thermal equilibrium. That is to say, the number of methyl radicals, chlorine atoms, and undissociated molecules of methyl chloride leaving a unit surface of the wire in every second would be equal to the number of the respective species hitting this surface in a unit of time, provided the wire is in an atmosphere of a hypothetical gas composed of CH_3, Cl, and CH_3Cl in an equilibrium corresponding to the temperature of the wire. We calculate the number of molecules hitting the unit surface, using the formula provided by the kinetic theory of gases:

$$Z_{CH_3} = \frac{P_{CH_3}}{(2\pi M_{CH_3} kT_s)^{1/2}}; \qquad Z_{Cl} = \frac{P_{Cl}}{(2\pi M_{Cl} kT_s)^{1/2}};$$

$$Z_{CH_3Cl} = \frac{P_{CH_3Cl}}{(2\pi M_{CH_3Cl} kT_s)^{1/2}}$$

Taking $P_{CH_3} = P_{Cl}$ and knowing that the total mass of the species leaving the wire must be equal to the mass of methyl chloride molecules *actually* striking the wire (the latter is obtained from the pressure and temperature of methyl chloride introduced to the apparatus), we calculate the equilibrium constant, K_1,

$$K_1 = \frac{(P_{Cl})^2}{P_{CH_3Cl}}$$

in terms of one unknown only, that is, P_{Cl}. Now the chlorine atoms are in equilibrium with the chloride ions and electrons and thus

$$K_2 = \frac{P_{Cl^-}}{P_{Cl} \cdot P_e}$$

P_{Cl^-} and P_e denoting the partial pressures of the hypothetical chloride ions and electron gases which are in thermal equilibrium with chlorine atoms. Since P_{Cl^-} is much smaller than P_{Cl}, the second equilibrium does not affect the first one. The ratio P_{Cl^-}/P_e is computed from the ratio of i_{Cl^-}/i_e, i_{Cl^-} and i_e denoting the currents due to the flow of chloride ions and electrons, respectively.

$$P_{Cl^-}/P_e = (i_{Cl^-}/i_e)\cdot(M_{Cl}/M_e)^{1/2}$$

M_{Cl} and M_e being the masses of the chlorine atom and the electron, respectively.

One concludes therefore that:

$$P_{Cl} = (i_{Cl^-}/i_e)(M_{Cl}/M_e)^{1/2}\cdot K_2^{-1}$$

Since K_2 is given by the known partition functions of electrons, chlorine atoms, and chloride ions, in conjunction with the known electron affinity of chlorine atoms, the measurement of i_{Cl^-}/i_e determines P_{Cl}, and by that K_1. The determination of the heat of dissociation is then straightforward.

Again it must be emphasized that all the methods discussed above are based on the assumption of accommodation coefficients equal to 1. Doty found, however, that the accommodation coefficients for both methyl chloride and carbon tetrachloride were appreciably smaller than 1. In spite of that he obtained a good straight line by plotting the logarithm of the quasi-equilibrium constant against $1/T$, and he concluded therefore that the "apparent" heat of reaction, given by the slope of this line, was identical with the "true" heat of reaction. His confidence was increased by the fact that the "apparent" heat of reaction estimated by him at 74 kcal./mole was well within the range of the "bond energies" of the C—Cl bond as quoted by Pauling at 66.5 kcal./mole (132) and by O. K. Rice at 73 kcal./mole (149). These values, however, represent the "average bond energy," while Doty tried to estimate the bond dissociation energy. The latter seems to be 80–81 kcal./mole, as computed from the heats of formation of methyl chloride and the methyl radical, respectively. It seems, therefore, that the results obtained from the quasi-equilibrium constant should be regarded with a good deal of suspicion.

I. The molecular beam method

If some molecule, say X_2, dissociates into 2X, then one may estimate the relative concentrations of X_2 and X in the equilibrium mixture by applying a molecular beam technique (see R. G. J. Fraser (59)). The investigation may be carried out either by separating atoms and molecules with the aid of a magnetic field and counting both species separately, or by investigating the velocity distribution in the beam.

The separation of the atoms and molecules in a mixed beam can be effected if the molecules are diamagnetic while the atoms have a magnetic moment. Performing a Stern–Gerlach experiment (63) on a mixed atomic-molecular beam one deflects the atoms right and left without influencing the molecules, which are unaffected by the field.

The first observations of this kind were made on bismuth by A. Leu (101), who measured the temperature dependence of the line which corresponded to Bi_2 molecules, and thus deduced that D(Bi—Bi) = 56 kcal./mole. This result was very rough, and in addition R. G. J. Fraser pointed out (63) that Leu made several mistakes in his interpretation of the experimental observations. Corrections introduced by Fraser reduced the value of D(Bi—Bi) to 26 ± 12 kcal./mole.

The technique was developed further by L. C. Lewis (103), who examined the dissociation energies of Li_2, Na_2, and K_2. His results are given in table 5. This work was repeated by W. Meissner and H. Scheffers (110), whose results checked those obtained by Lewis within 5 per cent.

The velocity distribution method applies the slotted-disc velocity sectors devised by B. Lammert (96), which make it possible to estimate the relative amount of molecules (or atoms) moving with some definite velocity. If the beam is composed of one species only, the plot of the fraction of the species moving with velocity ϑ against ϑ produces one maximum only which corresponds to the most probable velocity. If, however, two species are present in the beam, e.g., atoms and diatomic molecules, then the distribution curve shows two maxima. Analysis of such a curve might lead to the information required for the calculation of the bond dissociation energy.

TABLE 5

Dissociation energies of alkali metal molecules determined by molecular beam method

SUBSTANCE	D_0
	kcal./mole
Li_2	22.7
Na_2	16.5
K_2	15.0

This method was utilized by I. F. Zartman (226) for the investigation of the dissociation process $Bi_2 \rightleftharpoons 2Bi$. He concluded that under his experimental conditions, at 851°C., the beam was composed of 40 per cent bismuth atoms and 60 per cent bismuth molecules (Bi_2).

Similar work was carried out by Cheng Chuan Ko (91). This author estimated the equilibrium constant for the dissociation process $Bi_2 \rightleftharpoons 2Bi$ by measuring the distribution curve over the temperature range 827–947°C. The total pressure was estimated by an independent measurement of the rate of effusion. The accuracy claimed by this author was 1 per cent, but the estimated D(Bi—Bi) at about 77 kcal./mole cast doubt as to the reliability of the method.

J. The chemiluminescence method

A very elegant method for the estimation of the bond dissociation energy of the diatomic alkali metal molecules was developed by M. Polanyi (135). His studies of reactions between highly diluted halogens and alkali metals revealed the phenomenon of chemiluminescence which was explained by the occurrence of the reaction $Cl + Na_2 \rightarrow NaCl + Na^*$, where Na^* denotes an excited sodium atom which emits the observed radiation. The intensity of the chemiluminescence is dependent on the concentration of Na_2 molecules, and the latter decreases, of course, with increasing temperature. According to this mechanism the intensity of chemiluminescence should decrease with the overheating of the reaction zone, and the experiment confirmed fully this conclusion. The temperature dependence of the intensity of the chemiluminescence made it possible to estimate D(Na—Na) and the measurements by M. Polanyi and G. Schay (136) allowed them to calculate D(Na—Na) at 18 ± 2 kcal./mole.

This type of experiment carried out in Polanyi's laboratories by H. Ootuka made it possible to estimate D(Na—Na) at 19 ± 1 kcal./mole (127) and D(K—K) at 12.5 kcal./mole (128). These values compare favorably with the "best" values recommended by A. G. Gaydon (60): namely, D(Na—Na) = 17.8 kcal./mole and D(K—K) = 11.8 kcal./mole.

K. The explosion method

The heat liberated in the explosion of a hydrogen-oxygen mixture is used for heating a known amount of gas. Since the amount of heat liberated is known, it is possible to calculate the maximum temperature of the mixture providing the required specific heats of the components are known. The maximum temperature may be estimated from the maximum pressure developed in the combustion bomb. This is the principle of the method developed by Bunsen and by Nernst for direct measurements of the specific heats at constant volume (see, for example, A. Eucken (53)).

The estimation of the specific heat by spectroscopic methods makes it possible to compare the calculated and observable maximum temperatures. It was found that the observable temperature was frequently too low and it was assumed that the discrepancy was due to the dissociation process: e.g., $2H_2O \rightleftharpoons H_2 + 2OH$. It was feasible, therefore, to calculate the dissociation energy from the data obtained by the explosion method. This type of determination was carried out by K. Wohl and G. von Elbe (221) and K. Wohl and M. Magat (222); the best results were obtained by B. Lewis and G. von Elbe (102), who estimated D(HO—H) at 114 ± 1 kcal./mole.

The method is not very reliable, and has been criticized in an article published by A. Eucken in *Handbuch der experimentalen Physik* (53).

IV. THE KINETIC METHOD OF ESTIMATING THE BOND DISSOCIATION ENERGY

A. Principles

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 the two fragments, R′ and R″, produced by the rupture of the bond in question. It is very probable that the recombination of the fragments formed in the dissociation process does not require any activation energy,[10] 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.[11] 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 (see, for example, page 138). 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. Nevertheless, it should be stressed that, if the activation of the recombination process has a finite value, then the value of the bond dissociation energy obtained by the kinetic method will be too high. In such a case it will represent only the upper limit of 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, and in Section IV,D it is shown that this "experimental activation energy" is identical for all practical purposes with the bond dissociation energy. 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 estimated 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 experiments carried out in the region of 1000°K. Let us assume that both rate constants, estimated at T_1 and T_2, respectively, are uncertain by about 20 per cent each; then the maximum experimental error of the computed activation energy is:

$$E = 2 \times 2.3 \times \ln (1.2/0.8)/(10^{-4} \times 1000) \text{ kcal./mole} = 8.1 \text{ kcal./mole}$$

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,

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[10] This problem was discussed previously in Section I,G.

[11] The relationship between the experimental activation energy of the unimolecular dissociation process and the bond dissociation energy is discussed in detail in Section IV,D.

the main reaction, which is the subject of investigation, is accompanied by some side reaction the relative extent of which continuously increases or decreases with the temperature. The reader will find examples of such reactions in the following sections.

It is essential, therefore, to find experimental conditions under which all side reactions are suppressed as far as possible. Only under these circumstances can one expect to be able to determine accurately the "true" activation energy of the process from the temperature coefficient of the rate constant.

B. Estimation of the bond dissociation energy if the frequency factor of the unimolecular dissociation rate constant is known

In the preceding section we have discussed the difficulties encountered in the computation of the activation energy from the temperature coefficient. Fortunately these values of the activation energy can sometimes be checked by calculating the frequency factor of the unimolecular rate constant.

The absolute rate of the truly unimolecular reaction may be expressed by:

$$k = \nu \cdot e^{-E/RT}$$

where ν, the so-called frequency factor, should have a value of the order of 10^{13} sec.$^{-1}$ This result was deduced for the first time by M. Polanyi and E. Wigner (137), and the subsequent development of the theory of the absolute rate constants of unimolecular reactions has provided further arguments in favor of such an order of magnitude for ν (65).

In Section IV,D the theory of the absolute rate constant of a unimolecular dissociation process is discussed further, together with experimental evidence favoring the theoretical deductions. At this point we assume that the frequency factor of a unimolecular dissociation is known, and consider the consequences of such an assumption for the problem of determining bond dissociation energies by kinetic methods.

Suppose that the frequency factor of some unimolecular dissociation is known to be 1×10^{13} sec.$^{-1}$ This information might be utilized in two ways:

(a) If the temperature coefficient of the rate constant of the unimolecular dissociation has been determined, then we are able to calculate the experimental activation energy and from this the experimental frequency factor. If the latter entity comes out at about 1×10^{13} sec.$^{-1}$, then we have a further argument supporting the conclusion that the estimated "experimental activation energy" is the "true activation energy," i.e., is equal to the bond dissociation energy.

(b) If the temperature coefficient of the unimolecular rate constant has not been estimated, or if it cannot be estimated owing to some technical difficulties, then we are able to calculate the "true activation energy" from the absolute value of the rate constant determined at one temperature only.

Let us illustrate the latter 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:

$$k = 1 \times 10^{13} \times e^{-E/RT}$$

we derive

$$E = 2.3(13 - \log k) \cdot RT/1000 \text{ kcal./mole}$$

i.e.,

$$E = 2.3(13 + 2)2.800/1000 \text{ kcal./mole}$$

$$= 55 \text{ kcal./mole.}$$

The examination of the expression $E = 2.3(13 - \log k)RT/1000$ 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 per cent produces an error of only 1.1 kcal./mole in the E 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. Thus an error in ν by a factor of 5 produces in the above numerical example an error in E which amounts to 2.6 kcal./mole.

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 per cent in the estimated rate constants produce an error of 8.1 kcal./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 to this unimolecular decomposition can be estimated fairly accurately by the application of the expression:

$$E = (13 - \log k)2.3RT/1000 \text{ kcal./mole}$$ [12]

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 as the more re-

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[12] The value of 13 was chosen on both theoretical and experimental grounds. The experimental evidence is listed in Section IV,D, and it seems to indicate that for a variety of unimolecular dissociations (caused by rupture of one bond only) the "true" values of ν do not vary by more than a factor of 5 from 10^{13} sec.$^{-1}$

liable. This point, fully appreciated by E. T. Butler and M. Polanyi (35), is discussed on page 123.

C. Estimation of the differences in bond dissociation energies in series of similar molecules

In Section IV,B 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 RX, 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 $RX \rightarrow R + X$ are identical. If this is the case then the difference $D(R'—X) - D(R''—X)$, R′ and R″ 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 following expression:

$$D(\mathrm{R}'\text{—X}) - D(\mathrm{R}''\text{—X}) = 2.3RT \ln (k_2/k_1)$$

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 $D(R—X)$ requires neither a knowledge of the frequency factor, nor 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. (See, however, page 128 for an example of the misuse of this method.)

We must now examine evidence supporting the assumption of the constancy of the frequency factors in the series of unimolecular dissociations under discussion. There is evidence that in any series of reactions in which one varies the components without influencing the reaction centers (e.g., by substitution) the frequency factor (i.e., the temperature-independent factor) remains constant for the whole series.

Thus, C. K. Ingold and W. S. Nathan (85) estimated the activation energies for the hydrolysis of various substituted benzoic esters. The plot of the estimated activation energies *versus* log k (k being the rate constant of hydrolysis) gives a straight line, proving that the frequency factors remain constant throughout the whole series. These authors also drew attention to the results obtained by E. G. Williams and C. N. Hinshelwood (219) for the kinetics of benzoylation of various substituted anilines. A similar plot of E *versus* log k obtained by the latter authors gave a straight line which was parallel to that obtained by Ingold and Nathan. The idea of the constant frequency factors in a series of kindred reactions was developed further by L. P. Hammett (70), who devised a system of σ and ρ factors; ρ represents an entropy change constant for the same type of reaction, and σ represents the change in activation energy characteristic for each member of the series.

M. Szwarc (183, 186) estimated directly the frequency factors of a series of unimolecular dissociations of the type $C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot + H$, and found that, within experimental errors, they are identical for toluene, *m*-xylene, *p*-xylene, and *o*-xylene. The tabulated frequency factors of the xylenes are halved, since the presence of two methyl groups doubles the rate of the decomposition as a purely statistical effect. The same values for the frequency factors were obtained by M. Szwarc and A. Shaw (200) for the unimolecular dissociations of methylated naphthalenes. These results are given in table 6.

TABLE 6

Dissociation of methylated benzenes and naphthalenes

COMPOUND	THE FREQUENCY FACTOR FOR THE UNIMOLECULAR DISSOCIATION RH → R + H, CALCULATED PER METHYL GROUP
Toluene	2×10^{13} sec.$^{-1}$
m-Xylene	2×10^{13} sec.$^{-1}$
p-Xylene	2.5×10^{13} sec.$^{-1}$
o-Xylene	2.5×10^{13} sec.$^{-1}$
α-Methylnaphthalene	1.5×10^{13} sec.$^{-1}$
β-Methylnaphthalene	1.5×10^{13} sec.$^{-1}$

The direct estimation of the frequency factor is subject to some experimental error, e.g., the values quoted in table 6 are uncertain within a factor of 2–3. There is, however, a more accurate way of demonstrating the constancy of the frequency factors. It would seem that there is no relationship whatever between the frequency factor of a reaction and its activation energy. The theoretical treatment of this problem indicates that the causes of variations in activation energies and in frequency factors are to be traced to quite different sources. It is therefore extremely improbable that in a series of similar decompositions the variations in activation energy would be just balanced by the variation in frequency factor, thus leaving unchanged the rate constant of the reaction. For example, it was observed that the rate constants of the decomposition of toluene, *m*-xylene[13] (186), the *p*-, *m*-, and *o*-fluorotoluenes (196), and γ-picoline (151) were all equal within 25 per cent. It was demonstrated that all these reactions are of the same type:

$$RH \rightarrow R + H$$

There is no reason to expect changes in the C—H bond dissociation energies in any of these compounds (see reference 196), and the equality of all these rate constants is, in the writer's opinion, the strongest argument in favor of the assumption of the constancy of the frequency factors in a series of similar decompositions. The same conclusion follows from the results of M. Szwarc and A. Shaw (200), who found identical rate constants for the unimolecular decompositions of α-methylnaphthalene, β-methylnaphthalene, and 1,6-dimethylnaphthalene.[13]

We conclude, therefore, that there is full justification for computing the differences in bond dissociation energies caused by various substitutions in a given molecule, by comparing the relative rate constants of the respective *unimolecular* dissociation processes.

D. *Theoretical treatment of unimolecular dissociation*

In the theoretical treatment of unimolecular reactions we have to distinguish between two aspects of this phenomenon: activation and decomposition.

By activation we understand the process of energy transfer from the molecules of the system to some particular molecule which thus becomes "activated." This process is the result of a successful series of collisions in which the molecule eventually activated participates, and it is, therefore, essentially a bimolecular process obeying second-order kinetics. Hence the rate of activation, irrespective of the mechanism, is proportional to the partial pressure of the compound which yields the activated species and to the total pressure in the system.[14] The proportionality coefficient depends on the nature of the molecules composing the system, different molecules having different specific power of accepting or transferring energy.

By decomposition we understand the process of spontaneous dissociation of the "activated" molecule into products. The probability of this dissociation is characteristic of the "activated" molecule, being independent of the total pressure. It follows, therefore, that the rate of decomposition is proportional to the concentration of "activated" molecules.

A discussion of the mechanism and rate of the energy-transfer process is beyond the scope of this paper. We assume that in all cases discussed further the rate of activation is much higher than the rate of decomposition and that most of the "activated" molecules are deactivated by subsequent collisions with surrounding molecules. This assumption, which is the basis of Lindemann's theory, leads to the conclusion that the concentration of "activated" molecules is given approximately by the equilibrium distribution of the energy of the system amongst all the molecules of which it is composed. Provided that the pressure in the system is high enough,[15] the energy-transfer process will be sufficiently

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[13] The rates of decomposition of *m*-xylene and of 1,6-dimethylnaphthalene are halved, and thus they represent the "rate of decomposition per one methyl group."

[14] If the system contains only one type of molecule, the rate of activation is proportional to the square of the pressure.

[15] It seems that, for sufficiently complex molecules, the energy-transfer process is rapid even at pressures as low as a few millimeters of mercury. However, for small molecules containing three or four atoms, the pressure required seems to be much higher.

rapid to maintain the appropriate stationary concentration of "activated" molecules.

In order to calculate the rate of a unimolecular decomposition we apply the transition-state method. There is, however, some difficulty in defining the transition-state complex (sometimes called "activated complex"), and in this respect two different types of unimolecular decompositions should be distinguished:

1. Decompositions leading to the formation of two products, recombination of which involves an activation energy, e.g.:

$$C_2H_5Br \rightarrow C_2H_4 + HBr$$

2. Decompositions leading to the formation of two fragments, recombination of which requires no activation energy. This case is particularly important for us, as it covers the dissociation of the molecule into two radicals.

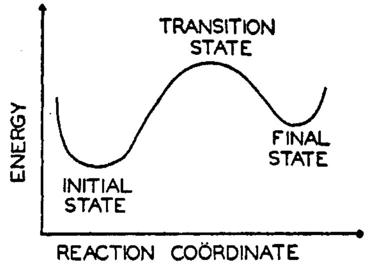

FIG. 1

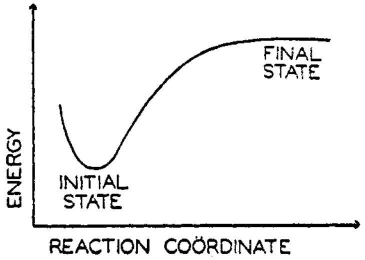

FIG. 2

In the dissociation processes of the first type we do not encounter any difficulties in the definition of the transition-state complex. On plotting the energy of the system as a function of the reaction path coördinate, one obtains the curve shown in figure 1. The hump of this curve represents the transition state which is, therefore, *completely* defined by the coördinates of this point. Figure 2, on the other hand, illustrates a decomposition of the second type, and because it does not show a hump a similar interpretation of the transition-state complex is impossible. In order to avoid the difficulties arising from the absence of a description of the transition-state complex, we adopt for the latter case a slightly modified treatment of the transition-state method, as described below.

Let us consider all the energy levels corresponding to various modes of motion of some particular bond in some particular molecule. These energy levels can be classified into two groups: (A) Energy levels which correspond to the proper vibration of the bond, i.e., for which the energy is smaller than the bond dissociation energy D[16] (see figure 3). (B) Energy levels which correspond to the translational mode of motion, i.e., for which the energy is greater than the bond dissociation energy D.[17] These two classes of energy levels are denoted in figure 3

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[16] The value of D used here is the dissociation energy *per molecule.*

[17] The energy levels corresponding to the translational mode of motion could be discrete only if the motion is limited in space, i.e., if the bond is enclosed in a "box." The length of this "box" is chosen arbitrarily as ds.

by A and B, respectively. It is obvious, of course, that the bond in question can be ruptured only if it is in a state which corresponds to any energy level belonging to class B.

Let us now assume that there is no interaction between energy levels which correspond to various degrees of freedom of the molecule. For such cases, the total partition function of the molecule can be represented as:

$$f_{\text{total}} = \prod_1^n f_i$$

where f_i denotes the partition function corresponding to the i^{th} degree of freedom of the molecule. We can represent f_{total} in a slightly different way:

$$f_{\text{total}} = f' \cdot f_k$$

where $f' = \pi' f_i$ represents the product of the f_i's for all i-values with the exception of $i = k$, and f_k represents the partition function corresponding to the vibrational degree of freedom of the bond in question.

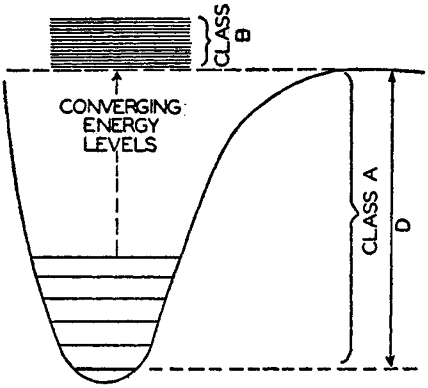

Fig. 3

The partition function f_k may be represented by:

$$f_k = \sum e^{-\epsilon_j/kT} + e^{-D/kT} \cdot f_{\text{transl}} \approx \sum e^{-\epsilon_j/kT}$$

the summation being taken over all vibrational energy levels, the j^{th} of them corresponding to the energy ϵ_j, taking $\epsilon_0 = 0$; D is the dissociation energy of the bond in question, i.e., the difference between the vibrational zero energy level and the convergence limit of the vibrational levels; and f_{transl} denotes the partition function of the translational levels belonging to Class B and measured from the energy level of the convergence limit taken as a zero.

If we confine our attention to the molecules for which the center of gravity of the bond in question is restricted to some segment ds along the direction of the bond,[18] then the partition function f_{transl} may be represented, with a fair degree of accuracy, as a translational partition function of "a particle in a box", i.e.:

$$f_{\text{transl}} = (2\pi\mu kT)^{1/2} \cdot h^{-1}\, ds$$

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[18] We assume the origin of the coördinates to be fixed at one end of the bond in question.

The fraction of the molecules which can decompose by the rupture of the bond in question (i.e., which contain the requisite amount of energy in the bond to be broken) and for which the center of gravity of this bond is confined to the segment ds is given by:

$$\frac{\text{Number of molecules which can decompose}}{\text{Total number of molecules}} =$$

$$= \frac{(\pi' f_i) \cdot e^{-D/kT} \cdot (2\pi\mu kT)^{1/2} \cdot h^{-1} \cdot \mathrm{d}s}{(\pi' f_i) \cdot (\sum e^{-\epsilon_j/kT} + e^{-D/kT} \cdot f_{\text{transl}})} \approx$$

$$\approx \frac{e^{-D/kT} \cdot (2\pi\mu kT)^{1/2} \cdot h^{-1} \cdot \mathrm{d}s}{\sum e^{-\epsilon_j/kT}}$$

This expression can be further simplified if we assume that the energy levels ϵ_j correspond to a harmonic oscillator so that

$$\sum e^{-\epsilon_j/kT} = 1 + e^{-h\nu_0/kT} + e^{-2h\nu_0/kT} + e^{-3h\nu_0/kT} + \cdots$$
$$= (1 - e^{-h\nu_0/kT})^{-1}$$

where ν_0 denotes the fundamental vibration of the bond in question. We arrive, therefore, at the expression:

$$\frac{\text{Number of molecules which may decompose}}{\text{Total number of molecules}} =$$

$$= (2\pi\mu kT)^{1/2} \cdot (1 - e^{-h\nu_0/kT}) \cdot h^{-1} \cdot e^{-D/kT} \cdot \mathrm{d}s$$

We can now assume that half of the molecules which can decompose (and for which the center of gravity is confined to the segment ds) are moving in the direction of decomposition with an average thermal velocity $(2kT/\pi\mu)^{1/2}$. The rate of decomposition is given, therefore, by the number of these molecules for which the center of gravity will pass the segment ds in a unit of time, i.e.:

$$\text{Rate constant of decomposition} = \frac{\frac{1}{2}(2\pi\mu k\,T)^{1/2} \cdot (1 - e^{-h\nu_0/kT}) \cdot h^{-1} \cdot e^{-D/kT} \cdot \mathrm{d}s}{(2kT/\pi\mu)^{-1/2} \cdot \mathrm{d}s}$$

$$k = \text{rate constant of decomposition} = (kT/h)(1 - e^{-h\nu_0/kT}) \cdot e^{-D/kT}$$

We have to distinguish between two extreme cases:

A. $h\nu_0 \ll kT$

B. $h\nu_0 \gg kT$

Assumption A: $h\nu_0 \ll kT$

In case A

$$(1 - e^{-h\nu_0/kT}) \approx h\nu_0/kT$$

and the expression for the rate constant is reduced to

$$k = \text{rate constant of decomposition} = \nu_0 \cdot e^{-D/kT}$$

This case, which was discussed by M. G. Evans and G. S. Rushbrooke (55), gives the correct results for either a very high temperature or very "soft" bonds.

It is necessary to analyze further the implications of the formula derived above for the rate constant of a unimolecular dissociation. We notice, first of all, that the nonexponential term is a constant which is truly temperature independent, and therefore

$$RT^2 \cdot \frac{\mathrm{d} \ln k}{\mathrm{d}T} = \frac{D}{kT^2} \cdot RT^2 = ND$$

where N = Avogadro's number. As the left-hand side is the Arrhenius activation energy (sometimes called "experimental activation energy"), we have shown that if assumption A is valid then the experimental activation energy of a unimolecular dissociation process in which one bond is ruptured is *exactly* equal to the dissociation energy of this bond. This provides a justification for the kinetic method of determining the bond dissociation energy.

Before we continue this discussion there are some apparent contradictions to be elucidated. It is known that for any reversible reaction

$$\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{C}$$

the heat of reaction is given by the difference between the activation energies of the forward and back reactions:

$$\Delta E = E_1 - E_2{}^{19}$$

We assume that the recombination of radicals does not involve an activation energy, and we might conclude, therefore, that the activation energy of the dissociation process is equal to the heat of reaction:

$$\Delta E = E_1 \qquad (E_2 = 0)$$

The heat of reaction at temperature T is of course different from the heat of reaction at 0°K., and thus we arrive at the conclusion:

$$\Delta E \neq \Delta E^0 = D$$

i.e.,

$$E_1 \neq D$$

which seems to contradict the previous statement.

In order to clarify this point we must note that E_1 and E_2 in the expression $\Delta E = E_1 - E_2$ have the meaning of "experimental activation energies," i.e., each of these activations can be represented by an expression of the type $RT^2 \cdot \mathrm{d} \ln k/\mathrm{d}T$. It was shown previously that for unimolecular dissociations:

$$RT^2 \cdot \mathrm{d} \ln k_1/\mathrm{d}T = E_1 = D = \Delta E^0$$

In order to find $RT^2 \cdot \mathrm{d} \ln k_2/\mathrm{d}T$ we write:

$$K_{\mathrm{eq}} = \frac{k_1}{k_2} = \frac{f_{\mathrm{final}}}{f_{\mathrm{initial}}} \cdot e^{-\Delta E^0/RT}$$

---

[19] The heat of reaction is measured here at constant volume.

K_{eq} = the equilibrium constant for $A \rightleftharpoons B + C$; f_{final} and $f_{initial}$ are the partition functions of products B and C, and of reagent A, respectively. Hence:

$$k_2 = \frac{f_{initial}}{f_{final}} \cdot e^{+\Delta E^0/RT} \cdot \nu_0 \cdot e^{-D/RT}$$

and because $\Delta E^0 = D$, we obtain:

$$RT^2 \cdot \frac{d \ln k_2}{dT} = RT^2 \frac{d(\ln f_{initial})}{dT} - RT^2 \frac{d(\ln f_{final})}{dT}$$

The left-hand side of this expression gives E_2, while the right-hand side gives $\Delta E^0 - \Delta E$. We see, therefore, that although there is no potential energy barrier for the recombination, there is an "experimental activation energy" which just accounts for the difference between D and ΔE. At 0°K. we get, of course:

TABLE 7

Frequency factors for various unimolecular dissociation processes in which one bond is ruptured

PROCESS	E	μ
	kcal./mole	*sec.*$^{-1}$
$C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$	77.5	$3 \times 0.7 \times 10^{12}$
m-$CH_3C_6H_4CH_3 \rightarrow m$-$CH_3C_6H_4CH_2 + H$	77.5	$6 \times 0.7 \times 10^{12}$
p-$CH_3C_6H_4CH_3 \rightarrow p$-$CH_3C_6H_4CH_2 + H$	76	$6 \times 0.8 \times 10^{12}$
o-$CH_3C_6H_4CH_3 \rightarrow o$-$CH_3C_6H_4CH_2 + H$	75	$6 \times 0.8 \times 10^{12}$
$C_6H_5CH_2Br \rightarrow C_6H_5CH_2 + Br$	50.5	1×10^{13}
$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2 + CH_3$	63	1×10^{13}
$C_6H_5CH_2NH_2 \rightarrow C_6H_5CH_2 + NH_2$	59	6×10^{12}
$C_6H_5CH_2COCH_3 \rightarrow C_6H_5CH_2 + COCH_3$	63	8×10^{13}
$N_2H_4 \rightarrow 2NH_2$	60	4×10^{12}
$CH_3COCOCH_3 \rightarrow 2CH_3CO$	60	6×10^{13}
$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO$	34	2×10^{13}
$CH_2{=}CHCH_2Br \rightarrow CH_2{=}CHCH_2 + Br$	47.5	5×10^{12}
$(C_6H_5)_3CC(C_6H_5)_3 \rightarrow 2(C_6H_5)_3C$	11	5×10^{12}
$(C_6H_5CO)OO(COC_6H_5) \rightarrow 2C_6H_5COO$	27-33	10^{12}-10^{14}
$(CH_3CO)OO(COCH_3) \rightarrow 2CH_3COO$	31	8×10^{14}
$C_2H_5OOC_2H_5 \rightarrow 2C_2H_5O$	31	5×10^{14}

$$\Delta E^0 = E_1 - 0 = D$$

The expression derived here for the rate constant of unimolecular dissociation demands that the frequency factor should be nearly equal to the fundamental vibration frequency of the bond in question. It is possible, therefore, to check the theory by comparing frequency factors determined experimentally with the corresponding vibrational frequencies. Table 7 lists the frequency factors obtained for various unimolecular dissociation processes in which one bond is ruptured. One observes that their orders of magnitude are 10^{12}–10^{13} sec.$^{-1}$ On the other hand, the corresponding fundamental vibrational frequencies are of the order of 10^{13}–10^{14} sec.$^{-1}$; hence the agreement appears to be reasonable. It seems, on the whole, that the frequency factors are lower by about a factor of 10 than the fundamental frequencies; this may indicate that in the activated complex that part of the molecule which is not involved in the decomposition is less flexible than it is in "normal" molecules.

Assumption B: $h\nu_0 \gg kT$

In case B

$$(1 - e^{-h\nu_0/kT}) \approx 1$$

and the expression for the rate constant is reduced to

$$k = \text{rate constant of decomposition} = \frac{kT}{h} \cdot e^{-D/kT}$$

The "experimental" activation energy measured by RT^2 d ln $k/\mathrm{d}T$ is given now by

$$E_{\text{exp}} = RT + D$$

We conclude, therefore, that at the temperature of about 1000°K. the "experimental" activation energy gives results which are too high by about 2 kcal./mole. The "experimental" frequency factor obtained from the expression $k = \nu_{\text{exp}} \cdot \exp(-E_{\text{exp}}/RT)$ should be greater than $kT/h \approx 10^{13}$ by about a factor of 3. It seems again that the theory predicts slightly higher values for ν_{exp} than are actually observed.

We arrive thus at the conclusion that the "experimental" activation energies yield values which are within $D + 2 > E_{\text{exp}} > D$. If $h\nu_0/kT$ is of the order of 1, the E_{exp} approximates closer to D than in case B. The same effect is caused by the anharmonicity of vibration; it makes $kT/h \cdot f_v$ less dependent on temperature and decreases the difference between E_{exp} and D.

Finally we have to consider the influence of the term $f^{\ddagger}/f_{\text{in}}$ (excluding the partition function linked with the bond to be broken). If the transition state is "softer" than the initial state, then the frequency factor contains an additional term increasing with temperature in the denominator. That helps to make the frequency factor temperature independent and approximates E_{exp} to D. On the other hand, the contrary is true if the transition state is "harder" than the initial state.

It seems adequate to summarize this discussion with the statement:

> The experimental activation energy defined by the expression RT^2 d ln $k/\mathrm{d}T$ gives a fair approximation to the bond dissociation energy, particularly if the experimental frequency factor is close to 10^{13} sec.$^{-1}$

E. Experimental problems in the determination of the rate of initial decomposition

Let us consider now the conditions which enable one to measure the rate of the primary unimolecular dissociation $\mathrm{RR'} \rightarrow \mathrm{R} + \mathrm{R'}$. 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 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 (per cent of decomposed molecules divided by time of contact). This idea was developed by F. O. Rice and his collaborators and is discussed more fully in Section IV,F (page 118).

An interesting case is encountered when nearly all the radicals produced are removed by their mutual recombination. Such a system approximates closely to the equilibrium state $R'R'' \rightleftharpoons R' + R''$. Hence, when a minute quantity of these radicals is removed by some *irreversible* process which produces molecules X, then the rate of formation of X depends on the equilibrium concentration of the radicals. The overall activation energy, corresponding to the process of X formation, involves, therefore, the activation energy of the reaction $R \rightarrow X$ (whatever its mechanism may be) and the heat of dissociation of $R' \cdot R''$. If the former is known, or can be independently estimated, then the heat of dissociation of $R' \cdot R''$ can be computed from the overall activation energy of X formation. This is the basis of a combined equilibrium and kinetic method, illustrated by the example given on page 127.

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 is very ambiguous and, in the writer's opinion, these reactions are not to be recommended for the estimation of the rate of initial dissociation.[20]

[20] See, for example, page 132.

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 mercury dimethyl takes place according to the equation

$$Hg(CH_3)_2 \rightarrow HgCH_3\cdot + CH_3\cdot$$

and it is followed by rapid decomposition of $HgCH_3\cdot$.

$$HgCH_3\cdot \rightarrow Hg + CH_3\cdot$$

Thus, the recombination of $HgCH_3\cdot$ and $CH_3\cdot$ radicals into the original molecules of mercury dimethyl is prevented. Now suppose that the recombination of methyl radicals into ethane 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:[21]

$$Hg(CH_3)_2 \rightarrow HgCH_3\cdot + CH_3\cdot$$

(*2*) When radicals initially formed are rapidly removed by some reactions. These eventually produce *stable* radicals which neither decompose into simpler fragments nor react with molecules present in the system. This is illustrated by two examples:

Example 1:

Decomposition of benzyl bromide produces reactive bromine atoms and relatively inert benzyl radicals:

$$C_6H_5CH_2Br \rightarrow C_6H_5CH_2\cdot + Br$$

If this reaction is carried out in an excess of toluene, then reactive bromine atoms are removed rapidly by the interaction with $C_6H_5CH_3$:

$$Br + C_6H_5CH_3 \rightarrow HBr + C_6H_5CH_2\cdot$$

producing inert benzyl radicals. The benzyl radicals may be continuously removed from the reaction vessel and they dimerize 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 bibenzyl.[22]

[21] A detailed discussion of this decomposition, investigated by E. Warhurst and G. B. Gowenlock, is reported on page 151.

[22] Decompositions of this type are discussed on page 136.

Example 2:

Primary decomposition of methyl nitrite takes place according to the equation:

$$CH_3ONO \rightarrow CH_3O\cdot + NO$$

The reactive $CH_3O\cdot$ radical interacts with a molecule of undecomposed nitrite and produces the unstable radical $\cdot CH_2ONO$:

$$CH_3O\cdot + CH_3ONO \rightarrow CH_3OH + \cdot CH_2ONO$$

Finally, the unstable $\cdot CH_2ONO$ radical decomposes and a stable NO radical is produced:

$$\cdot CH_2ONO \rightarrow CH_2O + NO$$

According to this mechanism the rate of initial decomposition may be measured by the rate of formation of nitric oxide.[23]

F. The determination of bond dissociation energy by the mirror technique

It was first demonstrated by F. Paneth and his collaborators (129, 130) that free methyl and ethyl radicals may exist in the gas phase. They have shown that these radicals reacted easily with metallic mirrors deposited on the walls of the tube, and the reciprocal of the time of removal of a "standard" mirror was taken as a measure of their "activities", i.e., an entity proportional to their concentration.

The mirror technique was further developed and improved by F. O. Rice and his colleagues (146, 147), who succeeded in demonstrating the presence of free methyl radicals amongst the products of decomposition of various organic compounds. Having proved that under their experimental conditions most compounds appeared to decompose homogeneously and according to a unimolecular law and that these decompositions involved a primary splitting of the molecule into two radicals, they deduced that the activation energies of these decompositions should measure the dissociation energies of the relevant bonds. It was further assumed that for small fractional decompositions the concentration of radicals at the end of the furnace is proportional to the rate of dissociation of an organic compound. This assumption may be sound if the recombination of radicals is negligible, as would be the case for low pressures and extremely short times of contact.

In the actual experimental set-up the vapor of an organic compound was passed rapidly through a silica tube, which was heated by means of an electric furnace to a temperature at which slight decomposition took place. The pressure was kept low (0.2–2 mm. of mercury) and the time of contact was very short, being of the order of 0.001 sec. Standard mirrors of antimony were placed at varying distances from the end of the furnace and the times of their removal were determined for each position. The time of removal of a mirror at the end of the

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[23] Decompositions of organic nitrites are discussed on page 141.

furnace was computed by extrapolation.[24] By this method the relative concentrations of radicals at the end of the furnace were determined for various temperatures of the decomposition and these data were used for the computation of the required activation energy (145).

F. O. Rice and W. R. Johnston (145) have discussed various objections which could be urged against this method of determining the activation energy. They argued, firstly, that the radicals originally formed undoubtedly decompose further and that, therefore, the activation energy of this process would be measured simultaneously; secondly, that the free radicals reacting with the surrounding molecules might start a chain reaction; and, thirdly, that, since the organic vapor passes through the furnace in about 0.001 sec., it is doubtful whether it reaches the temperature registered by the thermocouple.

With regard to the first of these objections, Rice and Johnston argued that the decomposition of the larger radicals into olefin molecules and methyl radicals has an activation energy of 40–60 kcal./mole lower than that of the initial dissociation of the parent compound. This is in their opinion due to the formation of a double bond, which takes place simultaneously with the dissociation process of the complex radical. The rate of formation of methyl radicals should, therefore, be equal to the rate of formation of the primary complex radicals and the activation energy measured should correspond to that of the primary dissociation process.

The second objection Rice and Johnston consider to be nonessential. Even if a chain process ensued, it would have no effect on the experimental measurements, since a reaction between a radical and molecule must of necessity lead to the formation of another radical. The chain termination seems to be negligible, because of the extremely short time of contact and low pressure.

Finally, the last objection was refuted by showing that changing of the diameter and length of the reaction vessel, as well as the rate of flow, had no appreciable effect on the final results. Similarly, no effect was observed when a preheater was fitted to the reaction vessel immediately in front of the main furnace. Moreover, the theoretical treatment of these problems by Herzfeld (80) seems to confirm fully the conclusion drawn from the experimental evidence above.

However, the following objection was not considered by Rice: The time of removal of a mirror at the end of the furnace was computed by extrapolation, the necessary data being provided by determining the times of the removal of mirrors placed at various distances from the furnace along the *cold* tube. The decay of radicals in the cold tube was quite different from the decay in the hot zone immediately following the end of the furnace. It is doubtful, therefore, if the extrapolated time of removal was correct. Moreover, the variation of the temperature of the furnace was changing both the temperature distribution and the length of the hot zone. This effect might systematically alter the error involved in the extrapolation yielding the time of the removal of the mirror at the end of the furnace. Any variation of the error with the temperature causes,

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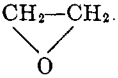
[24] A direct determination of this time would have been prevented by the sublimation of the mirror, were it deposited on the hot tube in the vicinity of the furnace.

of course, an appreciable error in the estimation of the temperature coefficient of the activity, i.e., in the activation energy determined. We doubt whether this objection could be refuted merely by the fact that variation of rate of flow did not produce a greater change in activation energy than ± 3 kcal./mole, which Rice considered as the experimental error of his determinations.[25]

The difficulties of the extrapolation discussed above were strongly emphasized by J. S. A. Forsyth (57). This worker has shown that nitric oxide apparently did not inhibit the reaction of methyl radicals at distances shorter than 4 cm. from the end of the furnace. He concluded that the gas leaving the furnace is still hot enough to decompose and to generate further quantities of radicals even at some distance from the furnace. He suggested that the "effective" end of the furnace should be taken as 4 cm. from its actual end.

TABLE 8

Bond dissociation energies estimated by mirror technique

COMPOUND	FURNACE TEMPERATURE	*E*
	°*K.*	*kcal./mole*
$CH_3—CH_3$	1179, 1233	79.5
$CH_3OCO—OCH_3$ (?)	1043, 1080, 1152, 1188	74.2
$CH_3CH_2—CH_3$	1010, 1080, 1152	71.5
n-C_4H_{10}	1010, 1080, 1152	65.4
n-C_5H_{12}	996, 1033, 1052, 1080	64.0
n-C_7H_{16}	1010, 1080	63.2
$CH_3CO—CH_3$	1010, 1080, 1134	70.9
$CH_3CO—H$ (?)	1116, 1152, 1179	69.4
$CH_3—CH_2OH$	1134, 1152, 1223	68.6
$CH_3O—CH_3$	1080, 1152, 1188	81.1
$C_2H_5OC_2H_5$	1010, 1080, 1152	68.6
	1052, 1088, 1134, 1188	44.0
$(CH_3)_2N—CH_3$	953, 1010, 1080	50.8
$CH_3NH—CH_3$	1080, 1116, 1152, 1188	52.0

To illustrate the application of the mirror technique we reproduce here table 8, taken from the paper by Rice and Johnston. These workers also showed their results by giving the plots of log of "activity" (i.e., time of removal of a mirror at the end of a furnace) against $1/T$, which gave excellent straight lines over a range of 150°C.

Consideration of table 8 leads to the following conclusions: In the first place, all the activation energies quoted seem to be definitely smaller than the relevant bond dissociation energies, taking for the latter values which are now considered to be the best. In the writer's opinion, this general trend may be attributed to errors in the extrapolated time of removal of the mirror at the end of the fur-

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[25] In Steacie's opinion, the experimental error in determining activation energies by the mirror technique may be as high as ± 10 kcal./mole.

nace. The hot zone following the reaction vessel is longer and hotter the higher the furnace temperature. Therefore the concentration of radicals in the region of mirror deposition corresponds to a smaller fraction of their initial concentration[26] the higher the temperature of the furnace. Consequently, the apparent activation energy is lower than the "true" activation energy.

The gradation of results presented in table 8 seems to be reasonable. We notice a decrease in activation energies in the series C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, and n-C_7H_{16}, although the recorded differences seem greater than would be expected, e.g., the difference between $D(CH_3—CH_3)$ and $D(C_2H_5—CH_3)$ is probably considerably smaller than the 8 kcal./mole reported. The results obtained for n-C_4H_{10}, n-C_5H_{12}, and n-C_7H_{16} leave us unable to decide which was the bond initially broken. Similarly, it is impossible to say whether the decomposition of dimethyl carbonate takes place at $CH_3OCO—OCH_3$ or at $CH_3OCOO—CH_3$, and whether, in the decomposition of acetaldehyde, the C—C or the C—H bond is primarily broken. It is interesting to note that the results obtained for dimethyl ether indicate that the dissociation energy of a C—O bond is greater than the dissociation energy of a C—C bond, a conclusion which is in accord with our present views. The difference in activation energies obtained for dimethyl ether and diethyl ether seems to indicate that, in the latter case, a C—C bond is broken and not a C—O bond. Finally, one notes that the activation energies obtained for amines are exceptionally low. The writer believes that $D[(CH_3)_2N—CH_3]$ and $D(CH_3NH—CH_3)$ are much higher, probably of the order of 70–75 kcal./mole.

The mirror technique was used by Rice and his colleagues in several other cases. F. O. Rice and M. D. Dooley (143) used this technique for determining $D(CH_3—H)$. They proved that under their experimental conditions CH_4 decomposes into $CH_3 + H$, and estimated the activation energy at 100 ± 6 kcal./mole; this result is in excellent agreement with the value of 101 kcal./mole for $D(CH_3—H)$ at present accepted as the most reliable. The same authors reinvestigated the thermal decomposition of ethane, demonstrated the formation of methyl radicals, and estimated the activation energy at 79.5 ± 3 kcal./mole (144).

The decomposition of ethyl nitrite was investigated by the mirror technique by F. O. Rice and E. L. Rodowskas (148). The activation energy of the process:

$$C_2H_5ONO \rightarrow C_2H_5O + NO$$

was estimated by them at 35 ± 3 kcal./mole (see also page 143).

We conclude that the mirror technique is an extremely sensitive tool for the detection of radicals. We do not think, however, that it can be accurate enough for the estimation of bond dissociation energies. The method is based on a calculation of the thermal coefficient of the rate constant and, as shown in Section IV,A, such a calculation is susceptible to errors resulting from the occurrence of various side reactions. The mirror technique fails to eliminate the

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[26] By "initial concentration of the radicals" is meant the concentration of radicals at the end of the furnace.

occurrence of possible side reactions and the time lag between the end of the reaction (products leave the furnace) and the actual measurements (products arrive at the mirror) is a source of appreciable errors which, in the writer's opinion, tend to decrease the observed activation energy. Perhaps the time lag could be eliminated by using the mass-spectroscopic technique described by G. C. Eltenton (52). The radicals produced in the reaction vessel leak through a small orifice directly into the ionizing chamber, where their presence can be detected in the usual way, since the ionization potential required for formation of the relevant ion from the radical is much lower than that required for formation of the same ion from the molecule.

G. The determination of the C—I *bond dissociation energy in organic iodides*

The C—I bond dissociation energy of various organic iodides was estimated by E. T. Butler and M. Polanyi (35) and by E. T. Butler, E. Mandel, and M. Polanyi (33), who investigated the rate of pyrolysis of a series of organic iodides by a flow technique. They measured the fraction of iodide decomposed by the amounts of free iodine formed in the reaction. In their opinion the use of a flow technique was advantageous, since the accumulation of the products resulting from an axtended period of flow made it possible (*a*) to work with a very small partial pressure of organic substance and (*b*) to limit the total decomposition to a very small percentage. Thus, by maintaining low concentrations of the initial and final products, the chances of secondary reactions were considerably reduced. These were further suppressed by the brief duration of the reaction, which was over in a second or less as the gases passed through the reaction vessel.

Since the C—I bond is the weakest bond in organic iodides, it is obvious that the first step in the pyrolysis of these compounds involves the rupture of this bond in preference to any other:

$$\mathrm{RI} \rightarrow \mathrm{R} + \mathrm{I} \qquad \text{(a)}$$

The formation of free iodine must be attributed to this reaction.[27]

Neither the radicals R nor the iodine atoms can be the final products of the decomposition. The appearance of I_2 suggests the reaction:

$$\mathrm{I} + \mathrm{I} \rightarrow \mathrm{I}_2 \qquad \text{(c)}$$

and this can take place either in the gas phase, by three-body collisions, or on the walls of the reaction vessel. Whether reaction c occurs in the reaction vessel itself, or in the tubes leading to the trap in which iodine is condensed has been left open. Radicals R must also be removed from the system by some secondary reactions which can be represented by the general equation:

$$\mathrm{R} \rightarrow \text{product}$$

---

[27] The experiments of Butler and Polanyi demonstrated that pyrolysis of many iodides produced hydrogen iodide in addition to free iodine. They explained the formation of hydrogen iodide by assuming an alternative unimolecular decomposition of the type:

$$\mathrm{C_2H_5I} \rightarrow \mathrm{C_2H_4} + \mathrm{HI} \qquad \text{(b)}$$

If reaction c is the only one which consumes iodine atoms, i.e., if the back reactions e and f

$$R + I \rightarrow RI \tag{e}$$

$$R + I_2 \rightarrow RI + I \tag{f}$$

can be neglected, and if the radicals R are removed from the system without initiating any chain decomposition of RI, then the rate of formation of iodine molecules measures the rate of the initial decomposition (equation a).

Butler and Polanyi tried to obtain further evidence for the occurrence and extent of back reactions e and f in the following ways:

(*a*) In some experiments mercury vapor, or nitric oxide, was admitted to the system. It is known that mercury vapor reacts readily with iodine atoms or iodine molecules (123) removing them from the system, while nitric oxide is well known for its readiness to combine with radicals (167); therefore, it was reasonable to assume that either of these substances must suppress the back reactions e and f. Actually, they found that admission of mercury vapor to ethyl iodide had no effect on the rate of decomposition, while admission of nitric oxide doubled the rate of decomposition, thus indicating only 50 per cent of back reaction.

(*b*) If the back reaction were only a minor disturbing factor, and if the initial decomposition were the actual rate-determining step, then the activation energies derived from the temperature coefficient of the rate constant would agree closely with the activation energy derived on the assumption of the frequency factor being 10^{13} sec.$^{-1}$ (see Section IV,B for details of the computation). On the other hand, if the back reactions were very fast, then the latter computation would yield a much higher value of the apparent activation energy. In fact, Butler and Polanyi found that for the decomposition of *n*-propyl iodide and *n*-butyl iodide the activation energies calculated from the temperature coefficients were 52 kcal./mole and 53 kcal./mole, respectively, whereas the activation energies computed on the basis of an assumed frequency factor at 10^{13} sec.$^{-1}$ came out at 50 kcal./mole and 49 kcal./mole, respectively.

On the basis of these two arguments Butler and Polanyi concluded that the rate of formation of iodine molecules approximates closely to the rate of initial decomposition of RI. They were aware, of course, of the fact that the main reaction was accompanied by various complicating reactions which made this approximation rather crude.[28] Therefore they did not consider the activation energies calculated from the temperature coefficient of the rate constant to be reliable. They were convinced, however, that no great error was introduced by calculating the activation energy of the primary process by the method in which the frequency factor was assumed at 10^{13} sec.$^{-1}$, particularly if the data used for these computations were taken from experiments performed at the lowest temperatures and with the shortest times of contact (*cf.* Section IV,B).

[28] The fact that the calculated unimolecular rate "constant" varied with changes in the time of contact, pressure, etc. demonstrated clearly that the decomposition is not a simple unimolecular reaction.

In consequence, the activation energies were computed in this way and identified with the relevant C—I bond dissociation energies. The results are given in table 9, taken from the original papers of Polanyi *et al.* The third column of table 9 gives the C—I bond dissociation energies which in the writer's opinion are more reliable, being computed on the basis of more recent evidence. Comparison of the results listed in columns 2 and 3 demonstrates that in many instances the original values of Butler and Polanyi are sound.

We shall now examine more closely the assumptions made by Butler and Polanyi. Intrinsically there is no reason to assume that the combination of iodine atoms to iodine molecules is more likely than the recombination of iodine atoms with R radicals. The mutual combination of iodine atoms *must* take place by a three-body collision if it occurs in the gas phase. On the other hand, if the dissociation process RI → R + I is truly unimolecular (as was assumed by Butler and Polanyi), then the recombination R + I → RI has to be a truly bimolecular process (under the experimental conditions which prevailed in the dissociation process). It follows, therefore, that R + I → RI is more likely to occur than $I + I + M \rightarrow I_2 + M$. The chances of recombination are further increased by the reaction:

TABLE 9

C—I *bond dissociation energies*

COMPOUND	*D*(C—I) (BUTLER AND POLANYI)	*D*(C—I) MOST RELIABLE VALUES AT PRESENT	
		Kilocalories per mole	References
	kcal./mole		
CH_3—I	(54)	54–55	(36, 206)
C_2H_5—I	52	51–53	(182)
n-C_3H_7—I	50		
Iso-C_3H_7—I	46		
n-C_4H_9—I	49		
tert-C_4H_9—I	45		
(CH_2=$CHCH_2$)—I	39	~34	(61, 163)
(CH_2=CH)—I	55		
$C_6H_5CH_2$—I	44	~37	(61, 182)
C_6H_5—I	54		
CH_3CO—I	(51)	~41–46	(37, 195)
C_6H_5CO—I	44		
CH_3COCH_2—I	45		
Cyclo-C_6H_{11}—I	49		
$C_6H_5CH_2CH_2$—I	50		
$CHCl_2$—I	42		
$CHBr_2$—I	41		
CH_2ClCH_2—I	46		

$$R + I_2 \rightarrow RI + I \tag{f}$$

It is known that iodine molecules react readily with radicals, and since the concentration of I_2 increases during the actual dissociation process, reaction f should be favored by a greater extent of decomposition. For example, a longer time of contact or a higher temperature of pyrolysis should increase back reaction f, and an examination of the data reported by Butler and Polanyi reveals indeed a decrease of the unimolecular rate "constant" with increasing time of contact. Besides, in some instances the apparent activation energy, calculated from the temperature coefficient of the rate constant, is too low, thus indicating a more efficient back reaction at higher temperature.

These arguments convince us that the back reaction cannot be prevented, at least efficiently enough, by the combination of iodine atoms to iodine molecules. However, Butler and Polanyi accumulated considerable evidence which pointed to the fact that in the pyrolyses of ethyl, propyl, and *n*-butyl iodides the back reaction was negligible. We conclude, therefore, that in the pyrolyses of these compounds the back reaction is prevented by a rapid removal of organic radicals R from the system.

There are two types of reactions which may remove radicals R from the system:

$$\text{(I)} \qquad R + R \rightarrow RR \text{ or}$$

$$R + R \rightarrow RH + \text{olefin}$$

$$\text{(II)} \qquad R + RI \rightarrow RH + R'$$

where R′ represents a radical of the type $\cdot CH_2CH_2I$. The efficiency of reactions of type I cannot be greater than the efficiency of the back reactions $R + I \rightarrow RI$ or $R + I_2 \rightarrow RI + I$. On the other hand, the efficiency of the reaction of type II might be greater, owing to a much higher concentration of RI as compared with the concentration of R.

There is additional evidence in favor of the assumed reaction:

$$R + RI \rightarrow RH + R'$$

The photochemical investigations by W. West and E. Ginsburg (214) and by W. West and L. Schlessinger (215) clearly demonstrated that at room temperature the back reaction, i.e., the re-formation of RI, was very efficient (the presence of a silver foil in the reaction vessel increased the rate of photolysis by a factor of 10 to 30). This means then that the reaction which removes the radicals has an activation energy, thus being efficient at high temperatures of pyrolysis and of little importance at low temperatures of photolysis. It is unlikely that the dimerization or disproportionation of radicals requires any appreciable activation energy (both being highly exothermic reactions), but it is plausible to attribute an activation energy to the reaction $R + RI \rightarrow RH + R'$.

The mechanism of pyrolysis of organic iodides, therefore, takes the following shape:

$$RI \rightarrow R + I$$

$$R + RI \rightarrow RH + R'$$

$$R' \rightarrow \text{olefin} + I$$

$$I + I \rightarrow I_2$$

The third reaction of this scheme is extremely plausible, as the C—I bond dissociation energy in the radical R′ (e.g., $\cdot CH_2CH_2I$) is considerably lower than D(R—I). An examination of the above scheme shows that it would lead to first-order kinetics, the unimolecular dissociation of RI being the rate-determining step. Two iodine atoms would be formed for every molecule of RI primarily decomposed.

It is the belief of the writer that the pyrolysis of ethyl, *n*-propyl, and *n*-butyl iodides approximates to this scheme. The unimolecular rate constants for *n*-propyl iodide and *n*-butyl iodide reported in table 1 of Butler and Polanyi's paper did not vary appreciably with changes of partial pressure of iodide and with different times of contact. The experimental frequency factors came close to the theoretically required value of 10^{13} sec.$^{-1}$ Similar conclusions might be drawn from the results of the pyrolysis of ethyl iodide, reinvestigated in Polanyi's laboratory by G. B. Gowenlock (68) and by M. Szwarc (182). The experimental activation energy calculated from the temperature coefficient of the rate constant was estimated at 54 kcal./mole by Szwarc and 55–56 kcal./mole by Gowenlock. The activation energy computed on the basis of frequency factors, assumed at 10^{13} sec.$^{-1}$, was 51–52 kcal./mole. This value agrees well with the $D(C_2H_5—I)$ estimated thermochemically at 51 kcal./mole. Nevertheless, closer analysis of the kinetics of these pyrolyses shows that various other processes participate to some extent in the overall decomposition and, notwithstanding all this extensive work, it has been impossible to elucidate finally the details of these reactions.

The kinetics of the pyrolysis of other iodides was much more complicated than those observed for ethyl, *n*-propyl, and *n*-butyl iodides. To illustrate the various complicating factors we shall discuss the pyrolyses of methyl iodide, benzyl iodide, and allyl iodide.

Reinvestigation of the pyrolysis of methyl iodide (182) demonstrated that the formation of iodine molecules was accompanied by the formation of methane. The rate of decomposition was much lower than expected, and it obeyed kinetics of an order higher than 1. It seems that the back reaction was much more efficient in this decomposition, indicating a higher activation energy for the reaction:

$$CH_3\cdot + CH_3I \rightarrow CH_4 + \cdot CH_2I$$

than for the reaction:

$$C_2H_5\cdot + C_2H_5I \rightarrow C_2H_6 + \cdot CH_2CH_2I$$

The formation of the radical $\cdot CH_2I$ is a further complicating factor. While a $\cdot CH_2CH_2I$ radical decomposes easily into an iodine atom and an ethylene *molecule*, the $\cdot CH_2I$ radical decomposes probably more slowly and then forms another radical, i.e., CH_2. It seems also that some steps of the decomposition of methyl iodide involve a heterogeneous wall reaction.

Reinvestigation of the pyrolysis of benzyl iodide (182) led to the postulation of the following mechanism:

$$C_6H_5CH_2I \rightleftarrows C_6H_5CH_2\cdot + I \qquad K_{eq}$$

$$I + I \rightleftarrows I_2 \qquad K_{I_2}$$

$$2C_6H_5CH_2\cdot \rightarrow C_6H_5CH_2CH_2C_6H_5 \qquad k_2$$

The benzyl radicals appeared very unreactive. They were not removed by the reaction $R + RI \rightarrow RH + R'$, and therefore the system approached an equilibrium state for R, I, and I_2. Consequently, the dimerization of benzyl radicals was the rate-determining step. For low temperatures and very small percentages of decomposition it was found that the unimolecular rate constant was inversely proportional to the square root of the time of contact. Denoting by X the amount of I_2 formed and by C the initial concentration of benzyl iodide (which we can regard as constant for very low percentages of decomposition) we derive the following expression:

$$[I] = (K_{I_2}\cdot X)^{1/2} \qquad ([I_2] = X)$$

$$[C_6H_5CH_2\cdot] = K_{eq}\cdot C/[I] = K_{eq}\cdot C/K_{I_2}\cdot X)^{1/2}$$

$$\frac{1}{2}\cdot\frac{dX}{dt} = k_2'[C_6H_5CH_2\cdot]^2 = \frac{k_2\cdot K_{eq}^2}{K_{I_2}}\cdot\frac{C^2}{X}$$

and on integration we obtain:

$$\tfrac{1}{4}X^2 = (k_2\cdot K_{eq}^2/K_{I_2}) = C^2t$$

$$\frac{X^2}{t^2C^2} = \text{const.}\ \frac{1}{t}$$

where

$$\text{const.} = \frac{4k_2\cdot K_{eq}^2}{K_{I_2}}$$

As the left-hand side is the square of the unimolecular rate constant we have derived the above empirical relationship: the unimolecular rate constant is inversely proportional to the square root of the time of contact.

The scheme discussed above represents only the first approximation of the actual decomposition of benzyl iodide. The participation of other complicating factors prevented the determination of the C—I bond dissociation energy in this compound.

The pyrolysis of allyl iodide was reinvestigated in a static system (163). It would appear that the following scheme represents the best first approximation to the actual reaction:

$$CH_2{=}CHCH_2I \rightleftarrows CH_2{=}CHCH_2\cdot + I$$

$$I + I \rightleftarrows I_2$$

$$CH_2{=}CHCH_2\cdot + CH_2{=}CHCH_2I \rightarrow \text{biallyl} + I$$

The kinetic evidence favors the last reaction rather than the dimerization of allyl radicals. It was not possible, however, to obtain conclusive results which would enable one to calculate the exact value of $D[(CH_2{=}CHCH_2){-}I]$.

Comparing the kinetics of the pyrolysis of benzyl iodide with that of allyl iodide we find that the rate of decomposition of allyl iodide was higher than the rate of decomposition of benzyl iodide. From this one might draw the conclusion that $D[(CH_2{=}CHCH_2){-}I]$ is smaller than $D(C_6H_5CH_2{-}I)$. This conclusion is, however, by no means certain. The postulated rate-determining steps are quite different for each case,

$$2C_6H_5CH_2\cdot \rightarrow \text{bibenzyl} \tag{a$_1$}$$

$$CH_2{=}CHCH_2\cdot + CH_2{=}CHCH_2I \rightarrow \text{biallyl} + I \tag{a$_2$}$$

and a closer inspection shows that the latter reaction should be faster than the former (if reaction a_2 does not involve any appreciable activation energy). In this connection we ought to emphasize that, when comparing rates of decomposition, one is entitled to draw conclusions as to the meaning of differences in bond dissociation energies only when the initial unimolecular dissociation is the rate-determining reaction.

We conclude this section with the following remarks:

(*a*) The pyrolysis of iodides is complicated by the occurrence of back reactions. The inertness of iodine in attacking organic molecules was considered a simplifying factor which, in practice, turned out to be the source of various difficulties.

(*b*) The gradation in the bond dissociation energies can be assessed if the initial dissociation process is the rate-determining step, which is not always the case.

(*c*) The amount of iodine produced mught be decreased by the addition of I_2 to the double bond in olefins. Such a reaction might occur in the gas phase, or more likely on the glass surface.

(*d*) In some cases the decomposition of RI into HI and olefin might be the main process in the pyrolysis of RI. Calculation of the rate of unimolecular split into a radical and an iodine atom is then particularly doubtful. (See, for example, the results of the pyrolysis of *tert*-butyl iodide (35).)

(*e*) The amount of I_2 produced might be increased by the occurrence of the reaction $RI + HI \rightarrow RH + I_2$ (122). This reaction becomes particularly important when the rate of formation of HI ($RI \rightarrow$ olefin $+ HI$) is very high, for example, in the pyrolysis of *tert*-butyl iodide.

H. Determination of the C—H *bond dissociation energy in toluene and related compounds*

It has been shown (183, 186) that the weakest bond in the toluene molecule is the C—H bond of the methyl group. In consequence one would expect the first step in the pyrolysis of this compound to be dissociation into hydrogen atoms and benzyl radicals:

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot + H \tag{1}$$

On account of their high reactivity the hydrogen atoms are rapidly removed by interaction with other molecules present in the system. If the extent of pyrolysis is limited to a very low fraction of decomposition, then hydrogen atoms formed by reaction 1 will be surrounded mainly by the molecules of undecomposed toluene and will be, therefore, most likely to interact with these.

The experiments revealed that a hydrogen atom will react with a toluene molecule in two ways:

$$C_6H_5CH_3 + H \rightarrow C_6H_5CH_2\cdot + H_2 \qquad (2)$$

$$C_6H_5CH_3 + H \rightarrow C_6H_6 + CH_3\cdot \qquad (3)$$

The first reaction produces a hydrogen molecule, while the second produces a methyl radical. The latter is surrounded by molecules of undecomposed toluene and reacts, therefore, rapidly with these, forming a methane molecule and another benzyl radical:

$$C_6H_5CH_3 + CH_3\cdot \rightarrow C_6H_5CH_2\cdot + CH_4 \qquad (4)$$

If the pyrolysis of toluene is carried out in a flow system, where the gases pass rapidly through the reaction vessel, then the benzyl radicals are quickly removed from the hot zone and eventually dimerize:

$$2C_6H_5CH_2\cdot \rightarrow \text{bibenzyl} \qquad (5)$$

In order to eliminate other possible secondary reactions, it is essential to prevent the decomposition of bibenzyl, and therefore it is imperative to work with short times of contact and high rates of flow. Furthermore, it is advantageous to work with low pressure, high temperature, and low fraction of decomposition, since all these factors prevent the dimerization of benzyl radicals in the hot zone. On the other hand, numerous investigations have proved that benzyl radicals are very stable and unreactive: they neither decompose nor initiate any chain reactions (see, e.g., the pyrolysis of benzyl iodide (182), of toluene (186), of ethylbenzene (189), of benzylamine (190, 192), and of benzyl bromide (194)).

We conclude from this outline that if the pyrolysis of toluene takes place according to the above mechanism, then each mole of hydrogen or methane produced corresponds to 1 mole of toluene primarily decomposed and should be accompanied by the formation of 1 mole of bibenzyl. Moreover, the kinetics of decomposition, measured by the rate of evolution of gaseous products ($H_2 + CH_4$), should reveal all the features of a truly unimolecular reaction.

Investigation of the pyrolysis of toluene by M. Szwarc (183, 186) fully confirmed these conclusions. The pyrolysis was investigated by a flow method in the temperature range 680–850°C. and under a pressure of 2–15 mm. of mercury. The experimental technique developed for these investigations made it possible to follow the reaction down to as little as 0.01 per cent of decomposition. The only gaseous products observed were hydrogen and methane in a constant proportion (1.5:1). In addition to gaseous products bibenzyl was isolated in quantities corresponding approximately to 1 mole of bibenzyl per mole of gas formed ($H_2 + CH_4$).

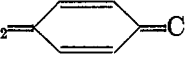
The rate of reaction was calculated on the assumption that 1 mole of gas produced corresponds to 1 mole of toluene primarily decomposed. It was found that the decomposition was a homogeneous gas reaction of the first order, the frequency factor determined experimentally being 2 × 10^{13} sec.$^{-1}$ and the activation energy 77.5 ± 1.3 kcal./mole. In view of all these facts, it seems that the author was fully justified in concluding that the estimated activation energy represents the dissociation energy of the C—H bond in toluene, i.e.:

$$D(C_6H_5CH_2\text{—}H) = 77.5 \pm 1.3 \text{ kcal./mole}$$

Further confirmation for the applicability of this method of estimating C—H bond dissociation energies is based on results obtained in the pyrolysis of compounds related to toluene. The compounds listed below were pyrolyzed and the experiments seem to indicate that they decomposed according to the mechanism suggested for toluene.

	COMPOUNDS	REFERENCE
1...	*p*-, *m*-, and *o*-xylenes	M. Szwarc (186)
2...	*p*-, *m*-, and *o*-fluorotoluenes	M. Szwarc and J. S. Roberts (190)
3...	α-, β-, and γ-picolines (methylpyridines)	J. S. Roberts and M. Szwarc (151)
4...	α- and β-methylnaphthalenes and dimethylnaphthalenes	M. Szwarc and A. Shaw (200)

Let us summarize the experimental results of these pyrolyses. The gaseous products were invariably hydrogen and methane, the H_2/CH_4 ratio being similar to that observed in the decomposition of toluene. The nonvolatile products of pyrolysis were isolated and identified as the relevant homologs of bibenzyl or substituted bibenzyls. Thus: *o,o′*-dimethylbibenzyl and *m,m′*-dimethylbibenzyl were isolated from the products of pyrolysis of *o*-xylene and *m*-xylene, respectively; the 2,2′-, 3,3′-, and 4,4′-difluoro-bibenzyls were isolated, identified, and described as products of pyrolysis of the respective fluorotoluenes (197); α,α-dinaphthylethane and β,β-dinaphthylethane were isolated and identified as products of pyrolysis of α-methylnaphthalene and β-methylnaphthalene, respectively; and the relevant dimethyldinaphthylethane was isolated and described as the product of pyrolysis of 2,6-dimethylnaphthalene (201).

The pyrolysis of *p*-xylene produced a polymer (185) and not the expected *p,p′*-dimethylbibenzyl. Nevertheless it was possible to show that the essential features of this pyrolysis remained the same as that of the toluene pyrolysis. The polymeric substance resulted from polymerization of CH_2CH_2, which was in turn produced by disproportionation of the primary fragments of the decomposition of *p*-xylene, i.e., the *p*-$CH_3C_6H_4CH_2\cdot$ radicals. The formation of molecules of the CH_2CH_2 type and their corresponding polymers seems to be characteristic of the pyrolysis of aromatic compounds having two methyl groups in para positions. In fact, the relevant quinonoid compounds and their polymers were observed in the pyrolysis of 1,4-dimethylnaphthalene, 2-chloro- or 2-fluoro-*p*-xylene, 2,5-dimethylpyrazine, 5,8-dimethylquinoline, and 2,5-lutidine (193).

Technical difficulties prevented the identification of nonvolatile products formed in the pyrolysis of picolines. It was demonstrated, however, that the crystalline product obtained in the pyrolysis of picoline had the molecular weight of the expected dimer.

The kinetics of pyrolysis of the xylenes and of the α- and β-methylnaphthalenes was thoroughly investigated. It was shown that all these decompositions were homogeneous gas reactions of the first order, the frequency factors and activation energies being given in table 10. From these data it is obvious that frequency factors, calculated per *methyl group*, are, within the experimental error, the same for all the compounds listed.

Our confidence in this assumed mechanism and the conclusions following from it is strengthened by the above facts, which suggest that the pattern of decomposition postulated for toluene is valid not only for this single compound but for a whole class of kindred compounds. Of particular importance is the inference drawn that the observed activation energies represent true dissociation energies of the C—H bonds in the respective compounds.

TABLE 10

Pyrolysis of methylbenzenes and methylnaphthalenes

COMPOUND	ACTIVATION ENERGY	FREQUENCY FACTOR
	kcal./mole	*sec.*$^{-1}$
Toluene	77.3 ± 1.3	2×10^{13}
m-Xylene	77.1 ± 1.9	$2 \times 2 \times 10^{13}$
p-Xylene	76.2 ± 1.5	$2 \times 2.5 \times 10^{13}$
o-Xylene	74.8 ± 1.1	$2 \times 2.5 \times 10^{13}$
α-Methylnaphthalene	73.5	1.5×10^{13}
β-Methylnaphthalene	73.5	1.5×10^{13}

Table 11 shows computed values of the C—H bond dissociation energies. This computation was performed by assuming the frequency factor to be a constant for the series, and the actual value chosen was 2×10^{13} sec.$^{-1}$ Justification for the use of this method of computation is discussed in Section IV,C (see page 107).

Consideration of table 11 leads to the following conclusions:

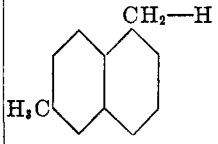
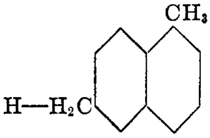
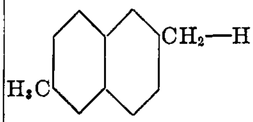
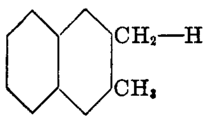
1. The substitution of an additional methyl group in the meta position in toluene seems to have no effect on the C—H bond dissociation energy. On the other hand, if this substitution takes place in the para or ortho position the C—H bond dissociation energy is weakened by 2.5 kcal./mole and 3.5 kcal./mole, respectively. This weakening effect is ascribed to hyperconjugation.
2. Substitution by a fluorine atom seems to have no effect on the C—H bond dissociation energy.
3. It seems that a change of a pyridine ring for a benzene nucleus influences the C—H bond dissociation energy, the gradation being $\gamma > \beta > \alpha$ for the three picolines.

4. A change of a naphthalene ring for a benzene ring decreases the C—H bond dissociation energy by 2.5 kcal./mole. It seems that the position of the methyl group (α or β) does not influence the C—H bond dissociation energy.

Lastly, we shall review the pyrolytic behavior of some compounds which were expected to decompose like toluene but actually behaved differently. The compounds in question are propene, 2-methylpropene ("isobutene"), cyclopentadiene, and ammonia. A consideration of their pyrolysis illustrates the limitations of this method and shows up the various complicating factors which may change completely the mechanism of the decomposition.

TABLE 11

Computed values of the C—H *bond dissociation energies*

COMPOUND	FORMULA	D(C—H) IN KCAL./MOLE (TO THE NEAREST 0.5 KCAL./MOLE)
Toluene	$C_6H_5CH_2—H$	77.5 ± 0.14
m-Xylene	*m*-$CH_3C_6H_4CH_2—H$	77.2 ± 0.18
p-Xylene	*p*-$CH_3C_6H_4CH_2—H$	74.8 ± 0.20
o-Xylene	*o*-$CH_3C_6H_4CH_2—H$	74.0 ± 0.55
p-Fluorotoluene	*p*-$FC_6H_4CH_2—H$	77.5–78.0
m-Fluorotoluene	*m*-$FC_6H_4CH_2—H$	77.5–78.0
o-Fluorotoluene	*o*-$FC_6H_4CH_2—H$	77.5–78.0
α-Picoline	$C_5NH_4CH_2—H$	75.5
β-Picoline	$C_5NH_4CH_2—H$	76.5
γ-Picoline	$C_5NH_4CH_2—H$	77.5
α-Methylnaphthalene	$C_{10}H_7CH_2—H$	75.0
β-Methylnaphthalene	$C_{10}H_7CH_2—H$	75.0
1,6-Dimethylnaphthalene	 or 	75.0
2,6-Dimethylnaphthalene		75.0
2,3-Dimethylnaphthalene		75.0

The pyrolysis of propene was investigated by M. Szwarc (187) by the experimental technique applied previously to the pyrolysis of toluene. Hydrogen and methane were found as products of decomposition. Assuming that the rate of decomposition is measured by the rate of formation of $H_2 + CH_4$, it was shown that the pyrolysis of propene was a homogeneous gas reaction of the first order, the first-order rate constant being given by $1 \times 10^{13} \exp(72{,}000/RT)$ sec.$^{-1}$ Other products of decomposition were identified as allene and ethylene. The amount of allene corresponded roughly to that of $H_2 + CH_4$ (in moles), while the quantity of ethylene seemed to be equivalent to the amount of methane.

The following mechanism, which is analogous to that suggested for the pyrolysis of toluene, accounts well for the nature of the observed products, their relative quantities, and the first order of the reaction.

$$CH_2{=}CHCH_3 \rightarrow CH_2{=}CHCH_2\cdot + H \tag{1'}$$

$$CH_2CHCH_3 + H \rightarrow CH_2{=}CHCH_2\cdot + H_2 \tag{2'}$$

$$CH_2{=}CHCH_3 + H \rightarrow C_2H_4 + CH_3\cdot \tag{3'}$$

$$CH_2{=}CHCH_3 + CH_3\cdot \rightarrow CH_2{=}CHCH_2\cdot + CH_4 \tag{4'}$$

$$2CH_2{=}CHCH_2\cdot \rightarrow CH_2{=}CHCH_3 + CH_2{=}C{=}CH_2 \tag{5'}$$

Postulation of step 1′ seems reasonable, since the high resonance energy of the allyl radical should decrease considerably the C—H bond dissociation energy in propene, making the rupture of this bond more likely than the breaking of the C—C bond. Step 5′ is different from the corresponding reaction 5 of the toluene scheme. The postulated disproportionation of allyl radicals accounts for the formation of allene, while step 5 would require the appearance of biallyl as the product of reaction. Reaction 1′, being the rate-determining step, is responsible for the first-order kinetics and for the frequency factor of 10^{13} sec.$^{-1}$ which is characteristic for a unimolecular process. The observed activation energy of 72 kcal./mole should represent, according to the mechanism postulated, the dissociation energy of the C—H bond in propene. The latter conclusion makes this mechanism rather doubtful, as the suggested value for $D[(CH_2{=}CHCH_2){-}H]$ seems to be too low, particularly since it leads to the value of 30 kcal./mole for the C—C bond dissociation energy in biallyl, a value which is obviously incompatible with the thermal stability of this compound.

Closer comparison of the benzyl and allyl radicals reveals an important difference between them. Both radicals have high resonance energies which facilitate their formation, but the thermal stability of the benzyl radical is mainly due to the fact that it cannot be decomposed into a still more stable fragment. On the other hand, such a decomposition is possible for the allyl radical, namely:

$$CH_2{=}CHCH_2 \rightarrow CH_2{=}C{=}CH_2 + H \tag{6}$$

Reaction 6 leads, of course, to the following chain mechanism:

$$CH_2{=}CHCH_3 \rightarrow CH_2{=}CHCH_2\cdot + H \tag{1'}$$

$$CH_2{=}CHCH_2\cdot \rightarrow CH_2{=}C{=}CH_2 + H \tag{6}$$

$$CH_2{=}CHCH_3 + H \rightarrow CH_2{=}CHCH_2\cdot + H_2 \tag{2'}$$

or

$$CH_2{=}CHCH_3 + H \rightarrow C_2H_4 + CH_3\cdot \tag{3'}$$

$$CH_2{=}CHCH_3 + CH_3\cdot \rightarrow CH_2{=}CHCH_2\cdot + CH_4 \tag{4'}$$

$$CH_2{=}CHCH_2\cdot + H \rightarrow CH_2{=}CHCH_3 \tag{7}$$

Step 7 represents the termination process. [29]

The application of the stationary-state method leads to the following expression for the rate of the overall decomposition:

$$d(H_2 + CH_4)/dt = (k_1k_6k_2/k_7)^{1/2}\,[C_3H_8]$$

which shows that the chain mechanism also requires first-order kinetics. Moreover we may assume that $k_2 \approx k_7$, since reactions 2 and 7 probably have the same collision factor and negligible activation energies. Hence we deduce:

$$d(H_2 + CH_4)/dt = (k_1k_6)^{1/2}\,[C_3H_8]$$

Now, since reactions 1 and 6 are unimolecular decompositions, both should require frequency factors of the order of 10^{13} sec.$^{-1}$; therefore the frequency factor of the overall reaction is also of the order of 10^{13} sec.$^{-1}$ It follows that the overall activation energy is

$$E_{act} = \tfrac{1}{2}(E_1 + E_6)$$

and since

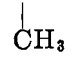
$$E_1 = D[(CH_2{=}CHCH_2){-}H] \text{ and } E_6 = D[(CH_2{=}\underset{\bullet}{C}CH_2){-}H]$$

$E_1 + E_6$ is the endothermicity of the process:

$$CH_2{=}CHCH_3 \rightarrow CH_2{=}C{=}CH_2 + 2H - 145 \text{ kcal./mole}$$

This means then that the proposed chain process accounts for the nature of the decomposition products, their relative quantities, the first-order kinetics, the frequency factor, and even for the observed activation energy.

The decomposition of the allyl radical into allene and a hydrogen atom is the complicating factor which makes the mechanism of the decomposition of propene essentially different from that suggested for toluene. The similar decomposition of the methylallyl radical, i.e.,



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2\cdot \rightarrow CH_2{=}C{=}CH_2 + CH_3\cdot$$

is responsible for the fact that the pyrolysis of 2-methylpropene (188) takes a course similar to that of propene.

The estimation of the C—H bond dissociation energy in propene and 2-methyl-

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[29] For discussion of the other termination processes see reference 187.

propene would be feasible if the length of the reaction chain could be estimated. The data provided by the decomposition of 2-methylpropene suggest that the length of the chain is approximately 10. The stationary-state method leads to the following expression for the length of the reaction chain in the decomposition of propene:

$$\ln \text{(length of chain)} = (1/2RT)\cdot(E_1 - E_6) - 1/2 \ln 3$$ [30]

Taking the length of the chain as 10, one derives

$$E_1 - E_6 \approx 11 \text{ kcal./mole}$$

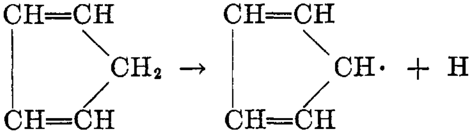
while

$$E_1 + E_6 = 145 \text{ kcal./mole}$$

(This is the endothermicity of the reaction $CH_2{=}CHCH_3 \rightarrow CH_2{=}C{=}CH_2 + 2H$)

Thus $E_1 = D[(CH_2{=}CHCH_2){-}H] \approx 78$ kcal./mole. This result seems to be plausible and leads to the frequency factor 2.5×10^{13} sec.$^{-1}$ for the initial decomposition process, a value which is in agreement with the results discussed previously (see page 131). Similar considerations lead to $D[(CH_2{=}CCH_2){-}H] = 76$ kcal./mole and 5×10^{13} sec.$^{-1}$ for the frequency factor of the initial decomposition of 2-methylpropene. It must be emphasized, however, that these results are highly spceulative and they call for an additional and independent evidence. Such evidence has been provided recently by a study of the pyrolysis of 1-butene (199; see also page 141).

A few experiments with cyclopentadiene were carried out in the Manchester laboratories, the technique described above being used again (unpublished results). It was expected that the molecule of cyclopentadiene would split into a hydrogen atom and the C_5H_5 radical



and that the hydrogen atoms would react with the excess of cyclopentadiene, producing H_2 and C_5H_5 radicals. It was also anticipated that the C_5H_5 radicals would be stable enough to emerge from the reaction vessel unchanged and eventually to dimerize. It was found, however, that a complete cracking of the molecule took place. The products of the decomposition contained H_2, CH_4, C_2 hydrocarbons, etc. No attempt was made to clear up the mechanism of this

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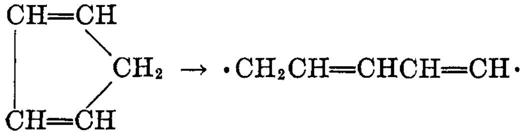
[30] ln 3 appears in this expression because statistical considerations require that the frequency factor of the decomposition of the C—H bond in the methyl group of propene be three times as great as for the decomposition:

$$CH_2{=}CHCH_2\cdot \rightarrow CH_2{=}C{=}CH_2 + H$$

pyrolysis. It may well be that the molecule breaks up by the scission of a C—C bond, i.e.,



with the subsequent decomposition of the diradical thus formed.

The thermal decomposition of ammonia (190) proved to be another instance of a pyrolysis from which no information on bond dissociation energy was obtained. It was expected that it would be possible to break the N—H bond and to produce hydrogen atoms and NH_2 radicals. Further, it was supposed that hydrogen atoms would react with ammonia, producing H_2 and more NH_2 radicals, and that the latter would dimerize in the outlet tube. The reaction, however, proved to be heterogeneous, a result which confirms the earlier observations of C. N. Hinshelwood and E. R. Burk (82), the products being H_2 and N_2 in the molar ratio of 3:1. Moreover, it is known that NH_2 radicals decompose rather than dimerize, and the products of their decomposition are H_2 and N_2.

I. The determination of bond dissociation energy by the "toluene carrier gas" technique

In the preceding section we described a method of estimating the C—H bond dissociation energy which can be summarized as follows: (*1*) Hydrogen atoms produced in the decomposition are rapidly removed from the system, forming H_2 (or CH_4) and thermally stable benzyl radicals (or their homologs or derivatives). (*2*) The benzyl radicals being inert and thermally stable neither decompose nor react, but pass out from the system when they eventually dimerize outside the hot zone. Therefore, no chain reaction ensues and the rate of formation of H_2 (and CH_4) measures the rate of initial decomposition of the compound investigated.

This method, with slight modifications, applies to the investigation of the pyrolysis of a number of compounds which split into two radicals by the breaking of one bond only. The technique is limited, however, by the condition that the dissociation energy of the bond in question must be smaller (preferably much smaller) than the C—H bond dissociation energy in toluene.

Let us assume that a molecule R—R′ decomposes by the rupture of the R—R′ bond into radicals R and R′, and that $D(\text{R—R}')$ is smaller than $D(C_6H_5CH_2\text{—H})$ i.e., smaller than 77 kcal./mole. We can, therefore, carry out the dissociation process $RR' \rightarrow R + R'$ at temperatures low enough to avoid the decomposition of toluene, which is used in this technique as a carrier gas. The radicals R and R′, being surrounded by molecules of toluene, are removed rapidly from the system by the reactions:

$$C_6H_5CH_3 + R \rightarrow C_6H_5CH_2\cdot + RH$$

$$C_6H_5CH_3 + R' \rightarrow C_6H_5CH_2\cdot + R'H$$

In the experimental set-up (similar to that described in the preceding section) the benzyl radicals pass out of the reaction vessel and eventually dimerize outside the hot zone. We conclude, therefore, that if the pyrolysis of RR′ takes place according to the scheme suggested above, then the rate of initial decomposition may be measured by the rate of formation of RH, or R′H, or bibenzyl. Moreover, the molecular ratio of RH:R′H:bibenzyl ought to be 1:1:1.

The appearance of bibenzyl amongst the products of decomposition makes it possible to discriminate between two modes of decomposition: namely, the decomposition into radicals (or atoms) and the decomposition into molecules. For example, ethyl bromide might decompose into ethyl radicals and bromine atoms, or into ethylene and hydrogen bromide. By using toluene as a carrier gas we should obtain bibenzyl as one of the products of reaction only if the decomposition takes place *via* radicals, whereas no bibenzyl would be produced if the compound decomposes directly into two *molecules.*

The most suitable compounds for this type of investigation are the benzyl derivatives of the general formula $C_6H_5CH_2X$, where X denotes an atom or a radical. The high resonance energy of the benzyl radical decreases considerably the C—X bond dissociation energy, making possible pyrolysis at conveniently low temperatures. Furthermore, the overall process is simplified by the fact that there is one radical (or atom) only, namely, X, which has to be removed from the system. The second fragment—the benzyl radical—remains unchanged and eventually gives rise to bibenzyl.

The important condition for the successful operation of the method is the high reactivity of X, which has to be removed rapidly from the system by the reaction:

$$C_6H_5CH_3 + X \rightarrow C_6H_5CH_2\cdot + HX$$

For example, the method fails in the case of benzyl iodide because the iodine atoms produced by the initial decomposition are too inert and unable, therefore, to react with toluene and to produce hydrogen iodide. This failure leads in consequence to back reaction and eventually to the equilibrium:

$$C_6H_5CH_2I \rightleftharpoons C_6H_5CH_2\cdot + I$$

which has been discussed on page 127.

The method was successfully applied in the pyrolysis of ethylbenzene (189), benzyl bromide (194), and benzylamine (192). The pyrolysis of ethylbenzene illustrates how the kinetics of decomposition could be simplified by using toluene as a carrier gas. The decomposition of ethylbenzene without carrier gas led to a chain reaction:

$$\left.\begin{array}{l} C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2\cdot + CH_3\cdot \\ C_6H_5CH_2CH_3 + CH_3\cdot \rightarrow C_6H_5C_2H_4\cdot + CH_4 \end{array}\right\}\text{initiation steps}$$

$$\left.\begin{array}{l} C_6H_5C_2H_4\cdot \rightarrow C_6H_5CH{=}CH_2 + H \\ C_6H_5CH_2CH_3 + H \rightarrow C_6H_5C_2H_4\cdot + H_2 \end{array}\right\}\text{propagation steps}$$

and some termination steps. Styrene and hydrogen are the main products of the pyrolysis required by the above mechanism. It was found, in fact, that the bulk of nongaseous material was composed of styrene, with small quantities of bibenzyl; the main gaseous product was hydrogen, which was present along with small quantities of methane and C_2 hydrocarbons (the latter resulted probably from some chain termination process; for example, $CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$, or $C_6H_5C_2H_5 + H \rightarrow C_6H_6 + C_2H_5\cdot$). The kinetics of the decomposition was hopelessly complicated and difficult to disentangle.

The character of the pyrolysis was changed radically when toluene was used as a carrier gas. The formation of the $C_6H_5C_2H_4\cdot$ radical, which was responsible for the chain propagation, was prevented by the reaction between methyl radicals and toluene:

$$C_6H_5CH_3 + CH_3\cdot \rightarrow CH_4 + C_6H_5CH_2\cdot$$

Since toluene was in great excess, the chance of reaction between methyl radicals and toluene was much higher than between methyl radicals and ethylbenzene. In consequence the products of the pyrolysis were methane and bibenzyl in molar proportions (1:1). The kinetics of the decomposition, measured by the rate of formation of methane, obeyed the first-order law, the activation energy being 63 kcal./mole and the frequency factor 1×10^{13} sec.$^{-1}$ It was concluded, therefore, that the rate of formation of methane measures the rate of initial decomposition of ethylbenzene into methyl and benzyl radicals and the observed activation energy of 63 kcal./mole represents the C—C bond dissociation energy in ethylbenzene.

There is a check on the values obtained for $D(C_6H_5CH_2—H)$ and $D(C_6H_5CH_2—CH_3)$. These two values, in conjunction with the relevant thermochemical data, make it possible to estimate the dissociation energy of the first C—H bond in methane at 103 ± 3 kcal./mole, and the results are in accordance with the $D(CH_3—H)$ estimated by other investigators, and particularly with the determination of G. B. Kistiakowsky and E. R. Van Artsdalen (88) (101 ± 1 kcal./mole).

The pyrolysis of benzyl bromide (194), investigated by the same technique, produced hydrogen bromide and bibenzyl in molar proportions of 1:1. The kinetics of the decomposition revealed all the characteristic features of a unimolecular reaction, obeying the first-order law and giving a frequency factor of the order of 10^{13} sec.$^{-1}$ The observed activation energy of 50.5 kcal./mole was identified, therefore, with the C—Br bond dissociation energy in benzyl bromide. It was again possible to check the deduction by using the available thermochemical data. The difference between $D(C_6H_5CH_2—H)$ and $D(C_6H_5CH_2—Br)$ was estimated calorimetrically by O. H. Gellner and H. A. Skinner (61) at 29 ± 3 kcal./mole. Since the direct pyrolytic estimation of both bond dissociation energies gave 77.5 ± 1.3 kcal./mole for the former and 50.5 ± 2 kcal./mole for the latter, the difference expected is 27 ± 3.3 kcal./mole. The agreement seems to be satisfactory.

The pyrolysis of benzylamine (192), investigated again by the same technique, produced ammonia and bibenzyl. This decomposition also revealed the characteristic features of the unimolecular reaction, and therefore the observed activation energy of 59 ± 4 kcal./mole was identified with the C—N bond dissociation energy in benzylamine.

The above technique was applied to investigations of the pyrolysis of other classes of compounds such as hydrazine (191), biacetyl (195), 1-butene (199), and a series of organic bromides (unpublished results).

The pyrolysis of hydrazine (191) provided an example of a mixed heterogeneous-homogeneous decomposition. It is well known that hydrazine decomposes heterogeneously into nitrogen and ammonia, or into nitrogen, hydrogen, and ammonia, according to the following stoichiometric equations:

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \qquad (h_1)$$

$$2N_2H_4 \rightarrow H_2 + N_2 + 2NH_3 \qquad (h_2)$$

The first mode of decomposition is predominant in reactions which take place on the surfaces of glass or silica, while the second represents the main reaction which takes place on the surfaces of platinum or tungsten wire. It was also demonstrated that the heterogeneous decomposition obeyed first-order kinetics.

The investigation of the pyrolysis of hydrazine at much higher temperatures, i.e., 660–780°C., revealed that in addition to the heterogeneous decompositions mentioned a homogeneous reaction took place in which a molecule of hydrazine dissociated into two NH_2 radicals.

$$N_2H_4 \rightarrow 2NH_2 \qquad (h_3)$$

It was possible to investigate this homogeneous reaction by using toluene as a carrier gas, since under these conditions the NH_2 radicals reacted with toluene, producing eventually bibenzyl. Hence the rate of formation of bibenzyl measured the rate of homogeneous dissociation (h_3).

The products of the pyrolysis contained, therefore, nitrogen, hydrogen, ammonia, and bibenzyl. Assuming that all the observed hydrogen was produced by reaction h_2, it was possible to calculate the amount of hydrazine decomposed and ammonia formed in this reaction. Nitrogen was formed in both reactions h_1 and h_2; deducting therefore from the total amount of nitrogen observed the amount of hydrogen (calculated in moles), one obtains the amount of nitrogen produced in reaction h_1. Thus it was possible to compute the amount of hydrazine decomposed and of ammonia formed in this reaction. Finally the amount of hydrazine decomposed and of ammonia formed in the homogeneous reaction (h_3) could be calculated from the amount of bibenzyl observed. Thus it was possible to calculate the total amount of ammonia formed in the pyrolysis and the total amount of hydrazine decomposed. Since both these quantities were observable, the above deductions could be checked. Table 12 illustrates the above method of computation. The activation energy of the homogeneous dissociation process (h_3) was estimated at 60 kcal./mole and the frequency factors at 4×10^{12} sec.$^{-1}$ Making the usual assumption, that the activation energy of the recombination process is negligible, it was deduced that $D(NH_2—NH_2) = 60$ kcal./mole.

The results obtained in the investigation of the pyrolysis of hydrazine may be checked against the results obtained in the pyrolysis of benzylamine, since having $D(NH_2—NH_2)$ and $\Delta H_f(N_2H_4)$ one is able to calculate $\Delta H_f(NH_2\cdot)$, and the latter value can be independently calculated from $D(C_6H_5CH_2—NH_2)$, $\Delta H_f(C_6H_5CH_2NH_2)$, and $\Delta H_f(C_6H_5CH_2\cdot)$. The calculation based on the estimated value of $D(NH_2—NH_2)$ leads to $\Delta H_f(NH_2\cdot) = 41 \pm 2$ kcal./mole, while that based on $D(C_6H_5CH_2—NH_2)$ gives $\Delta H_f(NH_2\cdot) = 35 \pm 5$ kcal./mole. The latter value relies on $\Delta H_f(C_6H_5CH_2NH_2)$ estimated by combustion by Petit (133a) in 1889. If the heat of combustion which he obtained was too low—which seems likely[31]—then the corrected value of $\Delta H_f(NH_2\cdot)$ would be higher, making the agreement between both methods of computation still closer.

TABLE 12

OBSERVED AMOUNT	EQUATION OF DECOMPOSITION	NH_3 CALCULATED	N_2H_4 DECOMPOSED
millimoles		*millimoles*	*millimoles*
H_2........0.25	$2N_2H_4 = H_2 + N_2 + 2NH_3$	$2 \times 0.25 = 0.50$	$2 \times 0.25 = 0.50$
N_2........$0.43 = 0.25 + 0.18$	$3N_2H_4 = N_2 + 4NH_3$	$4 \times 0.18 = 0.72$	$3 \times 0.18 = 0.54$
Bibenzyl..0.48	$N_2H_4 = 2NH_2$ (1 bibenzyl)	$2 \times 0.48 = 0.96$	$1 \times 0.48 = 0.48$
Total...		$NH_3 = 2.18$	$N_2H_4 = 1.52$
Observed		$NH_3 = 2.02$	

The pyrolysis of biacetyl (195) yields carbon monoxide and methane in the molar proportion 1:1. The amount of biacetyl decomposed was estimated as a difference between the amounts of biacetyl introduced and recovered (i.e., not decomposed), the latter two entities being determined directly. It was found in this way that each mole of biacetyl decomposed produced 2 moles of carbon monoxide and 2 moles of methane. These facts suggested that the mechanism of the decomposition of biacetyl is represented by the following equations:

$$CH_3COCOCH_3 \rightarrow 2CH_3CO\cdot \qquad \text{The slow, rate-determining step}$$

$$CH_3CO\cdot \rightarrow CH_3\cdot + CO \qquad \text{A very rapid reaction}$$

$$CH_3\cdot + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2\cdot \qquad \text{A rapid reaction}$$

and that the rate of formation of $CO + CH_4$ measures the rate of initial decomposition of biacetyl, which was found to obey the first-order kinetics. Hence, the activation energy estimated at 60 kcal./mole represents the $CH_3CO—COCH_3$ bond dissociation energy.

The value of $D(CH_3CO—COCH_3)$, in conjunction with the heat of formation of biacetyl, yields the heat of formation of the acetyl radical, which was computed

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[31] The minute amount of water or carbon dioxide which is likely to be in benzylamine makes the heat of combustion too low (0.5 per cent of either of these decreases the heat of combustion by about 5 kcal./mole).

at -11 kcal./mole. Having this value it was possible to calculate the various $CH_3CO—X$ bond dissociation energies from the relevant thermochemical data only.

The above value for the heat of formation of the acetyl radical was confirmed by the estimation of $D(C_6H_5CH_2—COCH_3)$. The pyrolysis of the latter compound was investigated also by the "toluene carrier gas" technique (195), and it was found to proceed analogously to the pyrolysis of biacetyl. The value of $D(C_6H_5CH_2—COCH_3)$ was estimated at $\sim$63 kcal./mole, and this, together with the required thermochemical data, led to $\Delta H_f(CH_3CO\cdot) \approx 10$ kcal./mole, in fair agreement with the previous estimate deduced from studies of the pyrolysis of biacetyl.

The pyrolysis of 1-butene (199) was similar to the pyrolysis of ethylbenzene. The initial decomposition produced methyl and allyl radicals:

$$CH_2{=}CHCH_2—CH_3 \rightarrow CH_2{=}CHCH_2\cdot + CH_3\cdot$$

Methyl radicals were removed by toluene and the progress of decomposition was measured, therefore, by the rate of formation of methane. The $CH_2{=}CHCH_2—CH_3$ bond dissociation energy was estimated at 62 kcal./mole, and this value led to $D[(CH_2{=}CHCH_2)—H] = 77$ kcal./mole. The latter C—H bond dissociation energy was estimated previously by investigating the kinetics of the decomposition of propene. These studies suggested a value of 78 kcal./mole for $D[(CH_2{=}CHCH_2)—H]$, which compares well with that obtained from investigations of the pyrolysis of 1-butene.

J. Dissociation energies of RO—NO *bonds*

E. W. R. Steacie and his collaborators investigated the kinetics of the pyrolysis of a series of organic nitrites, *viz.*, methyl (171), ethyl (172), *n*-propyl (173), isopropyl (174), and *n*-butyl nitrites (175). All these decompositions were studied by a static method over the temperature range of 170–230°C., the rate of reaction being measured by an increase of pressure. By packing the reaction vessel with short silica tubes (which increased the surface/volume ratio by a factor of 6–9) it was proved that all these processes were homogeneous gas reactions. Assuming that the increase of pressure was proportional to the amount of compound decomposed, Steacie deduced that all these pyrolyses followed the first-order law. This deduction was substantiated by the following two criteria:

1. The time required for an increase in pressure by some constant fraction of its initial value was constant. This meant that the time for partial decomposition was independent of the initial pressure.

   In most cases the constancy of the time for fractional decomposition was found to hold for initial pressures ranging from 50 to 350 mm. of mercury, and in the case of methyl nitrite even for higher pressures, up to 35 atm. (170).
2. The plot of the increase in pressure against time was in close agreement with the theoretically expected graph for a first-order reaction. This was further checked by comparing ratios of $t_{50\%}/t_{25\%}$, as obtained from ex-

periments, with the theoretical values for the same ratios derived on the basis of first-order kinetics. For example, in the decomposition of methyl nitrite the ratio of the times required to increase the pressure by 50 per cent and 25 per cent of the initial pressure was found to be 2.53. The final increase of pressure was 82.5 per cent of the initial pressure. Thus, the above increments of pressure correspond to 30.3 per cent and 60.6 per cent of the total decomposition. The theoretical value of $t_{60.6\%}/t_{30.3\%}$ is 2.58, in excellent agreement with the experimental value of 2.53.

The investigations also included the analysis of the products of each reaction. Although the analytical technique was rather crude, Steacie was able to conclude that the overall process of decomposition was represented stoichiometrically by the equation:

$$R'CH_2ONO \rightarrow NO + \tfrac{1}{2}R'CH_2OH + \tfrac{1}{2}R'CHO$$

Finally, the activation energies of these processes were estimated in the usual way from the temperature coefficients of the time of fractional decomposition. The results are summarized in table 13.

TABLE 13

Activation energies of decomposition of organic nitrites

COMPOUND	ν	E
	$sec.^{-1}$	*kcal./mole*
CH_3ONO	1.8×10^{13}	36.4
C_2H_5ONO	1.4×10^{14}	37.7
n-C_3H_7ONO	2.7×10^{14}	37.6
Iso-C_3H_7ONO	1.3×10^{14}	37.0
n-C_4H_9ONO	10^{13}	36.0

It follows from what was said that the decompositions of organic nitrites are homogeneous gas reactions of the first order, the frequency factor of the rate constants being 10^{13}–10^{14} $sec.^{-1}$ Consequently, Steacie concluded that all these pyrolyses are initiated by the same unimolecular split of the molecule of the organic nitrite. The results of the analysis of the products proves that the following reaction is the only possible[32] primary step, as suggested by Steacie:

$$R'CH_2ONO \rightarrow R'CH_2O\cdot + NO$$

This primary reaction must be followed by a sequence of rapid processes which remove the $R'CH_2O\cdot$ radicals. Several reaction schemes may be proposed which take these points into account.

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[32] One would expect the dissociation of the molecule of RONO to occur by the rupture of the RO—NO bond, because this bond seems to be the weakest one in the molecule of the organic nitrite.

$$\left.\begin{aligned} R'CH_2O\cdot &\rightarrow R'CHO + H \\ R'CH_2O\cdot + H &\rightarrow R'CH_2OH \end{aligned}\right\} \tag{A}$$

$$\left.\begin{aligned} &R'CH_2O\cdot + R'CH_2ONO \rightarrow R'CH_2OH + R'\underset{\cdot}{C}HONO \\ &R'\underset{\cdot}{C}HONO \rightarrow R'CHO + NO \end{aligned}\right\} \tag{B}$$

$$2R'CH_2O\cdot \rightarrow R'CH_2OH + R'CHO \tag{C}$$

Scheme A, originally proposed by Steacie and workers (171), does not seem to be likely. If a hydrogen atom is formed, then one expects it to have a much higher chance of collision with a molecule of the undecomposed nitrite than with an $R'CH_2O\cdot$ radical, since the concentration of these radicals is very much smaller than that of the undecomposed nitrite. Therefore, the probability of reaction D

$$R'CH_2ONO + H \rightarrow H_2 + R'\underset{\cdot}{C}HONO \tag{D}$$

would be very considerable, and this reaction could be neglected only if it either has a very high activation energy, or if the stationary concentration of $R'CH_2O\cdot$ radicals is very high. However, neither alternative seems to be acceptable.

Scheme C leads to the same result as scheme A, and yet it does not involve the improbable implications of the latter, but it requires a great stability of the $R'CH_2O\cdot$ radicals.

Scheme B, proposed by F. O. Rice and E. L. Rodowskas (148), seems to be the most plausible. It implies that the observed reaction rate is twice as high as the initiation rate, leaving all the other features of the kinetics identical with those required by the previous schemes. It is obvious, however, that all three schemes account equally well for the observed products of the reaction and for its unimolecular character.

The unimolecular character gains additional support from the studies of F. O. Rice and E. L. Rodowskas (148). These workers investigated the pyrolysis of ethyl nitrite in the region 400–500°C., using the mirror technique and carbon dioxide as a carrier gas. The activation energy was estimated by them as 35 ± 3 kcal./mole, and it was attributed to the initial rupture of the molecule of C_2H_5ONO into a $C_2H_5O\cdot$ radical and an NO molecule. The radicals removing the mirror were identified as $CH_3\cdot$, which can be interpreted in terms of the decomposition of the $CH_3CH_2O\cdot$ radical into a $CH_3\cdot$ radical and a CH_2O molecule. The high temperature of the pyrolysis and the dilution of ethyl nitrite with carbon dioxide favor the degradation of the $CH_3CH_2O\cdot$ radical, as suggested above.[33]

In the light of all these facts one may safely conclude that the activation energy of the dissociation process

$$RONO \rightarrow RO\cdot + NO$$

[33] The experiments of Rice and Rodowskas also demonstrate that in the absence of the carbon dioxide carrier no methyl radicals are produced.

is of the order of 34–37 kcal./mole. It is well established that the recombination of various radicals with nitric oxide molecules proceeds extremely easily, and this implies that the activation energy of the recombination process is very small, perhaps even zero. Hence, one arrives at the final result: *The dissociation energy of the* RO—NO *bond is of the order of 34–37 kcal./mole.*

There remains a further point to be elucidated: namely, the influence of the variation of the radical R in the nitrite molecule on the dissociation energy of the RO—NO bond. The activation energies listed in table 13 are not accurate enough to provide a satisfactory answer, and it is suggested that the problem might be solved by comparing the rate constants of decompositions of various nitrites, measured at the same temperature. On the assumption of a *constant frequency factor* the ratio of the rate constants leads to the difference in the dissociation energies of the various RO—NO bonds. The necessary data are provided in the paper by E. W. R. Steacie and W. McF. Smith (175) (table 14).

TABLE 14

Dissociation energies of RO—NO *bonds*

COMPOUND	RATE CONSTANT AT 190°C.	ΔD
	sec.$^{-1}$	*kcal./mole*
CH_3O—NO	0.97×10^{-4}	(0)
C_2H_5O—NO	1.9×10^{-4}	−0.6
n-C_3H_7O—NO	3.9×10^{-4}	−1.3
Iso-C_3H_7O—NO	3.7×10^{-4}	−1.2
n-C_4H_9O—NO	8.9×10^{-4}	−1.9

Inspection of table 14 shows that the rate constant increases, i.e., the bond dissociation energy decreases, in the series methyl, ethyl, propyl, butyl. Closer examination of Steacie's results, however, casts some doubts on the accuracy of the values quoted in table 14. The decompositions of nitrites are certainly accompanied by various side reactions, which may considerably affect the numerical results obtained from measurements of the increase of pressure. Some of the disconcerting factors are summarized as follows:

1. The suggested mechanism requires the final pressure to be twice the initial pressure. Actually the increase of pressure amounts only to 82 per cent for methyl nitrite, 86 per cent for ethyl nitrite, and it varies from 60 to 80 per cent in the case of butyl nitrite. (For n-propyl nitrite and isopropyl nitrite the increase of pressure reached the theoretically required value of 100 per cent.)
2. In some experiments a drop of pressure was observed in the last period of reaction, and in these cases it was necessary to consider the maximum value of the pressure as the final pressure.
3. The postulated mechanism requires all the noncondensable gas to be nitric oxide. In fact, the noncondensable gas obtained in the decomposition of methyl nitrite contained 81–88 per cent of nitric oxide and 6–10 per cent of carbon monoxide; that obtained from ethyl nitrite contained

88–94 per cent of nitric oxide and 1–3 per cent of carbon monoxide; that from *n*-propyl nitrite contained 90 per cent of nitric oxide; and that from isopropyl nitrite contained 82–84 per cent of nitric oxide.

4. The case of *n*-propyl nitrite is particularly doubtful, as considerable amounts of tarry materials and of carbon were deposited in the reaction bulb, the results being much less reproducible than those obtained for the lower nitrites.
5. The unimolecular rate constants calculated for the various periods of reaction were sometimes different; e.g., in the decomposition of ethyl nitrite the rate constant increased slightly towards the end of reaction, while in the decomposition of isopropyl nitrite it dropped considerably as the reaction proceeded.
6. A later investigation by A. G. Carter and M. W. Travers (38) demonstrated that the rate of production of nitric oxide resulting from the decomposition of methyl nitrite could not be represented by any simple kinetic expression. In the words of these workers there is ". . . . no justification for the statement that it [the decomposition] involves a first order reaction."

This last statement of Travers is, in our opinion, debatable, and we consider it most likely that the decomposition of organic nitrites in the main is governed by the unimolecular reaction:

$$\text{RONO} \rightarrow \text{RO}\cdot + \text{NO}$$

However, the disturbing factors listed above make the data presented by Steacie and his collaborators too uncertain for any conclusions to be drawn from them about the influence of the nature of R on the dissociation energy of the RO—NO bond. The present writer is inclined to believe that $D(\text{RO—NO})$ is of the order of 34–37 kcal./mole, probably tending towards the lower limit. It seems also that the dissociation energy of the RO—NO bond decreases along the series methyl, ethyl, propyl, butyl, but this trend is by no means established. The problem might be solved if it were possible to compare the *initial rates* of decomposition of various nitrites measured at the same temperature, which should be as low as possible.

K. The O—O *bond dissociation energy in peroxides*

The dissociation energy of the O—O bond in hydrogen peroxide has been estimated at 55 kcal./mole from the thermochemical data in conjunction with the measured value of $D(\text{H—OH})$. It seems, however, that the O—O bond dissociation energies in organic peroxides are considerably lower than $D(\text{HO—OH})$, although the existing observations do not permit one to draw any definite conclusions.

The kinetics of the thermal decomposition of various organic peroxides convinces us that the first step in these processes is the rupture of the O—O bond. Unfortunately, this primary dissociation is followed by various secondary reactions which complicate the overall kinetics to such an extent that the estimation of the activation energy of the initial dissociation from the overall activation energy is subject to considerable uncertainties. We may illustrate this point by discussing the kinetics of the thermal decomposition of benzoyl peroxide, acetyl peroxide, ethyl peroxide, propyl peroxide, and tertiary butyl peroxide.

The decomposition of benzoyl peroxide has been investigated by many workers. It has been shown that this decomposition produces carbon dioxide, benzoic acid, phenyl benzoate, and various other products, not all of which were identified. The first kinetic studies were performed by D. J. Brown (29), by F. I. Berezovskaya and E. K. Varfolomeeva (17), and by S. Kamenskaya and S. Medvedev (86) in 1940. The rate of reaction was measured by the rate of disappearance of peroxides. The reaction was found to be approximately of the first order, and the activation energy measured by the temperature coefficient of the overall process (over the temperature range 75–85°C.) was estimated at 30 kcal./mole (86). The very extensive studies of K. Nozaki and P. D. Bartlett (121) demonstrated that the overall process can be represented by two simultaneous reactions—a unimolecular decomposition and a chain reaction which obeys a kinetic of the 3/2 or second order. They suggested the following mechanism in order to account for the observed facts:

$$\left.\begin{array}{l}(C_6H_5CO)OO(COC_6H_5) \rightarrow 2C_6H_5COO\cdot \\ 2C_6H_5COO\cdot \rightarrow C_6H_5COOC_6H_5 + CO_2\end{array}\right\} \quad \text{Unimolecular decomposition}$$

$$C_6H_5COO\cdot + (C_6H_5CO)OO(COC_6H_5) \rightarrow C_6H_5COOC_6H_5 + CO_2 + C_6H_5COO\cdot \quad \text{Chain reaction}$$

$$C_6H_5COO\cdot + \text{solvent} \rightarrow \text{product} + \text{new radical} \qquad \text{Chain transfer}$$

The existence of a chain reaction was proved by demonstrating inhibition and initiation phenomena. The component rate constants for the unimolecular and chain reactions were computed from the overall kinetics, and the activation energies of the unimolecular dissociation were estimated at 30.7 kcal./mole and at 33.3 kcal./mole for decompositions taking place in acetic anhydride and benzene, respectively. The corresponding frequency factors of the unimolecular steps in the two solvents were calculated to be 6×10^{14} sec.$^{-1}$ and about 10^{16} sec.$^{-1}$ It is to be noted that the rate of the reaction depended on the nature of the solvent used (compare references 10 and 121), and it is most unfortunate that, owing to the low volatility of benzoyl peroxide, the reaction has not been investigated in the gaseous phase.

The complicating action of the solvent is caused by the chain-transfer reaction:

$$C_6H_5COO\cdot + \text{solvent} \rightarrow \text{product} + \text{new radical}$$

followed by the secondary chain process initiated by new radicals. One might expect, however, that if the above reaction leads to a stable radical, then the latter would terminate the chain process, and thus the rate of inhibited reaction would measure the rate of the initial dissociation. It was our belief that such a simplification of the process would be brought about by using toluene as a solvent, but the results of P. D. Bartlett and R. Altschul (9) and of K. Nozaki and P. D. Bartlett (121) did not confirm this expectation.

The importance of the chain process would be reduced in more dilute solutions, but the work of P. F. Hartman, H. G. Sellers, and D. Turnbull (74), who investigated the decomposition of benzoyl peroxide at various concentrations (the lowest concentration being 0.005 mole/liter) did not reveal any simplification of the reaction scheme. The results of these workers agreed very well with those obtained by Nozaki and Bartlett, and the activation energies and frequency factors reported by Turnbull *et al.* are presented in table 15.

TABLE 15

Frequency factor for the decomposition of benzoyl peroxide

SOLVENT	CONCENTRATION	E	ν
	moles/liter	*kcal./mole*	*sec.*$^{-1}$
Benzene	0.0050		
Benzene	0.025	29.9	1×10^{14}
tert-Butylbenzene	0.012	30.4	2×10^{14}
Cyclohexane	0.012	28.2	3×10^{13}
Methylcyclohexane	0.012	30.7	6×10^{14}
n-Octane	0.008	29.0	3×10^{13}

TABLE 16

Unimolecular rate constants for the decomposition of benzoyl peroxide

TEMPERATURE	$k \times 10^6$	TEMPERATURE	$k \times 10^6$
°*C.*	*sec.*$^{-1}$	°*C.*	*sec.*$^{-1}$
54*	1.83	80	33.5
64*	5.84	90	110.0
74*	19.3		

* These results were obtained by S. G. Cohen (40).

D. J. Brown (30) presented in his paper the data for the unimolecular rate constants (see table 16), covering a great range of temperature, and we may use them for the more accurate computation of activation energy and frequency factor. This leads to an activation energy of about 27.5 kcal./mole and a frequency factor of about 3×10^{12} sec.$^{-1}$

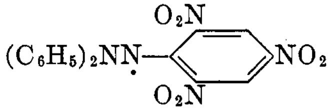
Investigations by B. Barnett and W. E. Vaughan (8) proved again that the decomposition of benzoyl peroxide is a composite reaction and can be treated as strictly of the first order only in infinitely dilute solutions. The activation energy of the first-order reaction in infinitely dilute solution was estimated at 31–32 kcal./mole. The rate of the reaction depended on the nature of the solvent, varying by a factor of 20.

All the data mentioned above indicate that the primary dissociation process

$$(C_6H_5CO)OO(COC_6H_5) \rightarrow 2C_6H_5COO\cdot$$

corresponds to an activation energy of about 27–33 kcal./mole. Since we favor a low value for the frequency factor (10^{12}–10^{13} sec.$^{-1}$), we therefore recommend the value 27–28 kcal./mole as a more reliable estimate for the above activation energy. Making the usual assumption that the recombination process does not require any activation energy we estimate $D(C_6H_5COO—OCOC_6H_5)$ at about 27–28 kcal./mole. This estimate, however, would be too low if the observed rate of reaction were given by the product of the rate of initiation and the length of the chain, e.g., a chain of about 100 cycles would make the "true" dissociation energy higher by about 3 kcal./mole.

An extremely elegant method of measuring the rate of dissociation of peroxides was developed by C. E. H. Bawn and Mellish[34] (13). These workers found that the stable and colored radical



is removed easily from solution by other radicals formed in the system, e.g., by radicals produced in the decomposition of benzoyl peroxide. Hence, the rate of the initial decomposition of peroxide is measured by the rate of disappearance of $(C_6H_5)_2N\underset{\bullet}{N}C_6H_2(NO_2)_3$, and the latter might be followed by any colorimetric method. Using this method Bawn and Mellish estimated $D(C_6H_5COO—OCOC_6H_5)$ at about 35 kcal./mole. The frequency factors were of the order 10^{14}–10^{15} sec.$^{-1}$, and the rate of dissociation was found to depend on the nature of the solvent.

The kinetics of the thermal decomposition of substituted benzoyl peroxides was investigated by D. J. Brown (30). The rate of decomposition of substituted peroxides was of the same order as the rate of decomposition of the unsubstituted compound. This seems to indicate that the influence of substitution on the O—O bond dissociation energy in benzoyl peroxides is not very considerable.

The thermal decomposition of acetyl peroxide was investigated both in the gaseous phase and in solution by O. J. Walker and G. L. E. Wild (209). The decomposition in the gaseous phase, at 100°C., produced ethane and carbon dioxide in the molar proportion 1:2, and Walker and Wild explained this result by postulating a reaction

$$(CH_3CO)OO(COCH_3) \rightarrow C_2H_6 + 2CO_2$$

The same products, however, would be obtained in a chain reaction:

$$(CH_3CO)OO(COCH_3) \rightarrow 2CH_3COO\cdot$$

$$CH_3COO\cdot \rightarrow CH_3\cdot + CO_2$$

$$CH_3\cdot + (CH_3CO)OO(COCH_3) \rightarrow C_2H_6 + 2CO_2 + CH_3\cdot$$

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[34] I am indebted to Professor Bawn for permission to quote his unpublished results.

It is most unfortunate that the above workers did not report the rate of the gaseous decomposition.

The liquid-phase decomposition of acetyl peroxide was investigated in toluene solution. The products of decomposition were different from those obtained in the gaseous phase, consisting mainly of methane and carbon dioxide in a molar ratio of about 1:1. Kinetically the reaction was of the first order, the activation energy being estimated at 31 kcal./mole (the frequency factor was 8×10^{14} sec.$^{-1}$). It seems, therefore, that the decomposition could be represented by the following mechanism:

$$(CH_3CO)OO(COCH_3) \rightarrow 2CH_3COO\cdot$$

$$CH_3COO\cdot \rightarrow CH_3\cdot + CO_2$$

$$CH_3\cdot + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2\cdot$$

the initial dissociation being the rate-determining step. If this mechanism is correct, then the O—O bond dissociation energy in acetyl peroxide would be about 31 kcal./mole.

The kinetics of the thermal decompositions of diethyl peroxide and dipropyl peroxide has been investigated by E. J. Harris and A. C. Egerton (72) and by E. J. Harris (71). Both reactions were proved to be homogeneous, first-order, gaseous decompositions, the rate being measured manometrically. The first-order rate constants remained unchanged over a wide range of initial pressure and were not influenced by the presence of foreign gases. As the initial pressure was raised, the character of the reaction suddenly changed at a definite value and became explosive. The nonexplosive decompositions of both substances had definite although very short induction periods. The experimental activation energy for the decomposition of diethyl peroxide was estimated at 31.5 kcal./mole, the frequency factor being 5×10^{14} sec.$^{-1}$; the corresponding values for dipropyl peroxide were 36.5 kcal./mole and 25×10^{14} sec.$^{-1}$ It seems very likely that the rate-determining step in these decompositions is the rupture of the O—O bond and that the above activation energies are equal to the corresponding O—O bond dissociation energies. The last conclusion, however, is not definite, because the mechanism of the decomposition is not yet quite clear. Harris suggested:

$$C_2H_5OOC_2H_5 \rightarrow C_2H_5OH + CH_3CHO$$

This suggestion is contradicted by the fact that in the decomposition of diethyl peroxide the final pressure increases to 2.17 times the initial pressure and in the decomposition of dipropyl peroxide to 2.5 times the initial pressure. More work is required for the determination of the O—O bond dissociation energy in these compounds.

The decomposition of tertiary butyl peroxide, investigated by N. A. Milas and D. M. Surgenor (1946) in a flow technique at temperature of 200–300°C., produced acetone and ethane. This finding can be understood in the light of the suggestion of P. George and A. D. Walsh (62) that the decomposition of a tertiary peroxide takes place by the breaking of the O—O bond, followed by the reaction:

$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3\cdot$$

The kinetics of the thermal decomposition of tertiary butyl peroxide was very thoroughly investigated by W. E. Vaughan and his colleagues. The work conducted in the liquid phase (142) demonstrated the presence of $(CH_3)_3CO\cdot$ radicals, since $(CH_3)_3COH$ was isolated amongst the products of decomposition. The studies in the gaseous phase (141) were carried out by a static manometric technique and by a flow technique, the latter being used only for the estimation of products. Thus it was shown that acetone and ethane were the main products of decomposition, accompanied by much smaller amounts of methane and methyl ethyl ketone, and the appearance of these products was accounted for by the following mechanisms:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot \rightarrow CH_3\cdot + CH_3COCH_3$$

$$2CH_3\cdot \rightarrow C_2H_6$$

$$CH_3\cdot + CH_3COCH_3 \rightarrow CH_4 + \cdot CH_2COCH_3$$

$$CH_3\cdot + \cdot CH_2COCH_3 \rightarrow C_2H_5COCH_3$$

The final pressure should be $3P_0$ (P_0 denotes the initial pressure of peroxide), both when ethane and when methane is the product of reaction.

The rate of decomposition was calculated on the assumption that the reaction obeys first-order kinetics and the computations were performed by the two methods:

(a) Assuming $P_{\text{final}} = 3P_0$ (as required by the stoichiometry)

(b) Assuming $P_{\text{final}} = 2.88P_0$

method (a) yielding rate constants higher than method (b).

The rate constants calculated by method (a) showed some fall-off towards the end of the run, while those calculated by method (b) were unchanged, and for this reason method (b) was used throughout the work. It was shown that the decomposition was a homogeneous gas reaction; that the first-order rate constant was not affected either by changes of the initial pressure of peroxide or by the addition of nitric oxide or propene; and that this rate constant was nearly the same when the decomposition was carried out in solution (142). It was concluded therefore that the observed rate of reaction measures the rate of initial decomposition of tertiary butyl peroxide into $(CH_3)_3CO\cdot$ radicals.

The activation energy was calculated at 39 kcal./mole from the temperature dependence of the rate constant, the relevant frequency factor being 3×10^{16} sec.$^{-1}$ Vaughan and his colleagues claimed therefore that

$$D[(CH_3)_3CO\text{—}OC(CH_3)_3] = 39 \text{ kcal./mole}$$

The above decomposition was reinvestigated recently by M. Szwarc and J. S. Roberts (198), who used a static method and added a great excess of toluene to the reacting mixture. The rate was measured by the rate of formation of $CH_4 + C_2H_6$, and the results indicated again that the reaction is homogeneous and obeys the first-order kinetics. The suggested mechanism is identical with that proposed by Vaughan:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot \rightarrow CH_3\cdot + CH_3COCH_3$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$$

or

$$CH_3\cdot + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2\cdot$$

The values of rate constants were smaller by about a factor of 2 than those obtained by Vaughan, and the activation energy was estimated from the temperature dependence of the rate constant at 33–34 kcal./mole, the frequency factor being $1\text{–}5 \times 10^{13}$ sec.$^{-1}$ On this basis a value of 33–34 kcal./mole was proposed for $D[(CH_3)_3CO\text{—}OC(CH_3)_3]$.

L. *Various methods*

The decomposition of mercury dialkyls has been investigated by E. Warhurst and G. B. Gowenlock (210). The technique was similar to that applied by E. T. Butler and M. Polanyi (35), and the extent of decomposition was measured by the rate of formation of mercury. It was demonstrated that the decomposition obeyed first-order kinetics. The activation energy was calculated by assuming the frequency factor to be 10^{13} sec.$^{-1}$ The following mechanism was suggested:

$$Hg(CH_3)_2 \rightarrow HgCH_3\cdot + CH_3\cdot \qquad \text{The rate-determining step}$$

$$HgCH_3\cdot \rightarrow Hg + CH_3\cdot \qquad \text{A rapid decomposition}$$

$$2CH_3\cdot \rightarrow C_2H_6$$

The decompositions of hydrazobenzene and phenylhydrazine have been investigated by M. J. S. Dewar (46). The decomposition was carried out in solution and the reaction was measured by the rate of disappearance of substrate. The reaction was proved to be of the first order, although the rate was dependent on the nature of solvent. The plot of log k against $1/T$ produced straight lines, and from their slopes the activation energies were estimated at 35–36 kcal./mole for hydrazobenzene and at about 48 kcal./mole for phenylhydrazine. The author suggests the following mechanism for these decompositions:

$$C_6H_5NH\text{—}NHC_6H_5 \rightarrow 2C_6H_5NH\cdot \qquad \text{The rate-determining step}$$

$$2C_6H_5NH\cdot + C_6H_5NH\text{—}NHC_6H_5 \rightarrow 2C_6H_5NH_2 + C_6H_5N{=}NC_6H_5$$

In conclusion, it is claimed that the observed activation energies measure the relevant N—N bond dissociation energies.

A similar mechanism was proposed by Miles (113) to account for the results of the pyrolysis of bibenzyl:

$$C_6H_5CH_2{-}CH_2C_6H_5 \rightarrow 2C_6H_5CH_2\cdot$$

$$2C_6H_5CH_2\cdot + C_6H_5CH_2CH_2C_6H_5 \rightarrow 2C_6H_5CH_3 + C_6H_5CH{=}CHC_6H_5$$

The pyrolysis was studied in the gas phase by means of a flow technique, and the rate was measured by the rate of formation of toluene. The activation energy was estimated at 45–48 kcal./mole and was identified with

$$D(C_6H_5CH_2{-}CH_2C_6H_5)$$

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VI. APPENDIX

This appendix contains three types of tables:

1. *The tables of bond dissociation energies determined directly*

The values quoted (table A1) were taken from the literature without introducing any corrections. They contain the data obtained from direct observations and not those calculated from heats of formation of the respective compounds in conjunction with heats of formation of radicals determined either by independent methods or by some guesswork. The values favored by the writer and considered by him as reliable are given in heavier type. Those which seem uncertain are indicated by question marks.

The bond dissociation energies for diatomic molecules were omitted, since an excellent compilation of these data is found in A. G. Gaydon's recent monograph (*Dissociation Energies*, Chapman and Hall, London (1947)).

The bond dissociation energies for triatomic molecules were calculated on the basis of the corresponding values for D(A—B) in the respective diatomic molecules. The values actually quoted were taken from recent papers by M. Wehrli and G. Milazzo (212) and by H. A. Skinner (164).

2. *The tables of heats of formation of radicals or atoms*

The values quoted in table A2 are computed on the basis of the respective bond dissociation energies. The values for the latter entities were either chosen from the literature or assumed on the basis of some observed regularities. It must be stressed, however, that in both cases the choice was a purely subjective one, reflecting the present opinion of the writer.

Every effort has been made to point out the assumptions on which these data are based, and the remarks added in the last column should help in this respect.

3. *The tables of "best" bond dissociation energies*

Assuming the heats of formation of radicals, as quoted in table A2, one may calculate the "best" bond dissociation energies (see table A3). This calculation requires a knowledge of the heats of formation of the respective compounds, and the data were taken from *Selected Values of Properties of Hydrocarbons*, or from the National Bureau of Standards monograph by F. R. Bichowsky and F. D. Rossini, or from modern publications. The references to the latter are given in a recent paper by J. S. Roberts and H. A. Skinner (150).

The values obtained in this way contain the uncertainties involved in the heats of formation of radicals (see Section IV,B) and in the estimation of the heats of formation of the respective compounds. The latter factor is of no significance in the case of hydrocarbons (and a few other compounds) for which modern and very accurate data are available.

The nature of the uncertainties is again stressed under the headings of the respective tables. The values determined directly are given in heavier type.

TABLE A1

Bond dissociation energies determined directly

Bond dissociation energies in teratomic molecules

MOLECULE X—A—Y	D(X—AY)	D(XA—Y)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole	*kcal./mole*			
H—O—H	115 ± 2.5	115 ± 2.5	$2H_2O + O_2 \rightleftharpoons 4OH$	1928	Bonhoeffer and Reichardt (25)
	115	115	Fluorescence	1934	Terenin *et al.* (203)
	117 ± 1	117 ± 1	Mercury-sensitized photolysis	1934	Senftleben *et al.* (168)
	114 ± 1	114 ± 1	Explosion method	1935	Lewis and von Elbe (102)
	113.5	113.5	$2H_2O + O_2 \rightleftharpoons 4OH$	1937	Avramenko and Kondrat'ew (6)
	118 ± 0.7	**118 ± 0.7**	$2H_2O + O_2 \rightleftharpoons 4OH$	1944	Dwyer and Oldenberg (50)
H—S—H	>78?	>78?	From D(S—H)		See Gaydon (60)
O—C—O	127	127	Thermochemistry		See Rossini *et al.*, *Selected Values of Properties of Hydrocarbons*
O—N—O	72	72	Thermochemistry		
Cl—N—O	37		$2NO + Cl_2 \rightleftharpoons 2NOCl$	1939	Beeson and Yost (41)
Br—N—O	28		$2NO + Br_2 \rightleftharpoons 2NOBr$	1934	Yost *et al.* (225)
O—N—N	39	? Owing to uncertainty in D(N—N)	Thermochemistry		
H—C—N	121?	?	Thermochemistry		Using ΔH_f(CN) = 100 kcal./mole
Cl—C—N	95?	?	Thermochemistry		
Br—C—N	83?	?	Thermochemistry		
I—C—N	71?	?	Thermochemistry		
Cl—Hg—Cl	80.5	80.5	Spectroscopic	1943	See Wieland (218) and Wehrli and Milazzo (212)
Br—Hg—Br	71.5	71.5	Spectroscopic	1943	
I—Hg—I	57	57	Spectroscopic	1943	
Cl—Hg—Br	77	70	Spectroscopic	1943	
Cl—Hg—I	74.5	62.5	Spectroscopic	1943	
Br—Hg—I	68	63.5	Spectroscopic	1943	

Cl—In—Cl	46	46	Based on spectroscopic D(In—Cl), D(In—Br), and D(In—I)	1943	See Wehrli and Milazzo (212)
Br—In—Br	42	42		1943	
I—In—I	42	42		1943	
Cl—Ca—Cl	176?	176?	Using spectroscopic data for the corresponding diatomic molecules	1949	Computed by Skinner (164)
Cl—Mg—Cl	136 ± 20?	136 ± 20?		1949	
Cl—Be—Cl	147 ± 15	147 ± 15		1949	
Cl—Cd—Cl	84 ± 5?	84 ± 5?		1949	
Br—Cd—Br	76 ± 10?	76 ± 10?		1949	
I—Cd—I	57 ± 10	57 ± 10		1949	
Cl—Zn—Cl	96 ± 5?	96 ± 5?		1949	
I—Zn—I	53 ± 15?	53 ± 15?		1949	

Bond dissociation energies of some inorganic molecules

COMPOUND	D	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
HO—OH	54	From D(H—OH)		
NH_2—H	<124	Predissociation	1928	Bonhoeffer and Farkas (24)
	<112	Mercury photosensitization	1935	Melville (111)
	<117	Fluorescence	1935	Terenin and Neumin (203)
	104	$NH_3 + H \rightleftharpoons NH_2 + H_2$		See Szwarc (192)
	104 ± 2	Pyrolysis of hydrazine	1949	Szwarc (191)
	100	Pyrolysis of benzylamine	1949	Szwarc (192)
H_2N—NH_2	60 ± 4	Pyrolysis of hydrazine	1949	Szwarc (191)
O_2N—NO_2	13	$N_2O_4 \rightleftharpoons 2NO_2$	1897	Schreber (160)
	12.85	$N_2O_4 \rightleftharpoons 2NO_2$	1919	Wourtzel (224)
	12.90	$N_2O_4 \rightleftharpoons 2NO_2$	1922	Bodenstein *et al.* (21)
	14.5–14.7	$N_2O_4 \rightleftharpoons 2NO_2$	1931	Verhoek and Daniels (207)
O_2N—NO	9.5		1929	Abel and Proisl (1)
	10	$N_2O_3 \rightleftharpoons NO_2 + NO$	1931	Verhoek and Daniels (207)

TABLE A1—*Continued*

Bond dissociation energies of hydrocarbons—1

TYPE C—H	D(C—H)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
C—H	80	Spectroscopic	1939	Herzberg (78)
CH_3—H	~98	Mirror technique (C_2H_6)	1933	Rice and Dooley (143)
	100 ± 6	Mirror technique (CH_4)	1934	Rice and Dooley (144)
	~103	Pyrolysis of CH_3I	1940	Polany *et al.* (11, 34, 35)
	101 ± 5	Electron impact	1942	Stevenson (177)
	~101	Electron impact	1942	Stevenson and Hipple (179)
	101 ± 1	Photobromination	1942	Kistiakowsky *et al.* (3, 4, 88)
	~101	Electron impact	1943	Stevenson (178)
	~101	Electron impact	1943	Hipple and Stevenson (83)
	103 ± 3	Pyrolysis of $C_6H_5C_2H_5$	1949	Szwarc (189)
		$CH_3 + H_2 \rightleftharpoons CH_4 + H$		See, for critical review, Wicke (217) and Steacie (168)
(CH≡C)—H	<121	Photodecomposition	1942	Cherton (39)
(CH_2=CH)—H	92?	Electron impact	1943	Stevenson (178)
CH_3CH_2—H	~102	$C_2H_5 + H_2 \rightleftharpoons C_2H_6 + H$	1942	Computed by Wicke (217)
	~100	$C_2H_5 + H_2 \rightleftharpoons C_2H_6 + H$	1946	Computed by Steacie (168)
	~97	Pyrolysis of C_2H_5I	1940	Polanyi *et al.* (11, 34, 35)
	~97	Electron impact	1943	Stevenson (178)
	~98	Photobromination	1944	Andersen and Van Artsdalen (5)
$CH_3CH_2CH_2$—H	~95	Pyrolysis of *n*-C_3H_7I	1940	Polanyi *et al.* (11, 34, 35)
$(CH_3)_2CH$—H	89?	Pyrolysis of iso-C_3H_7I	1940	Polanyi *et al.* (11, 34, 35)
(CH_2=$CHCH_2$)—H	~78	Pyrolysis of propene	1949	Szwarc (187)
	~77	Pyrolysis of 1-butene	1950	Szwarc and Sehon (199)

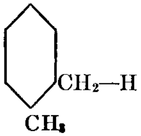
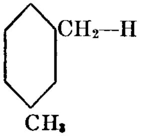
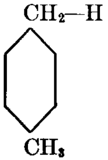
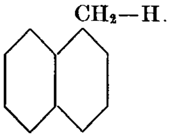
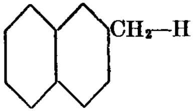
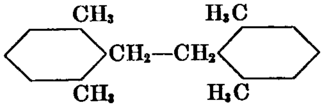
n-$C_3H_7CH_2$—H	~94	Pyrolysis of n-C_4H_9I	1940	Polanyi *et al.* (11, 34, 35)
$(CH_3)_3C$—H	86?	Pyrolysis of *tert*-C_4H_9I	1940	Polanyi *et al.* (11, 34, 35)
$[CH_2{=}C(CH_3)CH_2]$—H	~76	Pyrolysis of 2-methylpropene	1949	Szwarc (188)
$C_6H_5CH_2$—H	**77.5 ± 1.5**	Pyrolysis of toluene	1947	Szwarc (183, 186)
 CH_2—H CH_3	75 ± 1	Pyrolysis of *o*-xylene	1947	Szwarc (183, 186)
 CH_2—H CH_3	77 ± 2	Pyrolysis of *m*-xylene	1947	Szwarc (183, 186)
 CH_2—H CH_3	76 ± 1.5	Pyrolysis of *p*-xylene	1947	Szwarc (183, 186)
 CH_2—H	76	Pyrolysis of α-methylnaphthalene	1950	Szwarc and Shaw (200)

TABLE A1—*Continued*

Bond dissociation energies of hydrocarbons—1—Continued

TYPE C—H	D/C—H kcal./mole)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
 CH_2—H	76	Pyrolysis of β-methylnaphthalene	1950	Szwarc and Shaw (200)
$(C_6H_5)_3C$—H	~75	Dissociation of $(C_6H_5)_3CC(C_6H_5)_3$	1929	Ziegler *et al.* (228) Bent *et al.* (16)

Bond dissociation energies of hydrocarbons—2

TYPE C—C	D(C—C) kcal./mole	METHOD	YEAR	INVESTIGATORS AND REFERENCES
CH_3—CH_3	80 ± 6 82–87	Mirror technique Calculated from $D(CH_3—H)$	1933	Rice and Dooley (143) See $D(CH_3—H)$
$(CH_2{=}CHCH_2)$—CH_3	~**61.5**	Pyrolysis of 1-butene	1950	Szwarc and Sehon (199)
$C_6H_5CH_2$—CH_3	63 ± 1.5	Pyrolysis of $C_6H_5C_2H_5$	1949	Szwarc (189)
$C_6H_5CH_2$—$CH_2C_6H_5$	**47** 45–48	Pyrolysis of toluene Pyrolysis of bibenzyl	1947 1949	Szwarc (184) Miles (113)
 $(CH_3)_2C_6H_3CH_2$—$CH_2C_6H_3(CH_3)_2$	22?	Rate of thermal dissociation	1943	Coops *et al.* (42)

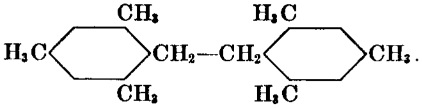
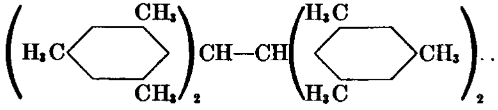
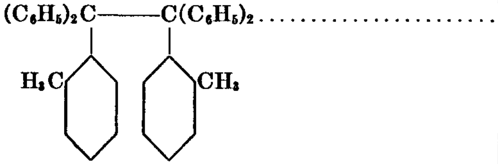
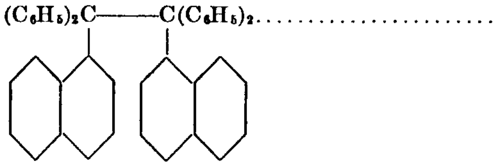
	22?	Rate of thermal dissociation	1943	Coops *et al.* (42)
	22?	Rate of thermal dissociation	1941	Coops *et al.* (41)
$(C_6H_5)_3C—CH(C_6H_5)_2$	<28	Rate of thermal dissociation	1937	Bachmann and Wiselogle (7)
$(C_6H_5)_3C—C(C_6H_5)_3$	11 ± 1	Equilibrium constant	1929	Ziegler and Ewald (228)
	11.6 ± 2	Equilibrium constant	1935	Müller and Müller-Rodloff (117)
	10	Equilibrium constant	1941	Preckel and Selwood (139)
	11.4	Equilibrium constant	1941	Preckel and Selwood (139)
	11.5	Equilibrium constant	1941	Preckel and Selwood (139)

TABLE A1—*Continued*

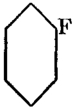
Bond dissociation energies of hydrocarbons—3

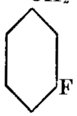
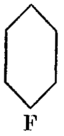
TYPE C=C	D(C=C)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
$H_2C{=}CH_2$	<162	Predissociation in Schumann ultraviolet	1934	Price (140)
	<159	Predissociation in Schumann ultraviolet	1935	Hilgendorff (81)

Bond dissociation energies of hydrocarbons—4

C≡C	D(C≡C)	METHOD	YEAR	INVESTIGATOR AND REFERENCE
	kcal./mole			
HC≡CH	<187?	Predissociation in Schumann ultraviolet	1934	Price (140)

Bond dissociation energies of halogen-substituted hydrocarbons—1

TYPE C—H	D(C—H)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
CH_2Br—H	~99	Photobromination of CH_3Br	1942	Kistiakowsky and Van Artsdalen (88)
CCl_3—H	~89	Photochlorination of CCl_3H	1934	Schumacher and Wolff (161)
	89 ± 2	Photobromination of CCl_3H	1939	Braunwarth and Schumacher (27)
CBr_3—H	93 ± 2	Photobromination of CBr_3H	1939	Braunwarth and Schumacher (27)
CH_2—H .... 	78	Pyrolysis of parent compound	1948	Szwarc and Roberts (196)

CH_2—H 	78	Pyrolysis of parent compound	1948	Szwarc and Roberts (196)
CH_2—H 	78	Pyrolysis of parent compound	1948	Szwarc and Roberts (196)

Bond dissociation energies of halogen-substituted hydrocarbons—2

TYPE C—Cl	D(C—Cl)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
CH_3—Cl	(74)?	Hot wire decomposition	1944	Doty (48)
CCl_3—Cl	≤70	$CCl_4 + Br_2 \rightleftarrows CCl_3Br + BrCl$	1949	Miller and Willard (unpublished results)

Bond dissociation energies of halogen-substituted hydrocarbons—3

TYPE C—Br	D(C—Br)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
CH_3—Br	~68	Pyrolysis of CH_3Br	1949	Szwarc and Sehon (unpublished results)
CF_3—Br	~65	Pyrolysis of CF_3Br	1949	Szwarc and Sehon (unpublished results)
CCl_3Br	45?	Photooxidation of CCl_3Br	1939	Franke and Schumacher (58)
	~52	Exchange Br_2 and CCl_3Br	1949	Miller and Willard (114)
	~57	Exchange Br_2 and CCl_3Br	1949	Davidson and Sullivan (44)

TABLE A1—*Continued*

Bond dissociation energies of halogen-substituted hydrocarbons—3—Continued

TYPE C—Br	D(C—Br)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
(·CHClCHCl)—Br	11 ± 3	Bromination of CHCl=CHCl	1938	Müller and Schumacher (118)
CHClBrCHCl—Br	51 ± 4	Bromination of CHCl=CHCl	1938	Müller and Schumacher (118)
(·CH=CH)—Br	8 ± 4	Photobromination of acetylene	1939	Müller and Schumacher (119)
(CH_2=$CHCH_2$)—Br	48–50 ~45	Pyrolysis of allyl bromide Pyrolysis of allyl bromide	1949 1949	Szwarc and Ghosh (194) Maccoll (107)
$C_6H_5CH_2$—Br	50 ± 2	Pyrolysis of benzyl bromide	1949	Szwarc and Ghosh (194)

Bond dissociation energies of halogen-substituted hydrocarbons—4

TYPE C—I	D(C—I)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
CH_3—I	~54 <58	Pyrolysis of CH_3I Absorption continuum	1940 1937	Butler and Polanyi (34, 35) Porret and Goodeve (138)
$CHCl_2$—I	42?	Pyrolysis of $CHCl_2I$	1945	Polanyi *et al.* (33)
$CHBr_2$—I	41?	Pyrolysis of $CHBr_2I$	1945	Polanyi *et al.* (33)
CHI_2—I	37?	Pyrolysis of iodoform	1945	Polanyi *et al.* (33)
C_2H_5—I	~52 ~51	Pyrolysis of C_2H_5I Pyrolysis of C_2H_5I	1940 1947	Butler and Polanyi (34, 35) Szwarc (182)
CH_2ClCH_2—I	46?	Pyrolysis	1945	Polanyi *et al.* (33)

CH_2ICH_2—I	<47	Photochemical decomposition	1930	Deduced from Schumacher and Wiig
(CH_2=CH)—I	~55	Pyrolysis of vinyl iodide	1940	Butler and Polanyi (34, 35)
n-C_3H_7—I	~50	Pyrolysis of *n*-C_3H_7I	1940	Butler and Polanyi (34, 35)
Iso-C_3H_7I	~46	Pyrolysis of iso-C_3H_7I	1945	Polanyi *et al.* (33)
(CH_2=$CHCH_2$)—I	39? 35–37	Pyrolysis of allyl iodide Pyrolysis of allyl iodide	1940 1948	Butler and Polanyi (34, 35) Szwarc and Shaw (163)
n-C_4H_9—I	~49	Pyrolysis of *n*-butyl iodide	1940	Butler and Polanyi (34, 35)
$(CH_3)_3C$—I	45?	Pyrolysis	1945	Polanyi *et al.* (35)
Cyclo-C_6H_{11}—I	49?	Pyrolysis	1945	Polanyi *et al.* (33)
C_6H_5—I	~54 >57	Pyrolysis of iodobenzene Pyrolysis of iodobenzene	1940 1947	Butler and Polanyi (35) Szwarc (182)
$C_6H_5CH_2$—I	44? ~39	Pyrolysis of benzyl iodide Pyrolysis of benzyl iodide	1940 1947	Butler and Polanyi (35) Szwarc (182)
$C_6H_5CH_2CH_2$—I	50?	Pyrolysis	1945	Polanyi *et al.* (33)

Bond dissociation energies of organic compounds containing oxygen—1

TYPE C—H	D(C—H)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
(HCO)—H	<78	Threshold in photolysis	1939	Gorin (67)
(CO)—H	<26 <12?	Photolysis, temperature coefficient Photolysis	1939 1939	Gorin (67) Remark by Style (180)

TABLE A1—*Continued*

Bond dissociation energies of organic compounds containing oxygen—2

TYPE C—C	D(C—C)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
CH_3—CO	<10	Photolysis	1934	Leermakers (100)
	<10	Photolysis	1936	Akeroyd and Norrish (2)
	<17	Photolysis	1939	Gorin (67)
	<18	Photolysis	1940	Herr and Noyes (77)
	<9	Photolysis	1940	Grahame and Rollefson (69)
	<9	Photolysis	1942	Blacet and Loeffler (20)
	<15	Photolysis	1943	Benson and Forbes (15)
CH_3—CHO	75 ± 2	Photolysis	1940	Grahame and Rollefson (69)
CH_3CO—$COCH_3$	60	Pyrolysis of biacetyl	1950	Szwarc and Murawski (195)
	<64	Threshold in photolysis	1942	Anderson and Rollefson (5a)
$C_6H_5CH_2$—$COCH_3$	63	Pyrolysis of $C_6H_5CH_2COCH_3$	1950	Szwarc and Murawski (195)

Bond dissociation energies of organic compounds containing oxygen—3

TYPE O—O	D(O—O)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
C_2H_5O—OC_2H_5	~30	Pyrolysis	1938	Harris and Egerton (72)
C_3H_7O—OC_3H_7	~35	Pyrolysis	1939	Harris (71)
$(CH_3)_3CO$—$OC(CH_3)_3$	39	Pyrolysis	1948	Rust, Vaughan, *et al.* (141)
	34	Pyrolysis	1950	Szwarc and Roberts (198)
CH_3COO—$OCOCH_3$	~30	Pyrolysis	1937	Walker and Wild (209)

$C_6H_5COO—OCOC_6H_5$	~30	Thermal decomposition in solution	1940	Kamenskaya and Medvedev (86)
	30–33	Thermal decomposition in solution	1946	Nozaki and Bartlett (121)
	28–30	Thermal decomposition in solution	1947	Hartman, Sellers, and Turnbull (74)
	~27.5	Thermal decomposition in solution	1948	Brown (30)
	~30	Thermal decomposition in solution	1949	Bawn *et al.* (13)

Bond dissociation energies of organic compounds containing oxygen—4

TYPE C—O	D(C—O)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
$CH_3—OH$	~90	Fluorescence	1934	Terenin *et al.* (203)
$C_2H_5—OH$	~90	Fluorescence	1934	Terenin *et al.* (203)
HCO—OH	~90?	Fluorescence	1934	Terenin *et al.* (203)
$CH_3CO—OH$	~90?	Fluorescence	1934	Terenin *et al.* (203)

Bond dissociation energies of organic compounds containing nitrogen—1

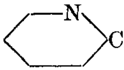
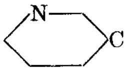
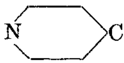
TYPE C—H	D(C—H)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
 $CH_2—H$	75	Pyrolysis	1948	Roberts and Szwarc (151)
 $CH_2—H$	76	Pyrolysis	1948	Roberts and Szwarc (151)
 $CH_2—H$	77	Pyrolysis	1948	Roberts and Szwarc (151)

TABLE A1—*Concluded*

Bond dissociation energies of organic compounds containing nitrogen—2

TYPE C—C	D(C—C)	METHOD	YEAR	INVESTIGATORS AND REFERENCES
	kcal./mole			
NC—CN	~100	Predissociation	1932	Hogness and Ts'ai (84)
	77?	Pyrolysis	1933	Kistiakowsky and Gershinowitz (87)
	146?	Pyrolysis	1940	White (216)
	<127	$H_2 + (CN)_2 \rightleftarrows 2HCN$	1942	Robertson and Pease (153)
	117-120	Lattice energy	1948	Glockler (66)
CH_3—CN	~105?	Fluorescence	1934	Terenin *et al.* (203)

Bond dissociation energies of organic compounds containing nitrogen—3

TYPE C—N	D(C—N)	METHOD	YEAR	INVESTIGATOR AND REFERENCE
	kcal./mole			
$C_6H_5CH_2$—NH_2	59 ± 4	Pyrolysis	1949	Szwarc (192)

Bond dissociation energies of organic compounds containing nitrogen—4

TYPE N—N	D(N—N)	METHOD	YEAR	INVESTIGATOR AND REFERENCE
	kcal./mole			
C_6H_5NH—NH_2	~48	Thermal decomposition in solution	1950	Dewar (46)
C_6H_5NH—NHC_6H_5	~35	Thermal decomposition in solution	1950	Dewar (46)

TABLE A2

Heats of formation of radicals or atoms in the gaseous state from elements in their standard states

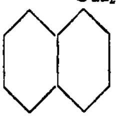
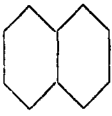
RADICAL OR ATOM	ΔH^0_f	METHOD	REMARKS
	kcal./mole		
H	+52.0	Spectroscopic	Rossini *et al.*, *Selected Values of Properties of Hydrocarbons* (1948)
Cl	+29.0	Spectroscopic	
Br	+26.7	Spectroscopic	
I	+25.5	Spectroscopic	
O	+59.2	Spectroscopic	
OH	+10.0	$2H_2O + O_2 \rightleftharpoons 4OH$	
CN	+100 ?	$(CN)_2 \rightleftharpoons 2CN$; D(CN—CN) = 127 kcal./mole	Uncertainty in interpretation
NO	+21.5	Calorimetric	
NH_2	+41 ± 2	Pyrolysis of hydrazine	
NO_2	+7.4	Calorimetric	
CH_3	+31 ± 1	Photobromination	Well established
CHO	0 ?	Decomposition of CHO	Very unreliable
C_2H_5	+26 ± 2	Photobromination	Might be slightly higher
C_2H_5O	−10 ?	Pyrolysis of C_2H_5ONO	Very unreliable; leads to $D(C_2H_5O—C_2H_5) < D(C_2H_5—O)$
$CH_2{=}CH$	+64 ?	Estimate	$D[(CH_2{=}CH)—H]$ seems to be $> D(CH_3—H)$
$CH{\equiv}C$	+123 ?	Photodecomposition	Very uncertain
CH_3CO	−4 to 8	Pyrolysis of biacetyl	Lack of modern combustion data
n-C_3H_7	+18 ?	Pyrolysis of n-C_3H_7I	Uncertain
Iso-C_3H_7	+12 ?	Pyrolysis of iso-C_3H_7I	Uncertain
$CH_2{=}CHCH_2$	+ 29.5 ± 2	Pyrolysis of 1-butene	Cross-checks: pyrolysis of propene and allyl bromide
$CH_2{=}C(CH_3)CH_2$	+20 ?	Pyrolysis of 2-methylpropene	
n-C_4H_9	+12 ?	Pyrolysis of n-C_4H_9I	
$(CH_3)_3C$	+3 ?	Pyrolysis of *tert*-C_4H_9I	Very uncertain
C_6H_5	+72 ?	Estimate	$D(C_6H_5—H)$ seems to be $>D$(CH —H)
$C_6H_5CH_2$	+37.5 ± 1.5	Pyrolysis of toluene	Cross-checks: pyrolysis of $C_6H_5C_2H_5$ and $C_6H_5CH_2Br$

TABLE A3

R′—R″ bond dissociation energies

Hydrocarbons

For uncertainties in $D(R'\text{—}R'')$ compare the table of ΔH_f of respective radicals
The bond dissociation energies estimated directly are set in heavy type

R″…… R′	H	CH_3	C_2H_5	$CH_2{=}CH$	$CH{\equiv}C$	n-C_3H_7	Iso-C_3H_7	$CH_2{=}CHCH_2$	n-C_4H_9	tert-C_4H_9	C_6H_5	$C_6H_5CH_2$
CH_3	**101**	**83**	82	90?	110?	79	74.5?	**60**	78	74?	91?	**63**
C_2H_5	**98**	82	82	90?	109?	79	75?	60.5	78	73?	91?	62
$CH_2{=}CH$	104?	90?	90?	101?		87?	85?	68.5?	86?	81?	101?	
$CH{\equiv}C$	121?	110?	109?			106?	103?				119?	
n-C_3H_7	95	79	79	87?	106?	76	72?	57.5	75	70?	88?	59
Iso-C_3H_7	89?	74.5?	75?	85?	103?	72?	66.5?	54.5?	71?	65?	83?	54.5?
$CH_2{=}CHCH_2$	**77**	**60**	60.5	68.5?		57.5	54.5?	38	56.5			
n-C_4H_9	94	78	78	86?		75	71?	56.5	74	69?	87?	57.5
$(CH_3)_3C$	85?	74?	73?	81?		70?	65?		69?	60?	78?	
$CH_2{=}C(CH_3)CH_2$	76?	60?	60?									
C_6H_5	104?	91?	91?	101?	119?	88?	83?		87?	78?	103?	76.5?
$C_6H_5CH_2$	**77.5**	**63**	62			59	54.5?		57.5		76.5?	47
o-$CH_3C_6H_4CH_2$	**74**	58	58									
m-$CH_3C_6H_4CH_2$	**77.5**	62	62.5									
p-$CH_3C_6H_4CH_2$	**75**	60	60									
CH_2 	**~76**											
 CH_2	**~76**											

R′—R″ bond dissociation energies

For uncertainties in $D(R'\text{—}R'')$ see the table of ΔH_f of respective radicals
The bond dissociation energies estimated directly are set in heavy type
The values of $D(R'\text{—}R'')$ calculated on the basis of ΔH_f of the respective compounds are denoted by an asterisk if the ΔH_f is uncertain

R″…… R′	H	Cl	Br	I	OH	NH_2	CN	CHO	$COCH_3$	NO_2	NO
CH_3	**101**	80	**66–67**	**54–55**	91 (**90**)	79	110? (**105**)	71–**75**	77?	57	
C_2H_5	**98**	80	65	**51–52**	93 (**90**)	78		71?	77?	52	
n-C_3H_7	95	77*		**50**	92	77*		71?	77?		
$(CH_3)_2CH$	89?			**~46**	~90				73?		
$(CH_3)_3C$	85?	75?	61?	**~45**?	91?	76?					
$CH_2{=}CH$	104?	86?		**55**?			121?	84*?			
$CH_2{=}CHCH_2$	**77**	58	**48**	**35–37**	71	64*	92*?	50?			
C_6H_5	104?	88?		**57**?	107*?	94*?	124*?	83*?			
$C_6H_5CH_2$	**77.5**		**50.5**	**39**?	73*	**59**	95*?		**63**		
CHO	79?				96? (**90**)	89?			59?		
CH_3CO	85?	82?	67?	**51**?	102? (**90**)	98?		59?	**60**		

It is necessary to acknowledge the existence of three previous communications attempting to systematize the data concerned with bond dissociation energies: a review by E. Wicke (217) published in 1942; a monograph by E. W. R. Steacie (168) published in 1946; and an extensive compilation by J. S. Roberts and H. A. Skinner (150) published in 1949. The data given in the present paper differ only slightly from those recommended by Roberts and Skinner. It seems, however, that Roberts and Skinner reported the various bond dissociation energies and heats of formation of radicals with an accuracy which is not warranted by the actual accuracy of the experimental determinations. They put the whole emphasis on the accuracy of thermochemical data used in their calculations, stressing to a lesser extent the uncertainties in the bond dissociation energies measured directly and consequently in the heats of formation of the radicals.